SLOW RELAXATION PHENOMENA ON THE GERMANIUM SURFACE

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ABSTRACT

Experiments on the "slow surface states" on germanium, the states with relaxation times the order of seconds or minutes, are reviewed. Methods of disturbing the charge in the states from equilibrium, and of detecting the return to equilibrium, are discussed. After a disturbance, it is found that the charge decays back in what is generally a non-exponential manner, and with a rate that is generally very temperature sensitive. Two models which have been suggested to explain the properties of the states are examined. One is the heterogeneous surface model, where it is proposed that inhomogeneities in the surface result in a variation in the lifetime from area to area over the surface. The other is the electron transfer model, where the surface is considered uniform, the non-exponential relaxation resulting from variations in the surface barrier with changes in surface charge. It is concluded that although neither model can satisfactorily account for the observed phenomena, possibly a combination of the two will.

I. INTRODUCTION

It has been concluded by many investigators[1-8] that there are two sets of surface states on the germanium surface. These have been termed "fast" states and "slow" states. The fast states have trapping time constants the order of fractions of a millisecond. The slow states exhibit relaxation times at room temperature the order of seconds to minutes. It is generally believed that the fast surface states are located at the interface between the germanium and the layer of germanium oxide. The slow states are probably located at the outer surface of the oxide. It is thus believed the long decay constants, observed with transitions to or from the slow states, arise because it takes considerable time for the charge to leak through the oxide layer. We shall be primarily interested here in effects related to the slow states.

The density of charge in the slow states normally appears to be in thermal equilibrium. This is concluded from the reversibility of any departure from equilibrium. If the density of charge in the slow states is disturbed and then the disturbance is removed, the original density will be re-established at some later time. The exact length of time required depends upon the experimental conditions.

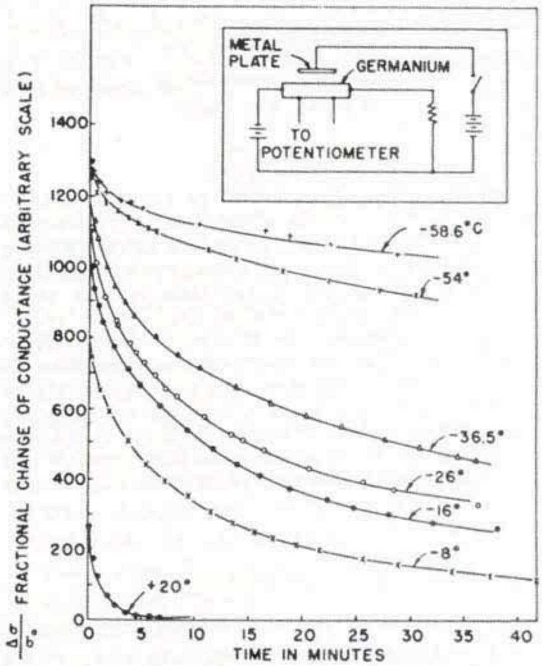


Fig. 1.—Relaxation of ac field effect at various temperatures. (After Morrison, reference 2.) The ordinate represents the fractional change in conductance from equilibrium. A block diagram of the method of measurement is shown in Fig. 1a.

Several stimuli have been used to disturb the charge density in the slow states. The one most often used is the field effect. If a field is applied normal to the surface, some or all of the induced charge will leak out to the slow surface states. When the conductance is measured (Fig. 1a), the initial change in conductance upon application of the field (due to that part of the induced charge entering the valence and conduction bands) is followed by a slow return toward the initial conductance value as the charge leaks out to the slow states. A second method of changing the density of charge in the slow states is through illumination. The illumination changes the quasi Fermi level, and the charge on the slow states adjusts with time to the new condition. Then, when the illumination is removed, the slow return to equilibrium of the conductance is again observed. A third method of disturbing the equilibrium density is through a temperature change. This method is particularly useful at low temperatures, where the times involved in the slow decay are long compared to the heating or cooling time. A fourth method, of considerable practical interest, is through biasing a *p-n* junction. The change in the quasi Fermi level arising as a reverse bias is applied causes slow adjustment of the charge on the slow states nearby. This has a marked effect on surface leakage in a transistor or junction, particularly if an inversion layer is present.

The measurement normally made to follow this slow adjustment of the slow states to equilibrium is the conductance. However, the work function has also been used successfully for this measurement by Pratt and Kolm.[8,9]

To explain the details of the phenomenon, two models have been proposed. The first was suggested by Kingston and McWhorter,[1] who assumed that the surface was heterogeneous, and that the shape of the curves was explainable in terms of a spectrum of time constants, the time constant fluctuating from area to area over the surface. A second model has been proposed by Morrison,[2] who suggested that the shape of the decay curves could be interpreted in terms of a uniform surface with electron exchange over the surface barrier acting as the rate-limiting step. When the charge in the surface states is perturbed from equilibrium, the rate of capture varies not only directly due to the change in the number of empty surface traps, but also indirectly through the dependence of the surface barrier height on the surface charge. In this "electron transfer" [10] model, the barrier height is assumed the controlling variable. A model similar in many respects to that of Morrison has been proposed by Pratt and Kolm.[8,9]

It is seen that the two models proposed to explain this particular phenomenon are similar to those suggested to explain chemisorption, where again heterogeneous surface effects and electron transfer effects could each explain the observed adsorption isobars. In fact, the general shape of the curves obtained in the relaxation studies, such as those to be shown in Fig. 1, are strongly reminiscent of adsorption-time curves normally observed. Thus a step toward the discrimination between the two models in this particular case may be of considerable importance in the problems of chemisorption. Such a step will be of particular interest in that in few materials to date have experiments been performed which will satisfactorily differentiate between the models.

Another area of research where a satisfactory model for our slow effects may be of prime interest is the area of excess, or $1/f$, noise. It has been concluded [1] that such a slow surface trapping phenomenon may well be the principal cause of the observed $1/f$ excess noise arising in a great variety of materials. It has also been shown mathematically that under certain conditions either the heterogeneous surface [1] or the electron transfer [11] models may lead to $1/f$ type noise. Thus a conclusive discrimination between the two models for even one isolated case will be an important step.

In the present manuscript we will outline the experimental observations which have been made, giving particular attention to those experiments which contribute information relating to the important problem of discrimination between the two surface models, the heterogeneous surface model and the electron transfer model.

II. EXPERIMENTAL OBSERVATIONS

1. *Field Effect Measurements*

Most of the experimental study of the slow decay has made use of an applied field to disturb the surface equilibrium on a free surface, and detected the electron trapping by measuring the conductance. The simplest approach in this study is that using a dc field.

Morrison [2] has published several curves showing the effects upon application of a dc field, which are reproduced in Fig. 1. The parameter involved is the temperature. At time zero the field is applied, resulting in an immediate conductance change. The induced charge leaks out to the slow states at a rate governed by the temperature; and with sufficient time, the conductance tends to return to its initial value. The experiments were performed on a *p*-type surface. The sample was *p*-type at low temperatures, intrinsic at room temperatures. The characteristics to be particularly noted are (a) the non-exponential form of the conductance decay, and (b) the strong temperature dependence of the rate.

Kingston and McWhorter [1] have made extensive studies using a sinusoidal alternating field with variable frequency. The results are shown in Fig. 2. At high frequency the relaxation has no effect, as the time constant is too great. Transfer of charge to the slow states does not occur, and the ac signal arising in the resistance measurement becomes independent of frequency. At very low frequencies the signal approaches zero, as the induced charge is able to leak out to the slow surface states fast enough to shield the sample from the field at all times. The sample used was high resistivity *n*-type, with a *p*-type surface when dry, *n*-type when wet ambients were used.

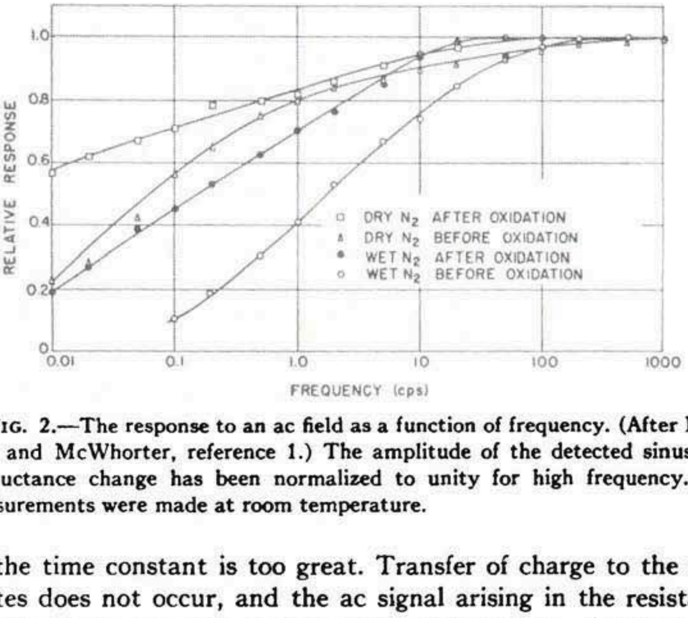


FIG. 2.—The response to an ac field as a function of frequency. (After Kingston and McWhorter, reference 1.) The amplitude of the detected sinusoidal conductance change has been normalized to unity for high frequency. The measurements were made at room temperature.

The distinctive features seem to be: (a) the amplitude observed varies approximately as log ω, where ω is the angular frequency, over portions of the curves; (b) the preparation of the surface and the gaseous ambient have a considerable effect on the response. Another important characteristic, not demonstrated in the curves, is the absence of harmonics in the detected signal. This absence is rather unexpected, considering the non-linearity of the decay characteristics.

Kingston and McWhorter have made measurements using a square wave field, obtaining in this manner results comparable to the dc field effect measurements. They report a non-exponential decay, but find the relaxation is insensitive to temperature possibly down to liquid nitrogen temperature. This latter result is in contradiction to those of other workers,[2,3,12] who find a very sensitive temperature dependence. No obvious reason presents itself to account for this discrepancy in results. It may be, for example, related to a difference in surface treatment or to the relatively low fields used in Kingston and McWhorter's experiments. In order to determine which, if either, of these explanations is correct, more experimental work is necessary.

Measurement of the contact potential during the slow relaxation has been made by H. H. Kolm and G. W. Pratt.[8,9] Following the application of a dc field, the contact potential at room temperature decays by a logarithmic law. These measurements will be discussed in more detail in another paper of this meeting.[11]

2. *The Use of Illumination and Heat to Disturb the Surface*

Several investigators [2,8,12] have disturbed the surface equilibrium by illumination or heating, and followed the decay of the conductance, contact potential, or saturation reverse current back to equilibrium. We will discuss in this section only the experiments performed on the free surface, leaving the more complex studies using junctions to the following sections.

Morrison [2] has done the only work to date using heating to disturb the surface equilibrium. With the sample at equilibrium at a low temperature (−44°C), he heated briefly to room temperature by Joule heating then cooled back to −44°. The surface conductance had changed, and decayed slowly back to its −44° equilibrium value. The decay curve was found to be the same as when illumination or field effect was used to disturb the surface. The results are shown in Fig. 3.

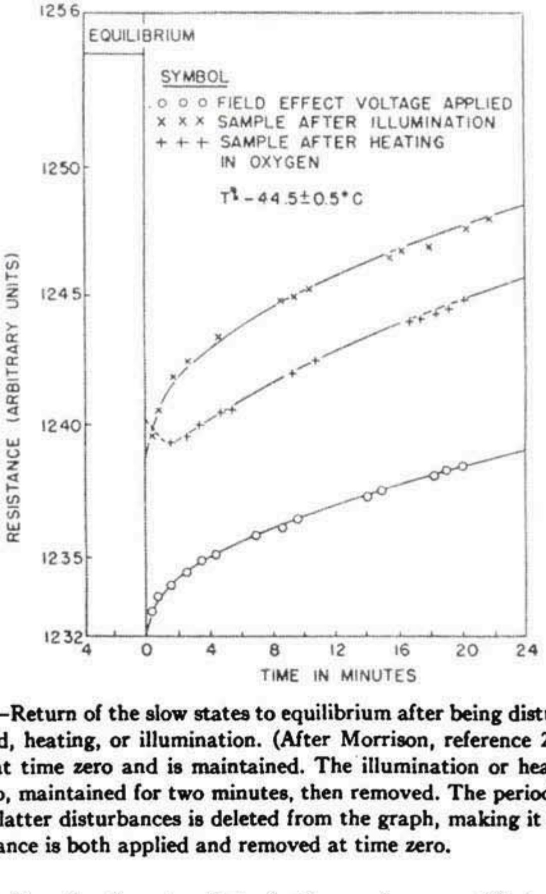


FIG. 3.—Return of the slow states to equilibrium after being disturbed by an applied field, heating, or illumination. (After Morrison, reference 2.) The field is applied at time zero and is maintained. The illumination or heat is applied at time zero, maintained for two minutes, then removed. The period of application of the latter disturbances is deleted from the graph, making it appear that the disturbance is both applied and removed at time zero.

Use of illumination to disturb the surface equilibrium on the free surface has been made by Morrison[2] and Kolm and Pratt,[9] the former studying conductance and the latter work function changes. Both found decay curves back to equilibrium after illumination resembling those arising from field effect disturbance.

Morrison studied the rate of change of the dark surface conductance as a function of time of illumination, using intensity of illumination and oxygen pressure as parameters. That is, the experiment measured the rate of displacing the surface states from their dark equilibrium value. Illumination caused a displacement from equilibrium corresponding to the trapping of electrons in the slow surface states. The initial rate of trapping was proportional to the photoconductance (proportional to the excess carriers present) and increased slightly as the oxygen pressure increased. The results are shown in Fig. 4, a plot of the dark conductance (measured while the illumination was briefly turned off) as a function of the time of illumination. The significant features are the influence of the photoconductance and the oxygen pressure on the rate of trapping.

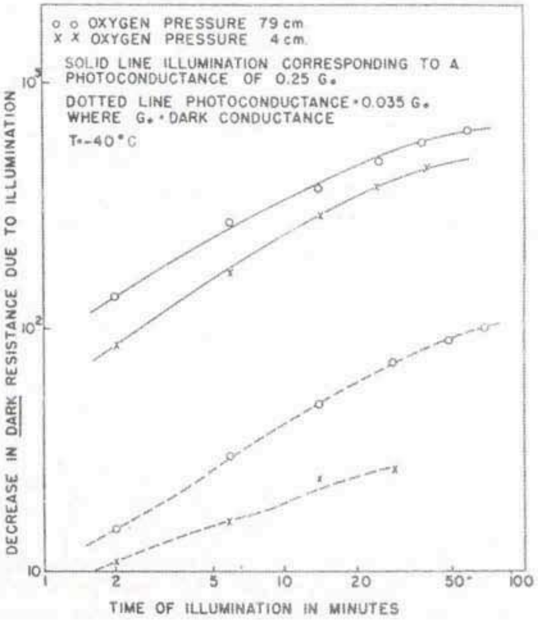


FIG. 4.—Departure from equilibrium of the charge density of the slow states when perturbed by illumination. (After Morrison, reference 2.) The measurements were made by briefly extinguishing the illumination, while measuring the dark conductance. The dependence of the process upon oxygen pressure and intensity is recorded.

3. *Measurements on Junctions and Channels*

Another method of disturbing the charge in the slow surface states from equilibrium is through the use of a bias on a junction or point contact. The quasi Fermi level will shift upon application of a bias; and in the surface region where this non-equilibrium situation is felt, the surface charge will adjust to the new condition.

This is obviously a more complex situation than in the case of a free surface, as in general the disturbance from equilibrium will vary from point to point around the surface. There have been two extensive sets of research using this effect. The first is by Kikuchi,[12] who described measurements on point contact diodes. He reported a slow decay or rise in the reverse current of germanium point contact diodes (and referred to similar effects in junction diodes) when stimulated by a change in reverse voltage or by illumination. The slow decay phenomena was not observed on all point contact diodes, appearing in only about 60 percent of those investigated. He observed non-exponential variations with time, which he was able to separate into two exponential decays, one with a time constant or 30–50 sec., and the other of 200–300 sec. The similarity between these time constants and those of the slow decay effect under discussion, together with similar illumination relaxation effects, leads to the belief that they are closely related effects. However, the complications of analysis arising when one considers effects at a point contact, together with the lack of knowledge about the surface band structure on his samples, makes the results difficult to interpret quantitatively. They are, however, of considerable qualitative interest.

The three effects which Kikuchi studied were: (a) what he termed the "photo-aftereffect," a slow decay of the dark reverse current to its equilibrium value after removing illumination, (b) "creep," a slow drift in the value of the saturation current upon application or removal of a reverse voltage, and (c) "creep of the photocurrent," a drift in the value of the short circuit photocurrent. He found that if a rectifier exhibited any of these effects, it exhibited all. Hence he concluded the effects were closely related. The rate of decay was found to increase with increasing temperature, varying a factor of three between 0°C and 10°C. The initial excess conductance in the "creep" effect was not linearly related to the voltage applied.

The second junction study is that of Statz et al.,[3,4,5] who have made extensive measurements on the conductance of channels developed across the base region of *p-n-p* transistors. The junctions are equally biased in the reverse direction (Fig. 5a) and because of the presence of a channel on the surface of the base region, the whole surface is at the same potential. In this case the surface over the base region has a relatively uniform quasi Fermi level, so the disturbance of the surface from equilibrium is uniform. Experimentally, when a sudden change is made in the bias voltage

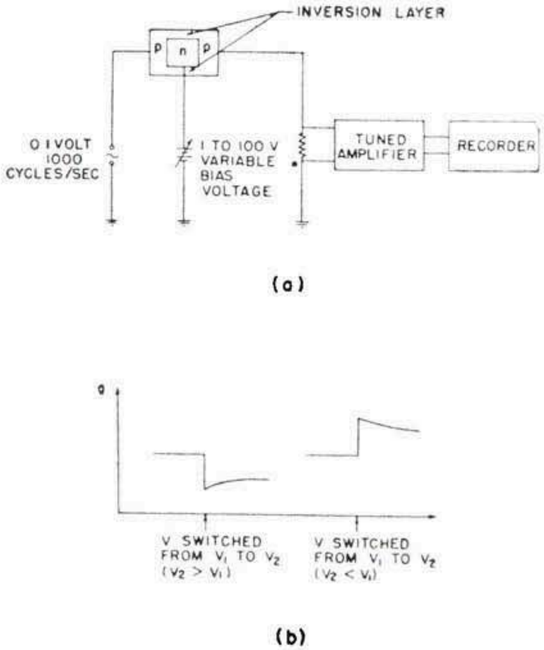


FIG. 5.—Slow state relaxation as observed by channel measurements. (After Statz, deMars, Davis, and Adams, references 3, 4 and 5.) Figure 5a shows the method of measurement, using a *p-n-p* transistor with a channel over the base region, and measuring the channel conductance. Figure 5b shows how the channel conductance varies with time after a change in the variable bias voltage.

the resulting change in channel resistance is followed by a slow decay of the resistance to new equilibrium value (Fig. 5b). The latter portion is apparently caused by the adjustment of the slow traps to the new quasi Fermi level.

The channel resistance is a measure of the density of holes in the channel, if the mobility were known. The mobility was calculated by Statz on the basis of Schrieffer's theory. With a calculation of the charge trapped at interface levels, the change of charge density in the slow surface states can be plotted as a function of time. Statz found an exponential dependence of the number of trapped carriers with time. The lifetime varied with temperature, increasing rapidly as the temperature decreased. Assuming the lifetime was governed by an activation energy, Statz et al. found 0.3 electron volts for the activation energy.

4. *Recent Experimental Observations*

In the hope of discriminating further between the heterogeneous surface and the electron transfer models (as will be discussed further in the next section) we have made a series of measurements of the relaxation characteristic of a 13 ohm-cm *n*-type sample at room temperature as a function of applied voltage. The surface was made strongly *n*-type by using a well-oxidized surface (exposed two weeks to air) and a helium ambient atmosphere with 50 percent relative humidity. The strongly *n*-type surface was necessary in order that the induced initial change in conductance be proportional to the applied voltage. As this requirement was approximately realized (see Fig. 4) it was assumed that a negligible fraction of the induced charge was captured by the valence band, and that the amount trapped by interface states was roughly proportional to the applied voltage. With these approximations the conductance varies linearly with the charge in the slow surface levels.

The results, showing the change in conductance as a function of time following application or removal of the field, are shown in Fig. 6. There are three characteristics to be emphasized in these curves. First, the variation with time is never exponential. Second, there appears to be some asymmetry between the curves representing the application and the removal of the field at very low disturbances, for $\Delta\sigma < 2$ units. Third, there is strong asymmetry at very high field strength. The asymmetry with low disturbances may arise for the following reason. When the applied voltage is switched on or off, there is a charge induced in the germanium which will in time leak to the slow states. When the voltage is applied, however, the induced charge is compensated by charge in the metal electrode, whereas when the voltage is removed the induced charge is compensated by charge on the slow states themselves. Thus the field near the germanium may be slightly different in the two cases, leading to different relaxation curves. Kingston and McWhorter[1] however have reported no such asymmetry in their results, even with a similar unidirectional field method of measurement.

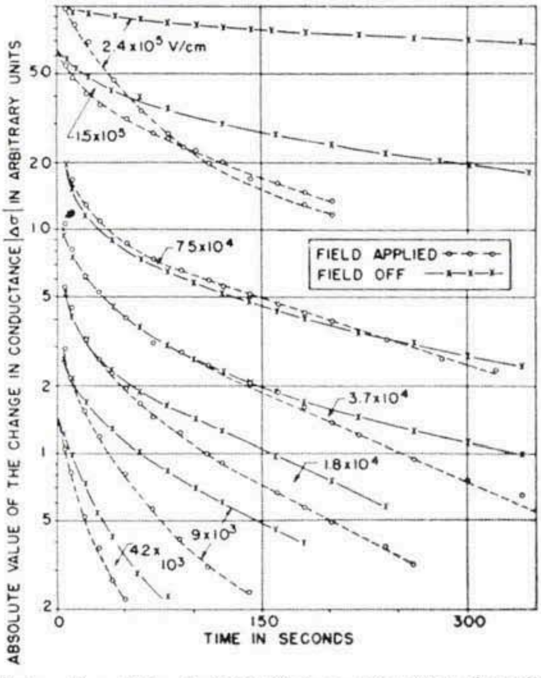


FIG. 6.—Relaxation of the dc field effect as a function of applied field. The measurements are at room temperature. The field is applied such that the metal plate is positive, the sample negative. The conductance increases upon application of the field, decreases upon removal.

To summarize the experimental results, it has been found by most workers that the relaxation is non-exponential, and depends strongly on the temperature. The rate of charge transfer is proportional to the excess carrier concentration, and depends strongly on the ambient atmosphere surrounding the sample. The return of the surface to equilibrium is not sensitive to whether the disturbance was caused by illumination, heating, or an applied field.

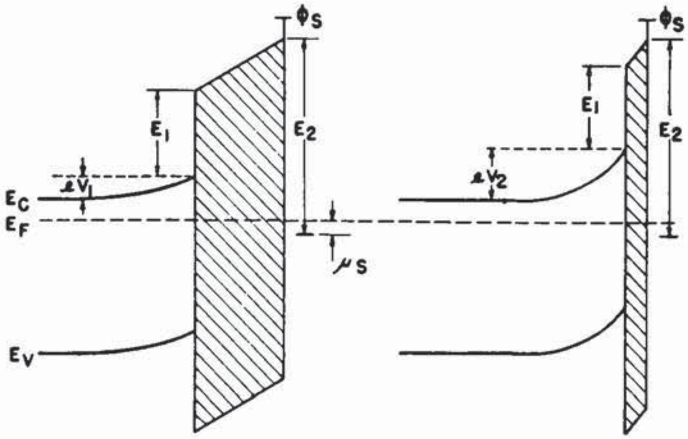
The first two characteristics, that of exponential decay and of the temperature dependence of the relaxation, are questioned by some dissenting observations. With respect to the former, Kikuchi[12] reports that one out of the eight samples which he studied showed a simple exponential decay at room temperature. Figure 1 shows a room temperature curve which is close to exponential. Statz et al.[3] claim that the number of excess charges in the surface states (as calculated from the experimental results) varies exponentially with time at temperatures above −20°C. Other measurements show non-exponential behavior at all temperatures, including room temperature. With respect to the temperature dependence of the rate, there has been only one experiment recorded which disputes this. Kingston and McWhorter[1] have reported temperature independence down to liquid nitrogen temperature. The other workers report a very sensitive temperature dependence.

III. INTERPRETATION

To date most investigators have interpreted the characteristics of the slow relaxation in terms of the following model. It has been assumed that the rate-limiting step in the relaxation process is the transfer of carriers over or through a barrier arising in the oxide layer, the charge becoming trapped in surface states in the oxide layer or on the outside of the oxide layer (Fig. 7 . In support of this model, it has been satisfactorily shown that electron transfer is rate limiting; for the rate of electron capture by the slow states is proportional to the number of excess carriers in the germanium, as was found in the illumination experiments of Fig. 3. The influence of the oxide has in the past been assumed, but has been recently verified by Lasser[13] in experiments relating the relaxation rates with the oxide thickness. The barrier model is supported by the observed temperature sensitivity of the relaxation rate.

Assuming the validity of the above general model there are many important details which remain to be cleared up. The questions of whether holes or electrons are transferred, whether the charge tunnels or goes over the potential barrier, the type of defect that constitutes the surface states, and whether the states are in the oxide or on the surface of the oxide, are relatively unexplored. We will discuss these problems in the above order.

With respect to the question of the type of carrier crossing the surface barrier, whether it is electron transfer or hole transfer, Statz and his co-workers[3] have concluded they are observing hole transfer in their experiments with a p-type surface on n-type



(a) THICK OXIDE (b) THIN OXIDE

FIG. 7.—A possible energy level diagram for the surface of n-type germanium. The slow states are represented as appearing at some energy E_2 below the "conductance band" of the germanium oxide, and are considered to be at a constant energy with respect to the Fermi level. Subject to these conditions, the influence of the oxide thickness is shown.

germanium. They conclude this on the basis of their calculation that the surface charge is controlled by the quasi-Fermi level for holes, and on their observation of an exponential decay. The latter is considered evidence since, if it were electron transfer, the barrier in the germanium would cause non-exponential effects to be observed. On the other hand, the interpretation of the asymmetric decay of Fig. 6 in terms of the electron transfer theory of the next section indicates that in this case, with an n-type surface, transfer is by electrons. For a positive field lowers the surface barrier for electrons, raises the barrier for holes, and as the fast decay occurs with a positive field, transfer of electrons is indicated.

Similarly, in Kingston and McWhorter's results of Fig. 2, lowering the surface barrier with water vapor decreases the time constants, indicating transfer of electrons.

Kingston and McWhorter[1] have pointed out that there are two possible methods of charge transfer across the oxide. The charge can go over the oxide barrier or tunnel through. The experiments to date have not been designed to distinguish between these possibilities. Both mechanisms of transfer can lead to an apparent activation energy in the decay constant,[3] as has been observed experimentally. With either mechanism, the rate of transfer will be affected by an applied field, as is observed; for the field appears to affect mainly the Schottky barrier[2] through which there can be no tunneling. The major difference between the two mechanisms should be observed in experiments investigating the effect of different oxide film thicknesses experiments which will be discussed by Lasser.[13] Assuming the energy levels are at the surface of the oxide (a question which will be discussed below), the time constant should vary in a very sensitive exponential manner with thickness if tunneling is the dominant mechanism for transfer; but should vary relatively slowly if the transfer is over the potential barrier in the oxide. An argument favoring tunneling as the dominant mechanism has been proposed by Kingston and McWhorter.[1] They suggest that tunneling through the oxide barrier may in some cases yield a slow variation in the decay rate with temperature. They therefore interpreted their observed temperature insensitivity as indicative of a tunneling mechanism. In the following discussions it will be assumed that transfer is over the potential barrier, for simplicity. However, the discussions should apply with only minor changes if the transfer is through the barrier.

Another question arising is with respect to the nature of the surface states, assuming they are on the outside of the oxide. The four possibilities we will discuss are: (a) Tamm states on the outer surface of the oxide, (b) states arising due to adsorption of oxygen, O^- levels, (c) states associated with doubly ionized oxygen, $O^{=}$ levels, (d) other adsorbed gases. There is no evidence clearly eliminating any one of these possibilities. However, it is possible to argue against Tamm states on the basis of the known presence of a large density of surface states due to adsorbed ions. The adsorbed ion concentration is so large that it appears to overwhelm all other surface states in controlling the surface band structure, so it is plausible to consider adsorbed ions as the more likely source of the slow surface states.

There have been many experiments showing that the adsorption of various gases has an effect on the relaxation constants, such as shown in Fig. 2. These, however, cannot be simply interpreted to conclude that any one of these gases provides the energy level under consideration. There is no easy way without a detailed model to separate direct effects, the addition or removal of slow levels, from indirect effects, in particular the changes in the time constant due to changes in the surface barrier upon adsorption. The choice between adsorbed oxygen and other adsorbates active on the surface is therefore a difficult one. However, it has been shown that the adsorption of water vapor (the most probable gas other than oxygen) is a reversible process at room temperature. Thus, as the relaxation effects occur in dried air or oxygen, water vapor is unlikely as the cause of the levels. Oxygen, however, is apparently irreversibly adsorbed at room temperature and below,[14] whereas the slow relaxation is a reversible process. A possible level is the $O^{=}$ level on the adsorbed oxygen, trapping on which may be reversible even when the direct adsorption is irreversible.[15] Pratt [16] has also suggested this for the level involved.

Of greater immediate importance than determining the exact nature of the slow states is the discrimination between the two possibilities: levels on the surface of the oxide or levels within the oxide, being the cause of the slow states. Not only will the importance of the phenomenon in chemisorption problems be diminished, but, if the slow states are in the oxide layer, the current theories of the process, as discussed in the next section, must be somewhat modified.

Although the problem of whether the slow surface levels are mainly in or on the oxide layer is far from solved as yet, there are several arguments which may be interpreted as indicative of trapping on the surface of the oxide. One argument is the lack of evidence for oxide levels in gas adsorption experiments, such as those of Brattain and Bardeen [17] and Morrison.[18] If the slow levels were levels in the oxide, these levels should shield the sample from the effects of gas adsorption in the same way they shield the sample from the effects of an applied field. The fact that this shielding is not complete is not conclusive evidence that the slow levels are not in the oxide as it may be merely a matter of relative concentrations, but the absence of any observed effects which can be attributed to shielding is indicative that oxide levels are not the dominant form of the slow levels. Another objection to oxide levels is the similarity between the use of illumination (or field effect) and heating to perturb the surface equilibrium (Fig. 3). The two methods would be expected to stimulate a different set of trapping levels if the levels possessed an array of energies, as may be expected (because of the band variation in the oxide, shown in Fig. 7) if the levels are dispersed through the oxide. The illumination experiments strive to distribute electrons into traps with a Fermi distribution characteristic of −44°C; the heating perturbation strives to attain a different equilibrium distribution, that characteristic of room temperature. Thus when the perturbation is removed the initial apportionment of charge in the traps should be different in the two cases. And, with the reasonable assumption that if the levels are spread through the oxide the time constants will correspondingly vary, the relaxation curves should be quite different in the heating and in the illumination experiments. Experimentally they are the same, which leads to the belief that the traps are not dispersed through the oxide.

Another example of experimental results suggesting that the slow surface states do not originate in the oxide is the observation of a simple exponential decay in many cases. Oxide trapping levels would be expected in the simplest case to give rise to a distribution of time constants, with the time constant varying with distance through the oxide. Thus, although the suggestion that the slow surface states are levels in the oxide has not been disproven, it is seen that there is some reason to favor the alternative model involving states on the oxide surface.

As described in the first paragraph of this section, the model commonly used to interpret the slow decay effects leaves unanswered many questions as to important details. We have discussed these questions, and attempted to draw tentative conclusions on the basis of known characteristics. Further experimentation is required to clear up these points in a satisfactory manner.

IV. SPECIFIC MODELS

1. *Heterogeneous Surface Model*

From the non-exponential relaxation curves which have been observed, it is apparent that a single lifetime model cannot generally apply. The two models which have been suggested to account for the non-exponential relaxation are the heterogeneous surface model, due to Kingston and McWhorter [1] and the electron transfer model suggested by Morrison.[2] Both models are based upon the theory of the surface relaxation as outlined in the first paragraph of the last section, and an energy band diagram of the general type shown in Fig. 7. In this paper we shall discuss the experimental evidence for and against the two models, and shall conclude that possibly each model has its range of validity.

The heterogeneous surface model is required [1] by the experimental observations of simultaneous non-exponential decay, linear response (the conductance shift was found to vary linearly with applied field, including a reversal of sign in the field), and the absence of harmonics in the response to a sinusoidal input signal. Based on these properties, the model may apply at low disturbances when non-linear decay does not occur, although it cannot dominate in the non-linear region of Fig. 6.

The characteristic non-exponential decay is demonstrated in the low field measurements of Fig. 6. As pointed out above, there are exceptions to this rule, for exponential decay has been observed in several studies. This is rather a serious drawback to the heterogeneous surface model; if the surface of the samples with non-exponential decay is as non-uniform as the model to be discussed will imply, the occurrence of a completely uniform surface should be a rarity indeed.

The linearity of the response with applied field is also demonstrated in Fig. 6 for applied fields less than 10^5 volts/cm. A non-linear effect at high fields was observed also by Kingston and McWhorter,[19] who, however, restricted their experiments and model to low field measurements. The apparent non-linearity at low voltages is not predicted by either theory, and was not observed by Kingston and McWhorter. It may be, as was discussed earlier, that this low voltage non-linearity may be characteristic of the particular method of applying the field used in the experiments of Fig. 6.

The absence of harmonics in the response of the field effect to a low frequency sinusoidal field is somewhat startling, considering the non-exponential variation of the field effect with time. This observation is the real basis for the heterogeneous surface model; for if each element of area has an identical decay characteristic (similar to that observed in Fig. 6), the output signal would be a badly distorted sine wave. Hence, it is assumed that each element of area decays exponentially, so that the number of charges in each element of area varies sinusoidally under a sinusoidal field. Thus, the assumption necessary to explain a non-exponential relaxation curve together with a sinusoidal response to a sinusoidal signal is a heterogeneous surface where each element of area decays exponentially but the time constant is different at different points along the surface. The elements of area over which the time constant is uniform should be the order of a Debye area as such an area is expected to act as a unit.[1]

The distribution of time constants along the surface can be calculated from curves such as Fig. 2. In the analysis, Kingston and McWhorter made the approximation that the amplitude (Fig. 2) varied as the log of the frequency. This approximation leads to a distribution $g(\tau)$ of the time constants τ, such that $g(\tau)$ varies as $1/\tau$ in the region where the logarithmic approximation is valid. Such a distribution of time constants yields a $1/f$ distribution for the noise power arising from these trapping levels in the same frequency range. The origin of this distribution of time constants of density varying as $1/\tau$ from τ about 0.02 to about 20 seconds was attributed to a variation in oxide thickness or to trapping levels in the oxide. We have discussed the possibility of levels in the oxide in the last section, showing that the evidence at hand indicates they are of minor importance in the process. However, the lifetime may vary considerably through the oxide thickness variation. If there is tunneling through the oxide barrier involved in the electron exchange, the spread in lifetime due to oxide variation will be very wide indeed. Even with no tunneling there may still be a spread in lifetimes, possibly due to the following effect. As the surface charge is discrete, the height of the barrier will vary along the surface, being at a minimum between surface ions. With a thin oxide, the minima will extend through the oxide, producing valleys through which the electrons can leak. The valleys will be less accentuated with a thick oxide, and the net energy necessary in electron transfer will be higher.

The mathematical expression for the distribution of oxide thicknesses in order to obtain the $1/\tau$ distribution of lifetimes is difficult to derive. Kingston and McWhorter show that if the lifetime can be expressed in terms of an activation energy E, then a uniform distribution of E's will give rise to a $1/\tau$ distribution of lifetimes. As the variation in E with oxide thickness is not clear, the model can be carried no further. If tunneling is the dominant mechanism for charge transfer, then E will be expected to be roughly proportional to the oxide thickness. Thus, in the region where there is a uniform distribution of oxide thickness, a $1/\tau$ distribution of time constants will be observed by this model.

The low field behavior, as shown in Figs. 2 and 6, may alternatively be described in terms of a limited number of time constants rather than Kingston and McWhorter's continuous spectrum of time constants. For example, Kikuchi [12] has analyzed his results in terms of two time constants. The results of Fig. 6 below 10^5 volts/cm can be approximately separated into two exponential decays, each with an initial conductance change proportional to the applied voltage and with the time constants independent of voltage. The time constants so obtained are in rough agreement with the values Kikuchi obtained. There are two difficulties with this suggestion. The first is fitting such a model to the experimental data of Kingston and McWhorter, shown in Fig. 2. These curves require more than two time constants to fit them adequately. Possibly three or four might provide an adequate fit. The second difficulty arises in developing a model which will yield single time constants over given small areas of the surface, as required to explain Kingston and McWhorter's sinusoidal response, and yet provide only two widely separated time constants as the net effect. It appears that probably more than two time constants are required.

It should be emphasized that the use of the term "heterogeneous surface model" as discussed above does not necessarily correspond with the normal use of the term, in which usage the energy of adsorption is generally presumed to vary from area to area in the surface. In fact, it has been suggested that in our case the energy level is independent of the particular element of surface area and the heterogeneity arises only with respect to the decay characteristics. There seems no evidence in these results indicating heterogeneity in the surface energy level.

2. *Electron Transfer Model*

The influence of the variation in the potential barrier with a variation in surface charge is considered dominant in the uniform surface model proposed by Morrison.[2] If, for example, there is an excess of negative charge over equilibrium on the surface in the model shown in Fig. 7, the barrier will be high. As the negative charge leaks back into the sample, the barrier will decrease. The variation in the potential barrier as the surface charge tends toward equilibrium is considered the dominant variable controlling the rate of charge transfer.

Consider the diagram of Fig. 7, assuming for example electrons are transferred between the conductance band and the surface states. If the surface barrier V_1 is suddenly changed by application of a field, the rate of electrons crossing from the conduction band to the surface states will be altered, as the barrier restricting the transition is changed by ΔV_1. The rate of electron transfer from the surface states to the conduction band is not altered, the barrier height remaining E_2. Thus, assuming to the first approximation that ΔV_1 is proportional to n, the excess charge induced by the field, we obtain

$$dn/dt = B - A \exp(\beta n) = B[1 - \exp(\beta n)] \qquad (1)$$

where the last form arises because, when $n = 0$, $dn/dt = 0$, for equilibrium. Here B is proportional to $\exp(-E_2 + \mu_s)$, and $\beta n = e\,\Delta V_1/kT$, with β inversely proportional to the capacity between the surface states and the induced carriers. The latter term in Eq. (1) thus represents the rate of electron transfer to the surface states; the first term the rate to the conduction band from the surface states. It is assumed in Eq. (1) that B and A vary much more slowly with n than $\exp \beta n$. By examining diagrams such as Fig. 7, it is clear that an equation of the form of

Eq. (1) is obtained with electron or hole transfer. If an inversion layer or an accumulation layer is present, however, the capacity is much larger and β is much smaller, as the induced charge then appears at the germanium-germanium dioxide interface. In this case a much larger disturbance is required to produce the nonlinear effects of Eq. (1). It has been shown [20] that a set of levels characterized by a decay curve of the form of Eq. (1) may develop $1/f$ excess noise.

The integration of (1) yields

$$1 - \exp(-\beta n) = A_0 \exp(-\gamma t) \qquad (2)$$

where $\gamma = \beta B$ and is the decay constant. With high $n(\beta n \gg 1)$, the model predicts a very asymmetric decay, depending on whether n is positive or negative. With $\beta n \ll 1$, an exponential decay should be observed.

Fitting the series of decay curves of Fig. 1 to Eq. (2), Morrison showed that γ could be represented by $A \exp(-E/kT)$, where E is the order of 0.5 ev. Physically E represents the equilibrium height of the barrier with respect to the Fermi level. The calculated value of β was shown to be reasonable on the basis of the model.

A more dramatic agreement of this theory with experiment is shown in Fig. 6, where the asymmetry of the decay curves at high voltages is apparent. This asymmetry is predicted from the theory; for from Eq. (1) if n is large and negative, $dn/dt \rightarrow B$. If n is large and positive, $dn/dt \rightarrow B \exp \beta n$, a relatively fast decay. It is easy to show that the asymmetry of Fig. 5 is in quantitative agreement with the theory, as the constants B, β, and γ can be easily calculated from the results. As concluded above, B can be calculated from the rate of decay of the "slow" decay near $t = 0$. The value of γ is known from the time constant for $\beta\Delta\sigma \ll 1$, in evidence at large t in all the curves except the high voltage "field off" curves. The value of β can be calculated simply from the "fast" decay as follows: The value of A_0 is $1 - \exp(-\beta n_0)$, where βn_0 for "fast" decay is large and positive, hence $A_0 \simeq 1$. As n decreases with time in the fast decay, βn becomes less than unity, and the curve for $t \rightarrow \infty$ becomes

$$\beta n = \exp(-\gamma t) \qquad (3)$$

Thus the curves for the high voltage "fast" decay at large t must be identical independent of the initial value of n, or the field applied. This phenomenon is observed in Fig. 6, with the curves for field strengths greater than 10^5 volts/cm. Extrapolating the linear portion of these curves back to time zero, Eq. (3) predicts that the intercept should have the value of $1/\beta$. Following these methods of evaluating β, γ, and B, it is found, using the arbitrary units of Fig. 6, that $B = 0.22$, $\gamma = 0.005$, and $\beta = 0.033$. From theory, these must be related by the simple form $\gamma = \beta B$. The result, $\gamma = 0.005$ and $\beta B = 0.007$, shows good agreement.

It must be emphasized that the observations of the asymmetric decay in Fig. 6 have been made for only one surface condition, and no predictions can be made to indicate what fields are necessary under different experimental conditions. The reasons why this particular surface condition was chosen are described with the details of the experiment.

3. *Synthesis of the Models*

It is apparent that a combination of the electron transfer theory, of major importance with large disturbances, and a heterogeneous surface model, which becomes apparent at lower disturbances, will satisfactorily account for most of the slow relaxation phenomena observed. However, there is a basic difference between the heterogeneous surface model as proposed by Kingston and McWhorter, and the heterogeneous surface model as obtained by assuming a "heterogeneous" electron transfer model. The time constant originates in a quite different manner in the two cases. The time constant from the electron transfer model depends on β, which is related to the capacity between the surface states and the induced charge. The time constant Kingston and McWhorter obtained, considering surface barrier variations unimportant, has no similar capacity dependence.

We can obtain an approximate rule to predict when the electron transfer heterogeneous surface should apply and when the Kingston and McWhorter heterogeneous surface should apply. In the derivation of Eq. (1) the variation of A and B with n was assumed insignificant relative to the variation in $\exp \beta n$. If β is so small that this assumption breaks down, then the electron transfer model breaks down. It can be shown using a simplified model that this occurs approximately when β is less than N_s^{-1}, where N_s is the charge density in the surface levels. Now N_s^{-1} is expected to be the order of 10^4 m^2 coul^{-1}. With a Schottky barrier, β should be the order of 4×10^5 m^2 coul^{-1}, whereas with an inversion layer, β should be the order of 4×10^2 m^2 coul^{-1}. Thus, with an inversion layer, the electron transfer model should break down, but may dominate when Schottky barrier effects are important.

Thus, there should be three surface models, (a) the Kingston-McWhorter heterogeneous surface model, where surface barrier variations with surface charge are unimportant, (b) the electron transfer model where surface barrier variations dominate, leading to non-linear effects, and (c) the low disturbance electron transfer model where despite the dominance of surface barrier variations the heterogeneous surface causes non-exponential relaxation effects.

It is possible that this distinction can account for the observed inconsistency in the low disturbance relaxation effects where sometimes exponential, sometimes non-exponential decays are observed. For example, if the surface heterogeneity arises through variations in β, then an almost exponential decay may be observed if the Kingston-McWhorter model is dominant for with this mechanism variations in β do not strongly affect the time constant.

V. CONCLUSIONS

The slow relaxation phenomenon observed on the germanium surface is a very provocative effect and, when some of the difficult points discussed above become clarified by further experimentation, should supply a wealth of knowledge concerning surface phenomena. In the present discussion we have been concerned mainly in the problem of distinguishing between the heterogeneous surface model (Kingston and McWhorter), and the electron transfer model (Morrison). It has been shown that neither model can adequately explain the observed phenomena, but some sort of combination of the two possibly will. The electron transfer model seems dominant when the disturbances from equilibrium are large. When the disturbance is small, which should lead to simple exponential decay by the electron transfer model, the heterogeneity of the surface becomes apparent. Then the variation of lifetime over the surface prevents the simple exponential decay from being generally observed.

The possibility of determining the relative importance of the two extreme models is obviously of great consequence in the understanding of chemisorption, and may be also in the understanding of excess noise. The importance of the relaxation effects in these fields is discussed more thoroughly by other authors in this volume, the chemisorption aspect by Pratt,[11] and the noise problem by McWhorter.[21]

DISCUSSION

J. N. ZEMEL (*U.S. Naval Ordnance Laboratory*): The dc field effects in germanium single crystals have just been discussed by Dr. Morrison. I should like to mention some recent experiments on PbS chemically deposited films which exhibit a dc field effect. The measurements were made in air using a 0.0013″ mica spacer between the film and the field effect electrode. The films were sealed in air and no attempt was made to regulate the temperature. The applied voltage ranged from 0 to 810 volts with both positive and negative voltages being used. The sign of the field effect indicated that the films were *p*-type in agreement with other studies on similarly prepared films. A characteristic resistance versus time curve is shown in Fig. 8 for the case of application of

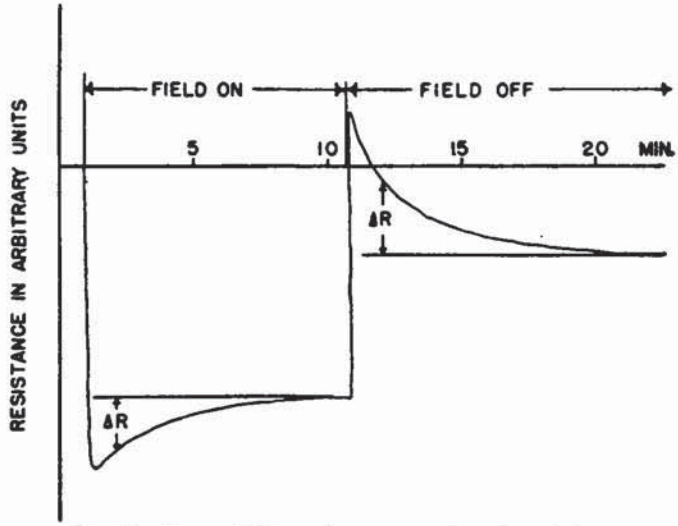


FIG. 8.—Trace of film resistance as a function of time.

−675 volts and recovery therefrom. The logarithm of the change in resistance, ΔR, for these two cases is plotted against time in Fig. 9. The quantity ΔR is based on the terminal value of the resistance after several time constants. For most of the applied

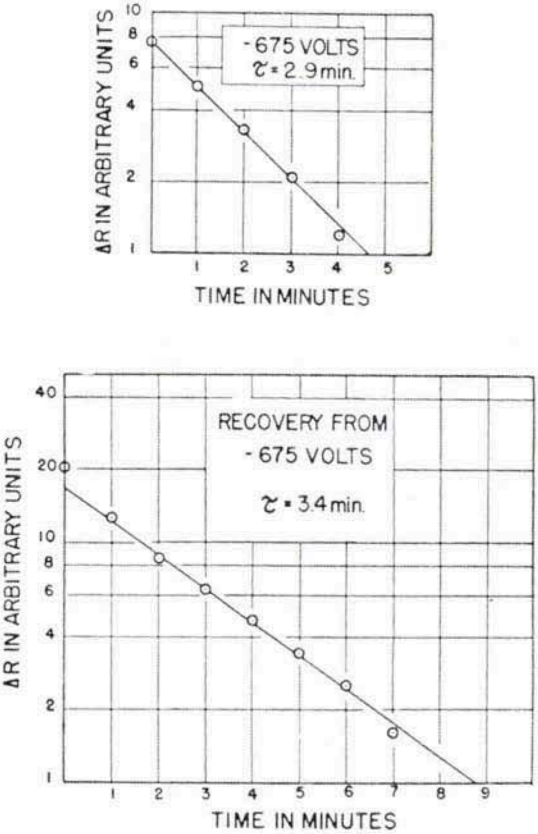


FIG. 9.—Time dependence of ΔR.

fields of either sign, the resistance did not recover to its original value. This became more pronounced with increasing voltage. The plot of log ΔR *vs.* t indicates a reasonably good exponential decay over approximately a decade of resistance.

The time constant varied with application of different voltage as shown in Fig. 10. Of interest are the different signs of the slopes of the log τ *vs.* voltage curves for the two cases, applied field and recovery from the applied field. In addition, the time constants are temperature dependent. A preliminary set of measurements indicate that the barrier responsible for the dc field effect is of

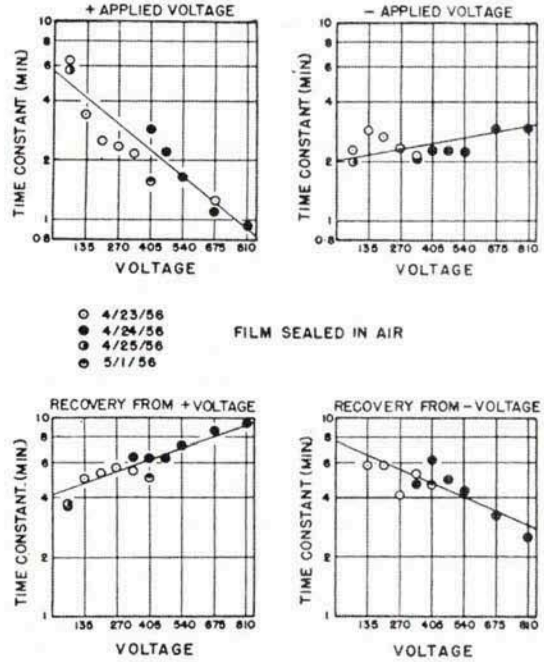


Fig. 10.—Voltage dependence of dc field effect time constants.

the order of 1.5 ev both for applied field and recovery from applied field.

The dc field effect can be described in terms of a Schottky type barrier where the time constants τ obey a relationship of the type

$$\log \tau \sim [Q \pm g(E)]/kT$$

where Q is the height of the barrier at zero field and $g(E)$ is the field dependence of the barrier. Further experiments are necessary to establish the value of Q and the form of $g(E)$.

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EFFECTS OF THICK OXIDES ON GERMANIUM SURFACE PROPERTIES *

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ABSTRACT

The effect of thick oxides on the transient change in the surface conductance of germanium induced by a transverse electric field has been studied experimentally. Oxide layers of various thicknesses were grown by heating etched samples in oxygen for various lengths of time at a variety of temperatures. It was found that the time constant for decay of the field induced surface conductance change was increased markedly as the oxide layer thickness increased. When a very thick oxide layer was grown by prolonged heating in oxygen at 500°C, no decay of conductance was observed. The heavy oxide layer was shown to diminish strongly or eliminate measurable effects of external ambients on the surface potential. Freshly etched samples which had been subjected to prolonged desiccation showed greatly lengthened decay time constants, indicating that water vapor may be the major source of outer surface states.

The existence of surface states at the surface of a germanium crystal has been well established. However, there is still much to be learned about the origin of these states and their interaction with the region immediately under the surface.

Surface states could conceivably originate in a number of ways:

(1) The termination of the lattice with germanium bonds not joined one to the other in the same manner as in the bulk of the material, giving rise to different energy states at the germanium-germanium oxide interface.

(2) Imperfections or impurities arising at either the germanium-germanium oxide interface or throughout the oxide.

(3) The presence of foreign impurity atoms which are physically or chemically joined to the outer germanium oxide surface.

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This study is concerned with the states present on the outer surface of the oxide or through its interior.

Since foreign impurities in the ambient atmosphere are known to affect the surface potential, it would be useful to know more about the relative numbers of states arising from these impurities and those which are associated with the oxide itself.

The field effect has been used in this investigation since it provides the most direct measurements of transfer of charge from the bulk of the germanium to the surface states. It has been found that the charge transfer to the various types of states can be distinguished by the different times required for the transfer to take place, making this approach a very fruitful one.

The application of a dc electric-field transverse to the surface of a freshly etched sample puts an increment of charge into the space-charge region and causes the conductance to change. This change shows an initial transient which may have a time duration from several microseconds to a millisecond. This is the time required for the charge to come into equilibrium with trapping states situated at the germanium-germanium oxide interface and for the product of the free-carrier densities to reach its equilibrium value. The new value of conductance then decays asymptotically with a time constant of the order of a second to the conductance value observed before the field was applied. This long time decay is believed to be produced by a charge interchange between the semiconductor space-charge region and the states in or on the surface oxide layer.[1] If this explanation is correct and if the states are on the outer surface of the oxide, it would be expected that as the oxide thickness is increased the decay time would be correspondingly increased. It would also be expected that the decay time would be affected by the density of the outer states; an increase in the state density causing the decay time to decrease. The growth of a thick oxide may also reduce the effects of ambient changes on the underlying semiconductor space-charge region and thereby stabilize a semiconductor device. For all the reasons stated above, oxide formation and its effects were studied.

The samples studied were 0.010 in. wafers of both *n*- and *p*-type single-crystal germanium.

The field effect measurements were made in a large sealed test tube into which various ambients could be introduced. A dc field was applied between plates and sample causing a change in surface conductance which was indicated by an imbalance of a resistance bridge, one arm of which was the sample itself (Fig. 1). Voltage changes reflecting variations in surface conductance were recorded on a fast dc recorder. The field-effect time constant is arbitrarily defined as the time required for the initial observed conductance change to decay to 40 percent of its original value.

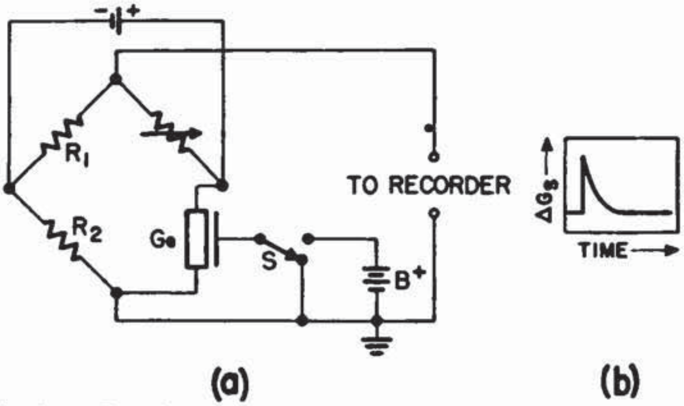

Fig. 1.—a. Experimental arrangement for dc field effect measurements. b. Typical dc recorder trace.

It has been found that as the oxide thickness is increased, the time required for the slow decay shows a corresponding increase. The oxides were grown by heating the samples in an oxygen atmosphere. Heating to various temperatures for different periods of time enabled different thicknesses of the oxide to be obtained. The effects of oxide formation could be observed also by allowing the sample to sit in room air for a period of a few weeks. Germanium wafers that had a 1-second time constant after being freshly etched had time constants of 20 or 30 seconds after being heated in an oxygen ambient at 100°C for 20 hours. Etching restored the one-second time constant but the half-minute time constants were again observed if the samples were stored in room ambient for about a month.

The fact that increased oxide thickness resulted in longer time constants indicates that the trapping states associated with the oxide lie principally at its outer surface rather than throughout the oxide region. If states did lie throughout the oxide region there would be no reason to expect that simply adding additional states would increase the time required for interaction to take place.

The time constant for the long time decay has also been found to be a strong function of the ambient surrounding the sample. It is important to point out that during the study of the field effects under different ambient conditions, the atmosphere about the sample was kept stationary. A gas-flow system had been used at first but then discarded due to the erratic and non-reproducible results obtained. In particular, it had been observed that flow about the sample could produce a change in the sign of the field effect and in the measured time constants. This may be explained by some sort of electrification phenomenon induced by the flow of the gas over the oxide surface of the sample or past the bounding surfaces of the system.

If a sample that had a time constant of about 20 seconds was placed in an atmosphere of 100 percent relative humidity, the time constant decreased to about 1 second. If the sample were then placed in a desiccated atmosphere and checked about 5 minutes later, the time constant had increased again to about 20 seconds. At the same time, of course, presence of the water vapor changed the surface potential. The effect of water vapor on the decay constants is explained by postulating that water vapor forms states on the outer oxide surface, thus increasing the state density and thereby the probability for trapping on the outer surface. Iodine and ammonia vapors were observed to have the same effect as water vapor in causing the time constant to decrease, as well as in altering the surface potential.

It can be seen that the lengthening of the time constants after heating in oxygen might be explained in terms of the removal of water-induced surface states, rather than as the effects of oxide formation. In order to eliminate this dichotomy of interpretations, samples were heated in both argon and oxygen ambients. A typical sample, which had a time constant of 1 second after etching, was heated for 4 hours at 100°C in argon and then for the same time in oxygen. Heating in argon produced no change in time constant; the oxygen treatment changed the time constant to 5 seconds. It follows from this that the oxides were formed on the germanium surfaces during the heat treatment in the oxygen atmosphere, and that these oxides inhibited to some extent interchange of charge between the germanium surface and the states on the outer surface of the oxide.

It was also of interest to measure the change of the time constant of a freshly etched sample stored in a desiccated atmosphere for extended periods. It was observed that this did indeed lengthen the decay constant. Thus, an initial decay constant of 1 second increased to 20 seconds after 4 hours in the desiccated atmosphere and to 5 minutes after 65 hours of desiccation. The latter decay constant fell to 4 seconds, however, after exposing the sample for 2 hours to room air of fairly low humidity. Thus, desiccated samples recover their original time constants on exposure to room humidities. That they do this much more rapidly than samples with grown oxide layers will appear in the later results. The lack of a lengthened decay time after heating in argon, as described in the paragraph above, may now be explained as being caused by the subsequent exposure of the sample to room humidity before testing. The observed effects of desiccation do indicate that removal of water vapor from the vicinity of a germanium surface either greatly reduces the density of the outer surface states or makes charge transfer through even a thin oxide layer more difficult.

As an oxide gets thicker, it should inhibit to a greater extent interaction between the atoms at the outer oxide surface and those of the underlying germanium. This suggests an application to protection of the surface of germanium devices. Samples were baked at 500°C in an oxygen atmosphere for periods long enough to form oxides which displayed interference colors. From these colors it was possible to get a measurement of the oxide thickness, and they were found to be the order of 0.3 microns thick. With these very thick oxides, dc field effects were observed that were immeasurably long in decay time. After the initial conductance change there was no observable decay (see Fig. 2a). Other samples with less thick oxide layers yielded decays with extrapolated time constants of several hours. These measurements show that for a period of several hours at least, there was no interaction between the outer ambient-induced states and the underlying material.

The thickly oxidized samples which showed no field-effect decay still did not show a decay after storage in room air for 1 month.

One of these samples was then placed in air of 88 percent relative humidity for several hours, and the field effect thereupon showed a very slow decay as in Fig. 2b. The sample was then exposed to water-saturated air for 1 hour, and the time constant dropped to 7 seconds. Upon drying the sample in a desiccated ambient for several hours, the time constant became immeasurably long again and remained so after 30 days' storage in room ambient.

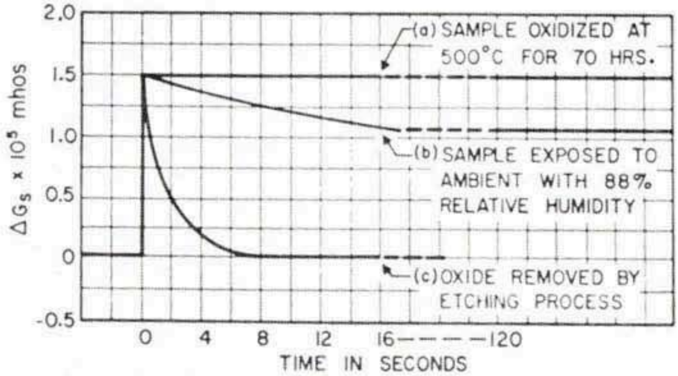

FIG. 2.—Field effect decays for various surface conditions.

In general, the field-effect decay time after exposure of the samples to some given humidity for a given time remained longer for the thicker oxide layers. The sharply increased effect of 100 percent humidity over 88 percent humidity is probably associated with the high solubility of the oxide in water, making possible a closer proximity of the water molecules to the germanium surface region when water vapor condenses. A thickly oxidized sample dipped directly in distilled water for several seconds showed a very sharp drop in time constant, and the oxide film was no longer visible. The effects of a humid ambient, including 100 percent humidity, could always be reversed by desiccation, and this indicates that no permanent damaging of the oxide structure occurred.

To check directly the protective action of the oxide, the heavily oxidized samples were exposed to wet (88 percent relative humidity) and dry-nitrogen cycling. The magnitude of variation in the surface conductance of the sample with respect to ambient change with a thick oxide layer on the sample was in a ratio of about 1 to 10 or 1 to 20 to the variation when no oxide layer was present, the former variation being about 0.02×10^{-4} mhos/square. It is therefore seen that the oxide layer did protect the germanium surface from influence by the ambient.

A thickly oxidized sample was then exposed to iodine vapor which is known to have a very strong effect in driving a surface p-type. The initial field effect of the sample, as with all the oxidized samples, showed an n-type surface. Exposure to the iodine vapor for an hour produced no change at all in the field effect.

This series of experiments indicates that there were no changes in the surface properties even after an hour of exposure to a strong ambient. To determine if there were any effects over much longer periods of time, measurements were made of the dc field effect before and after storing the samples in iodine for several days or more. Observations were made of the sign and the magnitude of the initial conductance change which occurs when the field is applied normal to the surface of the sample. There were no discernible effects on these quantities following the long storage in iodine. Since the sign and the magnitude of the field-effect conductance change are directly related to the quiescent surface potential, the above result shows that the thick oxide layer prevented the iodine from having its usual strong effect on the surface potential, even for exposures lasting a considerable period of time.

The lack of measurable effects on the oxidized germanium may be explained in one of two ways. First of all, if the oxide thickness is increased, the time required for the ambient-induced states on the outer surface of the oxide to reach equilibrium with the underlying germanium can become infinitely long. If this time is truly infinite, then the germanium surface is truly protected. The second explanation is that the change of surface potential required to bring the outer states into equilibrium is greatly reduced.

The second effect is deduced in the following manner. A change of ambient alters the levels and distribution of the outer states, and an interchange of charge, therefore, must take place between the outer states and the semiconductor space-charge region to bring the former into equilibrium with the Fermi level in the semiconductor. The charge interchange bends the semiconductor energy bands at the surface, changing the surface potential, and also produces a potential difference across the oxide layer. These effects are additive in moving the outer-state energy levels to an equilibrium position with respect to the Fermi level. Thicker oxide layers increase the potential difference produced across the oxide by a given charge interchange and minimize thereby the amount of the charge interchange required to bring the outer states to equilibrium with the Fermi level. The resulting change in surface potential is thereby minimized. This problem has been studied by Pratt and Neustadter.[2]

The work as discussed above has given a description of the times required for the surface potential to return to equilibrium but only an indication has as yet been given about the absolute value of the surface potential underneath the oxide. With the application of the dc field normal to the germanium surface the conductance may either increase or decrease. The sign of the change depends on the polarity of the applied field and the value of the surface potential, ϕ_s. The latter quantity is illustrated in Fig. 3 and is the difference between the Fermi potential and the intrinsic potential at the surface. The surface conductance is a function of ϕ_s, and as shown by Schrieffer,[3] the curve is characterized by a minimum in the conductance. Since the field effect senses the derivative of this curve, the change in a conductance of a sample with the negative potential applied to the germanium will be an increase if the surface potential is on the *n*-side of the

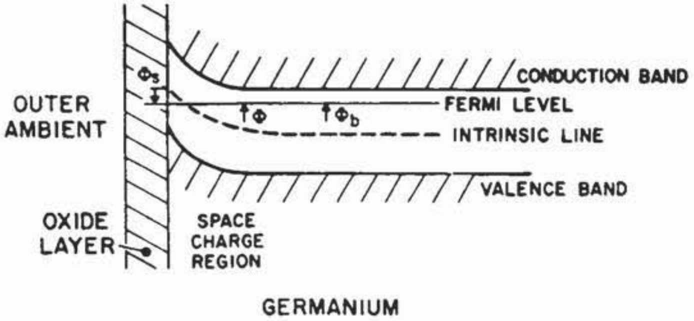

FIG. 3.—Schematic of energy band structure of semiconductor surface region.

minimum. If the surface potential were *p*-side of the minimum and the applied charge within certain limits, the conductance would decrease for the same applied polarity.

Since it was observed that the field effect of all of the samples after oxidation showed the surface potential to be on the *n*-side of the minimum, an attempt was made to determine the absolute value of the surface potential after the oxidation process. The field effect changes sign when the surface potential is about equal but of opposite sign to the bulk potential. (This is also the surface potential at which the minimum surface conductance occurs.) If it is assumed that the surface potential of germanium is established by what is in contact with the surface independent of the bulk properties, then by trying a series of heavily oxidized *p*-type samples of sufficiently low resistivities, a sample that shows a *p*-type field effect should be discovered.

An apparatus similar to that of Low [4] was used. It differed only in the elimination of the mica plate between the germanium and the metal plate and in the use of a 600-cycle ac field rather than a square wave. A definite *n*-type field effect was observed on all samples including those made of *p*-type material as low in resistivity as 1 ohm-cm, indicating that the oxide formation results in a surface potential corresponding to a resistivity at least as low as 1 ohm-cm *n*-type.

Measurements have also been made of the surface-recombination velocity at a heavily oxidized surface. Typical values of the surface-recombination velocity at these surfaces are in the neighborhood of 200 cm/sec. The *s* values are not only constant with different ambients in contact with the outer oxide surface but also remain constant after being stored for 500 hours at temperatures of 100°C in an argon atmosphere. Unoxidized samples do not show this stability when stored under the same conditions.

Assuming that the thick oxides can be formed on diode and transistor surfaces, they should serve to stabilize these devices. However, it is difficult to maintain many of the devices at the high temperatures required for thick oxide formation without having other deleterious effects come into play. It would therefore be advantageous to form the oxides at lower temperature if their desirable characteristics were still maintained. Two approaches to this problem are currently being made; one is by heating the samples in an ozone rather than a pure oxygen ambient in an attempt to form the oxide at a lower temperature; the other is by anodic oxidation in a non-aqueous solution at room temperature. Both of these approaches show promise in that surfaces treated this way show dc field-effect decay times which are relatively long.

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$1/f$ NOISE AND GERMANIUM SURFACE PROPERTIES *

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ABSTRACT

Recent experiments have shown that there exists a set of surface states in germanium with a relaxation time of the order of seconds or minutes. It is proposed that $1/f$ noise in germanium filaments arises from a fluctuation in the occupancy of these states. Such a process could alter the conductivity by producing (1) changes in the majority carrier concentration near the surface, as required to maintain charge neutrality, and (2) an injection-extraction of hole-electron pairs, due to a complex interaction between the surface recombination centers and the slow states. Two ways of obtaining a $1/f$ spectrum have been suggested as a result of field effect experiments on germanium. The first assumes that the time constant, τ, of the slow states varies over the surface with a $1/\tau$ distribution and the second involves a nonlinear effect of the surface barrier. Quantitative calculations are given for the first process and possible origins of the $1/\tau$ distribution are discussed. A review of some of the experimental and theoretical work on $1/f$ noise is also included.

I. INTRODUCTION

As has been discussed in several of the preceding papers,[1-4] recent experiments on germanium surfaces have shown that in addition to the fast-acting surface recombination centers there exists a set of slowly-acting surface states with relaxation times of the order of seconds and minutes. The surface recombination states are presumed to be located at the germanium-germanium oxide interface, while the slow states probably lie in or on the outside of the oxide layer. In this paper we will show how fluctuations in the number of charges in these slow states might account for the so-called excess or $1/f$ noise found in germanium. The first

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part, however, will be devoted to a review of some of the experimental and theoretical studies of $1/f$ noise, especially the work which pertains to germanium. Further references and discussion may be found in a paper on noise in p-n junctions by Petritz[5] and in van der Ziel's book.[6]

In thermal equilibrium any resistive device of resistance R, regardless of its internal structure, shows a mean-square voltage fluctuation across its terminals equal to $4kTR\Delta f$ in any frequency interval Δf (at least up to the infrared region). The application of a dc voltage or current will in general result in an additional amount of noise. Two classes of non-equilibrium fluctuations which are frequently observed under such circumstances, and which have been the subject of much investigation, are shot noise and $1/f$ noise. The term shot noise is now used to designate not only the current fluctuation resulting from the random emission of electrons from the cathode of a vacuum tube, but also the analogous current fluctuation in point-contact or p-n junction rectifiers, as well as the noise produced by the random generation and recombination of charge carriers in a semiconductor.[6] All of these fluctuations have in common a power spectrum which is flat out to the reciprocal of some characteristic time (e.g., the transit time of the electron in a vacuum tube or the lifetime of the carriers in a semiconductor) and which then falls off sharply with increasing frequency.

In contrast to this type of spectrum, many devices when biased with a dc current show an excess noise power which roughly obeys a $1/f^n$ law, with n approximately unity. Such a spectrum was first observed in vacuum tubes where it is known as "flicker noise," but it also occurs, for example, in carbon microphones and resistors ("contact noise"), thin metallic films, point-contact diodes and transistors, junction diodes and transistors, and even single-crystal germanium filaments. This second type of fluctuation, generally known as $1/f$ or excess noise, has been interpreted as arising from a resistance fluctuation since the mean-square voltage fluctuation increases approximately with the square of the dc biasing current.

In Fig. 1 there is shown a typical noise spectrum for an etched germanium filament. At very low frequencies the $1/f$ noise is the major component, but in this sample the shot noise becomes larger at about 200 cps. The shot noise then dominates until the angular frequency is approximately equal to the reciprocal of the minority carrier lifetime, about 50 μsec in this case. At higher frequencies the shot noise decreases sharply, and if the measurements had been taken to high enough frequencies, eventually only the thermal noise component would have been left.

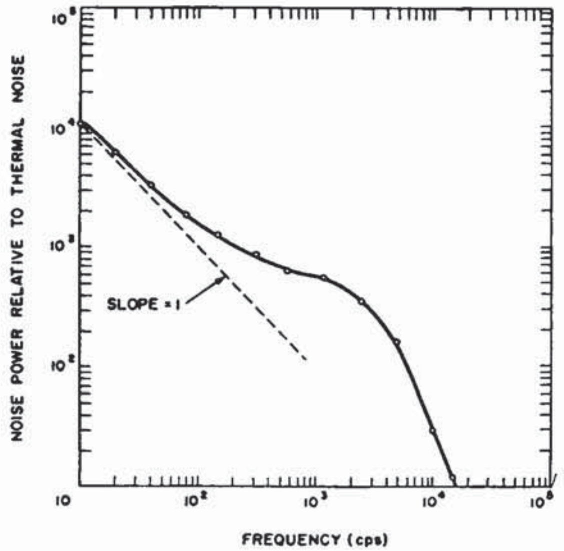

FIG. 1.—Noise spectrum of an etched germanium filament. [After Maple, Bess, and Gebbie, *J. Appl. Phys.* **26**, 490 (1955).]

The approximate $1/f$ law has been found to hold over a remarkably wide frequency and temperature range. In spite of the fact that the frequency range over which it is obeyed cannot be infinite because the total power must be finite, no low-frequency or high-frequency cutoff points have ever been observed for any of the devices mentioned above. Rollin and Templeton [7] found no significant deviation from a $1/f^n$ spectrum down to 2.5×10^{-4} cps for both carbon resistors and germanium filaments, and measurements have been made by Firle and Winston [8] on point-contact diodes down to 6×10^{-5} cps with the same observation. At the other end of the spectrum the $1/f$ noise appears to fall below thermal or shot noise before a high-frequency cutoff point occurs, although for carbon resistors [9] and point-contact rectifiers [10] the $1/f$ component is often still dominant at 1 Mc. In a measurement of the noise in carbon resistors as a function of temperature from 290°K to 4.2°K, Templeton and MacDonald [11] found that not only did $1/f$ noise still exist at liquid helium temperature, but even that the magnitude did not vary by more than a factor of ten or so over the entire temperature range. Russell [12] previously had reported the existence of $1/f$ noise in ZnO crystals at liquid helium temperature with an amplitude insensitive to temperature. Several other devices exhibiting $1/f$ noise, including germanium filaments,[13] have been measured down to 77°K with similar results.

There is some experimental uncertainty as to whether $1/f$ noise in germanium filaments is primarily a majority or a minority carrier effect. Several years ago Montgomery [13] reported that the noise amplitude was affected by magnetic fields in a way which corresponded to the change in lifetime of the minority carriers, and that the noise voltages measured across two adjacent segments of the filament were correlated with a time lag of approximately the minority carrier transit time. However, Montgomery made his measurements before Herzog and van der Ziel [14] had presented experimental evidence for shot noise in germanium filaments, and the effects of shot and $1/f$ noise were not separated in Montgomery's published results. When the work was repeated, exercising proper precautions to ensure that only $1/f$ noise was being measured, he was unable to get consistent results from the magnetic field experiment. The correlation effect apparently still existed, but the delay time could not be measured under the revised experimental conditions.[15] On the other hand, Bess [16] has recently deduced from measurements of Hall effect noise and voltage as a function of the angular orientation of the probes that $1/f$ noise is associated mainly with a fluctuation in the concentration of the majority carriers. The model to be presented in the next section actually gives two distinct effects, one associated with the majority and the other with the minority carrier, so that it is possible to account for the observations of both Montgomery and Bess.

This same work of Montgomery also suggested that the surface was the origin of the $1/f$ noise in single crystal germanium filaments. More recent results now leave little doubt that the noise is predominantly, if not entirely, a surface phenomenon. For example, Maple, Bess, and Gebbie [17] have found that a 10 to 20 db increase in $1/f$ noise, with no accompanying increase in the filament lifetime, may be produced by switching a filament from a dry nitrogen ambient to one of carbon tetrachloride. They have also obtained changes of several db in going from dry to wet ambients. The effect of surface treatment on noise magnitude is even more striking in point-contact rectifiers or *p-n* junctions. Kennedy [18] was able simultaneously to ruin the rectification characteristics and greatly increase the noise in reverse-biased junctions by such techniques as heating the diode or changing the gaseous ambient. However, the unit could always be restored to its former condition merely by re-etching, indicating that only surface changes had occurred. Several other workers have found that exposure of a *p-n* junction to water vapor can increase the $1/f$ noise by many orders of magnitude.[19,20]

The similarity of the $1/f$ noise from the various devices mentioned earlier certainly leads one to look for a common mechanism, but so far it has been difficult to get a satisfactory explanation for even one device. The basic difficulty is that a $1/f$ spectrum, in contrast to a shot noise spectrum, does not appear to be characteristic of any elementary process. However, it has been known for some time that by superimposing shot noise spectra of the type $\tau/[1 + (\omega\tau)^2]$, with a distribution function for the time constant τ which is proportional to $1/\tau$, a $1/f$ spectrum can be obtained.[21] Since the $1/f$ law may be obeyed over ten decades or more of frequency, this approach requires that the $1/\tau$ distribution of time constants cover a correspondingly large range. One plausible way to achieve the desired result was proposed at about the same time by van der Ziel [22] and duPré.[23]

Suppose that the time constants arise from a process involving an activation energy, such as the adsorption-desorption of an ion or the diffusion of an ion, so that τ is of the form $\tau_0 \exp(E/kT)$, where E is the activation energy. A uniform distribution of energies between E_1 and E_2 will then correspond to a $1/\tau$ distribution for τ between $\tau_1 = \tau_0 \exp(E_1/kT)$ and $\tau_2 = \tau_0 \exp(E_2/kT)$. Hence if the noise is produced by a large number of independent processes, each of which gives a shot noise spectrum of the form

$\tau/[1 + (\omega\tau)^2]$, with τ distributed as just described, the total power spectrum will be

$$G(\omega) \propto \left[\int_{\tau_1}^{\tau_2} d\tau/\tau\right]^{-1} \int_{\tau_1}^{\tau_2} (1/\tau)[\tau/(1 + (\omega\tau)^2)]d\tau. \tag{1}$$

If in the frequency range under consideration $\omega\tau_1 \ll 1 \ll \omega\tau_2$, then

$$G(\omega) \propto (kT/\omega)/(E_2 - E_1). \tag{2}$$

The result is a $1/f$ spectrum whose amplitude is only linearly dependent on T if $E_1 \ll kT \ln (1/\omega\tau_0) \ll E_2$ in the frequency and temperature range under consideration. However, as simple as this inequality may appear, the first half cannot be met at very low temperatures by ionic processes. The parameter τ_0 is at least as large as the reciprocal of the "jumping frequency," which is of the order of 10^{13}/sec.[24] Hence just to explain the measurements at liquid nitrogen temperature, which have been made in several devices up to a frequency of 1 Mc, we would need $E_1 \ll 0.09$ ev, and to account for the liquid helium measurements past 10 kc in carbon resistors and ZnO, $E_1 \ll 0.007$ ev. Since this last figure is so much smaller than activation energies for bulk or surface diffusion, or for adsorption-desorption processes, it would appear that such models must be ruled out.

Thus far the discussion has been for $1/f$ noise which was built up from a superposition of shot noise spectra. By using what appear to be highly specialized models, Richardson [25] and Bess [26] have been able to get $1/f$ spectra over a wide frequency range directly from ionic diffusion processes. Other studies by Miller,[27] Macfarlane,[28] and Petritz [29] have shown that diffusion in one dimension can approximate a $1/f$ low over about three decades of frequency. However, regardless of the detailed workings of a particular model, it is apparent on physical grounds that if E_1 is the minimum activation energy involved in the diffusion process and ν is the jumping frequency, then the most rapid fluctuations cannot have a time constant smaller than the order of $(1/\nu) \exp (E_1/kT)$. Therefore, the $1/f$ spectrum must begin to cut off at frequencies of the order of $\omega = \nu \exp (-E_1/kT)$, which leads to exactly the same result as before. Perhaps in some devices at higher temperatures an ionic process may play an important role, but not as a single model to explain all $1/f$ noise.

In addition to these ionic processes several wholly electronic mechanisms for $1/f$ noise have been proposed. In fact the idea of superimposing shot noise spectra was first suggested in connection with electronic lifetimes.[21] The trouble here, of course, is that the lifetime of a carrier is far too short to give a $1/f$ spectrum down to the very low frequencies where it has now been observed. Also there is no experimental evidence for a distribution of lifetimes. One electronic process that is known to give the very long times needed for $1/f$ noise is trapping, as indicated in luminescence work, for instance, where trapping times of hours and days have been observed in some semiconductors. It has sometimes been stated that if the traps were uniformly distributed in energy over a suitably wide range, then a $1/f$ spectrum would be obtained in the manner discussed above. As has been pointed out elsewhere,[20] however, this is not the case since the filling and emptying of a trap involves two time constants, the expected lifetime of the filled state and the expected lifetime of the empty state, and does not give rise to just a $\tau/[1 + (\omega\tau)^2]$ spectrum. A more careful analysis shows that at any one temperature one could obtain a $1/f$ spectrum by assuming an exponential distribution in energy, but that at any other temperature a different spectrum would result. An interesting variation of this model was recently proposed by Burgess,[30] in which he attempted to get a distribution of time constants not by assuming different energy levels for the traps, but rather by taking into account the fact that each trap really communicates with a whole spectrum of energy levels in the conduction or valence band. The electronic transitions from the various energy levels in the conduction or valence band to the trap level are not independent, however, since the trap can hold only one electron. This means that one cannot simply add up the shot noise associated with each possible transition as Burgess did, but instead must take into account the correlation between them. When this is done, only the usual shot noise type of spectrum is obtained,[31] in which the expected lifetimes of the filled and empty states are determined by suitably averaging over all transitions to the energy levels in the conduction and valence bands.[32]

An electronic process involving traps has also been proposed by Shockley [33] in an attempt to explain Montgomery's experimental results. For discussion purposes let us consider the case of an

n-type filament. Shockley suggested that a fluctuation in the carrier concentration might arise from the injection of hole-electron pairs from regions which were less n-type than the neighboring parts of the crystal, or which were actually p-type inclusions. Such injection will take place if these regions contain recombination centers, for an applied field will sweep out the excess holes and thus reduce the recombination rate. Since the generation rate remains constant, the region acts as a natural source of hole-electron pairs. So far this would only give a shot noise spectrum. However, Shockley pointed out that the ability of a recombination center to absorb or emit hole-electron pairs can be modulated by the emptying and filling of an adjacent trap. If one could obtain a $1/f$ spectrum for the trap modulation, then the regions would produce a $1/f$ noise.[34] It was implied that a uniform distribution of energy levels for the traps would give the desired result, but as was mentioned earlier, this procedure will not work.

II. QUALITATIVE DISCUSSION OF NOISE MODEL

In this section we shall describe qualitatively how fluctuations in occupancy of the slow states could give rise to $1/f$ noise, leaving the more detailed arguments until later. If possible, one always tries to analyze complex fluctuations as a sum of a large number of elementary processes which are independent of one another (or more precisely, uncorrelated), for then the total power spectrum can be obtained by simply adding up the spectra from the elementary processes. This approach fortunately can be followed in the present case, but the way in which to analyze the fluctuations is perhaps not immediately apparent. For instance, the filling and emptying of any one of the slow surface states, or traps as they will often be called for brevity, is not independent of the filling and emptying of every other trap. This is because of the very large density of the slow states, which has been shown by several experiments to be greater than $10^{13}/\text{cm}^2$. If only a fraction of these traps became filled, nearly all of the free electrons would be removed from the surface. Hence the chance that one of the remaining traps could also capture an electron would be reduced to zero, whereas for the traps to be independent, the capture probability would have to remain constant.

On the other hand, one cannot treat each charge carrier as a particle which behaves independently of all of the other carriers and try to follow it through its various states; e.g., first free and drifting down the sample, then trapped, then free again, etc. For even forgetting the fact that quantum mechanics would usually forbid distinguishing one carrier from another, there is an objection from the statistical point of view simply because charged particles interact with one another. The probability that a particular electron is in some given region of space depends on how many other electrons are there. If a majority carrier drifts out of the sample, or any smaller region of space for that matter, then within a dielectric relaxation time on the average it is replaced by another majority carrier.

A procedure which does prove to work, however, is to divide up the surface into small regions and ask how the concentration of holes and electrons changes with time in each separate region. Since the shot and thermal noise produced by the motion of the individual carriers is not being considered here, the rapid fluctuations in concentration due to carriers simply wandering through the region may be smoothed out by suitable short-term averaging. What we are interested in is the long-term, quasi-equilibrium change in concentration which occurs when one of these wandering carriers becomes trapped and remains in the region for a long time in the form of a localized, immobile charge. If a majority carrier is trapped, it is quite apparent that the average number of free majority carriers in the region is reduced by almost one to preserve charge neutrality (a fraction of the charge is neutralized by a small average increase in free minority carrier concentration). If a minority carrier is trapped, it might be thought at first that the average number of free minority carriers in the region would be reduced by almost one. This is not the case, however. The trapped minority carrier is simply a localized charge, and like any other charge will be neutralized mainly by majority carriers. The number of minority carriers will decrease only slightly, while the average number of majority carriers will increase by nearly one. Therefore, whether the trapped carrier is a hole or electron, the conductivity of the region will change by an amount corresponding to the gain or loss of approximately one majority carrier, and the change will persist for the duration of the trapping. This process will lead to a $1/f$ spectrum if either (a) each region gives directly a $1/f$ spectrum, or (b) each region gives a shot noise spectrum of the form $\tau/[1 + (\omega\tau)^2]$, where τ is the average time a carrier remains free while in the vicinity of a trap, and the τ's vary over the surface with a $1/\tau$ distribution. The second possibility and the experimental evidence for a $1/\tau$ distribution will be discussed in Section III, while the first will be discussed in Section IV.

Although we will show later that the above process gives the right order of magnitude for the $1/f$ noise, it completely fails to account for the correlation effects observed by Montgomery since the conductivity of each small region of the surface would fluctuate independently of the other regions. However, there is a second type of conductivity modulation arising from an interaction between the slow states and the recombination centers as a result of the behavior of the minority carriers. What has been tacitly assumed up to now is that when a voltage is applied to the sample in order to measure the $1/f$ resistance fluctuations, no disturbance is made in the carrier concentrations. This is a very good approximation for the majority carriers at the surface since their concentration is primarily determined by the necessity of neutralizing the charge in the traps. But the fluctuation of the minority carrier concentration in a given region is not determined by the trap occupancy of that region. These carriers are being constantly swept "downstream" by the applied field and replaced by ones coming from "upstream." If in some region the quasi-equilibrium state produced by a given trap occupancy is such that the majority carrier concentration is low and the minority concentration high, then when a longitudinal field is applied, this region loses its excess minority carriers but retains its low majority carrier density. (The region loses as many majority carriers as minority, but the percentage change in the majority carrier density is negligible.) Since the *p-n* product is now less than its thermal equilibrium value, the recombination rate of hole-electron pairs via the recombination states is reduced, while the thermal generation rate of these same centers remains constant.[35] Thus the recombination centers tend to restore the quasi-equilibrium state, with the result that the region acts as a net source for hole-electron pairs as long as the trap occupancy remains fixed. Conversely, a region which temporarily had a high majority carrier density would act as a net sink for hole-electron pairs.

Since this injection-extraction process will produce a change in the conductance of the sample which is correlated over approximately a life-path for the minority carriers, it could explain Montgomery's results. It will be shown that this latter process gives a $1/f$ noise of the same order of magnitude as the majority carrier effect discussed previously. Depending on the surface treatment and environment, one or the other could easily dominate.

While the injection-extraction process just described is similar in some ways to Shockley's model,[33] and was indeed suggested by this theory, it differs in two important respects. First of all, there were no assumptions introduced about the surface other than the existence of both recombination centers and the slow states or traps, for which there is now direct experimental evidence. Shockley, on the other hand, required the additional existence of certain crystalline imperfections. The other difference is somewhat complicated, but briefly it is this. In Shockley's model the noise was obtained by a modulation of the generation rate of the recombination centers in a fixed region. In the above theory the generation rate was assumed to be constant and there were no special regions. The noise arose from a variation of the recombination rate as a result of a varying p-n product; any given region would act at certain periods as a net injection center for hole-electron pairs and at other periods as an extraction center. Actually the generation rate does decrease when $|\phi_s| > |E_t - E_i|$,[36,37] where ϕ_s is the position of the Fermi level at the surface measured with respect to E_i, the Fermi level for intrinsic material, and E_t is the energy level of the recombination centers. Since ϕ_s changes as the occupancy of the slow states changes, these states could produce a third type of noise on a fairly strongly n- or p-type surface. Although the experimental evidence is slight, it appears that for most surface conditions this last noise effect can be neglected.[20,38]

III. $1/f$ SPECTRUM FROM A DISTRIBUTION OF TIME CONSTANTS

1. *Results of Field Effect Experiment*

The modulation of the surface conductivity of germanium by external electric fields (the "field effect" experiment) has provided much valuable information about the behavior of the slow states. Since such experiments have been reviewed in some detail by Morrison[4] in another paper, we will only summarize here the results pertinent to the $1/f$ noise model.

When the electric field is applied to the germanium surface, it is found that the conductance changes initially because of the induced charge, but then gradually decays back to its equilibrium value in a time of the order of seconds or minutes, in spite of the fact that the field is held constant. (It is just this long decay, and similar ones observed in other surface experiments, which indicate the existence of a large density of slow surface states.) The interesting thing about this conductance decay is that it is non-exponential, even when the applied fields are so small that the surface potential is changed by less than kT/q. The effect at such low fields is not due to a nonlinear process since doubling the applied field doubles the conductance change, reversing the polarity of the field reverses the sign of the conductance change without altering the rate of decay, and applying sinusoidal fields gives sinusoidal conductance changes at the same frequency with no harmonic distortion. In order to analyze these results we may divide the surface into small regions, as was done in the discussion for the $1/f$ noise. If the regions are of the order of a Debye length square (roughly $10^{-5} \times 10^{-5}$ cm), then the conductance of the different regions will vary essentially independently of one another when the electric field is applied.[39] The conductance change due to the i-th region would be expected to be proportional to $\exp(-t/\tau_i)$, where τ_i is the average time that a carrier induced in the i-th region remains untrapped. If there are traps with different capture cross sections in the i-th region, then τ_i would be given by some appropriate average over the various traps since the induced carriers would have only one effective "lifetime" in regions as small as those being considered here. The observed field effect decays can then be explained if it is assumed that the time constant τ_i varies from region to region with a distribution function which is approximately proportional to $1/\tau$.[40] To fit the experimental data, it is necessary that this $1/\tau$ distribution extend in many cases from the millisecond range to times at least as large as 100 sec, and probably much larger. (Experimentally the frequency response was measured instead of the decay transient, and since the lowest frequency used was 0.01 cps, the distribution function for τ could not be determined beyond about 100 sec.)

2. *Noise Produced by Majority Carriers*

As was mentioned earlier, a $1/\tau$ distribution of the time constants is just the result needed to give a $1/f$ spectrum for the noise. In order to show this and also to compute the magnitude of the noise we first need the spectrum for the fluctuations in carrier density from each separate region. This relation has been derived elsewhere on the assumption that all fluctuations are small enough to allow linearization of the governing equations.[20] Since the calculation is somewhat complicated, it will not be repeated here; the result, however, is quite simple. Each region gives a shot noise type of spectrum as if the free carriers within approximately a Debye length of the surface acted as independent particles, each with the same "lifetime" τ that occurs in the field effect experiment. More generally, it is as if an effective number of electrons, N_0, and an effective number of holes, P_0, participated in the trapping per unit area, giving for the spectrum of the number of charges trapped in the i-th region of area S,

$$G(\omega) = S(N_0 + P_0)\{4\tau_i/[1 + (\omega\tau_i)^2]\}. \tag{3}$$

The quantity N_0 is equal to $kT(n_0 - n_{s0})/qE_{s0}$, where n_0 and n_{s0} are, respectively, the equilibrium bulk and surface concentration of electrons, and E_{s0} is the equilibrium internal field at the surface (positive direction outward). If there is no space charge region at the surface and $E_{s0} = 0$, then

$$N_0 = n_0\{kT\kappa\epsilon_0/[q^2(n_0 + p_0)]\}^{\frac{1}{2}} = L_D n_0, \tag{4}$$

where $L_D = [kT\kappa\epsilon_0/q^2(n_0 + p_0)]^{\frac{1}{2}}$ is the Debye length, κ is the dielectric constant, and q the electric charge. Similar relations hold for P_0.

With a dc voltage V_0 applied to a sample of length L, each time a carrier is trapped or released the current will change by an amount $q\mu_{FE}V_0/L^2$, where μ_{FE} is the effective mobility measured in the field effect experiment at high frequencies. (If a large potential well exists at the surface, μ_{FE} may be much smaller than the bulk mobility.[41]) Adding up the contribution from each region, assuming a $1/\tau$ distribution for τ between a lower limit τ_1

and an upper limit τ_2, we obtain for the spectral distribution of the current fluctuations:

$$G_1(\omega) = \frac{4\ LC}{\ln(\tau_2/\tau_1)}\left(\frac{q\mu_{\mathrm{FE}}V_0}{L^2}\right)^2\left(\frac{\mathrm{N}_0 + P_0}{\omega}\right) (\tan^{-1}\omega\tau_2 - \tan^{-1}\omega\tau_1), \quad (5)$$

where C is the circumference of the filament. In the frequency range where $\omega\tau_1 \ll 1 \ll \omega\tau_2$,

$$G_1(\omega) \simeq \{LC/[\ln(\tau_2/\tau_1)]\}(q\mu_{\mathrm{FE}}V_0/L^2)^2(N_0 + P_0)/f. \quad (6)$$

The ratio of this noise to thermal noise is

$$n = (q/kT)\{1/[4\ln(\tau_2/\tau_1)]\}(V_0/L)^2[q(N_0 + P_0)\mu_{\mathrm{FE}}^2 C]/\sigma A f, \quad (7)$$

where σ is the bulk conductivity and A is the cross-sectional area of the sample.

To see what order of magnitude Eq. (7) predicts, we will consider a specific numerical example. Let us assume a filament 0.05×0.05 cm in cross section; a bulk resistivity of 30 ohm-cm n-type, corresponding to a majority carrier concentration of about $5 \times 10^{13}/\mathrm{cm}^2$ and a minority carrier concentration of about $1 \times 10^{13}/\mathrm{cm}^2$; a slightly more n-type surface, as might be produced by room air, with $\phi_s = 0.1$ ev; a dc biasing current of 1 ma; and $\tau_2/\tau_1 = 10^8$. If for this last quantity either 10^4 or 10^{16} were taken, the final answer would be changed only by a factor of two. With these numbers $(N_0 + P_0) \simeq 2 \times 10^{10}$ and $\mu_{\mathrm{FE}} \simeq \mu_n = 3600$ cm²/-volt-sec. The noise ratio n is then found to be approximately $10^4/f$, or about 10 at 1000 cps. Different values of ϕ_s could change this result by an order of magnitude either way.

3. *Noise Produced by Injection-Extraction Effect*

The calculation of the noise produced by the injection and extraction of hole-electron pairs is somewhat more complicated. For the sake of discussion, we will assume that the surface is n-type, and we will also make the important assumption that the slow states communicate primarily with the majority carriers, as seems to be the case experimentally. Since the applied field does not appreciably affect the concentration of the majority carrier, this last assumption means that the fluctuation in the trap occupancy is essentially unchanged by the presence of the field.

To a good approximation, the number of charges trapped in one region of the surface still fluctuates independently of the number trapped in any other region.

If we forget about fluctuations of the order of the minority carrier lifetime or faster, then the number of holes in the sample will be some function of the trap occupancy along the surface. (After a change in the trap occupancy, the hole concentration should reach a new quasi-equilibrium state in a time comparable with a lifetime.) Therefore, if we divide the surface into regions of area S as before, and denote the number of charges trapped in the k-th region by M_k and the total number of holes in the sample by P, the slow fluctuation in P is given to a linear approximation by

$$\Delta P = \Sigma_k \, (\partial P/\partial M_k)_0 \, \Delta M_k, \tag{8}$$

where the subscript 0 denotes that the partial derivatives are evaluated at equilibrium, i.e., for all of the $\Delta M_k = 0$. The number of excess holes in the sample due to generation from the recombination centers of the k-th region is

$$g^{(k)} \tau_p^{(k)} = Sr \, [n_i^2 - n_s^{(k)} p_s^{(k)}] \, \tau_p^{(k)}, \tag{9}$$

where r is the usual recombination coefficient, n_s and p_s are the surface concentration of electrons and holes, respectively, n_i is the intrinsic concentration of holes and electrons, and $\tau_p^{(k)}$ is the expected lifetime of the holes injected from region k. When M_k changes by one electron and the occupancy of the traps in the other regions is fixed, $p_s^{(k)}$ and $\tau_p^{(k)}$ do not change. The former is determined by the traps "upstream" and the latter by the traps "downstream." But $n_s^{(k)}$ will change by approximately $-\Delta M_k n_{s0}/(N_0 + P_0)$. Substituting Eq. (9) into (8) and using this relation, we find that

$$\Delta P = \Sigma_k \, r \, p_{s0} \, \tau_{p0} \, [n_{s0}/(N_0 + P_0)] \, \Delta M_k, \tag{10}$$

where τ_{p0} is the lifetime when all of the ΔM_k are zero. If bulk generation is negligible in comparison with surface generation, as is usually the case in the thin filaments used for noise measurements, then $r n_i^2 \tau_{p0} C = p_0 A$, where as before C is the circumference of the filament, A is the cross-sectional area, and p_0 is the bulk equilibrium concentration of minority carriers. (We will assume that the bulk is also n-type.) Since each hole-electron pair will produce a current $(\mu_n + \mu_p)qV_0/L^2$ when a dc voltage V_0 is applied, the fluctuation in the current due to the injection-extraction process is

$$\Delta I = (qV_0/L^2)[(\mu_n + \mu_p)Ap_0/C(N_0 + P_0)]\Sigma_k \Delta M_k. \qquad (11)$$

The discussion leading up to Eq. (5) shows that the change in current due to the majority carriers (here electrons) is $(-qV_0\mu_{\mathrm{FE}}/L^2)\ \Sigma_k\ \Delta M_k$, so that the total fluctuation in current is given by

$$\Delta I = (qV_0/L^2)\{[(\mu_n + \mu_p)Ap_0]/[C(N_0 + P_0)] - \mu_{\mathrm{FE}}\}\ \Sigma_k\ \Delta M_k. \ (12)$$

Using Eq. (3) for the spectrum of each ΔM_k and averaging over τ with the usual $1/\tau$ distribution, we obtain for the spectral distribution of the total current fluctuation:

$$G_I(\omega) = \frac{LC}{\ln(\tau_2/\tau_1)} \left(\frac{qV_0}{L^2}\right)^2 \left[\frac{(\mu_n + \mu_p)Ap_0}{C(N_0 + P_0)} - \mu_{\mathrm{FE}}\right]^2 \frac{N_0 + P_0}{f} \qquad (13)$$

in the frequency range where $\omega\tau_1 \ll 1 \ll \omega\tau_2$.

The ratio of the new component of the noise to that produced by the majority carriers is $[(\mu_n + \mu_p)Ap_0]^2/[\mu_{\mathrm{FE}}C(N_0 + P_0)]^2$. For the filament used in the previous calculation, this number would be about 80, but with different values for the parameters, the two processes could give about the same value for the noise. As has been mentioned before, both types of noise are of the right order of magnitude to agree with experiment.

4. *Possible Origin of* $1/\tau$ *Distribution*

While the purely phenomenological treatment of the $1/\tau$ distribution which has been used up to now is sufficient for the noise calculations, it would be far more satisfying if some physical explanation could be given. It seems certain from the very long times involved that there is a large potential barrier between the slow states and the germanium surface, and hence that these traps are not located at the germanium-germanium oxide interface. They could arise from imperfections in the oxide layer, or more probably, from ions adsorbed on the oxide surface. If the electron transfer to the traps takes place by thermionic emission over the barrier, then a variation in the barrier height from one region to another over the surface could give a $1/\tau$ distribution if the distribution in energy was uniform over a suitably wide range. This is just the idea discussed in Section I in connection with ionic processes.

Since 1/f noise is characteristically insensitive to temperature, an attractive alternative to thermionic emission is to assume that the electrons tunnel through the barrier. In this case the distribution of time constants could be caused by a uniform distribution in barrier widths, since τ would be given by $\tau = A \exp(Bw)$, where w is the barrier width and A and B are constants.[42] The proof is completely analogous to the one for activation energy processes. Such a uniform distribution of barrier widths would automatically be achieved if it were assumed that the traps were homogeneously distributed throughout the oxide layer. (Of course, the distribution would have to be coarse-grained enough to give a variation in τ from region to region.) On the other hand, if the traps are on the outside of the oxide, then a variation of the oxide thickness along the surface could give the desired distribution of barrier widths. For a variation of thickness from 20 to 40 Å, and a barrier height of one electron volt, the transition times may be shown to vary from the order of 10^{-4} to 10^{4} sec.[20]

IV. 1/f SPECTRUM FROM NONLINEAR BARRIER EFFECTS

If in the field effect experiment very large electric fields are applied to the germanium surface, then in addition to the nonexponential character of the conductance decay one finds certain nonlinear effects.[4] For example, with an n-type surface the initial change in conductance decreases more slowly when the germanium is made the positive electrode than with the opposite polarity. Doubling the applied voltage no longer leaves the rate of decay unchanged. Morrison has proposed that these effects arise because the rate of charge transfer to the slow states depends exponentially on the height of the surface barrier.[43] For fields which change the surface potential by more than kT/q, the equations cannot be linearized. He has also suggested that if this exponential dependence is taken into account, the variation of the barrier height with the number of trapped charges could lead directly to the observed 1/f spectrum without the necessity of assuming a distribution of time constants.[44]

Denoting by ΔM the trapped charge in excess of equilibrium, we have for the rate of change of ΔM

$$d\Delta M/dt = B[\exp(-q\Delta V/kT) - 1], \tag{14}$$

where B is the equilibrium rate at which charge crosses the barrier and ΔV is the change in barrier height produced by ΔM. Morrison assumes that ΔV is proportional to ΔM, so that Eq. (14) becomes

$$d\Delta M/dt = B[\exp(-\beta\Delta M) - 1], \tag{15}$$

where $\beta = (q/kT)\, dV/dM$. The integration of Eq. (15) gives

$$\Delta M = \beta^{-1} \ln [1 - A \exp(-\gamma t)], \tag{16}$$

with A the constant of integration and $\gamma = \beta B$. Equation (16) can be used to calculate the autocorrelation function, and the spectral distribution is then obtained by taking the Fourier transform. Assuming a Gaussian distribution for ΔM with a standard deviation ξ, Morrison finds that a $1/f$ spectrum will result in the frequency range:

$$\gamma \ll \omega \ll \gamma \exp(\sqrt{2}\beta\xi). \tag{17}$$

The difficulty with this model is that it requires far too large a variation in the barrier height. Since experimentally it is known that the $1/f$ spectrum in germanium filaments extends over more than eight decades of frequency, the ratio of the upper to the lower end of the frequency interval in Eq. (17) must satisfy the inequality:

$$[\gamma \exp(\sqrt{2}\beta\xi)]/\gamma \gg 10^8. \tag{18}$$

This means that the rms fluctuation in the barrier height would have to be

$$<\Delta V^2>^{\frac{1}{2}} = (kT/q)\beta\xi \gg (kT/q)(\ln 10^8/\sqrt{2}), \tag{19}$$

or greater than 0.3 ev at room temperature. The carrier concentrations at the surface would therefore have to vary by almost a factor of 10^6 either way. It is obvious that variations as large as these simply would not occur thermodynamically. It is also apparent from the calculations of the last section, which assumed a variation in the barrier height of the order of kT/q, that such fluctuations would produce a noise much too large to agree with experiment.

V. DISCUSSION

A major criticism which might be leveled against any theory linking the $1/f$ noise to the slow states is that the field effect experiment does not always indicate time constants as short as are needed for the noise. A typical set of frequency response curves for the field effect is shown in Fig. 2 of Morrison's paper.[4] Although some curves, like the one taken in dry nitrogen before oxidation, give a value for τ_1 (the lower limit of the $1/\tau$ distribution) less than 10^{-4} sec, others, like the curve taken in wet nitrogen after oxidation, show a τ_1 greater than 10^{-2} sec.

One way in which this difficulty could be overcome is to combine some of the features of Morrison's nonlinear model with the one based on a distribution of time constants. It was assumed in the calculations of Section III that the fluctuations were all small enough to permit linearization of the equations involved. If this were completely true, then certainly the predicted $1/f$ spectrum would cut off at $\omega = 1/\tau_1$, where τ_1 was determined from the field effect measurements at low field strengths. Actually if the rms barrier fluctuation is of the order of kT/q, many of the random statistical swings will carry the system well into the nonlinear region. Morrison's calculations show that this would have the effect of extending the high frequency end of the noise spectrum beyond $1/\tau_1$. Therefore the middle and low frequency end of the spectrum might arise from the $1/\tau$ distribution as before, but the high frequency end from the nonlinear effects.

One final point should be mentioned. Although most of the devices exhibiting $1/f$ noise differ markedly from single crystal germanium filaments in that the current passes through internal potential barriers, essentially the same noise model may apply. Fluctuations in the resistance can be produced by traps located in the barrier regions, since a variation in the trapped charge will cause a variation in the height of the barrier. If the traps communicate with the bulk by electrons tunneling through the barrier, then a $1/f$ spectrum will be obtained if the traps are simply distributed uniformly throughout the barrier region.

DISCUSSION

R. L. PETRITZ (*U.S. Naval Ordnance Laboratory*): Two important characteristics of 1/*f* noise are the large magnitude and lack of temperature dependence. The recent data of Morrison[45] shows that the time constant increases with decreasing temperature. If this is correct then both the model of McWhorter[46] and that of Morrison[47] should be quite temperature dependent. Another question is whether or not their theories can account for the large magnitude of 1/*f* noise as observed, especially when the current flow is across an oxide layer.

I wish to present the idea that the noise arises from local breakdown of barriers, and that the noise energy is supplied by the electric field. Consider first the case where current flows across a barrier as in an ordinary broad area metal-semiconductor contact or a point-contact transistor. The barrier across which the current flows is not of uniform thickness on a microscopic scale. In regions where the barrier is thin it can break down spontaneously, allowing bursts of current to pass. Such local breakdowns can occur while the barrier is still stable macroscopically. The duration of a given current pulse will depend on how long it takes for the local region to rebuild or "heal." Such a "healing" operation can be expected to take place since the electric field will be reduced upon breakdown because of the larger *IR* drop in the surrounding region.

The important feature of this model is that the energy of the noise pulses comes from the electric field, and is not of thermal origin. The randomness comes from the mechanism of the barrier instability—the actual triggering may be of thermal origin. The lack of dependence of the noise on temperature can also be explained because the noise energy is derived from electric fields.

It should be possible to build up a 1/*f* spectrum because the inhomogeneity of the barrier will naturally produce a variation in the degree of local stability. Very thin regions should be less stable and break down rather frequently; thicker regions should be more stable and break down only infrequently. The super-position of such a distribution can be expected to lead to something resembling a 1/*f* spectrum.

So far our description has been for current flow across a barrier;

it now remains to discuss how such a mechanism can describe noise observed in thin crystals where the surface current flow is in a channel parallel to the oxide layer on the germanium surface. Surfaces can be expected to be irregular on the microscopic scale. In a region of the surface where the oxide layer penetrates into the channel the local resistivity and the local field will be higher than average. Breakdown of this region will result in an increase in channel current. Again the energy of the noise pulse is derived from the electric field.

This model may also be applicable to strained crystals [48] which show an increase in $1/f$ noise. The strains produce inhomogeneities in the crystal which become the breakdown points.

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SURFACE STUDIES ON PHOTOCONDUCTIVE LEAD SULFIDE FILMS

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ABSTRACT

The photoconductive properties of lead sulfide films are sensitive to surface conditions because the film is polycrystalline and has a large surface to volume ratio. Furthermore, the diffusion length of minority carriers is much greater than the crystallite size, thus making the lifetime of hole-electron pairs produced in the photoconductive process a strong function of surface treatment. We review a recently developed model based on a system of crystallites of PbS, with an oxide layer surrounding each crystallite. The photoconductive time constant is related to the trapping of minority carriers by surface and/or volume states. Hall, resistivity, and time constant measurements as a function of temperature are analyzed to give the energy levels of the photoconductive traps. Field effect measurements show the presence of fast interface and slow outer surface states analogous to those in germanium and silicon. Further measurements are necessary to determine if the states probed by field effect measurements are the photoconductive traps.

I. INTRODUCTION

Fundamental semiconductor surface studies have been mainly centered on germanium and silicon. It is of interest to see if the basic ideas that have been developed are applicable to other semiconductors. A reasonably complete picture of the bulk properties of lead sulfide has been developed. The intrinsic energy gap is known to be 0.34 ev,[1,2] the scattering of holes and electrons has been studied,[3] donor and acceptor levels have been shown to result from deviations from stoichiometry [2] as well as from impurity atoms.[4] The details of the energy bands are less understood than for germanium, although the first theoretical wave function

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calculations which showed minima at k other than zero were made[5] for the lead sulfide crystal.

Our interest in the surface properties of PbS is related to its photoconductive properties. The PbS film is a sensitive photo detector in the visible and infrared region out to about three microns. PbTe and PbSe, other members of the lead salt family, extend this range to longer wavelengths. The high sensitivity of these detectors has been achieved only in the form of thin polycrystalline films. Such films, of the order of 0.1 to 1 micron thick, have a large surface to volume ratio. Furthermore, minority carriers can readily diffuse to the surface even for lifetimes as short as 10^{-9} secs. Therefore, time constant phenomena can be expected and are found to be very sensitive to surface conditions.

II. MODEL

A brief description of our model of the PbS film is given below; a more complete description will be found in reference 6. The film is composed of a system of crystallites of PbS with intercrystalline barriers of a physical size of about 10A. The intercrystalline barrier region is an oxide of lead or lead sulfide.[7] It occurs between the crystallites as well as on their outer surface. Figure 1 represents a series of crystallites with intercrystalline oxide barriers. The outer surface can be represented by a crystallite and a barrier as

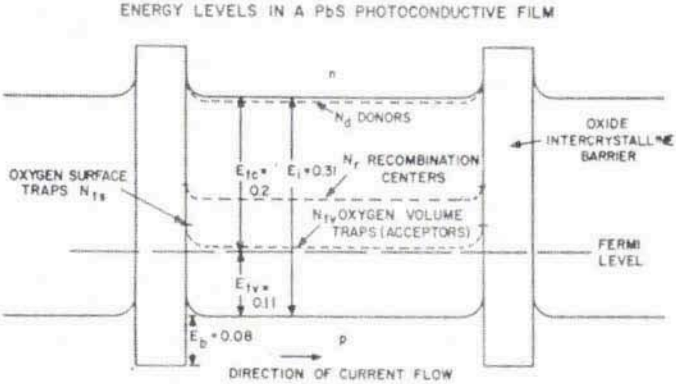

FIG. 1.—Energy levels in a PbS photoconductive film.

shown in Fig. 2. This barrier height may be considerably different from the intercrystallite barrier height.

The space charge region in the PbS crystallite has not been studied experimentally, but theoretical calculations have been made.[8,9] In the case of chemically deposited films it is likely that the space-charge region is of the accumulation type as shown in Figs. 1 and 2 because the sensitization occurs during the deposition process. Thus the whole crystallite is probably *p*-type, the surface being somewhat more *p*-type.

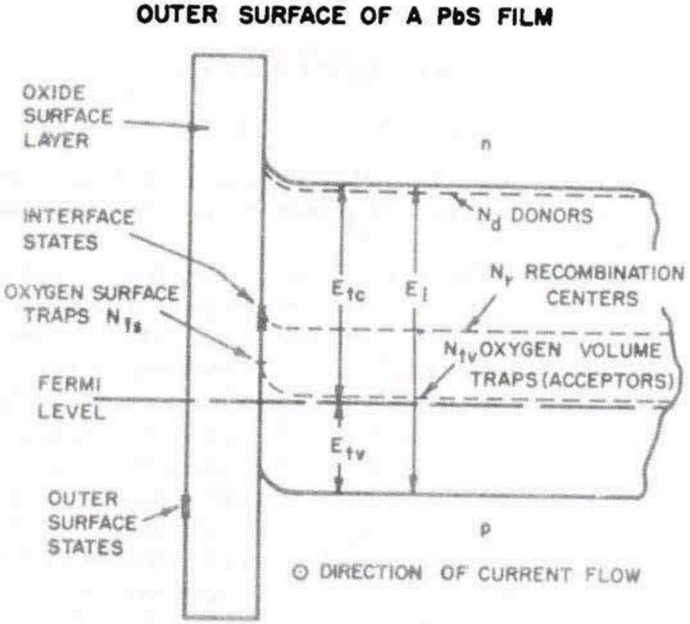

FIG. 2.—Outer surface of a PbS film.

In the case of evaporated films an *n*-type film is first deposited. Resistivity and thermo-electric-power measurements show that exposure to oxygen converts the film to *p*-type. The major part of the crystallite is therefore *p*-type but it is possible that an *n*-type region exists in the interior of the crystallite.

For the present we shall characterize the PbS crystallite by an average majority carrier density, *p*. This should be adequate for the chemically deposited film (accumulation type surface) and a first approximation to the evaporated film.

The conductivity of the film can be written [6] as

$$\sigma = q\,p\,\mu^*, \tag{1}$$

$$\mu^* = \mu \exp\left(-E_B/kT\right), \tag{2}$$

where E_B is the height of the intercrystalline barriers (Fig. 1) and μ^* is the effective mobility of the holes, as limited by barriers.

The Hall coefficient of this system [10] is

$$R_H = 3\pi/8q\,p, \tag{3}$$

and the effective mobility is related [6] to the Hall mobility by

$$\mu_H = R_H\sigma = 3\pi\mu^*/8. \tag{4}$$

It is necessary to make both Hall and resistivity measurements in order to separate effects arising from carrier density from those due to intercrystalline barriers.[6]

The response to radiation is directly proportional to the photoconductive time constant τ. The sensitization of films is accomplished by increasing τ.[11,12] In a freshly evaporated PbS film the photo-response is very small and τ is very short. During the sensitization process the time constant increases by at least three decades (from 10^{-7} to 10^{-4} sec). Exposure of freshly deposited PbSe films to various ambients,[11] including sulfur, selenium, and the halogens, showed that sensitization consisted of more than simply a shift of the Fermi level with respect to states already in the system. All of the above gases converted an n-type film to intrinsic and then to p-type, but only oxygen produced appreciable sensitivity. It was therefore concluded [11,12] that the oxygen introduced minority carrier traps (electron traps). Thus, when a hole-electron pair is created by absorption of a photon, the electron is trapped and the hole is free to conduct. The cross-section for a hole to combine with an electron in a trap is very small. When the electron escapes to the conduction band it can recombine with a hole through recombination centers. The photoconductive time constant, τ, therefore is the majority carrier lifetime and the change in conductivity is proportional to the change in the density of majority carriers.

III. DETERMINATION OF THE ENERGY LEVELS OF TRAPS AND BARRIERS

The energy levels of the traps and barriers are determined from the temperature dependence of the Hall coefficient, resistivity, and time constant. Figure 3 is a semilogarithmic plot of R_H, ρ, and μ_H versus $1/T$. The slopes of these curves give activation energies directly because the system is compensated and the Fermi level is fixed at or near the trap levels. Since the film is *p*-type, log R_H versus $1/T$ is a measure of the freezing out of holes, and its slope gives E_{tv}, the energy of the traps above the valence band. The

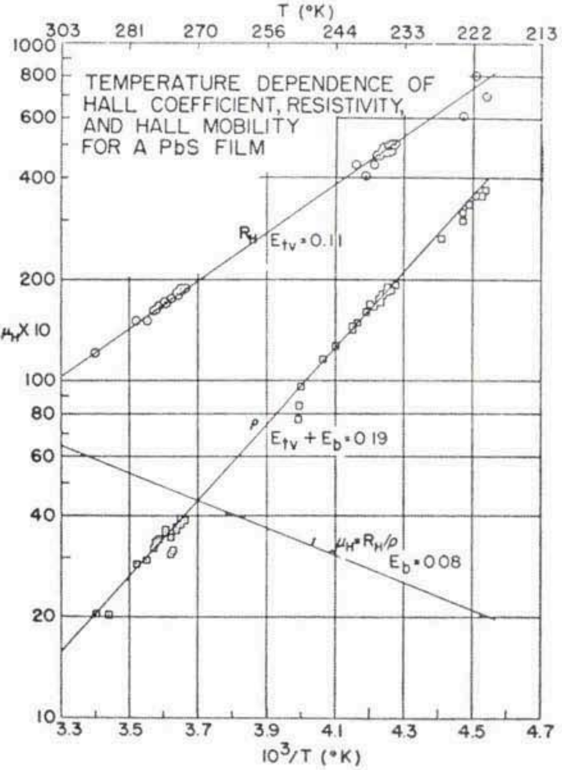

FIG. 3.—Temperature dependence of Hall coefficient, resistivity, and Hall mobility for a PbS film.

curve of log ρ *vs.* $1/T$ includes the effects of barriers. Its slope gives $(E_{tv} + E_B)$ and thus the barrier height is obtained.

The slope of log τ versus $1/T$ at room temperature (Fig. 4) gives the energy E_{tc}. This is because τ is proportional to the time an electron spends in a trap before being excited to the conduction band. At lower temperatures τ approaches a maximum, indicating that electrons are in the traps sufficiently long for holes to recombine with them.

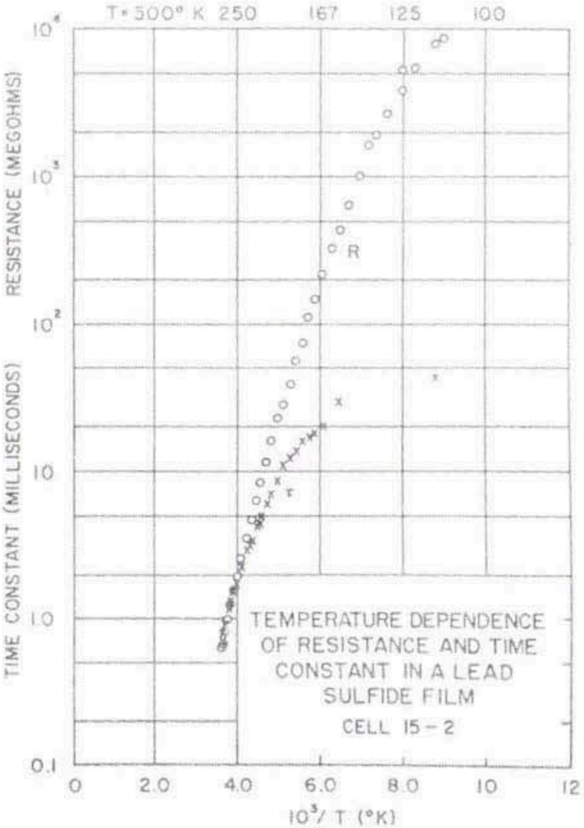

Fig. 4.—Temperature dependence of resistance and time constant in a lead sulfide film.

The resulting energy level diagram is shown in Fig. 1. A check on this interpretation is that $E_{tv} + E_{tc} = 0.31$ ev, in reasonable agreement with the intrinsic energy gap of lead sulfide. Note that we are not relating the slope of log ρ *vs.* $1/T$ to the intrinsic energy gap, as has been done elsewhere.[9]

Further evidence for our interpretation is that log R *vs.* $1/T$ (Fig. 4) does not change slope appreciably over the temperature range, 110°K to 300°K. It is unlikely that the freezing-out process being observed is an intrinsic one; rather one would expect an impurity effect to dominate at these temperatures.

Comparison of our Hall and resistivity curves with those observed on germanium doped with elements that provide deep traps[13] suggests further that oxygen provides a deep trap in lead sulfide. It is probable that these traps are on or near the surface of the PbS crystallites but the possibility of their being volume traps cannot be ignored. The field effect studies were undertaken in part to determine whether the traps are surface or volume states.

IV. FIELD EFFECT STUDIES

Field effect measurements are made on chemically deposited PbS films by placing a thin sheet of mica over the film, and a metal electrode on the mica. Application of a voltage to this condenser (film and electrode) changes the number of majority carriers in the crystallites. The geometrical surface area of the condenser represents only a part of the total surface area[14] of the film; thus the field effect does not probe the entire surface of the crystallites.

A typical fast field effect curve obtained by the Low technique[15] is shown in Fig. 5. The decay time is about 250 μsecs. This indicates the presence of interface states as shown on Fig. 2. Further measurements are required to determine the energy levels of these states and whether they are the photoconductive traps.

The quasi-equilibrium (ac) field-effect shows the surface to be *p*-type as in Fig. 2. The use of ambient gases and light to vary the surface potential may lead to information concerning the relation of space-charge regions to the mechanism of photoconductivity.

The dc field effect has been investigated by J. Zemel as reported elsewhere in this volume.[16] His Fig. 1 is a plot of a typical trace, and Fig. 2 shows log ΔR *vs* t. These results indicate the presence of slow outer surface states which we show schematically in Fig. 2.

V. CONCLUSIONS

Field effect studies show that the surface of lead sulfide photoconductive films resembles that of germanium in having fast interface and slow outer surface states. Photoconductive measurements indicate that the photoconductive properties are related to oxygen traps which are probably surface states but also may be volume states. Further experiments are necessary to determine if the states probed by field effect measurements are the photoconductive traps.

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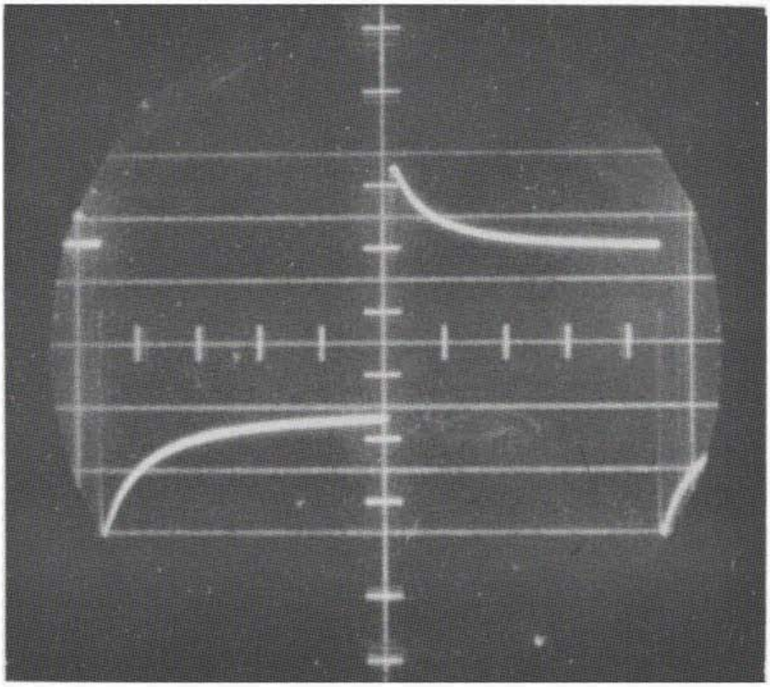

FIG. 5.—Fast field effect on a lead sulfide film. Conductance *vs.* time (200 μseconds per division).

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SURFACE STUDIES ON CLEAVED CRYSTALS OF LEAD SULFIDE

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ABSTRACT

A method for producing and maintaining clean surfaces on a semiconductor crystal is described. The clean surface is obtained by cleavage; contamination by active ambient gases is inhibited by use of atmospheric pressure of argon. The effect of adsorbed ambient on the crystal surface is studied by means of the Valdes lifetime experiment.

I. INTRODUCTION

A clean surface on a semiconductor crystal may be obtained by two different methods. In the first, currently used for germanium, one starts out with an initially dirty surface and tries to clean it by various ion bombardments, baking and annealing treatments in ultra high vacuum. In the second, which will be the subject of this paper, one starts out with an initially clean surface as obtained by cleavage of a crystal and tries to prevent it from becoming dirty.

It is generally agreed that a cleaved surface provides the nearest approach to an ideally clean surface. Germanium does not cleave easily while crystals of PbS may be readily cleaved along (100) planes. In this respect PbS offers a definite advantage over Ge as a material upon which to make studies of surface effects.

II. THE EXPERIMENT

A cleaved surface presents an array of unsaturated bonds on which an active gas such as oxygen or water vapor may be bound. The rate of coverage of such a surface may be inhibited by reducing the density of active molecules and by reducing their diffusion rate. These two quantities tend to go in opposite directions as the total pressure is reduced until the mean free path of the molecule is comparable to container dimensions. Pressure reduction beyond this results in a rate of surface coverage which depends only on density and is no longer diffusion limited. Most clean surface studies have been made in this region of pressure where, for example, at 10^{-10} mm of Hg coverage rates are so low that it takes several hours to form a monomolecular layer.

We propose another method for inhibiting the rate of coverage of a surface. If we have a low partial pressure of an active gas mixed in an atmospheric pressure of an inert gas, the diffusion rate of the active gas is reduced over that in a vacuum by approximately the ratio of partial pressure to total pressure. We assume for simplicity that the active gas and the inert gas have about the same molecular weight. The rate of coverage of a surface may therefore be decreased by orders of magnitude over the coverage under vacuum conditions by the inclusion of the inert gas at atmospheric pressure.

Let us compare the coverage time for the same oxygen density in vacuum and in argon at atmospheric pressure. For the oxygen density we shall use the value set by the limit of sensitivity of the mass spectrometer used for analyzing the argon, 50 parts in a million. This corresponds to a vacuum of 10^{-2} mm of Hg. For this pressure, if each molecule striking a surface stays there, the coverage time would be about 10^{-3} seconds.

In argon at atmospheric pressure the coverage would be diffusion limited. According to kinetic theory, diffusion is about 10^{5} times lower at atmospheric pressure than in a vacuum of 10^{-2} mm of Hg. Coverage time would be about 10^{5} times longer or about 10^{2} seconds in argon with the above oxygen content. An equivalent vacuum giving this coverage time would be about 10^{-7} mm Hg.

In the above analysis the estimate of oxygen content of the argon and the sticking probability of oxygen on PbS are believed to be conservative. On germanium for example the oxygen sticking probability[1] is about 10^{-2}. True values for these quantities may lead to a lower estimate of oxygen partial pressure than the one given. On the other hand convection currents in the argon atmosphere will increase the rate of coverage by an amount difficult to estimate. An experimental study may be the best way to evaluate this technique for keeping a surface clean.

The experimental set up has the advantage of providing in a relatively short time an evaluation of this technique of keeping a surface clean. We cleave the crystal in an atmosphere of pure argon. Since argon is more dense than air, we fill an open top container from the bottom as shown in Fig. 1. The rate of flow of argon is just sufficient to retard the diffusion of air in from the top of the container. It is less than $\frac{1}{2}$ liter per minute. A crystal, cleaver, tweezers, etc., are placed at the bottom of the container which is then flushed for about an hour with argon. By operating through the open top one can cleave the crystal, mount it in the sample holder and carry out the experiment entirely in the argon atmosphere. A loose fitting cover with suitable openings for the light beam and the point contact manipulator handle is placed on the box while carrying out experiments lasting several hours. This reduces the possibility of errors due to air currents.

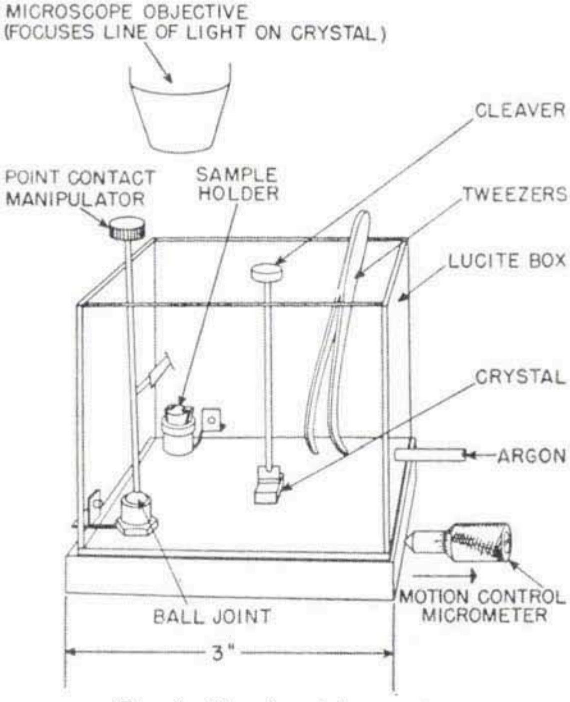

FIG. 1.—Experimental apparatus.

We have chosen to check the effect of ambients on cleaved surfaces by studying the lifetime of carriers by the Valdes method [2] which is simple and quite sensitive to surface effects such as inversion layers. Carriers are injected into an *n*-type crystal of PbS by a line of light. They diffuse away and are collected at a tungsten point. The signal is an exponential function of the diffusion distance. By making the assumption that the effective mobility is the same as the bulk mobility one can obtain the lifetime from the diffusion distance. The experimental behavior of the signal *vs* diffusion distance was studied over three orders of magnitude on these crystals and the data appeared to fit the Hankel function solution of the diffusion equation.

The time constant was measured on freshly cleaved surfaces as a function of time after cleavage. The results are shown in Fig. 2 for two different (100) cleaved surfaces from the same crystal. The cleaved surfaces were mirror-like. Sometimes one gets a small increase in τ the first 10 or 15 minutes after cleavage as seen on curve 1 of Fig. 2. It does not always appear as for example in curve 2 of Fig. 2. The lifetime was about 8 microseconds for both

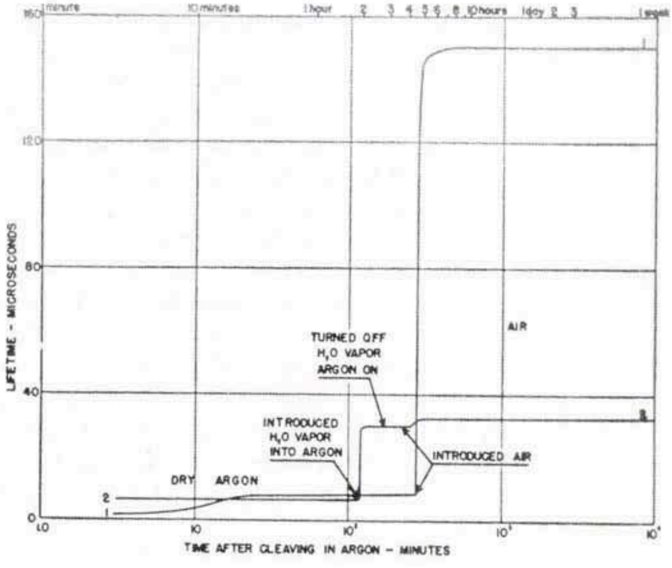

FIG. 2.—Time constant *vs* time after cleavage.

crystals in argon and remained at this value for several hours. The time was limited only by the available supply of argon.

The effect of different ambients was studied. In one case the argon was turned off after 4 hours so that air could diffuse into the container. The time constant rose quickly to a value of about 150 microseconds and remained there for 7 days. In the other case the dry argon was saturated with water vapor. Again the time constant increased rapidly stabilizing at 30 microseconds. The effect was not reversible and subsequent exposure to air produced no significant change over a period of several days.

III. ANALYSIS OF RESULTS

We shall not discuss the meaning of the lifetimes of carriers in PbS at this time. It is possible that the large values of τ we observe for PbS crystals may be due to an inversion layer and some of the storage effects described by B. H. Schultz.[3]

If we consider the values of time constant as representing the surface conditions we note three interesting features of these curves. First there is a plateau at about 8 microseconds for both crystals in argon. Second there is the drastic increase in time constant when the surfaces are exposed to appreciable pressures of active gases. Finally, the time constant immediately after cleavage is sometimes very short, of the order of a few microseconds, as in curve 1, Fig. 2. The fact that this is not always found as in curve 2, Fig. 2 is puzzling although it occurs more frequently than not in crystals studied so far.

Two alternate explanations may be offered for the observed behavior. If we assume that measurements for curve 2 were not made soon enough after cleavage to obtain the initial low value then one might interpret the results as follows. The initial one microsecond time constant represents the clean surface. The eight microsecond part of the curve represents a chemisorbed monolayer of oxygen contained as an impurity in the argon and the very large values of τ in air or water vapor represent chemical reaction between the ambient and the PbS such as the oxidation of the surface.

Experiments on the reaction of oxygen with thin films of PbS[4] suggest that at room temperature chemisorption is the predominant reaction and that chemical reaction between PbS and O_2 is considered to be negligible. At a higher temperature, 300°C, this chemical reaction occurs predominately. If these conclusions apply to clean surfaces on PbS crystals then the alternate explanation is that the long time constants observed when the surfaces are exposed to active gases may not be due to chemical reactions at the surface but may be due to a chemisorbed monolayer. The eight microsecond time constant under these conditions represents the clean surface. Minority carrier lifetime in these crystals as measured by the photoelectromagnetic-photoconductivity ratio method is also eight microseconds. The initial short time constant sometimes observed shortly after cleavage may be due to the presence of strains in the crystal resulting from the cleavage. This need not always occur at cleavage and when present may heal in a few minutes, due to ionic mobility. Further experiments, particularly in a high vacuum, may help decide between the two explanations.

IV. CONCLUSIONS

Cleaving a semiconductor crystal in an atmosphere of pure argon offers attractive possibilities for carrying out clean surface experiments. Preliminary experiments using rather simple techniques indicate that this method provides a surface condition on a cleaved crystal which changes drastically upon exposure to active ambients suggestive of the formation of a chemisorbed monolayer. Further experimental work is required to establish the preliminary conclusion that the method described produces a clean surface.

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INTRODUCTORY REMARKS:

BRIDGES OF PHYSICS AND CHEMISTRY ACROSS THE SEMICONDUCTOR SURFACE

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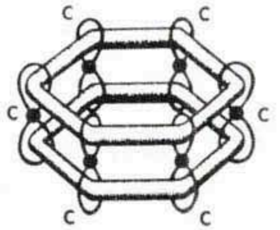
The introduction of this session marks a rather unusual meeting of investigators from fields of physics and of chemistry. It takes place around a subject which is becoming increasingly recognized as one of mutual interest and importance: the boundary of the solid. The *physicist's* attention was drawn to it mainly due to the influence of the boundary on the behavior of the atmosphere of electrical carriers, electrons and holes *within* the solid. On the other hand, the *chemist* has been concerned with its influence on the atmosphere of atoms and molecules *externally* surrounding the solid.

It is appropriate at an occasion like this to draw a brief sketch of some of the language and the basic concepts with which the two groups of investigators have dealt, especially with a view to analogous phenomena and experiences, and to concepts which do or may merge beyond the mere existence as analogies.

In our first lesson on solid state physics we discuss the splitting of energy levels and the creation of new ones when putting together a structure of very many individual atoms in a periodic manner. The quantum chemist is also well acquainted with this phenomenon. He has laboriously investigated the chemical and therefore electronic properties of first small diatomic and then larger and larger polyatomic aggregates.[1] Here, furthermore, the chemist too has been led from the concept of strictly localized bond electrons to that of wave functions extending continuously throughout the molecular aggregate. In butadiene, an aggregate of 10 atoms, or benzene (12 atoms) atomic p-orbitals of neighboring carbon atoms, overlap to form sausage-like continuous molecular π-orbitals (Fig. 1a). This implies equal "ownership" of electrons by the atom sites, and therefore mobility.[2] In fact, the treatment of these electrons as completely free electrons in a

(a) THE -MOLECULAR ORBITALS IN BENZENE



(b) REACTIVITY:

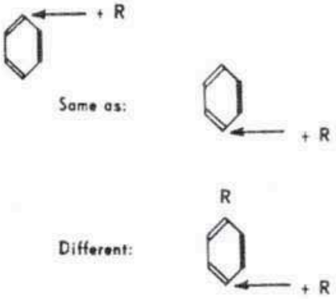


FIG. 1.—The benzene molecule. (a) Representation of nature of molecular orbitals. (b) Initial equivalence of any carbon position; but change of reactivity due to contact with chemical group at one spot.

simple potential box characterized by nothing but the dimension of the molecule leads to remarkably accurate quantitative prediction of energy levels in polyenes, polymethines, and cyanine dyes.[3] In this, the chemist has learned of mobility or common "belonging" of the electrons, and of the fact that this enables a profound redistribution of electron densities throughout a molecular structure when a chemical entity having a different electron energy level is contacted at one point (Fig. 1b). This is the "induction effect" of the organic chemist, whereby the addition of a chemical group to one carbon atom will change the reactivity of another carbon atom in the structure thereafter.[4]

Let us examine some of the worries of the physicist with the more macroscopic structure of the semiconducting solid. He has been concerned with the manner by which his otherwise periodic solid aggregate is terminated at the interface, and with what might be the resulting energy levels. The *mathematics* of an abruptly terminated periodic structure calls for *new* energy levels, for example the Tamm states. It is still not completely clear just what is the contribution of these idealized levels in the case of real surfaces. For by the time we are confronted with a real surface, chemical or structural alterations within the surface may have been brought about by the very same disturbance of periodicity which forces the mathematics into Tamm states; e.g. hydroxyl group termination in oxides, geometric lattice adjustments, etc.[5] However, the effect of entities *adsorbed* from the surrounding atmosphere on the energetics of the surface is being recognized as one real factor, as will be evident from the material presented at this meeting.

The chemist working on the other side of the surface has been aware of the existence of certain strong adsorption of atoms and molecules from gases or liquids on the solid interfaces. The relative specificity of some of these cases of adsorption, the energetics, and rate processes were remindful of chemical bond formation, and therefore the term chemisorption was coined, already implying electronic interaction with the solid. It was logical to consider the possibility of "compound formation" between adsorbate and the *solid as a whole*, accompanied by donation or acceptance of electrons by one or another depending on the relative position of the chemical potential in the adsorbate and in the solid (i.e. the Fermi level). This was described in detail by Dowden.[6] Such a contact between an adsorbate and a semiconductor must then lead to charge redistribution analogous to that occurring on contact between semiconductor and another, dissimilar solid. Possible consequences of the boundary layer phenomenon on amounts and heats of chemisorption were developed by Aigrain and Dugas,[7] Hauffe and Engell,[8] and Weisz,[9] consequences on sorption and catalytic rate processes by Weisz,[9] Hauffe [10] and Morrison.[11] As shown in a simplified, one-dimensional sketch in Fig. 2, an electrical potential will be built up within the solid until the magnitude of this potential is equal to and just opposes the chemical potential difference, E_0, between the contacting entities. In this process atoms or molecules on the surface involve an appreciable depth of the solid in charge rearrangement, this depth d_B being dependent on E_0, and on the concentration of donor or acceptor levels. There are three interesting observations to be made: a) the driving force is the chemical potential difference, b) the charge rearrangement is possible because of continuous electron (or hole) *mobility* throughout the structure, c) the resulting distance of involvement can be quite appreciable, compared to atomic or molecular dimensions.

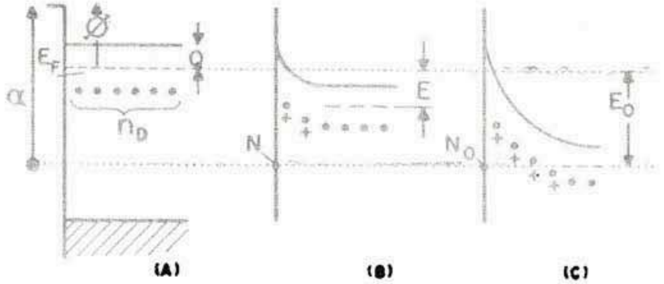


FIG. 2.—Energy diagrams of semiconductors (a) before, (b) after partial, and (c) after equilibrium chemisorption on surface. The abscissa represents depth (x) into the semiconductor (from reference 9).

[For the effective depth d_B, we have for the simplest case of the saturation layer

$$d_B = 10^3(\epsilon E_0/n_d)^{\frac{1}{2}},$$

wherein ϵ is the dielectric constant of the solid, E_0 is in ev's, and n_d the concentration of donors (or acceptors). This might be compared to the range of the Coulomb potential, d, originating from the individual surface charge before it drowns in thermal noise,

$$P_{ev} = 7.2 \times 10^{-8}/\epsilon d \approx kT/e.$$

For the example of $\epsilon \sim 5$, $E_0 \sim 4$ ev, we get $d_B > d$ when $n_d < 4 \times 10^{19}$.]

The chemist will readily recognize these three characteristics as rather analogous if not identical with the features of the aromatic or conjugated unsaturated molecule discussed above, the shifting of the electron distribution along the entire molecule on contacting one point with a foreign group. This important analogy will be carried further in a moment.

What are some of the most notable topics studied in chemisorption? a) The variation of heat of adsorption with amount adsorbed, b) rapid changes of the *rates* of chemisorption with amount adsorbed, c) the possible heterogeneity of the surface, as suggested by the observations (a) and (b).

Let us briefly examine these subjects in the light of chemisorption accompanied by charge transfer. As chemisorption proceeds, the potential of the electrical barrier layer grows; a progressive change of the Fermi level of the solid relative to the adsorbate molecule is effected. Thus the energy release for successive electron transfers changes.[7,8,9] Just as in the case of "induction" in the benzene molecule, adsorption modifies the electron distribution in the aggregate, and thus its energy state with respect to *succeeding* adsorption.

Now concerning the chemisorption rates. They have been observed to change in an exponential manner with the amount adsorbed,[12,13,14] i.e.

$$dn/dt = ae^{-bn};$$

or in its integrated form

$$n = (1/b)[\ln (t_0 + t) - \ln t_0]; \; t_0 = (ab)^{-1}.$$

This rate law is often referred to as the Elovich equation. In case of the barrier layer model, rates are limited by the ability of electrons to pass the potential barrier; and since this barrier rises with the amount adsorbed, a rate law with the amount adsorbed in the exponential is indeed a necessary consequence.[9,15]

Concerning heterogeneity, its existence cannot be generally challenged, of course. It can be seen, however, that it need not be invoked to explain the apparent spread in energetics encountered in the observations (a) and (b) above. This is true in the same sense as we do not feel compelled to conclude that there exist carbon atoms of inherently varying reactivities around a benzene ring in spite of the observed variations in reactivity on successive substitutions (Fig. 1).

What evolves from these considerations of the physicist and the chemist is that by way of the charge shift processes in the boundary, there is a profound mutual interplay between the external molecular atmosphere and the internal atmosphere of mobile charge carriers (electrons and holes). The common denominator being molecules trapped on the surface and acting as traps for charge carriers.

Adsorption processes may take place between solid, and gas *or* liquid atmospheres. Let us examine what types of interplay between such ambients and the electrical carriers within solids have been demonstrated. For a semiconductor-*liquid* contact, Brattain and Garrett [16] have demonstrated the ability of negative or positive ions adsorbed from an electrolyte to alter the surface conductivity type of germanium. Conversely, a direct demonstration of striking simplicity of ad- and desorption into the surrounding liquid upon alteration of the electronic state of a semiconductor was supplied by Hedvall.[17] He demonstrated on photoconductive red HgS adsorption of 42 percent of the dyestuff phenolphthalein from the surrounding solution upon illumination and redesorption on darkness; only weak adsorption, unaltered by illumination, resulted on the non-photoconductive black HgS. Further strength to the interpretation was given by the demonstration that the spectral response of dye adsorption was identical with that of the HgS's photoconductivity.

For semiconductor-*gas* contacts the effect of gas adsorption on the electrical properties of the solid have been amply demonstrated. For example, the work of Bevan and Anderson,[18] and of Morrison [11] demonstrated the large effects of oxygen on the conductivity of zinc oxide when the sample possesses regions of small particle size, i.e. where the surface-to-volume ratio becomes large. As another example, Weisz, Prater and Rittenhouse [19] have demonstrated for highly porous chromia-alumina changes of conductivity over several orders of magnitudes, as well as changes of semiconductor type (p- to n-) within seconds of a change in gaseous environment (Fig. 3).

The converse effect, i.e. of changing the amount of the adsorbate by introducing a change in the mobile carrier concentration

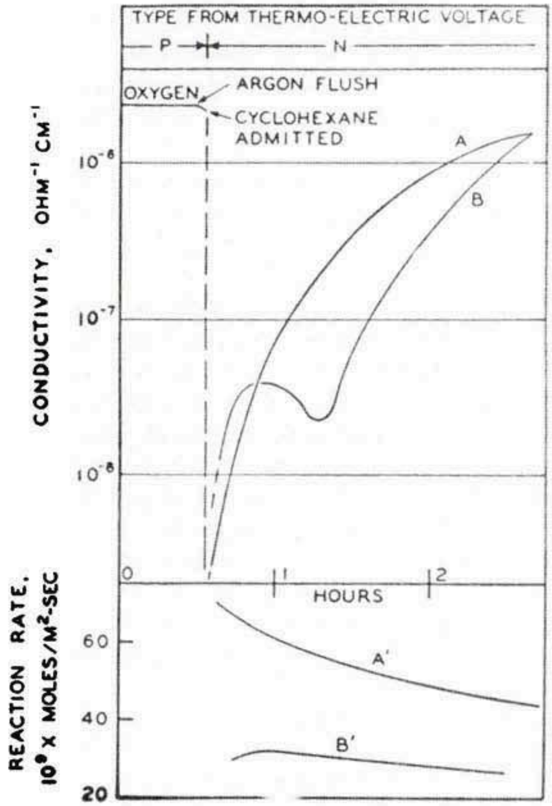


FIG. 3.—Sign of thermoelectric voltage, electrical conductivity, and catalytic reaction rate of chromia-alumina during dehydrogenation of cyclohexane (from reference 19).

below the solid surface, may be indicated by work such as that of Morrison [20] and of Pratt and Kolm.[21] They study the changes in work function, and thus variations in Fermi level of the surface when the carrier concentration is altered by a change in a normally applied electric field, or by a change in surface illumination. The observed surface potential changes are logarithmic with time, in the manner of the Elovich equation. Let us recall that the electron transfer model indicates the changes of surface potential with adsorbed amount n, which in turn is the variable described by the Elovich equation.

Such measurements are indirect in that they do not simultaneously and directly observe the species taken from or returned to the gaseous atmosphere. Changes of qualitative nature of the adsorbed traps rather than their number could be invoked in alternate explanations.

It appears that a *direct* demonstration of the alteration of the *gas* phase by a change of surface carrier concentration such as by the field effect or photoelectric effect still remains forthcoming. For such work some of the highly porous substances familiar to the catalytic chemist, such as Cr_2O_3, may be particularly suitable, since in such a material the ratio of surface atoms to volume atoms can be as high as 1/20 (corresponding to a surface area of 250 m^2/cc of solid). By illumination of 0.1 cm^3 of such material, liberation or capture of gas to the extent of only 0.1 percent of complete surface coverage would result in a change of gas pressure by 1 mm Hg in a surrounding volume of 10 cm^3.

So far I have discussed ad- and desorption, wherein the entity going on and off the surface is chemically the same. We have discussed a type of adsorption which involves rather drastic alteration of electronic make-up of the adsorbate molecules. Therefore, it is not unexpected that their chemical reactivities or stabilities can in some cases be appreciably altered *by* such a process. When surface adsorption leads to decomposition or other reactions which in the gaseous state would not take place, we have a case of "heterogeneous catalysis." Essentially, the molecules involved in desorption are chemically different from those in adsorption, Fig. 4. We must, of course, have the chemical conversion step $A^* \rightarrow B^*$, which may make some demands on the

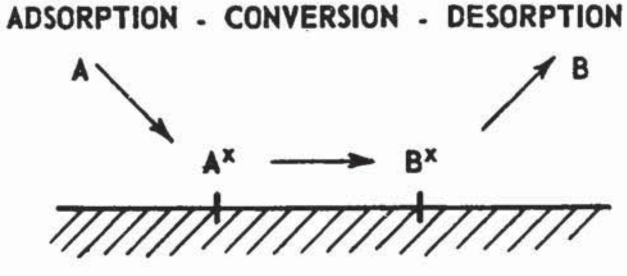


FIG. 4.—Schematic diagram of successive processes in surface catalyzed reaction.

type of electronic structure obtained by the chemisorption step, and thus on the type of semiconductor required. Much work has gone into investigating correlation between semiconductor types and their ability to produce certain chemisorbed species and thus to catalyze given chemical reactions. The following papers will deal with some of this work. One general and basic question arises from the fact that we encounter considerable specificity in catalysis in that a certain solid catalyst will catalyze certain very specific reactions out of the huge number of possible chemical transformations. Can a description of solid-adsorbate interaction based solely or mainly on certain relative energy states account for much of this specificity? Referring to Fig. 4 we observe that we wish to create a finite and presumably as large as possible number of A^* on the surface in order to obtain a desired and useful magnitude for the chemical rate $A^* \rightarrow B^*$. This would call for a semiconductor choice such that the chemical potential difference E_0 between it and the proposed adsorbate be *as large* as possible (see Fig. 2). On the other hand, we are now not interested in just obtaining chemisorption, but also in obtaining a *rate* of *ad-* and *desorption* of a magnitude to match the desired rate of conversion. The desorption step, however, will require an activation energy which increases with E_0. The desorption rate thus dropping exponentially with larger E_0, we are *sharply limited* in the choice of E_0 for a given, demanded rate. Even when we construct a case where the conversion A^* to B^* is such that the energy differential E_0 applicable to the product B and the solid is much different and smaller than for the initial molecule A, so as to facilitate desorption, then the rate of *ad*sorption depending on charge transfer across the electronic barrier will decrease rapidly with larger E_0. So, we get in this case into similar difficulties in the broadness of choice of E_0. In addition, the electronic adsorption process will require a certain minimum "vapor pressure" of charge carriers in the solid, that is a maximum activation energy Q for conductivity. Therefore, as pointed out by Weisz,[9] there exist rather narrow requirements for the relative energy states to accomplish a given chemical conversion, which conversely implies considerable catalytic selectivity for a given catalytic solid.

These remarks may suffice to indicate some of the more immediate relationships between catalysis and the remarks on chemisorption.

In such a sketch of possible relationships between the physical and chemical interests centering around the semiconductor surface, it is hard to ignore some related areas which are presenting a great challenge.

We realize that a difference in Fermi level of a conductive solid particle and the electronic energy states of the molecules of a surrounding fluid can result in charge accumulation at the particle surface, and that in a conductive solid this goes far beyond the case of stretching the negative charges a bit farther away from the positive nuclei in the sense of polarization by the induction of dipoles. The sign and the amount of charge on the surface of an immersed particle will depend on the electronic nature of the particle and on the chemical constituents in the fluid. Such particles with considerable net surface charge must then be expected to move in an electric field, and we find ourselves in the midst of the phenomena of colloid chemistry.

We have discussed the extent of electron redistribution which results from a surface contact, and the analogous "induction effect" in certain organic molecules when in this case a point contact is made. In 1941, Szent-Györgyi [22] pointed out that such capacity for electron flow and mobility leads to the ability of transmitting information and transporting energy through large chemical structures. He pointed out how the possible existence of continuous energy bands in proteins and other biological macromolecules could account for many of the most fundamental mysteries of biochemical processes. For example, the quantum efficiency in photosynthesis demands that the energy of quantum adsorption will find its way to the "trap" at which the actual chemical work is done. Similarly, the extensive and non-localized action of enzymes requires some mechanism of energy mobility. The proteins do form large and regular periodic molecular structures. Szent-Györgyi and co-workers [23] were able to demonstrate quantum induced phosphorescence of various dried proteins when a small quantity of dye molecules was incorporated to serve as activators. Similarly, photoconductivity was also demonstrated. Eley and co-workers [24] then showed proteins (fibrinogen, edestin) to possess electrical conductivity of a semiconductive character. These implications of electronic behavior of proteins in the characteristic manner of semiconductor solids, pointed out by

Szent-Györgyi at such an early date, reappear as particularly challenging. The rapid progress in biochemistry is vividly confronting us with the similarities between at least certain protein structures and sizable solid particles of periodic structure, as seen by the recently demonstrated model of the tobacco mosaic virus,[25] Fig. 5. The very uniform and nearly mathematical spiral coil structure is protein, and in this coil of protein is a slab of ano her material, nucleic acid. In recent work,[26] it was shown that neither of the two materials alone have the chemical, i.e. infectious virus properties. However, *recontacting* the two solid substances will immediately result in producing these characteristics.

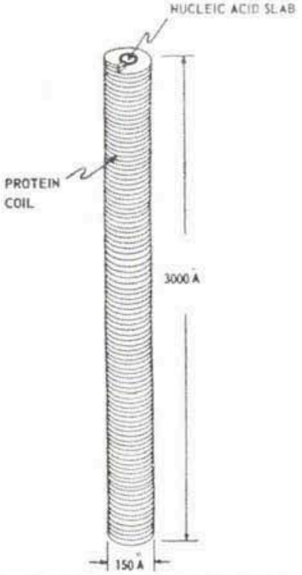


FIG. 5.—Model of the tobacco mosaic virus, as a contact of two solids, nucleic acid slab and protein coil (after reference 25).

Some of the present concepts which attempt to connect surface electronics and physical chemical processes are no doubt simple, insufficient, or wrong. Yet, it seems rather certain that a part of the mechanistic consequences of the electron mobility in semiconductive solids, the surface charge accumulation at contacts, and the interplay of surface traps with both the surrounding molecular and the internal electron atmosphere will greatly influence the understanding of many physical-chemical phenomena.

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GAS REACTIONS ON SEMICONDUCTING SURFACES AND SPACE CHARGE BOUNDARY LAYERS *

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ABSTRACT

The Fermi potential of a catalyst is related to the electronic exchange level of the reacting molecules. Applying a two-dimensional term scheme, the relations are generalized. On the basis of the results, one can determine whether an *n*- or *p*-type catalyst must be used for a reaction. Furthermore, the important role of the space charge in the catalyst is discussed, with its effects upon the reaction kinetics.

1. Formulation of the Problem

In all chemical processes which are accelerated by catalysts, the electronic interaction of the catalyst with the reacting molecules (initial substances, intermediate products and end products) plays a decisive role. In this connection the electronic interaction may manifest itself exclusively in polarization, or also frequently in a direct electron exchange. Experimental proof of the electron exchange between catalyst and reacting gases was provided some time ago by Wagner and Hauffe[1] for the decomposition of N_2O and the CO oxidation on oxides (NiO, CuO). The problem was again taken up only ten years later and dealt with more intensively by other authors, in particular by Garner and his collaborators[2] and Taylor and Schwab and their collaborators.[3] In the field of metal contacts, which is not dealt with in the present report, Schwab[4] and Suhrmann[5] among others were able to show the importance of electronic interaction.

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In order to distinguish cases in which the heterogeneous electron reactions to be catalyzed take place without intermediate electron donation to the layer and are catalyzed only by a lowering of the threshold by the action of stray surface fields, an incidental process which we shall keep in mind as "heterogeneous polarization catalysis," we shall in the following refer to heterogeneous catalysis with electron exchange as "electronic layer exchange catalysis" or briefly "layer exchange catalysis."

The following considerations will be limited to catalyses in which a direct electron exchange takes place between the reacting gas and the catalyst. This layer exchange catalysis is encountered frequently. At the present state of research, it is more readily accessible to quantitative treatment than the catalysis caused by electronic polarization phenomena. The electron theory of metals is considerably more difficult to manipulate than that of semiconductors (for example, oxides and sulfides and their mixed phases) where the mechanism of electron exchange can be described by laws (Boltzmann-statistics, ideal mass action law and electrochemical thermodynamics) familiar in the conceptual structure of chemistry. Therefore we will restrict ourselves to "semiconducting" catalysts in the present investigation.

From the chemical physics of solid inorganic compounds, it is known [6] that there exist solids, such as the alkali halides, which are pure ionic conductors in the temperature range of catalysis (if one disregards crystals which have been rendered photoconducting), and that there exist other solids, such as the oxides and sulfides, which represent practically pure electronic conductors. Whereas electron-conducting, nonmetallic solids (with the exception of intrinsic semiconductors) always differ from a stoichiometric composition, ionic conducting crystals are always nearly stoichiometric. In view of the requirement of overall neutrality, a substantial excess of electrons and holes is always connected with the appearance of localized charged defects which, in the absence of impurities, can only be caused by deviation from stoichiometric structure of the crystal. In oxides and sulfides the deviation from stoichiometry may be caused by an excess or deficiency of metal or non-metal, which leads to two types of electronic defects; in one case, we observe free electrons with an equivalent number of anion vacancies or cations in interstitial positions, and in the other case holes appear with an equivalent number of cation vacancies and/or anions in interstitial positions. In the sense of the band model concept, the first case represents the existence of free electrons in the conduction band, while the second case corresponds to holes in the valence band; in both cases the Fermi potential E_f is established simultaneously for both electrons and holes, but in the excess electron case it is equivalent to the electrochemical potential η_- which depends on the electron concentration. In the defect electron case it is equivalent to the electrochemical potential η_+ which depends on the hole concentration.[7]

Often we shall only have to deal with an electron exchange between the incident molecule and the conduction band in the case of an *n*-type catalyst, and the valence band in the case of a *p*-type catalyst. In this case the direction of the electron transfer will be determined by the relative position of the Fermi-potential and the electron exchange level (also referred to as the charge transfer level) of the molecular species appearing in the course of the reaction. As we shall show on the basis of a simple reaction, the ability to have influx and efflux of electrons from the molecule to and from the conduction or valence band of the catalyst will depend on the absolute position of η_- or η_+ and the charge transfer or exchange level of the gas molecule incident upon the surface.

Depending on the nature of the rate-determining step involving electron exchange, there may be a steady-state decrease or increase of the charge defect concentration in a certain thin boundary layer (50–200 A) of the catalyst. In this process the surface charge formed by the charges of the chemisorbed atoms and molecules is compensated by an equal and opposite charge within the boundary layer. This is accompanied by a deviation of the number of electrons and holes in the boundary layer (space charge boundary layer). The possible variation of an electric diffusion potential V_D during the process will first be ignored. Its frequently decisive effect on the course of the reaction will be discussed subsequently, making use of the well-known relation

$$\text{Fermi Potential} \equiv \eta_- = \mu_\ominus + V \text{ and } -\eta_+ = -(\mu_\oplus - V)$$

($\mu_\ominus = -\mu_\oplus$ = chemical potential in ev and V = electric potential).[7]

2. FERMI POTENTIAL OF THE CATALYST AND MECHANISM OF THE REACTION

In order to explain layer exchange processes we shall choose a simple reaction involving two species of molecules where one preferably *takes up* electrons while the other predominantly *gives off* electrons. This is the case, for example, with N_2O and CO or with O_2 and H_2, or with O_2 and CO. Taking the first-mentioned pair of molecules:

$$CO + N_2O \rightarrow CO_2 + N_2, \qquad (1)$$

which is connected with a negative free energy change, we shall have to consider the following steps of the reaction:

$CO^{(g)} \leftrightarrow CO^{+(\sigma)} + \ominus^{(\text{c-band})}$	(Chemisorption of CO on *n*-type catalyst)	(2a)
$CO^{(g)} + \oplus^{(\text{v-band})} \leftrightarrow CO^{+(\sigma)}$	(Chemisorption of CO on *p*-type catalyst)	(2b)
$N_2O^{(g)} + \ominus^{(\text{c-band})} \leftrightarrow O^{-(\sigma)} + N_2^{(g)}$	(Chemisorption of oxygen by N_2O on *n*-type catalyst)	(3a)
$N_2O^{(g)} \leftrightarrow O^{-(\sigma)} + N_2^{(g)} + \oplus^{(\text{v-band})}$	(ditto on *p*-type catalyst)	(3b)
$O^{-(\sigma)} + CO^{+(\sigma)} \leftrightarrow CO_2^{\times(\sigma)}$	(Electron exchange reaction without layer exchange)	(4)
$CO^{\times(\sigma)} \leftrightarrow CO_2^{(g)}$	(Desorption without layer exchange)	(5)

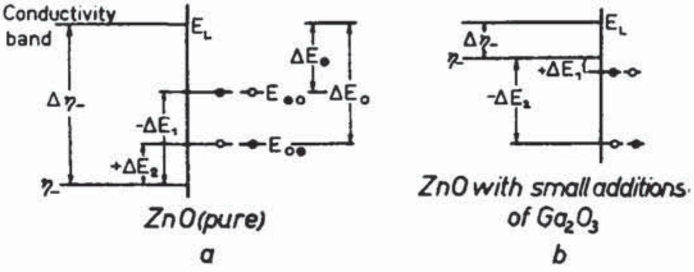
(The steps (6), (13), (16) and (17) discussed below are obtained by combining the steps formulated above. Moreover, the term "without layer exchange" means that no electrons enter or leave the catalyst layer as indicated by the probable reaction scheme above.)

The superscript σ represents chemisorption and $\times$ represents the uncharged state. In the above reaction scheme one of the steps (2) or (3) becomes rate-determining if the steps (4) and (5) take place sufficiently rapidly. Therefore, the rate can be accelerated by suitable choice of the Fermi potential in the catalyst.

The manner in which this can be accomplished in practice will be discussed in detail below.

2.1. *Reaction on an* n-*Type Catalyst*

The course of the reaction in this case is assumed to be described by the steps (2a), (3a), (4) and (5). The electronic exchange levels ("charge transfer levels") of CO and N_2O are designated by $E_{\bullet\circ}$ or $E_{\circ\bullet}$ depending on the sequence of the "states with electron" (●) and "without electron" (○). Since $E^{CO}_{\bullet\circ}$ and $E^{N_2O}_{\circ\bullet}$ are fixed, the problem is to change the position of the Fermi potential η_- in the *n*-type catalyst such that electron exchange (either donation or acceptance of electrons in the conduction band) which is energetically unfavorable to begin with, is accelerated. The E-values represent distance from the conduction band. For a given surface complex the position of the charge transfer levels is, of course, independent of the sequence ●○ or ○●. The notation is significant, however, in regard to the reaction kinetics; it indicates what type of charge transfer is involved in a reaction of the given direction. Several limiting cases of interest are illustrated in Figs. 1 and 2.



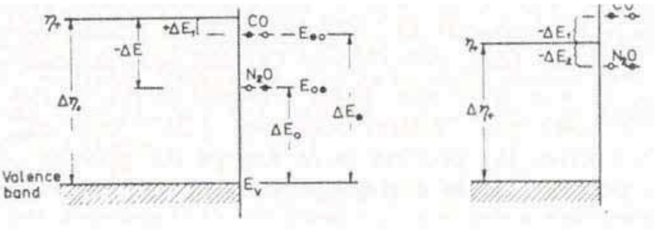
ZnO(pure)
a

ZnO with small additions of Ga_2O_3
b

FIG. 1.—Schematic representation of the positions of the Fermi potentials in an *n*-type catalyst and the transfer levels of molecules $E_{\bullet\circ}$ and $E_{\circ\bullet}$ at the surface.

Since —●— represents the electronically occupied state and —○— represents the electronically empty (unoccupied) state of the gas molecule at the surface (initial state at left, final state at right in the direction of the reaction), we use the symbol —●— in cases such as $CO^\times$ and N_2O^-, and the symbol —○— for the cases CO^+ and $N_2O^\times$. In our schematic energy level diagrams the exchange level $E^{CO}_{\bullet\circ}$ may be higher than the exchange level $E^{N_2O}_{\circ\bullet}$ in one case (Fig. 1 and 2), and lower in the other case.

Successful development of a catalyst would be determined by the choice of a suitable semiconductor (oxide or sulfide) with a



NiO (pure)
a

NiO with small additions of Li_2O
b

FIG. 2.—Schematic representation of the positions of the Fermi potentials in a *p*-type catalyst and the transfer levels of the molecules $E_{\bullet\circ}$ and $E_{\circ\bullet}$ at the surface.

Fermi potential η_- or η_+ which is quite close to both the $E^{CO}_{\bullet\circ}$ level and to the $E^{N_2O}_{\circ\bullet}$ level. In Fig. 1b for example the Fermi potential η_- is situated very favorably for the chemisorption of N_2O according to (3a), while the chemisorption of CO according to (2a) and thus the corresponding reaction (2a) + (4):

$$O^{-(\sigma)} + CO^{(g)} \rightarrow CO_2^{\times(\sigma)} + \ominus^{\text{c-band}} \qquad (6)$$

is inhibited. On the basis of this situation this semiconductor is probably a poor catalyst since the required energy expenditure $+\Delta E_1$ can only be attained at higher temperatures and frequently reaches the energy requirement for the homogeneous gas reaction.

Under these conditions we may assume a chemisorption equilibrium of the N_2O (which readily undergoes a charge reversal in this case) or the oxygen, which leads to a partial O^- occupation of the catalyst surface, causing a considerable decrease in the concentration or the chemical potential of the free electrons $\mu_\ominus$, down to a certain layer thickness (exhaustion boundary layer). As will be discussed in Section 3, this process causes the appearance of positive space charge in this boundary layer and of an electric diffusion potential V_D which must be allowed for in general in a refined examination of the reaction mechanism.

As indicated by the rate equation for the electronic charge transfer $-\bullet- \to -\circ-$ of the reaction (2a) and hence of the combined reaction (6)

$$(dN_{\circ}/dt)_{\text{c-band}} = -(dN_{\bullet}/dt)_{\text{c-band}} = i_{\text{th}\bullet} \cdot N_{\bullet} - \alpha_{\text{n}} n N_{\circ} \qquad (7)$$

($N_{\bullet}$ and $N_{\circ}$ represent surface densities of the $CO_{\bullet} = CO^{x}$ and $CO_{\circ} = CO^{+}$ occupation), this reaction is not noticeably favored by a decrease of the concentration of the free electrons n ($\sim \exp \mu_{\ominus}/\mathfrak{B}$), which does not influence $i_{\text{th}\bullet}$. The thermal emission $i_{\text{th}\bullet}$ of the ($CO^{\times}$) particles impinging on the surface or of the (O^{-}) particles present on it is governed by the known relation

$$i_{\text{th}\bullet} = \alpha_{\text{n}} K_{\text{n}} = \alpha_{\text{n}} n^{\circ} \exp(-\Delta E_{\bullet}/\mathfrak{B}) \text{ where } \mathfrak{B} = kT/e \qquad (8)$$

which can be derived from a comparison of the kinetic equilibrium condition:

$$i_{\text{th}\bullet} N_{\bullet} = \alpha_{\text{n}} n N_{\circ}$$

and the thermodynamic equilibrium condition:

$$\frac{N_{\circ} n}{N_{\bullet}} = K_{\text{n}} = n^{\circ} \exp(-\Delta E_{\bullet}/\mathfrak{B})$$

(n° = degeneracy concentration, α_{n} = statistical coefficient of the (n, $CO_{\circ}$)-recombination, $\Delta E_{\bullet}$ = distance of the level $E_{\bullet\circ}$ from the conduction band E_{c}). Thus $i_{\text{th}\bullet}$ does not depend upon the position of η_{-} but only upon the distance $E_{\text{c}} - E_{\bullet\circ} = \Delta E_{\bullet}$. Thus if the total reaction requires a $\ominus$-emission, the forward reaction (Fig. 1a) is completely independent of η_{-}. Only the appearance of a reverse reaction $\ominus + \circ \to \bullet$ becomes dependent upon η_{-} (proportional to n) and thereby makes the η_{-} position in Fig. 1a unfavorable. However, its contribution in turn depends upon $N_{\circ}$. We obtain the following equation for the forward reaction:

$$\begin{aligned} -(dN_{\bullet}/dt)_{\substack{\text{reaction} \\ \bullet \leftrightarrow \circ + \ominus}} &\equiv -(dN_{\bullet}/dt)_{\text{c-band}} \\ &= \alpha_{\text{n}} n^{\circ} \{N_{\bullet} \exp(-\Delta E_{\bullet}/\mathfrak{B}) - N_{\circ} \exp \\ &\qquad (-\Delta \eta_{-}/\mathfrak{B})\} \qquad (9) \end{aligned}$$

where $\Delta \eta_{-} = E_{\text{c}} - \eta_{-}$. From this it follows that the lowering of η_{-} is of importance only if the subsequent reaction with $N_{\circ}$ is too slow ($N_{\circ}$ large), and only if both energy levels are approximately equal, i.e., if the charge transfer reaction $-\bullet- \to -\circ-$

is no longer rate-determining. The discussion of the following schematic reactions is based on the fact that in all cases the reverse reaction can be neglected; only in this case is the corresponding forward reaction rate-determining.

To begin with, if one does not wish to limit oneself to the consideration of unidirectional overall reactions (with the assumption of negligible reverse reactions) but wishes to consider the more general case, one must include in the representation the forward and back reaction and the corresponding free energy change. Such considerations were examined by Schottky (unpublished diary pages). If we denote the available energy in a reaction by

$$\Delta F^{\circ} = (\Sigma \nu \mu)_{\text{final}} - (\Sigma \nu' \mu')_{\text{initial}},$$

for example for $CO^{(g)} + N_2O^{(g)} \rightarrow CO_2^{(g)} + N_2^{(g)}$, the corresponding expression for the charge transfer reaction $\bullet \rightarrow \circ + \ominus$ is:

$$\Delta F^{\circ} = \mu_{\ominus} - (\mu_{\bullet} - \mu_{\circ}) = E_c - \Delta\eta_- - [E_{\bullet\circ} - \mathfrak{B} \ln (N_{\circ}/N_{\bullet})]$$
$$= \Delta E_{\bullet} - \Delta\eta_- + \mathfrak{B} \ln \frac{N_{\circ}}{N_{\bullet}}.$$

From this we obtain the expression which determines the concentration ratio $N_{\circ}/N_{\bullet}$ of the electronically unoccupied and occupied states:

$$N_{\circ} = N_{\bullet} \cdot \exp [(\Delta F^{\circ} - \Delta E_{\bullet} + \Delta\eta_-)/\mathfrak{B}]. \qquad (10)$$

With the aid of this expression we obtain from (9):

$$-(dN_{\bullet}/dt)_{\substack{\text{reaction} \\ \bullet \rightleftarrows \circ + \ominus}} = \alpha_n n^{\circ} N_{\bullet} \exp (-\Delta E_{\bullet}/\mathfrak{B}) [1 - \exp (\Delta F^{\circ}/\mathfrak{B})]. \qquad (11)$$

Thus for the spontaneous course of the reaction in the overall ΔF° direction of the forward reaction, $-\bullet- \rightarrow -\circ-$, we must always have $\Delta F^{\circ} < 0$. As indicated by Eq. (11) the rate of the forward reaction for a given $N_{\bullet}$ and $\Delta E_{\bullet}$ depends only on the available free energy ΔF° of the reaction and is independent of the Fermi potential. It is seen, however, that as soon as a noticeable portion of the total available free energy ($\gg \mathfrak{B}$) is available for the reaction, only the rate of the forward reaction is controlling in all cases.

The relations Eq. (9) and Eq. (11) together with the statement that only forward reactions which (contrary to Eq. (9)) depend upon the product $nN_{\circ}$ or $pN_{\bullet}$ (p = concentration of holes) and hence upon the Fermi potential or η, for which we always have $\eta_+ = -\eta_-$ in the equilibrium state, might provide the basis for understanding how the doping by impurity ions in a catalyst will be of importance in regard to the course of the overall reaction. It will be of importance wherever the slowest step is of the recombination type.

According to Fig. 1b an activation energy for $\ominus$-emission can only appear for higher Fermi potentials. The incident CO molecules are discharged "instantaneously." The reverse reaction leads to negligible reoccupation. In the case of Fig. 1b according to Eq. (8), $i_{\mathrm{th}\bullet} = \alpha K_{\mathrm{n}}$ with $\exp(-\Delta E_{\bullet}/\mathfrak{B})$ may become very small. In the case $\eta_- > E_{\bullet\circ}$ the reverse reaction $\alpha_{\mathrm{n}} n N_{\circ}$ takes place very rapidly. However, if $N_{\circ}$ vanishes even more rapidly by a subsequent reaction step, the reverse reaction is also diminished in the present case. Corresponding to the equilibrium condition implied by Eq. (7)

$$i_{\mathrm{th}\bullet} N_{\bullet} = \alpha_{\mathrm{n}} n N_{\circ} \tag{12}$$

we still have $N_{\bullet}/N_{\circ} \gg 1$, but this is due only to the primary lifetime of the $N_{\bullet}$. Under these conditions $i_{\mathrm{th}\bullet}$ and consequently $\Delta E_{\bullet}$, which is independent of the Fermi potential over wide limits, becomes rate-determining. Thus in the present case a change in V_{D} or doping also has no effect on the process.

In the case of a rate-determining chemisorption of N_2O or a combined follow-up reaction

$$\ominus^{\text{c-band}} + \mathrm{CO}^{+(\sigma)} + \mathrm{N_2O}^{(\mathrm{g})} \rightarrow \mathrm{CO}_2^{\times(\sigma)} + \mathrm{N}_2^{(\mathrm{g})} \tag{13}$$

of the recombination type, doping, for example Ga_2O_3 in ZnO (Fig. 1b) in suitable quantities will cause an acceleration of the reaction due to an "upward" displacement of the Fermi potential, if $\Delta E_2 = \eta_- - E_{\circ\bullet}$ becomes as large as possible.

These relations become understandable if one considers the rate equation

$$-(dN_{\circ}/dt)_{\circ+\ominus\rightarrow\bullet} = \alpha_{\mathrm{n}} n N_{\circ} - i_{\mathrm{th}\bullet} N_{\bullet} \tag{14}$$

which determines the charge transfer in the follow-up step Eq. (13), i.e. $\circ + \ominus \rightarrow \bullet$. It is seen that the forward reaction is of the recombination type in which the concentration of the free electrons n and hence the Fermi potential η_- becomes controlling. In a manner analogous to Eq. (9) we obtain

$$-(dN_\bigcirc/dt)_{\bigcirc+\ominus\to\bullet} = \alpha_n n^\bigcirc\{N_\bigcirc \exp(-\Delta\eta_-/\mathfrak{B}) - N_\bullet \exp(-\Delta E_\bullet/\mathfrak{B})\}. \tag{15}$$

As indicated by these considerations, the successful catalysis of a reaction depends upon the choice of suitable n-type catalysts with an E_c which is located favorably with respect to $E_{\bullet\bigcirc}$ (i.e. $\Delta E_\bullet = E_c - E_{\bullet\bigcirc}$ very small) if a partial process involving an electron emission is rate-determining, or upon the choice of suitable catalysts with doping of higher-valence cations (for example, $ZnO + Ga_2O_3$, $TiO_2 + WO_3$), if a step of the recombination type is rate-determining.

2.2. *Reactions on a* p-*Type Catalyst*

Numerous experimental results indicate that for certain reactions, an n-type catalyst even on changing its Fermi potential η_- by doping, shows catalytic properties which are far inferior to those inherently possessed by a pure undoped p-type catalyst for the same reaction. This condition seems to prevail, for example, in the decomposition of N_2O.[8] The cause is found in that for numerous reactions the electron exchange between a p-type catalyst and the reacting gas molecules in slow recombination type reactions is determined by $\alpha_p p N_\bigcirc$, i.e. it is proportional to p and hence decisively dependent upon the Fermi potential of the catalyst, but independent of $\Delta E_\bigcirc$ over wide limits (Fig. 2).

The relations established for n-type catalysts can also be derived in a similar manner for a reaction occurring on a p-type catalyst. On the basis of the following considerations analogous reaction equations corresponding to Eq. (6) and Eq. (13) for the valence band mechanism must be formulated. These are:

$$O^{-(\sigma)} + CO^{(g)} + \oplus^{(\text{v-band})} \to CO_2^{\times(\sigma)} \tag{16}$$

and

$$CO^{+(\sigma)} + N_2O^{(g)} \to CO_2^{\times(\sigma)} + N_2^{(g)} + \oplus^{(\text{v-band})} \tag{17}$$

Following the above discussion we consider the forward reaction of Eq. (16), i.e., $\bullet + \oplus \to \bigcirc$, as the rate-determining step of the overall reaction Eq. (1). Corresponding to Eq. (9) we then obtain:

$$-\left(\frac{dN_\bullet}{dt}\right)_{\bullet+\oplus\to\bigcirc} = \alpha_p p^\bigcirc\{N_\bullet \exp(-\Delta\eta_+/\mathfrak{B}) - N_\bigcirc \exp(-\Delta E_\bullet/\mathfrak{B})\}. \tag{18}$$

Here p° represents the degeneracy concentration of the holes, $\Delta\eta_{+} = \eta_{+} - E_{\mathrm{v}}$, and $\Delta E_{\bullet} = E_{\bullet\circ} - E_{\mathrm{v}}$ (Fig. 2). It is seen that the forward reaction is of the recombination type and therefore dependent upon the hole concentration p or the Fermi potential. In order to catalyze this reaction one must add to a p-type catalyst suitable quantities of a lower valence cation, for example, Li_2O to NiO, in order to increase the hole concentration or to lower $\Delta\eta_{+}$. Since the reverse reaction of Eq. (16) is of no importance, the second term in the bracket expression Eq. (18) can be neglected.

If, on the other hand, the step Eq. (17) were to be rate-determining, i.e., $\circ \rightarrow \bullet + \oplus$, then, if only the forward reaction took place, the electron emission $i_{\mathrm{th}\circ}N_{\circ} \sim N_{\circ} \exp(-\Delta E_{\circ}/\mathfrak{B})$, which in turn determines the course of the reaction, is independent of the Fermi potential and hence is independent of doping. The present process is determined exclusively by the position of the valence band edge E_{v} with respect to that of the charge transfer level $E_{\circ\bullet}$. The smaller $\Delta E_{\circ}$, the more rapid is the combined follow-up reaction Eq. (17).

In the following chapter we shall show in which way the description of the electronic layer exchange mechanism can be generalized by a two-dimensional energy band model. Since this representation indicates for the first time quite generally when an n- or p-type catalyst is to be used for a reaction which is to be catalyzed and how the doping must be chosen, we shall develop in the following section some of its features, with several examples.

2.3. *Description of the Electronic Layer Exchange Catalysis in the Two-Dimensional Energy Scheme*

We shall assume that electron exchange between the molecules and the catalysts involves only one band (either the conduction band or the valence band), so that only one type of electronic charge carrier need be considered. The mechanism of electron exchange in a p-n catalyst, such as for example CuO, PbS, Ge, will be discussed in a paper to be published in the future. The effect of space charge layers which may develop in some cases will first be neglected. It would require a three-dimensional representation. This phenomena will be dealt with separately in a subsequent section.

As indicated in Fig. 3, the $E^{\mathrm{A}}_{\bullet\circ}$-values and the $E^{\mathrm{B}}_{\circ\bullet}$-values of a reaction $A + B = C + D$ have been plotted along the abscissa. The

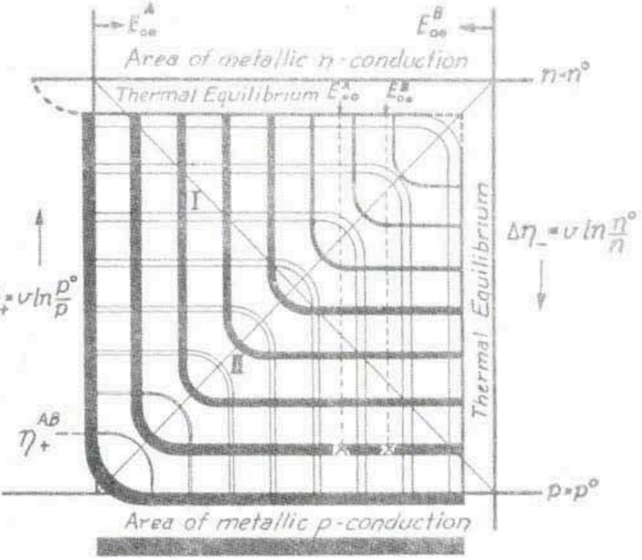


FIG. 3.—Two-dimensional energy level scheme according to Hauffe and Schottky. Black lines represent the forward reaction (—●— → —○—) and white lines represent the continuation reaction (—○— → —●—) on the catalyst.

ordinate shows the differences $\Delta\eta_{-}$ and $\Delta\eta_{+}$ of the Fermi potentials η_{-} and η_{+} of an arbitrary *n*-type and *p*-type catalyst as compared to the band edge levels in the interior of the semiconductor. Thus, $\Delta\eta_{-} = (E_c)_{\text{interior}} - \eta_{-}$ and $\Delta\eta_{+} = \eta_{+} - (E_v)_{\text{interior}}$, where E_c and E_v represent the band edge levels. However, the consideration can readily be applied to the case of band bending by taking $\Delta\eta_{-}$ to represent the distance: $(E_c)_{\text{outside}} - \eta_{-}$ and taking $\Delta\eta_{+}$ to represent the corresponding distance. In a corresponding manner the values for *n* and *p* appearing in the subsequent equations must be modified to allow for bending of the bands compared to the interior in such a way that they are no longer governed by doping exclusively but are also determined by surface charges.

Furthermore, the black curves represent the electron donating reaction (—●— → —○—) and the white curves represent the electron accepting reaction (—○— → —●—). In the representation the different widths of the black and white lines are intended to represent the energetic preference for the black mechanism or the white mechanism.

If we consider the process of electron donation to the semiconductor, i.e., —●— → —○—, as the forward reaction and correspondingly the process —○— → —●— as the follow-up reaction, then according to the energy scheme of Fig. 3 the forward reaction will be increasingly favored energetically the further one moves into the region at the bottom or toward the left. However, the further one moves to the top or to the right, the greater the energetic preference for the subsequent reaction.

If, for example, the electron-donating forward reaction is rate-determining, η_- must be made as small as possible, or $\Delta\eta_- = E_c - \eta_-$ must be made as large as possible; i.e., we must select a black horizontal line located as low as possible but without passing below the diagonal I, since otherwise the valence band mechanism would be favored over the conduction band mechanism. Of course, we can only go downward so far that the forward reaction rate is approximately equal to the rate of the follow-up reaction, indicated in the energy scheme by the equal width of the black and white curves. In the event the relative position of $E^{A}_{\bullet\circ}$ and $E^{B}_{\circ\bullet}$ (on the right-hand side in the schematic diagram) is such that the forward reaction is not sufficiently accelerated in view of the fact that η_- is still unfavorably located, then we must pass below the diagonal I and resort to the valence band mechanism by using a *p*-type catalyst. The fact that the diagonals I and II pass through the corners of the energy level square and that the black and white curves consequently have reflection symmetry is only one of the possible cases. Under these conditions electron exchange with the valence band enters the picture and we obtain for the forward reaction with a charge transfer: ● + ⊕ → ○:

$$-(dN_{\bullet}/dt)_{\text{v-band}} = \alpha_p p N_{\bullet} - i_{\text{th}\circ} N_{\circ} \tag{19}$$

the evaluation of which leads to Eq. (18) which has already been discussed.

Whether a reaction with the conduction band or the valence band is favored energetically is determined by a comparison of the first terms of Eq. (7) and Eq. (19) and thus depends upon whether

$$i_{\text{th}\bullet} \gtrless \alpha_p p. \tag{20}$$

Allowing for Eq. (8), the decision thus depends upon whether

$$\alpha_n n^{\circ} \exp\{-(E_c - E_{\bullet\circ})/\mathfrak{B}\} \gtrless \alpha_p p$$

or whether

$$\exp\{-(\mathrm{E}_c - \mathrm{E}_{\bullet\circ})/\mathfrak{B}\} \gtrless \frac{\alpha_p}{\alpha_n} \cdot \frac{\mathrm{p}^{\circ}}{\mathrm{n}^{\circ}} \cdot \frac{\mathrm{p}}{\mathrm{p}^{\circ}}. \qquad (21)$$

Corresponding to n°, p° represents the degeneracy concentration of holes.

If to a first approximation we introduce the simplification

$$(\alpha_p/\alpha_n)(p^{\circ}/n^{\circ}) \approx 1,$$

we move along the diagonal II of Fig. 3 and the limit is given by

$$\Delta E_{\bullet} = E_c - E_{\bullet\circ} = \mathfrak{B} \ln \frac{p^{\circ}}{p}.$$

However since

$$\Delta\eta_{+} = \mathfrak{B} \ln \frac{p^{\circ}}{p}$$

we must have $\Delta E_{\bullet} = \Delta\eta_{+}$ under these conditions.

In all cases where equilibrium has not yet been approached, we are interested only in the forward reaction (if the latter is slow), i.e., in the first term on the right-hand side of Eq. (7) and Eq. (19). On the other hand, if the follow-up reaction is very slow, acceleration of the initial or forward reaction will not help us at all, if we do not simultaneously catalyze this follow-up reaction. Thus in the case of a reaction mechanism with an electron-donating (—●— → —○—) initial or forward reaction, we must always compare both partial reactions $(dN_{\circ}/dt)_{\text{forward}}$ and $(dN_{\circ}/dt)_{\text{follow-up}}$.

If the reverse reaction rate of the initial reaction is very much greater than the follow-up reaction, we obtain

$$\alpha_n n N_{\circ} = \frac{N_{\circ}}{\tau_w}$$

and thus a limiting value for $\mathrm{n} = \mathrm{n}_{\text{lim}}$:

$$n_{\text{lim}} = 1/\alpha_n \tau_w \qquad (22)$$

(τ_w is the reaction time of the follow-up reaction or the mean life time of the chemisorbed molecule which is electronically unoccupied in the sense of a possible charge transfer, i.e., for example, $CO^{+(\sigma)}$ or $N_2O^{\times(\sigma)}$). This value represents a white horizontal line. Now if τ_w is very small, $n_{\lim}$ becomes very great, i.e., the horizontal line moves up to the top. Below this horizontal line the above condition applies: Follow-up rate < reverse reaction rate. Thus in order to obtain the reverse course (Follow-up reaction rate > reverse reaction rate), we must choose $n > n_{\lim}$.

Corresponding relations are obtained for the valence band if the reverse reaction rate is very much greater than the rate of the follow-up reaction. In this case

$$i_{\text{th}\circ} \cdot N_\circ = N_\circ / \tau_w \tag{23}$$

or

$$\alpha_p K_\circ = 1/\tau_w$$

if one considers the following relations:

$$i_{\text{th}\circ} \cdot N_\circ = \alpha_p p N_\bullet$$

and

$$p N_\bullet / N_\circ = p^\circ \exp\,(+\Delta E_\circ / \mathfrak{B}) = K_\circ.$$

If, for example, $\Delta E_\circ = E_{\circ\bullet} - E_v$ has a positive value, i.e., $\alpha_p \cdot K_\circ$ is very large or τ_w is very small, then $N_\circ$ cannot react rapidly enough in view of the abnormally rapid reverse reaction. An overwhelming occupation equilibrium sets in, at least as long as $\Delta\eta_+$ does not become too large. In this case the follow-up reaction which is slowed down due to the smaller value of $N_\circ$ becomes rate-determining. According to the expression for the limiting value of hole concentration $p = p_{\lim}$, for the valence band mechanism which is identical to Eq. (22),

$$p_{\lim} = 1/\alpha_p \tau_w \tag{24}$$

the follow-up reaction will be more rapid than the reverse reaction only if we choose p (black horizontal line) $> p_{\lim}$.

As a further explanation of the two-dimensional representation and following the above assumption for the N_2O decomposition, we shall choose $E^B_{\circ\bullet}$ to lie considerably below $E^A_{\bullet\circ}$ (i.e., further toward the right). Now in order to obtain a good catalytic effect one must choose a $\Delta\eta$-value for which the η-depending reaction rate (black in Fig. 3) is sufficiently high, while the white rate in this region of $\Delta\eta$ is not influenced (Fig. 3). For a reverse situation of $E_{\circ\bullet}$ and $E_{\bullet\circ}$ this same low $\Delta\eta$-value is expedient; however, the white reaction is weak in this region. If we were to move into the *n*-region (conduction band mechanism), the white reaction would be very rapid, but the black reaction would be very slow. Thus in order that conditions are not completely upset by one of the two partial reactions, $\Delta\eta$ must be chosen in such a way that the white and the black reaction rates are approximately equal. We thus choose a $\Delta\eta$ value in Fig. 3 such that the black and white curves have the same width, i.e., such that they have reflection symmetry in our representation.

If $E_{\bullet\circ}$ or $E_{\circ\bullet}$ for the partial processes of a reaction are located far to the left or the right side, respectively, of the abscissa in Fig. 3, then the rates of the electronic charge transfer of the two rate-determining partial processes and consequently also the overall reaction are to a first approximation independent of the position or the value of the Fermi potential in the catalyst for a moderate range of $\Delta\eta$. Under these conditions such a reaction would be equally well catalyzed by a *p*- or an *n*-type catalyst.

An unfavorable situation from the viewpoint of effective catalysis is encountered if $E_{\bullet\circ}$ lies at the right and $E_{\circ\bullet}$ lies to the left of the center of the abscissa in Fig. 3. Under these conditions the black and white curves which determine electron exchange fall on the center line (in our representation) of the ordinates, regardless of how far $E_{\circ\bullet}$ or $E_{\circ\bullet}$ lie to the right or to the left of center, respectively. For such conditions we only find moderately good catalysis.

The energy considerations represented schematically in Figs. 1 to 3 lead to an interesting general conclusion: The absolute position of the exchange levels of the reacting molecules determine whether it is possible in principle to obtain good catalysts for a certain reaction, even at low temperatures, or whether one can count only on moderately good catalysts in the most favorable cases, sufficiently effective only at higher temperatures.

As mentioned above, these relations might be responsible for the fact that one frequently finds very effective catalysts for certain industrial reactions while one has only found moderately effective catalysts for certain other reactions. This conclusion is of great significance in connection with the selective performance of the reaction of certain catalysts toward certain chemical processes.

2.4. *When Does the Follow-up Reaction Become Rate-Determining?*

In the preceding sections we dealt in a more qualitative way with the question as to when one or the other reaction step becomes rate-determining. In this connection one partial reaction was designated as the initial or forward reaction or the charge transfer reaction, while the other was denoted as the follow-up reaction. The question now arises how these relations can be represented more precisely. For this purpose we shall examine, for example, on an n-type catalyst (such as in Fig. 1) as a follow-up reaction the further reaction of the electronically discharged A-molecules with any arbitrary (charged or uncharged) B- or C-molecules. We shall assume, moreover, that the follow-up reaction is the rate-determining one so that no reverse reaction need be assumed. The rate of the continuation reaction is then:

$$dN_{\mathrm{F}}/dt = -(dN_{\mathrm{A}}/dt)_{\mathrm{continuation}} \sim N_{\circ}^{\mathrm{A}}/\tau_{\mathrm{w}}^{\mathrm{A}}. \tag{25}$$

In this case equilibrium is assumed to prevail in connection with the layer exchange reaction; it then follows from the corresponding mass action law and allowing for the conditions represented in Fig. 1:

$$\frac{N_{\circ}^{\mathrm{A}}\cdot n}{N_{\bullet}^{\mathrm{A}}} = K = n^{\circ}\exp\left(-\Delta E_{\bullet}/\mathfrak{V}\right)$$

where we have used the known relation

$$n = n^{\circ}\exp\left(-\Delta\eta_{-}/\mathfrak{V}\right)$$

for the rate of the follow-up reaction:

$$-\left(\frac{dN_{\mathrm{A}}}{dt}\right)_{\mathrm{contin}} = (1/\tau_{\mathrm{w}}^{\mathrm{A}})N_{\bullet}^{\mathrm{A}}\exp\left\{(\Delta\eta_{-} - \Delta E_{\bullet})/V\right\} \tag{26}$$

where $\quad (\Delta\eta_{-} - \Delta \mathrm{E}_{\bullet}) = \mathrm{E}_{\circ\bullet} - \eta_{-} = -\Delta E_{1}$ (Fig. 1).

It is seen that for the follow-up reaction the Fermi potential appears in the rate equation.

If on the other hand the layer exchange reaction $A_{\bullet} \rightarrow A_{\circ}$ is rate-determining, we obtain

$$\frac{dN_{\mathrm{v}}}{dt} = \left(\frac{dN_{\circ}^{\mathrm{A}}}{dt}\right)_{\text{charge transf.}} = N_{\bullet}^{\mathrm{A}}\cdot\alpha_{\mathrm{n}}n^{\circ}\cdot\exp\left(-\Delta E_{\bullet}/V\right). \tag{27}$$

For the relation between continuation and layer exchange reaction rates we obtain

$$\frac{dN_F}{dt} \Big/ \frac{dN_v}{dt} = \frac{\exp{(\Delta\eta_-/V)}}{\tau_w^A \alpha_n n^{\bigcirc}} = \frac{1/\tau_w^A}{\alpha_n n}. \tag{28}$$

It is seen that this velocity ratio is independent of $\Delta E_{\bullet}$. Moreover, the layer exchange rate is relatively high if τ_w^A is large.

We now consider the frequency factor preceding the exponential in Eq. (26). If we denote N_c as the surface concentration of an arbitrary molecular species C which continues to react with $A_{\bigcirc}$, we obtain:

$$\frac{1}{\tau_w^A} = \beta N_c \qquad \text{and} \qquad \beta = q_{th} \cdot d_{AC} = q_{th}\sigma$$

where q_{th} is given by the thermal velocity of $A_{\bigcirc}$ and C along the surface, and d_{AC} represents the diameter of the interaction cross-section of molecule $A_{\bigcirc}$ with C. Similarly we write for the recombination coefficient α_n:

$$\alpha_n = q_{el}\sigma_{\ominus A} = q_{el} a d_{\ominus A},$$

where q_{el} represents the velocity of the electrons or holes, a the lattice constant, $\sigma_{\ominus A}$ the effective cross-section of the $\ominus - A_{\bigcirc}$ reaction, and where $d_{\ominus A} \equiv \sigma_{\ominus A}/a$ has been introduced to obtain equal dimensions in the β-calculation. We thus obtain for the rate ration Eq. (28):

$$\frac{dN_F/dt}{dN_v/dt} = \frac{q_{th} \cdot d_{AC} N_c}{q_{el} \cdot d_{\ominus A} a n} = \frac{q_{th} y_c}{q_{el} x_-} \tag{29}$$

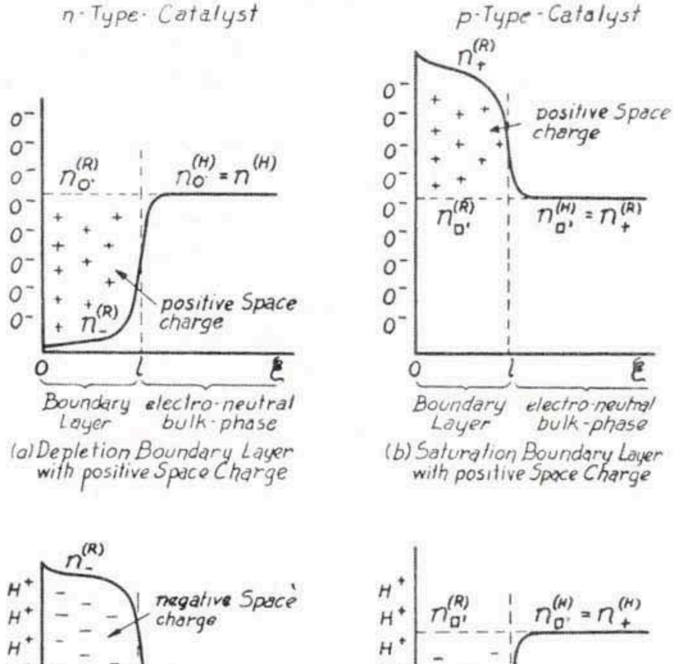
where d_{AC} and $d_{\ominus A}$ have been assumed to be of similar (atomic) order of magnitude and where $y_c = N_c/V$ and $x_- = an/V$ denote the number of C molecules per unit of surface or the number of electrons per lattice layer.

The derivation of the corresponding relations for a reaction taking place on a *p*-type catalyst presents no difficulties.

3. CATALYSTS WITH SPACE CHARGE BOUNDARY LAYERS

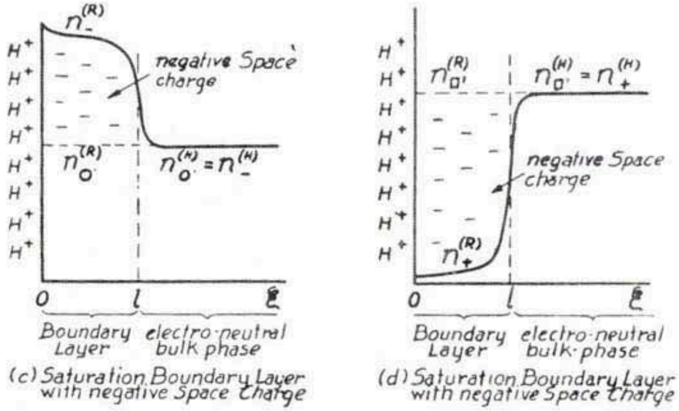
3.1. *Electron Exchange and Chemisorption*

As has been shown in the more recent literature,[9] electron exchange between a catalyst and the reacting gases is accompanied by depletion zones and enrichment zones of conduction electrons and holes down to a certain depth in the catalyst (50 to 500 A). This phenomenon produces positive or negative space charge in these zones, which we shall denote by depletion layers and enrichment layers respectively, according to Schottky[5] (Fig. 4). If



(a) Depletion Boundary Layer with positive Space Charge

(b) Saturation Boundary Layer with positive Space Charge



(c) Saturation Boundary Layer with negative Space Charge

(d) Saturation Boundary Layer with negative Space Charge

FIG. 4.—Schematic representation of the variation of concentration of free electrons n_- ($\equiv n$) and of holes n_+ ($\equiv p$) in the boundary layer and in the interior of an n-type and p-type catalyst during the chemisorption of oxygen and hydrogen.

inside the semiconductor (Index H) we set $\eta_+ = \mu_+(V = 0)$, the introduction of space charge boundary layers into our considerations leads to the following formulae:

$$\eta_+^{(\mathrm{H})} \equiv \mu_+^{(\mathrm{H})} + V^{(\mathrm{H})} = \eta_+^{(\mathrm{R})} \equiv \mu_+^{(\mathrm{R})} + V^{(\mathrm{R})} \tag{30a}$$

or

$$\mu_+^{(\mathrm{R})} = \mu_+^{(\mathrm{H})} + V_\mathrm{D} \tag{30b}$$

where R represents the uppermost location of the lattice plane, and V_D represents the diffusion potential. From Boltzmann's formulation one obtains the shape of the chemical potential or the concentration distribution of electrons, n_-, and holes, n_+, in the space charge boundary layers:

$$n_-^{(\mathrm{R})} = n_-^{(\mathrm{H})} \exp\left(-V_\mathrm{D}/\mathfrak{B}\right) \qquad (n\text{-type catalyst}) \tag{31a}$$

$$n_+^{(\mathrm{R})} = n_+^{(\mathrm{H})} \exp\left(+V_\mathrm{D}/\mathfrak{B}\right) \qquad (p\text{-type catalyst}) \tag{31b}$$

If we choose as an example the chemisorption of oxygen on a p-conducting oxide (for example NiO) and on an n-conducting oxide (for example ZnO), then the above formulations along with Poisson's equation lead to the chemisorption equations which have already been derived elsewhere (see Eq. (1.6)):

$$N_{\mathrm{O}^-}^{(\sigma)} = \left\{\left(\frac{\epsilon}{2\pi e}\right) \cdot p_{\mathrm{O}_2}^{\frac{1}{2}}\, V_\mathrm{D} \cdot K_2\right\}^{\frac{1}{2}} \qquad (p\text{-type catalyst}) \tag{32}$$

and correspondingly

$$N_{\mathrm{O}^-}^{(\sigma)} = \left\{\left(\frac{\epsilon}{2\pi e}\right) n_-^{(\mathrm{H})} \cdot \mathfrak{B} \ln \frac{p_{\mathrm{O}_2}^{\frac{1}{2}}\, n_-^{(\mathrm{H})}\; K_1}{N_{\mathrm{O}^-}^{(\sigma)}}\right\}^{\frac{1}{2}} \qquad (n\text{-type catalyst}) \tag{33}$$

Here ϵ represents the dielectric constant of the catalyst at the surface, and K_1 and K_2 are the mass action constants. Furthermore, $N_{\mathrm{O}^-}^{(\sigma)}$ is the surface concentration of the chemisorbed oxygen. These formulae are basically different from those for the physical adsorption of electrically neutral particles. As indicated by formulae (32) and (33), the geometric term (occupation number/-cm^2) of the Langmuir equation is replaced by the concentration of charged defects in the semiconductor, $n_-^{(\mathrm{H})}$ and $n_+^{(\mathrm{H})}$, and the diffusion potential V_D prevailing in the space charge boundary layer. Whereas in a p-type catalyst the quantity of chemisorbed gas is proportional to the fourth root of the oxygen pressure, in the case of an n-type catalyst it is proportional to the logarithm of the oxygen pressure. The experimental results can be interpreted in the light of this relation. The importance of space charge phenomena in the surface regions of a catalyst in connection with a catalytic reaction will be demonstrated in the following section with the aid of a simple reaction.

3.2. *The Fermi Potential and Space Charge Determine the Course of a Reaction*

In sections 2.1 and 2.2 we discussed the decisive importance of the position of the Fermi potential, η_- and η_+, in a catalyst as it affects the course of the reaction but without allowing for the effect of the space charge. The latter relations will only be discussed on the basis of the example of the decomposition of N_2O. It can be deduced from experimental results that for the decomposition of N_2O, n-conducting oxides are always poorer catalysts than p-conducting oxides.[7,8] As was found, moreover, the chemisorption which initiates the reaction (excluding the case of great enlargement of η_+) takes place sufficiently rapidly and the desorption reaction, i.e., the return of electrons to the catalyst, is sufficiently slow.[9,8] In the following considerations we shall write and evaluate only the reaction on a p-type catalyst (for example, NiO):

$$N_2O^{(g)} \rightleftharpoons N_2O^{-(\sigma)} + \oplus^{(R)} \qquad \text{fast,} \tag{34}$$

$$N_2O^{-(\sigma)} \rightarrow O^{-(\sigma)} + N_2^{(g)} \qquad \text{very fast,} \tag{35}$$

$$N_2O^{(g)} + O^{-(\sigma)} + \oplus^{(R)} \rightarrow N_2^{(g)} + O_2^{(g)} \quad \text{slow.} \tag{36}$$

Using (26), the rate equations corresponding to (34) and (36) are:

$$+dN^{(\sigma)}_{N_2O}/dt = k_1 p_{N_2O} - k_2 N^{(\sigma)}_{N_2O^-} \cdot n_+^{(R)} \tag{37a}$$

chemisorption initial reaction
or charge transfer reaction

or

$$+dN^{(\sigma)}_{N_2O}/dt = k_1 p_{N_2O} - k_2 N^{(\sigma)}_{N_2O^-} \cdot n_+^{(H)} \exp\,(+V_D/\mathfrak{B}) \tag{37b}$$

and

$$+dn_{O_2}/dt = k_3 N^{(\sigma)}_{O^-} \cdot n_+^{(R)} \cdot p_{N_2O} \tag{38a}$$

or

$$\frac{dn_{O_2}}{dt} = k_3 N^{(\sigma)}_{O^-} \cdot p_{N_2O} n_+^{(H)} \exp\,(+V_D/\mathfrak{B}). \tag{38b}$$

desorption reaction
(follow-up reaction)

Therefore, we obtain with Eq. (18)

$$\frac{dn_{O_2}}{dt} = k_3 \alpha_p N_{O^-} p^{\circ} \exp\,\{-(\Delta\eta_+^{(H)} - V_D)/\mathfrak{B}\} \cdot p_{N_2O} \tag{38c}$$

The formal rate constants $\boldsymbol{k}_3$, following the disucssion of section 2.4, contain the frequency factor and the energy difference between Fermi potential and ΔE ($= E^{A}_{\circ\bullet}$—valence band edge). $\boldsymbol{k}_3$ in (38) is thus not a purely statistical term, but contains an important energy difference which is determined by the Fermi potential and the exchange level $E^{A}_{\bullet\circ}$.

As indicated in particular by the rate equations (37b) and (38b), displacement of the Fermi potential η_+ downward, as indicated in Fig. 2, i.e., increasing the hole concentration $n_+^{(H)}$, increases the desorption rate (38b) while the chemisorption rate (37b), is decreased only at higher $n_+^{(H)}$. The boundary layer field or the quantity V_D which appears as an exponential term has a corresponding effect. As indicated by the experimental results in Fig. 5, in the case of the p-type catalyst NiO an addition of 0.1 mol % Li_2O causes a distinct increase in the rate of reaction, while an excessive addition of Li_2O of about 3–5 mol % slows down the N_2O decomposition very drastically. This is in agreement with the discussions of section 2.2. The excessive Li_2O content lowers the Fermi potential to such an extent that now the chemisorption according to (34) or (37b) becomes energetically much more difficult. The very rapid desorption is now no longer of interest

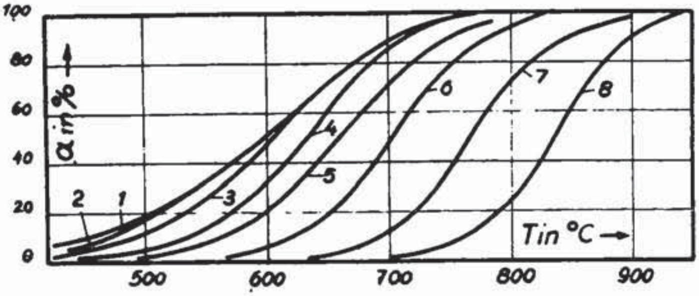


FIG. 5.—Temperature dependence of the degree of transformation of N_2O decomposition on NiO with various additions of Li_2O and In_2O_3 according to Hauffe, Glang and Engell. (Gas mixture 14 volume % N_2O and 86 volume % air; flow velocity at 25 mm diameter of reaction chamber: 1200 cm³/hour).

1. NiO + 0.1 mol % Li_2O
2. NiO + 0.5 mol % Li_2O
3. NiO + 1.0 mol % Li_2O
4. NiO (pure)
5. NiO + 1 mol % In_2O_3
6. CuO (pure)
7. NiO + 3.0 mol % Li_2O
8. Homogeneous and wall reactions.

in connection with the overall course of the N_2O decomposition The catalyst has been "poisoned" by excessive Li_2O doping.

Evidently the N_2O molecules which impinge on the excessively Li_2O-doped NiO behave like quasi "noble gas atoms" which are reflected from the surface without electronic interaction at the temperatures used.

Relations of this sort can readily be demonstrated in connection with other reactions as well and the required experimental evidence can be presented. Experiments for further corroboration of the considerations reported herein are in progress.

4. CONCLUDING REMARKS

As we were able to show in this paper, electron exchange between catalyst and gas molecules of the initial, intermediate, or end species is frequently of decisive importance in heterogeneously catalyzed reactions. Moreover, the relative difference in position between the Fermi potential of the catalyst and the charge transfer levels of the molecules has a decisive effect on the rate of these processes.

At present the quantities discussed here are today numerically still unknown. But the discussion indicates new methods which should be used in further investigating the mechanisms of catalysis. For example, the determination of Fermi potentials and of space charge phenomena in catalysts as well as the measurement of work functions and charge transfer levels (trapping levels) would appear to be most important. Only when these data are available will it be possible, with the aid of the rate equations from the kinetics of reactions, to approach an understanding of the true mechanism, which knowledge is bound to be useful for the purpose of discovering effective catalysts.

DISCUSSION

C. G. B. GARRETT (*Bell Telephone Laboratories*): Dr. Shockley has raised the question of catalysis at germanium surfaces, and the possible investigation of this by use of a *p-n* junction to control the electron and hole electrochemical potentials. In the special case of electrochemical reactions, this has already been done. Brattain and I have shown that, in the anodic oxidation of germanium, holes play a primary role in the rate-determining step in a way that must be very similar to that just discussed in more general terms by Dr. Hauffe. One can also show that, in the cathodic process—presumably the plating-out of hydrogen—it is electrons rather than holes that govern the rate-determining step.

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EXPERIMENTS CONNECTING SEMICONDUCTOR PROPERTIES AND CATALYSIS

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ABSTRACT

The connection between semiconductor properties of a solid and its catalytic action is to be considered as due to the electron transfer nature of catalytic reactions. Hitherto existing evidence is reviewed concerning catalytic reactions on *p*- and *n*-semiconducting oxides. It is corroborated by photochemical processes at semiconductor surfaces and by the consideration of Lewis acids and bases as catalysts. Finally, intrinsic semiconductors of *p*- and *n*-type show the same behavior in catalytic and photochemical reactions.

I. INTRODUCTION

Semiconductors are generally subdivided into impurity and intrinsic semiconductors. In the former, the forbidden zone is so broad (>1 ev) that electrons cannot cross it by thermal energy in the normal lattice. However, localized donor terms can be inserted within the forbidden zone near the conductivity level either by impurities or by reversible or irreversible electronic disorder (*n*-type conductors). Equally, acceptor terms can be produced in the same way near the lower edge of the forbidden zone (*p*-type conductors). E.g. NiO is a *p*-type conductor because in thermal disorder it contains excess oxygen and therefore some Ni^{3+} ions as acceptor terms. The number of these can be increased by insertion of ions of lower valence (Li^+, Ag^+) or decreased by introduction of ions of higher valence (Ga^{3+}, Cr^{3+}). These preparations will be named doped semiconductors. Correspondingly ZnO is an *n*-type conductor because of its thermal oxygen deficiency and hence the presence of Zn^0 or rather Zn^+ as donor levels. These can be increased in number by the insertion of ions of higher valence than Zn^{++} (Ga^{3+}, Al^{3+}) or decreased by lower valence ions (Li^+). It is this possibility of changing the conductivity and the concentration of carriers by doping without a simultaneous change in the bulk chemical character which enables us to study the catalytic behavior as a function of only this parameter.

Whereas in these impurity semiconductors either electrons in the conduction band or positive holes in the valence band are the mobile carriers, in intrinsic semiconductors such as germanium the forbidden zone is so narrow that pairs of carriers are formed simultaneously by thermal energy. A dissymetry of the number of carriers of each sign can again be produced by introducing donor or acceptor terms which on ionization give one carrier and one immobile charged ion. E.g. germanium is doped to an *n*-type conductor by addition of In or Ga and to a *p*-type conductor by As or Sb. Lately Welker has found that the so-called III-V-compounds, such as InSb or GaAs, behave in the same way as the tetravalent elements and can be doped in the same way. Here also, the study of the catalytic behavior is facilitated by the doping method. This is the same principle that has been used previously for the study of alloy catalysis with very dilute homogeneous alloys.[1] It is much more useful than the comparison of different catalysts differing not only in carrier concentration but at the same time in chemical character, lattice spacing, etc.

The idea of correlating semiconducting properties and catalytic action presupposes that catalysis has something to do with the electronic state of the solid. Up to ten years ago this was not at all self-evident. It was clear that some sort of chemisorption had to occur as a preparatory step to catalysis, but as for the nature of the bond between the molecule and the catalyst, only conjectures could be made. Lately this has considerably changed, and from the point of the catalytic reaction our knowledge is nearly as complete as from that of the solid. The change has been brought forth first by the study of alloy catalysis.[1,2] We now know that in a large number of reactions, if not in all, the catalytic activation consists in a transfer of electrons from the molecule to the catalyst or vice versa. As a first approximation, reactions may be divided in two groups: donor reactions in which electrons must be transferred to the catalyst. Hydrogenations and dehydrogenations clearly belong to this group. Metals having many free electron levels are good catalysts for these reactions, in agreement with the fact that hydrogen is chemisorbed on metals as protons giving off its electrons. To the same group belongs the oxidation of CO; e.g., with CuO as catalyst, it may be written:

$$\begin{array}{ll} 2CO + Cu^{++} \rightarrow 2CO^{+} + Cu & \text{(rate determining)} \\ Cu \rightarrow Cu^{++} + 2e^{-} & \\ 2e^{-} + 2CO^{+} + O_2 \rightarrow 2CO_2 & \text{(immeasurably fast)} \end{array}$$

(Later we will encounter a case where this reaction is not of the donor type.) The second group contains acceptor reactions involving molecules with high electron affinity such as O_2 or H_2O_2. H_2O_2-decomposition is catalyzed also in homogeneous systems by electron addition, e.g.:

$$\begin{array}{l} Fe^{++}_{aq} + H_2O_2 \rightarrow OH + OH^{-} + Fe^{3+} \\ OH^{-} + Fe^{3+} \rightarrow OH + Fe^{++} \\ OH + H_2O_2 \rightarrow O_2 + H_2O + H \quad \text{etc. (chain).} \end{array}$$

Similarly this reaction is catalyzed by electron rich alloys.

Thus, the task of connecting semiconductor properties to catalytic action reduces to the question whether donor reactions are catalyzed by *p*-type conductors and acceptor reactions by *n*-type conductors. According to the above principle we really should ask if an increase of *p*-type conductivity enhances the donor reaction catalysis and vice versa. Enhancing a reaction means increasing its rate or lowering its activation energy.

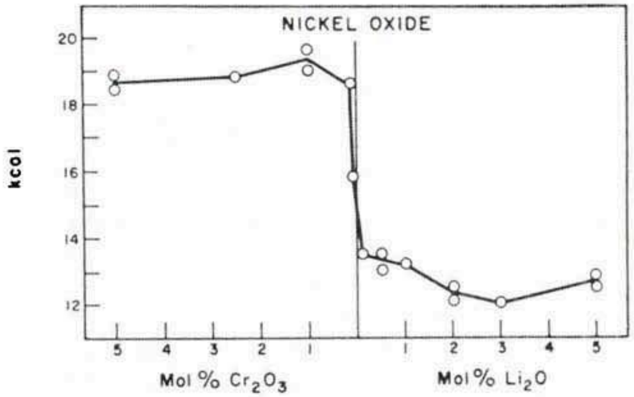
II. OXIDE SEMICONDUCTOR CATALYSIS

The first investigator to apply these criteria was C. Wagner[3] who tried to improve the catalysis of the nitrous oxide decomposition

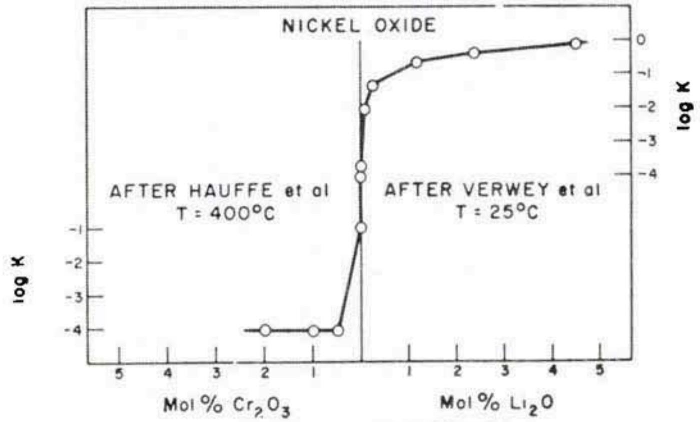
$$N_2O \rightarrow N_2 + \tfrac{1}{2}O_2$$

on ZnO by adding Ga_2O_3, i.e. by increasing the number of quasi-free electrons, considering N_2O as an electron acceptor. He did not find a positive effect, and different explanations, alien to our problem, have been brought forward (Cremer, Boudart[4,5]). Hauffe,[6] in a survey of his own and other experiments with various catalysts, was more successful. He was able to state that very generally *p*-type conductors are the best catalysts for this reaction. He concluded that the rate determining step is not the chemisorption of N_2O with electron transfer from the catalyst but the oxygen *de*sorption with transfer to the catalyst. The fact that on all *p*-type conductors the reaction order deviates from the first supports this view.

A systematic investigation with doped catalysts has been carried out by Schwab and Block.[7] They examined the carbon monoxide oxidation with Li- and Cr-doped NiO and with Ga- and Li-doped ZnO. With NiO they found, as shown in Fig. 1, that the activation energy drops on addition of Li^+ and increases on addition of Ga^{3+}, i.e. it is lowest at the highest positive hole



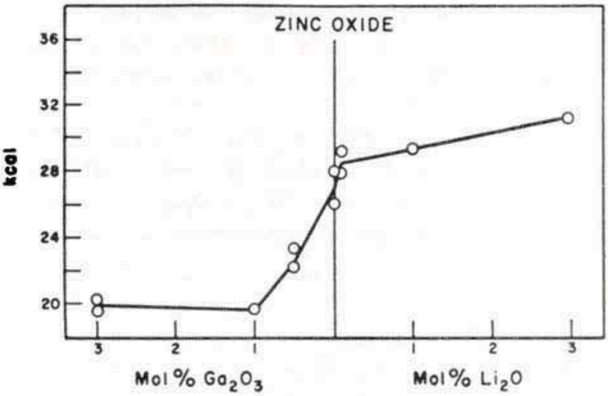
ACTIVATION ENERGY FOR CO-OXIDATION



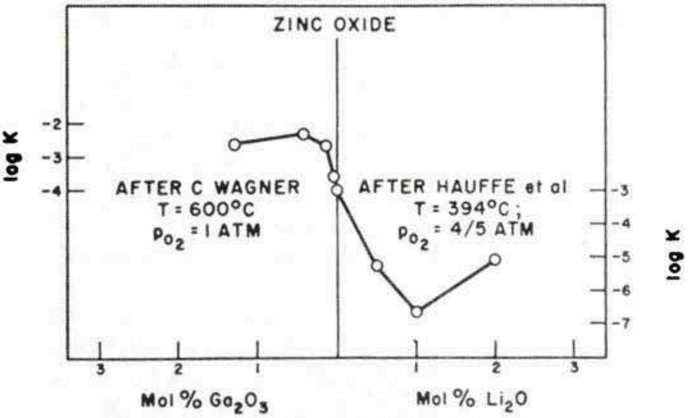
ELECTRICAL CONDUCTIVITY

FIG. 1.—Activation energy for catalytic oxidation of CO, and electrical conductivity, of NiO on doping with Cr or Li.

concentration. Hence, the rate determining step is the chemisorption of CO as a cation, as assumed above, and the order of the reaction is the first with respect to CO. However, with ZnO as a catalyst, Li^+ increases and Ga^{3+} decreases the activation energy as if here the free electrons were transferred from the catalyst to the gas. This result is shown in Fig. 2. As a matter of fact the kinetic behavior of the reaction on these catalysts clearly shows that in this case the chemisorption of oxygen is the rate determin-



ACTIVATION ENERGY FOR CO-OXIDATION



ELECTRICAL CONDUCTIVITY

FIG. 2.—Activation energy for catalytic oxidation of CO, and electrical conductivity, of ZnO on doping with Ga or Li.

ing step, and oxygen is an electron acceptor. Here for the first time, a clearcut connection has been established.

Unfortunately, nearly at the same time Parravano,[8] using the same reaction and similar catalysts, found exactly opposite results, and much discussion has been raised. It has been supposed that at Parravano's much lower temperatures chemisorbed gas layers might have entirely altered the electron balance in the catalyst surface. That this explanation is not very far from the truth appears from recent results of Block and Chon[9] who were able to reproduce the former results with CoO as catalyst, another *p*-conductor. It is rather remarkable that at high oxygen pressures this catalyst is self-poisoned, for it could be shown that Co_3O_4 is formed which is a *n*-type conductor.

There are other examples where the viewpoint of electron transfer could be successfully applied. Schwab et al.[10] reported that carbon monoxide combustion is catalyzed by zinc ferrite, $ZnFe_2O_4$, as shown in Figs. 3 and 4, faster and with lower activation

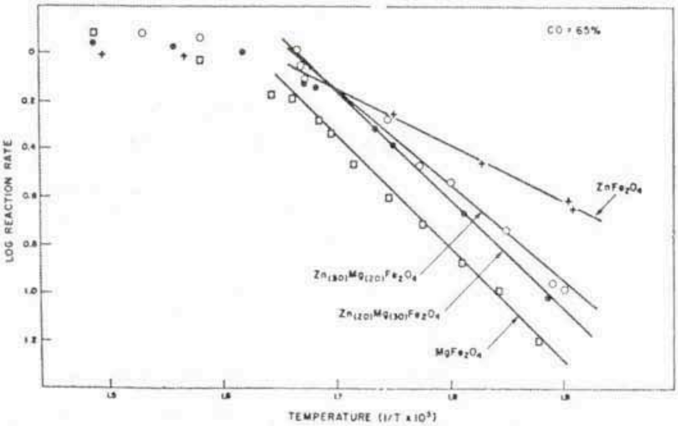


FIG. 3.—Rate of CO oxidation over Zn and Mg ferrites.

energy than by magnesium ferrite $MgFe_2O_4$. Now, zinc ferrite is a normal spinel, bearing all its Fe^{3+}-ions in octahedral sides, where they can easily act as electron acceptors for the donor CO, whereas in the inverse spinel magnesium ferrite only half of them are in this position. Magnetite Fe_3O_4, being also an inverse spinel, shows in Fig. 5 the same activation energy as magnesium ferrite,

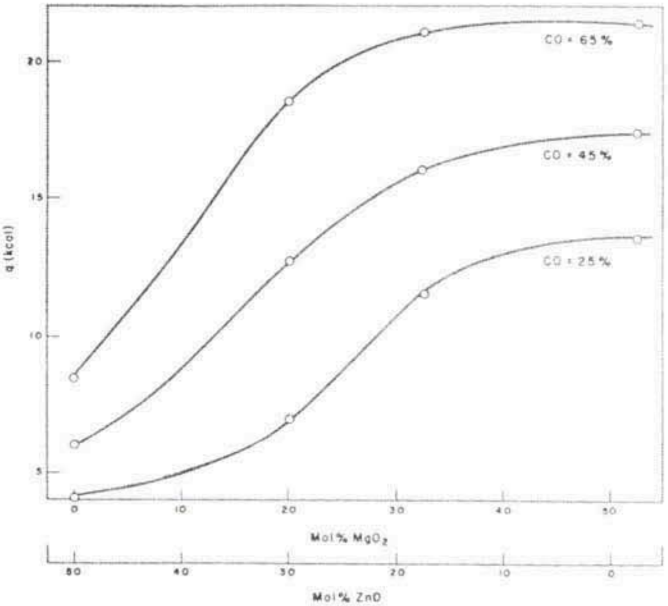


FIG. 4.—Activation energy for CO oxidation over (Zn,Mg)-ferrites.

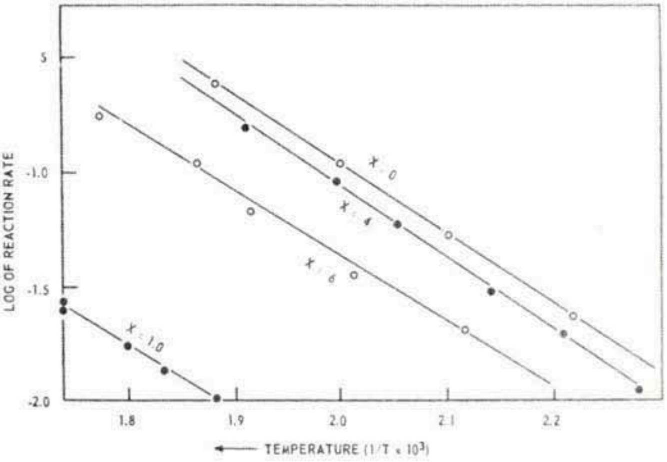


FIG. 5.—Rate of CO oxidation over xMgO·$(1 - x)$FeO·Fe_2O_3 ferrites.

but a frequency factor 30 times higher. This is explained by the easy charge transfer (semiconductivity) between octahedral Fe^{++} and Fe^{3+} ions. Characteristically enough, the acceptor reaction of H_2O_2 decomposition with both ferrites behaves in the opposite way although here not all the details are clear.

Another interesting example is ethylene hydrogenation with pretreated chromic oxide (Voltz and Weller [11]). Pretreatment with the acceptor O_2 increases the conductivity which is characteristic for a *p*-type conductor; however, O_2 poisons the hydrogenation. This would be a contradiction if it were not reasonable to assume that O_2-chemisorption produces a double layer on the surface the negative outer side of which repels the hydrogen electron. On the other hand hydrogen chemisorption decreases the conductivity by filling up the positive holes and increases the rate of hydrogenation because this chemisorption process is just identical with hydrogen activation.

III. OXIDE SEMICONDUCTOR PHOTOCHEMISTRY

In the previous examples electrons and positive holes exerted a catalytic action because they could come to the surface as mobile carriers whereas localized donor or acceptor terms, e.g. Li^+ ions in nickel oxide did not show such action. One can think about bringing the carriers to the surface by illumination instead of thermal excitation. This would mean that a semiconductor showing photoconductivity should be able to become a catalyst on illumination at temperatures where in the dark it is not. Hnojevij [12] tried this and, using the very sensitive Warburg-Barcroft technique, he was able to show that pure zinc oxide, entirely inactive in the dark, decomposes hydrogen peroxide when illuminated with white light. The mechanism obviously is excitation of electrons from the interlattice Zn^+ ions to the conductivity band by light, migration to the surface, chemisorption or immediate splitting of H_2O_2 and recharging of interlattice Zn^{++} giving Zn^+ in a similar way as in the Fe^{++} mechanism indicated above. The free energy of light accumulated in the excited electrons is high enough not only to split H_2O_2 but even to synthesize it, a reaction known long ago and here confirmed once more. It is very characteristic that luminescent zinc oxide preparations show both reactions with a much reduced rate. Obviously the luminescence activators, acceptor terms near the upper limit of the forbidden zone, bind the electrons in localized sites and thus keep the conductivity levels empty.

Pascher,[13] by using the same technique, was able to carry out a series of oxidations of organic compounds using ZnO or ZnS as photosensitizers. He observed oxidation of methanol, ethanol, xylene, hydroquinone, all being protodonor substances, but not of aniline or phenylene diamine which are bases and therefore electron donors.

IV. SURFACE ELECTRON TRANSFER

Of course, it is to be expected that, with a moderately conductive solid, the chemisorption layer formed may produce a dilution or an enrichment of electrons in the layers near the surface and thus build up a counter potential hindering further electronic transfer. An example is the oxygen poisoning of Cr_2O_3 for hydrogenation discussed above. It is mainly Hauffe [14] who rightly emphasizes this point especially in his study of surface oxidation of metals giving weakly conducting compact oxide layers. In the extreme case where no perceptible conductivity exists, only surface electrons can be transferred to the gas molecules and only surface holes can be filled therefrom. This would mean that amongst insulators, electron donors or Lewis bases will catalyze acceptor reactions and Lewis acids will be catalysts for donor reactions.

Both cases are verified by experiments. Thus Schwab and Hartmann [15] showed that nitrous oxide as well as ozone, both acceptor molecules, are decomposed faster the more basic the insulating oxide is (e.g. $BaO > SrO > CaO > MgO$). The well-known examples for Lewis acids are the acidic SiO_2-Al_2O_3 cracking catalysts (e.g.[16]), which show an ever-increasing industrial importance. By their acidic nature they attract electrons from hydrocarbons and so weaken the bonds in the carbonium-ion formed so that thermal decomposition can occur.

V. INTRINSIC SEMICONDUCTOR CATALYSTS

Whilst the oxidic catalysts treated above are always either *p*- or *n*-type and only the degree of this character can be modified by doping, intrinsic semiconductors offer the possibility of switching over entirely from the *n*- to the *p*-region for the same material. A basic change in the catalytic behavior should accompany such change. Weisz [17] has reported to us privately that he could not detect such catalytic changes with formic acid on silicon. Penzkofer [18] in our laboratory was more successful. He studied the dehydrogenation of formic acid vapor, the classical donor reaction with germanium of different preparation. At first sight, one would expect that *p*-type Ge (doped with In or Ga) would be a good catalyst requiring a low activation energy for this reaction and that *n*-type Ge (with As or Sb) would not catalyze. Experimentally, a certain catalytic effect is observed even with *n*-type Ge, obviously due to the positive holes existing as minority carriers. The activation energy is 40 kcal/mole (the same as with the insulating and neutral alkali halides). First we also were unable to notice any difference between *p*-type and *n*-type Ge, however when we thought about exposing freshly etched surfaces of both types to the formic acid vapor (etching with CP-4 which is essentially $HF + HNO_3$) the value for *p*-type Ge dropped distinctly to 32 kcal/mole and that for *n*-type Ge remained at its previous level.

The experiments have been extended by Krawczynski [19] from Ge to Si and to III-V-compounds and from dehydrogenation to ethylene hydrogenation. He found that this reaction with *p*-type Ge (10^{18} atoms$\cdot$cm^{-3} Ga or 10^{20} atoms$\cdot$cm^{-3} In) begins between 50 and 150°C and shows a sudden increase of its temperature coefficient at 450°C. With *n*-type Ge (10^{18} atoms$\cdot$cm^{-3} As), as in Fig. 6, the reaction does not become perceptible below 380°C and has so high a temperature coefficient that at 450°C it reaches the velocity of *p*-type Ge. It was also possible to change the catalytic response from this type to the previously described one by overdoping As-doped Ge with In. The activation energy of *n*-type and *p*-type Ge above 450°C is 22 kcal/mole from Fig. 7, for *p*-type Ge between 100 and 450°C, 3–6 kcal/mole. Obviously, by heating in the ethylene-hydrogen mixture to 450°C, *p*-type Ge is superficially changed to *n*-type Ge, the change being reversible only by heating in pure hydrogen. We suppose that the surface becomes (CH)-doped (5 electrons!). Similar results are obtained with *n*- or *p*-type Silicon, the activation energies being >11 and

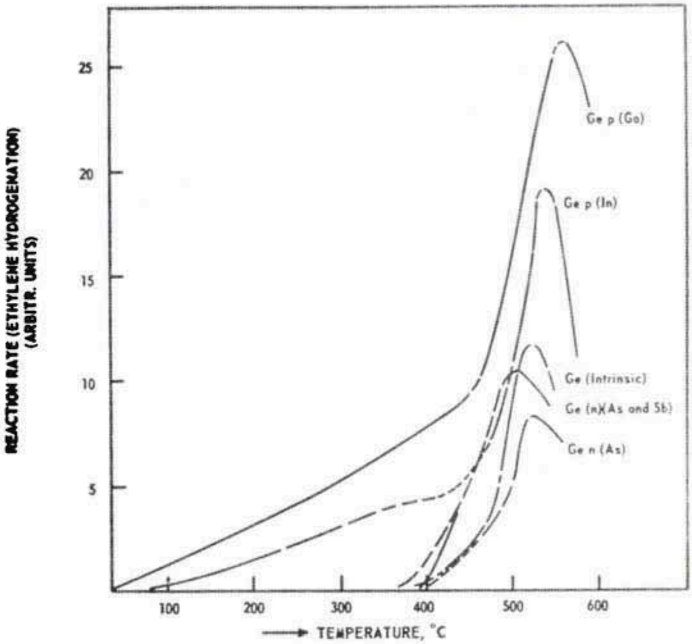


FIG. 6.—Reaction rate for hydrogenation of ethylene over various samples of Germanium, intrinsic, doped *n*-type with As or As and Sb, doped *p*-type with Ga or In.

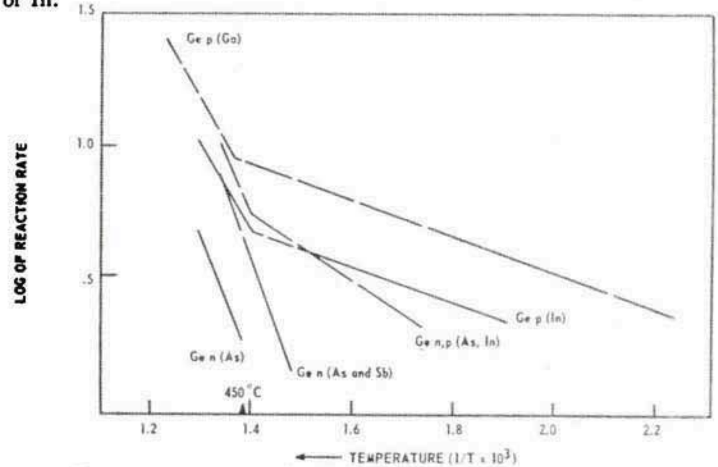


FIG. 7.—Arrhenius plot of hydrogenation rate of ethylene over Ge samples (see Fig. 6).

5 kcal/mole respectively. Corresponding effects are also observed with III-V-compounds; the respective values are for InSb 5 and 17 kcal/mole, for In As5 and 24 kcal/mole. In the latter case, the catalytic function of a technical *n*-type InAs could be totally changed to *p*-type behavior by depositing Indium on the surface from the vapor phase. All these experiments show distinctly that mobile positive holes are active in hydrogenation catalysis, even with these unusual catalysts.

In intrinsic semiconductors the width of the forbidden zone is so low that light absorption of wave lengths somewhat smaller than infrared is sufficient to produce carrier pairs, and still lower energies (longer waves) are sufficient to separate a carrier from an immobile impurity term. Thus, illumination of *n*-type Ge will produce a majority of free electrons in addition to the already established thermal dissociation equilibrium. As a consequence, *n*-type Ge, shaken with oxygen under water in a Warburg vessel, can be shown to be oxidized to GeO_2 or rather H_2GeO_3, and this reaction is accelerated by light. Figure 8 shows the experimental results of cumulative oxygen uptake during periods of darkness, and during illumination from a white incandescent lamp.

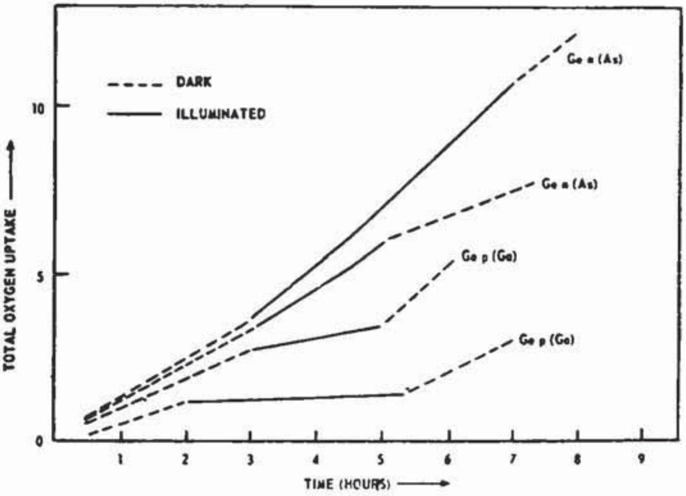


FIG. 8.—Cumulative oxygen uptake by *p*-type and by *n*-type samples of Ge, in oxygenated water, during darkness (- - - -) and during illumination (——).

What will happen to *p*-type Ge under the same circumstances? In the dark, the oxidation velocity is found to be somewhat lower than with *n*-type Ge because the free electron concentration is less, part of the positive holes being counterbalanced by immobile occupied acceptor levels. Now, on illumination, the oxidation is considerably retarded, sometimes even stopped. This can be explained by the assumption that illumination creates mobile positive carriers and that these recombine at the surface with the minority of free electrons in competition with the electron transfer to oxygen and hence with the oxidation of germanium.

VI. CONCLUSION

It may be remarked that the above summarized observations, coming from different sources and based on different methods, form a uniform picture for the relationship between semiconductor properties and catalysis. This can on one side be considered as a thorough confirmation of our concepts of semiconduction in a field at first view entirely alien. On the other side, however, even these concepts are a considerable support to modern catalysis theory as in its earlier stage was the theory of metals. We can say that one more gap between physics and chemistry has been closed, leaving both shores in a reinforced state.

DISCUSSION

W. H. BRATTAIN (*Bell Telephone Laboratories*): I would like to make the comment that, if the rate of reaction is dependent on illumination of the semiconductor surface, this photo effect sometimes can be used to determine which species, either electrons or holes, is controlling. In the simple case of light, of wave length short enough to be in the main absorption band, it will produce equal numbers of both species. If the semiconductor is extrinsic, the increase in concentration of the minority carrier will be much greater than that of the majority carrier. A reaction rate dependent on concentration of minority carrier will be increased. A good example of this is the anodic oxidation of germanium in electrolytes. The photoeffect here is very much greater on *n*-type germanium than on *p*-type. The reaction is controlled by the hole concentration. At high enough temperatures all semiconductors will be intrinsic and both concentrations will be increased equally. At low enough temperatures where most of the carriers are frozen out on the impurities, light of wave length just short enough to ionize the impurities will increase the concentration of majority carriers without appreciable change in the minority carrier. The intensity of these photo effects will depend on the lifetime of the added carrier concentration. Absence of photo effects may only mean that this life is very short. In some semiconductors the photo effects may be complicated by trapping of the minority carrier. For example, one might have a case where all the added minority carriers were trapped near the surface thus changing the surface potential without any change in the effective concentration of the minority carrier free to take part in the reaction.

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LONG TIME WORK FUNCTION CHANGES INDUCED BY LIGHT AND ELECTROSTATIC FIELDS *

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ABSTRACT

Long time changes in the work function of Au, Ge, and Si have been found to be induced by electrostatic fields or illumination. A description of the contact potential apparatus used in this investigation is given. Various possible models to explain the effect are examined.

It is suggested that chemisorbed gas on the surface acts as a semipermanent trap and that slow changes in this trap occupation are responsible for the long time processes. A model is advanced for the nature of the chemisorption bond of oxygen on Ge and from this the kinetics of adsorption are predicted.

I. INTRODUCTION

One of the classic tools used to study surface phenomena is the measurement of the work function. Any process which changes the potential barrier at the surface can be directly monitored by this technique. It has proven to be particularly useful in investigating the nature of the electronic interaction between chemisorbed atoms and the adsorbent surface. One can get information as to how the chemisorption bond is formed and as to its final form. The work function plays an important role in the electron transfer processes involved in adsorption and consequently in the kinetics and heat of reaction. In accord with these observations there is a direct relation between the work function of a surface and its catalytic properties.

In recent years a great deal of attention has been given to the properties of Ge and Si surfaces. One of the results of this work

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has been the concept of surface trapping. At present the generally accepted picture is that there are two kinds of surface traps, fast and slow. We will only be concerned with the latter type here. Changes in the slow trap occupancy are responsible for long time drifts (seconds to hours) in many surface properties. One can learn a good deal about this slow reaction by displacing it from equilibrium through an external agency and studying the details of the recovery when the disturbance is removed.

The measurements to be reported here concern long time changes in the work function of Au, Ge and Si which the authors discovered are induced by applied electrostatic fields and by illumination. It is interesting to note that this effect was first seen on Cu in 1912.[1] The results of the experiments on Au, Si, and Ge presented are only qualitative in nature. One cannot claim to have a truly quantitative description of such effects unless elaborate procedures are followed to ascertain the exact condition of the surface and of the gases used. However, even with this qualification, significant qualitative aspects stand out. There are two separate features of the contact potential measurements which must be examined. First that it is at all possible to induce changes in the work function with light or applied fields. The second feature is the magnitude of the changes and the details of the recovery process. It will be seen that the slow surface reaction responsible for the long time changes in the work function is also the cause of the drifts in the surface conductance and surface recombination velocity found by other workers for Ge and Si. Various mechanisms for the slow changes will be discussed and a model which seems to be consistent with the facts for Ge and Si will be proposed. A model will also be advanced for the nature of the chemisorption bond of oxygen on Ge and from this the kinetics of the adsorption will be predicted.

II. EXPERIMENTAL

1. *Experimental Method*

The Kelvin method of measuring contact potential differences is the only method which can be used in a gaseous atmosphere. It was adopted in the classic investigation of Brattain and Bardeen[2] and more recently by others; a direct comparison by Anderson[3] showed its results to be in good agreement with measurements by the electron beam method on metals in vacuum. The method consists in observing the displacement current which is generated by varying the capacity of a condenser formed of two samples to be compared. This displacement current vanishes if the contact potential difference of the two samples is compensated by a variable voltage source in series with the circuit, and the voltage required for compensation is then equal and opposite to the contact potential difference. Since measurements are made by a null method there is no need for accurate knowledge or control of the geometry.

In early applications of the method the electrodes were separated by a rapid motion and the null detection was performed with the aid of a ballistic galvanometer. It is customary practice at present to vibrate one of the electrodes and to amplify and display the ac signal thus generated. The signal obtained is proportional to the capacitance change produced by the vibration (or the fractional change in separation) and to the frequency of vibration. Since the vibrating electrode is driven electromagnetically at precisely the frequency at which the null detection must be performed, any increase in the product of amplitude times frequency of vibration (or the signal power) is accompanied by a proportional increase in the noise power picked up by the high impedance measuring circuit. Considerations of maximum feasible accuracy of positioning and optimum efficiency of the transducing process limit the sensitivity of the measurement to ± 10 millivolts for most practical purposes.

The vibrating electrode technique has three further disadvantages. Measurements in a controlled atmosphere or vacuum require a mechanical connection between one of the electrodes inside a sealed, electrostatically shielded chamber and a transducer located outside as remotely as possible. The elastic membrane or bellows through which such a connection must be made inevitably causes the vibrating electrode to shift when the pressure in the sealed container is changed. The application of an electrostatic field between the electrodes has a similar effect and usually causes the electrodes to touch. Finally, time-consuming repositioning is required if electrodes are to be changed for comparison purposes or if one of the electrode surfaces is to be made accessible for purposes of illumination, inspection or treatment.

It was found possible to eliminate all of the above shortcomings and to achieve a sensitivity of ±1 millivolt by adopting a rotating instead of a vibrating system. This method was adopted independently by Miller[4] for similar reasons. Our apparatus is shown schematically in Fig. 1 and pictorially in Fig. 2. Three samples are mounted on a turntable which rotates at about 1800 rpm below a stationary plate carrying three additional samples. The rotating samples are connected electrically to the turntable, which in turn is connected electrically by means of a sliding contact (and its grease-free ball bearings) to the metal frame of the apparatus and the electrostatic shield of nickel mesh which surrounds it. The three stationary samples are mounted on porcelain insulators and connected separately to the outside through shielded press leads. As shown in the schematic diagram, any one of the stationary electrodes can be connected to a reference

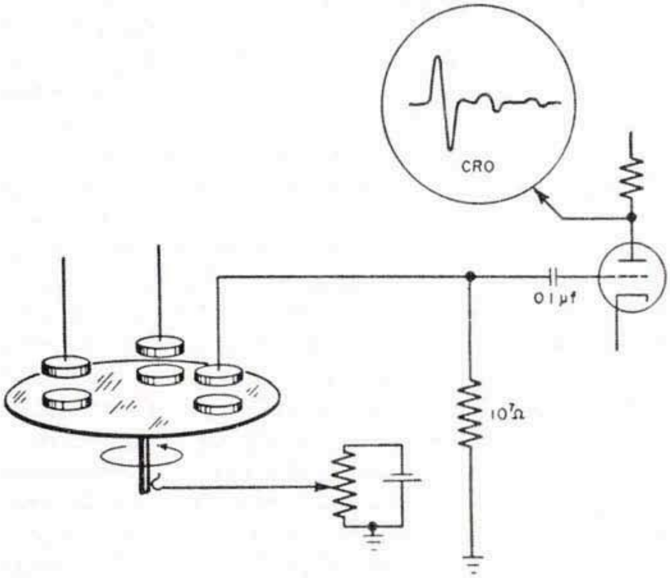

Fig. 1.—Schematic diagram of electrometer for work function comparisons by the Kelvin method.

"ground" through a high resistance, and the a-c voltage appearing across this grounding resistance can be amplified and displayed on an oscilloscope. The potential of the rotating electrode system (including the metal frame and the surrounding electrostatic shield) with respect to the reference "ground" can be adjusted by means of a calibrated potentiometer of relatively low impedance. A glass vacuum chamber surrounds the entire apparatus shown in Fig. 2, including its electrostatic shield (not shown). The turntable is connected to the rotor of a commercial induction motor (fan motor) by means of a shaft which is free to rotate about its axis in two grease-free ball bearings. The induction rotor protrudes below the electrostatic shield and is driven by a field coil assembly located outside the vacuum system. Adequate magnetic shielding

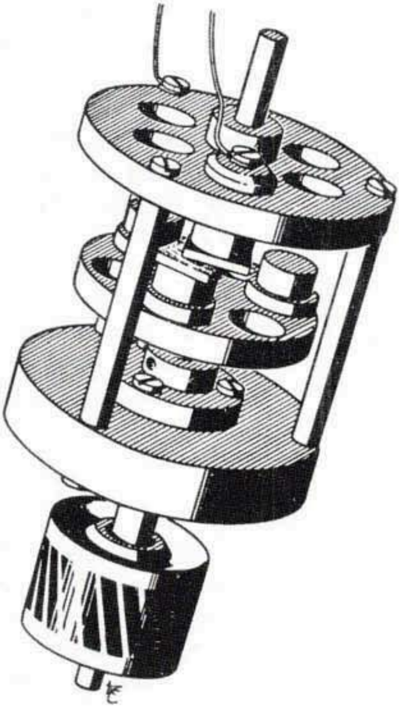

FIG. 2.—Rotating sample electrometer head for work function comparisons, electrostatic shield and vacuum chamber removed.

between the induction rotor and the samples is provided by the heavy circular base plate which is made of soft steel. With the exception of the commercial ball bearings, the porcelain insulators and the samples under investigation, all other metal components are of stainless steel or nickel. The system can therefore be baked and evacuated to 10^{-8} mm Hg.

To perform measurements the turntable is set into rotation, the null detection amplifier and oscilloscope is connected to one of the three stationary electrodes, and the potentiometer is adjusted so as to balance out each of the three displayed pulses in succession. The null detector is then connected in turn to the other two stationary electrodes and the balancing process is repeated. In this manner it is possible to observe continuously variations in the work function of six specimens, and the surfaces are readily accessible for illumination, etching, sandblasting, etc., without disturbing the critical alignment. By carefully reducing the electrode separation to a minimum, say 0.1 mm or less, it is possible to achieve a sensitivity of ± 1 millivolt. It should not be attempted to increase the sensitivity by increasing the resistance of the grounding resistor; if more than about 10^7 ohms is used, the sensing electrode is found to float at appreciable potentials due to ion collection from the flowing gas, photo-emission in vacuum, etc.

2. *Experimental Results*

If an electrostatic field of approximately 30,000 volt/cm (300 volts across a gap of 0.1 mm) is applied between two electrodes of gold, platinum, germanium or silicon, the work function of both electrodes is changed; this change builds up slowly and saturates in about one hour, and upon removal of the field it decays in a similar way. The possibility that this effect is stimulated by polarization of some insulating material in the circuit was eliminated by observing that no effect is induced if the voltage is applied without rotating the electrodes into alignment.

Our apparatus enables us to observe each of the two participating electrodes separately by referring them to one of the unaffected electrodes, and we were thus able to ascertain that there is no systematic difference between the changes induced in the anode and cathode. The work functions of both participating electrodes are changed by approximately equal amounts in opposite directions: the negative electrode becomes more electro-negative (its work function increases), and the positive electrode becomes more electro-positive. It is noteworthy that the direction of the change is always opposite to the change which would be induced by ion collection from the atmosphere (if the positive electrode collected negative ions); instead it corresponds to the direction of internal polarization of the electrode material.

The magnitude of the induced change depends on the history of a particular surface and is decreased somewhat by oxidation or contamination; for a freshly sandblasted surface of any material, the change in work function is of the order of 100 millivolts at saturation.

If the induced change is measured as a function of time after removal of the applied field, the observed decay is found to be linear if plotted against a logarithmic time base. If the measurement is performed with the two electrodes between which the field was applied, any slight difference in the magnitude of the changes induced in the two electrodes will cause the composite decay of both electrodes to appear curvilinear, even if the decay curve of each single electrode is linear. We therefore adopted the practice of always observing each of the two participating electrodes separately by using two other electrodes as references. The linearity of the decay slope for a single electrode thus obtained is the most highly reproducible feature of our observations.

The slope of the logarithmic decay curve for a given sample is reproducible within 10 percent under equal experimental conditions as long as the electrode is not contaminated or "poisoned." It is proportional to the absolute temperature within the limits of reproducibility, in the temperature range between 195°K and 373°K. The value of the slope varies between $\frac{1}{2}kT$ and kT for all the samples observed, regardless of the material. The six decay curves plotted in Fig. 3 are typical; they were obtained after alternately applying positive and negative fields to a single gold electrode.

The effect described above was observed on electrodes of gold, platinum, germanium and silicon (both p-type and n-type in each case), and regardless of the surface treatment applied (sandblasting, metallurgical polishing, chemical etching, and in some

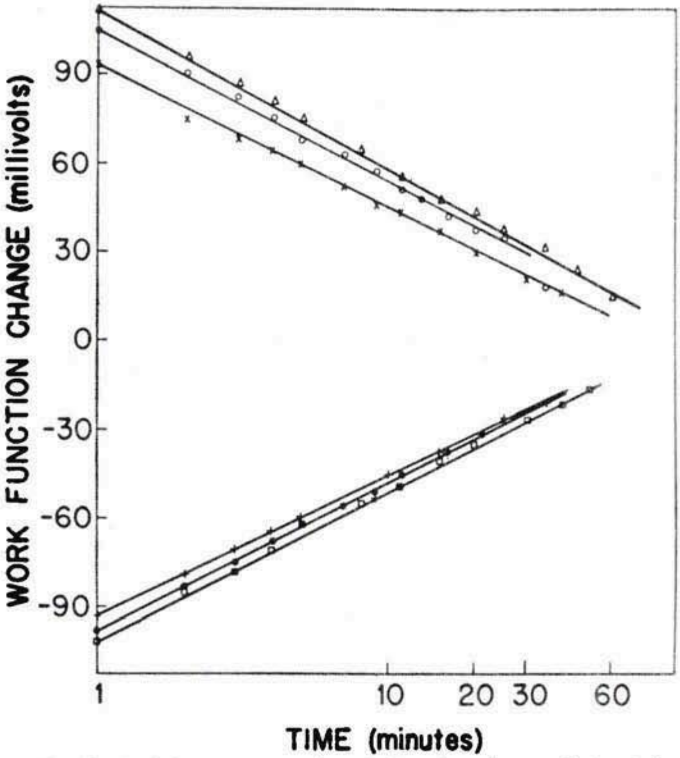

FIG. 3.—Typical decay curves of work function changes induced by alternately applying positive and negative fields (300 volts across 0.1 mm) to sandblasted gold electrode in dry nitrogen at atmospheric pressure and room temperature. The results of six consecutive runs are shown.

cases electrolytic etching). There appears to be no systematic dependence on the electrode material or surface treatment to within the limits of reproducibility.

The ambient atmosphere was also found to have no measurable effect; identical results were obtained in dry nitrogen, oxygen, hydrogen and helium; one notable exception is water vapor. If moisture is initially present, no change in work function is observed upon removal of the field. If moisture is introduced during a decay, the change in work function vanishes almost instantaneously. In this connection it should be pointed out that the first measurement of work function is performed about 15 seconds after removal of the field, so that a very rapidly decaying change would not be detected.

The effect also appears to be insensitive to pressure over a wide range. Measurements with all the materials were performed at pressures between 10^{-3} mm Hg and atmospheric. Several sandblasted gold electrodes were observed to show identical response after baking at 300°C in a vacuum of 10^{-8} mm Hg, again within the limits of reproducibility.

Finally it was observed that work function changes of comparable magnitude and decay rate can be induced by illuminating an electrode with incandescent light for a comparable period of time. Only several preliminary light experiments have been performed thus far, and these suggest that illumination decreases the work function of gold, while it increases that of germanium. The light-induced changes seem to be far less reproducible, in regard to both magnitude and decay-rate. It is possible that the picture is complicated in this case by the superposition of heating effects.

Some remarks are in order concerning the limits of reproducibility referred to repeatedly above. As was mentioned, the logarithmic decay slope of the field-induced work function changes was found to be reproducible within 10 percent as long as the sample in question was not contaminated or "poisoned." Samples occasionally retained their ability to react reproducibly for a period of months, apparently insensitive to repeated field applications, changes in ambient atmosphere, pressure or temperature, even insensitive to removal from the glass chamber and exposure to room air and the moisture of human breath. Not even exposure to ozone seemed to impair their response, although it caused an irreversible change in the work function of semiconductors. On other occasions samples were found to become "poisoned" several hours after a surface preparation, whereupon their response became erratic both as regards the magnitude and decay slope of the induced effect. Exposure to a roughing vacuum had no effect on "poisoned" samples, and their original reproducible response could only be restored by resurfacing. We have been unable thus far to identify the factor which governs this "poisoning." In observing the temperature dependence of the decay slope, all measurements were discarded if the initial slope at room temperature could not be reproduced at the end of the series.

One further systematic effect was observed which might prove of interest. It was found repeatedly that the work function of some electrodes is changed reversibly if they are left facing some other electrode for a period of time, even if no field is applied. These changes are usually of the order of 10 millivolts but have occasionally been observed to amount to 50 millivolts; they are most pronounced in the case of freshly prepared surfaces and seem to be independent of the surface treatment applied. The changes thus induced decay more slowly than the field induced changes. The work function of gold, for example, is increased if it remains near platinum; that of silicon is decreased upon exposure to germanium and increased upon exposure to the proximity of platinum. To avoid this "proximity effect" it was found necessary to make sure that the electrodes are not aligned when the apparatus is stopped between measurements. We might remark parenthetically that it was the original observation of this "proximity effect" which led to the development of the present apparatus and the discovery of the field effect.

In conclusion we wish to report briefly the results of an experiment which was performed in an effort to verify by direct means the hypothesis (to be elaborated in a subsequent section) that the observed work function changes are governed by a field-induced adsorption of gas. Such a phenomenon has been observed by Blüh,[5] but his experiment is not capable of measuring the time dependence of the process. A gold foil electrode was sealed into a re-entrant glass chamber of minimum volume which also contained a thermistor element, and the chamber was evacuated to about 10 microns and immersed in an electrolyte solution which served as a constant temperature bath. The ratio of surface area to volume and the pressure sensitivity of the thermistor element were such that the desorption of a monolayer of gas could have been observed with ease. The application of an electric field between the gold foil and the bath solution (through the glass envelope) was found to induce a sudden pressure drop. A similar drop was observed to accompany each change in the field direction, and upon repeated reversals of field the reaction gradually decreased and vanished. The system recovered its ability to react if left standing for several hours. No long persistent change analogous to the work function change was observed, but it should be pointed out that the characteristics of the several thermistors we tried showed a slow drift which might have masked any slow desorption effects.

III. THEORETICAL

1. *The Logarithmic Law Governing Surface Recovery*

In the experimental description it has been pointed out that the negative plate in the field effect suffered an increase in work function and that upon removal of the field the measured contact potential difference returns to its initial value linearly with the logarithm of the time over most of the observation period. This is shown in Fig. 3. The light induced effect although less well behaved than the field effect also decays in this manner. The logarithmic behavior is characteristic of an activated process where the activation energy can be represented as a linear function of the number of particles that have completed the process. This is of course essentially the idea of the boundary layer theory of chemisorption [6,7,8] where it is assumed that the adsorption of an atom on the surface results in the appearance of a positive or negative charge there depending on the electron affinity and the ionization potential of the adsorbate and the work function of the adsorbent. As the surface becomes increasingly covered with chemisorbed ions, the electrostatic potential energy of the adsorbed species becomes larger and larger until the electron transfer process which creates the chemisorption bond is no longer energetically favorable.

Let us now investigate the relationship between the boundary layer theory and the logarithmic change in the work function, without restricting ourselves to adsorption as the mechanism by which the work function changes. It is only necessary to assume a change in the charge trapped at the surface; just how it is trapped will be discussed further below. Let n_1 be a positive deviation from the equilibrium charge density produced at the surface by light or a field and let this decay away according to the expression

$$dn_1/dt = -A \exp\left[-(E_0 - E_1 n_1)/kT\right]. \qquad (1)$$

$(E_0 - E_1 n_1)$ is the activation energy for the decay as represented by a power series expansion in n_1 which is assumed to be small so that we need only retain the linear term. Both E_0 and E_1 are assumed positive here. The deviation at any time during the decay is

$$n_1 = (kT/E_1) \log (kT/E_1 A_1) - (kT/E_1) \log (t + \tau) \qquad (2)$$

Here A_1 is equal to $A \exp(-E_0/kT)$ and τ is given by

$$\tau = \frac{kT}{E_1 A} \exp \{E_0 - E_1 n_1(t = 0)\}/kT \qquad (3)$$

The work function ϕ is similarly expanded in a power series about the equilibrium trapped charge density at the surface n_0

$$\phi = \phi_0 + (\partial\phi/\partial n_1)_{n_0} n_1 + \tfrac{1}{2}(\partial^2\phi/\partial n_1^2)_{n_0} n_1^2 + \cdots \qquad (4)$$

Taking only the linear term and substituting for n_1 in Eq. (2) we find the time dependence of the work function to be

$$\begin{aligned} \phi(t) &= \phi_0 + \frac{kT}{E_1}\left(\frac{\partial\phi}{\partial n_1}\right)_{n_0} \log\left(\frac{kT}{E_1 A_1}\right) - \frac{kT}{E_1}\left(\frac{\partial\phi}{\partial n_1}\right)_{n_0} \log (t + \tau) \qquad (5) \\ &= A + B \log (t + \tau) \end{aligned}$$

This equation for the work function has an interesting feature. E_1 is the rate at which the activation energy for the charge transfer process changes with density of trapped charge. It seems reasonable to assume that this should be closely connected to the rate of change of the work function of the surface with trapped charge. If we set these two rates equal to each other, B in Eq. (5) reduces to $-kT$. Thus the slope of the work function *vs* log t plot should be approximately $-kT$ and this is seen to hold as shown in Fig. 3.

Equations (1) and (2) correspond to the case in which the trapped charge is increased by the disturbance. Experimentally it was found that this occurred when any of the materials investigated was used as the negative electrode in the field effect or in the case of germanium upon illumination. If the trapped surface charge is decreased, as always happens to the positive plate in the field effect, then the deviation at any time during the recovery is

$$n_1 = -(kT/E_1) \log (kT/E_1 A_1) + (kT/E_1) \log (t + \tau) \qquad (6)$$

An increase in trapped surface charge is meant to be an increase in trapped negative charge at the surface-gas interface corresponding consequently to an increase in ϕ. A decrease in trapped surface charge corresponds to a decrease in ϕ. According to Eq. (6) the work function of the positive plate will increase logarithmically after the removal of the field with a slope of approximately kT. The contact potential induced between the positive and negative electrodes should go to zero with a slope of $2kT$ as long as both electrodes are recovering.

In conclusion it seems very likely on the basis of these results that the process which governs the recovery of the surface system does obey the boundary layer theory of charge transfer.

2. *Mechanism Governing Work Function Changes*

Let us assume that the identification of the contact potential recovery with an activated process is correct. It then remains to catalogue the possible activated mechanisms and to decide which one or what combination of them is responsible for the observed effects. There seem to be two general possibilities both of which find support in the surface literature. First it may be that one upsets the adsorption-desorption equilibrium by fields or illumination causing an excess adsorption on or desorption from the surface. On removal of the disturbance there is a net desorption or adsorption respectively which is manifested by a change in the work function. The second general possibility is that the change in trapped surface charge arises not from a change in surface adsorption coverage but from a change in occupancy of traps of a semi-permanent nature on the surface. Such a trap might be an irreversibly chemisorbed gas atom or ion, a lattice vacancy at the surface, etc.

2.1. ADSORPTION-DESORPTION

The adsorption-desorption mechanism finds support in that it is well known that the kinetics of chemisorption and oxidation often obey the logarithmic relation.[9] The process of chemisorption involves the formation of a polar-covalent bond ranging from zero to 100 percent ionic. This of course alters the work function of the adsorbent surface. The plausibility of this mechanism rests upon the ability of electric fields or light to alter the adsorption equilibrium. The notorious activity of oxygen in surface reactions suggests that it is the oxygen adsorption-desorption status that we are concerned with. The heat of adsorption often drops from high values to quite low levels near complete coverage which would indicate that to a limited extent this adsorption may be regarded as reversible such that the coverage could be affected by a perturbation such as light or fields. Actually only a small fractional change in coverage can account for work function changes of 50 mv.

a Influence of external fields.—There is little evidence that electric fields transverse to the surface with a macroscopic strength of 30,000 volts/cm are able to affect adsorption. However, Blüh [5] has reported that adsorption of CO_2 and SO_2 is induced by application of such fields on the surface of aluminum plates. (Presumably there will be a considerable enhancement of the field very close to the surface due to microscopic irregularities. Thus the value of the macroscopic field may not be too significant.) Although one certainly cannot dismiss the possibility of fields changing the adsorption equilibrium considerable work must be done in this area before such an effect can be considered with confidence.

b. Influence of illumination.—The situation is somewhat different in the case of affecting the adsorption equilibrium by illumination of the surface. It has been observed that light causes a reversible desorption of oxygen from ZnO.[10] There is a readsorption which is linear with the log of the time when the light is extinguished. ZnO is an n-type semiconductor on whose surface a negative charge is built up by the chemisorption of oxygen resulting in an electric field in the ZnO just beneath the surface. The adsorption of light creates hole-electron pairs near the surface and this field draws the photo-holes to the surface. There they are believed to discharge chemisorbed O^- ions which, having lost their bond, desorb. This process has not been followed using the work function.

Kobayashi and Kawaji [11] have found that on ZnS there is a photo-enchanced adsorption of oxygen. Here it is supposed that photo-holes are drawn to the surface as in the case of ZnO. However, these holes are unable to annihilate a chemisorption bond but their presence lowers the potential barrier at the surface. This in turn is thought to lower the activation energy for chemisorption of O_2 leading to photoadsorption. The changes were followed by work function and pressure measurements on samples of approximately known surface area.

Evidence has been found by Cabrera, Terrien, and Hamon [12] that ultraviolet light increases the rate of oxidation of Al at room temperature. To explain this Cabrera [13] has elaborated a mechanism proposed by Mott in which the action of the light is to increase the trapped negative charge at the oxide-air interface causing an increased electric field in the oxide layer. This in turn enhances the motion of positive metal ions to the surface. It would be interesting to test this mechanism directly by measuring the change in work function due to illumination.

In conclusion although the effect of electric fields on adsorption is not unknown the influence of illumination is more widely established. The work function and pressure measurements of Kobayashi and Kawaji on ZnS are especially interesting since one can determine the increase in work function per adsorbed atom and from this infer the means by which chemisorption of gas traps charge at the surface.

2.2. SURFACE TRAPPING BY FIXED TRAPS

As mentioned above a second mechanism by which light or fields could lead to changes in the work function is by changing the occupation of a set of semipermanent traps on the surface. In the adsorption-desorption case the charge is regarded as trapped at the surface in the act of the formation of the chemisorption bond. This new mechanism would correspond to the chemisorbed atom having available empty levels so that it acts as an acceptor trap or filled levels at suitable energies so that it could act as a surface donor. Hence the trapping has nothing to do with adsorption. Of course there are other sources of surface traps such as lattice vacancies, interstitials, absorbed gas atoms, etc. As for surface vacancies, Tamm states, or other traps not involving adsorbed gas films very little is known at this time. The investigation of these questions requires special techniques such as those developed by Farnsworth [14] in his electron diffraction work. The identification of surface traps by these methods is just beginning to receive attention. There is a vast body of evidence to the effect that the chemisorption of oxygen does trap electrons. Its adsorption on an *n*-type semiconductor removes conduction electrons and increases the resistance while its adsorption on *p*-type semiconductors creates holes in the valence band. There is, however, the question of just how the electrons become trapped. Results on Ge and ZnS lead one to the conclusion that the trapping is not connected with the adsorption itself but is due to the chemisorbed atom acting as an acceptor. This will be fully discussed below. Aside from these conductivity changes due to oxygen chemisorption there is some other evidence of the trapping action of adsorbed oxygen. Morrison [15] has used a picture of ion adsorbed O^- covering ZnO in which some of the O^- can go to O^{--} by accepting an additional electron. He finds that this model can explain the change in conductivity with temperature of ZnO. Harada and Minden [16] have used a similar picture of ion adsorbed O^- covering PbS to explain the enhanced photoconductivity due to the exposure of the PbS film to oxygen. When the film is illuminated some photoelectrons become trapped as O^{--} on the surface leaving the photo-holes behind to conduct. The conductivity of PbS decreases as the result of oxygen chemisorption but the decrease in conductivity per adsorbed oxygen has not been measured nor has the O^{--} action been checked by change of work function with illumination. In keeping with the general lack of consistent behavior Sakamoto, Kobayashi, and Ishii [17] have found that exposure of a BaO film to oxygen decreases the photoconductivity.

3. *Surface Trapping on Germanium and Silicon*

Two mechanisms for surface trapping, by adsorption-desorption or by fixed traps, have been discussed. There is experimental evidence supporting both models. It has been pointed out that illumination can upset the surface charge distribution for systems governed by either mechanism and the influence of electric fields, although less familiar, seems likely to also be effective in actuating either process. We now turn to a discussion of long time changes in surface potential found for germanium and silicon. Our objective is twofold. First an attempt will be made to inter-relate the slow field and light induced changes in the work function to the slow changes in surface conductance and surface recombination velocity found by other workers. By examining the features of these long time changes the second objective of deciding what is the most likely of the two trapping models for germanium and silicon will be reached. The factors which govern this decision will also be applied to a discussion of the nature of the chemisorption bond of oxygen on germanium.

It has been proposed[2] that both germanium and silicon have two sets of traps on heir surface. One is a fast acting trap believed to be responsible for surface recombination with a time constant in the millisecond-microsecond range. The other is a set of slow acting traps in which adjustments of the trapped charge takes place over a period of seconds or minutes. We are concerned here with the slow traps whose existence is indicated by the work function drifts; by long time changes in the reverse current of a p-n junction as investigated by Statz et al.;[18] by the field effect measurements of Morrison,[19] Low,[20] and Kingston and McWhorter;[21] and by the slow changes in surface recombination velocity observed by Many et al.[22]

3.1. SLOW CHANGES IN SURFACE CONDUCTIVITY

The work function measurements on germanium and silicon can be brought into direct correlation with the reverse current voltage characteristics for p-n-p bars where emitter and collector are reverse biased to the base. Statz and coworkers found that suitable treatment of the surface of n-type silicon and germanium with oxygen can lead to the formation of a stable p-type layer just beneath the surface. Just as in the experiments which have shown a decrease in conductivity of n-type emiconductors due to oxygen chemisorption, the explanation for the inversion layer is that adsorption of oxygen leads to a negative surface charge. This is of such a magnitude that the resulting upward curvature of the energy bands lifts the valence band close enough to the Fermi level so that the material becomes p-type, forming a p-type skin on the n-type material. Statz et al. have been able to explain their experimental results by assuming that the slow states attain equilibrium with the holes in the p-type skin. An increase in reverse bias for his arrangement tends to decrease the hole density in the p-type layer on the n region. This causes a flow of electrons to the slow states which occurs over a period of several minutes. Since the conductance of the channel can be shown to depend on the amount of trapped surface charge, the slow leak of holes from the slow states is reflected by a slow conductance drift. These charge rearrangements at the surface postulated by Statz are in agreement with the charge transfers which must be taking place in the work function experiments although it is not possible to decide from Statz's work whether the trapping mechanism is by adsorption or by fixed traps. He does, however, estimate that the density of the slow traps is of the order of 10^{14} per cm^2.

Morrison's work [19] on the slow traps on germanium was done under conditions very similar to the contact potential measurements. The conductance of a germanium slab was measured under the influence of an external field normal to the surface, illumination, and temperature changes. Making the sample the negative plate, illumination, or heating caused an increase in the negative charge trapped at the surface. This would correspond to an increase in work function which agrees with the results of the contact potential experiments except for the temperature change which has not yet been tried. Upon removal of the disturbance, the surface charge distribution recovered to its initial condition in about one hour linearly with the log of the time exactly as the changes in work function decay. Experimental difficulties prevented an accurate determination by Morrison of the dependence of the conductance effects on oxygen pressure although he noted a slower decay at lower pressures. Low [20] has also reported slow changes in the conductance in his field effect experiments and noted that the drifts were faster in wet gases than dry and slower by about a factor of five at a roughing vacuum than at atmospheric pressure. Low suggests that a change in the adsorption-desorption equilibrium caused by the applied field might explain his results but regarded this as only a tentative conclusion. Kingston and McWhorter also find the long time changes in their field effect work with results in agreement with those of Low in that trapping is faster in wet ambients and the frequency response to the ac applied field shows only a very slight pressure dependence.

3.2. SLOW CHANGES IN SURFACE RECOMBINATION VELOCITY

Many, Margoninski, Harnik, and Alexander [22] have used the field effect technique to study relaxation effects in the surface recombination velocity of germanium. A transverse field is applied causing an abrupt change in the surface barrier which over periods of minutes to hours relaxed to nearly its initial value. Their interpretation is based on a set of slow traps on the surface which gradually attain equilibrium with changes in surface charge density. Using their curves and the results of Stevenson and Keyes[23] relating surface recombination to the surface potential barrier height it is seen that the fluctuations in charge trapped in the slow states amounts to changes in the surface barrier of about 80 mv. This is just the order of the work function changes that have been found by the authors to be induced by transverse fields. It is also of interest that the results of Many et al. taken at atmospheric pressure and at 10^{-4} mm Hg are very much alike, again suggesting a very small pressure dependence of the slow surface reaction.

3.3. WORK FUNCTION CHANGES WITH LIGHT

The long time changes in work function of germanium due to illumination have also been seen by F. Allen[24] in a very interesting series of experiments. He found that illuminating or darkening the surface caused slow drifts in the work function with time constants ranging from 5 seconds to 10 minutes. In the case of the longer drifts the work function changed by 30 to 50 mv. Allen was, however, set up to study surfaces cleaned by the Farnsworth[14] technique and was thus able to examine the long time changes on both uncleaned and cleaned surfaces. He found that the long time changes existed only on uncleaned surfaces and that they persisted at pressures of the order of 10^{-7} mm Hg which was the lowest possible pressure before baking the system. These changes could also be produced by heating in accord with Morrison's finding. No such drifts were found when the apparatus was baked at red heat and at a pressure of 10^{-8} to 10^{-10} mm Hg.

3.4. THE CASE AGAINST THE ADSORPTION-DESORPTION MECHANISM

The pressure dependence of the slow changes in work function and other surface properties is very significant as it provides a means by which one may distinguish between the two mechanisms proposed earlier of either adsorption-desorption or trapping by a fixed set of surface traps. The rate of recovery of the work function, conductivity, or surface recombination velocity would exhibit a marked pressure dependence if adsorption-desorption were the dominant process. For the surface reaction as suggested by Hauffe[25] for ZnO

$$\tfrac{1}{2}O_2^{(\text{gas})} + e^- \rightleftarrows O^{-(\text{adsorbed})}$$

the rate of adsorption is

$$dn/dt = k_a n_s P(O_2)^{\frac{1}{2}} \tag{7}$$

where n_s is the electron concentration at the surface. A pressure change from 760 mm Hg to a roughing vacuum of 10^{-3} mm Hg would correspond to a ratio of the rates at the two pressures of 10^3 while in Allen's experiment, where the slow change in work function was observed to be not markedly different at 10^{-7} mm Hg the rate ratio would be 10^5. None of the surface effects on germanium showing long time drifts have shown such a pressure sensitivity. Even if the rate of the surface reaction went as $P(O_2)^{\frac{1}{4}}$, this would amount to a factor of 30 between atmospheric pressure and 10^{-3} mm. The field and light induced work function changes reported by the authors were not examined quantitatively as a function of pressure but it is safe to say that no variations as large as a factor of ten were found in the relaxation rates between 760 and 10^{-3} mm. Therefore, the decided pressure insensitivity seems to rule out an adsorption-desorption mechanism for the slow changes on germanium and probably for silicon as well.

Aside from the absence of pressure dependence there is other very good evidence that the slow surface trapping reaction does not go by adsorption-desorption. If the adsorption of oxygen on germanium or silicon were by the ion-adsorption reaction such as that proposed for ZnO by Hauffe in Eq. (7), then every adsorbed oxygen would remove a conduction electron from the bulk. The surface barrier resulting, for example, from the depletion layer in n-type material required to neutralize the adsorbed O^- would be very sensitive to adsorption coverage. Small changes in the adsorption-desorption balance would lead to surface potential changes which would significantly influence the surface conductance, recombination velocity, and work function. However, if oxygen were adsorbed by a polar-covalent bond in which any negative charge on the oxygen is neutralized by the atom to which it is bound, then the surface potential would be quite insensitive to coverage. Any adsorption or desorption would have a very small effect on these barrier sensitive properties. It will be shown in a later section that ion-adsorption can be ruled out at once for germanium and silicon and that the polar-covalent model is in reasonable agreement with the experimentally determined facts describing the germanium-oxygen interaction. First, however, the possibility of chemisorbed oxygen acting as a fixed trap on germanium will be briefly considered.

3.5. CHEMISORBED OXYGEN AS A FIXED SURFACE TRAP ON GERMANIUM

From work performed in this laboratory[26] it is known that germanium rapidly chemisorbs a monolayer of oxygen and, due to the nature of the logarithmic adsorption law, it requires a period of several days to add a second oxygen atom per surface germanium atom. Robinson[27] has found that the heat of adsorption for the sparsely covered surface is very high, of the order of 120 Kcal per gram atom, and drops to about 30 Kcal per gram atom for roughly 1.2 oxygen atoms adsorbed per surface germanium atom. Therefore, it is to be expected that all of the germanium surfaces on which long time effects have been observed were covered by *at least* a monolayer of chemisorbed oxygen.

The fact that Allen[24] could remove the slow traps on germanium by baking at very low pressure strongly suggests that these traps are due to chemisorbed gas, most likely oxygen. The removal of the slow states under these conditions is to be compared with the results of Dillon[28] and Schlier.[29] Dillon measures the work function of a cleaned germanium surface and then admits O_2 which causes an increase in work function. This change in work function is not affected by subjecting the sample to high vacuum for long periods indicating that the chemisorption is irreversible. However, the clean surface work function is restored by heating at 500°C in vacuum for 15 minutes. Schlier finds that the clean surface electron diffraction pattern is also restored after the surface is contaminated with oxygen by a similar treatment.

In summary the fact that germanium surfaces which have exhibited the long time barrier changes have all had at least a monolayer of oxygen chemisorbed upon them, and that the long time changes disappear under conditions which also erase the changes in work function and electron diffraction pattern caused by oxygen chemisorption, lead to the almost inescapable conclusion that the slow states on germanium are due to chemisorbed oxygen atoms. Since O_2 is virtually irreversibly chemisorbed on germanium, a slow surface reaction based on this oxygen acting as a layer of acceptor and possibly donor traps would be essentially independent of pressure which is in agreement with experiment. As a final argument against the adsorption-desorption mechanism for germanium we will now consider the nature of the chemisorption bond.

4. *The Nature of the Chemisorption Bond*

The ion-adsorption model on which the boundary layer theory of chemisorption is based [6,7,8] only applies for cases in which a fraction of a percent of the surface is covered by adsorbed ions. Since both germanium and silicon are known to take up more than one oxygen per surface atom, one immediately looks for another type of adsorption bond. Let us assume that the chemisorbed oxygen is bound to the surface by the usual polar-covalent bond so that any charge on the oxygen is neutralized right at the atom to which it is bound with no necessity of a depletion layer. Consequently there is no trapping of electrons from the bulk in the formation of the adsorption bond. This is not in disagreement with the observations of Clarke [30] who found a decrease in conductivity of *n*-type germanium due to the adsorption of oxygen. Under conditions found by Dillon and Schlier to have removed the effects of adsorbed oxygen, Clarke found that the admission of oxygen resulted in the trapping of about 5×10^{11} electrons per cm^2 of surface whereas if ion-adsorption prevailed he would have noted a far greater trapping.

As a test of the above assumption about the adsorption bond we can make a rough calculation of the change in work function to be expected for the adsorption of a monolayer of oxygen on germanium. Pauling's methods [31] lead to an estimate for the ionic character of a free germanium-oxygen bond of 50 percent and of a bond length d of 1.88 A. We will restrict ourselves to the (100) face here as it has been most carefully studied. According to Schlier's[29] interpretation of the electron diffraction data, the clean surface is characterized by rows of surface atoms in the [110] directions coming together in pairs. Presumably the free bonds extending about the (100) plane will give rise to a substantial surface dipole moment. When a monolayer of oxygen is adsorbed, the displaced rows return to their normal lattice positions. Thus the change in work function $\Delta\phi$ we seek is made up by the *net* increase in surface dipole plus a small contribution from the atomic rearrangement. Allowing the ionic character of the germanium-oxygen bond to drop to 25 percent due to depolarizing forces[32] and assuming the normal geometry, one finds a surface dipole due to the oxygen of 2.92 volts. (The dielectric constant is taken as unity.) Since Dillon[26] measures $\Delta\phi$ to be only 0.28 volts, one concludes that the dipole moment of the clean surface must be quite high if this picture is at all accurate.

This model of a polar-covalent adsorption bond can be pushed somewhat further to predict the adsorption kinetics for the chemisorption of oxygen on germanium. The oxidation has been found[26] to obey the logarithmic law

$$n_a = A + B \log (t) \tag{8}$$

It was pointed out previously that this relation always results for an activated process in which the activation energy can be represented as a linear function of the coverage. In the ion-adsorption model the rate limiting step in adsorption is supposed to be the electron transfer through the potential barrier at the surface, the height of this barrier being essentially the activation energy. It seems that some systems such as germanium-oxygen react through an activated process in which changes in the activation energy can be related to changes in the work function even though the reaction does not go by a pure electron transfer or ion formation mechanism. An empirical relation between work function and activation energy was first pointed out by Rideal and Wansbrough-Jones[33] to be obeyed by some systems. This is

$$\phi - E_{\text{act.}} = \text{Constant} \tag{9}$$

Let us assume Eq. (9) for germanium so that the activation energy will vary with coverage as

$$E_{\text{act.}} = E_0 + E_1 n_a \tag{10}$$

The rate of adsorption is

$$dn_a/dt = K \exp\left[-(E_0 + E_1 n_a)/kT\right] \tag{11}$$

The value of E_1 will be taken as that which corresponds to an increase in work function of 0.28 volts for a monolayer of oxygen, $n_a = 0.625 \times 10^{15}$ atoms/cm², i.e. $E_1 = 4.48 \times 10^{-16}$ volt-cm². Integrating the rate equation one gets approximately

$$n_a = (kT/E_1) \log_e(t) + \text{Constant} \tag{12}$$

Thus the slope of the coverage *vs* $\log_e(t)$ plot is kT/E_1 which according to our determination is 1.28×10^{14} cm^{-2}. This is to be compared with the experimental value of Kafalas[26] of 1.41×10^{14} cm^{-2}. Furthermore, by observing the adsorption at different temperatures Kafalas is able to obtain another measure of the change of activation energy with coverage. This is approximately 1.24×10^{-11} cal-cm² as compared to the calculated value here of 1.04×10^{-11} cal-cm².

In conclusion we see that a model based on a polar-covalent adsorption bond is in very good agreement with the experimentally determined adsorption kinetics. A consequence of this type of adsorption is that the surface barrier sensitive properties will not be much affected by *small* changes in coverage which argues against adsorption-desorption as the source of the slow surface reaction. Furthermore, we see that the application of the Rideal, Wansbrough-Jones relation allows one to generalize the boundary layer theory of adsorption and to reasonably well describe the details of the chemisorption of oxygen on germanium.

IV. SUMMARY AND CONCLUSION

The experimental basis of this paper lies in the finding that electrostatic fields or light can induce long time changes in the work function of a Au, Ge, or Si surface. A new technique for measuring contact potentials by the Kelvin method was developed representing a considerable improvement in flexibility and accuracy in order to investigate this effect. It is shown that the experimental results can be related to the boundary layer theory of charge transfer. The relationship between the work function changes observed by the authors for germanium and silicon to the long time changes in other surface properties found by other workers is pointed out. Various models are suggested and examined with the conclusion that the slow surface reaction is the result of chemisorbed oxygen on the surface acting as an acceptor trap. In arriving at this conclusion we are led to consider the nature of the oxygen chemisorption bond on germanium. It is proposed that this is a polar-covalent bond and it is shown that this assumption combined with the Rideal, Wansbrough-Jones relation between activation energy and work function leads to an accurate prediction of the details of the adsorption kinetics.

DISCUSSION

C. G. B. GARRETT (*Bell Telephone Laboratories*): It ought to be possible to describe the long-time surface relaxation effects—particularly the photo-effects—by a purely thermodynamic argument, which evades the commitment to a precise form of words ("traps," "adsorption-desorption" etc.). Certainly the short-time surface photo-voltage on semiconductors is so describable. The thermodynamic approach is valuable in that it brings out that the slow passage of charge across the surface ought to depend not only on the barrier height, but also on the electrochemical potential for electrons (or holes, where these can be different). It also shows up a rather interesting difficulty. If the predominant electrochemical equilibrium at the surface is of the form $X \rightleftharpoons X^- + p$, then one can show from the Weisz type of reasoning that there should be long-time relaxation effects in the surface photo-voltage when the surface region of the semiconductor is rich in electrons, but not when it is rich in holes, since in the latter case the barrier height and the electrochemical potential for holes will have changed by equal amounts, so that the electrochemical equilibrium with the surface system will not have been upset. In the case that the surface equilibrium is of the sort $X \rightleftharpoons X^- - n$, one expects the long-time relaxation effects only at the other extreme. Some two years ago, Brattain and I looked at these long-time relaxation effects in the surface photo-voltage of germanium, and found them at *both* extremes. This seems to imply that the surface equilibrium is always with that carrier which is *less* plentiful in the surface region, in contradiction to common sense and to the conclusions drawn from the germanium-electrolyte experiments. So there seems to be a real difficulty, which cannot be evaded by mere changes in terminology, but must persist as long as one condition of the surface state, or trap, or adsorbed atom is neutral, and the other has one electronic charge.

G. W. PRATT, JR. and H. H. KOLM (*Lincoln Laboratory*): There are two points which should be remarked on in the above comment. A paradox is raised there concerning the existence of a slow reaction regardless of whether the carrier involved is of majority or minority type. Presumably the picture is that in the case where the slow traps are in equilibrium with the majority carrier at the surface, illumination which only changes the fractional majority carrier concentration at the surface by a negligible amount should only change the slow reaction equilibrium by a correspondingly small amount. There are two points which may serve to explain this situation.

First, light will undoubtedly directly affect the transition probability for a carrier at the surface going over or through the activation energy barrier which separates it from the slow trap. We know for example that one extracts electrons from a metal by proper illumination and we use this fact to measure the work function. Since the light effectively raises the temperature of the electrons at the surface, the equilibrium will be upset in this way independent of the carrier concentration at the surface.

The second point is that although the electrochemical potential of the majority carriers will only be changed by an amount proportional to the fractional change in majority carrier concentration, there will nevertheless be a change due to illumination. Since the potential barrier at the surface is *very* sensitive to the number of charged surface traps, this very small departure from equilibrium may still be observable through work function measurements.

Thus we see that light will affect two properties which enter into the trapping equilibrium. First, the transition probability into or out of the slow trap and secondly the number of available carriers to become trapped. The first change should be insensitive to carrier concentration and hence to be operative when the reacting carrier is either of majority type or minority type. One would expect the effect of changing the concentration to be much more marked in the minority carrier case but not entirely absent in the majority carrier case.

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THE OXIDATION OF METALS

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ABSTRACT

A discussion of the basic ideas of oxidation theory is presented in two parts: i) the formation of thin uniform films of oxide everywhere on the metal surface when no nucleation of the oxide is required. ii) formation of oxide nuclei when nucleation controls the beginning of the oxidation. In the former part, emphasis is given to the transit of electrons through the oxide layer. In the latter, the attempt is mainly to correlate the observations of Bénard and others with the existing ideas concerning the inhomogeneity of a surface, particularly the points where dislocations terminate.

1. INTRODUCTION

Several reviews on the theory of oxidation of metals have recently appeared which cover most of the developments in this field, so that a further discussion would at first sight appear unnecessary. Among them, one should mention, first of all, the book by K. Hauffe [1] and also the papers by Grimley and Stone in the book on Chemistry of the Solid State edited by W. E. Garner.[2] The present author feels, however, that these reviews have not sufficiently emphasized the relationship of the formation of an oxide to the more general theory of the growth of a phase according to nucleation theory, so that a short introductory paper emphasizing this point should be worth while.

From that point of view the description of the formation of an oxide falls into two parts.

i) The initiation of the oxide will always start at isolated nuclei, the frequency of their formation depending on a certain nucleation activation energy. This activation energy will, of course, be different on different regions on a crystal surface, so that their formation indicates the presence of regions on the surface of particularly high activity. The presence of impurities, of steps, the points where dislocations terminate, etc. are to be expected to play some role from that point of view. The realization of the necessity of nucleation in the formation of an oxide is very recent indeed, following the beautiful work of Bénard[3] and his collaborators. The interpretation of this work will be considered in Section 3, particularly from the point of view of its possible connection with dislocations.

ii) The further growth of the initial nuclei will be controlled by diffusion processes and the like, depending on another activation energy. Most of the earlier work on oxidation was carried out at high pressures of oxygen, where the activation energy for nucleation becomes very small, so that the controlling factor is the activation energy for diffusion. The formation of a continuous layer of oxide follows because of the nucleation at nearly every point on the crystal face. The theory of the formation of these layers is now well developed and has been fully described in the reviews mentioned earlier. The present author takes advantage of this occasion to discuss some points connected particularly with the transit of electrons through the oxide film which does not seem to have been properly considered. This will be done in Section 2.

It will be apparent that the comments presented in this paper are of a rather tentative nature. The point of view here presented is rapidly developing, and the object of this discussion is perhaps to suggest further experiments very badly needed.

2. CHEMISORPTION AND THE FORMATION OF OXIDE FILMS

Throughout this paragraph it will be assumed that the pressure of oxygen is so high that the activation energy for nucleation of the oxide is very small and consequently does not play any significant role. The rates are then controlled by the activation energies required for the motion of atomic units.

The first part, (a), will consider the process by which the first layer of oxygen is chemisorbed on the metal. Strictly speaking, this chemisorbed layer should be a thermodynamically stable system only if the pressure of oxygen is below the equilibrium pressure for the system metal-oxide-oxygen. However, the further growth of the oxide seems to require such a large diffusion activation energy that the chemisorbed layer remains in a metastable state for much higher pressures of oxygen.

In part (b) the formation of very thin films of oxide is discussed following the model proposed several years ago by Mott.[4] This model assumes the transit of electrons between the metal and the acceptor levels of adsorbed oxygen on the oxide. This question, which has been rather overlooked, will be discussed later in part (c). Part (d) will finally discuss briefly the further growth of the oxide to form thin films.

(a) *Chemisorption of oxygen.*—The first step in the process of oxidation is the formation of a chemisorbed layer of oxygen on the metal. Several excellent reviews have appeared recently which make a thorough treatment of it here unnecessary. It is, however, useful for our purpose to comment on this aspect of our problem as we still have to understand the transition from a chemisorbed layer of oxygen to the beginning of an oxide layer. Until fairly recently there were two different schools of thought, one which claimed that chemisorption on a clean metal surface did not require any activation, the other that it did. The indication now is that the second attitude is the correct one. The work by Trapnell and others [5] indicates that chemisorption requires an activation energy which increases with the amount adsorbed.

The following picture seems to represent the results. When O_2 is put in the presence of a metal surface at a relatively low temperature (below, say, 200°C) the surface is rapidly covered with a monolayer of oxygen. This "rapid uptake" occurs for all temperatures from −183°C up, the only known exception being, apparently, Au. The adsorption heat seems to be large (5–10 Kcal/mol) so that the bond is either covalent, ionic or most probably both. If the bond is ionic, one might expect the oxygen to be in the state O_2^- and to produce a high surface dipole. It seems more likely that the bond is partially or predominantly covalent, the oxygen being dissociated and producing a lower surface dipole. Once this monolayer is formed a subsequent "slow uptake" follows, so that as long as the temperature is below a certain lower limit, depending on the metal, the total amount of oxygen taken up is between 1 and 2 monolayers. The rate of uptake is proportional to $p^{\frac{1}{2}}$, where p is the oxygen pressure, and to $\exp(-\theta U/kt)$, where θ is the coverage and U an activation energy. The factor $p^{\frac{1}{2}}$ suggests dissociation of oxygen in the first layer. The nature of the activated process is likely to be a rearrangement of the chemisorbed layer which melts, so to speak, the crystal surface of the metal. This process should also tend to decrease the surface dipole as has been suggested by M. Green.[6] This decrease in the surface dipole should have both the advantage of decreasing the free energy and also making the continuation of the process on into an incipient oxide layer more difficult. Indeed, it seems hard to understand the stopping of the oxidation if the dipole is large, as it would always facilitate the beginning of oxidation by pulling metal ions through. It should be interesting to look for any change in the surface dipole during the "slow uptake" process by studying its influence on the photoelectric yield or contact potential.

A similar situation occurs in the case of semiconductors as Ge. According to the recent work of Green and Kafalas,[6] a chemisorption occurs at temperatures below 200°C which does not go beyond 2 monomolecular layers of oxygen. An interesting question, to which we will come back later, is whether or not electrons from donor levels in the semiconductors are contributing to the bonding of the chemisorbed layer. We believe this contribution to be negligible because the electrons have to diffuse against the field of the resulting Schottky layer.

(b) *Very thin oxide films.*—If the pressure of oxygen is higher than the equilibrium pressure for the equilibrium metal-oxide-oxygen system, the chemisorbed layer of oxygen is not stable so that a tendency for the continuation of the oxidation should always be present.

The occurrence of this further oxidation should follow the pattern of all nucleation processes, that is, it should be controlled by two independently activated processes. On one side there is the nucleation proper, being controlled by an activation energy which should decrease as the pressure of oxygen increases. As the equilibrium pressure for most of the metal-oxide systems is extremely low at low temperatures, one should expect the activation energy for nucleation to be small at these temperatures and ordinary pressures. If it is not small, then one should expect the oxidation to start from nuclei which will appear at the most favorable imperfect points on the crystal face (dislocations, impurities, etc., see Section 3).

On the other hand, the elementary atomic processes also require some activation energy, independent of pressure of course, which can only be overcome by increasing the temperature or by the presence of a very strong electric field (see below). It is probably this second activated process which is stopping the continuation of the oxidation at these low temperatures, as was suggested by the present author some time ago.[7] (This activated process is, of course, bound to be very sensitive to the presence of impurities.) If that is so, and the activation energy for nucleation proper is very small, one can understand the fact that once the oxidation starts because of the presence of an electric field, the oxide grows as a thin *amorphous* layer, the nucleation occurring everywhere simultaneously.

It is not clear at the present time when and how the chemisorbed layer of oxygen begins to transform into a very thin oxide layer. Apparently there is a transition from the bonding of adsorbed oxygen to the metal to the bonding of adsorbed oxygen to the oxide. The former has probably a predominantly covalent character with a small dipole moment, the latter a predominantly ionic character. Furthermore, if the acceptor surface levels due to the adsorbed oxygen lie below the Fermi level of the metal electrons, these electrons will fill up these levels and set up a strong electric field through the oxide which will overcome the activation energy that was stopping the motion of metallic ions. This idea was put forward by Mott.[4] It gives rise to an approximately logarithmic type of growth, so that the oxide forms as long as the electrons can continue to tunnel through the oxide layer or until the field becomes too small to pull ions through the oxide.

The formation of thin protective oxide films, according to this mechanism, seems to occur generally for all metals which oxidize. Figure 1 shows the result of recent careful experiments carried out by Cathcart, Hall, and Smith [8] on the oxidation of Na at low temperatures in the presence of pure oxygen. It is clear that protective films are also formed in spite of the fact that the ratio of equivalent volumes of oxide and metal is considerably lower than unity.

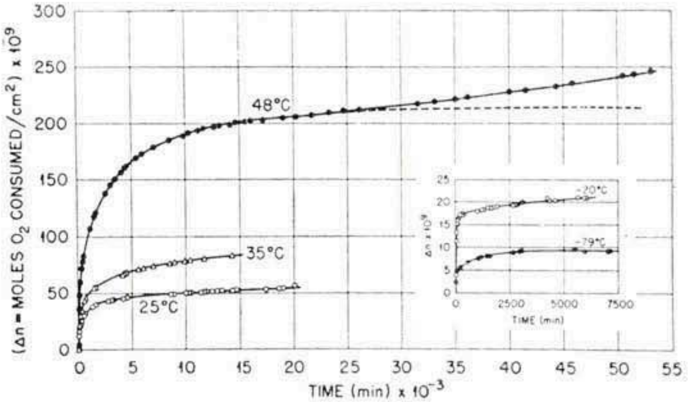

FIG. 1.—Oxidation of Na at different temperatures and atmospheric pressure, according to Cathcart, Hall, and Smith.[9]

In the original paper by Mott,[4] the following assumptions were made:

i) Electrons are able to establish an equilibrium between metal and adsorbed oxygen on the oxide in a time very small with respect to that required for an ion to diffuse through the oxide.

ii) The equilibrium contact potential V_0 between metal and adsorbed oxygen is supposed to be independent of temperature, oxygen pressure and oxide thickness.

iii) The total activation energy U for the solution of metal in the oxide at the metal-oxide interface, or of oxygen at the oxide-oxygen interface, is also assumed to be a constant.

Under those conditions, the rate of growth of the oxide layer was shown to be of the form

$$dX/dt = a\nu \exp\{-[U - eaV_0/X]/kT\} \tag{1}$$

The assumptions above are, of course, an oversimplification. As far as assumption (i) is concerned, it is clear that it will only be true as long as the electrons can tunnel through the oxide layer, and this limits its application to thicknesses smaller than say 20 A. If the electrons have to diffuse through the oxide, the equilibrium between metal and adsorbed oxygen ions could not be reached in any reasonable time, as the electrons would have to diffuse against their own field. This point will be discussed again later. Assumption (ii) is probably correct as soon as the thickness of oxide is a few monomolecular layers thick and the pressure of oxygen is sufficiently high so that there is plenty of adsorbed oxygen available. Engell and Hauffe[9] and Grimley[10] have analyzed carefully this point and shown how V_0 varies with the oxygen pressure. Finally, (iii) should be correct in the range of thicknesses in which (i) is satisfied.

If all these assumptions are satisfied Eq. (1) should be expected to hold. This seems to be the case in the experiments by Rhodin[11] on the oxidation of different crystal faces of Cu at low temperatures and high pressures. These experiments bring up another very important fact, which had already been observed earlier by Gwathmey and associates[12] for a higher range of temperatures and which will be discussed again in a later section, namely that the oxidation rates depend on the crystal face considered. This should not be surprising, as we are treating electrons and ions separately. The total heat released from the reaction must be independent of crystal face, but the two parts which compose it, namely the electronic heat (equal to eV_0) and the ionic heat (which is *not* related to U) could vary considerably from face to face due to differences in the surface dipole moment.

(c) *Transit of electrons.*—As soon as the thickness of oxide is large enough for the tunneling effect to be ineffective, we have to find another way for the electrons to be able to reach the surface oxide-oxygen. In the initial papers by Mott and the present author,[4] this problem was not treated correctly, although the authors were aware of its existence at the time of the publication of the review article in 1949. This point seems to have been overlooked by later authors, so that it might be worthwhile to comment on it briefly at the present time, a more thorough treatment being given elsewhere. The result of this treatment is that the current of electrons diffusing through the oxide layer will be very small, unless the field they create by the filling up of empty acceptor levels at the oxide surface is not much larger than kT/eX, X being the thickness of the oxide. The equilibrium metal-adsorbed oxygen which would establish a field V_0/X is therefore never reached, and the number of filled up levels at the adsorbed layer will be of the order of kT/eV_0 times what one would expect if the equilibrium could be established. The present picture for the formation of very thin oxide films is concluded to be a complicated one, namely, the rate initially obeys Eq. (1) but decreases rapidly as the field $F = V(X)/X$ decreases because X increases and $V(X)$ decreases in a complicated way.

The problem of the transit of electrons can of course be avoided if they reach the oxide surface via an external circuit. This can be done either by anodic oxidation in an electrolytic bath containing oxygen ions, or by anodic oxidation in a discharge tube. In both cases, there is the further advantage that the potential V_0 across the oxide film can be controlled and made so large that the thicknesses are considerably increased. Then the first two assumptions mentioned in (b) will be automatically satisfied, so that the law should be followed unless assumption (iii) is not correct. In fact, Vermilyea [13] by a set of beautiful experiments on the anodic oxidation of tantalum has shown Eq. (1) not to be correct. In a paper by Bean, Fisher, and Vermilyea,[14] the results have been interpreted by assuming that the source of ions is not located at the metal-oxide interface but occurs everywhere in the bulk of the oxide through the formation of vacancy-interstitial pairs under the influence of the very high field. Also the activation energy for dissociation will contain a term due to the interaction between the pair, so that this activation energy should increase as the field decreases. A similar increase in the activation energy U should occur when the ions are produced only at the metal-oxide surface, because of the image force acting on the ion, so that assumption (iii) should not be correct at sufficiently large thicknesses. (This is, of course, the same thing as the well-known Schottky effect in thermionic emission.)

(d) *Thin oxide films.*—If the temperature at which oxidation occurs is higher than the values considered in (b) a new factor must be taken into consideration which was entirely neglected there, namely the fact that the concentration of carriers in the oxide becomes appreciable, and therefore a space charge will be set up. As usual in all space charge problems, the mathematical treatment becomes exceedingly difficult and no simple analytical laws can be generally expected. However, on one hand, new and very interesting experimental results on the formation of thin oxide films have been recently obtained, particularly at the University of Virginia by a group under Gwathmey, and, on the other hand, attempts to treat the problem theoretically have been published by Hauffe[1] and collaborators, and by Grimley.[10] It is therefore useful to make some brief comments here as a continuation to the preceding sections.

First of all, in the original papers by Mott and Cabrera,[4] it was assumed that the field set up by the electronic equilibrium in metal-adsorbed oxygen could continue to be established at relatively large thicknesses of oxide, so that the field remains stronger than the field due to the space charges, and gives rise to simple parabolic or cubic laws. This point of view has been developed to great length by Grimley[10] in his recent review. However, in view of what we said in the preceding section this cannot be correct. It is clear that the electronic equilibrium in metal-adsorbed oxygen *cannot* be established as soon as the thickness of oxide is larger than that through which the electrons can tunnel.

The qualitative picture of what probably happens is easier to understand in the case of a *n*-type oxide such as Al_2O_3 where the oxide-oxygen surface does not play any important role (provided of course, the pressure of oxygen is sufficiently high). Here no further growth beyond the very thin film is possible until the concentration of electrons in the conductivity band in equilibrium with the metal is substantially increased. Some of these electrons will then be able to fill the adsorbed oxygen levels at the oxide surface (*without reaching equilibrium*) so that a field will be created in the oxide layer both because of the space charge and the surface charge thereby established; to this has to be added the positive space charge due to the ions being dissolved from the metal. The overall field will probably then be more important than the one which would be present if the metal was in equilibrium with the oxide. It is likely that at this stage the growth of the oxide will be mainly field controlled, the electrons establishing a quasi-equilibrium with the metal but *not* with the adsorbed layer.

In the case of a *p*-type oxide as Cu_2O, the picture should be very similar, although the fundamental role will be played by the oxide-oxygen surface. Whether or not the resulting law of growth will be approximately cubic as was suggested several years ago[7] remains to be seen.

The recent work by Gwathmey and his associates on the oxidation of different crystal faces of Cu deserves some special comments. The most important result is the large differences in rates on different crystal faces. This is clearly shown in Fig. 2

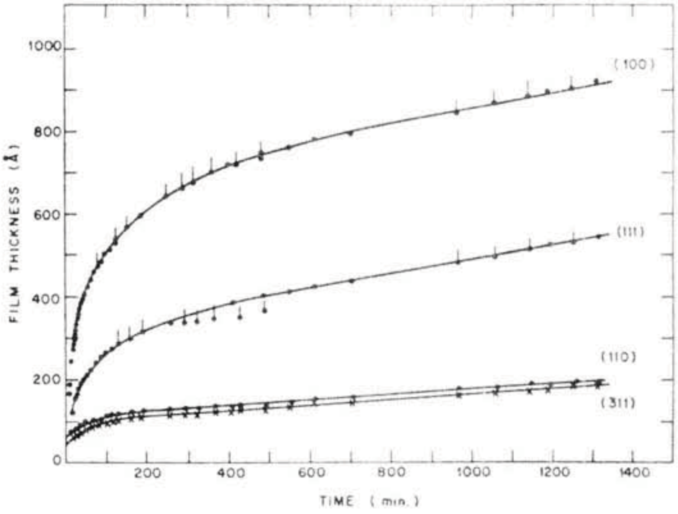

FIG. 2.—Oxidation on different crystal faces of Cu at 159°C and atmospheric pressure, from Young, Cathcart and Gwathmey.[15]

taken from the paper by Young, Cathcart, and Gwathmey.[15] One might suggest two main reasons for this behavior. In this range of temperatures the ions diffuse mostly via the grain boundaries in the oxide. Therefore the oxidation rate should depend on the grain boundary geometry, which clearly depends on the crystallographic orientation of the underlying metal and changes during the growth of the oxide layer. On the other hand, the dipole layer at every crystal face is likely to vary considerably from face to face, and contribute to the observed differences in rates. According to both interpretations the difference in growth rates should tend to disappear during oxidation at very high temperatures which seem to be in agreement with the experiments of Bénard and Talbot.[16]

3. THE ROLE OF DISLOCATIONS IN THE OXIDATION OF METALS

In recent years it has become apparent, both experimentally and theoretically, that we cannot consider a crystal surface as a homogeneous medium with every lattice point on the surface having the same properties. In the same way that the properties of the bulk of a crystal depend on the imperfections present, both geometrical imperfections of the lattice and impurities, so also must surface phenomena depend on similar surface imperfections. The effect of impurities should, of course, be more important on the surface than in the bulk, as adsorption is usually exothermic, while absorption is endothermic.

The experimental evidence is that besides the effect of impurities there are other points on the crystal face playing an important role in certain surface phenomena, namely the points where dislocations of the bulk crystal terminate at the crystal face. This is particularly clear in the case of etching. It has been known for a long time that etching under certain conditions occurs particularly at specific points on the surface (etch pits). Following the work of Lacombe,[17] which showed that these pits tend to be aligned in rows, Shockley and Read [18] suggested that etch-pits should be related to the presence of dislocations. This hypothesis has been confirmed by the work of Vogel,[19] Amelinckx [20] and many others, and has become the basis of an extremely powerful tool in testing the predictions of dislocation theory.

On the other hand, Bardolle and Bénard [3] and also Gulbransen and McMillan [21] and Harris, Ball, and Gwathmey [22] have shown that during oxidation within a specific range of temperatures and oxygen pressures the oxide film is very inhomogeneous, consisting of oxide nuclei separated by an apparently very thin continuous film of oxide. As discussed later, these nuclei might be due to several causes. The conclusion that they are connected with dislocations can only be stated when the nuclei are aligned in rows. However, it is worthwhile analyzing whether or not the experimental conditions for their observation are consistent with the assumption that they are connected with dislocations. Figure 3 gives an electron microscope picture of the oxide film on Cu taken from the paper by Harris, Ball and Gwathmey. Two types of nuclei are apparent in this picture, a large number ($\sim 10^{11}$ cm^{-2}) of small nuclei which are likely to be connected with impurities and a smaller number ($\sim 10^{8}$ cm^{-2}) of larger nuclei which are supposed to be connected with dislocations.

Many other processes should also indicate dislocations. Evaporation proper into an undersaturated vapor (thermal etching) should be the simplest process as well as the easiest to interpret. Work in progress by Young at the University of Virginia shows indeed the formation of evaporation pits which might also be connected with dislocations. It is also to be expected that dislocations might play a very important role in catalytic processes; preliminary work by Cunningham at the University of Virginia indicates that that is so.

There is still considerable doubt concerning the question of why pits should form at dislocations. From a rather naive point of view, one can suggest the two following main reasons for the specific activity of dislocations compared to that of the remainder of the surface:

i) The work required to evaporate a neutral atom from the metal into the surrounding medium might be different at the dislocation and far from it. This difference will be due to the strain energy concentrated around the dislocation and also to the presence of a different concentration of impurities at the dislocations. These might be the only factors present in the case of evaporation proper or perhaps during oxidation at high temperatures.

ii) The work function, the work required to take one electron from the metal, will probably also be different at the dislocation from what it is in the remaining surface. This would imply a corresponding change in the work needed to evaporate a metallic ion, so that the sum of the two is the same as in (i). The changes in work function will be extremely sensitive to impurities, so that the surface state connected with the impurity near the dislocation might be at a quite different level from that for the same impurity at a point on the flat face. This second factor, (ii), will be of fundamental importance in processes like electrolytic etching, oxidation at low temperatures, etc. It is difficult at the present time to discuss these processes, more experimental information is required before this can be done with profit.

Besides presenting a few general ideas we will limit ourselves

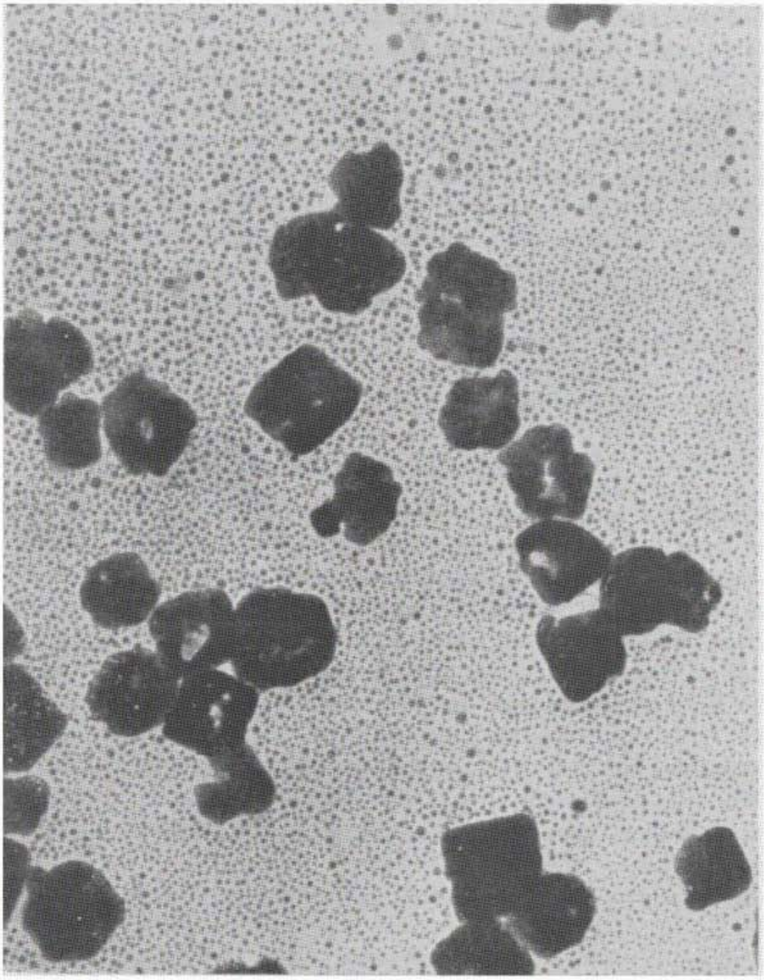

FIG. 3.—Oxide nuclei on a (111) face of Cu oxidized at 250°C and atmospheric pressure, from Harris, Ball and Gwathmey.[22]

in this paper to discuss the influence of factor, (i). Although there are differences between the formation of pits and the growth of oxide nuclei it will be useful for our purpose to discuss first in the next paragraph, (a), the initial formation of pits at dislocations and to establish the conditions necessary for it to occur. Then paragraph (b) will apply these ideas to the process of oxidation.

a) *Initial formation of pits at dislocations.*—It seems to be a general rule that the evaporation of a crystal into the surrounding medium proceeds by the movement of atomic steps or groups of them on the face of the crystal. Our problem is then to find out how these steps originate. The following classification of these sources can be given:

i) edges of the crystal.
ii) dislocations finishing at the surface and having a Burgers vector with a component normal to the surface.
iii) surface nucleation at dislocations with a Burgers vector parallel to the surface.
iv) surface nucleation on the remaining surface.

At sufficiently low rates of evaporation or more specifically when the difference in chemical potential $\Delta\mu$ between an atom in the crystal and in the surrounding medium is sufficiently small, only sources (i) and (ii) can operate. If the size of our crystal is very large only (ii) will be important and the steps will wind themselves forming spirals around the point of emergence of the dislocations according to the well-known mechanism proposed by Frank. However, the distance between successive turns of the spirals will be very large when $\Delta\mu$ is small, so that the surface of the crystal remains practically flat and no pit will be observed. It is only when $\Delta\mu$ is very large that the distance between steps becomes sufficiently small to make a pit visible, and then the internal part of the step begins to move also by surface nucleation.

It is to be expected that for roughly the same value of $\Delta\mu$ for which surface nucleation becomes effective at the center of a spiral, it will also become effective at dislocations with a Burgers vector of the same magnitude and parallel to the crystal face (iii). In both cases we can write for the rate of evaporation at the dislocations, an expression of the form

$$R_d = a\nu_d \exp\left[-(U_d + \Delta G_d^*)/kT\right], \qquad (2)$$

where $a \sim 10^{-8}$ cm is the height of a step, ν_d a frequency factor, U_d an activation energy for the motion of atomic units, and ΔG_d^* the activation energy for nucleation which will depend on all kinds of things, including the magnitude b of the Burgers vector of the dislocation, its character, its orientation both crystallographically and with respect to the surface, impurity content, etc. The production of observable pits will occur only when R_d is larger than a certain value, say

$$R_d > 10^{-5} \text{ cm/sec.} \tag{3}$$

The exact numerical value assumed is, of course, immaterial for our argument.

Finally, surface nucleation might also become effective all over the surface (iv) when sufficiently high initial values of $\Delta\mu$ are imposed. The rate of evaporation anywhere at the surface is given by an expression similar to Eq. (1) namely

$$R_p = a\nu_p \exp\left[-(U_p + \Delta G_p^*)/kT\right] \tag{4}$$

The frequency factor ν_p is expected to be larger than ν_d because nucleation can occur anywhere in the former case, but only at the dislocation in the latter, so that in some cases the factor $a\nu \exp(-U/kT)$ in Eq. (2) will be smaller than in Eq. (4). Then, as ΔG_p^* is always expected to be larger than ΔG_d^*, there will be a value of $\Delta\mu$ for which $R_p = R_d$. Clearly, if $R_p > R_d$ *no* pit can be formed, and therefore the condition

$$R_d < R_p, \tag{5}$$

along with Eq. (3), is necessary for the initial observation of pits.

It should be perfectly clear that the discussion above applies only at the very beginning of the evaporation of the metal. If the process is carried further, two effects have to be considered. First, above every point on the surface where nucleation initially occurred a diffusion and/or an electric field has to be established carrying away the material being evaporated. On the flat surface, where a linear field will be established, it will be very effective in decreasing the value of $\Delta\mu$ right at the surface and thereby decreasing the current. On the other hand the decrease of $\Delta\mu$ at a dislocation will be less marked as the diffusion field will be, at least initially, hemispherical. The pits at dislocations will therefore tend to expand at the expense of the flat surface, becoming more and more shallow until a steady state shape and a steady state current R_d is established. Second, the expansion of the pits will be the more rapid the larger R_d was initially, so that the more prominent pits will finally dominate all the others. It is therefore clear that etching can only give a lower limit for the number of dislocations ending at a crystal face; and that the number of pits observed should, if anything, decrease as the etching proceeds.

Let us now discuss the expressions for ΔG_d^* and ΔG_p^*. It is difficult at the present time to take account of all the possible factors which might contribute to the difference between these two activation energies. We shall limit ourselves to the only factor that can be treated rather simply, namely the strain energy. There are two reasons for doing this: first, the strain energy will no doubt be important in the case of a large Burgers vector, second, this treatment gives a qualitative picture of what is expected when the other factors are considered. Figure 4 represents the increase in free energy of the system by the formation of a surface nucleus of height a and radius r, both at a dislocation (ΔG_d) and away from it (ΔG_p).

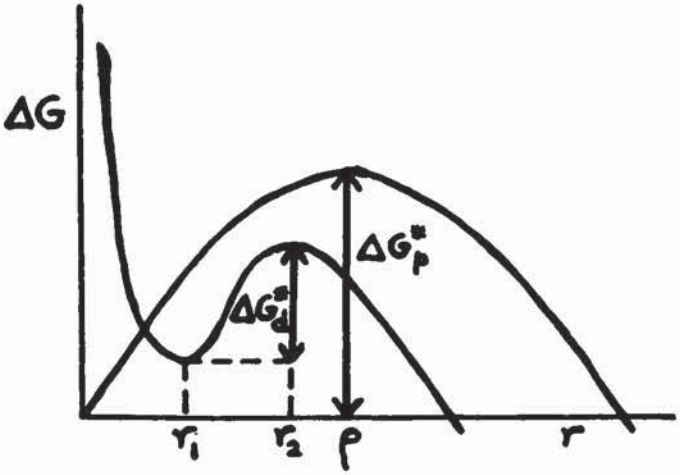

FIG. 4.—Activation energy for nucleation of a pit at a dislocation (ΔG_d) and away from it (ΔG_p).

In the latter case, there is a maximum $\Delta G_{\mathrm{p}}^{*}$ at $r = \rho$ given by

$$\Delta G_{\mathrm{p}}^{*} = \pi a \rho \gamma, \qquad \rho = \gamma \Omega / \Delta\mu, \tag{6}$$

where γ is the surface energy per unit surface of the edge of the step of height a, and Ω the molecular volume.

At the dislocation we have to consider the supplementary strain energy introduced in the crystal by the presence of the dislocation. Figure 4 shows that ΔG_{d} has a minimum and a maximum at two values of r, namely,

$$r_1 = \tfrac{1}{2}\rho[1 - \sqrt{1 - (4r_0/\rho)}],$$

which corresponds to a metastable equilibrium (minimum in the free energy) and

$$r_2 = \tfrac{1}{2}\rho[1 + \sqrt{1 - (4r_0/\rho)}],$$

which corresponds to an unstable equilibrium (maximum in the free energy). In these expressions

$$r_0 = \tau b^2 / 4\pi\gamma, \tag{7}$$

where b is the magnitude of the Burgers vector of the dislocation and τ is a combination of elastic constants having the characteristic value $\tau \sim 10^{11}$ erg/cm^3. r_0 is the stable solution when $\Delta\mu = 0 (\rho = \infty)$ and is equivalent to the existence of a hollow core along the dislocation as was suggested by Frank.[23] We see then that as $\Delta\mu$ increased r_1 increases and r_2 decreases until a critical value $\Delta\mu_{\mathrm{c}}$ is reached for which $\rho = 4r_0$ and $r_1 = r_2 = 2r_0$. Beyond $\Delta\mu_{\mathrm{c}}$ namely

$$\Delta\mu_{\mathrm{c}} = \pi\gamma^2\Omega / \tau b^2, \tag{8}$$

there is no equilibrium and therefore the dislocation should open up spontaneously without any need for nucleation. $\Delta G_{\mathrm{d}}^{*}$ is the difference between the maximum and the minimum of ΔG_{d} and becomes zero for $\Delta\mu = \Delta\mu_{\mathrm{c}}$. The following expression

$$\Delta G_{\mathrm{d}}^{*} = (\pi/12)(\gamma^2 a \Omega / \Delta\mu_{\mathrm{c}})[(\Delta\mu_{\mathrm{c}} - \Delta\mu)/\Delta\mu_{\mathrm{c}}]^{\frac{3}{2}}, \tag{9}$$

is valid for small $(\Delta\mu_{\mathrm{c}} - \Delta\mu)$ and sufficient for our purpose.

It is therefore clear that because of the strain energy, dislocations will open up and form pits, at least when $\Delta\mu$ at the dislocation is larger than Eq. (8). The parabola $\Delta\mu_{\mathrm{c}} = \pi[(\gamma a^2)^2/\tau a^3](a/b)^2$ is represented in Fig. 5 as a function of (a/b). We see that dislocations with a large b, as for instance those connected with polytypism, will open up under an extremely small $\Delta\mu$. Indeed for $a/b \sim 10^{-2}$, $\Delta\mu_c \sim 10^{-13}$ erg (assuming $\gamma a^2/kT \sim 1$), which would correspond to an undersaturation of the order 10^{-4} if the crystal is evaporating into its vapor or dissolving into a dilute solution. This has been

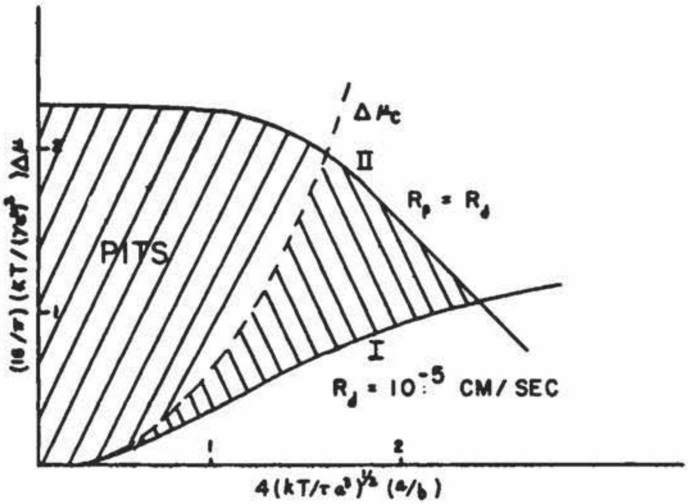

FIG. 5.—Showing the range of $\Delta\mu$ within which a dislocation with Burgers vector b is expected to initiate a pit.

shown to be the case by R. Coleman studying the dissolution of crystals of CdI_2 containing a dislocation with large Burgers vector. This is also the case in the large Burgers vector dislocations apparently present in germanium and silicon.

For small values of b however, namely $(a/b) \sim 1$, $\Delta\mu_c$ becomes quite large so that there is considerable doubt concerning the spontaneous opening up of such dislocations. There is no need, however, to reach the condition $\Delta G_d^* = 0$. In Fig. 5 the full curve I represents the values of $\Delta\mu$ necessary to make $R_d = 10^{-5}$ cm/sec, using Eq. (2) and Eq. (9). It is seen that this curve is considerably below the curve for $\Delta\mu_c$.

On the other hand, we still have to satisfy the second condition, Eq. (5). The full curve II in Fig. 5, represents the condition

$R_p = R_d$. For every dislocation, corresponding to a particular value of a/b there is a definite range of values of $\Delta\mu$, namely those within the two curves I and II in Fig. 5, for which nucleation of pits should initially occur. For $\Delta\mu$ below this range no pit should appear. For $\Delta\mu$ above this range, evaporation is so rapid everywhere, that no pit is allowed to form. The range of nucleation of pits becomes smaller and smaller as b decreases, and it finally disappears for $b < (\frac{1}{2})a$ if $\tau a^3/kT \sim 10$. This would indicate that strain energy alone should be (*just*) *sufficient* to form pits at elementary dislocations provided $\Delta\mu$ is of the order of $(\gamma a^2)^2/kT$. This is very sensitive to the value assumed for $\gamma a^2/kT$, assuming it to be between 1 and 10 one goes from relatively low undersaturations to ridiculously high ones.

In the argument above, we have entirely neglected the core energy of the dislocation by assuming that the strain energy obeys Hooke's law even at very small distances from the dislocation. This is clearly incorrect, so that we would expect our previous considerations to be doubtful for dislocations with an elementary Burgers vector. A phenomenological way of taking care of the core energy, as well as the presence of impurities near the dislocation, is to change the value of γ, assuming that it is indeed a function of the distance to the dislocation. If, for the sake of the argument, we assume $\gamma(r) = \gamma_\infty r/(r + \lambda)$ so that $\gamma(r)$ decreases as r decreases below a certain value λ, it is easy to show that the opening up of the dislocation can occur without the consideration of the strain energy. The activation energy for nucleation then becomes zero for $\Delta\mu > \gamma_\infty \Omega/\lambda$. It is therefore clear that if the magnitude of the Burgers vector b is small, such that $4r_0 < \lambda$ the opening up of the dislocation will occur more easily than it would if only the strain energy was present.

In conclusion, one might add in favor of the possible role of the strain energy in the nucleation of pits at elementary dislocations, that it predicts that the pitting should be more effective at isolated dislocations than at high angle grain boundaries where there is no strain energy. This is very often observed.

b) *The formation of oxide nuclei.*—The formation of oxide nuclei during oxidation differs from the formation of etch-pits in several respects. First of all, there should initially be a three dimensional nucleation process when a new phase is being produced. This three dimensional nucleation can be treated in a similar way to the two dimensional one considered in a). However, the results obtained depend on too many unknowns, namely the surface energies of the metal, the oxide, and the oxide-metal interface, so that at the present time there is not much to be gained by publishing the resulting formulae. It is clear, nevertheless, that the nucleation will depend very much on the crystal face considered and also on particularly active regions on a given face, namely, dislocations, large steps (or facets), precipitates of impurities, etc. The strain energy around a dislocation is here more effective than it is in the formation of a pit.

Once the three dimensional nucleus has been formed, its further growth will be very similar to that of a pit. Proper account has to be taken of the diffusion (or electric) fields occurring through the oxide. Also this further growth will differ according to whether the nucleus has been formed on the flat surface or on some active region.

When the nucleus has been formed on a perfect crystal, one should expect the nucleus to grow sidewise as the diffusion field will not control the current at the edges of the nucleus. We proceed to show how the thickness of the resulting layer can then be calculated, assuming for simplicity that there is no appreciable electric field in the oxide. Let $\Delta\mu$ be the difference in chemical potential of a metallic atom in the metal and in the oxide under equilibrium conditions at a given temperature and a given pressure of oxygen. As the thickness of oxide increases the total drop $\Delta\mu$ will be separated into $\Delta\mu_0$ occurring at the surface metal-oxide and $\Delta\mu - \Delta\mu_0$ occurring through the diffusion field in the layer of thickness X. $\Delta\mu_0$ will actually be a function of X to be determined by the condition that under steady state

$$a\nu \exp\left[-(U + \Delta G^*)/kT\right] = \Omega D_\mu(\Delta\mu - \Delta\mu_0)/X, \qquad (10)$$

where the left side represents the rate of evaporation R from the surface metal-oxide and the right side the diffusion current through the oxide. This is carried out in Fig. 6, where R_p represents the evaporation current (an expression of the type given by Eq. (4)) as a function of $\Delta\mu_0$. For a given value of $\Delta\mu$, $\Delta\mu_0$ will be given by the intersection between R_p and the straight line $(\Omega D_\mu/X)(\Delta\mu - \Delta\mu_0)$. As X increases this straight line turns counterclockwise around the point $\Delta\mu$. Once $\Delta\mu_0(X)$ is known the oxide thickness as a function of time will be determined by solving the equation,

$$dX/dt = \Omega D_\mu[\Delta\mu - \Delta\mu_0(X)]/X, \tag{11}$$

It is clear that after some time $\Delta\mu_0(X)$ will be small with respect to $\Delta\mu$, and Wagner's parabolic law of growth will be valid.

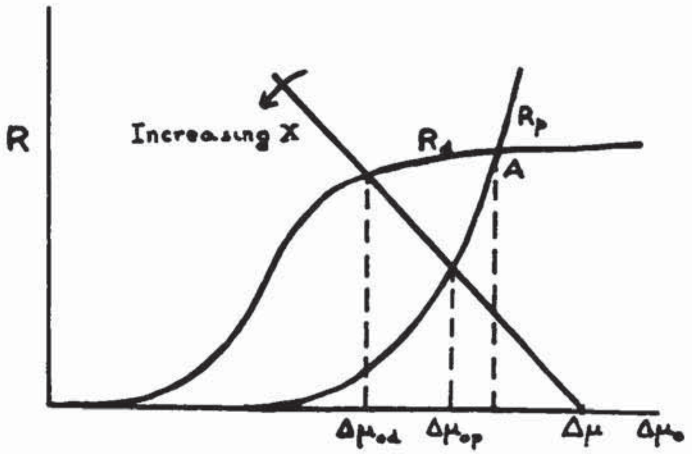

FIG. 6.—Determination of the drop in chemical potential $\Delta\mu_0$ at the dislocation (d) and away from it (*p*) as a function of the thickness X of oxide.

A similar situation will occur when the oxide nucleus has formed on a dislocation. At the beginning of its further growth the nucleus will grow hemispherically since the diffusion field from the pit formed around the dislocation will be hemispherical. Later, the increase in height of the nucleus will proceed according to the same equations (10) and (11) provided R_p is replaced by R_d. This is also represented in Fig. 6 where it has been assumed that R_p crosses R_d at the point A corresponding to a certain value of $\Delta\mu$. The following qualitative conclusions can then be deduced. We assume $\Delta\mu$ at high temperatures to be an increasing function of oxygen pressure. Then we must distinguish three possibilities: i) The oxygen pressure is so high that $\Delta\mu$ is far to the right of the abscissa of point A in Fig. 6. Then the nuclei cannot grow because $R_p > R_d$ for all values of X such that the straight line cuts both R_p and R_d beyond A. Only for large values of X is $R_d < R_p$ but then the difference will not be sufficiently large to make the nuclei apparent.

ii) The oxygen pressure is so low that $\Delta\mu$ is on the left side of the abscissa of point A. Again no nuclei will be observable because here both R_d and R_p will be small and practically equal.

iii) The oxygen pressure is such that $\Delta\mu$ is located near the abscissa of point A. Then the nuclei should become obvious at the beginning of the oxidation, as R_d remains larger than R_p in spite of the fact that X_d will also become larger than X_p. As the thickness increases it is clear that the nuclei will become less prominent, so that the formation of nuclei is only visible for a small range of oxygen pressures and a short time of oxidation, as Bénard[3] has concluded from his experimental work.

ACKNOWLEDGMENTS

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THE INTERACTION OF OXYGEN WITH CLEAN GERMANIUM SURFACES:

1. EXPERIMENT*

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ABSTRACT

Experimental methods for measuring the kinetics of the take-up of oxygen by virgin surfaces of germanium are described. The fresh surfaces used were created by crushing germanium disks in a vacuum. The effect of temperature, pressure of oxygen and germanium type was examined. The results show that over the experimentally accessible region, the take-up rate is given by $dN/dt = ae^{-bN}$, where a and b are constants and N is the amount of oxygen taken up at time t.

The take-up rate was independent of germanium type. The isosteric take-up rate was proportional to (pressure $O_2)^{\frac{1}{2}}$. Preliminary results for the isosteric activation energy have been obtained: $\Delta H^* = 5.5$ Kcals/mole at one monolayer oxygen coverage and $\frac{d(\Delta H^*)}{dN} = 1.4 \times 10^{-11}$ cals per additional oxygen atom adsorbed per cm^2 of germanium. Most of these measurements were taken at oxygen pressures ranging from 10 to 300 microns of Hg. Experiments at 60 mm Hg of O_2 gave an upper limit of surface coverage at 2.4 layers of oxide.

The variation of the heat of adsorption of oxygen on clean germanium surfaces as a function of coverage has been determined. The curve was found to be sigmoidal and the value of the heat of adsorption corresponding to zero coverage is about 250 Kcal/mole of O_2 adsorbed and decreases to about 75 Kcal/mole at monolayer coverage.

The surface oxidation of germanium is of considerable interest because the electrical behavior of a germanium surface cannot be thoroughly understood without a knowledge of the surface chemistry. This paper deals chiefly with the results of a study of the

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kinetics,[1] and of the heat of adsorption, of oxygen on clean germanium surfaces.

I. OXIDATION KINETICS

A. *Experimental Methods*

The kinetics of oxygen take-up on germanium were studied using an apparatus of the type shown in Fig. 1. The virgin surfaces were produced *in situ* by crushing single crystal disks under the glass drop-hammer: here advantage was taken of the fact that germanium is brittle and crushes easily under such treatment. The experiments were performed in an all-glass system with no stopcocks, grease or other components to interfere with the

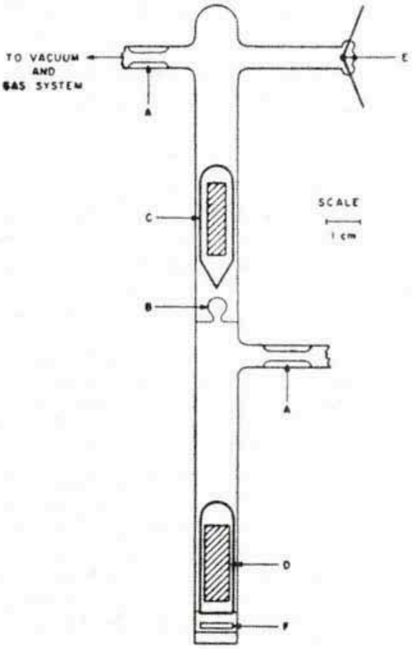

FIG. 1.—Adsorption chamber. A. Seal-off points; B. Bubble break-seal; C. Magnetically operated spike; D. Pyrex-encased iron drop-hammer; E. Thermistor pressure gauge; F. Ge disk.

measurement. The pressure measurements were made by the use of a glass-coated thermistor, employing a thermistor gauge circuit similar to that described by Dushman.[2] This gauge is particularly sensitive to pressure changes in the range 1 to 500 microns of mercury.

A typical run was carried out in the following manner: A disk of germanium (~1 cm diameter and 0.62 mm thick) was placed in the lower chamber of the apparatus (at F, Fig. 1). The lower chamber was then outgassed at about 350°C. Point A was then sealed off, and the germanium disk was crushed under the external-solenoid-operated drop-hammer (giving typically about 300 cm^2 of fresh germanium surface). A known quantity of oxygen was then introduced into the upper chamber and point A in the upper chamber was sealed off. The seal separating the two compartments of the apparatus was then punctured with drop-hammer C, and the change in oxygen pressure with time was monitored.

In a simpler version of the apparatus, a single chamber was used. Here the adsorption chamber was filled with oxygen to the desired pressure and the sample was then crushed in the presence of the gas. In this case it was not possible to examine oxidation kinetics while the sample was being crushed (from 2–5 minutes), but the total oxygen take-up and the kinetics after crushing had ceased, were recorded.

The dependence of oxidation rate on the pressure of oxygen was determined over the pressure range $1.5 \times 10^{-2} - 2.6 \times 10^{-1}$ mm Hg using a modified form of the apparatus described above. Two vessels containing oxygen at different pressures were isolated from the adsorption system by mercury cutoff valves. The sample was crushed in a vacuum, and the reservoir containing oxygen at the lower pressure was opened to the system. After the rate of adsorption was recorded, the second reservoir, containing oxygen at a higher pressure, was opened to the system, and the new adsorption rate was recorded.

The oxygen take-up was also determined at an oxygen pressure of 60 mm Hg. The germanium sample was crushed in the presence of oxygen, and the pressure changes measured using a mercury U-tube manometer. At this high oxygen pressure, percentage changes in pressure were exceedingly small, hence precise measurements of differences in meniscus heights were necessary.

The apparatus was thermostated to ±0.01°C and the pressure was determined using a cathetometer which could be read to ±0.01 mm. In this arrangement it was not possible to obtain differential readings while the sample was being crushed, hence the first differential measurement was taken 18 minutes after crushing began.

The dependence of the oxidation rate on temperature was examined in the following manner. A sample was crushed and exposed to oxygen at a specific temperature, and the rate of oxidation was measured. The temperature of the sample was then increased and kinetic data again recorded. In this manner it was possible to obtain data on the rate of oxidation at the same surface coverage, but at two temperatures.

B. *Results*

The results reported here have been normalized to surface areas determined by Rosenberg[3] using a modified BET method involving krypton as the adsorbate. While the precision of these determinations was good to better than 1 percent, the absolute accuracy of the derivation depends in general upon the particular adsorbent-adsorbate system. In the present case the conditions appear favorable and there is evidence that the accuracy may be better than 15 percent,[3] although Jacobs and Tompkins[4] claim that at best an absolute accuracy of 30 to 40 percent can be expected.

It was found that for all conditions (excepting possibly the case at 60 mm Hg of oxygen pressure) the oxygen take-up can be described by the equation

$$N = K \ln t + C \tag{1}$$

where $N = O_2$ take-up, and K and C are constants at constant temperature and pressure. Differentiating Eq. (1) yields the take-up rate $dN/dt = K/t$ and eliminating t, we have

$$dN/dt = ae^{-bN}. \tag{2}$$

Substituting experimental values in Eq. (1) we get

$$N = 0.17(8.4 \times 10^{14}) \log_{10} t + 8.4 \times 10^{14};$$
$$\text{at } 0.1 \text{ mm Hg of } O_2 \text{ and } 25°\text{C}$$

where N = atoms of oxygen adsorbed per cm² of germanium surface, and t = time (in minutes) of exposure to oxygen.

Samples of both *n*- and *p*-type germanium were used and it is of interest to note that identical results were obtained for both types.

In addition to knowing the surface area of a sample, it would be of help to know the number of surface sites per cm^2 presented by the crushed germanium. The number of broken valence bonds and the number of surface atoms per cm^2 for the three principal planes of germanium are:

(100)	1.25×10^{15} bonds and 6.25×10^{14} sites
(110)	8.83×10^{14} bonds and sites
(111)	7.22×10^{14} bonds and sites.

While the distribution of faces on a crushed surface of germanium is not known, if an assumed distribution of 40 percent (111), 40 percent (110), and 20 percent (100) is taken, this gives 7.7×10^{14} sites per cm^2. The true distribution would have to be drastically different to change this site density figure by more than 10 percent.

In the arrangement used, it was impossible to take pressure readings during the first 6 seconds of oxidation. However, the logarithmic growth was found to obtain throughout the whole period of possible measurement (6 seconds to 22 days). Beyond 22 days, the oxidation rate was too slow to be detectable with any degree of accuracy. During this period of observed logarithmic growth at room temperature, the surface coverage increased from 7×10^{14} to 1.5×10^{15} atoms of oxygen per cm^2 of sample or from 0.9 to 1.9 monolayers of oxide (using the value 7.7×10^{14} Ge atoms per cm^2 of surface).

The effect of O_2 pressure on the oxidation rate was measured in the 0.1 mm Hg range. The range was limited by the response characteristics of the thermistor gauge. Several runs were made and a typical result is shown in Fig. 2. Here the low pressure line (I) was obtained first, the pressure was then increased and curve (II) resulted. The straight line portions of curves (I) and (II) were parallel, showing that the pressure dependence of the rate is independent of surface coverage. The experiments gave

$$dN/dt \propto (P_{O_2})^{0.52}.$$

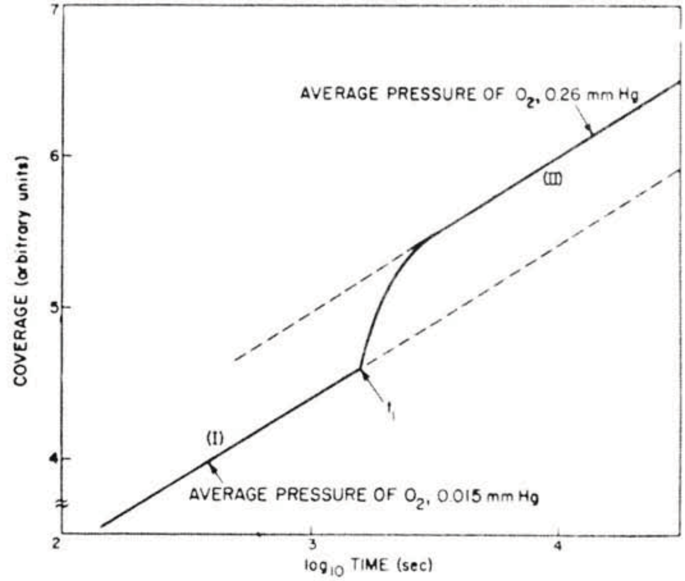

FIG. 2.—Coverage (arbitrary units) versus $\log_{10} t$ with a sudden pressure change at t_1.

It is difficult to obtain an estimate of the error in this power factor, but an upper limit would be ±10 percent.

The results of the run carried out at 60 mm Hg of O$_2$ pressure are given in Table I.

TABLE I

PRESSURE CHANGE *vs* TIME: GERMANIUM SURFACE AREA = 460 CM^2; VOLUME OF SYSTEM = 28.2 CC; INITIAL PRESSURE = 60.5 MM HG

TIME, SECS	PRESSURE CHANGE, MM HG	TIME, SECS	PRESSURE CHANGE, MM HG
1,080	0.469 ± 0.037	24,480	0.461 ± 0.046
1,800	0.480 ± 0.038	81,180	0.467 ± 0.035
3,400	0.470 ± 0.046	110,280	0.443 ± 0.030
5,280	0.437 ± 0.039	168,700	0.489 ± 0.040
10,680	0.471 ± 0.041		

The overall take-up amounted to 2.4 ± 0.2 layers of oxide. There was no statistically significant change in pressure after the first observation taken after 18 minutes of exposure of the sample to oxygen. Yet if we assume that a logarithmic take-up of O_2 is occurring and the constant (K) is unchanged (as is indicated by the low pressure studies), then there should have been a decrease in O_2 pressure of about 0.1 mm Hg over the time interval investigated. The indication is that at high coverages (2.4 atomic layers of oxide in this case) oxidation has either stopped or is proceeding at a rate slower than that predicted by Eq. (1).

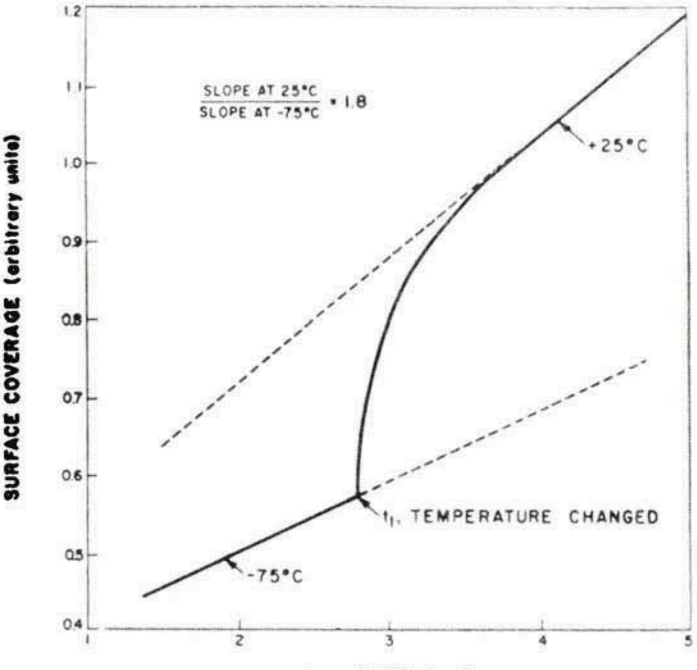

FIG. 3.—Coverage (arbitrary units) versus $\log_{10} t$, with a sudden temperature increase at t_1.

Figure 3 shows a typical run at −75°C followed by an abrupt change to 25°C. The 25°C curve is essentially a plot of N *versus* $\log_{10} t$ with an error in t. Thus, a plot of N versus $\log_{10} (t - t')$, (where t' is a time which takes account of the fact that the take-up at t_1 is less than the take-up which would have occurred if the entire experiment had been carried out at 25°C) would give the normal 25°C kinetics. When $t \gg t'$, the 25°C curve in Fig. 3 becomes a straight line, representing the pure 25°C kinetics.

The Arrhenius equation is assumed to apply, whence the energy of activation is given by,

$$\Delta H^* = \mathrm{R}[(T_1T_2)/(T_2 - T_1)] \ln (K_1/K_2)$$

where R is the gas constant per mole, T_1 and T_2 are the lower and higher temperatures respectively in degrees Kelvin, and K_1 and K_2 are the reaction rates at the same coverage values (N) at the low and high temperatures respectively.

At approximately 1 monolayer coverage, this gives $\Delta H^* = 5.5$ Kcals/mole. Since the two curves are diverging straight lines, the activation energy increases linearly with coverage; $d(\Delta H^*)/dN = 1.4 \times 10^{-11}$ cals per additional oxygen atom adsorbed per cm^2 of germanium surface.

No other pairs of temperature runs have been studied yet in sufficient detail to establish the validity of the linear dependence of energy of activation on coverage.

Kinetic studies were made on both samples crushed in a vacuum and samples crushed in an atmosphere of oxygen. The kinetics and total take-up for both cases gave the same results, indicating that desorption of oxygen from the walls of the apparatus did not affect the results of these experiments.

While samples were being crushed in vacuum, the pressure in the system was monitored. There was a measurable rise in pressure in each case which corresponded to approximately 10^{12} gas molecules per cm^2 of germanium surface or about 0.001 molecules per germanium surface atom. It is hardly likely that so slight an amount of inert gas could affect the results in any significant way.

II. THE HEAT OF ADSORPTION OF OXYGEN ON GERMANIUM

Oxygen is chemisorbed on virgin germanium surfaces with a high heat of adsorption. The apparatus described below was designed to measure the heat evolved in the chemisorption process as a function of oxygen coverage. The region of oxygen take-up investigated was from zero to about 1 monolayer of oxygen atoms. The two studies are interrelated and between them shed light on the overall interaction process.

A. *Description of Calorimeter*

The calorimeter used in the measurement of the heat of adsorption of oxygen on germanium is shown in Fig. 4. The essential features of the calorimeter are: (1) The use of a thermistor as the temperature sensing element. This has the advantage of a low heat capacity and high negative temperature coefficient of resistance; it has about four times the sensitivity of the more conventional platinum resistance thermometer or internal thermocouple. (2) The use of a thin wall, vacuum jacketed, and silvered inner bulb to minimize radiation and conduction losses. (3) The use of a calibrating nichrome coil, which is located along the bottom of the inner bulb and is connected to the tungsten leads by means of 0.002" copper wire to minimize any heat losses along the leads. Copper wire is used because its resistance is low compared with nichrome and the electrical energy dissipated as heat when calibrating the calorimeter will be localized inside the inner bulb and not dissipated along the wire coming from the tungsten leads.

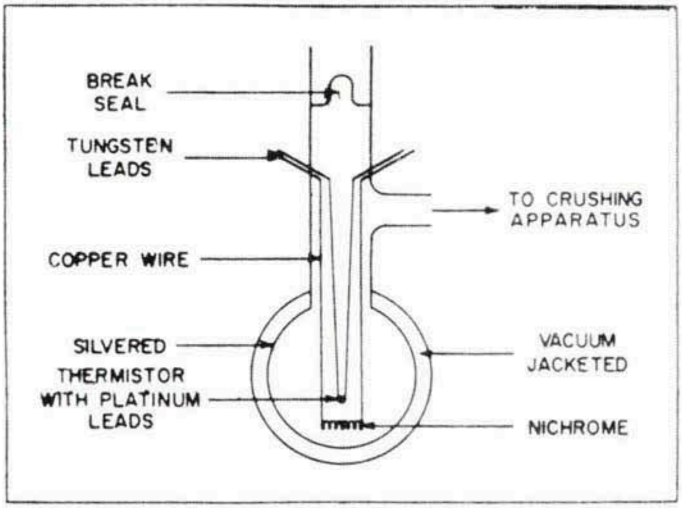

FIG. 4.—Calorimeter for heat at adsorption measurement.

B. *Preparation of Sample*

In order to obtain the largest possible temperature rise during measurement it is necessary to obtain a large ratio of surface area to mass of germanium. The germanium was sliced into thin wafers, 1 cm by 1 cm by 0.062 cm thick, CP-4 etched, and then loaded into the side arm of an all-pyrex crushing apparatus (Fig. 5) which was then sealed to a high vacuum system and outgassed overnight at 10^{-6} mm Hg and 300°C. The crushing apparatus was then sealed off under vacuum and each wafer was separately crushed for about 1 hour and transferred to the calorimeter. In this manner it was possible to obtain 5000–7000 cm^2 of fresh germanium surface from 2 grams of germanium.

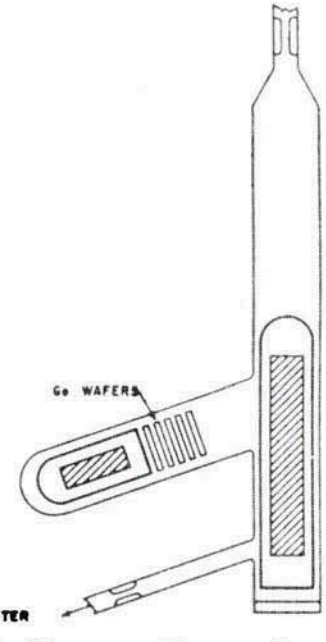

FIG. 5.—Vacuum crushing assembly.

C. *Experimental Procedure*

The calorimeter was sealed off from the crushing apparatus, placed in a well in a large copper block which was situated in a water bath thermostated at 25 ± 0.01°C and attached to the gas handling apparatus. With this arrangement temperature fluctuation should be less than ±0.001°C. Leads were connected to a Wheatstone bridge of which the temperature sensing thermistor formed one arm. Bridge unbalance due to a temperature change in the calorimeter resulted in the deflection of a high sensitivity ballistic galvanometer. The current flowing through the thermistor when its resistance was being measured was about 10 μamps and was insufficient to cause any temperature rise. The break-seal was then broken and the first increment of spectroscopically pure oxygen admitted, it was immediately gettered by the germanium. The temperature build-up and decay as a function of time as indicated by the deflection of the galvanometer was then obtained, the maximum deflection being noted. Successive doses were admitted and the heat evolved measured each time. After a certain amount of oxygen had been taken up by the germanium, it was found that the next dose was not taken up at once and the heat evolution could not be measured for this slow take-up. The calorimeter was then calibrated electrically by passing a given number of calories through the nichrome wire and observing the temperature-time curve for the system. If one assumes (to a first approximation) that the maximum deflection of the galvanometer is equal to the temperature rise in the calorimeter, a linear calibration curve of temperature *vs* heat input is obtained. The integral value of ΔH corresponding to each increment of oxygen is then calculated.

D. *Results*

Several preliminary runs have been completed and a composite plot of the heat of adsorption of oxygen in kilocalories per mole of O_2 adsorbed *vs* percent coverage is shown in Fig. 6. The percent coverage shown is given by the amount of oxygen taken up upon each addition divided by the amount that is taken up after a 1000-minute exposure. At low coverages the heat of adsorption appears to decrease slowly with coverage while at intermediate coverages the value of ΔH decreases rapidly with coverage. Values of ΔH corresponding to 65 percent coverage or greater cannot be determined experimentally because the take-up takes place too slowly.

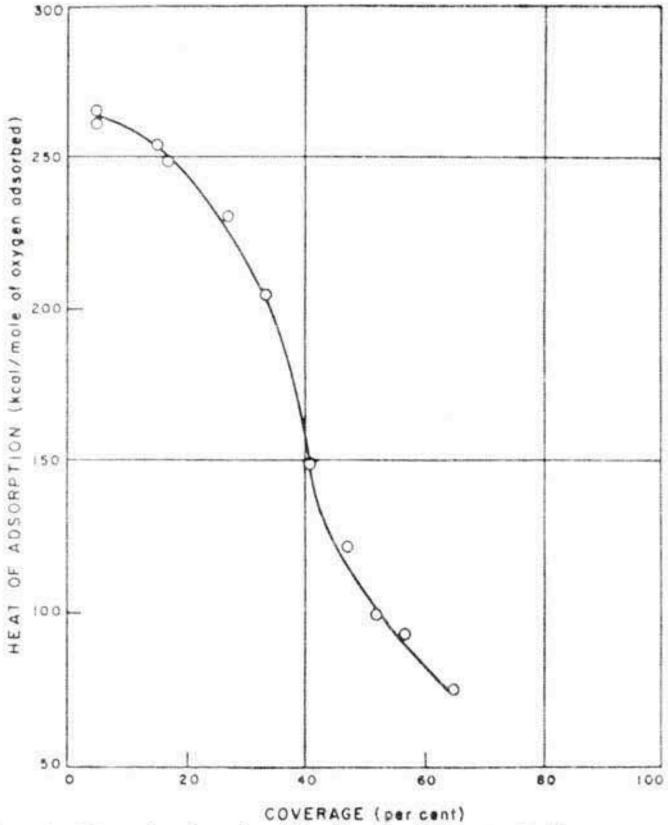

FIG. 6.—Heat of adsorption (Kcal/mole of O_2 adsorbed) versus coverage (oxygen take-up, 100% $\backsimeq$ 1.7 O per Ge).

E. *Discussion*

The results reported above are of a preliminary nature and experiments are in progress to check the validity of the calibration procedure. The error in the absolute value of ΔH may be as great as 25 percent; however, the error in determining the coverage is not higher than ±5 percent. After a 1000-minute exposure of clean germanium to oxygen at room temperature the oxygen take-up corresponds to 1.7 oxygen atoms per germanium surface atom (BET surface area). Using this relationship the rapid decrease of ΔH with coverage occurs at about 0.7 of a monolayer of oxygen.

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THE INTERACTION OF OXYGEN WITH CLEAN GERMANIUM SURFACES:

2. Theoretical Discussion

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ABSTRACT

The experimental data for the adsorption of oxygen on germanium are examined. The influence of adsorbate-adsorbate repulsion on the overall interaction process is discussed. Applying the treatment due to Roberts and Miller, it is shown that the configuration of oxygen on germanium at two-thirds of a monolayer coverage is a regular array with restricted surface mobility. Dipole-dipole interaction is considered and shown to be important for highly ionized species. The germanium-oxygen surface group is shown to be partly ionic having about 0.1 electron per oxygen atom.

Various mechanisms and kinetics for the logarithmic oxidation process are discussed. The logarithmic rate expression is shown to be of a non-specific nature, and various derivations are cited. No completely acceptable mechanism for the slow oxidation process can, as yet, be advanced.

The interaction of oxygen gas with virgin surfaces of a number of different metals [1] and germanium [2] has been the subject of recent investigations. These have disclosed an apparently new category of interaction process leading to ultra-thin oxide films, just a little beyond monolayer formation. Here the experimental data obtained for the germanium-oxygen system are examined. The possibility of establishing various diagnostic criteria for different interaction mechanisms is also considered. It will become apparent from the discussion that follows, that it is not yet possible to advance an interaction mechanism which can be taken to be completely acceptable. However, there is a sufficient body of experimental data to make an examination of some of the various possibilities worthwhile.

Our picture of the adsorbent, in this case the clean germanium surface, is the usual one of a two-dimensional lattice array which presents a periodic potential for adsorption. The valleys and peaks of the potential are periodic with the lattice, and there are as many valleys (and peaks) as there are surface atoms with broken valence bonds. Now, in the experiments on the Ge/O_2 system the surfaces were created by crushing the samples, and this leads to the exposure of different crystal faces, having a different character and a different number of adsorption sites per unit area. Thus evidence was provided of cleavage along the (111) plane as well as concoidal fracture. This experimental observation, taken together with the estimated relative energies required to separate the major faces of low crystal index, leads to the following crude guess for the distribution of low index faces: 40% (111); 40% (110); and 20% (100). Other crystal faces and a certain amount of surface heterogeneity are accepted as existing, but are considered to be of secondary importance in the context of this discussion.

I. THE HEAT OF CHEMISORPTION: THE $\Delta\bar{H}$ VERSUS θ CURVE

When a substance is chemisorbed, the strength of the union between the adsorbate and the surface is not only a result of the nature of the initial surface and the adsorbing species, but also depends upon how much adsorption has already occurred. Thus it becomes necessary to consider the adsorbate-adsorbate interaction if the overall interaction process is to be understood. The technique of dividing the surface interactions into independent groups and treating them separately, and later determining their total effect on the adsorption process, has had sufficient empirical success to warrant its continued application. In this section attention is directed to the influence of adsorbate-adsorbate interaction on the heat of adsorption for values of the relative surface coverage, θ, less than one. Of particular interest is the experimental $\Delta\bar{H}$ *vs* θ curve reported in the previous paper (Fig. 6), since the configuration of oxygen on the germanium surface at the start of the experimentally measured kinetics might well be helpful towards an understanding of the slow oxidation process.

The interpretation of the variation of the heat of adsorption with surface coverage has been treated by Roberts and Miller, using the methods of statistical mechanics. Here a brief outline of their model is given and the conclusions which arise out of their treatment are summarized. A full account of their arguments is given in Miller's beautifully written monograph[3] and his more recent paper.[4]

Miller and Roberts consider a regular surface array with each surface atom giving rise to an adsorption site. The adsorbate-adsorbent binding energy at essentially zero coverage is taken to be some fixed positive value, Q_0. As the surface fills up, adsorbate-adsorbate interactions come into play, and since there is mutual repulsion between adsorbed species their potential energy is raised by an amount q which depends on θ. This decreases the adsorbate-adsorbent binding energy, thereby giving a lower heat of adsorption; i.e.,

$$(\Delta\bar{H})_\theta = Q_0 - (q)_\theta.$$

It is assumed that the repulsive interaction which occurs is only important when species are adsorbed on nearest neighbor sites. On the basis of this model essentially three possibilities exist for adsorption with dissociation.

(i) The O_2 molecules adsorb randomly on pairs of neighboring sites and remain there, immobile. This gives a nearly linear $\Delta\bar{H}$ *vs* θ curve, which is described by,

$$\frac{\Delta\bar{H} - Q_0}{V} = -\frac{(z-1)^2\theta(2z-\theta)}{(z-\theta)^2},$$

where V is the interaction energy between two particles adsorbed on neighboring sites, and z is the number of nearest neighbors of any lattice point ($z = 4$ for rectangular arrays and 6 for close-packed hexagonal arrays).

(ii) The O_2 molecules adsorb and the oxygen atoms assume a Boltzmann distribution on the surface; that is, the energy required for the atoms to go from site to site is less than kT, resulting in complete mobility. This gives a sigmoidal curve similar to Fig. 6 of the previous paper, but with an inflexion point at $\theta = \frac{1}{2}$ for rectangular arrays and $\theta = \frac{1}{3}$ for hexagonal arrays. Up to $\theta = \frac{1}{2}$ ideally there are no nearest neighbors, and after $\theta = \frac{1}{2}$ each atom added finds itself with nearest neighbors. The equation for this curve on a rectangular array is

$$\frac{\Delta\bar{H} - Q_0}{zV} = -\left[1 - \frac{1 - 2\theta}{\{1 - 4(1-\eta)\theta(1-\theta)\}^{\frac{1}{2}}}\right],$$

where η is $e^{-V/kT}$.

(iii) The O_2 molecule adsorbs on a pair of sites; the atoms suffer strong mutual repulsion, so that they spring apart to next nearest neighbor sites, where they remain immobile until required to move by the threat of pair formation; the particles have a restricted mobility. This model gives a sigmoidal curve as well, but with the inflexion point at $\theta = \frac{2}{3}$ and $\theta = \frac{1}{2}$ for rectangular and hexagonal arrays respectively. Furthermore, there is not complete symmetry about the inflexion point: the curve after the inflexion point does not tend to parallel the θ axis as rapidly as the upper portion. For this case the calculation of $\Delta\bar{H} - Q_0$ is carried out in steps. Thus for a rectangular array from $\theta = 0$ to $\frac{1}{2}$, $\Delta\bar{H} - Q_0 = 0$. Between $\theta = \frac{1}{2}$ and $\theta = \frac{2}{3}$, $(\Delta\bar{H} - Q_0)$ per atom $= -2$ v. Between $\theta = \frac{2}{3}$ to $\frac{3}{4}$ $(\Delta\bar{H} - Q_0)$ per atom = (interaction energy for three groups of three first neighbors less the interaction energy for four groups of two first neighbors). This has been calculated as roughly -3.15 v. for an inverse seventh power law of repulsion. The steps in the $\Delta\bar{H} - Q_0$ *vs* θ curve are taken to be smoothed out by thermal motion. The array for $\theta = \frac{2}{3}$ is shown in Fig. 1. Figure 2 shows the $\Delta\bar{H}$ *vs* θ curve given by Miller.[8]

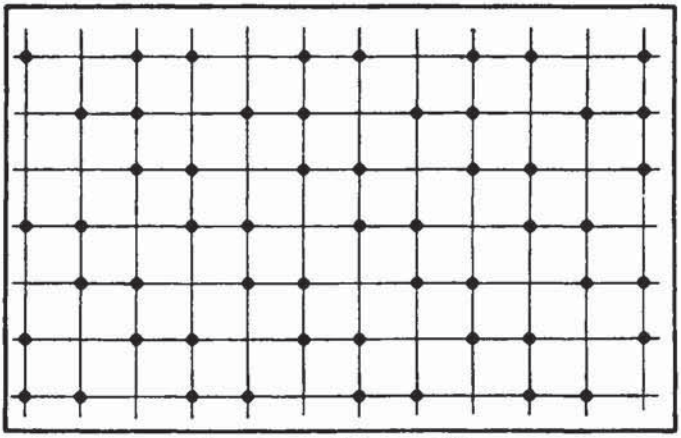


FIG. 1.—$\theta = \frac{2}{3}$ for case (iii).

Cases (i) to (iii) are for fixed nearest-neighbor interactions or for interactions varying with some high inverse power of adsorbate-adsorbate separation. The effect of long-range interaction would be to give an inflexion at about $\theta = \frac{1}{2}$ for cases (ii) and (iii).

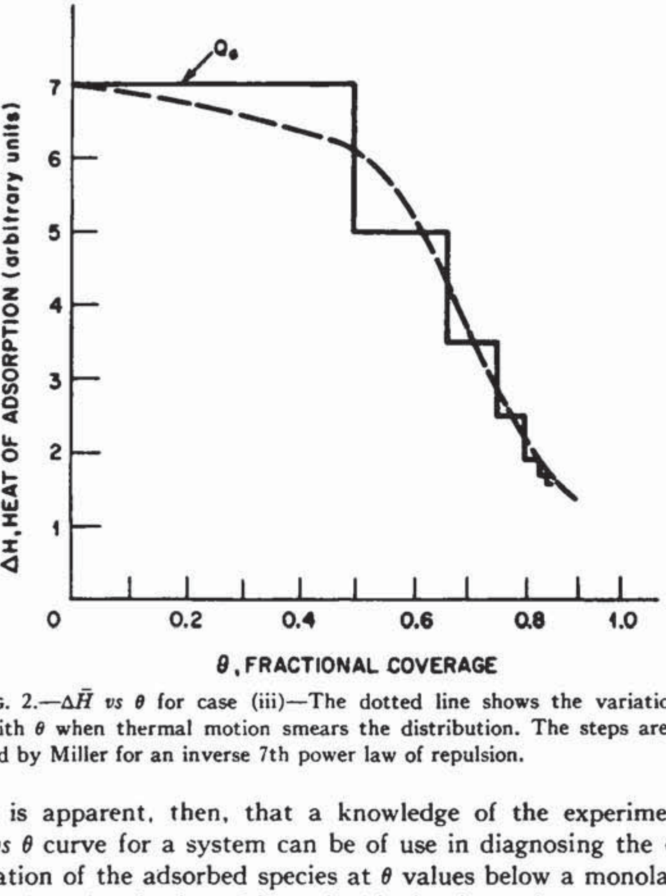


FIG. 2.—$\Delta\bar{H}$ *vs* θ for case (iii)—The dotted line shows the variation of $\Delta\bar{H}$ with θ when thermal motion smears the distribution. The steps are calculated by Miller for an inverse 7th power law of repulsion.

It is apparent, then, that a knowledge of the experimental $\Delta\bar{H}$ *vs* θ curve for a system can be of use in diagnosing the configuration of the adsorbed species at θ values below a monolayer. One serious drawback to this method is that it requires an accurate value of the absolute surface area of the adsorbent. The BET method gives surface area values which are probably not better in an absolute sense than 30 to 40 percent,[5] and even with the higher absolute accuracy (15 percent) claimed by Rosenberg [6] and some others, it would be difficult to distinguish between cases (ii) and (iii) above. We can, however, say that for the interaction of O_2 on germanium, assuming short-range repulsion, that either case (ii) or (iii) obtains.

The difference between cases (ii) and (iii) is considerable. On the one hand we have complete surface mobility, on the other, localized jumping under the influence of nearest neighbor repulsion. It is known from experiment that the initial binding energy of oxygen atoms to germanium is high (~250 Kcals/mole), and such large values of binding energy would militate against complete two-dimensional freedom. This argument is in agreement with other adsorption data. Furthermore, there appears to be a rough relation between the activation energy for desorption (ΔH_d^*) and the activation energy for surface jumping (ΔH_s^*). DeBoer[7] gives the rough relation:

$$\Delta H_s^* \approx \tfrac{1}{2}\Delta H_d^*.$$

ΔH_d^* for O_2 on Ge at low coverages must be $\gtrsim$ 12 Kcals/mole O_2 since no desorption of O_2 is observed, and the value may be much higher. For $\Delta H_d^* = 12$ Kcals/mole O_2, ΔH_s^* would have to be more than ten times smaller to obtain complete surface mobility. Thus the weight of evidence, up to this point, is in favor of case (iii).

For case (iii) to obtain we require that the nearest neighbor repulsion raise the potential energy of the nearest neighbor pair by about ($\Delta H_s^* - kT$). It remains to be seen whether such high values (≥ 12 Kcals/mole O_2) of nearest neighbor repulsion are possible for oxygen adsorbed on germanium.

The nearest neighbor distances on the germanium lattice are 4 A, (100), 4 A, (111), and about 3 A, (110), this last nearest neighbor distance being difficult to evaluate because the surface Ge-O bond makes an angle with the normal to the (110) plane and has a shorter bond length than the Ge-Ge bond it replaced. The largest atomic oxygen species that we know of is the $O^{=}$ ion, which has a radius of 1.40 A, according to Pauling.[8] Assuming a spherical ion, this leaves a gap of 1.2 A between adsorbate species on the (100) and (111) faces and approximately 0.2 A on the (110) face. The repulsion energy due to exchange interaction (which is the kind that varies very rapidly with distance) would most likely be small with such separations excepting for the (110) face. Thus if we take Fowler's calculations for the interaction energy for two neon atoms,[9] Fig. 3, which are similar in size to the $O^{=}$ ion (Ne = 1.12 A radius), the equilibrium distance is 3.20 A. The net interaction energy does not become positive until the particles are about 2¾ A apart; that is, a gap of about ½ A between the points of closest approach of the spheres. On this

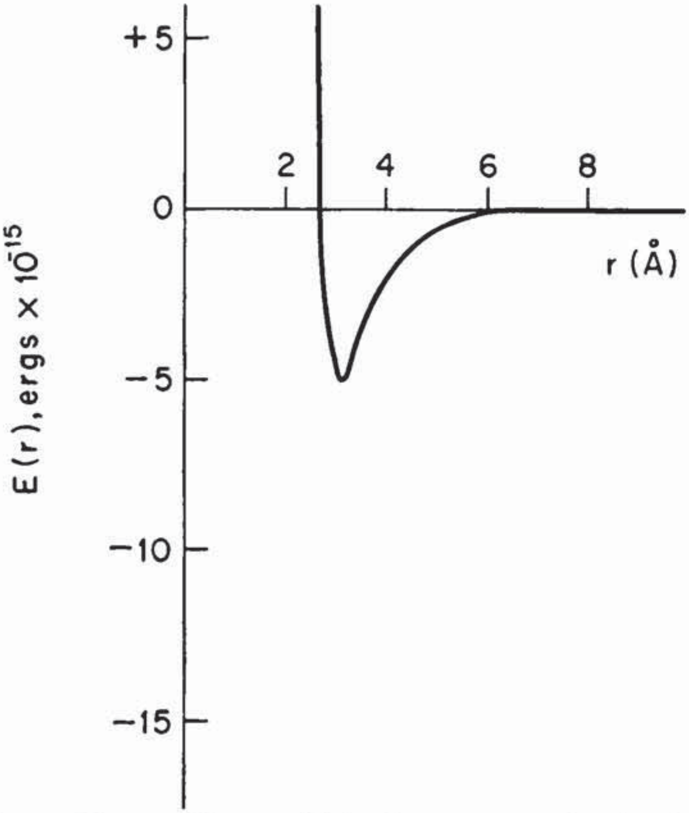


FIG. 3.—The potential energy of isolated near atoms as a function of their distance apart (after Fowler).

model it is difficult to see how high fixed interactions come about on the germanium lattice, except for the (110) face. Also there is evidence (next section) that the oxygen is not fully ionized, whence it would have an even smaller radius and give a larger gap between nearest neighbor species.

Another possibility exists, and that is that the oxygen species is not spherical, but is distorted giving rise to atoms roughly the shape of an oblate spheroid. This would bring the electron clouds of nearest species close together whence a large repulsion would result, Fig. 4. The distortion is imagined to come about because of the large electrostatic field set up between a negative oxygen ion and an underlying positive germanium ion. A surface dipole of ~1 D would have a field between oppositely charged ions of ~10^7 volts/cm.

The above models assume exchange force repulsions. However, there is the possibility of long-range dipole-dipole repulsion. A complete monolayer of dipoles would give an increase in potential energy of about 140 Kcals/mole O_2 if the dipole moment were 7.7 D. This is calculated using the expression

$$\Delta\, P.E. = 6N\mu^2K[1 + 1/3^{\frac{3}{2}} + 1/2^3 + 2/(\sqrt{28}/2)^3 + \cdots.]$$

This is essentially a Madelung type calculation for a two-dimensional array. The series is for the (111) lattice of germanium. N is Avogadro's number, μ is the dipole moment, and K is a numerical constant for converting the basic side on the (111) germanium lattice to one. The series was carried out to 19 terms and a correction was applied to the first five terms to account for the fact that we have real dipoles. For a lattice array on fifth neighbor sites and for $\mu = 7.7$ D, $\Delta\, P.E. = 4.4$ Kcals/mole O_2. Thus only high values of μ are capable of accounting for the magnitudes of the changes in the $\Delta\bar{H}$ *vs* θ curve. The weight of evidence then is in favor of case (iii) for the Ge/O_2 system.

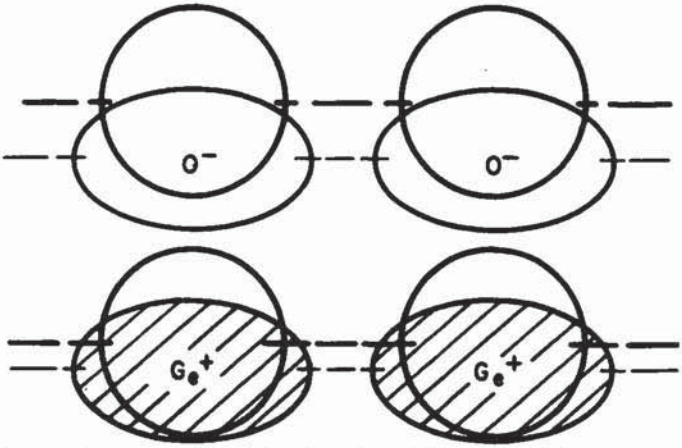


Fig. 4.—Representation of the distortion of the surface ionic species due to the field set up between them.

II. THE NATURE OF THE OXYGEN ON GERMANIUM

The magnitude of the heat of adsorption of O_2 on germanium at low coverages would be consistent with the idea that O_2 dissociates on adsorption. At the much lower heats observed when the surface begins to fill up and the kinetics become measurable, there is evidence for O_2 dissociation; i.e., the pressure dependence of take-up rate goes as (pressure $O_2)^{\frac{1}{2}}$. Thus it is very probable that oxygen atoms or ions are present on the germanium surface. The recent experiments carried out on germanium surfaces cleaned by ion bombardment methods can be of use in indicating the nature of the adsorbed oxygen atoms. The very rapid initial adsorption of oxygen on these surfaces indicates a high degree of surface cleanliness.

If the work function changes measured by Dillon[10] and the field effect and surface conductance experiments of Autler and McWhorter[11] are taken together, a value, admittedly crude, for the change in surface dipole produced as a result of O_2 adsorption can be obtained. The exact values of θ at which the physical changes were measured is not known, but since θ will change by about $\frac{1}{2}$ to $1\frac{1}{2}$ an exact knowledge of θ is not material to the broad argument.

Figure 5 (a) and (b) is a representation of the potential distribution in germanium before and after exposure to O_2. It is obvious that

$$\psi' - \psi = (\chi' - \chi) + (\phi - \phi').$$

Dillon gives the change in work function $(\chi' - \chi)$ as 0.28 ev on the (100) face, and $(\phi - \phi')$ is estimated[11] as 0.3 ev. This gives a change in the surface dipole of $\sim$0.58 ev. A crude electrostatic approach can be used to calculate what the change in work function should be for, say, a half monolayer of O^- ions. The work function of clean germanium surfaces is 4.8 ev. Thus the effective length of the surface dipole can be calculated using the relation,

$$d = \Delta V/4\pi\sigma,$$

where ΔV is the surface dipole (due to the displacement of the center of the electron cloud from the positive nucleus) and σ is the

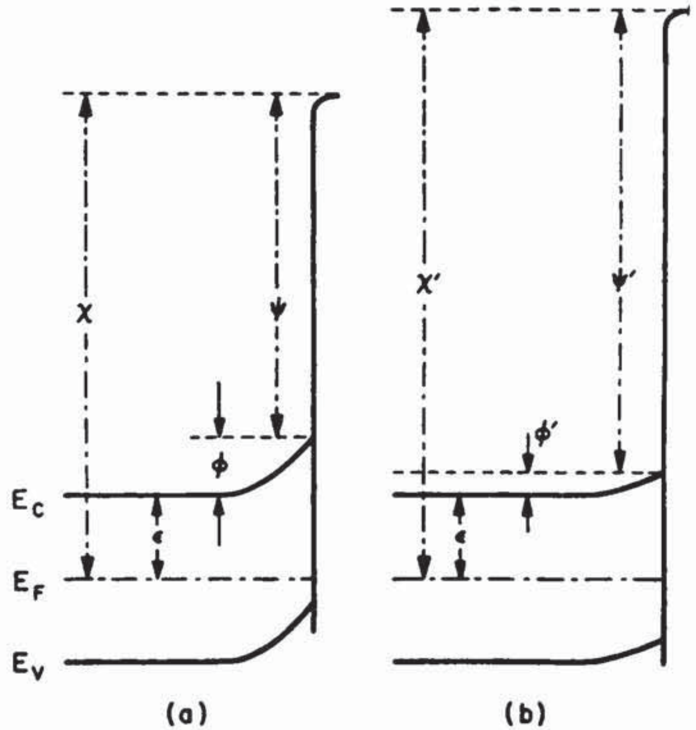


FIG. 5.—Schematic representation of the energy levels at, and near, a Ge surface: (a) before, and (b) after, exposure to O_2.

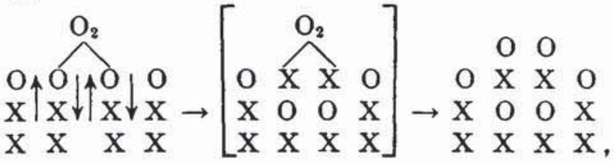
charge density per unit area (taken as $6.25 \times 10^{14} \times 4.8 \times 10^{-10}$). This gives $d = 0.435 \times 10^{-8}$ cm. When O^- ions are formed it is assumed that there is a shift of the negative charge so that the length of the surface dipole is now given by the internuclear separation between the Ge^+-O^- group. This internuclear distance is taken as 1.60 A, whereupon the change in work function is $4\pi\sigma\Delta d$, i.e. $\sim$6 volts, or approximately a factor of ten greater than the value observed. This would indicate that each surface oxygen carries approximately one-tenth of an electron charge, i.e., we have essentially a polar covalent bond. For more conclusive evidence it would be highly desirable to measure the changes in the surface electrical properties as a function of oxygen coverage, particularly in the range $\theta = 0$ to $\frac{2}{3}$. Admittedly such experiments would be fraught with difficulties.

III. POSSIBLE MECHANISMS FOR SLOW TAKE-UP

On the basis of the interpretation of the $\Delta \bar{H}$ *vs* θ curves we have it that at the inflexion point the surface configuration is, ideally, for a square array as shown in Fig. 1. The kinetics are not known for the build up of this film, and it is interesting to note that it is just the inflexion point that corresponds to the amount of O_2 that must be taken up before the kinetics are experimentally measurable (at the lowest temperature). This observation is independent of surface area determinations. It is taken that the starting point for the slow kinetics occurs with the value of θ corresponding to the inflexion point: this is not proved. However, the alternative of extrapolating the logarithmic kinetic relation to lower values of θ would imply a continuous oxide building process when there were few nearest neighbors of adsorbed oxygen. This seems unlikely except for a very heterogeneous surface, and even then the kinetics would not be continuous unless there were an almost continuous distribution in energy of surface sites. Even less likely is that the process of chemisorption of oxygen and the oxide formation process would have the same detailed kinetics, which implies an identity in mechanism. It seems reasonable to take it that a particular process starts when there is a critical change in the system which causes a large free energy change: this is certainly the case on the occurrence of nearest neighbor formation on a surface.

Any attempted explanation of the logarithmic take-up of O_2 by germanium must take account of the fact that the kinetics of the process are continuous, ranging from a starting value of $\theta = \frac{1}{2}$ to $\frac{2}{3}$ and terminating or slowing down at about $\theta = 2.0$ to 2.5; that the activation energy for the process apparently increases linearly with θ; and that the rate for any fixed value of θ increases as $(P_{O_2})^{\frac{1}{2}}$. For the metals of Lanyon and Trapnell we would have θ ranging from 1 to $1\frac{1}{2}$ or 2. Various mechanisms can be advanced.

(I) Lanyon and Trapnell[1] suggest several possible mechanisms; e.g.,



or the above process with interchange occurring in two steps. Also they consider interchange processes via lattice defects. This kind of mechanism is capable of giving an oxygen take-up of $\theta = 2$. If the process is allowed to continue by allowing a chain of O-X exchanges, an oxide layer of any thickness can be obtained, viz.:

$$\begin{array}{c} \uparrow\mathrm{O}\downarrow \\ \mathrm{X} \\ \uparrow\mathrm{O}\downarrow \\ \text{- - - -X- - - -} \\ \mathrm{X} \\ \mathrm{X} \end{array} \xrightarrow{+\text{oxygen}} \begin{array}{c} \mathrm{O} \\ \mathrm{X} \\ \mathrm{O} \\ \mathrm{X} \\ \mathrm{O} \\ \text{- - - -X- - - -} \\ \mathrm{X} \end{array} \quad \text{, and so forth.}$$

No reason is given for why these X-O exchanges should occur. But Lanyon and Trapnell do suggest that the heat of chemisorption would assist the exchange. This would imply that the exchange step occurs immediately after oxygen adsorption, so that the energy liberated has no time to become distributed through the system; to an order of magnitude this might be the time for 50 lattice vibrations to occur.

(II) Another possible mechanism for arriving at a very thin oxide layer is given below. It has the attractive feature of giving rise to a unique final configuration, and hence an intrinsic termination.

$$\begin{array}{cccc} & & & \\ \mathrm{O} & \mathrm{O} & \mathrm{O} & \mathrm{O} \\ \mathrm{X} & \mathrm{X} & \mathrm{X} & \mathrm{X} \end{array} \rightarrow \begin{array}{cccc} & \mathrm{O} & & \\ \mathrm{O} & \mathrm{X} & \mathrm{O} & \mathrm{O} \\ \mathrm{X} & & \mathrm{X} & \mathrm{X} \end{array} \rightarrow \begin{array}{cccc} & \mathrm{O} & & \\ \mathrm{O} & \mathrm{X} & & \mathrm{O} \\ \mathrm{X} & \mathrm{O} & \mathrm{X} & \mathrm{X} \end{array} \xrightarrow{+\mathrm{O}}$$

$$\begin{array}{cccc} & \mathrm{O} & & \\ \mathrm{O} & \mathrm{X} & \mathrm{O} & \mathrm{O} \\ \mathrm{X} & \mathrm{O} & \mathrm{X} & \mathrm{X} \end{array} \xrightarrow{\text{Finally}} \begin{array}{cccc} & \mathrm{O} & & \mathrm{O} \\ \mathrm{O} & \mathrm{X} & \mathrm{O} & \mathrm{X} \\ \mathrm{X} & \mathrm{O} & \mathrm{X} & \mathrm{O} \end{array}$$

This mechanism gives a final value of $\theta = 1\frac{1}{2}$ for a rectangular array. Furthermore, an argument can be made for its occurrence on the basis of strong repulsion between adjacent $\left(\begin{smallmatrix} \mathrm{O} & \mathrm{O} \\ \mathrm{X} & \mathrm{X} \end{smallmatrix}\right)$ groups as compared with $\left(\begin{smallmatrix} \mathrm{O} & \mathrm{X} \\ \mathrm{X} & \mathrm{O} \end{smallmatrix}\right)$ groups. If the drop in the $\Delta\bar{H}$ *vs* θ curve corresponds to $\theta \simeq \frac{1}{2}$, then this mechanism might well apply. This would not stretch the errors in the BET surface area data beyond its possible limits. However, there are serious objections to this case applying to the O_2-Ge system. Mechanism (II) might apply to the metals of Lanyon and Trapnell.

Without citing further examples it can be seen that it is a relatively simple matter to postulate various mechanisms for oxide layer formation up to $\theta = 2$. However, when the oxide layer is just greater than 2 we must invoke the migration of atoms which were in the second layer of the surface, or alternatively the penetration of the lattice by oxygen. The usual theories of the oxidation of metals where such migrations occur do not embrace such thin films, and it is apparent that no satisfactory mechanism has been advanced to explain the mechanism of formation of ultra-thin films. It should, however, be pointed out that the extent of O_2 take-up on germanium is not known with sufficient accuracy to warrant a more detailed examination of the possibilities for θ values beyond 2. This points to a need for a method for surface area determination with an absolute accuracy of better than 10 percent.

IV. LOGARITHMIC OXIDATION KINETICS

Several methods have been suggested whereby it is possible to arrive at the logarithmic rate expression:

$$\theta = \frac{1}{b} \{\ln (t + t_0) - \ln t_0\} \qquad (1)$$

(t_0 and b are constants and t is time measured from the beginning of the experiment). This expression applies to such a multiplicity of chemisorption processes [12] that it cannot be taken as indicative of a particular mechanism. Thus Weisz [13] has shown that in some cases adsorption on a semiconducting adsorbent, where electron transfer is the rate determining step, can give rise to a logarithmic expression. These arguments do not appear to be applicable to germanium since the temperature variation of adsorption rate obtained experimentally is considerably smaller than the variation with temperature of the number of electrons striking the barrier (which is the basis of Weisz's treatments).

Another possible interpretation of Eq. (1) is due to Porter and Tompkins.[14] Adsorption is assumed to occur on a non-uniform surface, such that the most active sites are covered first. There is then a slow (rate determining) migration from the active sites to less active sites where the adsorbate is finally trapped. This migration then uncovers the most active site for further adsorption.

There is, however, some evidence that this mechanism does not operate for oxygen adsorption,[1] since according to Lanyon and Trapnell the take-up rate on a partially oxidized surface is independent of the time for which such a sample has been allowed to stand in vacuo before being exposed to more oxygen. If the process were surface migration of adsorbate species there would be no reason why the process should not continue in vacuum. In fact, there is no apparent aging phenomena in the adsorbent-adsorbate system.

Landsberg [15] has given a detailed discussion of the logarithmic expression. He shows how such an expression arises from the simple assumption that the surface area which a particle invalidates on adsorption is different from the impact area of the molecule. The considerations are general and so no specific models were given.

Yet another possibility is to assume a linear increase of activation energy with coverage, so that the change of the free energy-distance relation for the rate determining step will be as shown on Fig. 6. Physically this can be argued as coming about in the

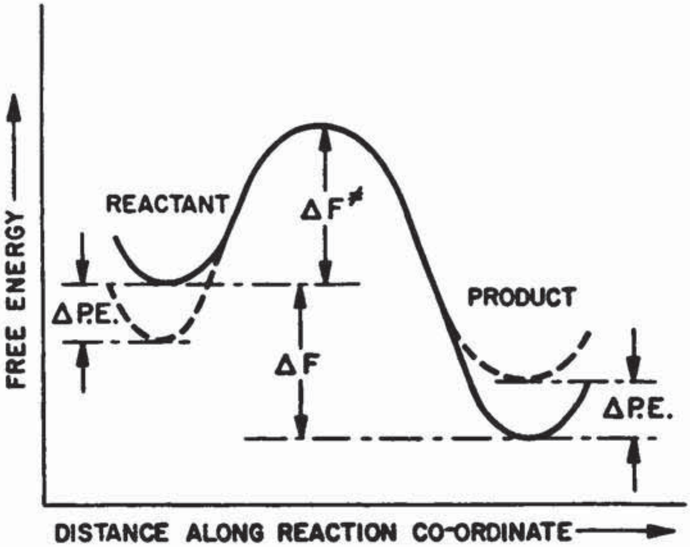


FIG. 6.—Free energy *vs.* distance diagram for the rate controlling step in oxide formation. The dotted lines are the changes in free energy due to lessened adsorbate-adsorbate repulsion on the reactant species and increased repulsion on the resultant species.

following way. Oxygen adsorbs in the vacant sites shown on Fig. 1; this starts the process of oxide formation. Thus at some sites on the surface X/O groups exchange, i.e.,

$$\text{- -}\begin{pmatrix}\text{O}\\ \text{X}\end{pmatrix}\text{- -} \rightarrow \begin{matrix}\text{X}\\ \text{O}\end{matrix}$$

The distribution of these exchanges is taken to be random on the surface. When such an exchange has occurred, the repulsion experienced by an adjacent $\binom{\text{O}}{\text{X}}$ group will be less and so its potential energy will fall, and it will be less likely to suffer an exchange (causing further adsorption). If these exchanges occur randomly on the surface, so that the occupancy of $\binom{\text{O}}{\text{X}}$ and $\binom{\text{X}}{\text{O}}$ groups in the first shell around an $\binom{\text{O}}{\text{X}}$ group is random, then a nearly linear drop of potential energy with coverage should result. This kind of approach parallels Miller and Robert's treatment for $\Delta\bar{H}$ *vs* θ for immobile adsorption with nearest neighbor interactions.

Then $\Delta\, P.E. = \text{const.} \times \theta$, i.e., $g\theta$, and if we say that $d\theta/dt = v_+ - v_-$, the forward and back rates respectively, then

$$\frac{d\theta}{dt} = K(c_+)\exp\left[-(\Delta F^{\ddagger} + \Delta\, P.E.)\right] - K'(c_-)\exp\left[-(\Delta F^{\ddagger} + \Delta F - \Delta\, P.E.)\right],$$

where (c_+) and (c_-) are the activities of reactants and products respectively, and K and K' are constants. Combining constants and neglecting changes in (c_+) and (c_-) which will only vary linearily, we have when $v_+ \geq 10\, v_-$ that

$$\frac{d\theta}{dt} = \text{Const} \times e^{-g\theta},$$

which is the kinetic law in the differential form. As v_+ approaches v_-, the rate will decrease and deviate from the logarithmic law, which is consistent with the high pressure O_2 experiments on germanium.

V. CONCLUSIONS

Following the work of Roberts and Miller it is apparent that the shape of the $\Delta\bar{H}$ *vs* θ curve can be used in diagnosing the configuration of adsorbate species at low oxygen coverage. This in some cases requires accurate values for the absolute surface area of the adsorbent. It is also apparent that the strong electric fields produced at the adsorption interface may have a strong influence on the nature of the adsorbate-adsorbate interaction energy. Large adsorbate-adsorbate potential energy changes can be brought about by dipole-dipole interaction, if fully ionized species occur on the surface, and to this end more careful studies of contact potential change as a function of coverage are needed. It is also by no means certain that a simple electrostatic approach in evaluating surface dipoles is adequate.

The mechanism for slow oxygen take-up is still an open question, and it would appear to be important to distinguish between configurations containing less than 2 oxygen atoms per surface site, and more than 2 oxygen atoms per surface site.

The kinetics for slow oxidation appear to be of a general kind embracing all manner of process and cannot be taken as diagnostic of a specific mechanism. Thus surface heterogeneity, adsorbate-adsorbate interaction, and semiconductor-barrier layers can all lead to a logarithmic rate expression.

Experimental determinations of $\Delta\bar{H}$ *vs* θ curves on different crystal faces would be a test of the short-range interaction theories. The interruption of a slow oxidation experiment as carried out by Lanyon and Trapnell[1] should cast light on the oxidation mechanism. Further kinetic runs at high coverages (high pressure experiments) would be helpful in distinguishing between some of the methods used for arriving at a logarithmic rate law. There is also the possibility of reversible adsorption of oxygen at high θ values and this would be interesting to study, since the entropy of adsorption could be obtained.

DISCUSSION

G. A. WOLFF (*Signal Corps Engineering Laboratories*): The speaker tried to estimate the chemical adsorption of oxygen on germanium on the basis of the experimentally determined surface area and of the assumed proportion of cleaved (111), (001) and (011) planes in germanium. The following experimental and theoretical results obtained might be helpful and contribute to the solution of this problem.

(1) Cleavage planes in silicon and germanium are (111), (001) and all the planes of the [011] zone between (111) and (001). There

is an indistinct cleavage of (001) and the neighboring planes, which might explain the conchoidal fracture in these materials.

The cleavage was determined as follows: Single crystal balls of the substance to be investigated were ground with silicon carbide or diamond powder, and the better the cleavage, the easier it was to chip away parts of the balls. Thus, the corresponding light figures show the cleavage as a function of crystallographic directions. Light figures are the projections of the light reflected from the planes of the "cleavage pits" when a parallel light beam is used and the screen is placed between light source and crystal. This method, which has been used by us mainly for the determination of the ratio of ionic to covalent bonding in crystals with sphalerite and wurtzite structure, shows for diamond a cleavage pattern of (111), (011) and all planes of the [011] zone between them, which differs from that of silicon and germanium.

(2) The ratio of the amount of cleaved surfaces for the different planes follows a canonical distribution law. This can be concluded from experiments on the triboluminescence, in particular, triboluminescence of the cubic arsenic trioxide with (molecular) diamond structure.

Triboluminescence is the light emitted when crystals are crushed. The distribution of the light flashes of less than 1 μsec duration, observed by photomultiplier and oscilloscope, is exponential with respect to their intensity. To each flash a microfracture of the crystal can be attributed which corresponds to a very small area of cleaved (111) plane. For cubic arsenic trioxide, which shows a temporary triboluminescence due to a decrease in lattice defects, the slope of the corresponding straight line in the $\log N_I^* - I$ diagram remains constant for each measurement at the different time interval. Here, N_I^* and I designate the number of light flashes of an intensity greater than I, and the intensity, respectively. The slope becomes more negative when impurities in the crystals increase the free surface energy of the cleavage planes, and possibly when the temperature decreases.

These results lead to the conclusion that for one single kind of cleavage plane the frequency of planar microfracture of a certain size follows the relation

$$N_S = N_O \exp(-AES)$$

where N_S and N_O are the numbers of the planes of the size S and O, respectively; E is the specific surface energy and A is a constant. This relation may be further extended to a relation between different planes, and thus determine the distribution of cleaving microplanes with respect to size.

(3) For the different crystal faces it is easy to determine the number of free bondings and thus estimate the chemical adsorption of a monoatomic layer of oxygen. Here, the general assumption is an undistorted crystal surface. A more detailed study suggests, however, that this is very likely the case for (111) and (011) in crystals with diamond structure, but not for any other plane. There is some evidence resulting from our habit studies that (113) in silicon and germanium is distorted as a result of a deformation of the upper crystal layers and that there is partial saturation of the residual bondings; there are also indications for (001); calculations show that the specific surface energy of a deformed (001) plane is considerably lower than that of the value for an undeformed (001) plane.

From these results it is concluded that adsorption on these planes may be less than calculated for an undeformed plane or that there is an additional activation barrier in adsorption. Distortions in crystal surfaces have been shown to exist in other crystals, particularly in the alkali halides.

M. GREEN: We are grateful to Dr. Wolff for his pertinent remarks. The fact that the (111) and (110) planes are favored in cleavage is most gratifying, since that is what we have assumed. However, these are qualitative or semi-quantitative conclusions; what is really desired is an exact knowledge of the distribution of crystal faces, and here the experiment on triboluminescence would appear to be promising, but again this is not yet on a quantitative footing.

I wonder if the method used for producing cleavage (grinding single crystal balls) is really comparable with our method which involves crushing under a drop-hammer.

C. G. B. GARRETT (*Bell Telephone Laboratories*): I should like to question the author's assumption that the oxidation process ceases after a well-defined, rather small number of layers of oxygen have gone down on to the surface. The experimental evidence, so far as it has been presented, suggests only that, after one to two layers of oxygen have been taken up, the experimental accuracy falls below that level which is required to establish the logarithmic oxidation law, so that one can no longer tell whether oxidation is continuing or not.

M. GREEN: It is not our claim that the experimental data obtained at high O_2 pressures gives proof that the oxidation process has come to a complete halt. The experiment indicates that the process is either proceeding more slowly than the extrapolated logarithmic interaction expression would lead us to expect, or, that it has come to a halt. Furthermore, our experiment was not sensitive enough to establish the nature of the O_2/Ge interaction law: it was merely able to show that there was a statistically significant difference between the amount of O_2 which should have been taken up had the logarithmic process pertained, and the observed amount of take up. In fact, no systematic decrease in O_2 pressure was observed over the time interval investigated. But a continued logarithmic interaction would have given a change in O_2 pressure which would have been more than four times the standard deviation of our observations; hence the statistically significant difference.

Dr. Garrett, however, raises the interesting question of what happens to a logarithmic process after long times. We consider one possibility in our discussion which leads to an expression which is the difference between a forward velocity and a reverse velocity, which by its very nature will finally give an equilibrium value. Another possibility is that a different (and slower) interaction process takes over.

J. T. LAW (*Bell Telephone Laboratories*): The measured heat of adsorption of oxygen on germanium as a function of the fraction of surface covered has been interpreted by the authors in terms of the theory of Roberts and Miller.[16] These workers showed that when the heat decreased rapidly at $\theta = 0.5$ the change could be ascribed to interactions between adsorbed particles on nearest neighbor sites. However, one must assure that the surface is homogeneous and that the adsorbed particles are mobile. For a powdered sample it is hard to believe that the first of these conditions is met. The first effect of heterogeneity would be to give heats of adsorption at near zero coverage which were considerably higher than those $\theta = 0.1$. In the curve shown there is no sign of a rise in this region. Do the authors interpret this as meaning that their surface was homogeneous or is it just a matter of the size of the initial dose of gas admitted?

On the question of mobility of the adsorbed species, is it not possible to calculate an entropy of adsorption from the heat and kinetic data and so decide this point? If the film is found to be immobile, one would be forced to the conclusion that the observed decrease in heat is occurring nearer to $\theta = 1$ than $\theta = 0.5$; and this would not be in disagreement with the measured BET areas. For immobile films the heat in the first layer will normally decrease linearly as a function of coverage.

M. GREEN: Heterogeneity must indeed be the case for our samples, if only because we have corners and edges. This will most likely give larger heat values at low coverages. However, our experimental method would not show up small differences in heat of adsorption, since we really measure an integral heat of adsorption (i.e. we measure total heat from $\theta = 0$ to 0.08 and so forth). The contribution to the heat due to extra active sites would have to be large to show up as a rise in our $\Delta\bar{H}$ *versus* θ curves. Thus it is indeed, as Dr. Law suggests, a matter of the size of the initial dose of gas admitted which smooths the curve in this region.

It is not possible to obtain the entropy of adsorption from our heat and kinetic data, since these do not overlap, i.e. we can measure heats of adsorption when the process is fast (essentially the heat is put in as a spike) and we can only measure kinetics when the process is slow (limited by the response time of our thermistor gauge). Certainly a knowledge of the entropy of adsorption would be useful; however I wonder if the interpretation is as clear cut as Dr. Law suggests.

The BET method gives the inflexion point at $\theta = 0.67$, which is still far from a monolayer. Hence one must conclude that the inflexion point in the $\Delta\bar{H}$ *versus* θ curve occurs well before a monolayer and so is not typical of monolayer-immobile film formation.

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THE HIGH TEMPERATURE OXIDATION OF GERMANIUM

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ABSTRACT

The oxidation rate of the (110), (111), and (100) faces of a germanium crystal have been measured between 500° and 700°C and at various oxygen pressures. The mechanism of the oxidation process in this range is discussed and compared with results previously reported at lower temperatures.

I. INTRODUCTION

A knowledge of the oxidation rate of germanium at and above room temperature may be of some importance in understanding the effect of an oxide film on the surface properties of germanium itself. It has been shown that at room temperature oxygen has a marked effect on surface conductivity,[1] contact potential,[2] etc., while long time changes associated with the Brattain-Bardeen [2] cycle have been ascribed to the formation and growth of an oxide film. In fact, whenever measurements are made on a surface not deliberately cleaned in vacuum, one is dealing with a germanium-germanium oxide-gas system. One way of understanding the effect of the oxide is to deliberately vary its thickness, for example, by preoxidizing at some elevated temperature.

Recently Green and Kafalas [3] have presented oxidation rates obtained on a cleaved germanium surface at temperatures between −195° and 87°C. At room temperature the oxidation rate obeys the equation

$$N = (0.16)(8.8 \times 10^{14}) \log t + 8.8 \times 10^{14}$$

where t is the time in minutes and N is the oxygen uptake at time t in atoms cm^{-2}. The pressure dependences of the oxidation rates in this temperature range have not been reported. Sun [4] has measured oxidation rates from 200° to 500°C and finds that the uptake at 200 minutes does not exceed 2.5×10^{14} molecules cm^{-2}, while the rates are approximately proportional to the pressure. The difference between Sun's results and those of Green and Kafalas may lie in the condition of the initial surface which was almost certainly less clean in Sun's work. Further work is required before the oxidation kinetics between room temperature and 500°C can be described with any certainty. Dennis, Tresler, and Hance[5] briefly studied the high temperature reaction with oxygen and noted that no apparent reaction occurred at temperatures below 600°C. At 730°C a glazed surface covered with white GeO_2 was obtained, while at higher temperatures appreciable volatilization of GeO occurred. The kinetics of the oxidation between 575° and 705°C were studied by Bernstein and Cubicciotti.[6] After oxidation the surface was covered with a thin blue oxide film, while at higher temperatures the sample was coated with a light colored powdery film. X-ray diffraction patterns showed lines corresponding to germanium dioxide. At all the temperatures investigated a deposit of white and/or brown powder was found on the walls of the reaction tube, presumably as a result of the evaporation of germanium monoxide. The existence of a volatile oxide complicates the reaction kinetics, and as we shall see later the oxidation rate is frequently just equal to the rate of evaporation of GeO.

We have measured oxidation rates from 500° to 700°C on the (100), (110), and (111) faces as a function of oxygen pressure, and between 550° and 700°C these are practically identical with those obtained by Bernstein and Cubicciotti.[6]

II. EXPERIMENTAL

The two principal means of following oxidation rates are (i) pressure change in a closed system, and (ii) weight change of the sample as determined with a microbalance. We have used the former of these as any loss of germanium due to evaporation of GeO would make weight measurements very difficult to interpret. The desired crystal face was located in a single crystal by means of an x-ray goniometer, and after cutting, the surface was etched with a mixture of nitric and hydrofluoric acids. The use of an etched surface almost certainly means that the measured rates apply to a surface initially covered with at least a monolayer of oxygen.

III. Results

The measured rates of oxidation of the (110) face from 500°–700°C are shown in Figs. 1–5. At all temperatures above 500°C the measured rates were found to be identical for the three crystal faces studied. This is shown in Fig. 6 where the slopes of the rate curves at 550°C for the various faces are plotted as a function

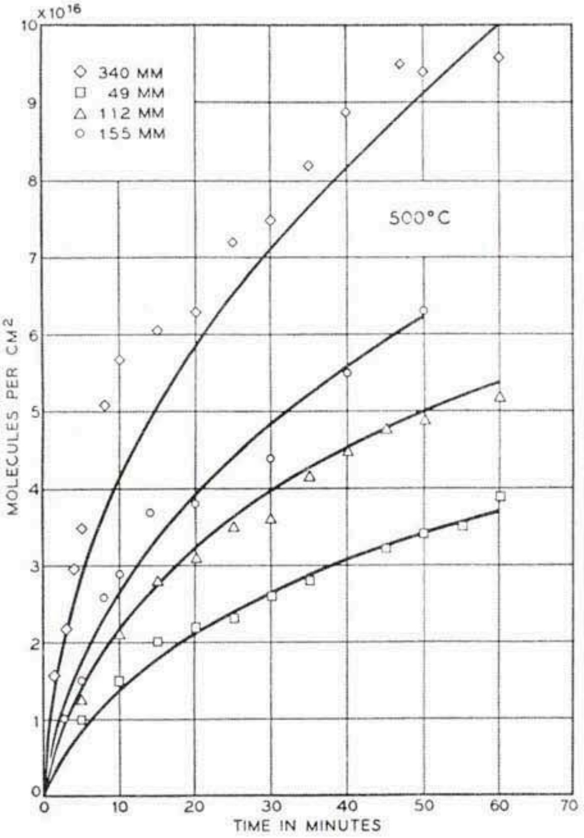


Fig. 1.—Oxidation rates of the (110) face at 500°C at various oxygen pressures. The curves were calculated using $N = 9 \times 10^{13} p^{\frac{1}{2}} t^{\frac{1}{2}}$.

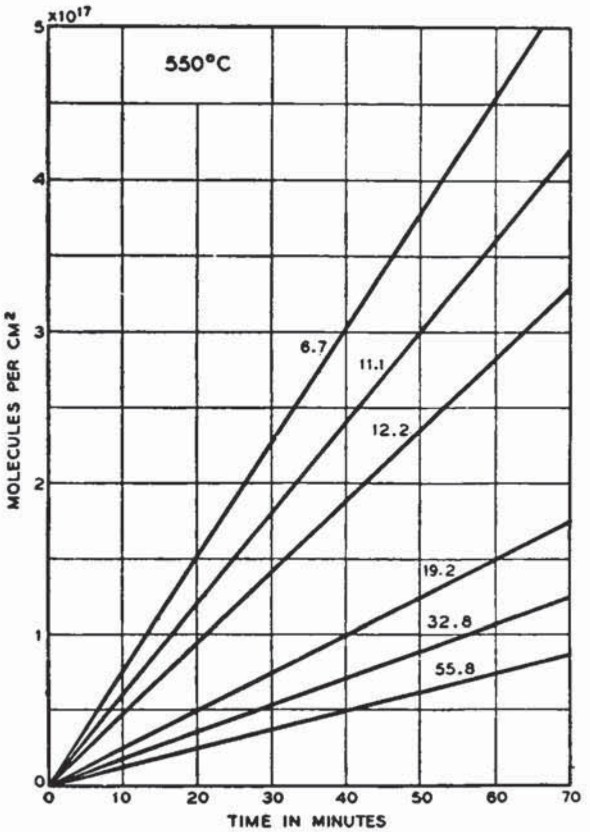


FIG. 2.—Oxidation rates at 550°C. The parameter is the total oxygen pressure.

of oxygen pressure. A single curve adequately describes the results. At 500°C oxidation only occurred on the (110) plane.

The most interesting feature of the results is the strong inverse dependence of oxidation rate on oxygen pressure at 550°C and above. For most metals, the oxidation rates at oxygen pressures above 1 mm are either independent of pressure or increase with increasing pressure. This effect was only found with germanium at 500°C as shown in Fig. 1. This was also the only temperature at which the oxidation rate was dependent on crystal orientation.

IV. DISCUSSION

We will first discuss the oxidation rates from 550°–700°C where no dependence on crystal orientation was found and the rates were inversely proportional to the oxygen pressure. The main difference between germanium and the metals whose oxidation rates have been measured lies in the existence of a volatile germanium monoxide. Although this material may be unstable in the solid form at all temperatures, there is strong evidence for its existence in the gas phase. Bues and v. Wartenberg [7] and Jolly

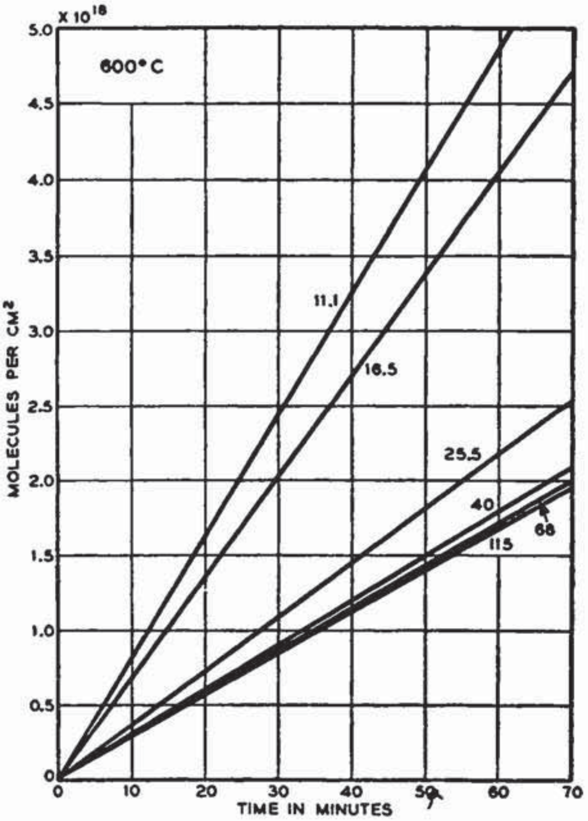


FIG. 3.—Oxidation rates at 600°C at various oxygen pressures.

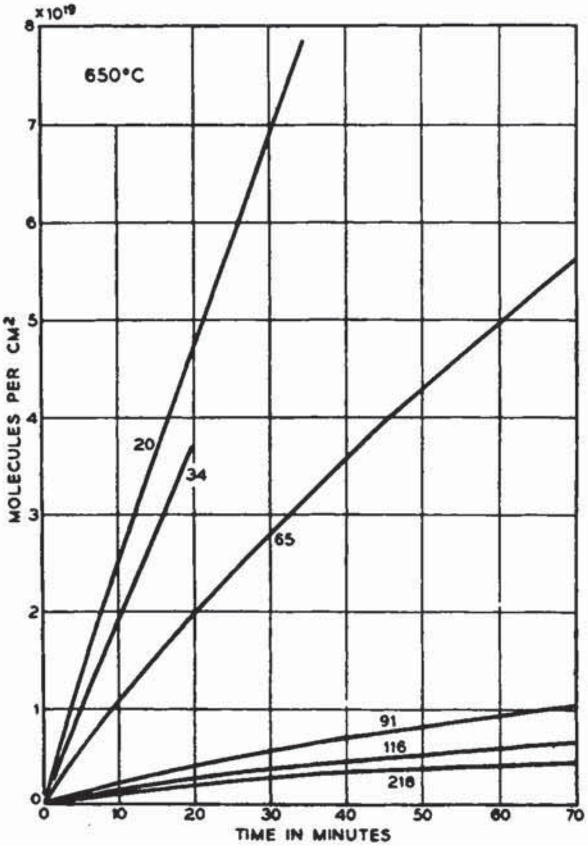


FIG. 4.—Oxidation rates at 650°C at various oxygen pressures.

and Latimer[8] have measured the vapor pressure of GeO over mixtures of Ge and GeO_2 corresponding to the reaction

$$\mathrm{Ge} + \mathrm{GeO_2} \rightleftharpoons 2\mathrm{GeO}_{(g)}.$$

From the vapor pressure data obtained by these workers we find that at temperatures above 550°C the vapor pressure of GeO is at least 10^{-3} mm of Hg, so that transport of this material through the gas phase could have a marked effect on the measured rates of oxidation.

To explain the observed oxidation rates let us consider five possible reactions:

$$Ge_l \rightarrow Ge^{\sigma} \tag{I}$$

$$Ge^{\sigma} + O_2 \rightarrow GeO_2^{\sigma} \tag{II}$$

$$Ge^{\sigma} + GeO_2^{\sigma} \rightarrow 2GeO^{\sigma} \tag{III}$$

$$GeO^{\sigma} \rightarrow GeO_{(g)} \tag{IV}$$

$$GeO_{(g)} + \tfrac{1}{2}O_2 \rightarrow GeO_{2_{(wall)}} \tag{V}$$

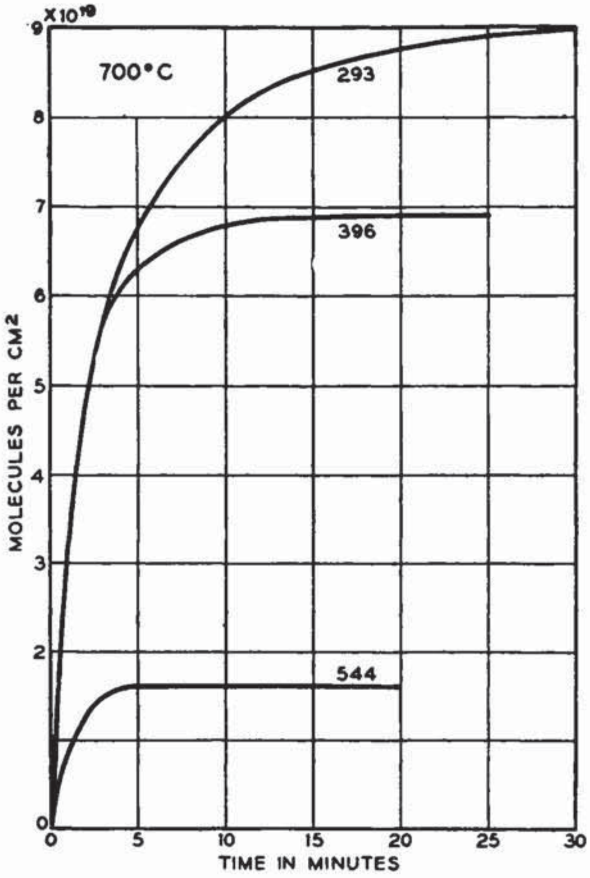


FIG. 5.—Oxidation rates at 700°C. The parameter is the total oxygen pressure.

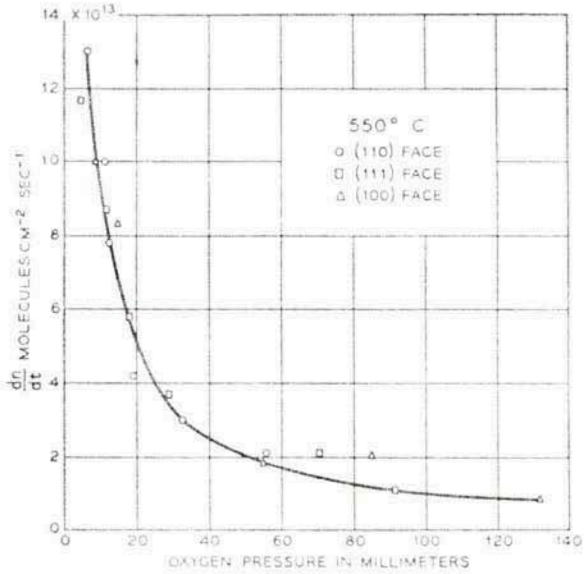


Fig. 6.—Oxidation rates at 550°C on the (110), (100), and (111) planes as a function of oxygen pressure.

where the superscript σ refers to material at the surface and the subscript i to material at the Ge-GeO$_2$ interface.

One could also include an equation for the formation of GeO$^\sigma$ from Ge$^\sigma$ and oxygen at the surface, but this only complicates matters without changing the form of the rate equation. Reaction (III) could also occur at the Ge-GeO$_2$ interface, but any GeO produced there would have to reach the solid-gas interface before it could evaporate and be detected by our measurements. As the diffusion of a GeO species through the GeO$_2$ layer is unlikely we have only considered (III) as a source of GeO at the solid-gas interface.

Let c_1 be the concentration of Ge$^\sigma$ in molecules cm^{-2} and c_2 be the concentration of GeO$^\sigma$ in molecules cm^{-2} and α be the number of molecular layers of GeO$_2^\sigma$. Then assuming that the rate of arrival of germanium at the surface is diffusion controlled,

$$dc_1/dt = K/\alpha - k_2c_1p^m - k_2c_1 \quad (1)$$

$$dc_2/dt = 2k_3c_1 - (\gamma/p)[f(c_2)] \quad (2)$$

The term $(\gamma/p)[f(c_2)]$ for the loss of GeO^g from the surface arises from the fact that this, too, is a diffusion process and $-(dc_2/dt) = D(dc/dx)$. The interdiffusion coefficient D for GeO diffusing through oxygen is inversely proportional to pressure, and we have included in γ the pressure independent part of D and the length of the concentration gradient along which diffusion occurs, hence $-(dc_2/dt) = (\gamma/p)[f(c_2)]$.

$$(d\alpha/dt) = k_2c_1p^m - k_3c_1. \tag{3}$$

The term p^m allows for any pressure dependence of reaction (II). We are also assuming that at the temperatures studied reaction (III) is well over the right-hand side, i.e., very little GeO^g dissociates to Ge^g and GeO_2^g. The only available data on the dissociation energy of GeO is from spectroscopic measurements. Drummond and Barrow [9] give a value of 7.0 ev or about 160Kcal mole^{-1}. From this we might expect that the assumption of little or no dissociation is reasonable.

From Eq. (1) at the steady state

$$K/\alpha = k_2c_1p^m + k_3c_1 \tag{4}$$

or

$$c_1 = K/[(k_2p^m + k_3)\alpha] \tag{5}$$

$$\therefore\ d\alpha/dt = \{K/[(k_2p^m + k_3)\alpha]\}(k_2p^m - k_3) \tag{6}$$

or, integrating from $t = 0$ where $\alpha = 0$,

$$\alpha^2 = 2K(k_2p^m - k_3)t/(k_2p^m + k_3) \tag{7}$$

and

$$c_1 = \left[\frac{K}{2[(k_2p^m)^2 - k_3^2]}\right]^{\frac{1}{2}} \frac{1}{t^{\frac{1}{2}}} \tag{8}$$

The amount of GeO_2^g formed (by reaction II) is given by

$$k_2c_1p^m = \left[\frac{K(k_2p^m)^2}{2[(k_2p^m)^2 - k_3^2]}\right]^{\frac{1}{2}} \frac{1}{t^{\frac{1}{2}}} \tag{9}$$

or the rate of oxygen removal by the formation of GeO_2^g is given by

$$-\frac{dn_1}{dt} = \left[\frac{K(k_2p^m)^2}{2[(k_2p^m)^2 - k_3^2]}\right]^{\frac{1}{2}} \frac{1}{t^{\frac{1}{2}}} \tag{10}$$

The rate of removal of oxygen molecules from the gas phase will be given by two terms,

$$-\frac{dn}{dt} = \frac{d[GeO_2^g]}{dt} + \frac{1}{2}\frac{dc_2}{dt}, \tag{11}$$

the second of which accounts for oxygen removal via reaction (V). It is assumed that the rate of this reaction is governed by the rate of arrival of $GeO_{(g)}$, and since two molecules of GeO are required for the removal of one oxygen molecule the rate is given by $\frac{1}{2}(dc_2/dt)$. GeO^{σ} evaporates at a rate

$$-\,dc_2/dt = \gamma'/p \quad \text{where } \gamma' = \gamma[f(c_2)] \tag{12}$$

or taking into account the limit for vacuum evaporation

$$-\,dc_2/dt = \gamma'/(\beta p + 1). \tag{13}$$

Equations (12) and (13) assume the evaporation process is diffusion controlled. The inverse dependence on pressure arises from the variation of the diffusion constant D with pressure. We have also assumed that the equilibrium vapor pressure of GeO is always attained at the surface, so that the evaporation rate is independent of c_2. If this assumption is not made the final equation gives a rate that is independent of oxygen pressure, for as the pressure is increased γ decreases but $f(c_2)$ increases and the product is nearly constant.

Adding the two terms for removal of oxygen from the gas phase we get

$$-\frac{dn}{dt} = \left[\frac{K(k_2p^{\mathrm{m}})^2}{2[(k_2p^{\mathrm{m}})^2 - k_3^2]}\right]^{\frac{1}{2}} \frac{1}{t^{\frac{1}{2}}} + \frac{\gamma''}{\beta p + 1} \tag{14}$$

where $\gamma'' = \gamma'/2$ (because two molecules of GeO are oxidized by one molecule of oxygen).

Let

$$\left[\frac{K(k_2p^{\mathrm{m}})^2}{2[(k_2p^{\mathrm{m}})^2 - k_3^2]}\right]^{\frac{1}{2}} = B. \tag{15}$$

Then

$$\Delta n = 2Bt^{\frac{1}{2}} + \frac{\gamma'' t}{\beta p + 1}\cdot \tag{16}$$

The assumption that the rate of evaporation of GeO^{σ} is independent of the concentration will obviously break down when c_2 becomes very small, since it must go to zero when $c_2 = 0$. We can take account of this by including an extra factor for the variation of the second term in Eq. (16) with c_2 when c_2 is very small. Let c_2' be the value of c_2 below which the equilibrium vapor pressure is no longer maintained. Then we write

$$\Delta n = 2Bt^{\frac{1}{2}} + \gamma''(1 - \mathrm{e}^{-c_2/c_2'})t/(\beta p + 1) \tag{17}$$

Then when $c_2 \gg c_2'$ the term in the final brackets equals unity and the vapor pressure is constant, below this value of c_2 the term decreases to zero with c_2.

This equation has the correct form to explain the experimental results. If the second term predominates with $c_2 \gg c_2'$ a linear rate is obtained. If the first term is important a parabolic or sum of parabolic and linear rates is obtained. With very thick GeO_2^g films both terms will approach zero and a protective film will be formed. In Eq. (17) the first parabolic term describes the formation of an oxide film on the surface while the second refers to the oxidation of GeO which has evaporated to the walls of the apparatus.

It now remains to fit this equation to the experimental data and see if the values of the constants required are reasonable.

The values of the constants in the term for evaporation can be calculated. Following the treatment of Fuchs[10] let us suppose that the concentration of vapor at a distance Δ from the surface is c^*, and that the equilibrium concentration at the surface is c_0 molecules cm^{-3}.

If the accommodation coefficient is λ, i.e., a fraction λ of the molecules which hit the surface condense, then the rate of evaporation into a vacuum is $\Gamma\lambda c_0$ molecules cm^{-2} sec^{-1}, where $\Gamma = (kT/2\pi M)^{\frac{1}{2}}$, k is Boltzmann's constant, and M the mass of the evaporating GeO molecule. Hence the rate at which molecules arrive at the plane, a distance Δ from the surface is $\Gamma\lambda(c_0 - c^*)$. This may be equated to the rate at which molecules leave by diffusion,

$$\Gamma\lambda(c_0 - c^*) = -D(\partial c^*/\partial x). \tag{18}$$

Assume a linear concentration gradient

$$c = Ux + W. \tag{19}$$

At the wall a distance L from the surface, $c = 0$. Therefore

$$UL + W = 0. \tag{20}$$

Then

$$\lambda(c_0 - c^*) = -DU/\Gamma. \tag{21}$$

Assume that the accommodation coefficient is unity and substitute for c^*

$$c_0 = U[(\Delta - L) - D/\Gamma]. \tag{22}$$

The rate of evaporation is equal to $-DU$ so on substituting for U we get

$$-\frac{dc_2}{dt} = \frac{-Dc_0}{\Delta - L - D/\Gamma} = \frac{Dc_0}{L - \Delta + D/\Gamma}. \tag{23}$$

Let

$$D = D_0 \times 760/p$$

Then

$$-dc_2/dt = \frac{c_0}{(L-\Delta)p/760D_0 + 1/\Gamma} = \frac{c_0\Gamma}{\Gamma Lp/760D_0 + 1} \tag{24}$$

assuming that Δ, the mean free path of the molecule, is small compared to the distance to the wall at all the pressures investigated. As $p \geq 5$ mm of Hg this is a good approximation. Hence, comparing coefficients of Eq. (13) and Eq. (24)

$$\gamma' = c_0\Gamma \tag{25}$$

and

$$\beta = \frac{\Gamma L}{760D_0}. \tag{26}$$

All the quantities in Eq. (24) can be calculated or estimated, so that the rates of evaporation of GeO^{σ} may be obtained and therefore the rates of uptake of oxygen due to its subsequent oxidation.

No data is available in the literature for the diffusion constant of GeO in oxygen. It is, however, approximately true that $D = K/M^{\frac{1}{2}}$, where M is the mass of the diffusing species. Using data for the diffusion of H_2, CO_2, and O_2 in oxygen K was found to be unity, and D for GeO equal to 0.106 at 273°K and 760 mm. On the basis of a simple theory D should vary as $T^{\frac{3}{2}}$, but Lonius[11] has found that the exponent is nearer 1.75. Using $D = D_0(T/273)^{1.75}(760/p)$ the values of D at 760 mm and various temperatures have been calculated and listed in Table I. The average velocity (Γ) of GeO molecules leaving the surface was obtained from $\Gamma = (kT/2\pi M)^{\frac{1}{2}}$ and the product $c_0\Gamma$ from

$$c_0\Gamma = 3.95 \times 10^{20} P_{\mathrm{mm}}(M/T)^{\frac{1}{2}} \text{ molecules cm}^{-2}\text{ sec}^{-1} \tag{27}$$

where P_{mm} is the vapor pressure of GeO.

The value of the vapor pressure of GeO over a mixture of GeO_2 and Ge is not well established. Data have been obtained by Bues and Wartenburg[7] and by Jolly and Latimer.[8] The values obtained by Jolly and Latimer have been used in the present calculations. The inaccuracies in the vapor pressure data will make the calculated values of the oxidation rate equally uncertain but should at least give values correct within an order of magnitude. In the derivation of Eq. (24), the accommodation coefficient λ was assumed to be unity. If we include it in the final equation we get

$$-dc_2/dt = \frac{\lambda c_0 \Gamma}{\lambda \Gamma L p/D_0 + 1}. \tag{28}$$

In general λ will be less than unity and probably between 1 and 10^{-3}.

From the values listed in Table I it is possible to calculate dc_2/dt from 773° to 973°K and at any pressure. From these results

TABLE I

CALCULATED QUANTITIES FOR THE DIFFUSION OF GeO THROUGH OXYGEN

TEMP. °K	P_{mm}	Γ	$c_0\Gamma$	ΓL	D
773	4.0×10^{-4}	1.08×10^4	5.3×10^{16}	5.4×10^3	.68
823	3.2×10^{-3}	1.12×10^4	4.1×10^{17}	5.6×10^3	.76
873	2.0×10^{-2}	1.15×10^4	2.5×10^{18}	5.75×10^3	.84
923	1.3×10^{-1}	1.18×10^4	1.6×10^{19}	5.9×10^3	.92
973	6.3×10^{-1}	1.22×10^4	7.5×10^{19}	6.1×10^3	1.01

the second term in Eq. (11) can be evaluated and hence the linear parts of the rate curves predicted. Unfortunately it is impossible to carry out an independent calculation of the first term which includes several rate constants. The best that we can do is to calculate it at a given pressure and use this value to fit data obtained at the same temperature but different pressures.

The oxidation rates at 550° and 600°C are shown in Figs. 2 and 3 as linear curves. However, at very short time intervals ($\leqslant 3$ minutes) they were practically parabolic. Because of the difficulty of obtaining accurate data at the beginning of the run only the linear portions were plotted, by moving the zero of time to +3 minutes. We believe that this initial region describes the growth of an oxide film. This film grows until its growth rate is just equal to the rate of evaporation of GeO. It then remains at a constant thickness and the oxidation curve becomes linear with respect to time.

The above theory predicts that the linear part of the rate curves describes the diffusion of GeO through the oxygen atmosphere. In Table II the experimental and calculated (from Eqs. (11) and (28)) values of dn/dt in molecules cm^{-2} sec^{-1} at 550° and 600°C are given as a function of oxygen pressure. The calculated values are all higher than the experimental ones although the agreement is satisfactory. The difference could be due either to inaccurate vapor pressure data for GeO or the use of unity for the accommodation coefficient, λ. In general λ will be less than one and therefore reduce the calculated value of dn/dt.

TABLE II

CALCULATED AND EXPERIMENTAL VALUES OF dn/dt IN MOLECULES $CM^{-2}SEC^{-1}$

OXYGEN PRESSURE	dn/dt (CALCULATED)	dn/dt (EXPERIMENTAL)
	$T = 550°C$	
6.7	2.6×10^{15}	1.3×10^{14}
11.1	1.7×10^{15}	1.0×10^{14}
12.2	1.6×10^{15}	7.8×10^{13}
19.2	1.0×10^{15}	4.2×10^{13}
32.8	6.0×10^{14}	3.0×10^{13}
55.8	3.6×10^{14}	2.1×10^{13}
	$T = 600°C$	
11.1	1.2×10^{16}	1.3×10^{15}
16.6	8.4×10^{15}	1.1×10^{15}
40.0	5.5×10^{15}	6.1×10^{14}
68.0	2.0×10^{15}	4.9×10^{14}
115.0	1.2×10^{15}	4.7×10^{14}

To check the validity of the hypothesis that diffusion of GeO away from the surface is the rate determining step, a run was carried out using a low partial pressure of oxygen in an O_2-N_2 mixture. The value of dn/dt obtained was practically identical with that found at the same total pressure when oxygen alone was present.

At temperatures above 600°C no comparison of theory and experiment is possible as the oxidation curves are no longer linear. That evaporation of GeO is still important is shown by the inverse dependence of rate on oxygen pressure, but this process is reduced and finally (at 700°C) prevented by the growth of a protective film of GeO_2. Once a stable GeO_2 film has been formed at 700°C no further oxidation is observed even if the oxygen pressure is lowered. The difference between the uptakes at the various pressures is due to the amount of GeO that can evaporate before a complete GeO_2 film is formed. This will obviously be greater at the low pressures.

In view of the recent interest in "clean" germanium surfaces it may be worthwhile to speculate about the vacuum rate of evaporation of GeO above room temperature. There is some evidence [12] that a germanium surface that has been cleaned by ion bombardment, annealed, and subsequently exposed to oxygen can be restored to its "clean" condition merely by heating to about 400°C. Indeed some reversal of electrical properties has been observed at temperatures as low as 200°C.

Assuming that $\log p$ against $1/T$ is linear from the measured range to room temperature, values of the vapor pressure of GeO have been obtained, and from these (by Eq. (27)) vacuum evaporation rates. These are plotted in Fig. 7 as the number of monolayers evaporating per minute, as a function of temperature. From the present oxidation results we may expect that these numbers are about one order of magnitude too high, but they at least show the minimum temperature (~400°C) at which GeO evaporation need be considered as an oxygen removing mechanism.

V. EFFECT OF CRYSTAL ORIENTATION ON OXIDATION RATE

As mentioned earlier, we have carried out oxidation measurements on the (100), (111), and (110) faces from 500°–700°C. At 550°C and higher temperatures no dependence of rate on crystal orientation was found. This is to be expected if the oxidation process is indeed diffusion controlled. The slopes of the rate curves at 550°C for the three faces are shown in Fig. 6 as a function of oxygen pressure. A single curve describes all the results.

At 500°C no removal of oxygen from the gas phase by the (100) and (111) faces could be detected over a period of two hours at oxygen pressures between 50 and 700 mm. This was in contrast to the (110) face where appreciable oxidation occurred, as shown in Fig. 1. The curves were obtained from the relationship $\Delta n = 9 \times 10^{13} p^{\frac{1}{3}} t^{\frac{1}{3}}$ and satisfactorily describe the experimental data. At this temperature the results show that diffusion through

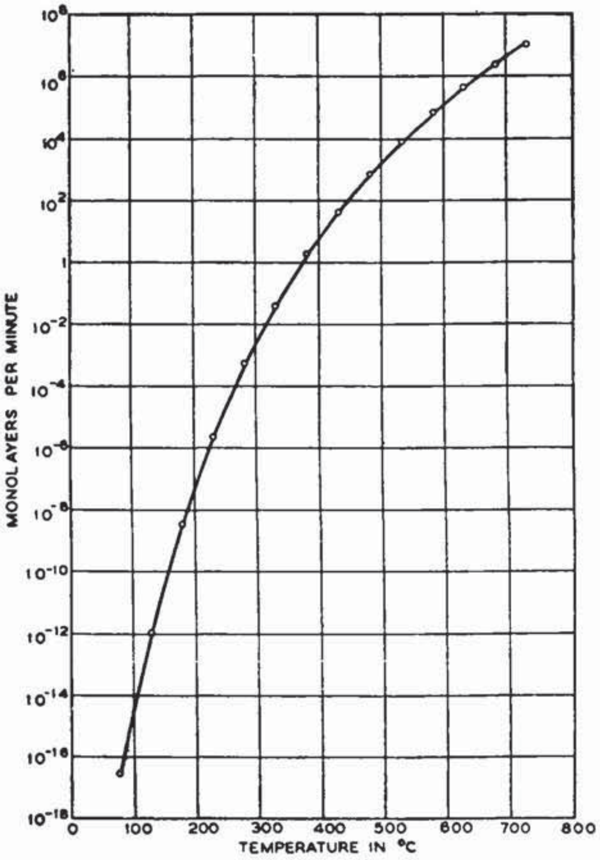
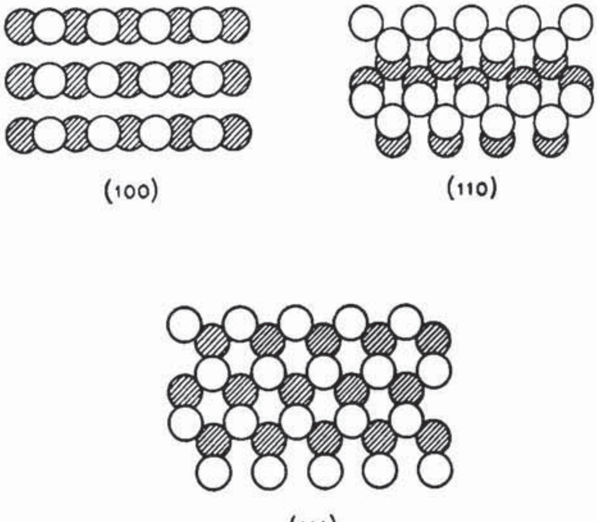


FIG. 7.—The rate of evaporation of GeO (in monolayers $\min^{-1}$) as a function of temperature.

the gas phase is unimportant, so the rate determining step must be either the removal of a germanium ion from the lattice or its transport across the oxide film. For any difference between crystal faces to be important, the former of these must be operative. In Fig. 8 the arrangement of germanium atoms on the (100), (111), and (110) faces is shown. On the (100) face each surface atom is bonded to two atoms in the layer below while on the (111) face each surface atom is bound to three in the next lowest layer. These numbers remain constant even when the surface layer



(100)

(110)

(111)

FIG. 8.—Orientation of the surface atoms on the (100), (110), and (111) planes.

is partially depleted. On the (110) face, however, each surface atom is bound to two neighboring surface atoms but to only one atom in the underlying layer. Thus if one atom is removed from the surface the bonding of the two neighboring atoms is weakened, and one can get progressive removal along the chain. From the crystal structure therefore it does not seem unreasonable that the (110) plane is more reactive than either the (100) or the (111). Further measurements at temperatures below 500°C are needed for confirmation.

VI. CONCLUSIONS

Our knowledge of the oxidation process can be summarized as follows:

At and above 550°C the oxidation process is controlled by the diffusion of GeO away from the surface, and no effect of crystalline orientation is found.

Between room temperature and 550°C little data is available, but our results suggest that in this region the (110) plane oxidizes more readily than either the (100) or the (111) and that the rate of oxidation is controlled by either the removal of a germanium ion from the lattice and/or its transport across the oxide film.

At room temperature the only data is that of Green and Kafalas[3] on a cleaved surface which should consist mainly of the (111) cleavage plane. At this temperature where adsorption is important a difference due to the different packing of the various planes should be found. For example the number of surface atoms for the various planes are: (100), 6.3×10^{14}; (110), 9.0×10^{14}; and (111), $7.2 \times 10^{14}\ \text{cm}^{-2}$.

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SHORT CONTRIBUTION: VACUUM MICROBALANCE STUDIES ON SINGLE CRYSTAL GERMANIUM *

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The following is a preliminary report on studies made with a quartz microbalance similar in design to those used by Rhodin and Gulbransen.[1] The sensitivity of the balance was 0.1 to 0.2 μg. Buoyancy effects were less than the sensitivity at all pressures used. The balance was enclosed in a mercury pump vacuum system that was capable of pressures of 10^{-9} to 10^{-10} mm. The samples could be heated to 900°C with an external heater that necessarily heated the quartz tube surrounding the sample. Because of the delicacy of the balance, high currents could not be passed through the samples for Joule heating. Provisions were made for argon bombardment.[2] See Fig. 1 for more details.

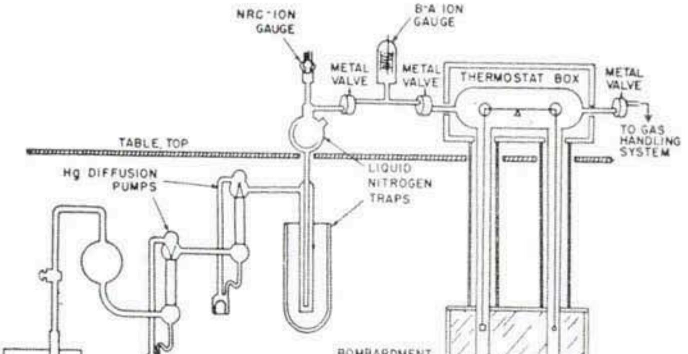

FIG. 1.—Vacuum microbalance system.

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The samples studied were oriented germanium wafers. The specimens were lapped, and about 0.004″ was removed from each face by etching with CP-4 leaving a wafer 0.003″ to 0.005″ thick. The geometric area of the samples was 10 to 15 cm². This was 10 to 100 times the area of a counter-balancing sphere.

In general, the vacuum system was baked out at 200° to 250°C for 12 to 36 hours. The tubes enclosing the samples were baked out at 300° to 400°C for a like period.

A complete study of adsorption and oxidation on germanium single crystals was contemplated. The many complications that arose are pertinent to the discussion of surface treatments.

A very large rise in pressure (to 10^{-5} mm) was observed on heating a previously unheated sample to 250° to 500°C. This pressure rise was accompanied by a corresponding weight loss that was nearly complete after several hours at 400°C. For one sample that weighed 0.2962 grams and had a geometric area of 10.6 cm², a loss of 4.3 μg was observed. It would be difficult to account for this loss in terms of any reaction involving germanium oxides since their vapor pressures are low at this temperature. Mass spectrographic experiments carried out by Robinson et al.[3] of Lincoln Laboratory and by S. Wolsky and H. Papazian [4] of this laboratory indicate that relatively large amounts of CO and other gases are evolved from the bulk of the germanium on heating. Robinson et al. report a gas mixture consisting largely of CO (50 ppm) and small amounts of CO_2, N_2, and H_2 evolved from samples crushed in vacuum. Wolsky and Papazian similarly observed CO, CO_2, H_2, H_2O, and N_2. No O_2 was observed by either group. If the 4.3 μg evolved from the sample discussed above were entirely CO, the bulk concentration would be 10^{18} molecules/cc or 38 ppm.

In addition to the gas evolution at medium temperatures (200° to 450°C), a large continuing weight loss was observed in the 750° to 800°C range. A sample that was heated at 500°C for 17 hours at 10^{-6} mm lost 4.4 μg, and the weight had reached an approximately constant value. As the temperature was increased to 750°C, the pressure in the system rose. An increased rate of weight loss that was constant for several hours was observed. At 750°C, the rate of weight loss was 0.5 μg/min., or about one atomic layer of Ge/min.; at 800°C, the rate was 2.0 μg/min. Approximately these same values were observed on other samples.

The rate did not seem to be affected by initial pressure or bakeout history of the sample. In a system that had been initially at a pressure of 5×10^{-9} mm, the pressure rose to 10^{-5} to 10^{-6} mm when the sample was at 800°C. In cases where no sample was in the system, this rise was of short duration and it was possible to obtain pressures of $\sim 10^{-8}$ mm at high temperatures. When the sample was in the system, the high pressures remained over several hours. A metallic deposit was observed on the quartz. No brown deposit indicating germanium monoxide was observed in any experiment. Pitting due to thermal etching of the germanium was observed on occasions.

The above observations cannot be explained in terms of loss of impurities, adsorbed gases, or dissolved gases. They seem to indicate the removal of germanium from the surface. The mechanism of weight loss is not known. Dushman[5] states that the vapor pressure of germanium is 10^{-6} mm at 897°C, but because of an error of approximately 20°C in the melting point, this figure is in doubt. There is a possibility that oxygen or water vapor, which might have come from or through the quartz surrounding the sample, reacts with the germanium to produce a volatile oxide. One might expect a brown deposit in this case, and as stated none was observed. Law[6] and Cubicciotti and Bernstein[7] state that above 700°C a protective layer of GeO_2 is formed that prevents the formation of volatile GeO. (Their experiments were carried out in a pressure range above 1 cm. The pressure in our system was usually 10^{-5} to 10^{-9} mm.) Our observations were that the weight loss rate increased by a factor of about four as the temperature increased from 750° to 800°C. Although the weight loss mechanism is still in doubt, one should probably avoid heating the quartz envelope, if possible, in preparing clean surfaces.

The following observations were made on a sample subjected to the argon bombardment treatment developed by Farnsworth, et al.[2] The sample studied had (100) orientation of the faces, weighed 0.2426 gram, and had a geometric area of 10.3 cm^2. After a 24-hour bakeout of the system, a pressure of 5×10^{-9} was obtained. The sample was prebaked at 750°C for 3 hours. Argon bombardment was carried out at 10^{-4} mm of argon. An 80 μa ion current at 600 volts was used for 6 minutes. A subsequent 400° to 450°C bakeout for $\frac{3}{4}$ of an hour was performed. An initial pressure rise on this bakeout was observed. A total weight loss of

5μg or about 5 argon atoms/surface atom (using the geometric area) or 10^{18} argon atoms/cc occurred. In another case, a sample that weighed 0.1976 gram and had a geometric area of 10.8 cm^2 was prebaked at 700°C for 1 hour. An ion current of 40 μa was maintained for 21 minutes. A weight loss of greater than 100 μg was obtained during the bombardment. On bakeout at 200°C a loss of 11.5 μg was measured. Further heating at 400° to 450°C for 35 minutes resulted in a loss of an additional 0.9 μg. Even after 1 hour the sample was losing weight slowly.

These considerations demonstrate the difficulties in interpreting adsorption and oxidation of samples treated as above. Room temperature oxidation kinetics at 3 mm oxygen were observed on samples prepared both by argon bombardment and by high temperature heating. Little qualitative difference was observed in the adsorption of oxygen for the two surface treatments. In general, a rapid uptake of oxygen was observed in the first minutes. This was followed by a period of more than a thousand minutes, and in one case, 8 days during which no measurable weight change occurred. This result is similar to those of Green and Kafalas,[8] but since no careful BET measurements have accompanied each oxidation, direct comparison cannot yet be made. In the case of the oxidation of an argon bombarded sample demonstrated by the curve of Fig. 2, an improved estimate of the area has been made by counting the etch pits. On the flat

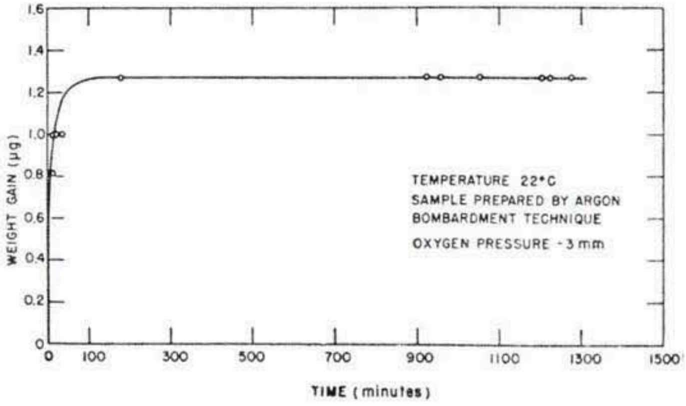

FIG. 2.—Oxidation of germanium.

portion of the curve, the weight increase was 1.27 μg. Using the adjusted area a calculation shows that the sample adsorbed 1.6×10^{15} atoms/cm^2. Green and Kafalas found 1.3×10^{15} atoms/cm^2 for the same time on crushed samples. Obviously, this calculation does not prove that the surfaces are identical in the argon bombarded and cleaned cases. A more careful study may clarify this point.

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