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Gallium Arsenide Electrode Behavior

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ABSTRACT

The anodic dissolution reaction of GaAs was found to proceed quantitatively in well-stirred solutions of KOH and $HClO_4$ with the formation of soluble, tripositive Ga and As compounds. Disintegration of the anode was noted under natural convection. Passivity ensued at high anodic currents in $HClO_4$ electrolyte, with an abrupt active-passive transition and a gradual passive-transpassive transition. In H_2SO_4 electrolyte, the passive region extended to the highest attainable anodic potentials. No substantial differences in electrochemical behavior were found between Ga(111) and As($\bar{1}\bar{1}\bar{1}$) surface orientations. The influence of the semiconductor properties of p-type GaAs on the cathodic polarization was confined to low current densities. Galvanostatic anodic-cathodic cycling revealed significant details of the photopotentials and eliminated the hysteresis in the cathodic polarization curves.

It was anticipated that, following the diversion of much research emphasis in semiconductor physics from germanium and silicon to compound semiconductors, workers in the field of semiconductor electrochemistry would also turn to the latter materials. It happens, however, that germanium and, to a lesser extent, silicon possess physical and chemical properties which are peculiarly favorable for revealing effects of bulk semiconductor properties on electrode behavior. For this and other reasons, the literature, at the beginning of the present investigation, contained a bare handful of papers on gallium arsenide electrochemistry—so fundamental a characteristic as the stoichiometry of the anodic dissolution reaction had not been established.

Williams (1) had concluded from his study of photovoltaic effects at binary-semiconductor/electrolyte interfaces that GaAs behaves as an inert electrode capable of exchanging electrons with a redox couple in the solution. This conclusion was based on observations that the electrode potential of n-type GaAs *vs.* saturated calomel varied in the same direction as the oxidation potential of the redox couple, and became strongly more negative on illumination. Subsequently, Haisty (2) experimented with photoetching and gold chemiplating of GaAs. Plating was observed at the nonilluminated and etching at the illuminated region on n-type material. The reverse occurred for p-type material when the photovoltage had the opposite sign. The results obtained by the two investigators are consistent except for the matter of inertness. Haisty noted that in fairly concentrated acid or base the anodic oxidation products were soluble, but in other electrolytes a film was formed.

A study of electrolytic polarization and photopotentials for both n- and p-type GaAs was carried out by Pleskov (3), who reported that the limiting anodic current for n-type is proportional to the incident light intensity at low values of the latter. Breakdown was observed to occur at a critical potential which varied in an inverse manner with the bulk electron concentration. The occurrence of avalanche breakdown and the low magnitude of calculated hole diffusion currents as compared to observed anodic currents, together with imperfect saturation of the latter led the author to conclude that holes are supplied mainly by space charge generation. Influences of semiconductor properties on cathodic polarization behavior were not as pronounced as the chemical effects responsible for hysteresis in the recorded curves.

In a meeting presentation, Greenberg and Sanders (4) reported measurements of current multiplication at n-type GaAs electrodes. They obtained sharp saturation of the anodic current and, for the ratio of limiting anodic current to absorbed light intensity, the values 2.1 and 1.5 in 1.0*N* HCl and 1.0*N* KOH, respectively. Anodic current resulted in dissolution of the crystals, whose surfaces acquired "unstable brown films."

Such was the state of knowledge of the GaAs/electrolyte interface. The observed similarities and differences with respect to germanium and silicon electrodes

were generally in accord with what was known or anticipated concerning the electronic and chemical properties of GaAs. Recently, three rather more extensive studies of GaAs electrochemistry have been published. Included are the measurements of differential capacitance and cathodic reduction of surface oxides by Birintseva and Pleskov (5), the determination of the hole participation factor and the current efficiency of anodic dissolution by Efimov and Erusalimchik (6), and the investigation of the anodic dissolution mechanism for (111)- and $(\bar{1}\bar{1}\bar{1})$-oriented surfaces by Gerischer (7). Certain findings of the present research are in disagreement with earlier reported results; these and some previously unexplored electrochemical features will be elaborated on.

Stoichiometry of the Electrode Reactions

One bit of information presently unavailable, yet essential for the calculation of standard potentials of possible electrode reactions, is the standard free enthalpy of formation ΔG°_{298} of gallium arsenide. Thermochemical data (8) for several related compounds are presented in Table I, which also lists electronegativities from Pauling (9) and from a more recent compilation (10) [two and three significant figures, respectively]. No correlation is evident between the standard enthalpies of formation of the compounds GaSb, InAs, and InSb and differences in electronegativities of the constituent elements. As a rough approximation, the unknown ΔH°_{298} for GaAs was taken to be the same as that of InSb (−3.5 kcal/mole).

When this assumed value is combined with the standard entropy of formation from Table I, the quantity −3.1 kcal/mole is obtained for ΔG°_{298} of GaAs. The absolute error cannot be so great as to alter the conclusions to be drawn from Table II; namely, that the 6-electron anodic reactions are favored over the corresponding 8-electron reactions in both acid and alkaline solution and that cathodic hydrogen evolution is much more probable than arsine formation.

Experimental

Gallium arsenide electrodes were fashioned in the form of (111)-oriented disks, 4-mm or 8-mm diameter, and of the order of 1-mm thick. The (111), "A" or gallium faces were distinguished from the $(\bar{1}\bar{1}\bar{1})$, "B" or arsenic faces by etching the initially abraded surfaces in $1HF:1H_2O_2:1H_2O$. The identification of polarity according to the chemical etch patterns was confirmed for one pair of surfaces by means of anomalous x-ray dispersion. The crystals from which electrodes were cut had the following characteristics

n-type (undoped)	0.85 ohm-cm, 2.0 x 10^{15} carriers/cm^3, mobility 3700 cm^2/v-sec
p-type (Zn-doped)	0.012 ohm-cm, 4.2 x 10^{18} carriers/cm^3, mobility 125 cm^2/v-sec

Table I. Electronegativities and thermochemical data

	IIIA	VA	III-V	$-\Delta H^\circ_{298}$
	Ga	As	GaSb	5.0 ± 0.2 kcal
Pauling	1.6	2.0	InAs	7.4 ± 0.6 kcal
Gray	1.81	2.18	InSb	3.5 ± 0.1 kcal
	In	Sb		
Pauling	1.7	1.9		
Gray	1.78	2.05	GaAs: $\Delta S^\circ_{298} = -1.4$ cal/deg	

Table II. Standard potentials for some GaAs electrode reactions

	ΔG°, kcal	E°, v
$GaAs + 2H_2O = Ga^{+3} + HAsO_2(aq) + 3H^+ + 6e^-$	−16.5	+0.11
$GaAs + 4H_2O = Ga^{+3} + H_3AsO_4(aq) + 5H^+ + 8e^-$	+9.8	−0.05
$GaAs + 8OH^- = H_2GaO_3^- + AsO_3^- + 3H_2O + 6e^-$	−128.0	+0.92
$GaAs + 12OH^- = H_2GaO_3^- + AsO_4^{-3} + 5H_2O + 8e^-$	−159.3	+0.86
$GaAs + 3H^+ + 3e^- = Ga + AsH_3(g)$	+47.0	−0.69
$GaAs + 3H_2O + 3e^- = Ga + AsH_3(g) + 3OH^-$	+102.8	−1.47

The provision of suitably low resistance electrical contacts proved an important consideration, particularly for n-type electrodes. A satisfactory procedure consisted of sputtering gold onto a clean, freshly abraded surface and then effecting some penetration of the gold into the GaAs surface layer by heating in a reducing atmosphere (H_2/N_2 mixture) for ½ hr at 300°C. For the majority of experiments a bead of indium was alloyed to the gold layer, thus permitting a reliable pressure contact to be made. Where accurate electrode weight changes were required, "precipitated silver metal" was compacted between the sputtered gold layer and a metal rod.

Current-voltage characteristics of pairs of contacts affixed to opposite faces of the same specimen were measured. Electrical contacts were considered satisfactory when the combined resistance of contacts plus electrode was constant and not significantly greater than the resistance of electrode alone (as calculated from the bulk resistivity) over the current range of interest. Thereupon the superfluous contact was removed. Of the previously cited publications dealing with aspects of GaAs electrode behavior, only that of Pleskov (3) makes specific note of concern with and the means employed for circumventing rectification and high resistance at the metal-GaAs contacts.

Electrodes were cemented with Apiezon W black wax into a circular recess at the end of a glass capillary tube. The wax and projecting edge of the GaAs disk were then coated with commercial purified paraffin, excluding all but the desired face from contact with the electrolyte. It was thus possible to make advantageous use both of the adhesiveness of the black wax and the chemical inertness of the paraffin. The surface was most often wet-abraded (3000-mesh garnet) before mounting as indicated and subsequently was generally chemically polished (10 v/o Br_2 in methanol) before insertion in the electrochemical cell.

A Pyrex cell was employed which could accommodate up to three working electrodes, symmetrically situated with respect to a pivotal Luggin capillary. The counter electrode compartment was separated from the main body of the cell by a glass frit. A stream of purified, deoxygenated nitrogen served to purge both the cell volume and the electrolyte in a connected solution reservoir. Reagent grade salts and perchloric acid were used without purification; sulfuric acid and alkaline solutions were made up from Acculute volumetric standards. The distilled water used had room temperature resistivity in excess of 10^{-6} ohm-cm and was obtained from an all-Pyrex still fed with demineralized and Millipore-filtered water. The cell temperature was 25°C throughout and, unless otherwise noted, experiments were carried out in room light and with magnetic stirring of the electrolyte.

Results and Discussion

Over-all electrode reactions.—In agreement with the observations of other investigators, n-type GaAs electrodes were found to exhibit a large, negative photovoltage on open circuit; p-type electrodes showed a smaller, positive photovoltage in the solutions studied. Furthermore, the limiting anodic current for n-type was both very small in the dark and extremely sensitive to light. Gas was evolved at appreciable current densities during cathodic but not anodic polarization; the steady-state anodic reaction was always GaAs dissolution. In a number of cases a loosely adherent brown coating formed on the anode; this substance was isolated and found by x-ray diffraction to be gallium arsenide rather than some oxidation product. [Greenberg and Sanders (4) and Gerischer (7) reported a dark coating, whose identity was correctly established by the latter.]

The indicated disintegration or undermining of the anode could be eliminated by effecting vigorous mass-transport conditions at the interface. Table III summarizes coulometric measurements carried out on ini-

Table III. Coulometry of the anodic dissolution reaction for p-GaAs, 20 ma/cm²

Expt. No.	Surface	Disk diameter, mm	Electrolyte	Electron number
1	A(111)	4	0.5*N* KOH	5.88_0
2	A(111)	8	0.5*N* KOH	5.92_6
3	B($\bar{1}\bar{1}\bar{1}$)	8	0.5*N* KOH	5.99_2
4	B($\bar{1}\bar{1}\bar{1}$)	8	1.0*N* $HClO_4$	5.99_8
5	A(111)	8	1.0*N* $HClO_4$	6.10_0

tially abraded p-type anodes at 20 ma/cm² and 25°C, with magnetic stirring of the electrolyte. Anode weight losses were determined directly. In general, as techniques were refined the electron number more closely approached the value 6; the single instance of an apparent electron number in excess of 6 appeared to be due to severe attack of the rim of the GaAs disk, leading to possible exposure of the edge of the gold film to the electrolyte.

Following anodic dissolution, a positive test was obtained for arsenite in the electrolyte. It appears certain that gallium arsenide normally undergoes anodic dissolution with the formation of trivalent gallium and trivalent arsenic, a conclusion in agreement with that expressed in ref. (6) and (7). Moreover, the stoichiometry is the same for both surface polarities. In experiments 2-5 of Table III, the cathode was a GaAs disk of surface polarity opposite to that of the anode. There were no weight changes of the cathodes, within weighing errors, attending prolonged cathodic hydrogen evolution at current densities of 20 and 80 ma/cm². Evidently, arsine formation is not a significant part of the cathodic process at the current densities indicated.

Electrode polarization characteristics.—Preliminary anodic etching experiments with an n-type GaAs hemisphere in 0.5*N* KOH, carried out perforce under strong illumination, gave some indication of a reduced rate of attack along the [110] zone, including the (111) plane, as compared to the ($\bar{1}\bar{1}\bar{1}$) plane. However, the anodic etch patterns were not nearly so well defined as those obtainable with germanium hemispheres—one infers a lower degree of crystalline perfection for the GaAs—and the polarization experiments to be described allow little distinction to be made between the electrode kinetics of nominally A and B surfaces. On the other hand, anodic dissolution of both surfaces is definitely retarded relative to other orientations. Only one example is given by the photographs of Fig. 1, which depict the surface of an n-type electrode of B($\bar{1}\bar{1}\bar{1}$) surface polarity following anodic etching in 2*N* NaOH under illumination. There is clear evidence of higher-than-average current density at the rim of the disk; there also appears to be little remaining of the original surface orientation. The major reflecting planes in this particular etch pattern were identified as ($\bar{2}\bar{2}3$) by means of a two-circle goniometer.

Figures 2 and 3 illustrate the similarity in polarization behavior of the nominally A and B surfaces. The data points were obtained potentiostatically and represent quasistationary current densities measured at roughly 30-sec intervals. It is apparent that little quantitative significance can be attached to rest potentials in this system. On the other hand, the anodic polarization behavior was nicely reproducible, obeying a Tafel relation over at least four decades of current density. Within experimental error, Tafel slopes were the same (82 mv) for both electrodes.

The upward swing of the anodic curves at the highest current densities is an indication of a resistive component of the electrode potential measured *vs.* the saturated calomel half-cell. Thus, the data at high

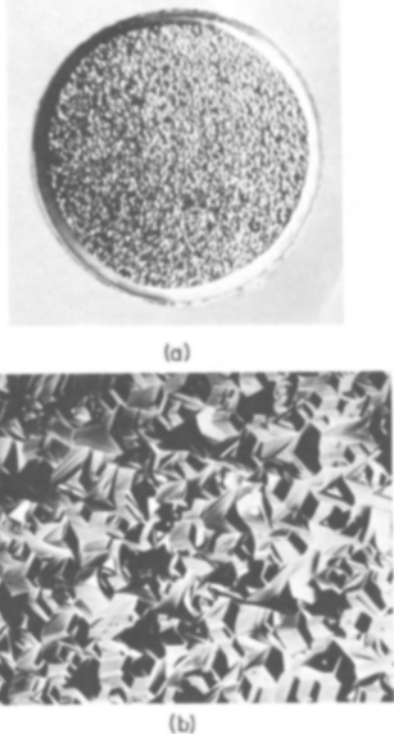

Fig. 1. Etch pattern resulting from anodic dissolution in 2N NaOH of an n-GaAs disk, 4-mm diameter, with B($\bar{1}\bar{1}\bar{1}$) surface orientation. Magnification before reproduction: (a) 20X, (b) 160X.

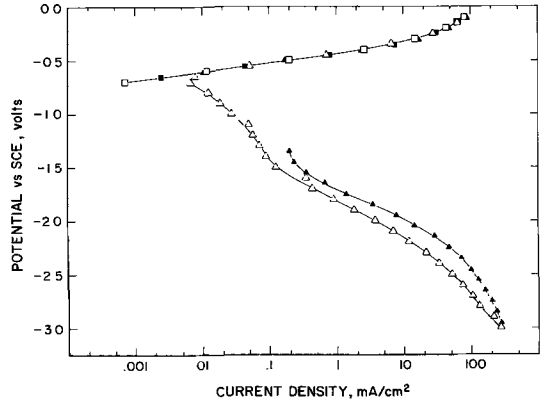

Fig. 2. Anodic and cathodic polarization curves for a p-GaAs, A(111) electrode in 0.5N KOH, 25°C: △, incr. $|\eta|$; ▲, decr. $|\eta|$; □, incr. $|\eta|$ (repeat); ■, decr. $|\eta|$ (repeat). The symbol η in this and subsequent figure captions stands for "overpotential."

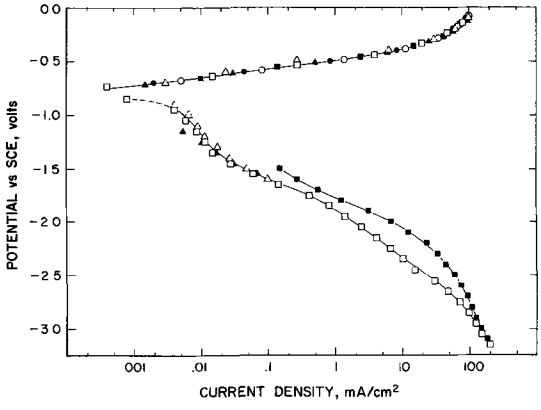

Fig. 3. Anodic and cathodic polarization curves for a p-GaAs, B($\bar{1}\bar{1}\bar{1}$) electrode in 0.5N KOH, 25°C. Sequence of measurements: △, ▲, □, ■, ○, ● (see Fig. 2 caption).

anodic overpotentials, when replotted as potential, U, *vs.* (linear) current density, j, yield straight lines with slopes, $R = dU/dj$, equal to 2.8_3 and 3.0_5 ohm-cm^2 for the A and B electrodes, respectively. The indicated magnitude of R is too large to be accounted for by the corresponding quantity for semiconductor bulk plus electrical contact to the back surface and is probably determined by the effective resistance (11) between electrode and Luggin capillary tip. Actually, for these and other cases it was found that the subtraction of jR from the measured electrode potentials apparently overcompensates for ohmic resistance; the corrected Tafel plots invariably leveled off at high current densities.

The cathodic behavior was more strongly influenced by chemical factors than by bulk semiconductor properties. Note in this regard the absence of an electron-limited current, together with an insensitivity to illumination at all but the lowest cathodic currents. These findings are in general agreement with those of Pleskov (3). The curves reported here were obtained subsequent to anodic polarization, and it is clear from examination of Fig. 2 and 3 that beyond a certain region of cathodic overpotential the nature of the GaAs surface becomes altered so that the polarization curve is not retraced on decreasing the overpotential. By way of comparison, Birintseva and Pleskov (5) obtained evidence for the anodic formation of a surface oxide phase in acid solution, but only of the order of one monolayer of cathodically reducible oxidation product in alkaline solution.

In addition to a shift of approximately 0.8v to more positive potentials, as compared to the 0.5N KOH electrolyte, the anodic polarization curves for p-type GaAs in 1.0N $HClO_4$ exhibit a passive region. Results for one surface orientation only are shown (Fig. 4), since the data for the second are virtually superposable, even to the extent of reproducing all details of the complicated cathodic behavior. The effect of prior anodic polarization on the cathodic behavior was more pronounced in the acid electrolyte, consistent with more extensive oxidation of the electrode surface. As in the alkaline electrolyte, the cathodic behavior of the p-type electrodes employed was much more a function of their chemical than of their semiconducting nature.

In 1.0N $HClO_4$ the anodic Tafel slope was 68 mv. The resistive contributions to measured overpotentials in the prepassive region were 1.5_4 and 1.8_8 ohm-cm^2 for an A and a B electrode, respectively, multiplied by

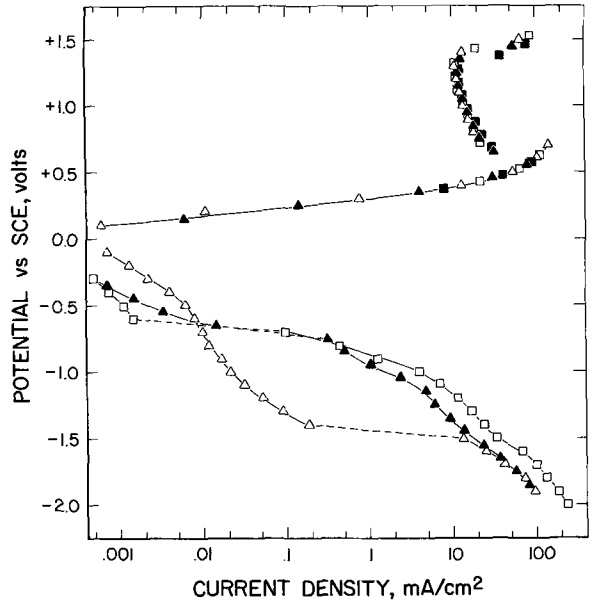

Fig. 4. Anodic and cathodic polarization curves for a p-GaAs, B($\bar{1}\bar{1}\bar{1}$) electrode in 1.0N $HClO_4$, 25°C. Sequence of measurements: same as Fig. 2.

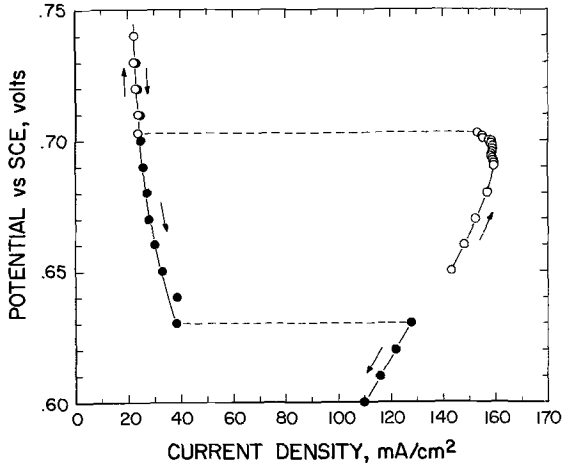

Fig. 5. Details of the active-passive transition for a p-GaAs, B($\bar{1}\bar{1}\bar{1}$) electrode in 1.0N $HClO_4$, 25°C.

current density. The transition from active to passive condition was abrupt; the critical potential could be located potentiostatically to within 1 mv (Fig. 5). Reestablishment of the active condition was attended by pronounced hysteresis, although the passive-to-active transition was equally abrupt. In the absence of stirring, current densities were lower in the prepassive and throughout the passive regions, but intense light had no perceptible effect on the kinetics.

By contrast to the active-passive transitions, that between passive and transpassive regions was gradual with, moreover, a drifting of the current at a fixed electrode potential. It is possible that the former is, in reality, continuous in keeping with the suggestion of Osterwald (11) relative to the effect of an included jR component.

Anodic polarization in $HClO_4$ to the extent indicated by Fig. 4 (about 30 sec/point) resulted in deep pitting of the GaAs surface and heavy attack of the rim. Although, as shown in Fig. 6, the pits formed on an A and a B surface are readily distinguishable (as in chemical etching), the microtextures of the rest of the surface and, indeed, of the pits themselves proved to be rather similar. The passive film is not thought to be the dark coating which appeared at high anodic current densities, since the latter could be dislodged mechanically, but was not reduced electrochemically.

The most pronounced effect of changing the anion from perchlorate to sulfate was the extension of the passive region to the most positive attainable potentials. The anodic polarization data given in Fig. 7 are for an A(111) surface orientation; results were virtually identical for a B($\bar{1}\bar{1}\bar{1}$) electrode as well as for

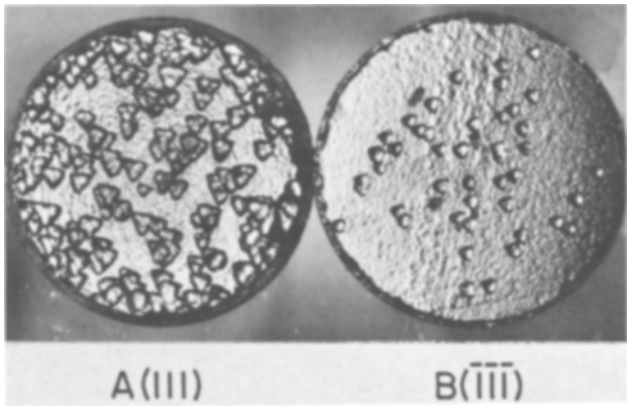

Fig. 6. Gross appearance of differently oriented p-GaAs electrodes, 8-mm diameter, following anodic passivation experiments in $HClO_4$.

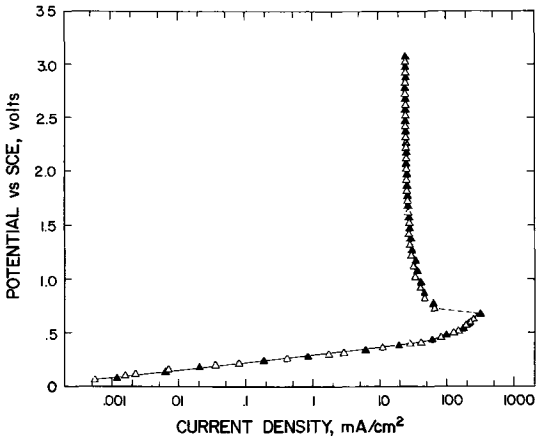

Fig. 7. Anodic polarization behavior of a p-GaAs, A(111) electrode in 1.0N H_2SO_4, 25°C: △, incr. η; ▲, decr. η.

a second A(111) electrode. The value of b derived from Fig. 7 is 62 mv. The active-passive transition was abrupt in both directions, but without appreciable hysteresis.

Additional comparisons of passivation characteristics in the two solutions are interesting. Thus, the Flade potential in 1.0*N* H_2SO_4 and that for the direction of increasing overpotential in 1.0*N* $HClO_4$ have sensibly the same value, namely about +0.70v *vs.* SCE; however, the maximum current density is greater in the former (~325 as compared to ~150 ma/cm²), as is the passive current density (~25 as compared to ~15 ma/cm²). The difference in *p*H between normal solutions of sulfuric and perchloric acid is thought to be insufficient to account for differences in passivation behavior, especially since hydrogen ion is a product of the anode reaction. One is led to a consideration of the probable composition of the passive film.

Both the sulfate and perchlorate of trivalent gallium have appreciable solubilities, as confirmed in separate experiments. It was also found that a gallium arsenite could not be isolated, although gallium arsenate was precipitated in the *p*H range 2-8. Arsenic trioxide is known to be only moderately soluble in acid solution, as noted by Straumanis and Kim in their report (12) on the growth of As_2O_3 crystals on GaAs etched with dilute and concentrated HNO_3 and also with aqua regia. (It would be difficult to reconcile their identification of the product as As_2O_3 with the known reducing properties of this substance were it not readily demonstrable in the laboratory that the oxidation of solid As_2O_3 by the reagents employed proceeds very slowly at room temperature.) Haisty (2) identified a dark blue film formed on p-type GaAs in dilute KCl by photogalvanic etching as β-Ga_2O_3, which is also the product of thermal oxidation (13). However, as noted previously, oxide films were formed only at intermediate *p*H's.

The published observations most pertinent to the passivation behavior of GaAs are possibly those of Revesz and Zaininger (14), who obtained a Ga_2O_3-As_2O_5 film by anodic oxidation of p-type GaAs in acetic anhydride saturated with KNO_3. They concluded that the film was essentially amorphous with a Ga/As atom ratio of 1.3, possibly a glass modification of the silica-like composite oxide $GaAsO_4$. It is conceivable that an anodic film of this nature is formed at sufficiently high current densities in aqueous acid electrolytes, leading to retardation of the anodic dissolution reaction. The rate of the implied further oxidation of arsenic to the +5 state would likely be enhanced by perchlorate and so result in diminished passive and maximum prepassive currents relative to H_2SO_4 electrolyte.

The narrowness of the range of passive potentials observed in $HClO_4$ is probably a consequence of the

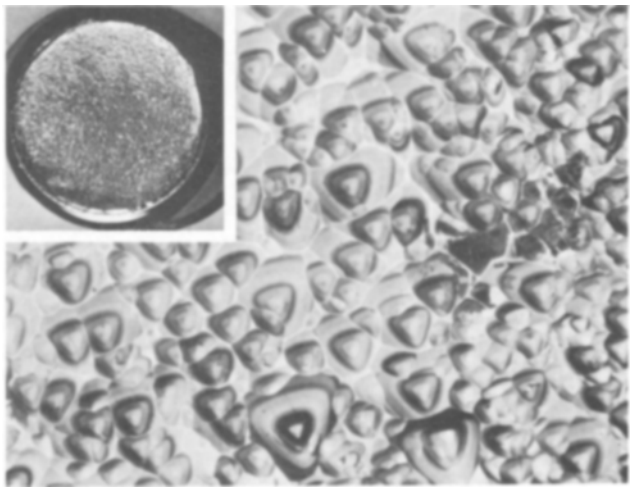

Fig. 8. Gross appearance (inset) and surface features of a p-GaAs, A(111) electrode, 4-mm diameter, following anodic passivation experiments in H_2SO_4. Magnification before reproduction: 200X.

severe pitting which occurs (Fig. 6). The absence of pits on GaAs electrodes having undergone similar anodic treatment in H_2SO_4 provides a marked contrast (Fig. 8). Visible in the latter figure are vestiges of a loosely adherent, dark film of GaAs. The strongly nonuniform distribution of electrode current density associated with pitting and transpassivity is probably also responsible for the hysteresis in the active-passive transition observed in $HClO_4$ electrolyte. There follows a consideration of some experiments performed with the aim of understanding better the cathodic behavior.

Cathodic photopotentials.—It was of interest to explore further the photoresponse of p-type GaAs cathodes. The absence of an electron-limited current has been noted here as well as by others, although Pleskov (3) found the overpotential for hydrogen evolution to be greater for p-type GaAs ($p = 2 \times 10^{18}$ cm^{-3}) than for n-type ($n = 10^{18}$ cm^{-3}). It seems clear that at the higher current densities the electrons required for the cathodic process are either generated at a sufficient rate within the electrode or at its surface or are derived from the valence band. The abrasion of the back surface prior to applying the gold contact is not thought to be a factor because of the very short lifetime and consequent short diffusion length of minority carriers in GaAs (15).

Initially, the positive photopotential was enhanced by application of a small cathodic current. The clear indication is that the negative space charge was increased in the way expected for consumption of minority carriers by the cathodic reaction. Continuous illumination at very low cathodic current densities

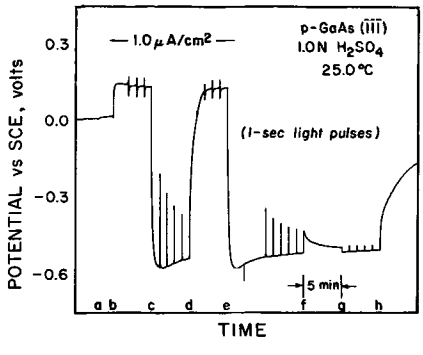

Fig. 9. Charging curves and photopotentials at a low current density. Events: a, begin magnetic stirring; b and d, begin anodic charging; c and e, begin cathodic charging; f to g, continuous illumination; h, current off.

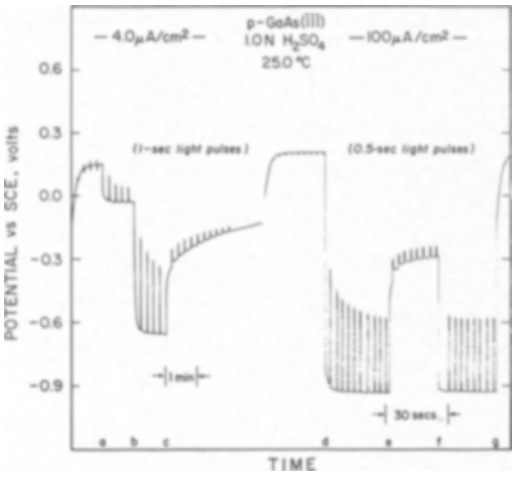

Fig. 10. Charging curves and photopotentials at intermediate current densities. Events: a, anodic current off; b, d, and f, begin cathodic charging; c and e, cathodic current off; g, begin anodic charging.

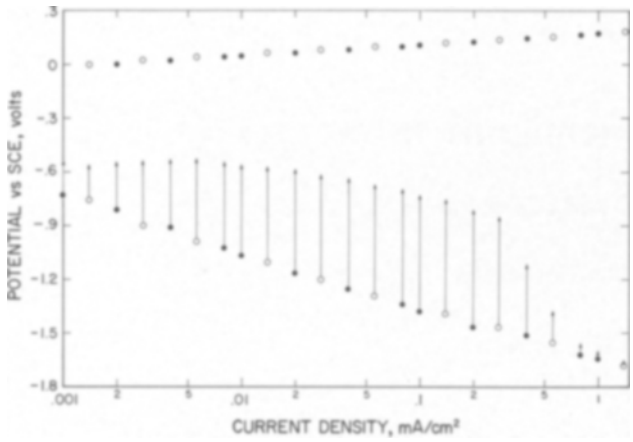

Fig. 11. Galvanostatic anodic-cathodic polarization of a p-GaAs, A(111) electrode in 0.99N Na_2SO_4/0.01N H_2SO_4; pH 2.85, 25°C. *Arrows indicate the change of cathodic potential under illumination.* ○, incr. $|\eta|$; ●, decr. $|\eta|$.

caused the magnitude of the photopotential to decrease more rapidly than in the dark (Fig. 9). The contribution of continued cathodic current to the observed relaxation of the photopotential may result from the change in the chemical state of the surface, with an attendant adjustment of the potential difference across the interface. Superposed on this effect is that of continued illumination (Fig. 9), which appears to be associated with a trapping phenomenon; possibly the light is absorbed by trapping centers and effects the release of minority carriers.

At somewhat higher cathodic current densities (Fig. 10), the cathodic photopotential becomes both larger and less time dependent. At still higher current densities, the cathodic charging curve is characterized by overshoot and, eventually, by greatly diminished photoresponse.

It was found that the quasistationary potentials obtained from cyclical charging yield polarization curves in which much of the previously encountered complicated cathode behavior is absent (Fig. 11). Evidently, the chemical state of the GaAs surface is altered in a more reproducible way as a consequence of anodic-cathodic cycling. From Fig. 11 it is seen that not only do the curves for increasing and decreasing overpotential coincide, but the cathodic branch has now a well-defined Tafel region. The values of the coefficient b in the given electrolyte are 62 mv for the anodic branch and 300 mv for the cathodic. The anodic photopotentials (not shown) were small throughout.

The following interpretation of the cathodic photopotentials is offered. Up to about 10 μa/cm^2 the cathode potential under illumination is sensibly constant, indicating that the light was sufficiently intense to bring the surface region to the flat-band condition (not that for the unpolarized electrode, which occurs at a potential slightly more anodic than the rest potential, but that corresponding to the new surface configuration brought about by cathodic current). Thereafter the light potential begins to fall off and for a decade or so of current density does so in parallel with the dark potential. In this range, increments of overpotential fall largely across the space-charge region. At still higher current densities an increasing fraction of the applied overpotential falls across the interface, with the consequence that the chemical state of the surface becomes more drastically altered—conceivably, surface As atoms are removed as arsine, leaving a Ga surface—and the light potential approaches the dark. Eventually, the semiconductor nature of the p-type GaAs is no longer manifest in its cathodic behavior.

Remarks

Certain difficulties experienced in studies of gallium arsenide electrochemistry stem from the compound nature of the electrode material; in most instances it probably does not make sense to think in terms of the composition GaAs in the immediate vicinity of the interface with the electrolyte. That is, one must consider that the existence of a surface layer with Ga/As atom ratio different from unity is the probable state of affairs. Thus, the usual picture of the Helmholtz layer may not be adequate for the electrode side of the interface.

The indistinguishability in polarization behavior of the (111) and $(\bar{1}\bar{1}\bar{1})$ surface orientations may be related to the factor just mentioned. There is also the likelihood, as mentioned earlier, that as a consequence of preferential etching, little of the real surface retains the (111) or $(\bar{1}\bar{1}\bar{1})$ orientation. Finally, as suggested by Gerischer (7) to explain similarities in anodic behavior, dismantling of the crystal by anodic reaction probably proceeds by removal of Ga and As atoms in pairs rather than singly.

There are serious discrepancies in the literature regarding the participation of holes in GaAs electrode processes. A photoinjection method indicated that 2.8-4.0 holes (4) are required per GaAs unit entering the electrolyte at the limiting anodic current. On the other hand, studies based on the redox method developed by Gerischer and Beck (16) for germanium give variously 1-6 (6) and 6 (7) for the same quantity.

A great deal more knowledge has to be gained before the contributions of different possible sources to the supply of minority carriers can be sorted out. Probably generation-recombination in the field of the space charge region is more important than in the volume, but the relative importance of thermal generation-recombination at the surface is not known. Some results presented here point to trapping as a factor in the charge distribution, whereas other authors have invoked field-induced ionization of deep lying impurities. In short, it may not be profitable to attempt to fit the electrochemical behavior of compound semiconductors wholly within the simple model which works well for germanium.

Acknowledgments

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Note added in proof: Since this paper was written, two items of especial pertinence have appeared in the literature. It has been reported that $-\Delta G^\circ_{298}$ for GaAs is of the order of 9 kcal/mole [A. S. Abbasov *et al.*, *Doklady Akad. Nauk S.S.S.R.*, **170**, 1110 (1966)]. Hence, the standard oxidation potentials of Table II are too positive by $0.26/n$ v, where n is 3, 6, or 8. Recently, Gerischer and Mattes [*Z. physik. Chem. Neue Folge*, **49**, 112 (1966)] have demonstrated convincingly the attainability of electron-limited currents with p-GaAs cathodes. Observations of others to the contrary are probably not ascribable to cathodically produced electron-hole generation centers, as may form on Ge cathodes. Very likely, it will be found that certain techniques of producing contacts to the back surface result in obliteration of the inherent limiting current.

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Transient Response of Chemically Interacting Solid-Gas Systems

I. Theoretical Considerations

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ABSTRACT

The transient response of the rate of a surface reaction between gas and solid phases is discussed mathematically. The over-all reaction is assumed to be the results of two elementary steps: adsorption of reactants and desorption of products. Expressions for the nonsteady rates of the two steps are derived and applied to the case of simultaneous occurrence of both steps. This results in a surface catalyzed reaction. It is shown how the analysis of the transient response permits the determination of some of the fundamental parameters of the elementary steps including the values of the step rate constant, the nature and concentration of the adsorbed intermediates. The contribution of nonsteady state kinetics to the elucidation of basic problems on the reactivity of solid surfaces is outlined.

The elementary steps of solid-gas reactions involve physical and chemical phenomena taking place at different rates. This is particularly valid for chemical changes occurring at a phase boundary, since the peculiar environment and structure of a phase boundary provides a wider spectrum of possibilities and conditions. Thus, a range of reaction relaxation times is to be expected in heterogeneous kinetics: from rapid electronic transitions, to slow transfer of atoms or ions among surface positions, and between surface and bulk phases. A detailed study of these various processes is a formidable, but necessary task for reaching a comprehensive understanding of heterogeneous and surface processes.

In the past, studies have been performed on the nonsteady rate of reaction of FeO in CO_2-CO and H_2O-H_2 mixtures (1) and of decomposition of HCOOH on Pd (2). In general, relatively high temperatures are preferred for these investigations, since the identification of the physical process corresponding to the measured relaxation times may be carried out with more confidence.

In view, however, of the fact that many surface reactions, mostly catalytic, take place at lower temperatures with fast rates, it is pertinent to inquire how far the pattern of physicochemical behavior emerging from high-temperature studies can be extrapolated to the lower temperatures of interest. To investigate this problem and to find out the extent to which low-temperature results may be utilized to extract meaningful information about surface-gas interactions, we have analyzed theoretically the transient response of chemically interacting solid-gas systems and performed experimental investigations to test the theoretical analysis.

Two considerations guided the present effort: first, the scattered but extensive literature reports of initial drifts of surface activity of many solids used as catalysts; in some cases, the direction of the activity change with time was qualitatively related to and found consistent with the reaction scheme derived from steady state velocity information (3); second, a close scrutiny of the nonsteady state behavior should be of great interest for mechanistic studies in hetero-