J. Phys. Chem. Solids Pergamon Press 1960. Vol. 14. pp. 137–141. Printed in Great Britain.

SECTION IV. COMPOUND SEMICONDUCTOR SURFACES

RECENT WORK ON SURFACE PROPERTIES OF II–VI SEMICONDUCTORS

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RECENT work concerned with the semiconductor properties of single crystals of II–VI compounds has revealed several important surface effects. Zinc oxide has received by far the most attention, in part because its bulk properties are better known(1) and in part because its surface effects are often found to interfere with measurements of bulk properties. Therefore this work will be reviewed first, and work on the related materials CdS and CdSe will be mentioned later. Finally some of the problems encountered in using such data to interpret phenomena in sintered and thin film material will be discussed.

The surface charge and potential of a zinc oxide single crystal can be changed by chemical reaction with the environment, exposure to light in the near ultraviolet, application of a transverse electric field or bombarding with ions or electrons. The change in potential has been with respect to a bulk material which is *n*-type or near intrinsic, since material with significant *p*-type character has not been produced, nor have space charge layers with significant *p*-type character been produced by the adsorption of negative ions. The effects are properly attributed to surface conditions because they can be observed at room temperature and below, where diffusion of atomic species into the bulk is negligible. Equilibrium, however, is generally not attained rapidly at temperatures below about 300°C.

The surface chemical reaction between zinc oxide and its own atmosphere of zinc and oxygen is of fundamental importance in reaction systems involving zinc oxide. Analogous to treatments of imperfections in the bulk one might define intrinsic surface imperfections such as zinc vacancies and excess zinc atoms, noting, however, that this would be an oversimplification unless one took into account the various types of occupied and unoccupied sites. Instead, without further definition, we will denote the density of surface acceptor atoms as $[O(s)]$ indicating that they are oxygen atoms, and the density of surface donor atoms as $[Zn(s)]$. The equations for the evaporation of oxygen and zinc, are

$$2\,O(s) \rightleftarrows O_2(g) \qquad (1)$$

$$Zn(s) \rightleftarrows Zn(g) \qquad (2)$$

and since the product of zinc and the square root of the oxygen vapor pressure is a function of temperature only, one also has

$$[O(s)]^2[Zn(s)] = K_3 \qquad (3)$$

in which K_3 is known. In the case of ZnO the oxygen to zinc pressure ratio can be changed through an extremely wide range. For example, at 300°C a pressure of oxygen of 1 atm implies an equilibrium pressure of zinc of about 10^{-40} atm.

The surface atoms may be considered as mostly neutral, but with ionization occurring at some according to the reactions

$$O(s)+e^- \rightleftarrows O^-(s) \quad K_4 = [O^-(s)]/[O(s)][e^-] \qquad (4)$$

$$Zn(s) \rightleftarrows Zn^+(s)+e^-$$
$$K_5 = [Zn^{+1}(s)]\,[e^-]/[Zn(s)] \qquad (5)$$

In non-equilibrium cases any one of the reactions (1), (2), (4) and (5) may be rate limiting, and more complicated situations are to be expected.

Reversible data for the surface conductivity of this system has been reported by THOMAS and LANDER(2) for zinc pressures in the range from 1 to 10^{-8} mm of Hg and temperatures between 300° and 500°C and they are reproduced in Fig. 1. The saturation value of $2\times10^{-4}\ \Omega^{-1}$/square corresponds to about 2 per cent of a monolayer of positive charge compensated by electrons with average mobility taken equal to 100 cm^2/V sec in a space charge layer beneath. Because the quantity adsorbed is not strongly dependent on zinc pressure the heat of adsorption of excess zinc must be high. Neglecting the degree of ionization of the excess zinc, an estimated value is about 10 kcal/mole for the concentration range explored. One hopes that further work with such tools as the field emission microscope, or slow electron diffraction would resolve the ambiguities in the model presented above.

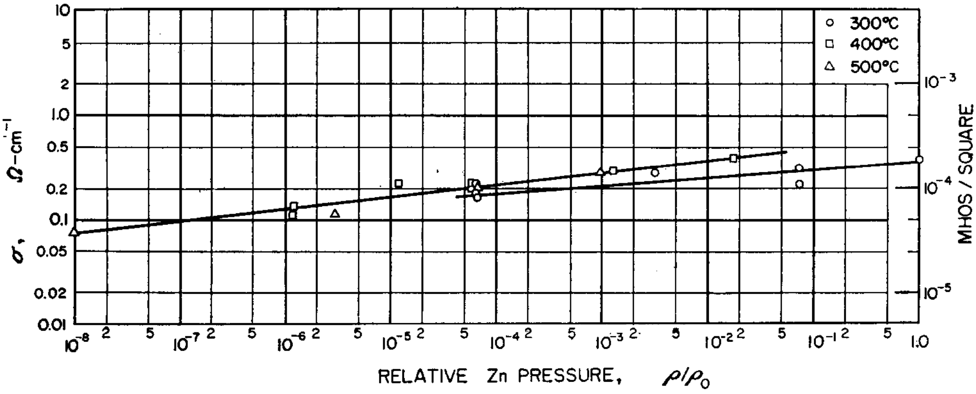

FIG. 1. Conductivity of 0·001 in. crystal at various temperatures as a function of zinc relative pressure.

Data for the temperature dependence of conductivity are given in Fig. 2 for a succession of "frozen-in" states. Similar results were obtained by evaporating minute quantities of zinc on to a crystal held in vacuum at room temperature. With increasing conductivity (increasing concentration of excess zinc) the slopes decrease and at the highest conductivities there is little temperature dependence in the range to liquid helium. This is presumably the result of overlapping donor orbitals. Because of the probable presence of traps at and near the surface the significance of the limiting slope at low concentrations has not been explained, and values for the energies of ionization species are not known.

HEILAND(3, 4) has reported that hydrogen produces large and similar surface effects, but in that work the surface concentrations of hydrogen and excess zinc resulting from reduction of zinc oxide are not known. More generally it is believed that strong reducing agents produce excess positive charge and strong oxidizing agents excess negative

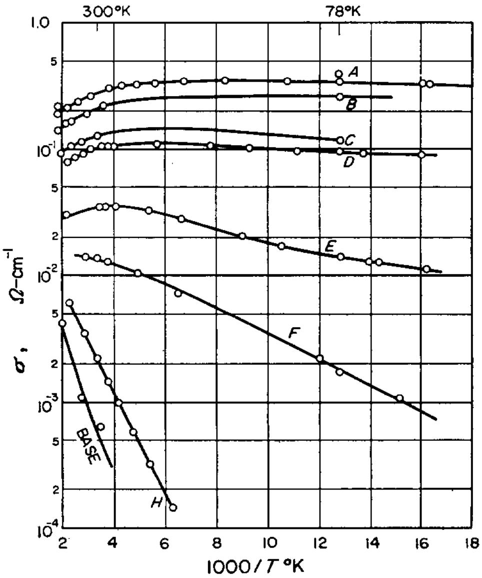

FIG. 2. 0·0019 in. diameter crystal conductivity as a function of temperature for different zinc coverages.

charge on zinc oxide surfaces, but chemical reduction or oxidation need not take place. Thus Thomas finds that cesium evaporated onto ZnO at room temperature behaves much like zinc.(5)

Large increases in conductivity of zinc oxide can also be obtained by exposure to ultraviolet light.(4) The results are dependent on ambient as well as on the intensity and frequency of the light. Since it was found that an increased conductivity produced in a crystal in vacuum at room temperature in this way is permanent, but could be reversed by exposure to oxygen, Collins and Thomas(6) concluded that light results in a desorption of lattice oxygen atoms, a process which may properly be called photolysis. Changes in conductivity due to trapping processes unaccompanied by oxygen desorption are also possible and in particular it was observed that after a change in conductivity produced at liquid nitrogen temperature the initial state was regained at about −150°C by warming the crystal in the dark. Presumably the oxygen does not desorb at very low temperatures. Data obtained by Krusemeyer(8) show that the efficiency of the process (the number of surface charges produced per absorbed photon) is near unity when the surface is far from saturation, and with sufficiently intense light saturation values of conductivity correspond to about 1 per cent of a monolayer of charge. Rates of change of conductivity, which are a function of the ambient, were also reported. Furthermore, surface photoconductivity can be produced by light with a frequency in the exciton range(7) (about 3·3 eV in zinc oxide). Earlier work on photoconductivity in thin films and sintered samples has been reviewed by Heiland *et al.*(1)

Field effect data as a function of surface conductivity have been obtained at 70°K by Heiland(4) and as a function of contact potential and surface conductivity at room temperature by Krusemeyer(8), who observed a range of contact potential from about −0·1 V to about +0·5 V with respect to the bulk potential (Fig. 3). In this range field effect mobility of different crystals varied from about 1 to about 100 cm²/V sec, and it was concluded from the nature of the variation of conductivity with contact potential that the low values were caused by surface states rather than by screening of the field by ions in the space charge region. Application of the electric field to crystals in vacuum produced slow changes in surface potential. Krusemeyer also reported a quantitative treatment of the hole-trapping process which is in good agreement with the experimental results.

Takaishi(9), and Krusemeyer and Thomas(10) have analyzed the equilibrium adsorption and charge transfer process at semiconductor surfaces (represented for ZnO by equations 1 to 5) as a function of partial pressure and composition of reacting vapor, and Garrett has extended this type of analysis to a treatment of the absolute rates of catalytic reactions involving charge transfer in semiconductors.(11)

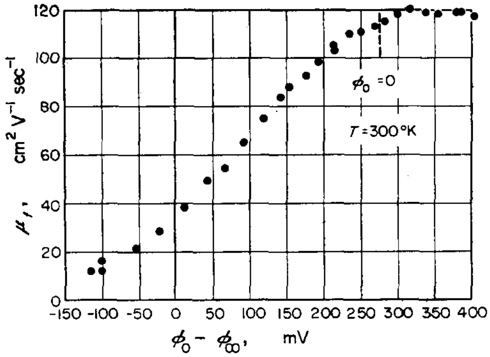

Fig. 3. Field effect mobility versus surface potential.

Dewald(12) has measured the capacitance of single crystal zinc oxide electrodes in contact with aqueous electrolytes. He observed no surface-state effects over a wide range of bias (about 2 V) and bulk electron density (10^{14}–10^{19} electrons/cm³). Variable surface dipoles and effects of low-lying donors (e.g. boron at 0·3 eV) were observed.

Work on surface effects in CdO and ZnS single crystals has not been reported but effects have been observed in the photoconductivity response of CdS and CdSe single crystals. Bube(13) has reported a study of the "photostimulated, temperature dependent, reversible sorption of oxygen" resulting from treatment of (*n*-type) CdSe crystals at 300°C for 3 hr in vacuum which apparently left excess cadmium near the surface (a result similar to the *A* and *B* type surface effects in zinc oxide reported by Heiland(1)). Subsequently conductivity was observed to decrease by as much as 5 orders of magnitude with exposure to oxygen at lower temperatures and this was accompanied by an increased sensitivity of photoresponse (Fig. 4). Similar effects were observed by **Bube**⁽¹⁴⁾ in work with CdS single crystals. As a matter of practical technology one notes that there is a variable fraction of photoconductive response in these materials which depends on the state of the surface and which can be altered by temperature, atmosphere, incident light and electric field.

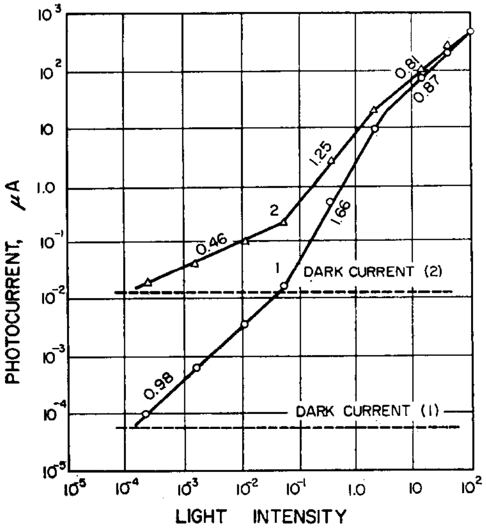

Fig. 4. Variation of photocurrent (for 1·5 V) as a function of light intensity at 75°C for crystal in (1) low-conductivity state, and (2) high-conductivity state. Light intensity of 100 corresponds to 900 ft-cd.

In summary, study of the surface properties of single crystals of II–VI semiconducting compounds exhibits large effects due to non-stoichiometry. Thus, in comparison with group IV elements, a more complex intrinsic chemistry must be taken into account. However, one does not have to worry so much about surface oxide films, at least on oxides. The relation between contact potential and conductivity appears to be better understood, and some surface trapping and recombination effects observed are very different (in zinc oxide recombination effects appear to be negligible). Many experimental techniques and much of the theory developed in work on germanium and silicon is readily adaptable to these materials, but, even in the case of zinc oxide, much remains to be done. Thus one might consider use of low voltage electron diffraction and the field emission microscope to obtain improved models of surface structure, analysis of combined measurements of surface conductivity, Hall coefficient and magnetoresistance as developed by **Zemel** and **Petritz** with germanium,⁽¹⁵⁾ the surface p.e.m. effect, infrared absorption and conductivity, space charge effects on drift mobility as developed by **Harrick**⁽¹⁶⁾ (but not with zinc oxide where the hole life-time is presumably too short), electron spin resonance and extensive studies of chemical reactions at surfaces.

The remainder of this review will be concerned briefly with properties of II–VI compounds in sintered or thin film form. These have practical application in catalysis, photodevices, luminescence, thermionic emission and transistor-like devices. The importance of surface properties is much greater in such material and space charge effects at intergranular boundaries or across individual grains may dominate the semiconducting properties. **Hutson**⁽¹⁷⁾ has reviewed the problem of interpreting the results of experiments. In general, detailed knowledge of the bulk and surface chemical and physical properties as well as the granular geometry is required in order to arrive at quantitative predictions. However, some properties may be dominated by surface effects through a wide range of grain size. **Sorrows**⁽¹⁸⁾ has reviewed work on thin films of lead sulfide and reported results of a study in which field effect and photoresponse were observed to have identical time constants. Thus the rate of transfer of charge into majority carrier traps (presumably at the surface) was the rate limiting process for both effects, and the density of charge of the traps determined the photoconductivity. The variation of photoresponse was correlated with trap density which could be changed by oxygen treatment. Further work will be reported by **Zemel** and **Varela**⁽¹⁹⁾.

A note of caution should be raised regarding the interpretation of data for material in sintered or thin film form. In some work it is likely that a simple model of the surface and intergranular regions may not be appropriate because of the precipitation during cooling of one or more insoluble phases. For example, several studies have been reported of the semiconducting and catalytic properties of zinc oxide containing various concentrations in the range from 0·1 to 2 mol% of impurities such as lithium on one hand and indium or gallium on the other which respectively reduce and enhance conductivity.(1, 20) In one such study by RUDOLPH(21) *p*-type conductivity was reported for a material doped with 2 per cent lithium.(21) However, it is known that although lithium and indium oxide are moderately soluble in zinc oxide at high temperatures, insoluble compounds tend to precipitate on cooling. Thus THOMAS(22) found that the solubility of indium in zinc oxide ranges from 3×10^{19} atom/cm^3 at 1300°C to about 1×10^{17} at 800°C and he has studied the precipitation on dislocations at lower temperatures in single crystals. The precipitated phase was not identified but it is known that at least three phases exist in the $ZnO–In_2O_3$ system. Similar results have been obtained with lithium,(23) which, however, has a somewhat higher solubility, but diffuses at a lower temperature.

PIPER and WILLIAMS(24) review the properties of sintered electroluminescent materials (ZnS dominates the field) and the basic mechanisms of electroluminescence. The acceleration of conduction electrons to optical energies in regions of high field is the excitation process. These regions occur at grain boundaries and, similar to surface regions, their properties are no doubt sensitive to grain boundary composition, which may be readily affected by the ambient at moderate temperatures.

Finally, it should be noted that surface effects may dominate the behavior of sintered material and thin films even at high temperatures. DEREN *et al.*(25) have discussed the temperature dependence of conductivity of zinc oxide in the range to 700°C in terms of the equilibria for oxygen chemisorption. The range in which reversible effects are observed is a function of sintering temperature and ends at about 400°C for material sintered below 1000°C. They conclude that conductivity in material sintered at temperatures much higher than 1000°C is determined by bulk properties.

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