

LETTER TO THE EDITOR

Some Comments on the Validity of Hall Effect Studies to Surface Phenomena

The recent paper by Chon and Pajares (1) in this journal regarding "Hall Effect Studies of Oxygen Chemisorption on Doped Zinc Oxide" contains so many simplifications and assumptions that we consider it to be misleading. Thus, changes in Hall coefficient are said to reflect changes in carrier concentration at the surface of a semiconductor. The work of Petritz (2) is quoted as proof. In our view the theory of Petritz is not entirely applicable to polycrystalline samples. The theoretical derivation in this paper is for long thin crystals and assumes no external effects. In a polycrystalline sample the surface states of each microscopic crystal would be considerably altered by the surface fields of neighboring crystals (3).

The use of the basic Hall equation, viz, $V_H = (3 \pi/8) \cdot (1/R) \cdot I \cdot B$, where V_H is the Hall voltage; $R =$ the Hall coefficient; $I =$ the current density; and $B =$ the magnetic field, was justified by Chon in an earlier paper (4). In it was stated that Volger's treatment (5) of cubes with good conducting properties embedded in a poor conducting media showed that any Hall voltage generated would essentially be due to the cubes. However, this was a theoretical proof and made no attempt to show how one could calculate the current density of a polycrystalline sample. In such a sample the geometric cross-sectional area of a pressed pellet would not be the same as the sum of the cross-sectional areas of individual crystals. Thus the measured voltage at two Hall probes in a polycrystalline sample is not the true Hall voltage.

Although Chon and Pajares' paper does

not actually state where the electrons come from in bonding oxygen to the surface it suggests that they are removed from the conductivity band of the zinc oxide. This, in our opinion, is questionable and depends on whether one accepts the views of Haufler (6) or Vollkenskstein (7). Most workers tend to apply the concepts of Haufler but this has been questioned lately (8).

In the Vollkenskstein theory, adsorbed particles, whether atoms or molecules, would form acceptor levels on the surface of the semiconductor. Electrons could then come into the levels from three sources, viz, (i) the conduction band of the catalyst, (ii) the donor levels of any doping materials, or (iii) the valence band of the catalyst. The determination of Hall coefficients cannot distinguish between any of these mechanisms as it only measures a net $(n-p)$ value (n is the number of electrons in the conduction band and p is the number of positive holes in the valence band). Whichever mechanism predominates depends on the position of the acceptor levels in the forbidden energy gap but generally it can be assumed that electrons would come from donor levels in a doped semiconductor (10). Electrons cannot come from the conductivity band as occupancy of this band would be zero if it were not for promotion of electrons from either donor levels or from the valence band. Thus, a drop in conductivity electrons simply implies that there are less free electrons in the donor levels for promotion into the conductivity band. (The actual fraction of donor electrons promoted would probably not alter as in adsorption

the Fermi level is effectively unaltered although admittedly there would be a secondary effect of change in surface states of the semiconductor due to adsorption.) Promotion of electrons from the valence band is easily discounted. The acceptor levels of this adsorbed species having higher energy than the valence band but lower energy (in general) than the doped donor atoms would preferentially accept electrons from the donor states. Also the removal of electrons from the valence band would cause an increase in conductivity of the semiconductor which, according to one worker, is not so for oxygen adsorbed on zinc oxide (3). If mechanisms predominate involving removal of electrons from donor levels, then a ratio of 1:1 for $(n-p):(O_2 \text{ adsorbed})$ is not necessarily evidence of an adsorbed species O_2^- . The only case when this would be so is if the donor levels are so close to the conduction band that practically all electrons left in the donor levels after adsorption are promoted into the conduction band.

For gallium-doped zinc oxide, Chon and Pajares do not give any value for the energy of the donor level. If we are to assume a previous paper (4) donor levels would be very near the conduction band and hence for the particular system an $(n-p):(\text{molecules } O_2 \text{ adsorbed})$ ratio of 1:1 would be reasonable evidence of O_2^- . However, generally this is not so.

If the gallium-doped zinc oxide sample of Chon and Pajares has donor levels very near the conduction band their results imply an accuracy of 0.1%. This appears excessive for Hall measurements on polycrystalline samples, particularly when one considers the effects quoted at the beginning of this letter. However, as the results appear to confirm the work of other authors, it may be that for the system being studied the low surface area of the samples makes surface field effects negligible and that the pellet pressing and final sintering of the pellets reduces gaps between the constituent crystals to a minimum.

In the experimental section of their paper it is stated that the use of a dual

Hall AC method avoids the need to balance out misalignment voltages. This is undoubtedly true but the use of an AC method introduces the further complication of probe pickup which, in the case of large probes, can be greater than the Hall voltage. This effect is caused by the alternating magnetic field interacting with the misalignment voltage from the current passing through the sample and generating an emf of the same frequency as the Hall voltage. Minimizing this effect is difficult and is usually accomplished by feeding bucking signals of the appropriate frequency and phase onto the Hall probes (9). The use of thin platinum probes (0.001 in.) and a sample of high conductivity (and thus low misalignment voltages) might make this effect very small in Chon's work; but nevertheless we feel it is worthy of mention.

In conclusion we might add that while the results of Chon and Pajares appear to confirm the results of other workers we think that they are particularly fortunate in the system they have chosen and their reasonings might not apply to other systems. To study the mechanism of bonding in a semiconductor catalyst, it is necessary to have much more information about acceptor levels of the absorbate molecule and this involves combination of both conductivity and Hall effect measurements. We do not believe that it is possible to obtain both sets of results to the accuracy required by use of conventional measuring techniques on a polycrystalline sample.

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Received November 11, 1969