JOURNAL OF CATALYSIS 2, 315–323 (1963)

Oxygen Chemisorption and Surface *p*-Type Behavior of Zinc Oxide Powders

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Received January 25, 1963

It is shown that the weak chemisorption of oxygen which is observed in the temperature range 20–130°C on powder samples of zinc oxide, either pure or with additions of Li^+ or Ga^{3+}, can exert a positive influence on the electrical conductivity of the oxide. The dependence of the conductivity on the oxygen pressure, as well as the sign of the Seebeck voltage, points to the presence of *p*-type inversion layers on the surface.

Treatment of the samples in high vacuum at 450°C removes the *p*-type surface layers and the normal *n*-type behavior can thereafter be observed.

In the course of previous work on the influence of hydrogen chemisorption on the surface conductivity of zinc oxide semiconductors (*1*), experiments were performed to determine the behavior of the samples in the presence of air. These experiments revealed that in the temperature range 20–130°C the behavior of the powders was not that expected of a typical *n*-type semiconductor such as ZnO. The observed effects have been further investigated and the results of this investigation are presented in this paper.

EXPERIMENTAL METHODS

Conductivities of the powder samples were measured in the apparatus described previously (*1*). Ac conductivities in the range 10^{-1}–10^{-10} mhos were measured by means of an ac bridge (Wayne Kerr B 221) operating at 1592 c/sec and dc conductivities by means of a Wheatstone bridge for high resistances. Voltage intensity curves were determined in order to ascertain the influence of non-ohmic constants.

Seebeck voltages were recorded by means of a vibrating reed electrometer. The powder was held between two platinum electrodes about 5 cm apart, one junction was kept as 0°C, and the temperature difference between the electrodes, about 10–15°C, was measured by means of a precision potentiometer connected to Pt, Pt-Rh wires sealed to the Pt electrodes.

The air admitted to the samples was purified through silica gel and soda lime.

The samples investigated were as follows:

pure ZnO obtained from high purity Zn C_2O_4 by thermal decomposition at 450°C in air (ZO);

pure ZnO prepared by the same method and sintered at 900°C in air (ZO-S);

high purity ZnO from Johnson Matthey sintered at 900°C in air (ZO-J);

ZnO + 0.35 mole % Ga_2O_3 prepared by impregnation of ZO with gallium nitrate and sintering at 900°C in air (ZG);

ZnO + 0.70 mole % Li_2O also prepared by impregnation with lithium nitrate and sintering (ZL).

Further details on sample preparation have been reported previously (*2*). The results are best illustrated by graphs which refer to particular samples. The behavior illustrated by the figures was, however, confirmed for a number of different preparations and can therefore be considered as representative of the type of sample under examination.

Although ac and dc conductivities might differ according to conditions, the general patterns illustrated by the figures, which refer to ac conductivities, were confirmed by dc measurements.

EXPERIMENTAL RESULTS

The Conductivity of Fresh Samples

Fresh samples constitute powders which did not undergo any preliminary surface treatment. Figures 1A and 1B illustrate the behavior of the conductivity of two different ZO-S samples as a function of temperature. Curve 1 of Fig. 1A was obtained by raising the temperature slowly from room temperature (r.t.) to 450°C in 1 atm of purified air. The broken curve was obtained by subsequent slow cooling to r.t.

It can be appreciated that upon cooling the conductivity falls below the sensitivity limit of the ac bridge at about 175°C and remains below this limit down to r.t. To restore the initial conductivity, the sample must be left overnight (about 12 hr) in the presence of air. After the sample was left overnight curve 2 was obtained if the temperature was raised as for curve 1.

Curve 3 was obtained by raising the temperature, after cooling the sample to r.t., and allowing it to stand in the presence of air for only about 3 hr. Curve 1 of Fig. 1B is similar to curve 1 of Fig. 1A (broken line corresponds to the cooling curve), while curve 2 was obtained by the following procedure: After leaving the sample overnight in the presence of air a conductivity value corresponding to the square point was measured; air was then pumped out and the conductivity fell as indicated by the arrow; readmission of air did not appreciably alter the conductivity and by raising the temperature thereafter curve 2 was obtained. There is an appreciable correspondence between curve 2 and the broken cooling curve.

The behavior of ZL samples is illustrated by Fig. 2. Curve 1 is the first rising temperature curve followed by the broken cooling curve. Curve 2 was obtained after leaving the sample for 12 hr in air at r.t. Curve 3 was obtained by a similar procedure to that giving curve 2 of Fig. 1B. It should be noted that in the case of ZL samples evacuation lowered the conductivity as for ZO-S, but readmission of air rapidly restored the conductivity close to its initial value. The results for ZG samples are illustrated by Fig. 3.

Curve 1 is the first rising temperature curve followed by the broken cooling curve. Curve 2 was determined the following morn-

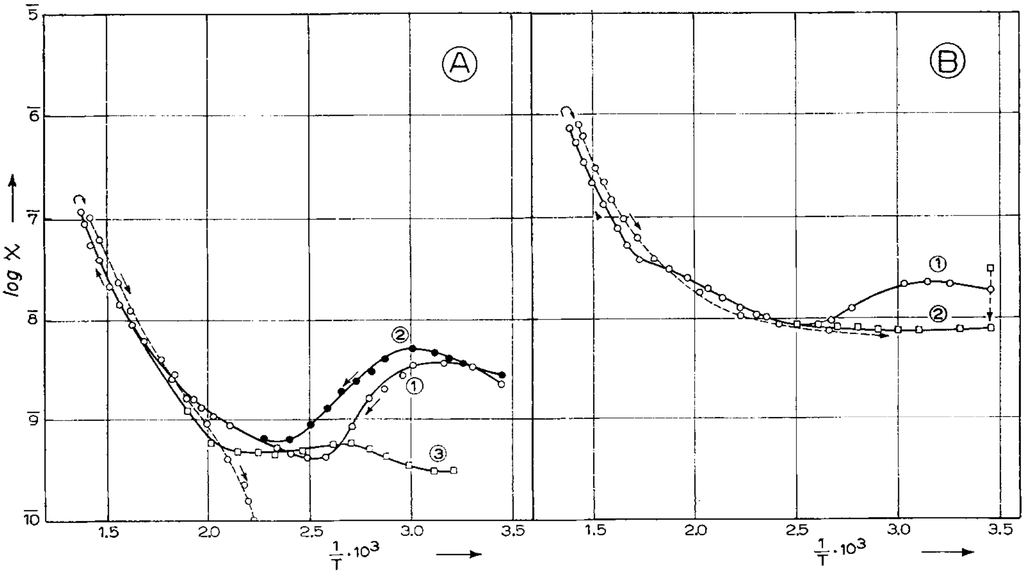

FIG. 1. Conductivity as a function of temperature for two sintered ZnO(ZO-S) samples. Heating and cooling curves determined under conditions specified in the text.

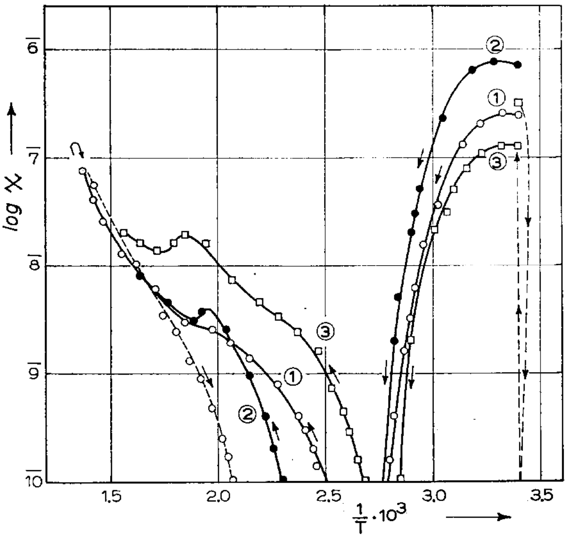

FIG. 2. Conductivity as a function of temperature for ZnO + Li_2O(ZL) samples. Heating and cooling curves determined under conditions specified in the text.

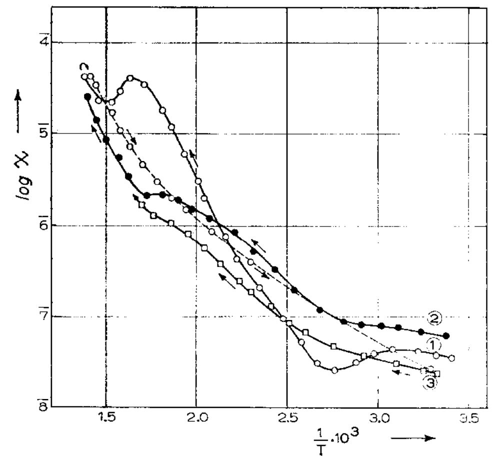

FIG. 3. Conductivity as a function of temperature for ZnO + Ga_2O_3 (ZG) samples. Heating and cooling curves determined under conditions specified in the text.

ing. Curve 3 was obtained by raising the temperature shortly after completion of a cooling experiment. This curve is similar to curve 3 of Fig. 1A.*

The decrease in conductivity observed at r.t. when the air pressure is reduced can be followed by slow evacuation of the sample, since the response of the conductivity to a pressure decrease is in fact very rapid. In Figs. 4, 5, and 6 conductivities have been plotted as a function of the air pressure for ZO-S and ZO-J, ZL, and ZG, respectively. If air is readmitted to ZO and ZL samples, and sufficient time is allowed for restoration of the initial conductivity at atmospheric pressure, essentially the same pressure dependence will be observed in a successive experiment at decreasing pressure. ZG samples differ somewhat in this respect in that their conductivities at atmospheric pressure tend to decrease in successive experiments (compare curves 1 and 2 of Fig. 6).

The rate of increase in conductivity upon readmission of air is strongly dependent on the type of sample. The process is fastest with ZL and slower with ZG. In any case, the rate of increase in conductivity is much lower than the corresponding rate of decrease observed when the pressure is lowered. The kinetics of the conductivity increase was not studied in detail. Figure 7 illustrates the type of kinetics observed with ZL samples when air was admitted at constant pressure. ZO-J samples behaved similarly though with much less pronounced maxima.

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* The origin of the conductivity maxima observed around 290°C has previously been discussed by J. Derén, J. Haber, and J. Wilkowa, *Z. Physik* **155**, 453 (1959).

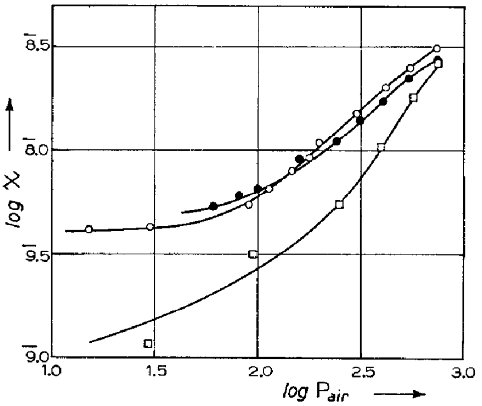

FIG. 4. Conductivity at 20°C as a function of the air pressure (in torr). Sintered ZnO samples. □, ZO-S; ○, ZO-J; ●, ZO-J after treatment in high vacuum at 450°C and successive treatment in air at the same temperature.

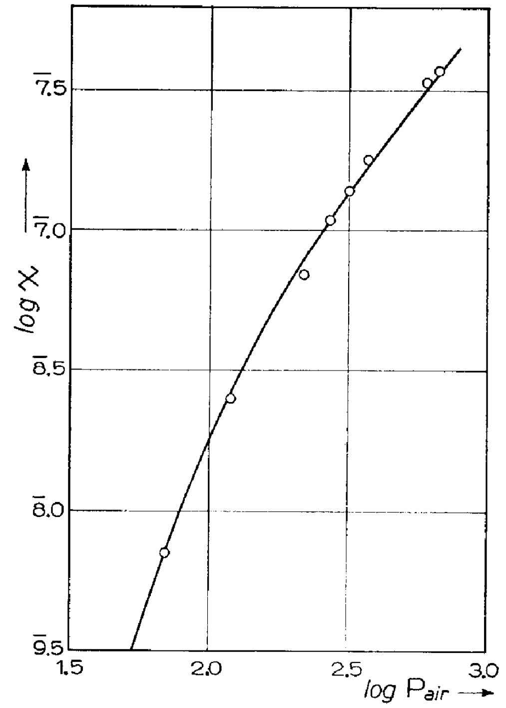

FIG. 5. Conductivity at 20°C as a function of the air pressure (in torr) of ZnO + Li_2O (ZL) samples.

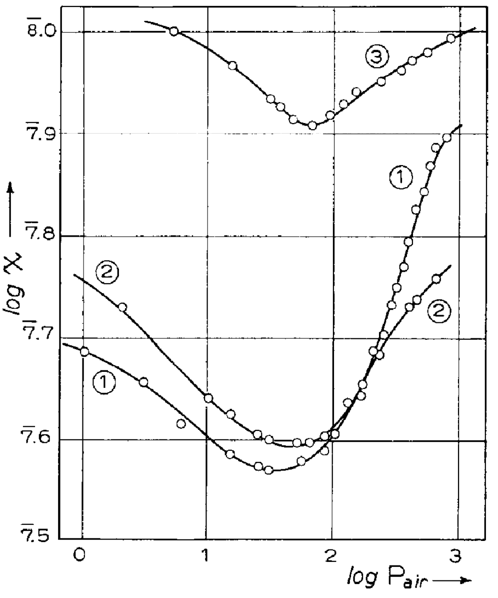

FIG. 6. Conductivity at 20°C as a function of the air pressure (in torr) of ZnO + Ga_2O_3 (ZG) samples. Curve 1, fresh samples; curve 2 determined after curve 1; curve 3 determined after treatment in high vacuum at 450°C and successive treatment in air at the same temperature.

The Conductivity of Samples Treated in High Vacuum at 450°C

Treatment of the samples in high vacuum at 450°C led to a progressive increase in conductivity until a limiting value was eventually reached. In Fig. 8 rising temperature curves in air for fresh ZO-S, ZL, and ZG samples have been plotted for comparison with the corresponding curves obtained in high vacuum after 2 hr treatment at 450°C. The latter curves are reproducible both in the raising and lowering of the temperature. It should be noted that the conductivity values of the samples treated at 450°C in high vacuum were considerably higher than the corresponding conductivities of fresh samples in the entire temperature range studied. ZL samples are an exception below about 70°C. Conductivities of the samples treated in high vacuum at 450°C increase in the order ZL, ZO-S, ZG over the whole temperature range: This agrees with the established behavior of single crystals. It is also evident from Fig. 8 that conductivity values at r.t. of fresh samples in air increase in a different order, namely: ZO-S, ZG, ZL. It has been found that conductivity values of pure and doped samples in air at r.t. generally fall within 2 orders of magnitude.

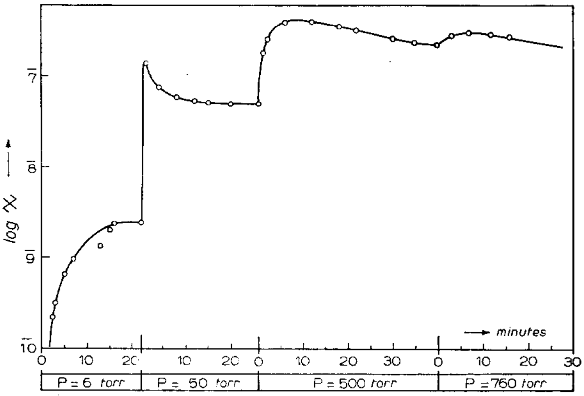

FIG. 7. The variation in conductivity with the time after air admission at constant pressure on a ZnO + Li_2O sample, at 20°C.

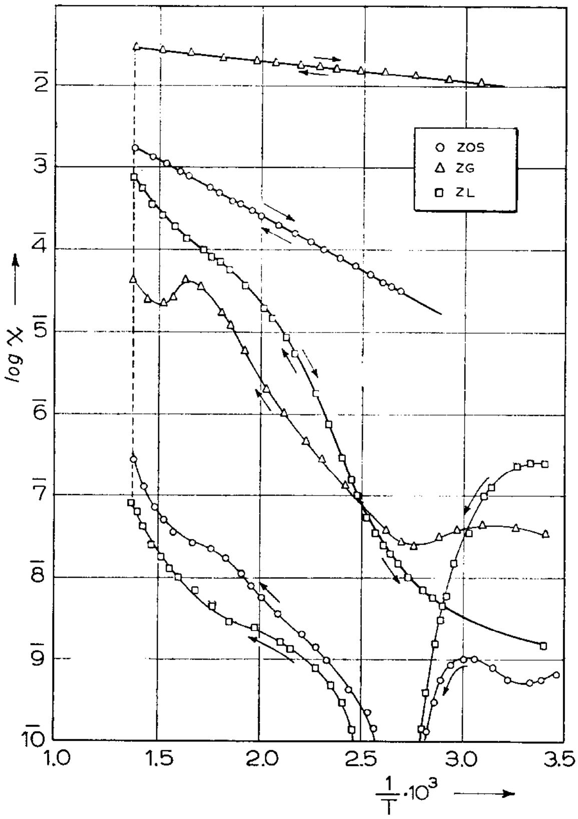

FIG. 8. Conductivity as a function of temperature of fresh ZO-S, ZL, and ZG samples in air (thin lines) and of the same samples in high vacuum after treatment at 450°C (thick lines).

Since the conductivity of fresh samples can vary within a factor of 10 among different batches of the same material, the order of the conductivity values in fresh samples can therefore differ from the one shown in Fig. 8. However, fresh ZL samples generally exhibit the highest conductivity. Similar results for r.t. conductivities of pure and doped samples in air have been reported previously by Papazian, Flinn, and Trivich (*3*).

Figure 9 illustrates the influence of oxygen on the conductivities at r.t. of samples treated in high vacuum at 450°C. In the case of ZO-S, ZO-J, and ZG samples conductivity is decreased by admission of air, the decrease being a function of the air pressure. Pumping at r.t. on these samples does not restore the initial high vacuum conductivity. This value can only be reproduced by repeating the treatment in high vacuum at 450°C. The behavior of ZL is different: The conductivity is insensitive to air in the pressure range 10^{-5}–10^{-2} torr, while higher pressures bring about a conductivity increase, as for fresh samples. In this case, evacuation of the samples at r.t. almost completely restores the initial conductivity in high vacuum. If samples treated in high vacuum at 450°C are submitted at this same temperature to a treatment of about 2 hr in 1 atm of purified air the behavior of the fresh samples is more or less completely restored according to the type of sample. This is evident from Fig. 4 for ZO-J and from curve 3 of Fig. 6 for ZG. The behavior of ZL is fully restored.

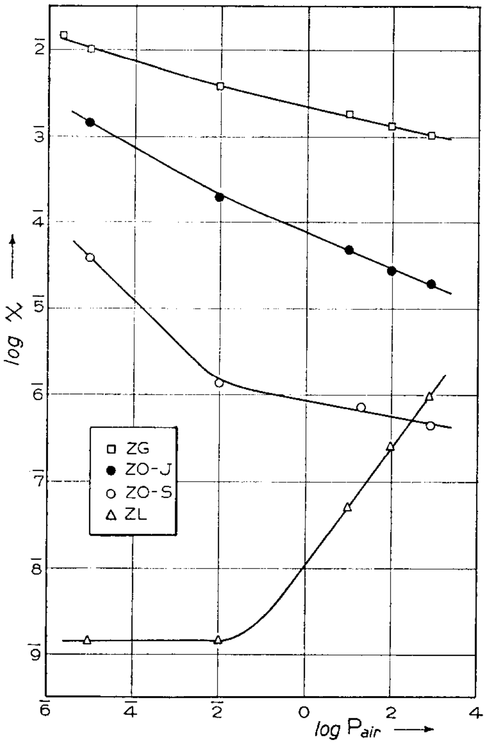

FIG. 9. Conductivity at 20°C as a function of the air pressure (in torr) of ZG, ZO-J, ZO-S, and ZL samples treated in high vacuum at 450°C.

The Seebeck Voltage

Measurements of Seebeck voltages (SV) on powder samples of high ohmic resistance, such as those employed in these experiments, are not accurate. However, the general trends observed by measuring Seebeck voltages, as a function of the oxygen pressure, of samples submitted to different surface treatments were reproducible. Figure 10 illustrates the results obtained with a ZO sample. The corresponding values of the conductivity are given in Fig. 11. For fresh ZO samples at atmospheric pressure, the sign of the Seebeck voltage was positive, corresponding to *p*-type conduction. A decrease in pressure entrained a decrease in the voltage and a parallel decreased conductivity. Below about 10^{-1} torr, the Seebeck voltage changed its sign, which then corresponded to *n*-type conductivity. If the sample is kept under vacuum and the pressure subsequently increased, the SV sign remains negative and its value increases with increasing pressure. The conductivity remains low and practically constant. If the sample is then treated at 450° in air, the conductivity at r.t. increases as shown by the arrow in Fig. 11 and the positive SV sign again shows the onset of *p*-type conduction. The behavior of the Seebeck voltage of a ZO sample treated in high vacuum at 450°C is also given in Fig. 10 Trends observed with ZO-S samples are generally similar, but the scattering of the points is much higher. In one case, the scattering at the same pressure was such as to include negative SV values.

DISCUSSION

The results reported in Figs. 1–6 can be easily interpreted if one admits that (1): a weakly bound, reversibly chemisorbed oxygen is present in the temperature range 20–130°C; (2) chemisorption of oxygen in

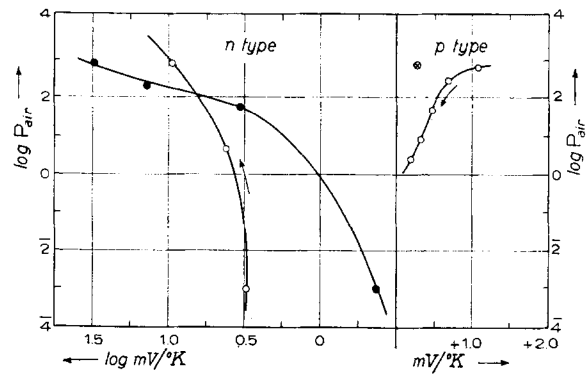

FIG. 10. Seebeck voltage as a function of the air pressure of a nonsintered ZnO sample (ZO); ○, fresh sample; ⊗, after evacuation at room temperature and treatment at 450°C in air; ●, after treatment in high vacuum at 450°C.

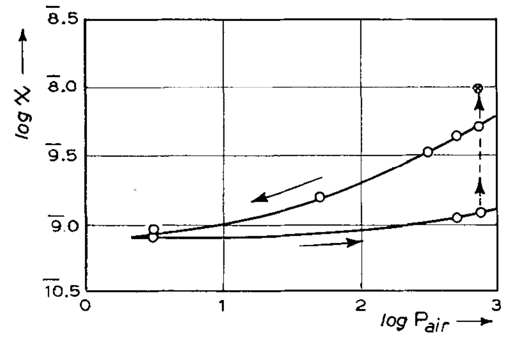

FIG. 11. Conductivity as a function of the air pressure for a nonsintered ZnO sample (ZO), ○; conductivity at atmospheric pressure after evacuation at room temperature and treatment in air at 450°C, ⊕.

this form exerts a *positive* influence on the surface conductivity of fresh ZO samples. The existence of weakly chemisorbed oxygen at low temperatures has recently been demonstrated by a number of authors (4), although the nature of the chemisorbed species cannot presently be clearly defined; O^-, O^{2-} ions or O_2^- molecule ions have been suggested as possible chemisorbed species.

The possibility of a positive influence of oxygen chemisorption on the surface conductivity of ZnO has been envisaged theoretically (*5*) and will be examined in the course of this discussion. The behavior of the samples in the thermal cycles illustrated by Figs. 1–3 can be understood if one considers that the weakly bound oxygen is progressively desorbed on raising the temperature. The ensuing decrease in conductivity is not compensated for by the normal increase in conductivity until higher temperatures are reached. The comparatively high surface/volume ratio of powders undoubtedly enhances these surface effects. It should be mentioned in this connection that measurements done in this laboratory using pellets obtained by pressing and sintering show that similar effects are present but they are less pronounced. Oxygen readsorption upon cooling is a slow process compared to desorption, as clearly brought out by the experiments discussed in connection with the data reported in Fig. 7. The hysteresis observed upon cooling is therefore explained by the fact that the amount of weakly chemisorbed oxygen that can be readsorbed during a cooling experiment is not sufficient to restore the high surface concentration of adsorbed oxygen and the high conductivities observed during the first heating of the samples.

The disappearance of the maxima in the low-temperature region, or their reduction in the case of ZL samples, can also be interpreted along these lines. The evidence for the existence of a positive influence of adsorbed oxygen on the electrical conductivity is clearly provided in Figs. 4, 5, and 11. The positive influence of oxygen is quite remarkable on ZL samples, where conductivities can vary by more than a factor of 10^4. The positive effect of oxygen is indeed so large as to alter the order of r.t. conductivities of the fresh samples in air with respect to the order observed with samples treated in high vacuum at 450°C and which corresponds to the order observed with single crystals. It should be appreciated that while the treatment at 450°C in high vacuum enhances the conductivity of all the samples examined in the whole temperature range, ZL samples are an exception below 70°. This exception is a consequence of the large positive influence of oxygen on the conductivity for fresh ZL samples.

On the basis of the results illustrated by Figs. 1–7 one is led to the conclusion that the surface of fresh samples behaves as if it were of a *p* character. This is true for ZO and ZL samples in the pressure range studied, while ZG samples, with their conductivity minimum at about 40 torr, apparently change over from *p*- to *n*-type behavior around this pressure. Treatment of the samples in high vacuum at 450°C completely changes their behavior toward oxygen at room temperature. The influence of oxygen on the r.t. conductivity of ZO and ZG becomes negative, as expected for an *n*-type surface, and essentially irreversible. ZL samples are less severely modified by this treatment in that they maintain their *p*-type character above 10^{-2} torr. The idea that positive holes might contribute to the surface conductivity of fresh samples receives further support from the measurements of the Seebeck voltage. In interpreting these results it should be remembered that in polycrystalline samples consisting of grains with surface conductivities which differ from bulk conductivities, the major contribution to the measured Seebeck voltage comes from the regions of the grains with the highest conductivity.

This point has recently been discussed by W. Fulkerson (*6*)[*] in connection with Seebeck voltage measurements of polycrystalline CdS films. When the surface conductivity is high with respect to the bulk conductivity, the contribution of the surface layer to the total Seebeck voltage is high and the presence of hole conduction on the surface is evidenced by the sign of the Seebeck voltage. A decrease in air pressure entrains a decreased conductivity and a corresponding decrease in the Seebeck voltage. In fact, the *n*-type contribution which is always present becomes more and more important until one reaches a condition of surface coverage where the *n*-type contribution predominates. At this point, the sign of the Seebeck voltage is reversed. In the *n*-type region, which is observed with samples treated in a vacuum either at r.t. or at 450°C, the adsorption of oxygen increases the Seebeck voltage in agreement with the decrease in *n*-type character entrained by oxygen adsorption in this region (see below). Treatment in air at 450° of vacuum-treated samples, restores the behavior of the conductivity observed with fresh samples as well as the sign of the Seebeck voltage.

The possibility of bulk *p*-type conductivity can be theoretically envisaged for ZnO. Experiments carried out by Lander (*7*) did show, however, that ZnO single crystals cannot be made *p*-type even by strong doping with lithium. To our knowledge, *p*-type conduction in ZnO has only been reported by Rudolph (*8*) for polycrystalline sintered rods of ZnO, strongly doped with lithium (2%) at high temperatures ($\simeq$1000 °K).

The possibility of *surface p*-type conduction for ZnO in an oxygen atmosphere has been theoretically discussed by Krusemeyer and Thomas (*5*). They have shown that the interaction of oxygen with an initially bare *n*-type surface first creates a "depletion layer" on the surface, with an ensuing decrease in the surface concentration of majority carriers. In this region, an increase of the oxygen pressures will further depress the concentration of quasi-free electrons and the conductivity, therefore, will be correspondingly lowered. When the upward bending of the semiconductor bands near the surface, caused by chemisorbed oxygen, is such that the upper limit of the valence band has become sufficiently close to the Fermi level, electrons can be transferred to the acceptor oxygen molecules directly from

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[*] If one considers a single grain with a temperature gradient across it, the surface and the interior of the grain can be treated as separate sources of two emf's, V_s and V_i, with corresponding internal resistances R_s and R_i. The voltage V, measured across the grain is then given by $V = -V_s - \{[R_s/(R_s + R_i)]\ [V_i - V_s]\}$. It follows that for $R_i \ll R_s$, $V \cong -V_i$ and for $(R_s/R_i)V_i \ll V_s$, $V \cong -V_s$.

the valence band. At this stage, quasi-free holes will start to contribute to the surface conduction and an "inversion layer" with p character is formed. An increase in oxygen pressure will then increase the hole concentration on the surface and the conductivity will be correspondingly increased.

Although a quantitative comparison of our data with the theory of Krusemayer and Thomas is not possible the general trends observed in our experiments seem to be consistent with this theory.

Fresh samples are characterized by almost stoichiometric surfaces with a comparatively high concentration of chemisorbed oxygen. These conditions cause the presence of an inversion layer on the surface. This explains why the conductivity decreases when the pressure is lowered and why the Seebeck voltage sign corresponds to p-type conduction.

Furthermore, the addition of lithium, which depresses the Fermi level of the semiconductor, would favor the formation of the inversion layer. This might explain the large effects observed on these samples. The addition of gallium, on the other hand, raises the Fermi level. As a consequence the "inversion layer" present at high pressures changes over to "depletion layer" at about 40 torr, and the observed effects are smaller than those observed with either ZO or ZL.

Treatment of the samples in high vacuum at 450°C destroys the surface layers and very likely eliminates some surface lattice oxygen, thus creating a more defective n-type surface (*1*). The behavior of samples treated in high vacuum, with the exception of ZL, is typical of an n-type surface where oxygen adsorption gives rise to a "depletion layer." In this case, the amount of oxygen that can be adsorbed at r.t. in the pressure range studied is not sufficient to give rise to an "inversion layer" except in the case of ZL samples which possess a lower Fermi level. The inversion layer can again be formed on the surface of these samples by treatment in air at 450°C. This treatment can partly restore the surface conditions which are present in the fresh samples. A result of the theory of Krusemayer and Thomas is that very large changes in the oxygen pressure are necessary to convert a depletion layer into an inversion layer. This result, apparently, would rule out the possibility of observing the behavior of ZnO in both the n and the p region. One appreciates, however, that in our experiments the state of the surface is not varied simply by changing the oxygen pressure, but by submitting the samples either to appropriate surface treatments or by modifying the position of the Fermi level by doping with Li or Ga. This is formally equivalent to a variation of the oxygen pressure within very wide limits.

ACKNOWLEDGMENT

We wish to thank Dr. G. Ghersini for his help in performing some of the experiments.

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