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Autor: Ruppel, W. / Gerritsen, H.J. / Rose, A.
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An Approach to Intrinsic Zinc Oxide

by W. Ruppel, H. J. Gerritsen and A. Rose.

Laboratories RCA Ltd., Zurich, Switzerland.

(2. VIII. 1957.)

Abstract. The resistivity of layers of finely divided zinc oxide powder approaches about 10 powers of ten closer to intrinsic zinc oxide than do single crystals. The electrical properties of these layers can be analyzed as if the material were homogeneous. These properties include the formation of depletion layers and the large rectifying action obtained with ohmic and blocking contacts. The finely divided state appears here mainly to allow surface adsorbed oxygen to simulate the effects it would have if it could be diffused into the volume of the bulk material.

A. Introduction.

Extensive investigations have been carried out on zinc oxide in the form of single crystals and sintered layers. The room temperature resistivities reported in these papers are in the range of 10^{-2} to 10^6 ohm.cm, that is, in the range of semiconductors. These values are strikingly small compared with the intrinsic resistivity of zinc oxide which should be of the order of 10^{25} ohm.cm as expected from a forbidden gap of 3,2 eV. The present paper extends the range of resistivities, measured at room temperature, to about 10^{17} ohm.cm. This value is still small compared with the intrinsic resistivity but is some ten decades higher than has yet been achieved in single crystals.

The high insulation was made possible by three techniques: the use of finely powdered material; the avoidance of adsorbed moisture and the use of electrically blocking contacts. While measurements on powdered materials are normally suspect, the use of the finely divided state is believed here to facilitate a closer approach to the intrinsic properties of zinc oxide. And, in fact, the data to be described are consistent with the zinc oxide powder regarded essentially as a homogeneous material.

B. The finely divided state.

Macroscopic ZnO single crystals are known to be highly *n*-type probably due to excess zinc acting as donors. Their volume conductivity ranges between about 10^{-2} and 10^6 ohm. cm¹)²).

The surfaces of these crystals in air are known to be much more insulating as a result of chemisorbed oxygen. At thermal equilibrium, an insulating electron depletion layer under the surface is formed (fig. 1).

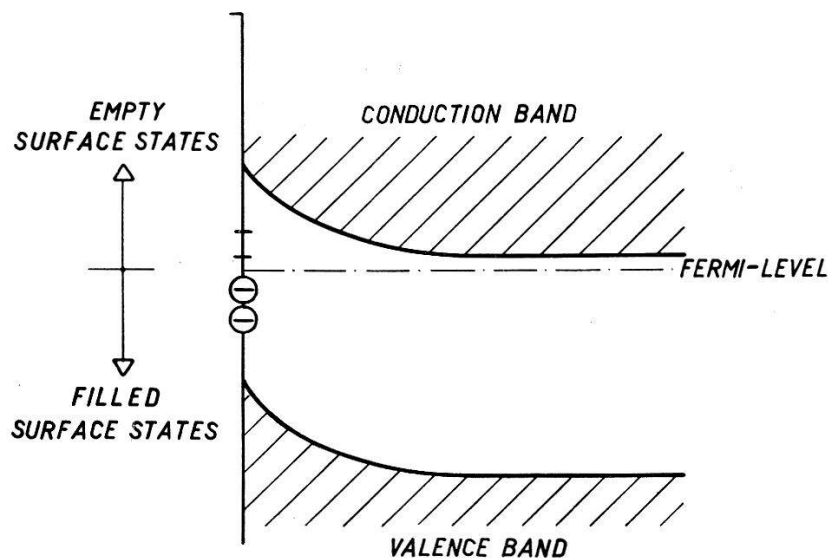


Fig. 1.

The surface of a ZnO crystal at thermal equilibrium.

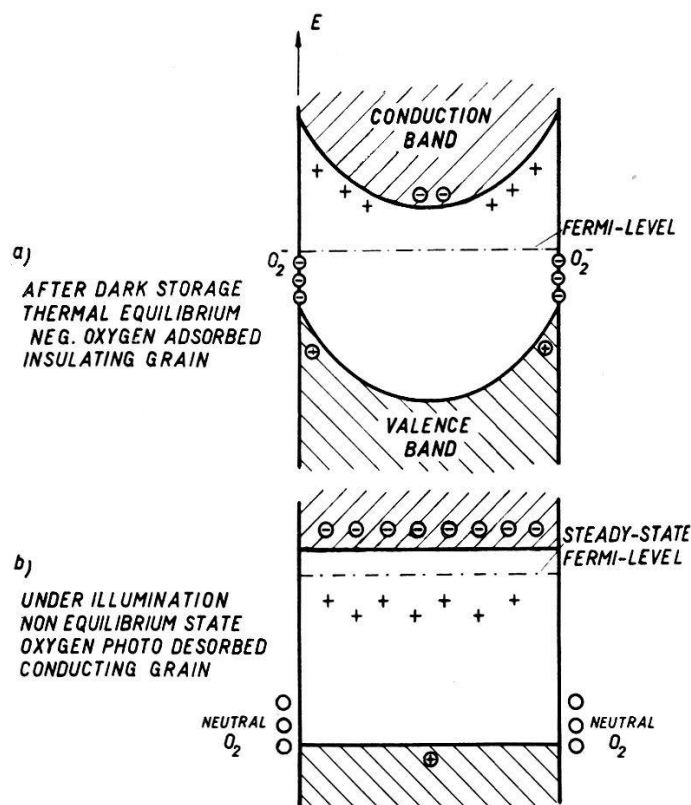


Fig. 2.

ZnO powder particle of the size of 10^{-5} cm a) before and b) after illumination.

In ZnO powder with a grain size of about 10^{-5} cm the thickness of the electron depletion layer becomes comparable with the grain size. For this reason the insulation of ZnO powder may be expected

to be high relative to that of large crystals (fig. 2a). By breaking up a large crystal into small grains, the ZnO becomes on the average more stoichiometric and approaches closer to intrinsic behavior.

The use of the finely divided state may be looked upon as one way of doping a material with elements that do not diffuse readily into the volume. Prolonged heating of single crystals of zinc oxide in an atmosphere of oxygen, for example, has not succeeded in diffusing enough oxygen into the crystals to make them insulating*). In the finely divided state, oxygen adsorbed on the surface is the equivalent of oxygen uniformly diffused into the volume. A volume doping of 10^{15} atoms/cm³ corresponds to a mean spacing of impurity atoms of 10^{-5} cm, namely the dimensions of the zinc oxide powder grains used in this investigation. Actually, as many as 100 oxygen atoms per grain still approximates uniform doping. The occurrence of an increase in resistivity in ZnO powder compared with bulk material is analogous to the formation of highly insulating necks in sintered layers proposed by MORRISON and MELNICK³).

C. The Avoidance of Moisture.

Surface leakage due to adsorbed moisture is a common difficulty in trying to achieve high insulation. This type of spurious leakage is naturally even more pronounced for finely divided powders. It was found in the case of the zinc oxide powder that a typical room temperature resistivity less than 10^{10} ohm.cm could easily be increased some powers of ten by heating the powder to 100° C. As the powder approached room temperature again, it soon became more conducting. This behaviour is clearly caused by adsorbed moisture.

Thin layers of zinc oxide powder mixed in a silicone resin have been developed by GREIG and YOUNG⁴) for use as a photosensitive insulator in a special photographic process. These layers were found to show a decrease of resistivity with increasing temperature indicating that moisture was not playing a significant role.

Further measurements on the zinc oxide — resin mixture showed that the resin served mainly to avoid the parallel leakage paths caused by adsorbed moisture and did not contribute any significant resistance in series with the zinc oxide grains. The observation of saturated primary photocurrents for light strongly absorbed at the negative electrode**) was clear evidence that electrons could pass

*) G. HEILAND, private communication.

**) See the accompanying paper "Photoproperties of Zinc Oxide with Ohmic and Blocking Contacts" which will be referred to by II.

freely from one grain to the next over a path of several hundred grains. Also, the observation of normal photocurrents many powers of ten higher than the dark current would not have been possible if the dark resistance were due to the photo-insensitive resin. Finally, a DC measurement of the dielectric constant of the layer gave a value of 8 to be compared with a value of 10 used for single crystals⁵). If the insulation of the layer were localized at the grain boundaries, the apparent dielectric constant would have been considerably higher than 10.

The silicone resin appeared mainly to act as a convenient substitute for dry air and served to reveal rather than obscure the properties of the ZnO in the coating.

D. Ohmic and Blocking Contacts.

a) Ohmic contacts.

The tests of good ohmic contacts are their freedom from noise and their ability to show ohmic behaviour at low voltages even down to microvolts. Such contacts are not easily found. For many purposes, quasi-ohmic contacts are sufficient. These contacts show ohmic behaviour above a few volts but not necessarily at very low voltages. A small voltage is expended at the electrodes to break through the contact resistance. In this sense, metal electrodes made quasi-ohmic contact to the zinc oxide layers and showed ohmic behaviour in the range of a few volts to several hundred volts. Using silver paste or mercury contacts, the resistivity of the zinc oxide layers was observed to be about 10^{14} ohm.cm if the layer had been kept in the dark for about a day. This is believed to be the thermal equilibrium value for the "dark adapted" zinc oxide powder.

If the zinc oxide powder were now exposed for some minutes to daylight, the resistivity dropped to 10^6 ohm.cm and recovered only slowly in the dark. About one day was required to recover the dark adapted resistivity of 10^{14} ohm.cm. It is likely that the oxygen adsorbed on the grain surfaces is negatively charged in the dark and is neutralized under illumination by a photo-excited hole, the free electron going to the interior of the grain (see Fig. 2)*). It is likely that the neutralized oxygen is mechanically retained by the

*) The effect of straightening the band structure in the grains by the photo-generated excess charge is exaggerated in the figure. Even under strong illumination a significant curvature of the energy band will remain.

resin. When the light is removed, the free electrons drain off into the oxygen again. This is a slow process limited by the small capture cross-section of the oxygen centers for free electrons and by the large density of traps. In brief, the approach to high insulation caused by surface adsorbed oxygen requires a comparatively long time and levels off at 10^{14} ohm.cm.

b) *Blocking contacts.*

In contrast to the behaviour with ohmic contacts it was found that if an electric field was applied to the zinc oxide powder through blocking contacts, a still higher resistivity was achieved in a much shorter time. Blocking contacts to the ZnO powder layer could be realized in the following ways:

1. By the negative ions from a corona discharge in air.
2. By the negative ions of an electrolyte.
3. By a *p*-type semiconductor.

The experimental results to be discussed in the following are those obtained with the negative ions from a corona discharge in air acting as the blocking electrode. Since the free electron life time in the corona discharge in air at atmospheric pressure is less than 10^{-4} sec, negative ions of oxygen, nitric or nitrous oxides will be formed and deposited rather than free electrons⁶).

These ions strike the surface of the ZnO layer under the field of the corona discharge and enhance the density of adsorbed negative ions in the surface of the layer beyond the thermal equilibrium value. The ions form a negative blocking contact and give rise to an electron depletion layer inside the ZnO. This depletion layer is superposed on the electronic "sub-barriers" due to the thermal equilibrium oxygen adsorption around each grain. While the local depletion layers formed by oxygen adsorbed on each grain have the dimensions of individual grains (10^{-5} cms), the thickness of the depletion layer formed by negative ions from the corona discharge deposited on the surface of the powder layer is 10^{-3} cm or more and extends over hundreds of grains as if these were parts of a homogeneous material. As will be described below, the thickness of the macroscopic depletion layer could be controlled from values well in excess of 2×10^{-3} cm, the thickness of the powder layer, down to approximately 1×10^{-3} cm. The control was effected by photo excitation of the layer prior to the corona charging.

The blocking action of negative ions such as OH^- and O^{--} was estimated⁷) to correspond to electron energy levels of these contact-

ing ions several electron volts below the conduction band of zinc oxide.

The resistivity of the ZnO layer in the case of a blocking contact was measured by observing the decay time of the surface potential. The surface potential was detected by means of a conducting electrode brought close to the surface and connected to an electrometer.

Under the corona discharge the surface of a 2×10^{-3} cm thick layer of zinc oxide charged up to about 500 volts. It is believed that field emission from the blocking electrode limited the further increase of voltage. The time for this voltage to decay to half value was several hours. From this a resistivity of the zinc oxide layer at room temperature was computed to be 10^{16} ohm.cm. Since independent tests on the resin alone gave a value no higher than 10^{16} ohm.cm this value must be taken to be a lower limit for the zinc oxide. The fact that the resistivity with blocking contacts is at least 100 times higher than the value measured with ohmic contacts is evidence that a depletion layer was formed. Further, from a measurement of the total charge deposited to reach 500 volts, the thickness of the depletion layer was computed to be equal to the thickness of the zinc oxide layer. That is, for effective depletion layers thicker than the sample, the measured value approaches the sample thickness and the behaviour of the sample approaches that of a simple condenser.

In order to get more definite evidence of the depletion layer formed by the blocking contact, the zinc oxide layer was converted into a semiconductor by exposure for about a minute to room light. From previous experience this photo induced conductivity required a time in the order of a day to decay to the "dark adapted" value. Thus, measurements could be made on the light-exposed layer, for some time after the exposure, with confidence that the material remained a semiconductor.

The charging of such a "light adapted" layer even with a high current corona discharge required a few seconds. From the magnitude of the charging current and the layer thickness the charging time would be expected to be 0.1 seconds. The maximum voltage reached was now only about 250 volts in contrast to the 500 volts for a "dark adapted" layer. The charging time of a few seconds was interpreted as the time required to form a depletion layer. Time is required to drain off not only the free carriers out of the layer but also the trapped charges. This observation is discussed further in the next section.

When the charging rate was reduced so that the rate of rise of potential was limited by the current reaching the surface, significant differences between the barrier properties of "dark" and "light adapted" zinc oxide were observed. In Fig. 3 the build up of the surface potential is plotted for a relatively insulating layer in which the ZnO grains are in thermal equilibrium with the surrounding oxygen (dark adapted sheet) and for a semiconducting layer in which the excess free carrier concentration did not yet decay from a previous exposure to light (light adapted sheet). The

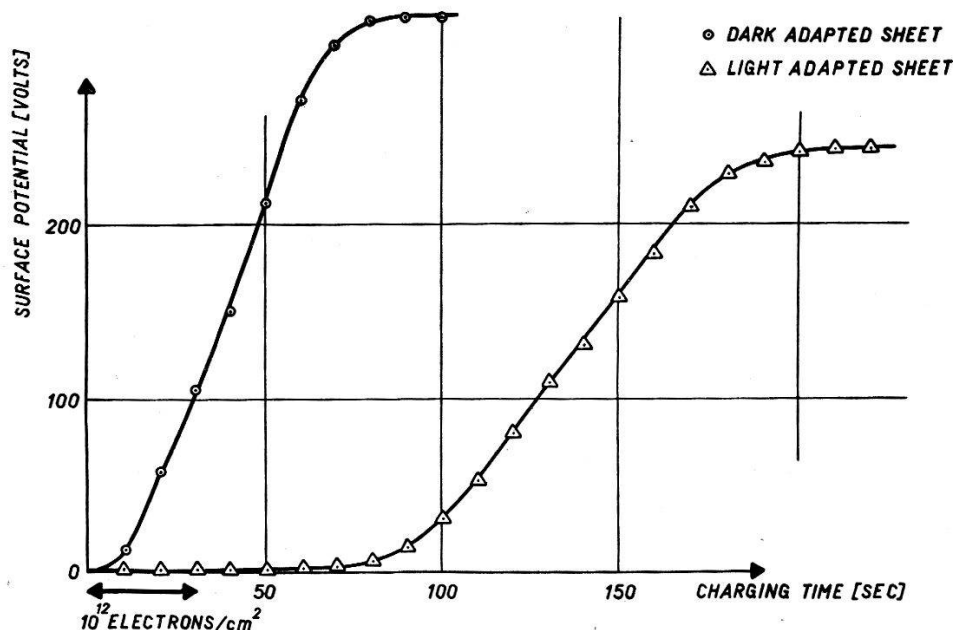


Fig. 3. Charging curves of a "dark adapted" and a "light adapted" ZnO layer.

charging time is plotted along the abscissa and is a measure of the amount of charge incident on the layer. On the ordinate the negative surface potential of the layer is plotted.

In case of the "dark adapted" layer (left curve) the surface potential of the ZnO layer rises almost immediately when the corona discharge is applied until finally saturation occurs. In case of the "light adapted" layer (right curve) the charging curve deviates in the following ways from that of a "dark adapted" layer:

1. When the corona discharge is started, a certain amount of negative charge strikes the layer without raising its surface potential essentially above zero.
2. In the region where the potential rises, the slope of the increase in potential is about a factor of 2 smaller than in the case of a "dark adapted" layer.
3. The saturation of the potential as a function of the incident charge in the "light adapted" state occurs at a lower potential than in the "dark adapted" state.

E. Discussion.

The charging of a "dark adapted" layer approaches the charging of a simple condenser. Since, by virtue of the high thermal equilibrium resistivity, the electron depletion layer will be larger than the thickness of the ZnO layer, most of the positive charge is localized on the grounded back electrode and only little in the positive space charge region in the ZnO layer.

If the depletion layer thickness is computed from the free carrier density ($\sim 10^3/\text{cm}^3$) above, the thickness is some meters and is unrealistically large. A more significant value is obtained by adding the density of trapped electrons at the thermal equilibrium value of the Fermi level (see II), namely $10^{14}/\text{cm}^3$. For this density of available charge, the depletion layer is 10^{-2} cm thick or about five times the actual layer thickness. This thickness is sufficient to account for the simple condenser behavior.

In the case of the light adapted layer, the conductivity at the free surface was relatively high owing to the strongly absorbed component of the light. The volume conductivity, while several powers of ten higher than in the dark adapted state was still considerably lower than the conductivity at the surface. The result was that when the first oxygen ions were deposited on the surface, the "available" (i.e. free and shallow trapped) electrons from only the surface layers were forced to leave the zinc oxide layer and go into the grounded electrode. The dipole thickness formed by the negative oxygen ions and the positive charges left behind by draining off the "available" surface electrons was probably less than 10^{-5} cm. For such a small dipole layer thickness the voltage built up in the first 70 seconds of charging time may be computed to be less than a volt as observed in Fig. 3. When the available surface electrons are exhausted, further charging forces available electrons out of the volume of the zinc oxide layer. The dipole layer thickness then becomes larger and a significant rise in surface voltage is observed corresponding to the part of the curve in Fig. 3 beyond 70 seconds.

From the slope of this part of the curve, the thickness of depletion layer may be computed to be about 1×10^{-3} cm or half the actual thickness of the zinc oxide powder layer. The density of available electrons needed to give a 10^{-3} cm thick depletion layer is $4 \times 10^{15}/\text{cm}^3$ and fits in well with independent photo conductive observations showing a rise in trap density near the Fermi level as the latter moves from its "dark adapted" value towards the conduction band.

The fact that high insulation is obtained in only a few seconds by a heavy corona deposit of negative oxygen ions whereas some

hours are required when the oxygen is thermally adsorbed on the individual grains is quantitatively accounted for in paper II. It need only be mentioned here that the removal of a free electron by thermally adsorbed oxygen requires 10^{-4} sec while the removal of a free electron by an applied field requires only 10^{-8} sec. This is the same ratio of recovery times just referred to. The inclusion of the densities of trapped electrons in this argument increases both times by a factor of 10^8 so that the characteristic observed times are in the range of seconds and hours respectively.

Passing mention should be made of the fact that the charge storage time of "light adapted" zinc oxide layers was considerably less than a second when charged with a positive corona in contrast to about 10^5 seconds when charged with a negative corona. These two charge storage times are a measure of the forward and back currents of the zinc oxide layer regarded as a rectifier. The rectification ratio is then at least 10^6 and the back current is in the order of 10^{-11} amps/cm² at 200 volts.

F. Acknowledgements.

The present paper is part of an investigation of the basic physical processes occurring in a new electro-photographic technique developed by C. J. YOUNG*) and H. G. GREIG*). The writers have profited from their experience and are indebted to them for most of the materials used in this work. During the later stages of the work, the writers have also had many helpful discussions with J.A. AMICK*).

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*) RCA Laboratories, Princeton, New Jersey.