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Effects of an Electrically Conducting Layer at the Zinc Oxide Surface

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Measurements of the electrical properties of high-resistivity zinc oxide (ZnO) are strongly influenced by the sample ambient. Temperature-dependent Hall-effect measurements were performed on Li- and Cu-doped bulk crystals in both air and vacuum. Repeating the measurements under a given test ambient produced stable results. Changing the ambient systematically changed the measured results. We explain this behavior in terms of a surface conducting channel that exists in vacuum but is destroyed upon exposure to air. We propose that the surface conducting layer is eliminated in air due to changes of the surface condition. Repeating the measurements under a given test ambient produced stable results. Changing the ambient systematically changed the measured results. We explain this behavior in terms of a surface conducting channel that exists in vacuum but is destroyed upon exposure to air. We propose that the surface conducting layer is eliminated in air due to changes of the surface condition. This feature of the untreated ZnO surface may relate to reports of large scatter and poor reproducibility of electrical data on p-type ZnO samples. [DOI: 10.1143/JJAP.44.7271]

KEYWORDS: ZnO surface, electron accumulation layer, Hall-effect measurements, electrical conductivity

ZnO is a promising material for electronic and optoelectronic devices due to its fascinating physical properties (e.g., wide band-gap, high excitonic binding energy, high saturation velocity, and large piezoelectric fields) and the ability to fabricate heterostructures by using MgZnO or CdZnO alloys. Potential devices include high power, high speed or high temperature electronics and blue or UV light emitters. In addition, ZnO shows promise for nanostructured or high temperature electronics and blue or UV light emitters. In addition, ZnO shows promise for nanostructured or high temperature electronics and blue or UV light emitters. In addition, ZnO shows promise for nanostructured or high temperature electronics and blue or UV light emitters. In addition, ZnO shows promise for nanostructured or high temperature electronics and blue or UV light emitters.

Unusual interaction of ZnO with the environment was shown, for example, with hydrogen and oxygen. The chemisorption of ambient gases at the ZnO surface is known to have a significant influence on the surface conductivity of ZnO crystals. The surface properties particularly impact ZnO nanostructures due to their large surface to volume ratio.

In the late 1970s and early 1980s electron accumulation layers at the ZnO surface were studied considerably. This electron accumulation layer has been produced by exposure to atomic hydrogen or He ions as well as irradiation with electrons or UV light. Annealing of the samples usually destroys the accumulation layers irreversibly. In contrast, here we report a surface conducting channel that appears upon annealing in a modest vacuum in the dark without additional effort. It appears to be the native intrinsic state and, therefore, is relevant for the interpretation of electrical measurements (e.g., Hall results), may influence growth since the formation energy of defect generation depends on the Fermi level, and is significant for fabrication of devices such as Schottky contacts. Despite the renewed interest in ZnO, a detailed study of the surface properties, in particular, their influence on the electrical behavior of crystalline ZnO, has remained to be reassessed.

Most of the semiconductor device applications are currently hampered by the lack of control over the electrical conductivity. As-grown ZnO usually exhibits n-type conductivity, and the cause for this residual doping is heavily debated. Recent reports on the p-type electrical properties of ZnO have been based on measurements conducted under only a single set of experimental conditions, for example, in vacuum or in the dark. There has been very little assessment of the effect of the ambient on the measurements of the electronic properties of ZnO. In this paper we demonstrate that the electrical properties of high resistivity ZnO bulk material are dominated by the surface. We also suggest that failure to recognize and control this phenomenon may have been a contributing factor in numerous reports of irreproducibility and extreme scatter in measurements of electrical conductivity in ZnO. In particular, the electrical behavior of epitaxially grown p-type films might be completely obscured by the surface conductance.

The basic phenomenon that we have observed is illustrated in Fig. 1 with an electrical measurement on high-resistivity ZnO. The sample is a platelet of Cu-doped bulk ZnO that has been metallized in the Van der Pauw geometry for resistivity and Hall-effect measurements. The figure shows the time dependence of the measured resistivity at a constant temperature of 305 K after turning off the vacuum pump and venting the sample chamber to the laboratory ambient. The resistivity rises by nearly one order of magnitude over a period of several hours. We hypothesize...

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Fig. 1. Resistivity of a Cu-doped ZnO bulk sample monitored as the sample ambient was changed from vacuum to air.
that this response arises from an electrically conducting surface channel that is present for a relatively clean surface, which results in a low resistivity. Evidence for the presence of this surface conducting channel is presented below. Exposure of the surface to ambient air destroys the surface channel and leads to a high resistivity. The transition process is reversible, as shown below. By annealing the sample at high temperatures the transition between the two states can be accelerated. The destruction of the surface channel progresses at a low rate at 305 K as shown in Fig. 1, whereas the recovery process requires much higher temperatures (>500 K) to be activated.

Multi-temperature-cycle Hall measurements were performed between 80 and 730 K with a Van der Pauw contact geometry on various doped and undoped bulk samples. The samples were grown by the pressurized melt-growth technique and cut into rectangular platelets sized 5 × 5 mm². The sample thickness is about 0.5 mm. Ti/Au contacts were thermally evaporated in the four corners of the samples. Hall measurements on samples with high n-type background (e.g., unintentionally doped, N-doped or K-doped bulk crystals) typically revealed resistivity values of 0.2 Ω cm, carrier concentrations of 5 × 10¹⁷ cm⁻³ and mobilities of 100 cm²/(V s) at room temperature. At 730 K these values change only slightly [0.3 Ω cm, 3 × 10¹⁷ cm⁻³, 30 cm²/(V s)]. Their electrical properties remain stable even upon changing the environment (e.g., from vacuum to air).

This is completely different for high resistivity samples in which the n-background is highly compensated by Li- or Cu-doping. Their room temperature resistivity is much higher than in the unintentionally doped samples (>10⁸ Ω cm (Cu-doped), >10⁶ Ω cm (Li-doped)). We performed SIMS analysis (Secondary ion mass spectroscopy) indicating doping concentrations in the order of 10²¹ cm⁻³ (Cu-doped), 10²⁰ cm⁻³ (Li-doped). Unfortunately, these results are not based on suited SIMS standards which results in large error bars. However, the fact that the n-background doping of 5 × 10¹⁷ cm⁻³, which we see in the unintentionally doped sample grown by the same method, is highly compensated suggests doping concentrations larger than 10¹⁸ cm⁻³.

Beside a high resistivity these Li- or Cu-doped samples exhibit pronounced changes under temperature-cycled measurements in various ambient conditions. Figure 2 shows the temperature-dependent resistivity of a Li-doped bulk sample in air and vacuum. Before the first measurement the sample was exposed to ambient air for several weeks. Without any additional treatment it was installed in the Hall chamber, which was flooded with ambient air. The first temperature cycle revealed a change in resistivity of over seven orders of magnitude, but the sample returned to the high-resistivity starting point upon completing the temperature cycle. After evacuating the chamber to <0.1 Pa, the second temperature cycle was performed. The resistivity again decreased from >10⁸ Ω cm (300 K) to almost 10⁵ Ω cm (650 K), as observed during the first temperature cycle, but this time reaches only <10⁵ Ω cm upon completion of the temperature cycle. A third temperature cycle was performed immediately upon completion of the second cycle and the temperature-dependent resistivity curve is observed to closely track that of the preceding cycle. After turning off the vacuum and flooding the chamber with ambient air, it was possible to return to the high-resistivity starting point by performing a number of temperature cycles.

Cu-doped bulk crystals behaved similarly to the Li-doped samples discussed above. However, due to their higher conductivity it was possible to also measure the carrier mobility and concentration with high precision. The temperature-dependent resistivity, mobility and carrier concentration of a Cu-doped sample in vacuum and air are depicted in Figs. 3(a)–3(c), respectively. The data reveal that at room temperature (RT) the apparent carrier concentration is higher and the resistivity and effective mobility are lower in vacuum than in air. The RT mobility of the sample decreases from 60 cm²/(V s) in air to 10 cm²/(V s) in vacuum. All data indicated n-type conductivity.

As an explanation for the phenomena described above we propose that there exists an electrically conducting channel at the ZnO surface. Under vacuum this channel appears upon annealing. The channel is evident only for samples showing a high bulk resistivity, and it seems to be the “native” state of the ZnO surface. In this state the electrical bulk properties are obscured completely by the surface channel. A SiO₂ passivation layer that was deposited by electron beam deposition was found to preserve this surface channel. The low temperature properties of this channel reveal a constant carrier concentration. As indicated in Fig. 3(b) the carrier density in the channel is approximately 2 × 10¹² cm⁻², which appears reasonable for a surface channel. The carrier mobility within the channel is relatively low and further decreases with lowering temperature [Fig. 3(c)]. This suggests strong surface scattering and a thermally activated transport mechanism between localized states (e.g., a hopping process). The surface behavior of ZnO described above does not occur or is screened in the case of high n-type doping. Exposure to ambient air destroys the surface channel, most probably due to adsorption processes at the surface possibly in combination with surface reconstruction. In this regime the electrical properties are determined by the bulk properties of the crystal. In Fig. 3(b) the slope of the temperature-dependent carrier concentration in air reveals an activation energy of approximately 360 meV for the transport mechanism in the bulk crystal.
Fig. 3. Results from temperature-dependent Hall measurements on a Cu-doped ZnO bulk crystal in air and vacuum. (a) Resistivity. (b) Carrier concentration. (c) Mobility.

A similar observation of surface conductivity was previously reported for diamond. However, in that case the surface channel appeared only in air and was destroyed by exposure to ultra high vacuum. A mechanism was proposed in which a redox reaction in a thin adsorbed water layer provides the electron sink for a subsurface hole accumulation layer. This behavior turned out to be unique because of the low (even negative) electron affinity of diamond.

In contrast, the electron affinity of ZnO is high compared with other available semiconductor materials. The Fermi-level at the surface of ZnO is likely to be pinned at a position above the conduction-band-minimum. This pinning position is related to the fact that the conduction band of ZnO occurs at a low energy (below the vacuum level) on an absolute energy scale. A similar situation occurs in InN, where a high surface accumulation of electrons has indeed been reported. We thus expect that in this “intrinsic” state ZnO will exhibit a high surface conductivity due to the accumulation of electrons in the potential well near the surface.

Evidently, annealing in vacuum produces this “intrinsic” state, as we have shown that such anneals result in a low measured resistivity. When exposed to air, the samples become highly resistive. We hypothesize that this is due to adsorption of species which act as surface acceptors, and hence compensate the electrons that are present near the surface. This may coincide with surface reconstructions and the build-up of adsorbed molecules resulting in a reduced band bending. Hence, the smaller overlap of conduction band and Fermi-level diminishes the surface conductivity. The chemisorption of oxygen on ZnO surfaces is one candidate for this behavior. The adsorption at moderate temperatures involves an electron transfer from the semiconductor to the adsorbate and reduces the band bending.

In summary, annealing experiments have elucidated a new feature of ZnO samples that has profound consequences for electrical measurements. Samples that were measured to be semi-insulating (i.e., exhibiting a high resistivity) in their as-received state became conducting upon annealing up to about 650 K in vacuum. Since it is highly unlikely that impurity diffusion can take place in the bulk at these relatively modest temperatures, we propose that the observed effect is due to the surface. Indeed, subsequent annealing in air (as opposed to vacuum) recovered the original resistivity (an effect unlikely to be explained by motion of impurities in the bulk). We propose that there is an electron conducting surface channel that is present in vacuum but which disappears upon exposure to an air ambient. The fact that the measured conductivity of the sample exhibits such remarkable changes by annealing at modest temperatures and that the effect is so sensitive to the environment may shed light on the puzzling observations that have been reported in the context of p-type ZnO samples. Such samples have sometimes been observed to undergo type conversion, and are also known to change as a function of time. It is quite possible that uncontrolled surface conductivity was causally connected with such observations.

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