Bulk, interface and surface properties of zinc oxide

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Zinc oxide (ZnO) is a highly developed oxide semiconductor that has been widely employed in industry as varistor ceramics, transparent conductor films, surface acoustic wave resonators, and so on. However, many questions about its fundamental properties remain unanswered. For instance, density functional theory simulations are currently contradicting the common conception established by many experimental scientists that non-stoichiometry is the primary factor inducing the native conductivity of ZnO. Thus, it may be necessary to reconstruct the conceptual models of the solid-state chemistry and physics of oxide semiconductors. In this context, this paper gathers the knowledge and suggestions presented in previous studies and attempts to find directions for the next steps in further scientific and technological development of ZnO-related materials and structures.

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1. Introduction

Zinc oxide (ZnO) is a well-known ceramic material and has been used for many ceramic devices such as varistors. For example, because its conductivity can be controlled by doping, ZnO has been developed as a useful oxide conductor, and the piezoelectricity of ZnO is useful for electromechanical coupling devices such as surface acoustic wave resonators. In recent years, the scientific and technological development of ZnO materials has progressed significantly. For example, the quality of ZnO thin films has been improved, and high-quality bulk single crystals have become commercially available. Owing to these achievements, we can now precisely control the material properties and fabricate ZnO-based device structures. Indeed, many attempts to fabricate ZnO-based devices such as surface acoustic wave resonators and light-emitting diodes have made conducted worldwide.

Although a lot of research and development on ZnO-based materials and structures has been performed, there are still many unanswered questions. The most critical of these is which factor is responsible for the origin of native n-type conductivity of ZnO. In general, it has been accepted that native donors such as oxygen vacancies or zinc interstitials are formed in ZnO, and their concentration increases when ZnO is heated under a low oxygen partial pressure (P_po2) or a high zinc vapor pressure. In fact, some experimental studies have indicated that the electric conductivity of ZnO is correlated with its non-stoichiometry, and, indeed, the carrier concentration increases after annealing under a high zinc vapor pressure. As a consequence, n-type conduction of undoped ZnO has been attributed to those native defects for many years. However, recent investigations including a few theoretical studies have suggested the possibility that native n-type conduction is not caused by native point defects. Those theoretical studies have made two very important predictions: (1) that oxygen vacancies in ZnO do not create shallow donor levels and instead create very deep donor levels and (2) that zinc is very unstable in the interstitial position in ZnO. Thus, a new understanding of ZnO is needed to bridge the divide between the experimental results and theoretical predictions.

The native donor issue is the most fundamental problem, but first, some other questions remain unsolved. For instance, we do not have clear understanding of what the essential roles of additives in ZnO varistors are. In this paper, the research relating to these fundamental issues in the chemistry and physics of ZnO is reviewed in order to discuss the direction and strategy for solving these fundamental questions relating to ZnO and related materials.

2. Preparation of ZnO crystals

It is always true that high-quality single crystals are necessary for scientific investigation and technological developments, and this is also the case for research and development related to ZnO. For defect-related studies, the purity of the crystal determines the accuracy and reliability of the experimental results. For the growth of ZnO crystals, there is one critical problem: zinc is highly volatile, which makes growing a ZnO crystal from molten ZnO impractical. Therefore, bulk ZnO crystals are not easily obtained.

In 1990s to 2000s, there were two major developments in ZnO crystal growth: the growth of high-purity ZnO single crystals using a chemical vapor transport (CVT) method and the growth of large (>75 mm in diameter), high-crystallinity ZnO single crystals using the hydrothermal (HT) method. Figure 1 shows a ZnO ingot grown using the HT method. Indeed, the production of high-purity crystals made a huge contribution to our understanding of the solid-state physics of ZnO, in that it allowed optical detection of the impurity- and defect-related electronic states. On the other hand, the fabrication of crystals using HT methods has made a great contribution to development of device structures, which can now be fabricated using homoepitaxy because of the availability of a commercial supply of ZnO wafers with high crystallinity. Thus, the crystals produced using the CVT and HT methods have led to significant advances in ZnO science and technology.
However, those methods are not very convenient for the growth of doped crystals or alloy crystals, especially since they use the vapor phase or aqueous phase and can be regarded as purification methods. A possible way to grow ZnO with extrinsic elements is to use an inorganic solvent (flux) for ZnO growth. The concept of such flux methods is shown in Fig. 2. Indeed, large-scale (>50 mm in diameter) bulk crystals of (Zn,Mg)O alloy and doped ZnO have been produced using a seeded flux method called liquid phase epitaxy (LPE). The concept of the LPE growth method is also shown in Fig. 2. In this process, the growth of a large crystal requires a large substrate, and so the large ZnO wafers obtained using the HT method enable the large-scale LPE growth of doped ZnO crystals and ZnO-based alloy crystals. Then, self-stand (Zn,Mg)O alloy wafers can be obtained by simply removing the substrate after the LPE process. In this way, the LPE technique enables us to assess the bulk properties of ZnO-based alloys and doped ZnO, as described later.

### 3. Electric conductivity of bulk ZnO

#### 3.1 Nominally undoped ZnO

The most important physical properties of ZnO used in industrial applications is its electric conductivity. Typical results of Hall effect measurements of bulk ZnO single crystals grown using the CVT and HT methods (hereafter, these are called CVT crystals and HT crystals) are shown in Fig. 3. For the CVT crystals, the presence of a shallow donor is indicated by the relatively small slope describing the temperature dependence of the electron concentration \( n[^e] \). On the other hand, the slope of the \( n[^e]-T^{-1} \) plot for the HT crystal is much larger than that of the CVT crystal. The large activation energy for electric carriers in HT crystals is often explained as due to contamination with acceptor elements, i.e., lithium, used as mineralizers during HT growth. In fact, a relatively high concentration of Li, on the order of \( 10^{18} \text{ cm}^{-3} \), could be found in the as-grown HT crystals. It is also well-known that annealing the HT crystal to remove Li reduces its electric resistivity. The electron mobility \( \mu[^e] \) of CVT crystals reaches \( 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) at room temperature and increases with increasing temperature owing to the reduction in the scattering of carriers by phonons. For the HT crystals, \( \mu[^e] \) depends on the impurity concentration, and high-purity HT crystals also show high \( \mu[^e] \) values around \( 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) at room temperature.

As mentioned above, the observation of shallow donors in high-purity (99.9999% grade) CVT crystals led to the current discussion of whether native defects such as oxygen vacancies and zinc interstitials are the origin of the conductivity. DFT calculations have predicted that such native defects cannot lead to the formation of shallow donor states. Instead, the researchers proposed that hydrogen that was unintentionally incorporated into the ZnO is the origin of the shallow donor states in nominally undoped ZnO. Therefore, experimental studies on intentional hydrogen doping have been performed extensively after this prediction. For instance, a remote plasma technique has been used for intentional doping of hydrogen in to ZnO.
indicated in Table 1, it has been demonstrated that hydrogen incorporation increases \( n[e] \) in ZnO.\(^{2,3} \) The hydrogen concentration analyzed by secondary ion mass spectrometry\(^{33} \) and the \( n[e] \) values determined by Hall effect measurements\(^{34} \) were in good agreement, close to \( 1 \times 10^{19} \text{cm}^{-3} \), which provides evidence that the hydrogen inserted into the ZnO lattice actually induces the shallow donor state in ZnO.

These results confirm that hydrogen is one of the impurity elements causing the electric conductivity of ZnO. However, it is still difficult to conclude that native defects such as oxygen vacancies are not the origin of the shallow donor state in nominally undoped ZnO and that hydrogen is the only reason for the conductivity of nominally undoped ZnO. For instance, it is true that hydrogen impurities form very shallow donor levels, but it is also true that the hydrogen in ZnO is not thermally stable.\(^{35} \)

Therefore, the conductivity of ZnO quenched from high temperatures is not easily explained as due to hydrogen impurities. A serious hazard for investigations of the effects of defects in ZnO is impurities in the source materials. For instance, photoluminescence (PL) measurements performed at low temperatures revealed that even high-purity CVT crystals\(^{24} \) exhibit bound-exciton luminescence originating from group III impurities. On the other hand, quantitative analyses of very minor impurities, such as Ga with an abundance on the order of \( 10^{15} \text{cm}^{-3} \), are not very easy to perform. Thus, further investigations are needed to reach to the final answer to whether native donors cause the conductivity. Here, it should also be emphasized that role of hydrogen impurities in oxides must be further investigated. For instance, the hydrogen concentration in some oxide semiconductors reaches \( \sim 10^{20} \text{cm}^{-3} \) (\( \sim 1 \text{mol\%} \)), and controlling the reaction between an oxide semiconductor and humidity is likely an essential matter for controlling its properties.\(^{36,37} \)

### 3.2 Doped ZnO

It is well-known that ZnO heavily doped with impurities such as Al, Ga, and In shows a very low resistivity on the order of \( 10^{-3} \Omega \text{cm} \).\(^{38-41} \) Here, it should be noted that the electric conductivity (or \( n[e] \)) of heavily doped ZnO is sensitive to the growth conditions, such as the oxidation conditions.\(^{42} \) It is also notable that physically deposited ZnO films often show high conductivity, even if they are not intentionally doped.\(^{43} \) For the most part, such very high conductivity (or high \( n[e] \)) appears in metastable or non-equilibrium systems. In fact, heavily In-doped ZnO thin films exhibiting high conductivity transform to the so-called homologous layered structure expressed as \( \text{In}_2\text{O}_3(\text{ZnO})_m \) after annealing.\(^{39,40} \) It is also notable that the metastable structure appears not only in heavily doped systems but also in alloy systems. For instance, (Zn\(_{1-x}\)Mg\(_x\))O alloy with \( x \approx 0.5 \) can be obtained by physical deposition, e.g., pulsed laser deposition, but the solubility limit of MgO in the ZnO lattice is approximately \( x = 0.15 \) at around 1000°C.\(^{54} \) For investigations of the fundamental properties of ZnO, we need to find the material parameters under thermal equilibrium. In this respect, the developed bulk crystal growth methods have been very useful.

The highest dopant concentrations recorded in our studies are listed in Table 2. One of the conventional ways to determine solubility limit at elevated temperatures is to measure the concentration profile of the impurities in the samples prepared by ion implantation, as described in the literature.\(^{43,46} \) For instance, as shown in Fig. 4, the dopant concentration in the implanted and annealed sample shows a plateau, and the dopant concentration at the plateau corresponds to solubility limit. In contrast, correlating the lattice parameter to the dopant concentration is not a very useful way to evaluate the dopant solubility, because lattice parameters do not change much for low impurity concentrations. As can be seen in the table, the solubility of group III dopants in the ZnO lattice is close to \( 0.1 \text{mol\%} \) (\( 4 \times 10^{19} \text{cm}^{-3} \)). The results shown in the table also indicate that dopant solubility increases with increasing preparation temperature. It is also notable that the \( n[e] \) in ZnO doped with group III elements is very close to the concentration of those impurity elements if the samples were prepared under equilibrium conditions.\(^{28} \)

### 3.3 Codoping

“Codoping” is a memorable term in the history of ZnO. In particular, there has been a race to obtain p-type ZnO around the world, and there was a theoretical prediction that codoping both nitrogen and a group III element could lead to p-type ZnO.\(^{47} \) Thus, numerous studies were launched to examine the effects of codoping both theoretically and experimentally. In this paper, one example of codoping is illustrated.\(^{48} \) Figure 5 shows the \( n[e] \) in polycrystalline ZnO codoped with Al and Li. For the nominally undoped sample, \( n[e] \) was nearly constant regardless of whether

<table>
<thead>
<tr>
<th>Element</th>
<th>Temperature (°C)</th>
<th>Concentration (cm(^{-3}))</th>
</tr>
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<tbody>
<tr>
<td>Ga(^{11} )</td>
<td>800</td>
<td>( 1 \times 10^{19} )</td>
</tr>
<tr>
<td>850</td>
<td>( 2 \times 10^{19} )</td>
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</tr>
<tr>
<td>900</td>
<td>( 4 \times 10^{19} )</td>
<td></td>
</tr>
<tr>
<td>Al(^{22} )</td>
<td>800</td>
<td>( 1 \times 10^{19} )</td>
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<tr>
<td>Ga(^{22} )</td>
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<td>800</td>
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</tr>
<tr>
<td>850</td>
<td>( 1.3 \times 10^{19} )</td>
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![Fig. 4](image-url)

**Fig. 4.** Indium concentration profiles of as-implanted and annealed ZnO single crystals. [T. Nakagawa et al., *Jpn. J. Appl. Phys.*, 47, 7848–7850 (2008).]
the annealing was carried out in Ar gas or O₂ gas. However, the \( n[e] \) of the codoped sample was very sensitive to the annealing atmosphere, even if the concentrations of Al (\( n[Al] \)) and Li (\( n[Li] \)) were the same. If we assume that Al and Li can compensate each other as follows, there is no need to consider \( P_{\text{O}} \) during annealing:

\[
\text{Li}_2\text{O} + \text{Al}_2\text{O}_3 \rightarrow 2\text{Li}^{+}_{\text{Zn}} + 2\text{Al}^{+}_{\text{Zn}} + 4\text{O}^-_\text{O} \quad (1)
\]

However, the experimental results indicate that Al-donor characteristics appear after annealing in Ar gas, whereas the compensation described in Eq. (1) appears after annealing in O₂ gas. Therefore, we need to consider whether Li ions always sit at substitutional Zn sites or not, because Li ions have relatively small atomic radii and can probably sit at interstitial sites. At any rate, it is evident that native defects contribute to the charge compensation behavior in codoped, nominally compensated ZnO.

Next, the effect of annealing on the \( n[e] \) in nominally undoped ZnO is discussed. As shown in Fig. 5, the \( n[e] \) of nominally undoped ZnO varies slightly with annealing conditions. In fact, the \( n[e] \) in nominally undoped ZnO slightly increased after annealing in Ar gas, indicating that annealing under a relatively low \( P_{\text{O}} \) causes \( n[e] \) to increase. However, this result is not conclusive evidence that native defects cause the native donor states. As shown in Fig. 6, sintering ZnO in a conventional tube furnace causes surface contamination, particularly with Li and Al, and as shown in Fig. 5, ZnO codoped with Li and Al responds to the annealing conditions. Thus, there is a possibility that the very slight change in the \( n[e] \) of the nominally undoped ZnO is due to the presence of a very small amount of unintentional impurities. This is, indeed, the most serious problem in studying the annealing was carried out in Ar gas or O₂ gas. However, the the concentration of unintentional impurities is known with sufficient accuracy. Therefore, whether the conductivity of nominally undoped ZnO is due to native defects is an unanswered question right now. I personally desire further development of the state-of-the-art technology for materials synthesis and characterization for solving this question. In addition, we must not forget about the contributions of kinetics. It is possible that metastable structures are formed in ZnO even after high-temperature treatment. From this viewpoint, a very clean environment that can provide insignificant impurity incorporation even after 1-year-long high-temperature annealing is desirable to perform experiments to obtain the final answer for the unsolved questions.

4. Grain boundaries in ZnO ceramics and films

The grain boundary (GB) properties of ZnO have been extensively studied, because they directly affect the performance of ZnO-based structures and devices. In particular, the rectification behavior originating from the potential barrier at the GBs has been utilized to fabricate ZnO varistors, and, on the other hand, mitigating the electron scattering at GBs has been a strategy for improving the electric conductivity in transparent electrode films made from ZnO.

Owing to the development of methods for the growth of bulk single crystals, artificial grain boundaries can now be prepared in ZnO, and many studies on artificial GBs have been reported. The most important result is that obvious rectification behavior is not obtained at the artificial GBs made by direct bonding of two ZnO single crystals. On the other hand, obvious rectification behavior such as that observed in polycrystalline varistor ceramics is only obtained when an insulating layer is inserted between two ZnO single crystals. In fact, since the invention of ZnO varistors, transition metal doping, particularly doping with Co, and the presence of a GB layer such as a Bi₂O₃ layer have been considered essential for obtaining highly nonlinear current–voltage (I–V) characteristics at GBs in ZnO varistor ceramics. The results of these artificial GB studies confirm that both of those two conditions are really necessary for obtaining very steep junction breakdown behavior. However, to the author’s knowledge, no reasonable explanation of the role of the transition metals in ZnO varistors has been proposed. As indicated in the previously published paper, it is likely that Co-doping of ZnO did not affect the electric transport properties of bulk ZnO so it is probable that the transition metal doping affects the interface/surface properties of ZnO.

The results of the artificial GB studies indicate that the GBs in polycrystalline ZnO are not very active when the ZnO is not doped with transition metals. This raises the question of whether the GBs in polycrystalline ZnO thin films cause their very low \( \mu[e] \). The relatively low \( \mu[e] \) in polycrystalline ZnO films has often been discussed in terms of potential barrier formed at the GB. Indeed, \( \mu[e] \) in ZnO films shows thermal activation and/or further strange behavior, indicating that a localized state contributes to the lowering of \( \mu[e] \). However, there is another possible explanation of the relatively low \( \mu[e] \) in polycrystalline ZnO films, namely, that each ZnO grain contains many defects causing carrier scattering. Films with low \( \mu[e] \) often show very high diffusivity of the anions and cations in their lattice, which
means that these films do contain many defects, and physical deposition of ZnO films, particularly at lower temperature, is one cause for the formation of metastable structures, as mentioned. Therefore, defects must be considered in discussions about the degraded $\mu(e)$ in polycrystalline ZnO films.

5. Polarity of ZnO

One hint suggesting the answers to the questions regarding the GB properties of ZnO is their polarity dependence. Since ZnO has a wurtzite-type lattice, it has electric polarization along the c-axis. In other words, one of two c-faces of ZnO, i.e., the (0001) surface, is terminated by Zn and the other, the (0001) surface, is terminated by O. In fact, in some reports,\textsuperscript{54,57} it has been suggested that the current transport at the artificial GBs made from ZnO single crystals depends on the polarity of the ZnO. This behavior indicates that the contact between the (0001) face of ZnO and Bi$_2$O$_3$ shows deeper breakdown behavior than the contact between the (0001) face of ZnO and Bi$_2$O$_3$. The origin of such polarity-dependent junction properties has not been well-understood till now. The effects of polarity on the junction properties are also important for the formation of a two-dimensional electron gas at the ZnO/(Zn,Mg)O interfaces.\textsuperscript{59} One possible reason for the polarity dependent properties is internal electric polarization due to the crystalline symmetry. Indeed, the X-ray photoelectron spectra obtained from (0001) and (0001) faces of wurtzite-type structures are different from each other, as shown in Fig. 7.\textsuperscript{61–63} It is noted that the impurity incorporation behavior also depends on the crystalline polarity. In particular, the defect structure and impurity concentrations in the crystalline sectors with the (0001) and (0001) faces are different from each other.\textsuperscript{64–66} Hence, the difference between the impurity concentrations in the (0001) and (0001) sectors is another possible reason for the observed polarity-dependent features. Further study is needed to clarify the role of crystalline polarity on the electronic structure of the polar surfaces and interfaces involving the polar surfaces.

6. Summary

The properties and characteristics of ZnO semiconductors have been reviewed. Thanks to the development of new methods for materials synthesis and characterization, some important facts have been discovered. First, it was found that hydrogen has a significant effect on the electronic and optical properties of ZnO. Second, polarization along the c-axis is likely important not only for the piezoelectricity but also for electron transport through the polar surface. However, several very important questions remain unanswered. In particular, the origin of the electric conductivity in nominally undoped ZnO is still unclear. To obtain a clear answer to this question, further developments in materials synthesis technology, such as purification of the source material, and further development of materials characterization techniques, such as quantitative analysis of very minor impurities, are absolutely needed. In the future, the author wishes to investigate the essential physics and chemistry governing the properties of ZnO and related materials and devices in order to enable the development of the electric devices necessary for sustainability of modern human life.

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References


Fig. 7. Valence band spectra of ZnO obtained from different facets. The polarity dependence can clearly be seen for the spectral feature around 5 eV. [J. Williams et al., Appl. Phys. Lett., 100, 051902-1–3 (2012).]


Naoki Ohashi received PhD from Department of Inorganic Materials, Faculty of Engineering, Tokyo Institute of Technology in 1992. He served as an assistant professor in the same department in 1993–1999. After one year appointment in Department of Materials Science and Technology, Massachusetts Institute of Technology, he joined National Institute for Research in Inorganic Materials (NIRIM), Japan as a senior researcher in 2000. NIRIM was reorganized as National Institute for Materials Science (NIMS) in 2001 and he has been the director of Environment and Energy Materials Division, NIMS since 2011. His specialty is structure-composition-property relationship in inorganic materials.