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High Conductivity in Gallium-Doped Zinc Oxide Powders

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Gallium-doped zinc oxide powders have been prepared with electrical conductivities at 25 °C as high as 300 Ω^{-1} cm^{-1}, more than 1000 higher than previously reported. All materials prepared can be represented as $Zn_{1-x}Ga_xO$, $Zn_{1-y}Ga_yO_{1+(y/2)}$, or a combination of these two. For $Zn_{1-x}Ga_xO$, the room-temperature conductivity increases monotonically with increasing x up to 2.7%, which is the limit of Ga solubility for this formulation at our synthesis temperatures of 1000 to 1200 °C. Conductivities measured from 4.2 to 500 K showed only a very small temperature dependence. An ESR peak ($g = 1.96$), attributed to the conduction electrons, broadens with increased doping level. The hexagonal unit-cell edges increase with increasing x over the entire range of x. For the low conductivity $Zn_{1-y}Ga_yO_{1+(y/2)}$ series, the level of Ga substitution can reach at least 4.0%.

Introduction

Zinc oxide based materials have many interesting and useful properties. Applications of such materials are especially attractive on consideration of the low cost and lack of toxicity of zinc oxide. Important uses of zinc oxide include catalysts, luminescent materials, fungicides, surface acoustic wave devices, varistors, and transparent conductors. So-called transparent conductors have low optical absorption in the visible region of the optical spectrum and are good electrical conductors. Other transparent conductors such as SnO_2:Sb, In_2O_3:Sn, and Cd_2SnO_4 are toxic and/or more costly. Some applications of transparent conductors require films. Examples of these applications are transparent electrodes for optoelectronic devices, transparent heat mirrors for solar energy utilization, and coatings to heat the surface of glass windows. Powders of transparent conductors also have important applications such as additives to polymers and paper to prevent buildup of static electricity. Highly colored conductors such as carbon are undesirable in some of these applications.

Electrical transport properties of doped zinc oxide have been reported for sintered specimens, single crystals, and thin films. Only n-type doping enhances conductivity. Work prior to 1959, mainly on sintered specimens and single crystals, has been reviewed by Heiland et al.[1] The conductivity of unintentionally undoped zinc oxide[2] is reported to be as high as $\sim 4 \times 10^{-3}$ Ω^{-1} cm^{-1} at 400 °C. However, it is our observation that the conductivity of zinc oxide is highly dependent on its impurity level. Very low doping levels can result in conductivity variations of many orders of magnitude. Thus, reports of good conductivity in undoped zinc oxide are presumably due to unintentional doping. Lower valent cations such as Li^+ substituting for Zn^{2+} do not produce p-type conductivity but instead decrease conductivity. Many higher valent cations substituting for Zn^{2+} cause an increase in conductivity. Most of the literature on zinc oxide does not indicate the purity of the zinc oxide used and does not discuss contamination issues. Thus, this literature is of little value when attempting to understand the transport properties of undoped zinc oxide.

The conductivity of zinc oxide samples has been found to increase after heating under low oxygen partial pressure,[3] under hydrogen,[4] or with zinc vapor.[5] These different treatments have not necessarily produced different materials. The effect in all three cases is likely to be the same; that is, to increase the cation-to-anion ratio in zinc oxide. Sintered zinc oxide pellets intentionally doped with another element have given conductivities of ~ 1 Ω^{-1} cm^{-1} at 400 °C for aluminum doping and $\sim 10^{-2}$ Ω^{-1} cm^{-1} at 400 °C for chromium doping.[5] In the case of gallium doping, conductivities of $\sim 10^{-2}$ Ω^{-1} cm^{-1} at 600 °C and ~ 10 Ω^{-1} cm^{-1} at 800 °C have been reported.[6,7] We have synthesized doped zinc oxide thin films[8] and powders. The conductivities that we report here on Ga-doped zinc oxide powders are the highest such values reported for any doped zinc oxide powders and are also higher than reported for doped SnO_2 powders.

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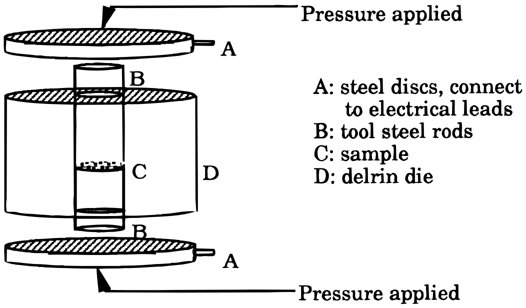

Figure 1. Schematic of the conductivity measuring cell. Parts A and B were gold plated for good electrical contact.

Experimental Section

Reagents were Ga metal (4N, Strem Chemicals), Ga_2O_3 (5N, Johnson Matthey), and Reagent Grade ZnO (99.7+%, Strem Chemicals) or high purity ZnO (5N, Johnson Matthey). We did not observe any difference in conductivities of samples prepared from high purity ZnO vs reagent grade ZnO. This is because our doping levels are much higher than the impurity levels in the zinc oxide reactants we employed. Thus, reagent-grade ZnO was used in the synthesis of samples reported here. Appropriate mixtures were ground together in an agate mortar and pestle before sealing in predried silica tubes under vacuum (~50−100 mTorr). Samples were homogeneous in color under an optical microscope after as little as 1 h heating at 1200 °C. Quenching samples from 1200 °C into cold water did not produce a noticeable change in the electrical conductivity of the products. Two standard synthesis conditions were then adopted. The samples were heated at either 1000 or 1200 °C for 10 h using heating and cooling rates of 300 °C/h. This heating time was used in an effort to ensure that equilibrium was achieved. Most of the samples were prepared from only ZnO and Ga metal according to the formula $ZnGa_xO$, where x is in the range 0.1−5.0%. These were then samples prepared under low oxygen partial pressure. Samples were also prepared at higher oxygen partial pressures by replacing some of the Ga metal with Ga_2O_3. Gallium-doped ZnO thin films were prepared by rf magnetron sputtering.[8]

The conductivities of Ga-doped zinc oxide powders were measured using the resistivity probe of a LakeShore AC susceptometer, Model 7000. Because the samples were in powder form, measured conductivities are affected by the powder density and contacts between grains. Thus, the conductivities were measured at various applied pressures. A schematic of the measuring cell is shown in Figure 1. The diameter of the pressing die is 0.5 in. The measuring contacts were gold plated to achieve low contact resistance; the short circuit resistance was ~0.0003 Ω. Typical samples were ~2 g with a thickness of ~3−5 mm and a density in the range 75−90% of theoretical. The samples used in the conductivity measurements were not ground after synthesis. The measured conductivities generally decreased slightly if the samples were ground. The conductivities of the powders also decreased slightly if they were removed from the cell and then measured a second time. These results suggest that conductivity is somewhat degraded when sintered agglomerates are broken up. The break up of the agglomerates was confirmed by SEM (Figure 2). The temperature dependence of the conductivity was studied from 4.2 to 500 K using the four-terminal technique on sintered pellets.

X-ray diffraction data and unit cell dimension refinements were obtained using a Siemens D-5000 diffractometer and its analysis program. Scanning electron microscopy (SEM) was used to evaluate morphology and particle size. Electron microprobe analysis (EMPA), based on wavelength-dispersive spectroscopy, was used to determine the actual dopant concentration of the doped powders. In the EMPA analysis, 5−15 points were probed. The average is used as the measured value, and the standard deviation is the error bar shown for that point. The solubility of the dopant was determined from these data. Hall measurements were used to determine the carrier concentration and mobility on thin films.[8] This approach was not considered readily applicable to powders. Therefore, the carrier concentrations for the powders were assessed through iodimetric titrations.[9] The apparent mobilities of doped ZnO powders were estimated using these carrier concentrations and the measured conductivities. The carrier concentrations obtained from iodimetric titrations are not necessarily free carrier concentrations because some of the titratable electrons may be trapped.

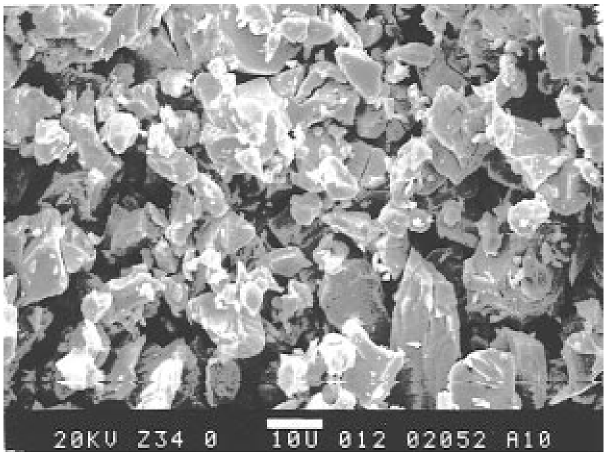

Figure 2. SEM micrograph of a 2% Ga-doped sample after being pressed at 4 tons/cm^2.

ESR studies were performed using a Bruker ESP 300 E ESR spectrometer operating at X-band (9.4 GHz). All spectra were recorded at room temperature. Highly conducting samples (such as those with more than 1 at. % Ga doping) were difficult to critically couple. Spectra were recorded with 100 kHz magnetic field modulation. The amplitude of the modulation was kept below 20% of the line width of the ESR signal.

Results

All the results presented refer to samples prepared at 1200 °C unless otherwise indicated. When prepared at low oxygen pressure (ZnO + Ga only), the Ga-doped zinc oxide powders showed a light blue color for low doping levels and a blue-black color for heavy doping. However, even the most highly colored products have the optical absorption typical of the so called transparent conductors. For example, 1-μm-thick films with a conductivity of ~1800 Ω^{-1} cm^{-1} showed greater than 85% transmittance of light in the visible range.[8] Powders of highly conducting zinc oxide do not show noticeable color in composites when used at the levels required to alleviate static electricity buildup. The light blue color of lightly doped zinc oxide lightened to white and the blue or black color to light green upon heating the powders in air to 900°C or above for 3 h. SEM showed that the particles are approximately equilateral (Figure 3). For samples prepared at 1200 °C, the particle sizes were ~15 μm for 0.5 at. % Ga doping and ~20 μm for 2 at. % Ga doping. Particle sizes were ~7 μm for 2 at. % Ga doping when a synthesis temperature of 1000 °C was employed. Higher temperatures and higher doping levels result in larger particles.

The X-ray diffraction data showed only clean ZnO type patterns. The X-ray cell dimension refinements showed that both a and c increased with doping and leveled off at a Ga reactant concentration of about 3 at. % (Figure 4). The expansions of a and c were less than

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(9) Wang, R. P.; Sleight, A. W.; Platzer, R.; Gardner, J. A. *J. Solid State Chem.*, in press.

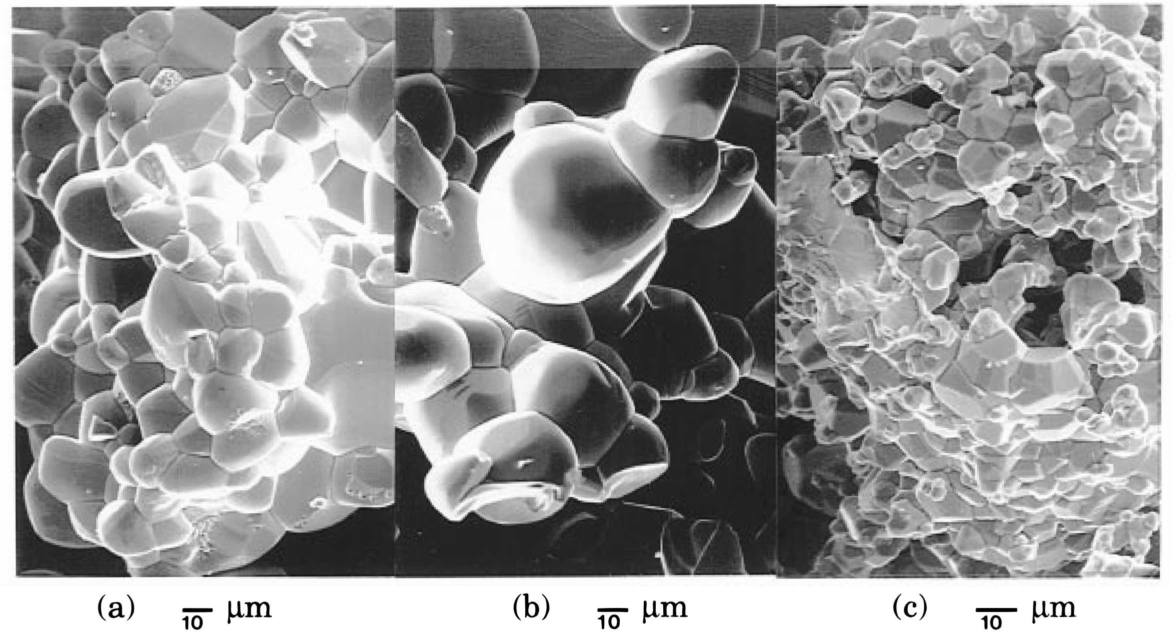

Figure 3. SEM micrographs of (a) 0.5% [1200 °C synthesis], (b) 2% [1200 °C synthesis], and (c) 2% [1000 °C synthesis Ga-doped ZnO powders.

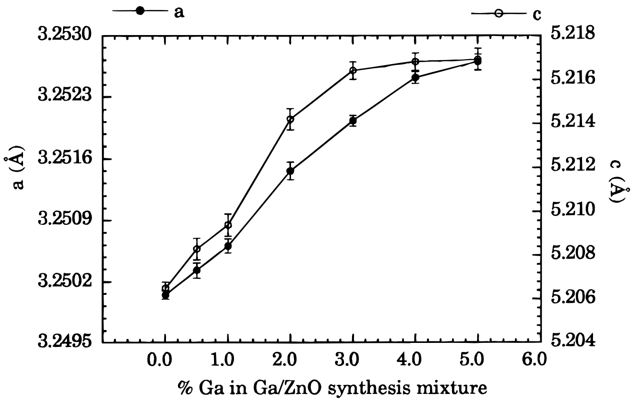

Figure 4. Cell dimensions of Ga-doped ZnO as a function of the percent Ga in the reactant mixture.

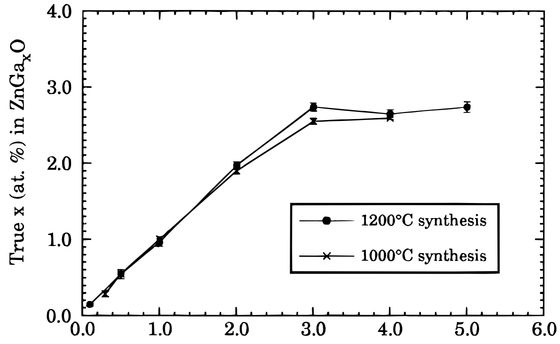

Figure 5. Actual doping level from EMPA of Ga-doped ZnO prepared with increasing atomic percent of Ga.

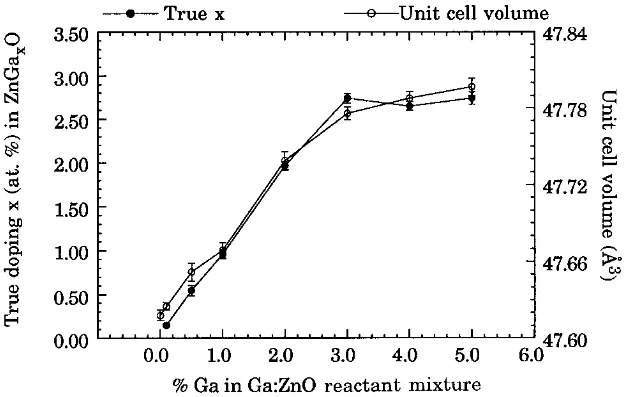

Figure 6. Actual doping level and the unit cell volume of Ga-doped ZnO obtained by increasing the percent Ga in the synthesis.

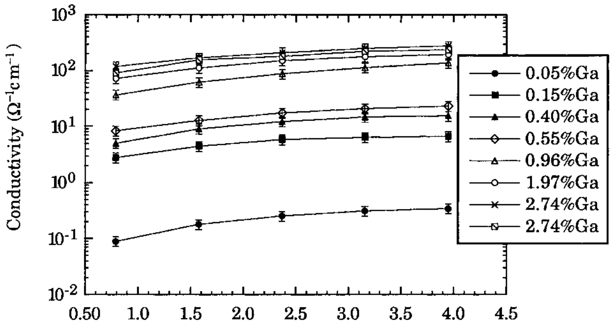

Figure 7. Conductivity of Ga-doped ZnO at various applied pressures. The dopings labeled are the true doping levels.

0.1% and 0.2%, respectively. EMPA gave a solubility limit of 2.7 at. % Ga in ZnO for equilibration at either 1200 or 1000 °C under metal vapors (Figure 5). Figure 6 shows the actual doping concentration and the unit cell volume for samples prepared with various starting compositions. The similarity of these two curves indicates the expansion of the lattice is directly related to x in $Zn_{1-x}Ga_xO$.

Figure 7 shows the conductivity measured at various applied pressures. The higher the pressure, the denser the powder and the better contact between the particles. Therefore, the measured conductivity increases with applied pressure. Higher Ga doping levels give higher conductivity. The conductivity measured at the pressure of 4 tons/cm^2 is used in other plots of conductivity. The error bars on all the conductivity plots are estimated to be 20% of the measured value. This estimation was based on repeated measurements of many

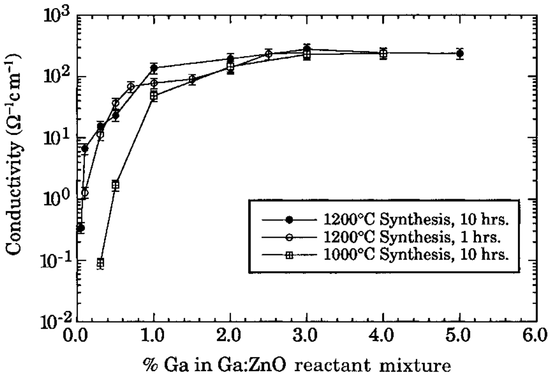

Figure 8. Conductivity of Ga-doped ZnO samples at two different synthesis temperatures.

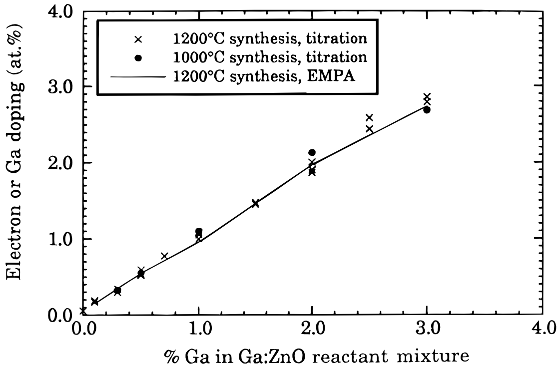

Figure 9. Apparent electron doping levels of Ga-doped ZnO obtained from iodimetric titration and the Ga-doping concentration analyzed by EMPA.

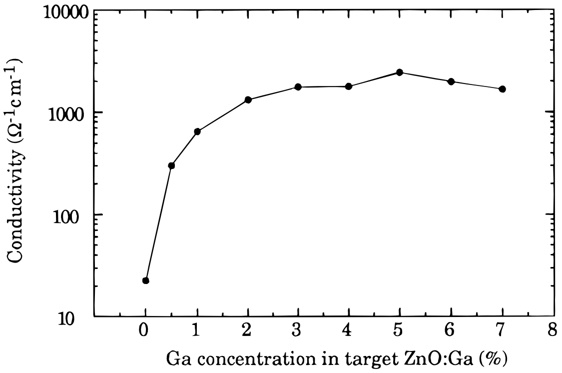

Figure 10. Conductivity of Ga-doped ZnO thin films.

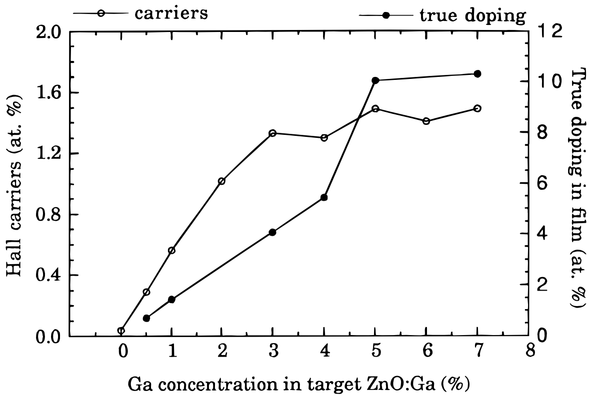

Figure 11. Carrier concentration obtained from Hall measurements and the doping level obtained from EMPA on Ga-doped ZnO films.

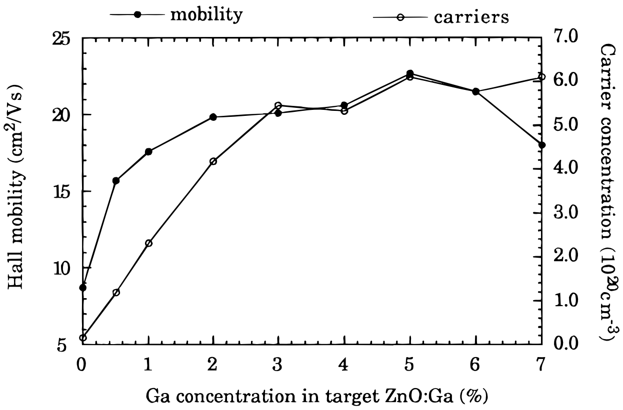

Figure 12. Room-temperature Hall mobilities and carrier concentrations of Ga-doped ZnO films.

freshly prepared samples. Within this error range, no frequency dependence of the conductivity was observed for several Ga-doped zinc oxide samples over the frequency range of 1 Hz−1 MHz. Thereafter, the frequency was fixed at 5 Hz for all measurements shown here. The measurement temperature was room temperature unless otherwise indicated.

Figure 8 shows the conductivity for samples synthesized at 1200 and 1000 °C using different Ga-to-ZnO reactant ratios. Materials prepared at 1200 °C consistently gave higher conductivities than those prepared at 1000 °C, an effect which was more pronounced when the doping level was less than 1 at. %. The conductivity of the samples synthesized at 1200 °C for different lengths of time did not show significant differences. The maximum conductivity of Ga-doped ZnO samples is ~300 Ω^{-1} cm^{-1}. EMPA showed the same dopant concentration for samples with the same reactant concentrations regardless of whether the synthesis temperature was 1200 or 1000 °C (Figure 5). Furthermore, iodimetric titrations suggested that the number of carriers is essentially the same in the powders prepared at 1000 and 1200 °C (Figure 9). The differences in the conductivity of powders prepared at these two temperatures is then likely not intrinsic but is instead related to their different microstructures. Lower synthesis temperatures resulted in smaller particles. Thus, there are more grain-to-grain contacts in the materials prepared at lower temperatures. Therefore, the finer powder prepared at lower temperatures showed lower apparent conductivity.

Thin films of Ga-doped ZnO gave even higher conductivity (Figure 10). The conductivity reached ~1800 Ω^{-1} cm^{-1} at 4 at. % doping level. Thin films can be doped with as much as 10 at. % Ga, but the free carrier concentration from Hall data never exceeds 0.015 electrons/formula unit (Figure 11). Figure 12 shows Hall mobilities and carrier concentrations of Ga-doped ZnO thin films. The Hall mobilities are in the range 9−22 cm^2/V s. The mobility obtained from an In-doped ZnO single crystal[10] was also of the order of 10 cm^2/V s. The apparent mobilities for Ga-doped ZnO powders were calculated using the measured conductivity and the number of carriers obtained from iodimetric titrations. Figure 13 shows the estimated mobilities of samples synthesized at 1200 or 1000 °C. The carrier concentrations are essentially the same for samples prepared at those different temperatures. The highest apparent

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[10] Rupprecht, H. *J. Phys. Chem. Solids* **1958**, *6*, 144−54.

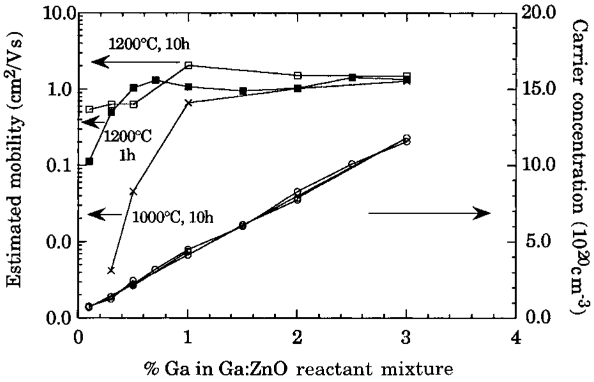

Figure 13. Estimated mobilities and the electron doping concentrations obtained from iodimetric titration of Ga-doped ZnO powders.

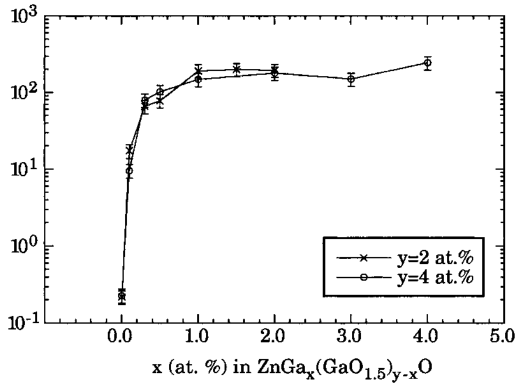

Figure 14. Conductivity of samples prepared with 2 and 4 at. % Ga and different oxygen contents; × refers to the reactant compositions.

mobilities in these powders are about a factor of 10 lower than those for films and single crystals. However, the iodimetric titrations may overestimate the number of free carriers by some unknown amount. Thus, the actual mobilites may be somewhat higher than indicated in Figure 13.

In addition to the Ga content, the oxygen concentration in doped zinc oxide is a crucial factor for its conductivity. To study the conductivity at different oxygen contents, we maintained a constant Ga reactant composition of 2 or 4 at. %, which is below or above the solubility limit in the case where Ga metal is the only source of Ga. Samples were prepared by mixing appropriate amounts of Ga metal, Ga_2O_3, and ZnO according to the formula $ZnGa_x(GaO_{1.5})_{y-x}O$ where $y = 2$ or 4 at. %. The total cation content is fixed at $1 + y$ in each case, and the total amount of oxygen is $1 + 1.5(y - x)$, which is then less for larger x. Figure 14 shows the conductivity of these samples versus x, *i.e.*, fixed gallium content but different oxygen content. The conductivity increased with decreasing oxygen content and leveled off above $x = 1\%$ for both cases. Figure 15 shows the actual Ga doping for samples prepared according to $ZnGa_x(GaO_{1.5})_{0.04-x}O$. The Ga content can increase to at least 4% if the oxygen content is increased. However, this additional Ga doping does not improve the conductivity.

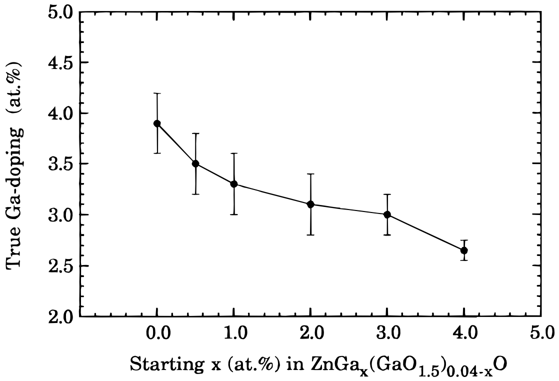

Figure 15. Actual Ga doping levels for samples of Ga-doped ZnO prepared with 4% Ga and different oxygen contents.

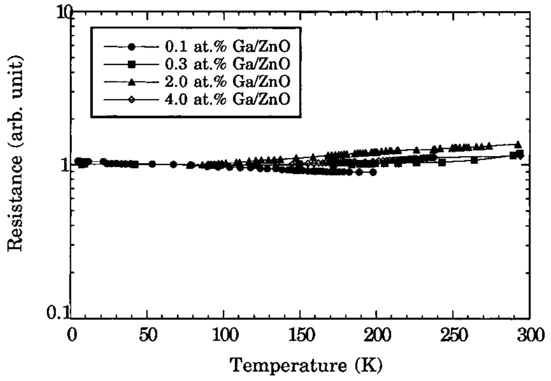

Figure 16. Temperature dependence of the conductivity of Ga-doped ZnO pellets below room temperatures normalized to 1.0 at 4.2 K.

The conductivity of Ga-doped ZnO samples prepared from Ga and ZnO only varied slightly with temperature for samples with 0.1 to 2.7 at. % Ga doping. The change of the resistance from room temperature to 4.2 K is generally less than 20% for all samples (Figure 16). These samples can be heated in air to 200 °C for more than 20 h without noticeable degradation of their conductivity. The small temperature dependence of conductivity indicates these samples are in the heavy doping range.[11] Using the Mott criteria[12]

$$n_c^{1/3}a_H = 0.3, \quad \text{where } a_H = 10.6\ \text{Å},\ \epsilon = 8.5,\ m_e^* = 0.4m_e$$

we obtain $n_c = 2.25 \times 10^{-19}$ cm^{-3} or 0.06 at. %. Thus, the carrier concentrations in all samples prepared from Ga and ZnO only were above the Mott criteria.[12] This is consistent with our iodimetric titration results.

Previous ESR studies[13-15] have given a g value of 1.96 for conduction electrons in ZnO. We have observed the same ESR signal from Ga-, Al-, Ge-, and In-doped ZnO powders. Figure 17 shows the ESR line width ΔH_{pp} of this signal ($g = 1.96$) at various Ga-doping levels. Since the conduction electrons are delocalized in Ga-doped powders, the increase of the ESR line width with increase Ga concentration is presumed to be mainly caused by the interactions between Ga dopants. At even higher concentration (>1 at. % Ga doping), an ESR signal was difficult to detect due to the high conductivity of the sample. In a 3 at. % Ga-doped sample, a very sharp ESR signal was observed ($\Delta H_{pp} = 0.54$ G), which

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(12) Dietz, R. E.; Hopfield, J. J.; Thomas, D. G. *J. Appl. Phys.* **1961**, *32*, 2282.

(13) Müller, K. A.; Schneider, J. *Phys. Lett.* **1963**, *4*, 288–91.

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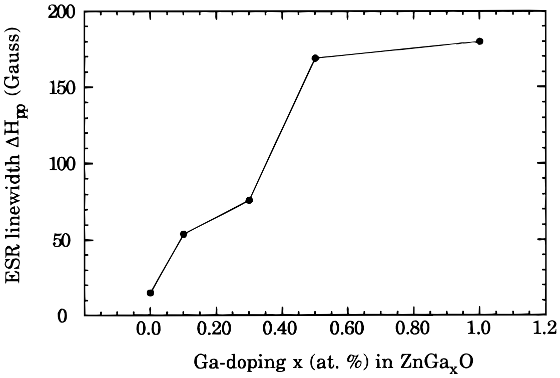

Figure 17. Line width of the ESR peak from the conduction electrons in Ga-doped ZnO.

Table 1

model	formula	defect types	e$^-$ per *x*
1	$ZnGa_xO$	$[Ga^{\bullet}_{i}]$	1e$^-$/*x*
2	$ZnGa_xO$	$[Ga^{\bullet\bullet\bullet}_{i}]$	3e$^-$/*x*
3	$Zn_{1-x}Ga_xO_{1-x}$	$[Ga^{\bullet}_{Zn}, V^{\bullet\bullet}_{O}]$	3e$^-$/*x*
4	$Zn_{1-x}Ga_xO$	$[Ga^{\bullet}_{Zn}]$	1e$^-$/*x*
5	$Zn_{1-x}Ga_xO_{1+(x/2)}$	$[Ga^{\bullet}_{Zn}, O^{\bullet\bullet}_{i}]$	none
6	$Zn_{1-(3x/2)}Ga_xO$	$[Ga^{\bullet}_{Zn}, V^{\bullet\bullet}_{Zn}]$	none

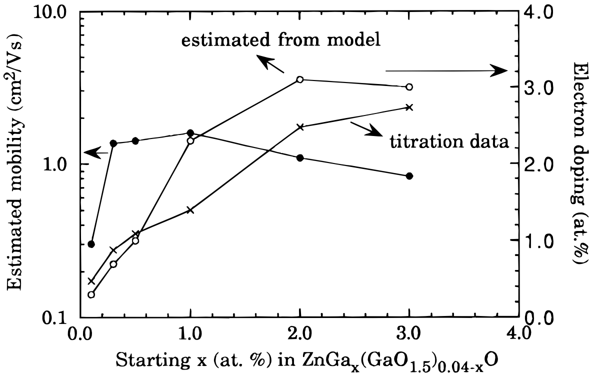

Figure 18. Estimated mobilities and the carrier concentrations obtained from iodimetric titrations and model estimates.

may have resulted from the spin–spin interaction of the conduction electrons.[16]

Discussion

The conductivity levels of Ga-doped zinc oxide powders obtained in this work are much higher than those previously reported for powders of doped tin oxide or doped zinc oxide.[5–7] Furthermore, these high values were measured at room temperature, whereas other studies of doped zinc oxide used measuring temperatures above 700 °C to obtain significant conductivity. We attribute our higher conductivity to our high synthesis temperatures and highly reducing conditions in closed systems. Our highly conducting samples have been equilibrated with metal vapors (Zn + Ga) at a pressure considerably in excess of 1 atm. We explored several low-temperature synthesis routes to doped zinc oxide powders. All products showed low conductivities. Nonetheless, films of doped zinc oxide prepared on substrates heated to only 200 °C produced conductivities somewhat higher than we obtained in powders. This indicates that some nonequilibrium synthesis techniques can give high conductivities even when low synthesis temperatures and low synthesis pressures are used.

Many different situations could be considered upon doping zinc oxide with Ga. A few of the more likely possibilities are in Table 1.

All formulations ignore the possibility of zinc oxide itself being nonstoichiometric. This is a reasonable approximation because our doping levels are very high relative to the nonstoichiometry of zinc oxide. The maximum established nonstoichiometry[9] in zinc oxide can be represented as $Zn_{1.0003}O$. Although our levels of Ga doping are much higher than the level of excess Zn in zinc oxide, the Ga_i models (1 or 2) are suggested by the presumed dominant mechanism for nonstoichiometry of zinc oxide. This formulation would result in three free carriers for every dopant Ga atom (2) if we assume complete ionization to Ga^{3+}. Such a model cannot readily be distinguished from an oxygen vacancy model (3) which also gives three carriers per Ga dopant atom. However, we may exclude models (2) and (3) because both Hall data and iodimetric titrations indicate that the number of carriers per dopant atom never exceeds one. Another possibility is that interstitial gallium is ionized only to Ga^+ (model 1). In this case, each Ga dopant atom would produce only one free carrier per dopant. However, the iodimetric titrations would still show three electrons per Ga dopant atom because iodine would oxidize Ga^+ to Ga^{3+}. Thus, models 1–3 are all excluded.

The fourth formulation suggests simple substitution of Zn by Ga. In this case, every dopant Ga atom would produce just one free carrier, assuming ionization of the dopant to Ga^{3+}. The last formulations (5 and 6) would give no carriers with Ga substitution. These are merely a $ZnO-Ga_2O_3$ solid solution. The dominant defect mechanism could be either oxygen interstitials (5) or cation vacancies (6).

We conclude that Ga doping under our most reducing conditions occurs according to model (4) while doping under our most oxidizing conditions occurs according to model (5) or (6). When zinc oxide and gallium metal and/or gallium oxide are used as reactants, relevant reactions to consider are

$$x\mathrm{Ga} + \mathrm{ZnO} \rightarrow \mathrm{Zn}_{1-x}\mathrm{Ga}_x\mathrm{O} + x\mathrm{Zn} \tag{7}$$

$$(z/2)\mathrm{Ga}_2\mathrm{O}_3 + (1-z)\mathrm{ZnO} \rightarrow \mathrm{Zn}_{1-z}\mathrm{Ga}_z\mathrm{O}_{1+(z/2)} \tag{8}$$

Reaction 7 is justified by the relative Gibbs free energies of oxide formation at 1185 K: −703 kJ/mol for Ga_2O_3 and −228 kJ/mol for ZnO. The elemental zinc is a vapor under synthesis conditions. Due to an intentional temperature gradient of about 5 °C, the Zn metal condenses in a cooler part of the tube away from the oxide. Thus, this zinc metal is not an impurity in the oxide powder produced. For samples prepared with only Ga and ZnO as reactants, only formulation (4) and reaction (7) apply where the carrier concentration equals the Ga-doping concentration. This is supported by the fact that the Ga doping concentration analyzed by EMPA is the same as the carrier concentration obtained from iodimetric titration (Figure 9).

In the case where samples were prepared with Ga, Ga_2O_3, and ZnO at fixed total Ga content (y), both reactions (7) and (8) must be considered. For small

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[16] Gonzalez, C.; Block, D.; Cox, R. T.; Hervé, A. *J. Cryst. Growth* **1982**, *59*, 357–62.

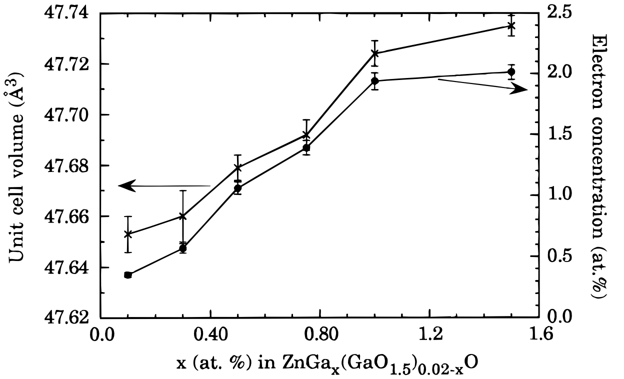

Figure 19. Unit-cell volumes derived from X-ray refinements and electron concentrations obtained from iodimetric titrations at different Ga-to-Ga_2O_3 ratios of 2 at. % Ga-doped ZnO powders.

values of x ($x \leq y/3$), the number of free carriers will be $3x$. For higher values of x, the carrier concentration is limited to the total Ga content because the oxygen-to-total cation ratio does not drop significantly below 1.0. Figure 18 shows the estimated mobility and the carrier concentration obtained from the iodimetric titration using the model just discussed.

Despite the fact that Ga^{3+} is smaller than Zn^{2+}, an expansion of the unit cell occurs on Ga substitution into the Zn site in ZnO according to $Zn_{1-x}Ga_xO$. One rationalization might be that Ga is formally in a +2 rather than a +3 oxidation state and that Ga^{2+} is larger than Ga^{3+} or Zn^{2+}. However, it is not clear that hypothetical Ga^{2+} would actually be of a size to account for this expansion. Furthermore, our data suggest that gallium doped into zinc oxide is ionized to Ga^{3+} which is smaller than Zn^{2+}. Thus, it is more appropriate to view both Zn−O and Ga−O distances as slightly expanded from the values expected for Zn^{2+} and Ga^{3+}. This expansion is expected because the electrons in the conduction band are antibonding. Thus, as their concentration increases with increasing level of Ga doping according to $Zn_{1-x}Ga_xO$, the Zn−O and Ga−O distances should increase as well. Figure 19 shows the unit-cell volume derived from X-ray cell dimension refinements and the electron concentrations obtained from iodimetric titrations at different Ga-to-Ga_2O_3 ratios of 2 at. % Ga-doped ZnO powders. Smaller cell volumes are, in fact, found as samples are oxidized and the concentration of antibonding electrons in the conduction band decreases. However, such samples must also have interstitial oxygen or cation vacancies which may have some influence on the cell volume.

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