Production of native donors in ZnO by annealing at high temperature in Zn vapor

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Zinc oxide crystals grown by the seeded chemical vapor transport method have been annealed in zinc vapor at 1100 °C for 30 min. These thermochemical reduction treatments produce a deep red coloration in the crystals and increase their *n*-type electrical conductivity. Electron paramagnetic resonance (EPR), optical absorption, and Hall measurements were used to monitor changes in the crystals. After an anneal, an intense optical absorption band is present that extends from the band edge out to approximately 550 nm, and the EPR signal near $g=1.96$ (due to shallow donors and/or conduction-band electrons), the free-carrier absorption, and the Hall electron concentration are all larger. Hydrogen was not present during these anneals, thus leaving oxygen vacancies and zinc interstitials as candidates for the added donors. Neutral oxygen vacancies are produced at high temperature by the additive-coloration mechanism, and are responsible for the broad near-edge absorption band. The observed increase in the number of free carriers is a result of either (1) the formation of zinc interstitials or (2) having the ground state of the neutral oxygen vacancy near the conduction band. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2117630]

The identity of the donors in ZnO that are responsible for the material's pervasive *n*-type conductivity continues to be a topic of considerable interest.[1,2] Group III impurities such as Al, Ga, and In can easily substitute for Zn ions and form shallow donors.[3] These impurities are present at trace levels in most ZnO crystals and can account for a significant portion of the observed *n*-type conductivity. Other donors, such as hydrogen, zinc interstitials, and oxygen vacancies, are also often invoked to explain observed electron concentrations. Both theory[4] and experiment[5] support the shallow donor role of hydrogen, while other experiments[6–8] demonstrate that hydrogen in the form of OH^- ions can serve as a passivator for acceptors. Hall measurements on electron-irradiated ZnO have provided supporting evidence that zinc interstitials may be a residual shallow donor.[9] Neutral oxygen vacancies are considered to be a major component of the defect structure of ZnO,[10] but their production conditions and their electrical and optical properties have not been unequivocally established. It is accepted by some investigators[11–16] that the ubiquitous green luminescence is a measure of oxygen vacancies in ZnO, but clear evidence for this association is still lacking since the often-referred-to papers[17,18] misidentified the electron paramagnetic resonance (EPR) signal that was used to verify the presence of oxygen vacancies. These authors[17,18] believed that the EPR signal at $g=1.96$ represented singly ionized oxygen vacancies, when in fact it is due to shallow donors and/or conduction-band electrons. An EPR signal near $g=1.995$ has been unambiguously assigned to singly ionized oxygen vacancies.[19–21]

In the present article, we describe the results obtained when a ZnO crystal is annealed at 1100 °C in zinc vapor. This study provides information about the production and behavior of native donors in this material. Optical absorption, EPR, and Hall data were acquired from a pair of crystals, one as-grown and the other annealed. When heated at high temperature in zinc vapor, the ZnO crystal turned red (i.e., a broad absorption band peaking in the blue was formed) and its *n*-type electrical conductivity increased. Although data is presented in this article from only one pair of samples, we have observed similar results from additional vapor-transport and hydrothermally grown ZnO crystals.

The bulk ZnO crystals used in this study were grown by the seeded chemical vapor transport method at Eagle-Picher (Miami, OK). Two *c*-plate samples with dimensions of $4.5 \times 3.5 \times 0.5$ mm^3 were cut from an optically polished larger *c*-plate. One sample was used as a reference (representing the before anneal state) and the other was annealed at high temperature in Zn vapor. In this thermochemical reduction process, the ZnO crystal was placed in a quartz tube (10 cm long, 6 mm inner diameter, and 8 mm outer diameter) along with 0.2 g of zinc metal. The tube containing the crystal and zinc metal was evacuated. During this pumping stage, a flame from a torch was passed over the tube to remove contaminants. The torch was then used to seal the tube while maintaining the vacuum inside. The resulting capsule was placed in a furnace that had been preset at 1100 °C (the zinc metal vaporizes at approximately 906 °C). After 30 min, the capsule was quickly removed from the furnace. The surface damage produced during the anneal was eliminated by polishing with colloidal silica.

Infrared absorption data were taken with a ThermoNicolet Nexus 870 fourier-transform infrared spectrometer and the visible/ultraviolet absorption data were taken with a Cary 14 spectrophotometer. The EPR data were obtained using a

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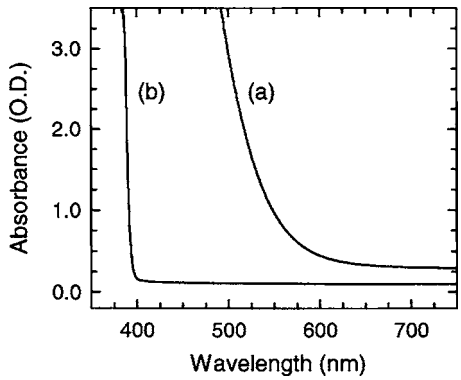

FIG. 1. Optical absorption from ZnO crystals. These data were taken at room temperature with unpolarized light propagating along the *c* axis. (a) After an anneal at 1100 °C for 30 min in zinc vapor. (b) Before the anneal.

Bruker EMX spectrometer. A van der Pauw geometry was used in the Hall measurements.

Heating in zinc vapor at high temperature caused the ZnO crystals to turn a deep red color. Figure 1(a) shows the optical absorption spectrum of an annealed sample, taken at room temperature with unpolarized light propagating along the *c* axis of the crystal. For comparison, Fig. 1(b) shows the absorption spectrum from the reference sample (i.e., the untreated sample) taken under similar conditions. An intense band peaking in the "blue" has been produced by the thermochemical reduction treatment. This extrinsic absorption feature is off-scale in Fig. 1, but its trailing edge in the 500–600 nm region is exponential and can be fit by a Gaussian-shaped band with a peak value of 3.03 eV (409 nm) and a full width at half maximum of 0.78 eV. Other investigators have reported the presence of this absorption feature in ZnO crystals,[22–25] but none have assigned it to a specific defect.

Heating in the zinc vapor also produced a significant increase in the EPR signal at $g=1.96$. This signal is due to shallow donors and/or conduction-band electrons.[26] Data illustrating the changes in this EPR signal are presented in Fig. 2. These data were taken at 15 K, the microwave frequency was 9.466 GHz, and the magnetic field was perpendicular to the *c* axis. The signal in Fig. 2(a), taken after the anneal, is narrow (about 0.24 G wide) and very intense. In comparison, the signal in Fig. 2(b), taken from the untreated reference sample, is broad with low intensity. A double integration of each spectrum indicates that the sample heated in zinc vapor has approximately four times more "area" under its absorption curve than the untreated sample. As the temperature was increased from 15 to 45 K, the signal from the annealed sample in Fig. 2(a) became progressively broader and less intense while the signal from the untreated reference sample in Fig. 2(b) became progressively narrower and more intense. These opposite temperature dependences suggest that the EPR signal in the annealed sample is dominated by electrons in the conduction band while the EPR signal in the untreated reference sample primarily represents electrons localized at donors or in an impurity band.[27,28]

Along with the introduction of the blue absorption near the band edge and the increase in the shallow donor/conduction band EPR signal, heating in zinc vapor produced a more than tenfold increase in the Hall electron concentration. The treated sample had an electron concentration of 1.5×10^{18} cm^{-3} and a mobility of 110 cm^2 V^{-1} s^{-1}, while the untreated sample had a concentration of 1.3×10^{17} cm^{-3} and

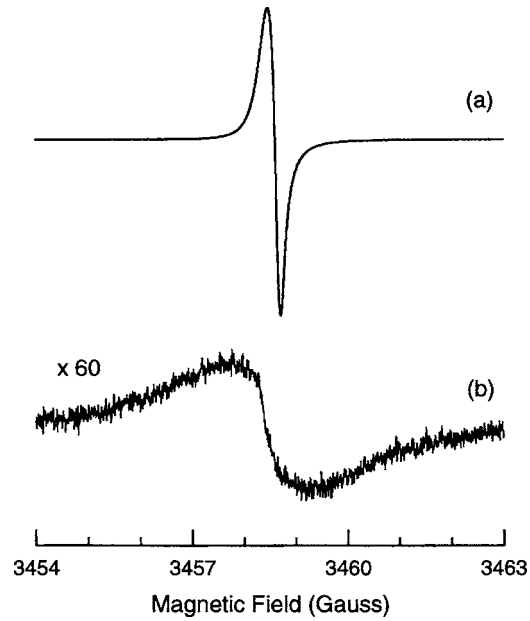

FIG. 2. EPR spectrum of shallow donors and/or conduction band electrons in ZnO crystals. These data were taken at 15 K. (a) After an anneal at 1100 °C for 30 min in zinc vapor. (b) Before the anneal. This latter spectrum has been enhanced by a factor of 60.

a mobility of 150 cm^2 V^{-1} s^{-1}. This decrease in mobility for the treated sample is consistent with the increase in free carriers. Additional evidence for an increase in shallow donors is provided by infrared absorption data taken in the 1–8 μm region. Figure 3(a) shows the room-temperature absorption spectrum of the sample annealed at 1100 °C in zinc vapor. For comparison, Fig. 3(b) shows the absorption spectrum from the reference sample (i.e., the untreated sample). At 4 μm, the absorption in the annealed sample is approximately 4.2 times greater than in the untreated sample. An analysis of the temperature dependence of this free carrier absorption in the crystal annealed in zinc vapor, following an approach[29] used for oxygen vacancies in BaO, gave an activation energy near 40 meV. We also monitored the 500 nm green emission (at 5 K with 325 nm excitation) before and after heating in zinc vapor, but found little change in its intensity. The tail of the 409 nm absorption band in Fig. 1 overlaps this green emission band, but will have only a minor effect on its intensity since the emitted light is produced in a small region near the surface (<1 μm depth).

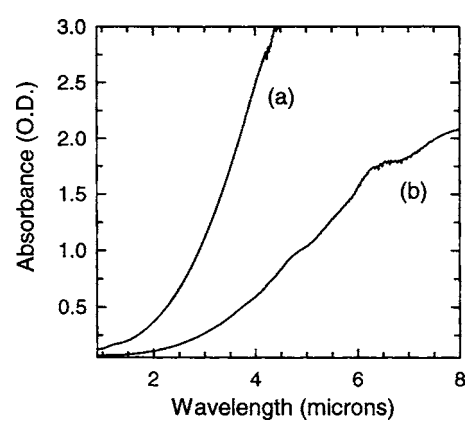

FIG. 3. Infrared absorption from free carriers in ZnO. These data were taken at room temperature. (a) After an anneal at 1100 °C for 30 min in zinc vapor. (b) Before the anneal.

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We now turn to a discussion of the identity and production mechanisms for the additional donors that are formed during the anneal at high temperature in zinc vapor. These new donors could be either neutral oxygen vacancies or zinc interstitials, or a combination of the two. Very little hydrogen was present in our system during the high temperature anneals, and it is not considered to be a candidate for the additional donors. Furthermore, it is generally agreed that hydrogen diffuses out of ZnO well below 1100 °C.

The reducing nature of our thermochemical treatments is expected to form oxygen vacancies at the surface that then diffuse into the bulk of the crystal. This process, referred to as "additive coloration," has been widely used to produce oxygen vacancies in MgO, CaO, SrO, and BaO crystals[29,30] and sulfur vacancies in ZnS crystals.[31] At the high temperature, oxygen ions emerge at the surface of the ZnO crystal and join with zinc atoms from the vapor to form a "new" layer of ZnO on the surface. The crystal is "growing" as a result of this combining of zinc from the vapor and oxygen from the bulk. The electrons given up at the surface by the incorporated zinc atoms convert the newly formed oxygen vacancies to the neutral charge state. These neutral oxygen vacancies then migrate into the crystal. Zinc interstitials could also form at the same time as the oxygen vacancies, since the surrounding zinc vapor is an obvious source of zinc atoms that could diffuse into the crystal.

Neutral oxygen vacancies, by themselves, could explain all of our experimental results if the ground state of this donor is near the conduction band. This would mean that one of the two electrons at the neutral oxygen vacancy could easily be thermally excited to the conduction band and thus contribute to the free-carrier absorption, the Hall electron concentration, and the EPR signal. Even though the remaining electron would still be localized at the oxygen vacancy, its EPR signal would not be easily observed because of nonresonant microwave losses from free carriers. In BaO,[29] neutral oxygen vacancies produced by the additive coloration process have their ground state close to the conduction band and significant concentrations of free carriers are observed along with an intense visible optical absorption band. Similar behavior could also occur in ZnO. We note that Smakula's equation, using an oscillator strength of 0.8 and an index of refraction of 2.4, gives a defect concentration of 1.7×10^{18} cm^{-3} for the absorption band in Fig. 1(a).

First-principles calculations have predicted that oxygen vacancies are deep donors in ZnO.[32–35] If the ground state of the neutral oxygen vacancy is deep in the gap, then the blue optical absorption band that gives rise to the red coloration could still be explained by the formation of oxygen vacancies, but the increase in free carriers would require the formation of zinc interstitials. We have found that an anneal at 1100 °C in phosphorus vapor makes ZnO crystals red and increases their *n*-type conductivity. This suggests that zinc interstitials may not be the sole reason for the increase in conductivity, and thus supports placing the ground state of the neutral oxygen vacancy near the conduction band.

In summary, we heated ZnO in zinc vapor and produced red crystals with significant concentrations of free carriers. Neutral oxygen vacancies are responsible for the absorption band in the blue (that causes the red appearance) and either zinc interstitials or neutral oxygen vacancies are responsible for the increase in free carriers. This study has demonstrated the efficiency of the thermochemical reduction process in modifying the optical and electrical properties of ZnO by introducing native donors, and it has established an optical "signature" for the presence of oxygen vacancies in ZnO.

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