Evidence for Native-Defect Donors in n-Type ZnO

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Recent theory has found that native defects such as the O vacancy $V_O$ and Zn interstitial $Zn_i$ have high formation energies in \textit{n}-type ZnO and, thus, are not important donors, especially in comparison to impurities such as H. In contrast, we use both theory and experiment to show that, under N ambient, the complex $Zn_i-O$ is a stronger candidate than H or any other known impurity for a 30 meV donor commonly found in bulk ZnO grown from the vapor phase. Since the Zn vacancy is also the dominant acceptor in such material, we must conclude that native defects are important donors and acceptors in ZnO.

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Semiconducting ZnO has generated great interest in the past decade because of advances in bulk and epitaxial growth that have opened the door for new photonic and electronic applications, such as UV light emitting diodes and transparent transistors \cite{1,2}. Previous research had established that ZnO was always \textit{n}-type and that the dominant donors were usually shallow with activation energies of between 30 and 60 meV \cite{3,4}. Because it was also known that the crystal growth was typically Zn-rich, the O vacancy $V_O$ or the Zn interstitial $Zn_i$ \cite{5,6}. This model was strongly challenged in the year 2000 when Kohan et al. showed theoretically that both $V_O$ and $Zn_i$ have high formation energies in \textit{n}-type ZnO and that, furthermore, both are deep, not shallow, donors \cite{7}. More recent theory has concluded that $Zn_i$ is actually a shallow donor, rather than deep \cite{8,9}, as has also been suggested by electron-irradiation experiments \cite{6}; however, its high formation energy would still limit its participation in the conductivity of \textit{n}-type material. Also in the year 2000, the defect-donor model was further challenged by Van de Walle’s theoretical result that H is always a donor in ZnO, that it is easily ionized, and that it has a low enough formation energy to be abundant; thus, Van de Walle suggested that it was likely to be a dominant background donor in ZnO materials that were exposed to H during growth \cite{10}. This proposal has been amenable to testing, because H-containing, high-quality, bulk ZnO, grown by a seeded chemical vapor transport (SCVT) technology, has been commercially available for the past few years. For the most part, these tests have confirmed that a shallow donor due to H exists in SCVT ZnO and can contribute significantly to the conductivity \cite{11–16}. This fact, coupled with the theoretical evidence of high formation energies for the native donors \cite{7}, has led to a prevailing opinion that native donors do not play a significant role in the conductivity of as-grown ZnO. In contrast, we will offer evidence here that native donors can contribute significantly to conduction in ZnO but as complexes, rather than isolated elements.

The main sample used in this study was a 5 mm $\times$ 5 mm $\times$ 0.42 mm piece cut from a wafer grown by the SCVT technique at ZN Technology, Inc. \cite{17}. Material of this type is of very high quality, with peak electron mobility $\gtrsim 2000 \text{cm}^2/\text{V}\cdot\text{s}$, 300 K carrier concentration in the $10^{16} \text{cm}^{-3}$ range, and photoluminescence (PL) linewidths under 0.5 meV, as shown in Figs. 1 and 2 \cite{4}. The sample was first annealed at 715 °C, in order to release most of the H \cite{14,15}, then was irradiated with high-energy electrons to create point defects, and finally was annealed again at temperatures from 200–500 °C, in order to investigate the annihilation of the point defects. As seen in Fig. 1, several sharp PL lines appear in the region 3.357–3.365 eV, and these spectral features are usually assigned to transitions of excitons bound to neutral donors ($D^0X$ transitions), in which the donor remains in its ground state ($n = 1$) during the transition. Some of these lines have been tentatively identified; for example, the lines at 3.35964 eV ($I_8$ or $I_{8a}$ in...
the literature) and 3.36042 eV ($I_6$ or $I_{ba}$) have been assigned to GaZn and AlGn, respectively. (See Ref. [18] for an excellent review of PL in ZnO.) All of the spectra presented in this work are normalized to the $I_4$ line, because it is relatively isolated and also not expected to change significantly as a result of annealing or irradiation treatments. However, the most dominant PL line in this particular sample before annealing is the $D^{0}X$ line at 3.36270 eV ($I_4$), now almost universally assigned to interstitial H [16,18]. This identification results at least partially from annealing experiments, because $I_4$ disappears for anneals above 600 °C, in good correlation with the effusion of H from the sample [14–16,19]. Our sample behaves in the same way, as evidenced by the strong reduction of $I_4$ after an anneal of 715 °C (curve 2 in Fig. 1). Not shown in Fig. 1 is a two-electron satellite (TES) replica of $I_4$, appearing at 3.32961 eV. A TES transition is one in which the donor is left in an excited $n = 2$ state after the collapse of the exciton. If the donor associated with $I_4$ follows a hydrogenic model, then the ground-state $(n = 1)$ energy of this donor should be given by $4/3(3.36270 - 3.32961) = 44.1$ meV. Other TES transitions, also not shown, are seen near 3.32 eV and may be associated with $I_6$ and $I_8$ [18]. If so, then the hydrogenic model would predict ground-state energies of 53–55 meV for these donors, presumably associated with GaZn and AlGn. Thus, the donors identified from PL are H, at 44 meV, and GaZn and AlZn, at about 55 meV.

To create point defects, we have used the Van de Graaff electron accelerator at Wright State University. The sample was irradiated on the Zn face (0001) with 1 MeV electrons three separate times, making a total fluence of $3 \times 10^{17}$ cm$^{-2}$. The PL spectrum after the third irradiation is presented as curve 3 in Fig. 1. A new sharp defect line at 3.36070 eV, which we will designate as $I_D$, is generated by the irradiation. Concomitantly, a triplet feature, comprised of energies 3.33711, 3.33793, and 3.33840 eV, is also generated. These will we designate $I_{D,TES1}$, $I_{D,TES2}$, and $I_{D,TES3}$ This triplet has an intensity about 100 times less than that of $I_D$, and this reduction is about the same as that observed for the TES line of H compared with its parent line, $I_4$. Thus, the defect triplet at 3.338 eV clearly is related to $I_D$, and, if the hydrogenic model holds, the associated energy is $4/3(3.3607 - 3.3379) = 30.4$ meV. This value is less than that predicted from an empirical version of Haynes' rule presented in Ref. [18]. However, that version was developed for simple, isolated impurities, Al, Ga, In, and H, and there is no reason to expect that it should hold for a defect-related complex. Both $I_D$ and its TES triplet are greatly reduced for anneals greater than 500 °C (not shown), evidently due to defect recombination. It is important to note at this point that the as-grown sample, represented by curve 1 in Fig. 1, has two small lines at the energies of $I_{D,TES1}$ and $I_{D,TES2}$, respectively, and possibly also a line in the $I_D$ region, although obscured by $I_6$. This is our first indication that the as-grown sample contains defect-related donors.

We next discuss the temperature-dependent mobility $\mu$ and carrier concentration $n$, shown in Fig. 2. To avoid clutter, we show curves representing only four stages in the evolution of this sample: (1) as-grown; (2) annealed at 715 °C for 1/2 hour in flowing N$_2$ gas; (3) irradiated with 1 MeV electrons, in three equal stages up to a total fluence of $3 \times 10^{17}$ cm$^{-2}$; and (4) annealed at 400 °C, following previous anneals beginning at 200 °C. It should be noted that a final anneal at 500 °C (not shown) eliminated almost all of the irradiation damage and basically returned the $\mu$ and $n$ curves to those of stage 2. [Note that a return to the $\mu$ and $n$ curves of stage 1 (as-grown) is of course impossible, because the H content was lost in stage 2, the first 715 °C anneal.]

The mobility data (inset in Fig. 2) were fitted to an accurate charge-carrier scattering theory, described elsewhere [20], and the only fitting parameter was the acceptor concentration $N_A$. The carrier concentration data of Fig. 2 were then fitted to the charge-balance equation:

$$n + N_A = \sum_i \frac{N_{Di}}{1 + n/\phi_{Di}},$$

where the subscript $i$ denotes a particular donor and where $\phi_{Di}$ is a function of $T$ and $E_{Di}$, the donor energy [cf. Eq. (8) of Ref. [20]]. The fitting parameters in Eq. (1) are the donor concentrations ($N_{Di}$'s), donor energies ($E_{Di}$'s), and acceptor concentration $N_A$. Excellent fits to the $n$ vs $1/T$ data in Fig. 2 were obtained by also including a degenerate surface layer in the analysis [20,21].

The PL results discussed above determined the energies of three different donors, calculated from their respective TES lines: 55 meV, possibly associated with GaZn and/or AlZn; 44 meV, associated with H; and 30 meV, produced by irradiation and thus associated with a defect. Indeed, the 30 and 44 meV energies turn out to be good fitting parameters for two of the three donors required to fit our Hall-effect data, but the third donor is best fitted with about 75 meV, rather than 55 meV. The carrier concentration fits are

![FIG. 2 (color online). Temperature-dependent carrier concentration for ZnO sample. The solid lines are theoretical fits. The inset shows the experimental mobility curves after the same four treatments.](image-url)
shown as solid lines in Fig. 2, and the fitting parameters are given in Table I. Two major conclusions are evident from the results: (1) the 44 meV H level essentially disappears during the 715 °C anneal, in agreement with the PL data; and (2) a 30 meV level is produced by irradiation but also exists in the as-grown sample and the sample annealed at 715 °C. It should be emphasized that the choice of 30 meV as a Hall fitting parameter is not dependent on the fact that the PL analysis also found a donor at 30 meV. Indeed, a donor of this energy has been found previously by a number of groups to give good fits to ZnO Hall-effect data [3,4,6]. To help identify this 30 meV donor, we appeal to theory.

First of all, we calculate the expected 1 MeV-electron-bombardment production rates of Zn and O Frenkel pairs from molecular dynamics simulations [22]. The threshold energies were calculated by giving a randomly chosen O or Zn atom a recoil energy in a random direction in an experimentally controlled angular window of 15 degrees around the desired (0001) direction. The interatomic interaction model for the ZnO system will be published elsewhere [23], but the potential development principles are described in Ref. [24]. To account for the experimental situation with a beam acceptance angle, the threshold was determined as the average over the direction-specific thresholds obtained within the 15° angular window.

For Zn-face (0001) irradiation at 300 K, the threshold for O displacement is 44 eV, and that for Zn displacement, 34 eV. We then apply the McKinley-Feshbach relativistic cross-section formula [25] to give effective production rates of 0.18 cm⁻¹ for O displacement and 0.30 cm⁻¹ for Zn displacement. Thus, we would expect that our fluence of 3 × 10¹² cm⁻² would produce O₇ and V₀ concentrations of about 5 × 10¹⁶ cm⁻³ and Zn₇ and Vzn concentrations of about 9 × 10¹⁶ cm⁻³. Either of these numbers is consistent with the observed 30 meV donor concentration of about 2 × 10¹⁷ cm⁻³ in the irradiated sample (see Table I), because the value 2 × 10¹⁷ cm⁻³ is actually an upper limit. That is, the mobility after such a heavy irradiation is almost certainly reduced by electrical inhomogeneity, and, thus, it is artificially low, leading to artificially high donor and acceptor concentrations. However, the concentration of Zn₇ should still be about twice that of V₀, and, moreover, there is abundant evidence that V₀ is a deep, not shallow, donor [7-9,26]. Thus, Zn₇ is a much better candidate for the irradiation donor than V₀. However, there also is evidence that isolated Zn₇ is mobile at room temperature, so that it likely has to form a complex to be stable [27,28].

A search for potential complexing partners for Zn₇ immediately suggests N, which easily substitutes for O in the ZnO lattice and which indeed has a concentration of about 10¹⁷ cm⁻³ in ZnO material of the type we are using [29]. Thus, we have examined the formation energy, binding energy, and (0/ +) transition energy of the complex Zn₇–Oₗ using first principles calculations. We applied density functional theory (DFT) within the local density approximation (LDA) and used Vanderbilt-type ultrasoft pseudopotentials, as implemented in the VASP code [30]. To obtain defect formation energies, defined elsewhere [31,32], a supercell approach was used, with a ZnO supercell size of 96 atoms. The main result of the calculation is that the binding energy of the Zn₇–Oₗ complex is about 0.9 eV; thus, the complex should be stable at room temperature. The formation energies of the Nₒ, Zn₇, and Zn₇–Oₗ species in ZnO depend on the Fermi energy and the partial pressures of the elements or, in other words, the chemical potentials of the elements, during growth. The secondary-ion mass-spectroscopy measurements [29] found a N concentration [N] of about 1 × 10¹⁷ cm⁻³. Based on our calculated formation energies of Nₒ, Zn₇, and Zn₇–Oₗ, together with the measured N concentration ([N] = [Nₒ] + [Zn₇–Oₗ]), we estimate a N chemical potential of 0.92 eV below the N₂ precipitation limit (assuming Zn-rich and charge-neutral growth conditions and a growth temperature of 950 °C). The calculated formation energy [33] shows that, during growth, Nₒ⁻ acts as the dominant acceptor and Zn₇⁺ as the dominant donor, with the Fermi energy pinned at about 1.0 eV above the valence band where the two defects have approximately the same energy, about 1.4 eV. The corresponding defect concentrations are on the order of 10¹⁵ cm⁻³. The concentration of the Zn₇–Oₗ complex is about 2 orders of magnitude lower, as determined from the reaction Nₒ + Zn₇ → Zn₇–Oₗ + 0.9 eV and the associated detailed-balance relationship [Nₒ][Zn₇]/[Nₒ][Zn₇–Oₗ] = exp(–E_b/kT). Here we use Nₒ(ZnO) = 4.28 × 10²² cm⁻³ and E_b = 0.9 eV. At T = 950 °C, we get [Zn₇–Oₗ]/[Zn₇] = 0.012, which means that only about 1/100 of the Zn₇ ions take part in formation of the complex. However, during cooldown, it is expected that the formation of the complex will accelerate, assuming a sufficiently low Zn₇ diffusion barrier. As the temperature cools to about 500 °C, the quantity [Zn₇–Oₗ]/[Zn₇] approaches unity, which means that about half of the Zn₇ are already bound in the com-

| Table I. Fitting parameters for mobility and carrier concentration data. |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                | E_D1 (meV)      | N_D1 (10¹⁶ cm⁻³)| E_D2 (meV)      | N_D2 (10¹⁶ cm⁻³)| E_D3 (meV)      | N_D3 (10¹⁶ cm⁻³)| N_A (10¹⁶ cm⁻³) |
| As-grown       | 30              | 0.45            | 44              | 3.0             | 75              | 2.0             | 0.13            |
| 715 °C         | 30              | 0.74            | 75              | 3.2             | 0.7             |
| Irradiated     | ~20             | 75              | 0.13            | ~20             |
| 400 °C         | 30              | 1.35            | 75              | 0.4             | 1.2             |

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plexes. At room temperature, $[\text{Zn}_I\text{-N}_0]/[\text{Zn}_I] = 10^9$, so that nearly 100% of the Zn$_I$ are in complexes. With other impurities (such as H$_I$) in the sample, the above balance conditions would vary somewhat, but the main conclusions should remain the same.

The electronic transition energy of Zn$_I$-N$_0$ is somewhat uncertain, due to the well-known LDA gap error. However, our calculations show that the donor level of Zn$_I$-N$_0$ is shallower than that of isolated Zn$_I$, which itself is argued to be a shallow donor [8,9]. In addition, a wave function analysis of Zn$_I$ shows delocalization, which is characteristic of a shallow level. In short, although the (0/+ ) transition energy of Zn$_I$-N$_0$ cannot be accurately calculated, it is entirely consistent with the observed value of 30 meV. Further details of these calculations will be published elsewhere.

It is also interesting to compare the 0.9 eV binding energy with the activation energy for irradiation-defect annealing in ZnO, measured previously as 1.7 eV [34]. The difference between these two energies, 0.8 eV, should be the motional energy for Zn$_I$ and is a reasonable value for an interstitial.

Other evidence for a Zn$_I$-N$_0$ complex comes from optically detected magnetic resonance experiments in epiztal N-doped ZnO [35]. An observed spin-1/2 center was consistent with a Zn interstitial, possibly in association with an N atom, since it was not observed in a sample with lower N content. Besides Zn$_I$, other donors, such as H, are also believed to associate with N [14,36]. However, H-N would be neutral, whereas Zn$_I$-N has a shallow-donor level.

Finally, other Zn$_I$-acceptor complexes that behave as shallow donors are also predicted to be stable. For example, very recently Wardle et al. [37] have used DFT to show that Zn$_I$-Li$_{Zn}$ is bound by 0.7 eV and has a shallow-donor transition. This result further strengthens and generalizes our assertion that Zn$_I$-related shallow donors can exist and be important in as-grown ZnO.

In summary, we have carried out extensive low-temperature photoluminescence and temperature-dependent Hall-effect measurements on irradiated ZnO and have identified a defect-related donor at about 30 meV, which also exists in as-grown ZnO. We have further carried out molecular dynamics simulations, to show that the expected production rate of Zn$_I$ is consistent with the concentrations of the 30 meV donor after irradiation, and density functional calculations to show that the Zn$_I$-N$_0$ defect complex is a shallow donor with a sufficient binding energy to explain the annealing data. Thus, the conclusion is that native-defect-related donors can exist in n-type ZnO and contribute to its conductance.

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[17] ZN Technology, 910 Columbia Street, Brea, CA 92821, USA.
[33] See EPAPS Document No. E-PRLTAO-030548 for the calculated defect formation energy. This document can be reached via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).