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## Residual Native Shallow Donor in ZnO

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High-energy electron irradiation in ZnO produces shallow donors at about  $E_C - 30$  meV. Because the production rate is much higher for Zn-face (0001) than O-face (000 $\bar{1}$ ) irradiation, the donor is identified as a Zn-sublattice defect, most likely the interstitial  $Zn_I$  or a  $Zn_I$ -related complex. The donor energy is quite close to that of the unirradiated sample, and of other samples discussed in the literature, strongly suggesting that  $Zn_I$  (and not  $V_O$ ) is the dominant native shallow donor in ZnO. An exceptionally high displacement threshold energy ( $\sim 1.6$  MeV) is quantitatively explained in terms of a multiple-displacement model. [S0031-9007(99)08717-7]

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ZnO is a common and widely used semiconductor material, which crystallizes in the wurtzite phase and has a direct band gap of 3.437 eV at 2 K. Until now, the commercial applications, including piezoelectric transducers, varistors [1], phosphors, and transparent conducting films, have mainly involved polycrystalline material; however, recent successes in producing large-area single crystals [2] have opened up the possibility of a nearly lattice-matched substrate for GaN, a blue and uv light emitter [3]. Moreover, it has been found that ZnO itself is a very bright blue and uv light emitter, and optical uv lasing has already been demonstrated [4], even at 300 K [5]. With the resurgence of interest in commercial applications, it is important to point out that many of the fundamental properties are poorly understood; e.g., no impurity or defect donors or acceptors have been positively identified, say, in terms of energy. Because most ZnO material is strongly  $n$ -type, it has long been assumed that the dominant donor is a native defect, either the O vacancy  $V_O$ , or the Zn interstitial  $Zn_I$  [6]. Kroger [7] assigned  $V_O$  and  $V_{Zn}$  as the dominant donor and acceptor species, respectively, but a *shallow* donor state for  $V_O$  has never been proven to exist. In fact,  $V_O$  has been identified in electron paramagnetic resonance (EPR) studies as a *deep* donor [8], although the energy has not been measured. Correspondingly, Vanheusden *et al.* [9] argued that, since the free carrier concentration  $n$  was much larger than  $[V_O]$  in their samples, there had to be another source of donors, possibly  $Zn_I$ . Various other authors have postulated either  $V_O$  or  $Zn_I$  as the dominant donor in their particular samples.

The expected hydrogenic donor energy is given by  $E_D = 13.6m^*/\epsilon_0^2 = 66$  meV, since the polaron effective mass is  $m^* = 0.318m_0$ , and the relative static dielectric constant is  $\epsilon_0 = 8.12$  [10]. Optically, at least by photoluminescence (PL),  $E_D$  is difficult to measure directly, because most of the near-band-edge PL strength involves exciton collapse, not free-to-bound transitions; indeed, Reynolds *et al.* [11] see no free-to-bound transitions in

the ZnO used in the present study, but at least seven transitions due to excitons bound to neutral donors. Fortunately, sometimes an exciton bound to a neutral donor will collapse and leave the donor in an excited ( $n = 2$ ) state, and, if the donor is hydrogenic, then the ground-state energy will be just  $(4/3)[E(n = 1) - E(n = 2)]$ . Reynolds *et al.* [11] used this fact to get a donor binding energy of about 56–58 meV (close to the expected value) for three of the donors associated with the donor-bound-exciton lines mentioned above. Temperature dependent Hall (TDH) measurements were applied to this same material [2], and energies of 31 and 61 meV were found for two donors of concentration  $1 \times 10^{16}$  and  $1 \times 10^{17} \text{ cm}^{-3}$ , respectively. The larger of these TDH donor energies is consistent with the hydrogenic model; however, the shallower one is not. In an older work by Wagner and Helbig [12], again a shallow level (38 meV) was measured. In fact, in the samples that we have examined, a shallow donor of energy 25–35 meV always dominates the low-temperature electrical data, although various deeper donors are often evident at higher temperatures ( $T > 300$  K). Thus, we hypothesize that the donor at approximately  $E_C - 30$  meV is a native defect, and support that claim below.

To create defects, we have used high-energy (1.0–2.0 MeV) electrons from a Van de Graaff accelerator. The sample stage was under vacuum and water cooled, and typical current densities were 10–20  $\mu\text{A}/\text{cm}^2$ . The ZnO samples, of approximate dimensions 6 mm  $\times$  6 mm  $\times$  0.5 mm, were cut from 2-in.-diam. wafers, which were themselves cut from a boule grown by a vapor-transport technique [2]. The crystals were of very high quality, with peak mobilities of about 2000  $\text{cm}^2/\text{Vs}$  (see inset of Fig. 1), and donor-bound-exciton PL linewidths as narrow as 0.1 meV, at 2 K.

Most of the energy loss in high-energy electron bombardment occurs from electron-electron, rather than electron-nucleus, collisions [13]. Such  $e$ - $e$  collisions

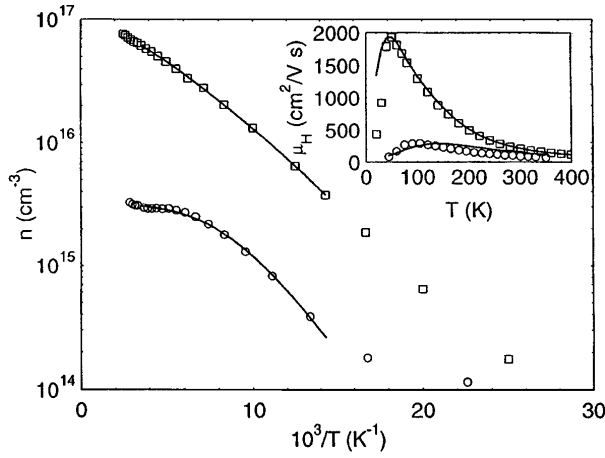


FIG. 1. Carrier concentration vs  $T^{-1}$  for an unirradiated ZnO sample (squares) and one irradiated at 2.0 MeV to a fluence of  $1.2 \times 10^{17} \text{ cm}^{-2}$  (circles). The inset shows mobility vs  $T$  for the two cases.

limit the electron range to about 0.7 and 1.7 mm, for 1- and 2-MeV electrons, respectively. Most of the analysis here will concern 2-MeV electron irradiation, because little damage is seen, either optically or electrically, for  $E < 1.6$  MeV. At 2 MeV, the electrons will easily penetrate the 0.5-mm samples. If a relativistic electron of energy  $E$  makes a *direct* hit on a nucleus, it will transfer a maximum energy  $E_m$  given by [13]

$$E_m = \frac{2E(E + 2m_e c^2)}{Mc^2} = \frac{2.147 \times 10^{-9} E(E + 1.022 \times 10^6)}{A}, \quad (1)$$

where  $m_e$  and  $M$  are the electron and ion masses, respectively,  $A$  is the atomic weight, and the energies are in eV. The threshold energy  $E_{th}$  necessary to produce an atomic displacement is then just given by the condition  $E_m = E_d$ , where  $E_d$  is the displacement energy. Since very little damage is seen for  $E < 1.6$  MeV, the implication is that  $E_{th} > 1.6$  MeV, or  $E_d > 138$  eV for Zn ( $A = 65.38$ ), or  $E_d > 563$  eV for O ( $A = 16$ ). These values of  $E_d$  are much too high when compared with those of As displacement in GaAs (10 eV) [14], N in GaN (11 eV) [15], Si (13 eV) [16], and even C in diamond (80 eV) [17]. However, as we shall show later, *effective* values of  $E_d$  can be much higher if the *stable* defects are only those which involve *multiple* atomic displacements, along a chain of atoms.

Automated Hall-effect measurements were performed after each irradiation and covered a temperature range of 15–400 K. The contacts, In dots soldered to the corners of the square samples, were Ohmic even at the lowest temperatures. One sample was irradiated along the (0001) direction (Zn-face up), and the other along the (000 $\bar{1}$ ) direction (O-face up). Six irradiations, each of fluence  $4 \times 10^{16} \text{ e}/\text{cm}^2$ , were performed per sample and are designated as follows: I0, no irradiation; I1, 1.0 MeV; I2, 1.3 MeV;

I3, 1.6 MeV; I4, 2.0 MeV; I5, 2.0 MeV; and I6, 2.0 MeV. The TDH data for I0 and I6, O face, are shown in Fig. 1 as squares and circles, respectively. (Note that  $n$  in this figure is already corrected for the Hall  $r$  factor; i.e.,  $n = rn_H = r/eR$ , where  $R$  is the measured Hall coefficient.) The solid lines are accurate theoretical fits, calculated according to the following scheme [2]. First, the Hall mobility  $\mu_H$  vs  $T$  is fitted by solving the Boltzmann transport equation, using Rode's method [10], at each temperature; in this initial fit,  $n$  is approximated by  $n_H$ . The only fitting parameter is the acceptor concentration  $N_A$ , since the ionized-defect scattering rate varies as  $2N_A + n$  in an  $n$ -type sample, assuming singly ionized defects or impurities; all of the other scattering parameters are taken from the literature [2]. From this fit, a set of  $r$  factors can be calculated, and then the true  $n = rn_H$  can be used to determine a better value of  $N_A$  ( $r$  varies from 1.2–1.6 as a function of  $T$ ). Finally, the charge-balance equation is solved:

$$n + N_A = \sum_i \frac{N_{Di}}{1 + n/\phi_i}, \quad (2)$$

where  $\phi = (g_0/g_1) \exp(\alpha/k) N_C' T^{3/2} \exp(-E_{D0}/kT)$ . Here,  $g_0$  and  $g_1$  are the degeneracies of the unoccupied and occupied states, respectively,  $k$  is Boltzmann's constant,  $N_C'$  is the effective density of conduction-band states at  $T = 1$  K, and  $E_{D0}$  and  $\alpha$  are defined by the donor energy  $E_D = E_{D0} - \alpha T$ . In Fig. 1, we have used a single-donor model to fit just the data between about 80 and 300 K; below 80 K, impurity-band (or defect-band) effects cause the curves to bend upward, and, above 300 K, deeper donors become important. The fitting parameters given by the solid lines in Fig. 1 are the following: I0:  $N_A = 0.25 \times 10^{16}$ ,  $N_D = 8.6 \times 10^{16} \text{ cm}^{-3}$ , and  $E_{D0} = 34$  meV; I6:  $N_A = 15.9 \times 10^{16}$ ,  $N_D = 16.2 \times 10^{16} \text{ cm}^{-3}$ , and  $E_{D0} = 27$  meV. Note that a lower value of  $E_{D0}$  would be expected for the I6 case, because of increased screening effects due to the higher  $N_D$ ; i.e.,  $E_D = E_D(N_D = 0) - \beta N_D^{1/3}$ , where  $\beta$  is usually between 2 and  $3 \times 10^{-5} \text{ meV cm}$  for various semiconductor materials.

Although  $N_A$  has increased greatly by the end of the irradiation sequence, still the same shallow level is dominant, at least below  $T = 250$  K. Since  $n \ll \phi$  in the high- $T$  region, Eq. (2) gives  $n = N_D - N_A$ , and, since  $N_A \gg n$ ,  $N_D$  and  $N_A$  are almost equal and are being produced at nearly the same rate. In Fig. 2, we show  $n_H$  (300 K) and  $\mu_H$  (80 K) for both the O-face and Zn-face samples, noting that  $n_H$  (300 K)  $\cong N_D - N_A$  and  $\mu_H$  (80 K)  $\propto N_A^{-1}$ . Clearly, the threshold for  $N_A$  production is between 1.6 and 2.0 MeV, and the production is much higher for Zn-face irradiation. In this direction (Zn-face up), Zn displacement is “easy” because the Zn atoms are knocked into an interstitial region; however, in the other direction (O-face up), the Zn atoms have a short-bonded O atom directly beneath them, so that Zn displacement becomes more difficult [14].

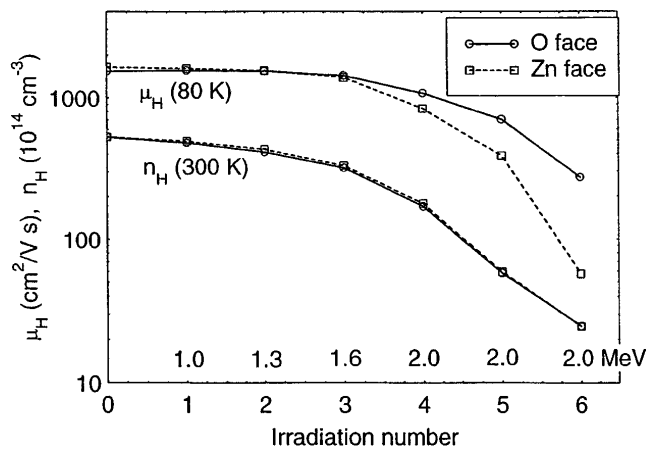


FIG. 2. Hall concentration at 300 K and mobility at 80 K as a function of irradiation schedule for two ZnO samples, one with the Zn-face up, and the other with the O-face up. The fluence for each irradiation was  $4 \times 10^{16} \text{ cm}^{-2}$ .

The opposite conclusions hold for O atoms, of course. Thus, the data of Fig. 2 suggest that Zn displacement is dominant, and the simplest explanation is that  $\text{Zn}_I$  (or a  $\text{Zn}_I$  complex) is the donor being produced, and  $V_{\text{Zn}}$  (or a  $V_{\text{Zn}}$  complex), the acceptor. Although no defect theory in ZnO has been carried out, to our knowledge, still, in analogy with theoretical results in ZnSe [18], we might expect  $\text{Zn}_I$  to have  $(0/+)$  and  $(+/++)$  states near the conduction band minimum. Our analysis has been based on single-charge-state donors and acceptors, which would hold if the 30-meV energy corresponds to  $(0/+)$ ; however, the analysis could be easily revised to include double-charge-state defects and the main conclusions would not change.

The conclusion that  $\text{Zn}_I$  is the dominant donor in our as-grown ZnO is based on the identification of a Zn-sublattice donor which happens to have the same energy as that of the dominant donor in the as-grown sample. However, there should also be O-sublattice defects created at 2 MeV, as found by Smith and Vehse [19], using EPR experiments. Moreover, Locker and Meese [17] have found a threshold for carrier removal at 0.31 MeV, but it appears only after first irradiating their sample at  $>0.90$  MeV. They argue that the 0.31 MeV threshold is due to O displacement, and that the one at 0.90 MeV is due to Zn displacement. However, if  $V_O$  is a deep donor, as found by the EPR experiments [8], then it cannot remove carriers in  $n$ -type material; in fact, it should not be seen by electrical measurements at all if  $E_F$  is near the conduction band. We believe, rather, that the carrier removal may occur by the *destruction* of the hydrogenic ( $\sim 60$  meV) donors. Consistent with this scenario, the I0 data for both of our samples are best fitted at high temperatures with a second donor, of roughly hydrogenic energy, but this level is barely evident after the I6 irradiation, as seen in Fig. 1. Two-donor fits to the I0–I6 data sets show a systematic removal of

the hydrogenic donor, which is largely responsible for the negative slope of  $n$  (300 K) seen in Fig. 2. One possible model for the hydrogenic-donor destruction is a replacement reaction, often observed in Si [20]. That is, a host interstitial (in this case  $\text{O}_I$ ), displaced during the irradiation, migrates to a substitutional donor (say,  $\text{Cl}_O$ ) and replaces it, thus destroying a donor. The  $V_O$  left behind, being deeper, does not contribute to  $n$  (300 K). It also might be conjectured that  $\text{O}_I$  could be an acceptor (as, e.g., is  $N_I$  in GaN) [15]; however, then we should see a strong decrease in  $\mu$  (80 K) and, in fact, very little decrease is seen until  $E > 1.6$  MeV. Thus, we believe that our data cannot be explained by O-sublattice damage.

It is still necessary to explain why the apparent displacement energy  $E_d$  is so large. That is, from Fig. 2, we see that the threshold energy  $E_{\text{th}}$  for significant electrical changes is  $\sim 1.6$  MeV, and we have assigned the donors and acceptors being produced above this energy to  $\text{Zn}_I$  and  $V_{\text{Zn}}$ , respectively. If the  $\text{Zn}_I$  results from a simple displacement, then, from Eq. (1),  $E_d \cong 138\text{--}198$  eV, which is much too high. In fact, Van Vechten has calculated  $E_d(\text{Zn}) \cong 18.5$  eV and  $E_d(\text{O}) \cong 41.4$  eV from a thermodynamic model [21], and Locker and Meese have estimated  $E_d(\text{Zn}) = E_d(\text{O}) \cong 57$  eV from their experiments [17]. We believe that the resolution to this problem lies in the idea of multiple displacements along a chain of atoms. That is, suppose  $E_d(\text{Zn}) = 18.5$  eV and suppose the electron energy is just high enough to displace a Zn atom; then, from Eq. (1), we calculate  $E_{\text{th}} = 0.4$  MeV. However, the  $\text{Zn}_I$  will be positively charged, and the  $V_{\text{Zn}}$  negatively charged, and they will probably recombine immediately. On the other hand, if  $E$  is higher, then the collision may give the Zn atom enough kinetic energy (KE) to knock out the O atom directly below it. For nonrelativistic particles, the maximum energy that a particle of mass  $M_1$  and energy  $E$  can transfer to a particle of mass  $M_2$  is

$$T_m = \frac{4M_1M_2}{(M_1 + M_2)^2} E \equiv RE. \quad (3)$$

If  $T_m(\text{O}) > E_d(\text{O})$ , then the O atom will be displaced and will itself have  $\text{KE}(\text{O}) = T_m(\text{O}) - E_d(\text{O})$ . This process can go on; i.e., if  $R\text{KE}(\text{O}) > E_d(\text{Zn})$ , then the O can knock out the Zn below it, etc. At some point, the last  $\text{Zn}_I$  knocked out will be far enough from the parent  $V_{\text{Zn}}$  to avoid immediate recombination. Let  $m$  be the total number of atoms displaced; e.g.,  $m = 3$  would denote Zn-O-Zn, and  $m = 5$ , Zn-O-Zn-O-Zn. Then it can be shown that the effective threshold energy, for  $m$  odd and  $m > 1$ , is given by

$$E_{d,\text{eff}}(\text{Zn}) = E_d(\text{Zn}) + \frac{E_d(\text{O})}{R} + \frac{E_d(\text{Zn})}{R^2} + \frac{E_d(\text{O})}{R^3} + \dots + \frac{E_d(\text{Zn})}{R^{m-1}}. \quad (4)$$

This expression can also be written in closed form, but, since  $m$  is usually small, Eq. (4) is more illustrative. If  $m$

is even (e.g.,  $m = 6$ ; Zn-O-Zn-O-Zn-O), then the formula becomes

$$E_{d,\text{eff}}(\text{Zn}) = E_d(\text{Zn}) + \frac{E_d(\text{O})}{R} + \frac{E_d(\text{Zn})}{R^2} + \frac{E_d(\text{O})}{R^3} + \dots + \frac{E_d(\text{O})}{R^{m-1}}. \quad (5)$$

If the O atoms are hit by the electrons, then we simply interchange “Zn” and “O” in Eqs. (4) and (5). For ZnO, Eq. (3) gives  $R = 0.6318$ . Thus, using Van Vechten’s value of  $E_d(\text{Zn})$  and  $E_d(\text{O})$ , and  $m = 3$ , we calculate  $E_{d,\text{eff}}(\text{Zn}) = 130$  eV. According to Eq. (1), the electron energy required to transfer 130 eV to a Zn atom would be about 1.55 MeV, in good agreement with the data of Fig. 2. It is also interesting to note that if O atoms are hit by the electrons, then, for  $m = 2$  (O-Zn),  $E_{d,\text{eff}}(\text{O}) = 71$  eV, and  $E_{\text{th}} = 0.38$  MeV, and, for  $m = 4$  (O-Zn-O-Zn),  $E_{d,\text{eff}}(\text{O}) = 248$  eV, and  $E_{\text{th}} = 0.94$  MeV. These values are in satisfactory agreement with the thresholds observed by Locker and Meese [17]. We, of course, do not know the accuracy of the values of  $E_d(\text{Zn})$  and  $E_d(\text{O})$  calculated by Van Vechten, but it is interesting that, when used with the multiple-displacement model, they can well explain both our data and the data of Locker and Meese.

Note that some interesting complexes can be generated from these multiple displacements. For example, the Zn-O-Zn process could lead to  $V_{\text{Zn}}\text{-ZnO-O-Zn-Zn}_I$ , with the  $\text{Zn}_I$  possibly drifting away. Theoretical analysis of the stabilities and electronic energies of the various possible complexes would be quite helpful in making assignments.

Photoluminescence measurements on irradiated ZnO samples show changes in the relative intensities of the donor-bound-exciton lines, but no new ones. These changes can possibly be correlated with the changes observed in the 60-meV TDH donor, but there is no clear correlation with the 30-meV TDH donor. The detailed PL results will be published elsewhere [22].

In summary, we have shown that electron irradiation of energy  $E > 1.6$  MeV creates significant concentrations of donors and acceptors in ZnO while lower energies cause little electrical damage. Because the defect production rate is much higher for (0001) Zn-face irradiation than for O-face irradiation, we assign the donor to  $\text{Zn}_I$  and the acceptor to  $V_{\text{Zn}}$ , or their complexes. The threshold energy of 1.6 MeV cannot be explained by simple  $\text{Zn}_I$ - $V_{\text{Zn}}$  (Frenkel pair) production, but is in good agreement with a multiple-displacement model (Zn-O-Zn) in which existing theoretical estimates [21] of the primary displacement energies of Zn and O are used as input parameters. This model also can explain the thresholds observed in earlier ZnO electron-irradiation experiments and should be useful for other semiconductor systems as well. The  $\text{Zn}_I$  donor has an energy of about  $30 \pm 5$  meV, the same as that observed in our as-grown material and in that of others;

thus,  $\text{Zn}_I$  (and not  $V_{\text{O}}$ ) is the dominant residual native shallow donor in ZnO.

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