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Self-compensation in semiconductors: The Zn vacancy in Ga-doped ZnO

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Self-compensation, the tendency of a crystal to lower its energy by forming point defects to counter the effects of a dopant, is here quantitatively proven. Based on a new theoretical formalism and several different experimental techniques, we demonstrate that the addition of 1.4 \times 10^{21} \text{cm}^{-3} Ga donors in ZnO causes the lattice to form 1.7 \times 10^{20} \text{cm}^{-3} Zn-vacancy acceptors. The calculated $V_{\text{Zn}}$ formation energy of 0.2 eV is consistent with predictions from density functional theory. Our formalism is of general validity and can be used to investigate self-compensation in any degenerate semiconductor material.

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I. INTRODUCTION

Self-compensation (SC) in semiconductors, the formation of acceptor-type lattice defects to counter donor-type impurity dopants or vice versa, has been theoretically predicted to occur in wide-band gap semiconductor materials; however, its existence has seldom been proven because of the difficulty in measuring and matching impurity and point-defect concentrations with donor ($N_D$) and acceptor ($N_A$) concentrations. In this paper, we develop a new theoretical formalism to determine $N_D$ and $N_A$ in degenerate semiconductor materials and then use it to investigate an important transparent-electrode material, Ga-doped ZnO.\textsuperscript{1–3} Then from secondary-ion mass spectroscopy (SIMS) results, we show that $N_D \approx \text{[Ga]}$, as expected, and from positron annihilation results that $N_A$ is consistent with $[V_{\text{Zn}}]$, where $V_{\text{Zn}}$ is the Zn-vacancy. Finally, from further comparison with SIMS measurements and the application of density functional theory (DFT), we show that $N_A$ can be explained only by $V_{\text{Zn}}$, and not any other impurity or point defect. These results conclusively demonstrate SC in highly doped ZnO, and by inference, SC is also possible in other transparent-electrode materials. If present, it will impose a limit on the ultimate conductivity that can be attained, at least under conditions of thermodynamic equilibrium. Indeed, for our ZnO sample the room-temperature resistivity is 2.0 \times 10^{-4} \Omega\text{-cm}, but elimination of the Zn vacancies would improve it to 0.9 \times 10^{-4} \Omega\text{-cm}, nearly a record for ZnO. Finally, as a check on the model, the value of $[V_{\text{Zn}}]$ is consistent with that expected from theoretical formation energies.

II. THEORY

Our theoretical formalism is based on finding an analytical expression for mobility $\mu(N_D, N_A, T)$ and then fitting this expression to the experimental mobility $\mu_{\text{exp}}(T)$ obtained from Hall effect measurements. The Hall experiment also measures carrier concentration $n$, which in degenerate materials immediately yields a second relationship: $n = N_D - N_A$, independent of temperature. Degeneracy also simplifies the mobility calculations, because (1) no energy averaging is necessary since all scattering occurs at the Fermi energy, $E_F$; (2) $E_F$ is a simple and well-known function of $n$; (3) Matthiessen’s rule ($\mu_{\text{tot}}^{-1} = \mu_{\text{el}}^{-1} + \mu_{\text{ph}}^{-1} + \mu_{\text{bdry}}^{-1}$) applies exactly,\textsuperscript{4,5} and (4) the major scattering is due to ionized impurities and the relevant theory (Brooks–Herring, B-H) contains only well-known parameters.\textsuperscript{4} In thin films, we must also consider scattering due to boundaries (surfaces and interfaces), and at higher temperatures, we must include phonon scattering. Thus, $\mu_{\text{tot}}^{-1} = \mu_{\text{el}}^{-1} + \mu_{\text{ph}}^{-1} + \mu_{\text{bdry}}^{-1}$, where $\mu_{\text{bdry}}$ is to be fitted to the experimental mobility, $\mu_{\text{exp}}$. Another scattering mechanism, that due to charged grain boundaries,\textsuperscript{6} may also be important if $n \leq 10^{20} \text{cm}^{-3}$; however, that is not the case for our samples, or indeed for most competitive transparent-conducting-oxide materials.

The degenerate form of the B-H equation is usually written as $\mu_{\text{ii}}(n, N_{ii}) = \mu_{\text{ii0}}(n) n / Z^2 N_{ii}$, where $N_{ii}$ is the concentration of ionized impurities (or defects) of charge $Z$, and $\mu_{\text{ii0}}(n)$ is given by\textsuperscript{4,5}

$$
\mu_{\text{ii0}}(n) = \frac{24\pi^3}{e^3 m^2} \frac{1}{n} \ln[1 + \gamma(n)] - \frac{n_{\text{th0}}}{T^3 n},
$$

where $n_{\text{th0}}$ is the Fermi-Dirac integration constant.

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where
\[
y(n) = \frac{3^{1/3} 4\pi n^{6/3} \epsilon_0 \hbar^2 n^{1/3}}{e^2 m^*}.
\]

Here, \(\epsilon_0\) is the static dielectric constant and \(m^*\) is the effective mass. Usually, it is assumed that \(Z = 1\), and if so, then \(\mu_{ii}(n, N_i) = \mu_{ii}(0)(1 - K)/(1 + K)\), where \(K = N_A / N_D\) is the compensation ratio, and \(\mu_{ii}(0)\) can be identified as the maximum possible mobility at a given concentration \(n\) because it is the value of \(\mu\) when \(N_A = 0\). However, for this study, it will be necessary to relax the condition \(Z = 1\), and also we will need to generalize the B-H equation to allow for multiple types of donors and acceptors. To carry out this generalization, we recognize that each group of donors and acceptors will scatter electrons independently, and thus we can add their respective scattering rates, i.e. the inverse mobilities, essentially invoking Matthiessen’s rule again:

\[
\mu_{ii}^{-1} = \mu_{ii}(0)^{-1} \sum D_{ij} N_{Dj} + \sum Z_{Aj} N_{Aj}
\]

\[= \mu_{ii}(0)^{-1} \sum D_{ij} N_{Dj} + \sum Z_{Aj} N_{Aj} - \sum Z_{Aj} N_{Aj}.\]

In our sample, we will show that there is one main donor, Ga, with \(Z_D = 1\), and one main acceptor, the isolated Zn vacancy \(V_Zn\), with \(Z_A = 2\) (in \(n\)-type material). In this case, Eq. (3) becomes \(\mu_i(N_D, N_A) = \mu_{ii}(n)(N_D - 2N_A)/(N_D + 4N_A)\).

For high-temperature analysis, we must add scattering due to optical and acoustic phonons. The optical phonons interact mainly through the polar potential, at least in ZnO, and the optical phonons interact through the piezoelectric \(\chi\) and \(\mu_{ph}(n, T)\). The acoustic phonons, interacting through the deformation potential, give a mobility according to the Matthiessen’s rule:

\[\mu_{ph}(n, T)^{-1} = \mu_{pe}(T)^{-1} + \mu_{aw}(n, T)^{-1} + \mu_{ph}(n, T)^{-1}.
\]

Finally, in thin films, we can have scattering at the boundaries, the surface, and interface. Here, we offer a simple, heuristic model that seems to work well for thicknesses \(d\) above, say, 20 nm. Under the logical assumption that the boundary-scattering-limited mean free path (mfp) should increase as \(d\) increases, we postulate that mfp = \(d/C\), where \(C\) is a constant that depends on the particular system being studied. The relevant velocity for scattering should be the Fermi velocity, so the mobility becomes:

\[\mu_{bdry}(d, n, C) = \frac{d/C}{m^* v_{Ferm}(n)} = \frac{d/C}{\hbar (3\pi^2 n)^{1/3}}.
\]

The value of \(C\) can be determined by growing multiple samples with various values of \(d\) and fitting \(\mu_{expt}\) vs \(d\) to Eq. (8), below. For example, ZnO layers grown on SiO\(_2\) by pulsed laser deposition (PLD) in O\(_2\) at 400°C and annealed in forming gas (5% H\(_2\) in Ar) at 400°C were well fitted with \(C = 4.4\) and PLD ZnO layers grown on Al\(_2\)O\(_3\) in Ar at 200°C required \(C = 2.5\). Fortunately, however, an accurate value of \(C\) is not a requirement for obtaining good values of \(N_D\) and \(N_A\) for our sample of thickness \(d = 278\) nm. This can be seen immediately by inserting the measured values \(C = 2.5\) and \(n = 1.1 \times 10^{21}\) cm\(^{-3}\) into Eq. (7) to get \(\mu_{bdry} = 527\) cm\(^2\)/V\(\cdot\)s. Since \(\mu_{expt} \leq 50\) cm\(^2\)/V\(\cdot\)s for all samples in this study, boundary scattering is not a major component of the mobility; however, we will still include it for maximum accuracy.

We now combine Eq. (3) with our earlier equation, \(\mu_{ii}(N_D, N_A)^{-1} = \mu_{expt}^{-1} - \mu_{ph}(n, T)^{-1} - \mu_{bdry}(n, d)^{-1}\), to get:

\[\mu_{ii}(N_D, N_A)^{-1} = \mu_{ii}(0)^{-1} \frac{Z_D^2 N_D + Z_A^2 N_A}{Z_D N_D - Z_A N_A} = \mu_{expt}(T)^{-1} - \mu_{ph}(n, T)^{-1} - \mu_{bdry}(n, d, C)^{-1},\]

where the only unknowns are \(N_D\) and \(N_A\). Finally, we solve Eq. (8) simultaneously with \(n = Z_D N_D - Z_A N_A\):

\[N_D = \frac{n}{Z_D(Z_D + Z_A)} \times \left\{ \frac{\mu_{ii}(0)}{\mu_{expt}(T)} \left[ 1 - \text{corr}(d, n, C, T) \right] + Z_A \right\},\]

\[N_A = \frac{n}{Z_A(Z_D + Z_A)} \times \left\{ \frac{\mu_{ii}(0)}{\mu_{expt}(T)} \left[ 1 - \text{corr}(d, n, C, T) \right] - Z_D \right\},\]

where

\[\text{corr}(d, n, C, T) = \frac{\mu_{expt}(T)}{\mu_{ph}(n, T)} + \frac{\mu_{expt}(T)}{\mu_{bdry}(d, n, C)}.
\]

Here, \(\text{corr}(d, n, C, T)\) may be thought of as a correction term (normally small) due to phonon scattering at high temperatures and boundary scattering at small thicknesses. For our unannealed sample, at \(T = 20\) K, \(\text{corr} = 0.001 + 0.062 = 0.063\), and at 300 K, \(\text{corr} = 0.131 + 0.054 = 0.185\). Thus, it is always best, if possible, to measure \(\mu_{expt}\) at as low a \(T\) as possible, say, \(T < 100\) K, to avoid the phonon terms altogether. In this regard, measurements at liquid-nitrogen...
temperature (77 K), if available, should be quite sufficient in most cases. Also, thicker samples are better for avoiding the boundary scattering correction. However, if thick samples and low-temperature measurements are not possible, then Eqs. (9) and (10) can be applied with only slightly reduced accuracy.

III. EXPERIMENT

Eight, 1-cm × 1-cm pieces were cut from a 278-nm-thick ZnO film grown on a 3-inch Al2O3 substrate by PLD at 200 °C in an atmosphere of pure Ar. We have earlier showed that the unusual process of PLD growth in pure Ar, without any O2 in the growth ambient, produces highly conductive ZnO.12

For the present samples, the as-grown, room-temperature (RT) resistivity was 1.96 × 10−4 Ω-cm, without any additional processing, such as annealing. However, to test whether even lower resistivities could be obtained by further processing, we subjected seven of the pieces to rapid thermal annealing in forming gas (5% H2 in Ar) for 10 min at various temperatures from T2 = 300–600 °C. The minimum resistivity obtained was 1.46 × 10−4 Ω-cm, at T2 = 500 °C. Although these annealing results are of interest for practical applications, we wish to emphasize that the main conclusion of this paper, the existence of self-compensation in the form of Zn vacancies, depends only on analysis of the unannealed sample.

Hall effect measurements were carried out over the range 20–300 K. The mobilities for the unannealed sample and those annealed at 450, 500, and 600 °C are shown in Fig. 1. The fits to the curves, using Eq. (8), are also shown, as solid lines. In the fittings, the following parameters in Eqs. (1)–(6) were taken from the literature: ε0 = 8.12εvac, ε1 = 3.72εvac, T0 = 837 K, E1 = 3.8 eV, Ppe = 0.21,9 and cl = 1.4 × 1013 N/m2.13

For the remaining two parameters, the constant C = 2.5 in (7) was determined from a μ-vs-T analysis, discussed in Ref. 12, and an effective mass m∗ = 0.34m0. The best fit of μ vs T for the unannealed sample, as demonstrated by the solid line in Fig. 1. (The upper and lower dashed lines are calculated using different values of m∗, respectively.) Note that our best-fit m∗ is larger than the literature value 0.318m0 or the value 0.30m0 that we and others have typically used for nondegenerate samples.14 However, it is expected that the conduction band (CB) may be somewhat nonparabolic at the Fermi energy (E_F = 1.3 eV at n = 1.1 × 1021 cm−3), and so our higher value of m∗ may be taken as a measure of the CB nonparabolicity at E_F. Using m∗ = 0.34m0 along with the other parameters mentioned above, we fit Eq. (8) to the mobility data for the unannealed sample and those annealed at 450, 500, and 600 °C. The values of ND and NA producing the best fits are displayed in Fig. 1. For the unannealed sample, ND = 1.45 × 1021 and NA = 1.71 × 1020 cm−3, where we have assumed that ZD = 1 and ZA = 2. Below we will compare with SIMS to show that ND consists mainly of the dopant Ga, with slight contributions from H and Al, but that NA cannot be due to any impurity.

To quantitatively assess the possible impurity involvement in ND and NA, secondary-ion mass spectrometry (SIMS) measurements were performed. Calibrations of individual impurities were accomplished with ion-implanted standards. For maximum calibration accuracy, the peak concentration of a given impurity in the implanted standard was designed to be about the same as the expected concentration of that same impurity in the sample itself. A mass scan of all elements was carried out to determine which were of a sufficient concentration to contribute significantly to the > 1021 cm−3 donors and the > 1020 cm−3 acceptors, and thus only impurities of concentration > 1018 cm−3 were considered further in the analysis. Three impurities, all normally donors, satisfied this criterion: Ga (∼1.4 × 1021 cm−3), H (∼1–9 × 1018 cm−3, depending on depth and anneal conditions), and Al (∼3 × 1018 cm−3). Thus, as expected, the donors are dominated by Ga, but H and Al are also included in the total SIMS-derived donor concentration, i.e. SIMS-ND = [Ga] + [H] + [Al]. The SIMS-ND’s are plotted in Fig. 2 for the unannealed sample and those annealed at 500 and 600 °C, and they are compared with the Hall-ND’s calculated from the respective mobilities at 20 K. In the unannealed sample, the excellent agreement between the Hall- and SIMS-ND’s, along with the good fit to the overall temperature dependence demonstrated in

![FIG. 1. (Color online) Experimental (points) and theoretical (solid and dashed lines) mobilities for Ga-doped ZnO samples grown at 200 °C in pure Ar and annealed at various temperatures in forming gas.](image1)

![FIG. 2. (Color online) A comparison of donor concentrations determined by Hall mobility analysis (solid lines) and SIMS measurements of [Ga] + [H] + [Al] (dashed lines).](image2)
Fig. 1, shows that the scattering model is basically sound and should also be applicable to the annealed samples. Consider the sample annealed at 600 °C: here the SIMS-N_D has dropped about 10%, with the drop split about evenly between decreases in [H], expected to leave the sample at 600 °C, and [Ga]. However, the Hall-N_D has decreased much more, about 45%. Since [Ga] itself drops by only about 5%, the large decrease in N_D has to come from the loss of donor character in some of the Ga atoms, and this can possibly occur through reactions at 600 °C that produce neutral forms of Ga, such as Ga_2O_3 or ZnGa_2O_4. Confirmation of such possibilities will have to await further investigation.

IV. DISCUSSION

We now turn to the identity of the acceptors, of concentration N_A = 1.71 \times 10^{20} \text{ cm}^{-3}. No impurities, except possibly Ga itself, can account for a concentration this high. If Ga were involved, then the associated acceptor would likely be Ga_2Zn, a singly charged complex. In that case, we would have Z_A = 1 and Eqs. (9) and (10) would give N_D = 1.64 \times 10^{21} and N_A = 5.40 \times 10^{20} \text{ cm}^{-3}. For Ga to account for all the acceptors, and all of the donors except H and Al, we would need [Ga] = N_D - [H] - [Al] + N_A \approx 2.0 \times 10^{21} \text{ cm}^{-3}, and that is outside the error of our SIMS values, [Ga] \leq 1.4 \times 10^{21} \text{ cm}^{-3}. Thus, we conclude that the dominant acceptor must be a doubly charged point defect at a concentration of about 1.7 \times 10^{19} \text{ cm}^{-3}. The potential acceptor-like point defects are the Zn vacancy, V_Zn, the O interstitial, O_I, and the O antisite, O_Zn. To get an estimate on which of these defects is most likely, we can assume quasi-equilibrium growth conditions (Fig. 1), shows that the scattering model is basically sound and should also be applicable to the annealed samples. Consider the Zn vacancy, V_Zn, the O interstitial, O_I, and the O antisite, O_Zn. To get an estimate on which of these defects is most likely, we can assume quasi-equilibrium growth conditions and compare the formation energies E_F's calculated from density functional theory (DFT). It turns out that for n-type material, under either Zn-rich or O-rich growth conditions, the E_F's for both O_I and O_Zn are at least 2 eV higher than that of V_Zn. The concentration of a particular species can be approximated by C \approx N_{sites} \times \exp(-E_F/kT_G), where N_{sites} is the density of sites available for that species and T_G = 473 K is the growth temperature. For V_Zn, N_{sites} \approx 4 \times 10^{22} \text{ cm}^{-3} and C = N_A = 1.7 \times 10^{20} \text{ cm}^{-3}, so that the predicted E_F(V_Zn) \approx 0.22 \text{ eV}. Theoretical values for E_F(V_Zn) have been calculated by DFT, but these values depend on the choices of exchange and correlation functionals. In Ref. 7, localized functionals (GGA approximation, in this reference) are used and E_F(V_Zn), for a Fermi energy E_{Fermi} at the CB minimum (E_{CB, min}), ranges between +1.8 eV for Zn-rich growth to −1.9 eV for O-rich growth. In Ref. 8, several local and nonlocal combinations of functionals are compared, and a screened exchange (sX) functional, which produces an accurate band gap E_g = E_{CB, min} − E_{V, max} = 3.41 eV, gives E_F(V_Zn) = +4.1 eV for Zn-rich growth and +0.2 eV for O-rich growth. However, E_F in our samples will in general be different from 3.41 eV because the extremely high concentration (~10^{21} \text{ cm}^{-3}) of Ga atoms will affect it in several ways: (1) the CB will be shifted downward because of exchange and correlation effects arising from the donor electrons (band gap narrowing or renormalization); (2) the host CB states will hybridize with the Ga donor states and induce nonparabolicity; and (3) the donor electron will fill states well into the CB and thus effectively increase the band gap (Moss–Burstein effect) for the nondegenerate DFT case, the new equilibrium band gap will be E_DFT(n) = E_{CB(k_{Fermi})} − E_{V, max}. To determine E_DFT(n), some relevant information can be obtained from a simple optical absorption (OA) threshold measurement, which gives E_{Opt, abs} = 3.85 eV for a sample with n = 1 \times 10^{19} \text{ cm}^{-3}, grown on double-side polished Al_2O_3 (in order to carry out absorption measurements). The OA experiment was performed with the light direction parallel to the c axis which means the light is polarized perpendicular to the c axis. For such a polarization, transitions are allowed from either of the two top, nearly degenerate, valence bands (Γ_7 and Γ_9 symmetry) to the lowest conduction band (Γ_2) at k = 0.20 Since the absorption transition is vertical in k space, we can write E_{Opt, abs} = E_{CB(k_{Fermi})} − E_{VB(k_{Fermi})} = E_DFT(n) + E_{V, max} − E_{VB(k_{Fermi})}. Thus, E_DFT(n) = E_{Opt, abs} − (h^2/2)[k_F^2/m_{hh}^{*} + k_F^2/m_{hh}/], where m_{hh}^{*} and m_{hh}/ are the effective masses of the heavy holes, perpendicular and parallel to the c axis, respectively, and k_{Fermi} = (3\pi^2 n)^{1/3}. Also, k_F^2 = (k_{Fermi})^2 = k_{Fermi}^2 = (3\pi^2 n)^{2/3}. Unfortunately, m_{hh}/ and m_{hh}/ are not well-known quantities, but some recently reported values are m_{hh}/ = 0.8m_0 and m_{hh}/ = 5.0m_0. The optical-absorption threshold will occur at the highest point in the VB consistent with k = k_{Fermi}, and for n = 10^{19} \text{ cm}^{-3}, that point is k_F = k_F = 0, and k_F = k_{Fermi} = 3.1 \times 10^9 \text{ m}^{-1}, giving E_DFT(n) = 3.85 − 0.073 = 3.78 eV. Interestingly, the new value of E_{CB, min} − E_{VB, max} is then 3.78 − 3.78/2m_0^{*} = 3.78 − 1.07 eV = 2.71 eV, which may be taken as the renormalized band gap. Our E_F(V_Zn) values for the sX functional must therefore be corrected by −2(3.78 − 3.41) = −0.74 eV, and thus we get E_F(V_Zn) = +4.1 − 0.7 = 3.4 eV for Zn-rich growth and +0.2 − 0.7 = −0.5 eV for O-rich growth, respectively. For comparison, another DFT approach (LDA + U) gives E_F(V_Zn) = +1.8 eV for Zn-rich growth and −1.9 eV for O-rich growth, before corrections for E_{Fermi}, and thus 1.1 eV and −2.6 eV, respectively, after corrections. Clearly, our Hall-effect-derived value +0.2 eV is within the theoretical ranges presented in both of these works, and thus our hypothesis that the dominant acceptor is V_Zn is consistent with the predictions of DFT.

Finally, we consider the question of direct evidence for large quantities of V_Zn in our samples. For this, we apply positron annihilation spectroscopy (PAS), a technique that is very sensitive to negatively charged vacancies, such as V_Zn in ZnO. To get good signal strength, we used two thicker PLD samples, one Ga doped and the other undoped. The PAS-determined concentrations of isolated Zn vacancies [V_Zn] were \geq 10^{19} \text{ cm}^{-3} for the Ga-doped sample and \leq 10^{18} \text{ cm}^{-3} for the undoped sample. (The lower limit on [V_Zn] for the doped sample is due to saturation of the PAS signal at [V_Zn] \approx 10^{19} \text{ cm}^{-3}.) Two conclusions are evident: (1) [V_Zn] is at least 10^{18} \text{ cm}^{-3} and thus must be the dominant acceptor since it is far larger than any impurity of acceptor-type character; and (2) [V_Zn] of the undoped sample is more than an order of magnitude below that of the Ga-doped sample, showing that the heavy donor incorporation produces large quantities of compensating point-defect acceptors. (It should also be noted that a signal sometimes seen for vacancy clusters was at least two orders of magnitude smaller than that for isolated vacancies, showing that only the latter are important.)
and intensities of the peaks near 1.8 eV. In the near-band-edge region (3.5 eV) in order to compare the relative doped ZnO samples grown at 200 °C. We might associate the ratio = 1.64 to be immediately applied to other ZnO results already present in the literature. As an example, consider the ZnO sample with one of the lowest ever reported resistivities, ρ = 8.12 × 10⁻³ Ω·cm.²⁶ It was grown by PLD on quartz at 300 °C to a thickness of 200 nm, and Hall effect measurements gave = 30.96 cm²/V·s and = 1.46 × 10⁻²² cm⁻³ at room temperature. From these values of and , we can use Eqs. (9) and (10) to calculate = 1.76 × 10²¹ and = 1.50 × 10³⁰ cm⁻³, under the assumption that = 0.34m₀ and = 2.5. Then, assuming that = [VZn], as with our sample, we get EF(VZn) ≈ 0.27 eV, very close to our value of 0.22 eV. The higher N₀ = 1.76 × 10²¹ cm⁻³, compared with our value of 1.45 × 10²¹ cm⁻³, may be due to the higher Ga content in their target, 5% vs our 3%. In any case, the close overall agreement between these two studies, especially the very high concentrations of acceptors of near equal magnitudes, is totally consistent with the idea of point-defect compensation in heavily-doped semiconductors.

V. SUMMARY

In summary, we have quantitatively demonstrated self-compensation in a highly doped, wide-band gap semiconductor, ZnO. To accomplish this task, we have developed a theoretical formalism to calculate donor and acceptor concentrations from mobility measurements in degenerate semiconductors and have applied it to Ga-doped ZnO. In conjunction with Hall effect, SIMS, and PAS measurements, we have shown that N₀ is comprised mostly of Ga with small contributions from H and Al, and that = is due to Zn vacancies. The Zn-vacancy concentration is consistent with that predicted by density functional theory for nearly stoichiometric growth conditions.

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Fig. 3. (Color online) Cathodoluminescence spectra for Ga-doped ZnO samples grown at 200 °C in pure Ar and annealed at 300 and 550 °C, respectively, in forming gas. The dashed curve represents the 300 °C sample intensity normalized to that of the 550 °C sample in the near-band-edge region (3.5 eV) in order to compare the relative intensities of the peaks near 1.8 eV.

Optical evidence for [VZn] is also found. Depth-resolved cathodoluminescence (DRCL) measurements have shown that bands in the 1.7–2.1 eV region correlate well with VZn concentrations.²⁴ Indeed, these bands are not strong in most as-grown, nondegenerate ZnO samples, which instead are dominated in the deep region by a green band at 2.4–2.5 eV.²⁵ However, high-energy electron irradiation in such nondegenerate samples produces electron-paramagnetic-resonance lines known to be due to VZn and also a strong photoluminescence band at 1.8 eV, attributed to shallow-donor-VZn pair (DAP) recombination.²⁵ Our present, unannealed, Ga-doped sample also has a dominant peak near 1.8 eV, as shown in Fig. 3. In agreement with the presence of VZn. Here, we compare the samples annealed at 300 and 550 °C, because neither of these samples had been subjected to postanneal processing. Our Hall effect analysis gives N₀ = 1.44 × 10²¹ and = 1.64 × 10³⁰ cm⁻³ for the 300 °C sample (very close to N₀ and of the unannealed sample), and N₀ = 9.25 × 10²⁰ and = 0.33 × 10³⁰ cm⁻³ for the 550 °C sample. In Fig. 3, the dashed curve is the 300 °C sample intensity normalized to that of the 550 °C sample in the near-band-edge region (~3.5 eV), in order to visually compare the relative intensities of the peaks near 1.8 eV. Qualitatively, the 300 °C sample has a larger 1.8-eV peak, in agreement with the larger found from the Hall effect analysis. More quantitatively, we might associate the ratio = I(1.8 eV)/I(3.5 eV) with R₀ = N₀/N₀, and thus compare R₀(300)/R₀(550) = 2.5, and R₀(300)/R₀(550) = 3.4, which should be considered to be satisfactory agreement considering the many unknown factors affecting the optical line intensities. Thus, the DRCL measurements give further evidence that heavy donor doping induces VZn acceptors.

Although our experimental work in this investigation has concentrated on the Zn vacancy in ZnO, the mobility model presented here is applicable to all degenerate semiconductors for which values of , , , and are available. (Note that Ref. 9 lists such values for 19 materials.) In particular, the formulas for and [Eqs. (9) and (10)] can be immediately applied to other ZnO results already present in the literature. As an example, consider the ZnO sample with one of the lowest ever reported resistivities, ρ = 8.12 × 10⁻³ Ω·cm.²⁶ It was grown by PLD on quartz at 300 °C to a thickness of 200 nm, and Hall effect measurements gave = 30.96 cm²/V·s and = 1.46 × 10⁻²² cm⁻³ at room temperature. From these values of and , we can use Eqs. (9) and (10) to calculate N₀ = 1.76 × 10²¹ and = 1.50 × 10³⁰ cm⁻³, under the assumption that = 0.34m₀ and = 2.5. Then, assuming that = [VZn], as with our sample, we get EF(VZn) ≈ 0.27 eV, very close to our value of 0.22 eV. The higher N₀ = 1.76 × 10²¹ cm⁻³, compared with our value of 1.45 × 10²¹ cm⁻³, may be due to the higher Ga content in their target, 5% vs our 3%. In any case, the close overall agreement between these two studies, especially the very high concentrations of acceptors of near equal magnitudes, is totally consistent with the idea of point-defect compensation in heavily-doped semiconductors.

V. SUMMARY

In summary, we have quantitatively demonstrated self-compensation in a highly doped, wide-band gap semiconductor, ZnO. To accomplish this task, we have developed a theoretical formalism to calculate donor and acceptor concentrations from mobility measurements in degenerate semiconductors and have applied it to Ga-doped ZnO. In conjunction with Hall effect, SIMS, and PAS measurements, we have shown that N₀ is comprised mostly of Ga with small contributions from H and Al, and that = is due to Zn vacancies. The Zn-vacancy concentration is consistent with that predicted by density functional theory for nearly stoichiometric growth conditions.

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