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Ga-related photoluminescence lines in Ga-doped ZnO grown by plasma-assisted molecular-beam epitaxy

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Low-temperature photoluminescence (PL) and temperature-dependent Hall-effect (T-Hall) measurements were carried out in undoped and Ga-doped ZnO thin films grown by molecular-beam epitaxy. As the carrier concentration increases from 1.8×10^{18} to 1.8×10^{20} cm⁻³, the dominant PL line at 9 K changes from I_1 (3.368–3.371 eV) to I_{DA} (3.317–3.321 eV), and finally to I_8 (3.359 eV). The dominance of I_1 , due to *ionized*-donor bound excitons, is unexpected in *n*-type samples but is shown to be consistent with the T-Hall results. We also show that I_{DA} has characteristics of a donor-acceptor-pair transition, and use a detailed, quantitative analysis to argue that it arises from Ga_{Zn} donors paired with Zn-vacancy (V_{Zn}) acceptors. In this analysis, the Ga_{Zn}^{0/+} energy is well-known from two-electron satellite transitions, and the $V_{Zn}^{0/-}$ energy is taken from a recent theoretical calculation. © 2009 American Institute of Physics. [DOI: 10.1063/1.3080204]

ZnO materials have potential applications in optoelectronics and spintronics.^{1–4} Although *p*-type doping has attracted more recent attention in ZnO research, *n*-type materials with high crystallinity and controllable electron carrier concentration (*n*) are also indispensable toward the applications. For example, controllable *n* is important for ZnO-based dilute magnetic semiconductor materials because their magnetic properties can be modulated by *n*.^{5–7} Also, group-III-doped ZnO with large *n* is a potential candidate for replacing conventional transparent conducting oxides such as indium tin oxide. Among group-III elements, Ga is an excellent *n*-type dopant in ZnO with a more compatible covalent bond length (1.92 Å for Ga–O and 1.97 Å for Zn–O) than that of Al or In (2.7 Å for Al–O and 2.1 Å for In–O).

Ga-doped ZnO has been widely studied;^{8–14} however, among the Ga-related excitonic transitions, only excitons bound to *neutral* Ga_{Zn} donors (I_8 in the literature) have been commonly reported. This is in part due to the strong tendency for ionized donors to become neutral under light excitation because of the reaction $D^+ + e^- \rightarrow D^0$. In this paper, we report systematic photoluminescence (PL) studies of high-quality Ga-doped ZnO thin films with various *n*. Variations in the energies and strengths of three dominant donor-related PL emissions with increasing *n* are discussed in detail.

ZnO thin films were grown on *r*-plane sapphire substrates using plasma-assisted molecular-beam epitaxy (MBE). An undoped sample (A) and eight Ga-doped samples (B–I), with room-temperature electron carrier concentration *n* ranging from 1.9×10^{18} to 1.8×10^{20} cm⁻³, were prepared. The *n* of each sample was tuned by the Ga incorporation controlled by the Ga effusion cell temperature. The 300 K (10 K) *n* values of samples A–I are 0.19 (0.18), 0.55 (0.36), 0.96 (0.88), 1.5 (1.5), 2.3 (2.2), 2.5 (2.4), 3.6 (3.5), 7.4 (7.4), and 18 (18), respectively, in unit 10¹⁹ cm⁻³. The *n* values do

not show strong temperature dependence since they are basically degenerate.

Reflection high-energy electron diffraction (RHEED) measurements were performed *in situ* on the as-grown samples in the MBE system. Hall-effect measurements were carried out using a Quantum Design physical properties measurement system at 10 and 300 K, and a LakeShore 7507 system from 15 to 320 K. X-ray diffraction (XRD) measurements were performed using a Bruker D8 Advance x-ray diffractometer. PL measurements were carried out using a home-built PL system with temperature control over a range of 8.5–300 K. The 325 nm wavelength of a He–Cd laser was used as an excitation source and a photomultiplier tube was used to detect the PL signals. The resolution of the PL system was 0.15 nm, which is about 1.5 meV in the ultraviolet emission region.

Figure 1 shows the XRD spectra of undoped sample A and heavily Ga-doped sample G. Only the ZnO and GaZnO (11 $\bar{2}$ 0) peaks are observed in the samples, indicating that both samples are single crystalline and the heavy Ga doping does not significantly degrade the crystallinity of the film. The insets in Fig. 1 show the RHEED patterns of the two samples. Note the change from the streaky pattern of the undoped sample to the spotty pattern of the Ga-doped

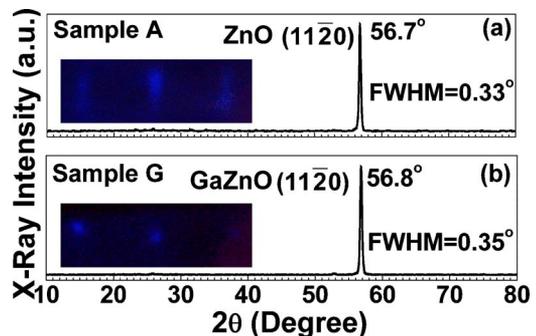


FIG. 1. (Color online) XRD patterns of (a) undoped ZnO sample A and (b) heavy-Ga-doped ZnO sample G. The insets show the RHEED patterns of samples A and G, which are streaky and spotty, respectively.

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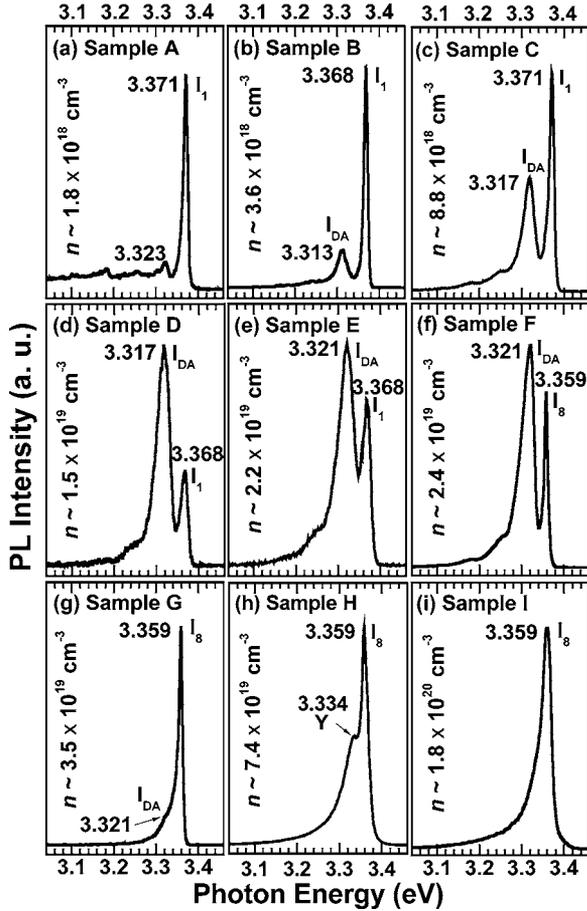


FIG. 2. PL spectra measured at 9 K for samples A–I [(a)–(i)].

sample, which indicates that the surface of the film becomes rougher after heavy Ga doping.

Figures 2(a)–2(i) show the 9 K PL spectra of samples A to I. In the nine spectra, three basic PL peaks, designated I_1 , I_8 , and I_{DA} , are dominant: I_1 , at 3.368–3.371 eV, is found in samples A to E; I_8 , at 3.359 eV, in samples F to I; and I_{DA} , at 3.313–3.321 eV, in samples B to G. The I_8 line is the commonly accepted as the neutral Ga donor-bound-exciton recombination.^{8,15,16} The I_1 line lies above the common neutral donor-bound-exciton lines, $I_9(\text{In})$, $I_8(\text{Ga})$, $I_6(\text{Al})$, and $I_4(\text{H})$, which span the range of 3.357–3.363 eV but below the free A exciton line at 3.377 eV. It has been seen in the past^{16,17} but never unambiguously identified. More recently, however, it has been associated with an exciton bound to an ionized Ga donor.^{18,19} In almost all n -type ZnO samples, the intensity of I_1 is much less than that of I_8 ; however, several of our samples show exactly the opposite relationship, and we will give the reasons below.

The PL lines occurring in the region of 3.30–3.32 eV have been variously assigned in the literature to many different transitions, including those involving acceptor-bound excitons, donor-acceptor pairs (DAPs), and free electrons to neutral acceptors.²⁰ In fact, more than one mechanism may contribute to luminescence in this region. Here we will argue that DAP transitions best describe line I_{DA} in our case. Immediate support for this assignment arises from a study of the excitation-power dependence of the luminescence in sample E, Fig. 2. In this sample, the I_{DA} transition energy clearly blueshifts with excitation power (not shown), whereas that of I_1 does not. This is a strong indication that

I_{DA} represents a DAP transition. Further support is presented below.

We propose that I_{DA} consists of transitions between neutral Ga_{Zn} donors and neutral Zn-vacancy (V_{Zn}) acceptors, or acceptor complexes. Obviously Ga_{Zn} donors should be abundant in our samples but V_{Zn} acceptors also have low formation energies and are common in n -type ZnO.²¹ In this scenario, the DAP transition would be written as $\text{Ga}_{\text{Zn}}^0 + V_{\text{Zn}}^0 \rightarrow \text{Ga}_{\text{Zn}}^+ + V_{\text{Zn}}^-$. The photon emitted in this transition should have an energy

$$E_{DA} = E_g - E_D(\text{Ga}_{\text{Zn}}^{0/+}) - E_A(V_{\text{Zn}}^{0/-}) + E_{\text{coul}} - E_{\text{vdW}}, \quad (1)$$

where $E_D(\text{Ga}_{\text{Zn}}) = 55$ meV from analysis of two-electron satellite spectra^{15,16} and $E_A(V_{\text{Zn}})$ is estimated to be about 180 meV, as recently determined from density-functional theory (DFT).²² The term $E_{\text{coul}} = e^2/4\pi\epsilon r_{DA}$ is the Coulomb energy arising from the proximity between the donor and acceptor, and E_{vdW} is the van der Waals (vdW) polarization energy associated with the dipole-dipole interaction.²³ The vdW term is very small compared to the Coulomb term when r_{DA} is large, and hence is generally neglected. However, when r_{DA} is small (say, < 2 nm), the contribution from the vdW term needs to be considered. The traditional vdW term is in the form of

$$E_{\text{vdW}} = \frac{e^2}{4\pi\epsilon r_{DA}} \left(\frac{b}{r_{DA}} \right)^5 \quad (2)$$

as proposed by Dean²³ in GaP materials, with b a constant for a given donor and acceptor. However, it was later found that this equation gives a very unsatisfactory result in II-VI materials, especially in the region of closer pairs ($r_{DA} < 3$ nm).²⁴ Instead, an exponential form

$$E_{\text{vdW}} \text{ (eV)} = 0.06823 \times \exp[-1.312 \times r_{DA} \text{ (nm)}] \quad (3)$$

was employed by Neumark²⁵ to achieve a good fit. We will use Neumark's formula as a reasonable approximation for our samples because E_{vdW} is rather small compared to E_{coul} and thus high accuracy in E_{vdW} is not required.

Consider the PL spectrum for sample F in Fig. 2. Here I_8 is strong and I_1 does not appear in the linear plot, which indeed is typical of most ZnO samples that we have examined. To apply Eq. (1), we need to know the donor and acceptor concentrations, N_D and N_A , respectively. Measurement of these quantities requires temperature-dependent Hall-effect (T-Hall) measurements, and to analyze the T-Hall data, we employ a general two-layer algorithm outlined in Ref. 26. The fitting results are $N_{D1} = 6.3 \times 10^{19} \text{ cm}^{-3}$, $N_{D2} = 7.0 \times 10^{18} \text{ cm}^{-3}$, $N_{A1} = 4.0 \times 10^{19} \text{ cm}^{-3}$, and $N_{A2} = 2.0 \times 10^{18} \text{ cm}^{-3}$; and $d_1 = 440$ nm and $d_2 = 20$ nm. Here N_{Di} , N_{Ai} , and d_i , are the donor concentration, acceptor concentration, and thickness of layer i , respectively. Layer 2 is probably representative of the surface and/or interface regions and is not of importance in this study. In the dark, at 10 K, the neutral donor concentration in layer 1 is $N_D^0 \approx N_D - N_A = 2.3 \times 10^{19} \text{ cm}^{-3}$, and the neutral acceptor concentration is $N_A^0 \approx 0$ since almost all of the acceptors will be negatively charged. In the light, photogenerated electrons will create more D^0 through the reaction $e + D^+ \rightarrow D^0$, and photogenerated holes will create A^0 through the reaction $h + A^- \rightarrow A^0$. Of course, some of the photogenerated electrons and holes will also form free excitons, $h + e \rightarrow X$, and at 10 K most of these excitons will bind to neutral donors, forming D^0X . (Note that

neutral acceptors are rarely seen in ZnO.) If these three reactions are the only ones available (or at least are dominant), then the photogenerated neutral donors and acceptors must be equal: $\Delta D^0 = \Delta A^0$. Since clearly $D^0 + \Delta D^0 > \Delta A^0$, the average distance between neutral donors and acceptors will be determined by the average distance between neutral donors, i.e., $r_{DA} \approx (3/4\pi N_D^0)^{1/3} \approx 2.2$ nm, assuming $N_D^0 \gg \Delta N_D^0$. Then, applying Eqs. (1) and (3), $E_{DA} = 3.437 - 0.055 - 0.18 + 0.081 - 0.004 = 3.279$ eV. If on the other hand, it is assumed that the light neutralizes *all* of the donors, then $E_{DA} = 3.307$ eV. With this and other uncertainties, including that in the DFT value [$E_A(V_{Zn}^{0/-}) = 0.18$ eV], our range of 3.279–3.307 eV is in good agreement with the experimental value, 3.321 eV. This agreement, along with the aforementioned observation of a blue shift with excitation intensity, justifies the assignment of I_{DA} as a DAP transition involving Ga_{Zn} donors and V_{Zn} acceptors.

The other main PL line in Fig. 2(f), I_8 , is almost universally acknowledged to be the $\text{Ga}_{Zn} D^0X$ line. The existence of this line is entirely expected from the high concentration of neutral donors available for the reaction $D^0 + X \rightarrow D^0X$. Although the relative strengths of I_8 and I_{DA} depend upon many factors, certainly one of these factors is the photogenerated neutral-acceptor concentration ΔA^0 . Indeed, as more Ga donors are added to the ZnO (cf. samples G, H, and I in Fig. 2), the reaction $e + h + D^0 \rightarrow D^0X$ may become more and more dominant over the reaction $h + A^- \rightarrow A^0$, thus favoring I_8 over I_{DA} .

Finally, we must explain the dominance of ionized donor-bound excitons in low-Ga-doped samples, such as sample A, which has only background Ga doping. The occurrence of strong D^+X transitions, represented by I_1 , is very unusual. To explain this phenomenon, we again turn to the T-Hall fitting,²⁶ which for sample A [Fig. 2(a)] gives $N_{D1} = 1.33 \times 10^{20} \text{ cm}^{-3}$, $N_{D2} = 6.5 \times 10^{19} \text{ cm}^{-3}$, $N_{A1} = 1.30 \times 10^{20} \text{ cm}^{-3}$, and $N_{A2} = 2.5 \times 10^{19} \text{ cm}^{-3}$ and $d_1 = 199$ nm and $d_2 = 1$ nm. Again, only layer 1 is of any importance, and in the dark we get $N_D^0 = N_D - N_A \approx 3 \times 10^{18} \text{ cm}^{-3}$ and $N_D^+ \approx N_A = 1.3 \times 10^{20} \text{ cm}^{-3}$. (Note that the compensation ratio N_A/N_D is close to one for sample A. However, this is often the case in as-grown ZnO; see, e.g., Table I in Ref. 26.) Thus, $N_D^+ \gg N_D^0$, so that in weak light the ionized donor-bound excitons $D^+X(I_1)$ might be expected to dominate over the neutral donor-bound excitons $D^0X(I_8)$. Even in stronger light, it takes three reactions to make D^0X from D^+ : (1) $e + h \rightarrow X$, (2) $e + D^+ \rightarrow D^0$, and (3) $X + D^0 \rightarrow D^0X$. The DAP analysis [Eq. (1)] for sample A follows that given earlier for sample F, and the results are that $E_{DA} \approx 3.243$ eV if there is almost no *additional* donor neutralization from the photoexcitation, and $E_{DA} \approx 3.334$ eV if all of the donors are neutralized and participate in DAP recombinations. The experimental value $E_{DA} \approx 3.323$ eV falls in this range; however, the accuracy of this value may be poor because the I_{DA} intensity is quite weak and the line may overlap with other PL lines in this region. For example, there is a well-known line at 3.333 eV that often appears in ZnO. Further analysis of the relative line intensities and energies would require more detailed knowledge of the various capture cross sections and other factors and is beyond the scope of this work.

In summary, we have carried out PL and Hall-effect measurements for a series of Ga-doped ZnO thin films grown by MBE. For high Ga doping, the PL spectra are dominated

by the neutral-Ga donor-bound exciton I_8 at 3.359 eV, and for low Ga doping, the ionized-Ga donor bound exciton I_1 at 3.371 eV. The low-Ga spectra in this study demonstrate one of the first ever observations of higher I_1 intensity than that of I_8 , and this phenomenon is explained by the T-Hall result that $[\text{Ga}^+] \gg [\text{Ga}^0]$ in these low-Ga samples. For intermediate Ga doping, a line that ranges from 3.31 to 3.32 eV, designated as I_{DA} , is dominant. We have shown that I_{DA} has characteristics of a DAP transition, and have used a detailed, quantitative analysis to argue that it arises from Ga_{Zn} donors paired with Zn-vacancy (V_{Zn}) acceptors. The success of our analysis depends upon, and lends credence to, a recent theoretical calculation of the $V_{Zn}^{0/-}$ acceptor transition energy.

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