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Phosphorus-doped *p*-type ZnO thin films were grown on sapphire by radio-frequency magnetron sputtering. The photoluminescence (PL) spectra revealed an acceptor bound exciton peak at 3.355 eV and a conduction band to the acceptor transition caused by a phosphorus related level at 3.310 eV. A study of the dependence of the excitation laser power density and temperature on the characteristics of the PL spectra suggests that the emission lines at 3.310 and 3.241 eV can be attributed to a conduction band to the phosphorus-related acceptor transition and a donor to the acceptor pair transition, respectively. The acceptor energy level of the phosphorus dopant was estimated to be located 127 meV above the valence band. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1895480]

In recent years, wide band gap optoelectronic research based on ZnO has been stimulated by the need for blue and ultraviolet solid-state light emitters and detectors. ZnO-based optical devices are expected to be highly efficient and practical due to the large exciton binding energy (~60 meV), the high radiation resistance, the availability of large area ZnO substrates, the amenability to wet chemical etching, and relatively low materials costs.[1,2] However, ZnO has several drawbacks, including lack of reproducible and high quality *p*-type material. Several groups have recently reported on the growth of *p*-type ZnO using a pure metal Zn target in a N_2O plasma, using a ZnO target mixed with P_2O_5.[3,4] Several research groups have also proposed a co-doping method where N and group III elements such as Ga and Al are used as dopants to produce *p*-type ZnO.[5–8] In addition to co-doping methods, it has been reported that *p*-type ZnO thin films can be grown by doping ZnO thin films with As contained in the GaAs substrate or with N, a popular *p*-type dopant that has been used by many research groups.[9–13] We recently reported on a reproducible and effective route to the production of *p*-type ZnO thin films with a high hole concentration by sputtering a ZnO target mixed with P_2O_5 at high temperatures followed by a rapid thermal annealing process.[14] As-grown ZnO films doped with phosphorus have been shown to have an electron concentration of 10^{16}–10^{17} cm^{-3} and these films can be converted to *p*-type ZnO by a rapid thermal annealing process at a temperature above 800 °C under a N_2 ambient.[14] Hall measurements of a phosphorus doped *p*-type ZnO (*p*-type ZnO:P) film showed a high hole concentration of 1.0×10^{17}–1.7×10^{19} cm^{-3}, a mobility of 0.53–3.51 $cm^2/V\,s$, and a low resistivity of 0.59–4.4 Ω cm.[14] In this study, we further investigated the effects of phosphorus doping on the optical properties of ZnO thin films by means of photoluminescence (PL) measurements. The emission lines at 3.355, 3.310, and 3.241 eV were found to be phosphorus-related peaks and the acceptor energy level of phosphorus dopant was estimated to be at 127 meV above the valence band.

The undoped ZnO thin film was grown on a *c*-plane sapphire (a-Al_2O_3) at 900 °C by the radio-frequency magnetron sputtering of an undoped ZnO target. *p*-Type ZnO:P thin films were also grown on a *c*-plane sapphire (a-Al_2O_3) at 700 °C by doping phosphorus into ZnO thin films using a ZnO target mixed with 1 wt% P_2O_5. Typical film thicknesses of undoped and phosphorus ZnO were 1 and 0.4 μm, respectively. Hall measurements were carried out in the Van der Pauw configuration using a direct current of 0.2 μA and a magnetic field of 320 G (BIO-RAD HL5500PC). These measurements showed that the undoped ZnO has an electron concentration of 1.73×10^{12} cm^{-3}, an electron mobility of 21.2 $cm^2/V\,s$, and a resistivity of 1.71×10^5 Ω cm and the *p*-type ZnO:P has a hole concentration of 5×10^{18} cm^{-3}, a hole mobility of 2 $cm^2/V\,s$, and a resistivity of 2 Ω cm. PL spectra of *p*-type ZnO:P thin films were obtained using a He–Cd laser (λ=325 nm) over a range of temperatures (10–80 K) and excitation laser power densities (6–30 mW/cm^2) in order to study the phosphorus related energy levels in the band gap.

The PL spectrum of an undoped ZnO showed two strong peaks at 3.363 eV with a full width at half maximum (FWHM) of 7 meV and at 3.352 eV with a FWHM of 8 meV,

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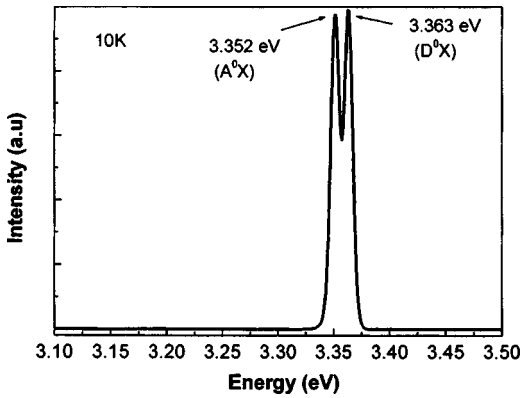
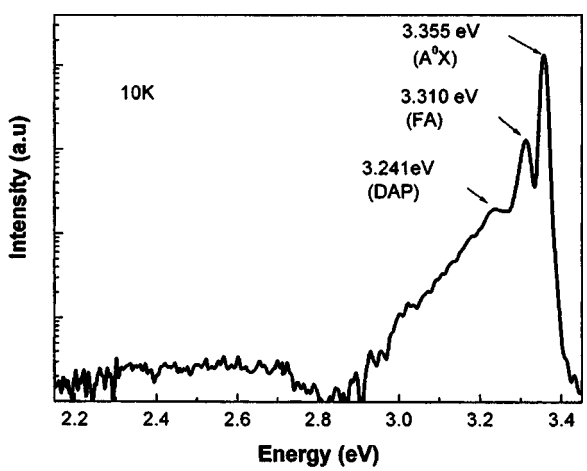
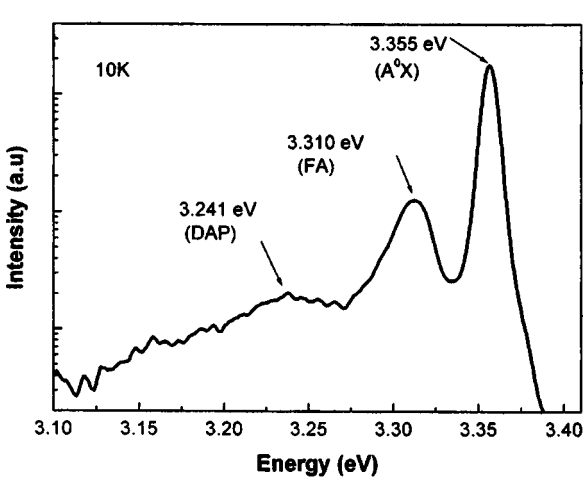


FIG. 1. PL spectra of undoped ZnO films measured at 10 K.

as shown in Fig.1.[15] The peak at 3.363 eV can be assigned to a donor bound exciton (D^0X) having a donor binding energy of 56 meV.[16] The peak at 3.352 eV has been previously identified as an acceptor bound exciton (A^0X) having an acceptor binding energy of 94 meV.[17] Figure 2(a) depicts the PL spectrum of *p*-type ZnO:P, in which the PL peaks appear at



(a)



(b)

FIG. 2. PL spectra of *p*-type ZnO:P films measured at 10 K. (a) Wide scale of the PL spectra, from a deep level to band edge emissions; (b) narrow scale of the PL spectra showing near band edge emissions.

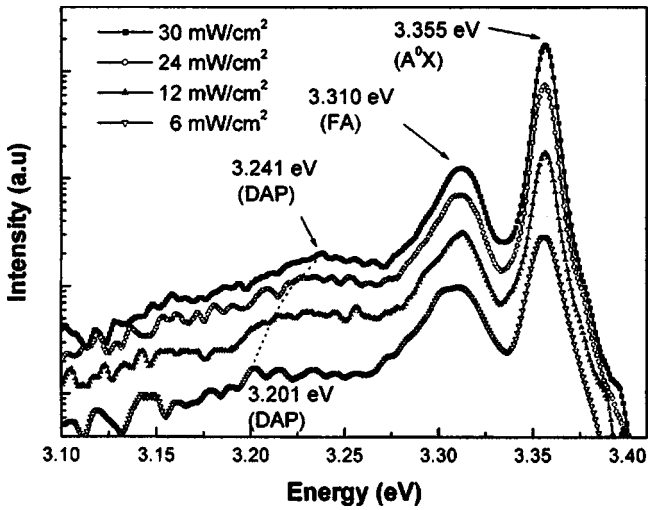


FIG. 3. The dependence of excitation power density on the PL spectra of a ZnO:P film at a laser power density of 6–30 mW/cm² at 10 K.

3.355, 3.310, and 3.241 eV without any strong deep level emission. Deep level emission is related to a variety of defects such as donor defect Zn interstitial (Zn_I), O vacancy (V_O), acceptor defect Zn vacancy (V_{Zn}),[18] and antisite defect O substitutional Zn (O_{Zn})[19] due to the poor stoichiometry of ZnO. The very weak deep level emission indicates that the *p*-type ZnO:P has very few native donor and acceptor defects and the observed acceptor related PL emissions and hole concentration are not due to the native defects but are due to the phosphorus dopant in ZnO. In Fig. 2(b), the PL spectrum of phosphorus-doped ZnO film clearly shows a peak at 3.355 eV which can be attributed to A^0X and two other peaks at 3.310 and at 3.241 eV which are related to acceptors. Peaks at 3.310 and 3.241 eV were not observed on the PL spectrum of undoped ZnO, as shown in Fig.1. These new peaks shown in Fig. 2(b) were observed only on the intentionally phosphorus-doped *p*-type ZnO and suggest that they are closely related to phosphorus-related acceptor transitions. We further investigated the origin of PL emissions at 3.310 and 3.241 eV by studying the laser power density and temperature dependence of PL since the origin of the emission for a phosphorus dopant have not been reported yet.

For a donor to acceptor pair (DAP) transition, the energy of the photon resulting from radiative recombination is given by

$$h\nu_{\mathrm{DA}} = E_g - E_D - E_A + \frac{e^2}{4\pi\varepsilon R_{\mathrm{DA}}}$$

where E_g, E_D, and E_A are the band gap, donor and acceptor binding energies, respectively, ε the dielectric constant, R_{DA} the distance between the involved donor and acceptor.[20] When the excitation intensity is increased, the number of occupied donor and acceptor centers increases and their average distance R_{DA} decreases. Consequently, it would be expected that the emission line of the pair band would shift to higher energy with increasing excitation intensity due to the Coulomb term. Figure 3 shows the laser power density dependent PL spectra of *p*-type ZnO excited by laser power densities in the range from 6 to 30 mW/cm² at 10 K. As shown in Fig. 3, the peak position at 3.310 eV is independent of the laser power density at 10 K, whereas the peak at 3.241 eV shifts to the lower energy side with decreasing laser

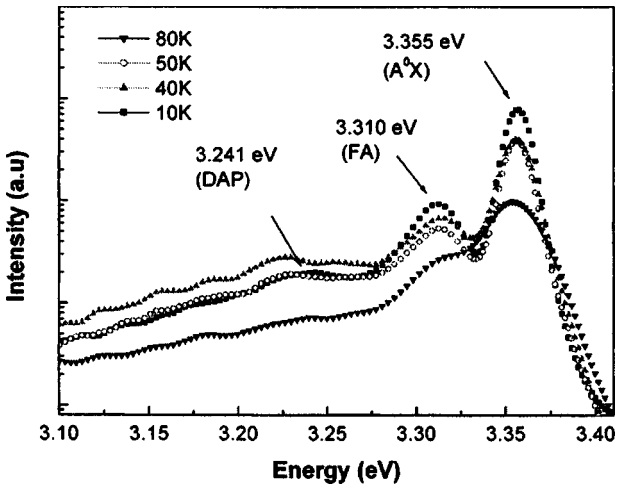


FIG. 4. Temperature dependent PL spectra for a ZnO:P film in the temperature range of 10–80 K.

power density. This observation strongly suggests that the origin of the emission peak at 3.241 eV is from the DAP transition and the emission peak at 3.310 eV can be attributed to the conduction band to acceptor transition [or free electrons to the acceptor (FA) transition].

The temperature dependent PL spectra of a *p*-type ZnO:P film was also measured and these data are shown in Fig. 4. The integrated intensity of the peak emission at 3.310 eV decreases gradually with increasing temperature, as shown in Fig. 4, exhibiting the thermal characteristic of the FA transition.[21] However, the peak intensity of the emission at 3.241 eV increased with increasing temperature from 10 to 40 K, as shown in Fig. 4. The increase in peak intensity at 3.241 eV can be explained by the thermal release of electrons from the shallow donor level.[22] This result and the shift of the peak at 3.241 eV to the high energy side with increasing excitation power as shown in Fig. 3 indicates that the emission at 3.241 eV is due to the DAP transition. Previous studies of PL have shown that the FA and DAP emissions appear at 3.322 and 3.204 eV for *p*-type ZnO:As,[23] respectively, and DAP emission is observed at 3.238 eV for *p*-type ZnO:N.[10] The PL results in this study show that the DAP emission at 3.241 eV from *p*-type ZnO:P is very similar to results for N-doped *p*-type ZnO and the FA emission peak from *p*-type ZnO:P is significantly different from that of As doped *p*-ZnO.

The acceptor energy of the phosphorus dopant was estimated from the FA transition at 3.310 eV PL spectra of *p*-type ZnO:P. The FA energy is given by

$$E_{FA} = E_g - E_A + \frac{k_B T}{2},$$

where E_g and E_A are the band gap and acceptor energies, respectively. The optical binding energy of phosphorus acceptors can be estimated from the equation $E_{FA}(3.310\ \text{eV}) = E_g(3.437\ \text{eV}) - E_A + (k_B T/2)$. Since the thermal energy term can be neglected at 10 K, we obtain an E_A value of 127 meV at a hole concentration of 5×10^{18} cm^{-3}. The analysis of PL spectra showed that the acceptor energy levels of As doped and N doped *p*-type ZnO are in the range of 115–164 meV at a 4×10^{17} cm^{-3} hole concentration,[23] and 170–200 meV at a 9×10^{16} cm^{-3} hole concentration,[10] respectively. The shallow acceptor energy level of 127 meV suggests that the use of phosphorus as an acceptor in ZnO would be very desirable, in terms of obtaining a high hole concentration in *p*-type ZnO.

In summary, a thermal activation of phosphorus-doped ZnO thin films showed a good *p*-type conductivity with a hole carrier concentration of 5×10^{18} cm^{-3} at room temperature. The PL spectra revealed an acceptor bound exciton peak at 3.355 eV and phosphorus-related peaks at 3.310 and 3.241 eV. A temperature dependence study and the dependence of laser power on the PL spectra at 10 K revealed that the emission line at 3.241 eV is due to a DAP transition and the emission line at 3.310 eV can be attributed to the FA transition. The acceptor energy level was estimated to be located at 127 meV above the valence band, resulting in a high hole concentration in the *p*-type ZnO:P compared to As or N doped *p*-type ZnO.

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