

Research Article

Study of Ultraviolet Emission Spectra in ZnO Thin Films

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Photoluminescence (PL) of ZnO thin films prepared on c-Al₂O₃ substrates by pulsed laser deposition (PLD) are investigated. For all samples, roomtemperature (RT) spectra show a strong band-edge ultraviolet (UV) emission with a pronounced low-energy band tail. The origin of this UV emission is analyzed by the temperature dependence of PL spectra. The result shows that the UV emission at RT contains different recombination processes. At low temperature donor-bound exciton (D⁰X) emission plays a major role in PL spectra, while the free exciton transition (FX) gradually dominates the spectrum with increasing temperatures. It notes that at low temperature an emission band (FA) appears in low energy side of D⁰X and FX and can survive up to RT. Further confirmation shows that the origin of the band FA can be attributed to the transitions of conduction band electrons to acceptors (e, A⁰), in which the acceptor binding energy is estimated to be approximately 121 meV. It is concluded that at room temperature UV emission originates from the corporate contributions of the free exciton and free electrons-to-acceptor transitions.

1. Introduction

ZnO, with a direct band gap of 3.37 eV and a binding energy of exciton as high as 60 meV at room temperature (RT), has been extensively studied as a candidate material for ultraviolet (UV) light emitting diodes (LEDs) and laser diodes (LDs) [1–3]. To realize the application of these devices, it is necessary to fabricate undoped ZnO thin films which avail to obtain a stable high-yield exciton emission at RT. However, it is well known that the fabrication of the high quality ZnO films is rather difficult. Because it is common to use Al₂O₃ as the substrate for the growth of ZnO thin films, 18% lattice mismatch between ZnO and Al₂O₃ results in the presence of various native defects in ZnO thin films [4–7]. These defects often control directly or indirectly doping, compensation, minority carrier lifetime, and luminescence efficiency. Consequently, it is very important to understand behavior of these defects in ZnO-based materials. Photoluminescence (PL) emission spectroscopy is a useful method to examine the quality of the grown ZnO thin films, which may provide important information on understanding the carrier recombination processes and the role of defects in ZnO.

In the reported PL spectra, the origin of the room temperature UV emission was extensively studied. Most of the authors suggested that the UV emission at RT originates from free exciton recombination [8–12]. However, Ohashi et al. reported that the most intense emission at RT for undoped crystals was not free-exciton recombination but was related to an unspecified localized state [13]. Zhao and Willander found that the room temperature UV emission contains two different transitions, in which one is related to the ZnO free-exciton and the other is related to the free-to-bound transition [14]. Up to now, the room temperature UV emission is still in debate. In addition, the controversies on PL properties also present to some UV emission bands obtained at low temperature. For example, the 3.31 eV emission band observed in a great variety of ZnO materials has been interpreted controversially. Many authors have assigned this UV emission band to longitudinal-optical (LO) phonon replicas of the excitons (FX-LO) [15, 16], acceptor-bound excitons (A⁰X) [17], electron-hole recombination from donor acceptor pairs (DAP) [18], free electron-to-acceptor transition (e, A⁰) [19], and so forth. Noticeably, the 3.31 eV emission band is also frequently observed in intentionally p-doped ZnO [20–25].

Most of the works revealed that it is as a test criterion of p-type conductivity formed by substitutional acceptors. Recently, a remarkable work was reported in undoped ZnO epitaxial layers grown on a-Al₂O₃ substrates, in which the 3.31 eV emission band observed at low temperature originates from a (e, A⁰) transition. And they give clear evidence that the localized acceptor states causing the 3.31 eV luminescence should be associated with the stacking faults rather than the substitutional impurities [19].

On the other hand, the measurements of the electrical properties in undoped ZnO thin films grown on Al₂O₃ substrate show n-type conductivities with low electron mobilities of <100 cm²V⁻¹s⁻¹, which is quite smaller than 300 cm²V⁻¹s⁻¹ based on the reported value in ZnO films grown on lattice-matched ScAlMgO₄ substrates [2]. Such low electron mobility implies the existence of the scattering mechanisms due to unknown localized states. In conclusion, until now the impact of these defects on the optical and electrical properties of ZnO is still a subject of much debate. The clarifying of the PL origin not only can deepen and enrich the research of the impurity and defect behaviors but also is more advantageous for the development of ZnO-based devices.

In this paper, we report near band edge UV luminescence in the ZnO thin films grown on c-Al₂O₃ substrates by PLD method. The mechanism of the UV emission band is investigated by the temperature dependence of PL spectra. The 3.31 eV emission band observed at low temperature is assigned to the transitions of conduction band electrons to acceptors. It is suggested that at room temperature UV emission is composed of two recombination processes. One is the free-exciton emission (FX), another is the free electron-to-acceptor emission (e, A⁰).

2. Experiment

ZnO thin films were fabricated on c-Al₂O₃ substrates by using a KrF excimer laser (Lambda Physics Compexpro 205, $\lambda = 248$ nm, $\tau = 20$ ns pulse duration). The laser beam was focused onto a rotating target at a 45° angle of incidence, and the energy density of the laser beam at the target surface was maintained at about 2 J/cm². A 99.99% purity ZnO ceramic target with the thickness of 4 mm and the diameter of 60 mm was used as source materials.

Al₂O₃ substrates degreased in acetone and methanol for 10 min, respectively, and then etched in a hot (160°C) solution of H₂SO₄:H₃PO₄ = 3:1 for 15 min., followed by a rinse in deionized water and dried by the high-pure nitrogen gas before being loaded into the growth chamber. Prior to growth, the chemical cleaned substrates were thermally treated at 800°C in high vacuum atmosphere ($\sim 6 \times 10^{-4}$ Pa) for about 30 min to remove the surface contaminants. Sequentially, ZnO was deposited on this treated substrate at 700°C for 120 min. In the growth process, O₂ partial pressure in the growth chamber was varied from 0.2 to 5 Pa. The repetition frequency of the laser was 5 Hz, and the target-substrate distance was 8.5 cm.

After growth, the sample quality was confirmed by a Rigaku O/max-RA X-ray diffractometer with Cu K_α radiation ($\lambda = 0.1542$ nm). Photoluminescence spectra were measured at different temperatures. The sample was attached to the cold finger of an optical cryostat in conjunction with a cryogenic refrigerator and cooled down to ~ 10 K. The 325 nm line of a He-Cd laser with a power of 20 mW was used as the excitation source. The photoluminescence from the sample was dispersed through a monochromator (ZLX-FS Omniλ-3005) and detected by a photomultiplier tube (Hamamatsu R928) followed by a photon counter (Zolix DCS200PC). The carrier concentration and Hall mobility were measured by ET-9007 Hall measurement system through the Van de Pauw method.

3. Results and Discussion

Figure 1 shows the patterns of X-ray diffraction (XRD) for four samples of ZnO thin films grown on c-Al₂O₃ substrates at different O₂ partial pressures in the growth chamber, which are 5, 3, 1, 0.5 Pa for the samples A, B, C, and D, respectively. It is noted that besides the Al₂O₃ (006) peak, only ZnO (002) and (004) diffraction peaks can be observed for all samples. This indicates that the grown ZnO thin films have the wurtzite structure with a high *c*-axis orientation. To further confirm the crystal quality of the ZnO films, XRD (103) ϕ -scan measurements were performed. The inset of Figure 1 shows the measured result for the sample A. It is clearly seen the six peaks separated by 60° with almost same intensities, indicating the formation of a sixfold symmetric single-crystal ZnO.

Figure 2 shows photoluminescence (PL) spectra in UV region range for the above samples at RT excited by a He-Cd laser with 325 nm line. As seen in Figure 2, one UV emission band with a central wavelength of 377.5 nm (3.284 eV) can be observed for the four samples. It is obvious that this UV emission band has a large linewidth (>100 meV) and one shoulder (arrow in the figure) can be clearly seen at lower-energy side of this peak. The ZnO RT UV emission is extensively reported as a characteristic excitonic emission in the literatures [8–12]. In addition, Most of the works indicated that low-energy band tail of UV peak at RT is associated to LO-phonon replica of free exciton [16, 21].

In order to study the origin of the room temperature UV emission band, the temperature dependence of the PL spectrum from the ZnO thin films grown on a sapphire substrate has been measured. Figure 3 shows the PL spectra at various temperatures for the sample A. At 10 K, the spectrum mainly composed of a strong emission of D⁰X band and a weak band labeled FA located at 3.355 and 3.309 eV, respectively. As temperature increases to 50 K, the FA-LO band appears in low energy side of the band FA. In addition, one peak (FX) can be clearly observed in high energy side of D⁰X band at 50 K and becomes stronger and stronger with temperature increasing to 130 K. At 90 K, the FX at 3.370 eV is comparable in intensity to the remaining D⁰X emission at 3.350 eV. As the temperature increases from 130 to 260 K, the intensity of D⁰X band decreases rapidly and the FX emission

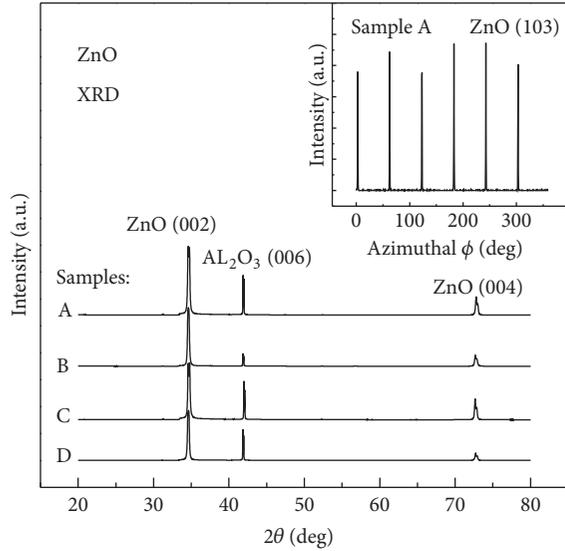


FIGURE 1: XRD spectra of ZnO thin films grown on $c\text{-Al}_2\text{O}_3$ substrate. The inset is ϕ -scan curve of the (103) reflection of sample A.

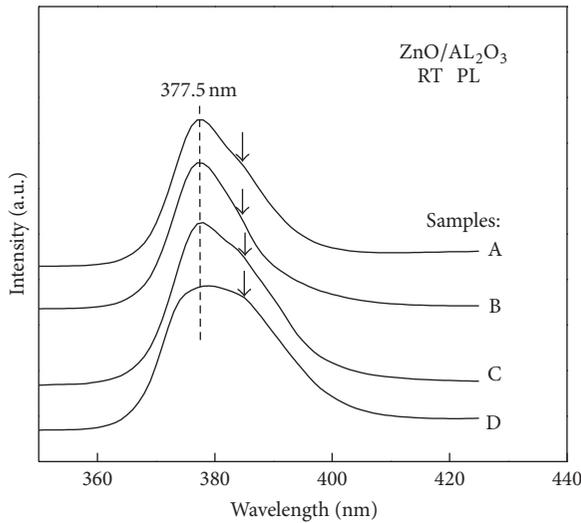


FIGURE 2: UV PL spectra of the grown ZnO thin films at room temperatures.

band becomes increasingly important in spite of its intensity decreases with increasing of temperature. It notes that at 110 K an emission band labeled FA-2LO appears in low energy side of the FA-LO band, and the bands of FA, FA-LO, and FA-2LO can survive up to 260 K. Significantly, a careful study of these bands should be necessary to consider because of their contribution to the room temperature UV emission.

Figure 4 shows the fitted spectra by multi-peaks of Lorentzian line shape at the four typical temperatures. According to their energy values, the FX and D^0X peaks were attributed to the emission of free exciton and the recombination of excitons bound to neutral donors, respectively. As reported in [18], D^0X assigned to donor-bound excitons with 10–15 meV binding energy dominates in low temperature

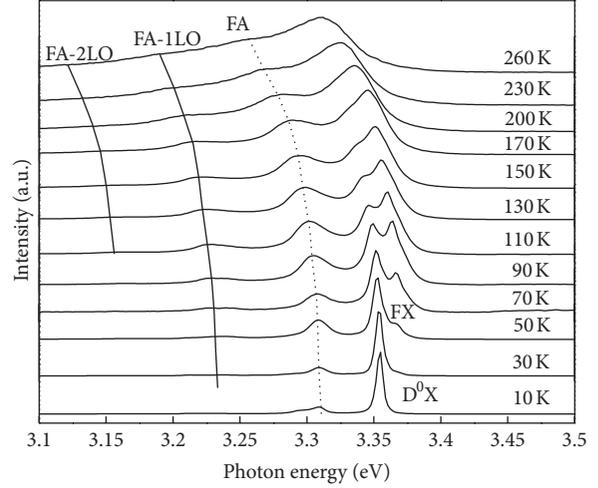


FIGURE 3: Temperature-dependent PL spectra of sample A. The spectra were normalized and shifted vertically for clarity.

spectra and the free-exciton recombination plays a major role in high temperature. By comparing with the peak positions of the FA and FX, two peaks have the energy spacing of about 47 meV, which is less than the energy of ZnO LO phonon [17]. Therefore, it can be believed that the FA peak should be associated with the impurity or defects rather than the first LO phonon replica of the free exciton recombination (FX). In our previous work, PL spectrum at 80 K of undoped ZnO thin film grown by plasma-assisted molecular beam epitaxy (P-MBE) clearly shows the first and the second LO phonon replica of FX (FX-LO and FX-2LO) [21]. In this paper, the fabrication of the samples was used by PLD method on a deviation from the stoichiometric ratio condition. The measure of the film thicknesses shows the increase of the growth rate with increasing O_2 partial pressure. This indicates that the growth of the films is on a rich-Zn condition, resulting in the observation of FA emission related to the defects. For FA-LO and FA-2LO bands, we note that the energy differences between the FA-LO and FA-2LO bands to the FA band are close to one and two LO phonon energies of ZnO. This implies that FA-LO and FA-2LO bands should correspond to the first and the second LO phonon replica of the FA band.

Figure 5(a) exhibits the temperature (T) dependence of integral PL intensities (I) for FX band. One can clearly see that at high temperature, the emission intensity represents the decrease with temperature increasing due to the thermal quenching. The dependence of I on T for FX band can be fitted by the following formula

$$I = \frac{I_0}{1 + A \exp(-E_a/(k_B T))}, \quad (1)$$

where I_0 is the peak intensity at temperature $T = 0$ K, A is a parameter, E_a is the activation energy in the thermal quenching process, and k_B is the Boltzmann constant. From the plots (solid line), the thermal activation energy is estimated to be 59 meV for FX band. This value agrees well with the free exciton binding energy of ZnO (~60 meV) [1–4].

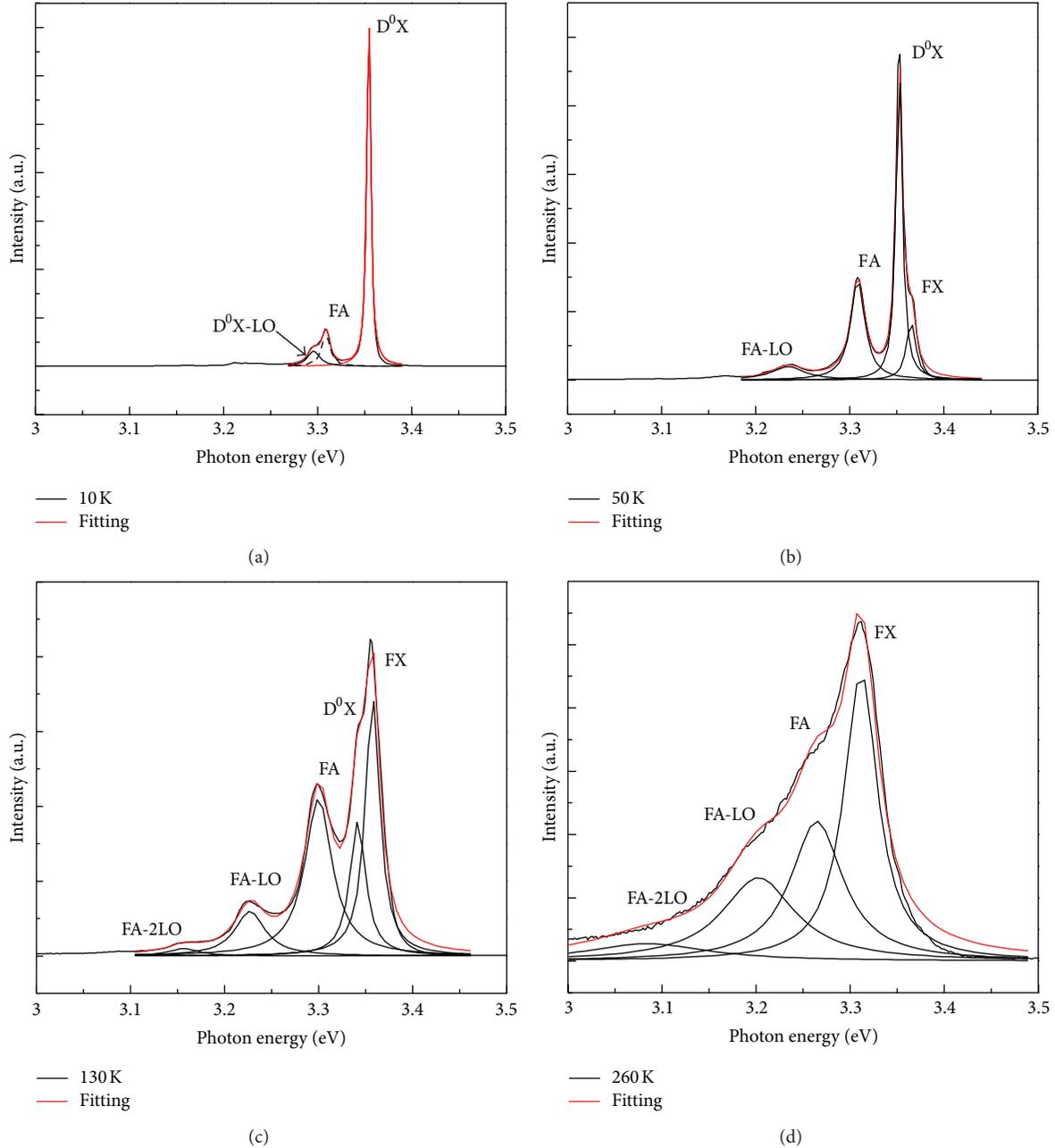


FIGURE 4: The fits of PL spectra by Lorentzian line shape at 10 K (a), 50 K(b), 130 K(c) and 260 K (d).

Figure 5(b) shows the intensity ratio R_0 of FA to FA-LO (FA/FA-LO) as a function of temperature. It can be seen that the R_0 value presents a downtrend as the temperature increases. In the same temperature range, the phonon replicas could be much stronger than the no-phonon recombination due to self-absorption, but the intensity ratio of the first to the second LO-phonon replica should increase linearly with temperature [26, 27]. As shown in Figure 5(b), it is found that R_0 is decreased with the temperature from 90 to 260 K. Thus, FA-LO band is not the second LO replica of FX, but rather is the first LO replica of FA, that is, FA band cannot be the first LO replica of FX.

Although we excluded that the FA band is from the first LO replica of the free exciton, the luminescence band still exist many other controversial luminescent mechanisms [14, 15, 17, 18, 28]. The comparison with literature [14, 19, 28] strongly suggests that the observed FA band originates from free-to-acceptor transition, that is, the recombination of an electron from the conduction band with a hole bound to an acceptor state, labeled (e, A^0) . A further confirmation of this assignment will be demonstrated below. In Figure 3, PL spectra exhibit that the FA band at low energy side of D^0X and FX can be clearly observed in whole temperature range from 11 to 260 K. At lower temperature (<130 K),

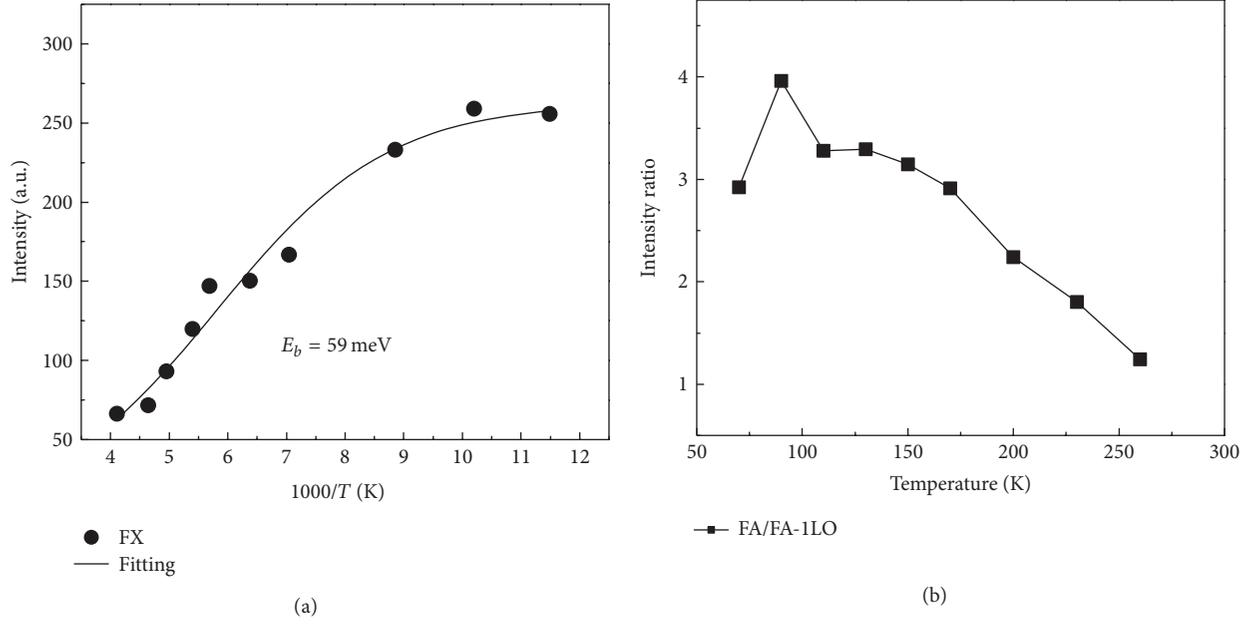


FIGURE 5: (a) The integrated intensity of the FX emission as a function of the temperature for sample A. The solid lines are the curves fitted by formula (1). (b) The intensity ratio I_0 of FA emission to FA-LO emission at various temperatures for sample A.

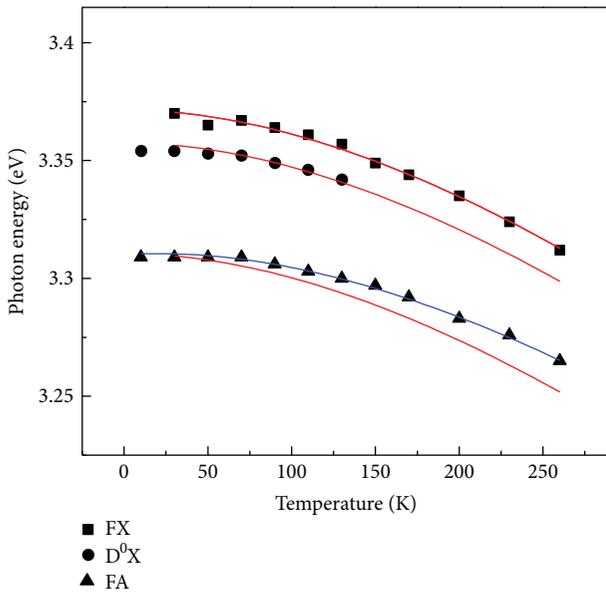


FIGURE 6: Temperature dependences on the peak energies of FX(■), D^0X (●) and FA(▲) emissions for ZnO thin films grown on c- Al_2O_3 substrate. The solid lines are the curves fitted by formula (2).

the intensity of the FA, and FA-LO bands gradually becomes strong with increase temperature. At 130 K, four evident emission peaks labeled FX, D^0X , FA, and FA-LO are located at 3.360 eV, 3.346 eV, 3.301 eV, and 3.227 eV, respectively. With further increases in ZnO sample temperature, the FA band decreases in relative intensity and becomes more pronounced at the high-energy tail. This is a typical feature of the free-to-bound transition [19]. In undoped ZnO, typical donors

have binding energies in the range of 46–63 meV [29], while acceptor binding energy is larger (>100 meV) [30]. Due to the release of the electrons from donors with smaller binding energy, the electron concentration in the conduction band increases with increasing temperature (<130 K), resulting in the FA emission intensity increases. For >130 K, the observed thermal quenching of the FA band is related to hole release from acceptors.

In order to verify that the recombination of free-to-acceptor is responsible for the observed FA band, the temperature dependent peak position is analyzed, as shown in Figure 6. The open circles in Figure 6 are the data generated from the FA band. Because the temperature dependence of the free-to-bound transition energy differs from the bandgap energy by $k_B T/2$, a curve-fitting analysis of the temperature dependence of the FA transition energy by using the following formula [31]:

$$E_{\text{FA}}(T) = E_g(T) - E_a + \frac{1}{2}k_B T, \quad (2)$$

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{(T + \beta)},$$

where $E_g(T)$ and $E_{\text{FA}}(T)$ are the temperature-dependent band gap energy and FA band energy, respectively, E_a is the acceptor binding energy, k_B is the Boltzmann constant, α and β are constants, $E_g(0)$ is the band gap energy at $T = 0$ K. The blue curves in Figure 6 represent the results of the best fit according to (2). The energy E_a is obtained to be 121 meV. The fitted values of $E_g(0)$, α and β are equal to 3.440 eV, 8.6×10^{-4} eV/K and 800 K, respectively, which are in good agreement with those reported by Wang and Giles [31]. This fact provides evidence that the observed FA transition has

the characteristic of the free-to-bound transition. In Figure 6, the FX and D^0X peak energies from PL spectra are also plotted with solid square and solid circle symbols. As can be seen, although the FX, the D^0X , and the FA transition energies are reduced with increasing temperature, the change of their transition energies is different. The transition energies of the free and bound excitons show similar temperature dependence as the band-gap energy (red lines). Hence, the redshift of the FA emission peak is significantly smaller than the FX and D^0X . This further identifies the FA band as a free-to-bound transition.

Though we identify the FA band as a free-to-bound transition, a further investigation is required to clarify this bound state is donor-like or acceptor-like. Because this band around 3.310 eV always appears in p-type ZnO, not only in N-doped [20, 21] but also in P-doped [22, 23], and As-doped [24, 25] samples, it has been assigned to (e, A^0) transition related to these substitutional acceptors. However, this luminescence band has indeed frequently been observed in undoped ZnO samples, especially in ZnO nanostructure materials [14, 15, 17, 18]. In our previous works, the 3.31 eV luminescence assigned (e, A^0) transition is observed in N-doped p-type ZnO thin films [21] and ZnO nanowalls [28]. If these reported results in undoped ZnO are consistent with p-type ZnO, that is, the observed luminescence band around 3.31 eV is related to acceptors, it is necessary to discuss the origin of the acceptors in undoped n-type ZnO.

Recently, some research results confirm the existence of certain acceptor states in n-type ZnO with relatively high concentrations [19, 32]. Janotti and Van De Walle given the acceptor/donor concentration ratio of 0.41 in ZnO:Ga samples and suggested the dominant acceptors are likely zinc vacancies (V_{Zn}) and/or neutral complexes related to V_{Zn} . Indeed, the theoretical study shows that V_{Zn} is deep acceptor with a low formation energy, and it can act as compensating centers in n-type ZnO [5]. Simultaneously on the experimental, V_{Zn} has been directly identified as the dominant acceptor in as-grown ZnO [7]. On the other hand, Schirra and Schneider reported that the acceptor states related to stacking fault in ZnO films grown on a- Al_2O_3 substrates [19], in which the 3.31-eV luminescence assigned to (e, A^0) transition is found to be related to a high local density of acceptors in conjunction with crystallographic defects. The existence of these acceptors with the estimated concentration of $10^{18} \sim 10^{20} \text{ cm}^{-3}$, which might exceed the donor concentration, will play a vital role for the electrical properties [19, 32]. From this consideration, the room temperature electrical properties of ZnO films were measured by the four-probe van der Pauw method. Based on these measurements, the grown samples show n-type characteristics with a resistivity of the order of $10 \Omega \cdot \text{cm}$. In addition, obtaining such high resistivity corresponds to a mobility of $10 \text{ cm}^2 (\text{V s})^{-1}$ and a carrier concentration of 10^{15} cm^{-3} . It is well known that undoped ZnO films has a nature of the residual n-type conductivity due to donor-like intrinsic defects, such as oxygen vacancies (V_O) and interstitial zinc atoms (Zn_i). In the majority of the pertinent works [2, 3], the obtained carrier concentration

in undoped ZnO films is the order of $10^{16} \sim 10^{18} \text{ cm}^{-3}$. Obviously, these values are much higher than that of our sample. Thus, high resistivity in our work is suggested to be due to the compensating effect formed by large numbers of acceptor states. Here, the acceptors likely arising from the native defects will cause the electrical properties degradation. Not only such, these acceptor states will bring important influence on room temperature UV emission. To identify the acceptor origin need further investigation in detail.

4. Conclusion

In summary, we have performed a detailed study about photoluminescence properties of ZnO thin films grown on c- Al_2O_3 substrates by pulsed laser deposition. The origin of UV emissions at RT is studied carefully by measuring different temperature spectra of ZnO thin films. The result shows at low temperature donor-bound exciton emission plays a major role in PL spectra, while the free-exciton transition gradually dominates the spectrum with increasing temperatures. The room temperature UV emission contains two different transitions. One is related to the ZnO free-exciton and the other is related to the free-to-bound transition. The focus is put on the confirmation of this the free-to-bound transition observed at 3.309 eV at low temperature. It is strongly suggested that the 3.309 eV band originates from free-electrons-to-acceptor recombination. The acceptor binding energy is estimated to be about 121 meV.

Acknowledgments

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