Temperature-Dependent Excitonic Luminescence in ZnO Thin Film Grown by Metal Organic Chemical Vapor Deposition

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In this study, the excitonic luminescence behaviors of ZnO thin films in the temperature range of 10–300 K were investigated. The photoluminescence (PL) spectrum exhibits the bound-exciton emission and the donor-acceptor recombination accompanying its multiphonon replicas at low temperatures. The observed features exhibit redshift with an increase in temperature, and the temperature dependence of the peak position was analyzed by the Varshni empirical expression. The study showed the dominant presence of bound excitonic transition below 160 K or free excitonic transition at higher temperatures for the observed PL spectrum. The free exciton emission can be observed up to room temperature. The Debye temperature of ZnO was evaluated by taking into account the elastic constants of ZnO and utilized as a parameter in the Varshni empirical expression giving an accurate description of the free exciton emission behavior up to room temperature.

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1. Introduction

Zinc oxide (ZnO) is a well-known wide-direct-gap II–VI semiconductor of wurtzite structure. The material has attracted considerable attention as a promising candidate for optoelectronic devices in the visible and ultraviolet (UV) regions due to its wide band gap of 3.7 eV and large exciton binding energy of 60 meV at room temperature.[1–4)]

It has been known that the excitonic emission of ZnO is very sensitive to the crystal quality and to the presence of defects. The powerful and nondestructive method of photoluminescence (PL) spectroscopy has been used in the study of the optical properties of the impurities, excitons, and exciton–impurity complexes in ZnO. The effects of annealing and growth processes on the low- and high-temperature emission properties of ZnO thin films[3,4)] as well as a more systematic temperature-dependent study on the emission characteristics of bulk ZnO[5)] and phosphorous-doped ZnO nanowires[6)] have been reported. These studies point to the dissociation of the observed bound-exciton peak at low temperatures into free excitons at high temperatures.

In this study, we investigated in detail the temperature-dependent emission characteristics of ZnO single crystal thin films grown by metal organic chemical vapor deposition (MOCVD). The variation in the excitonic peak position of ZnO films as a function of temperature was fitted with the Varshni empirical relationship. In addition, the Debye temperature derived by taking into account the elastic constants of ZnO was substituted into the Varshni empirical expression that yielded an accurate description of the temperature dependence of the emission characteristics of free excitons at high temperatures. The derived curve was extrapolated to estimate the band gap of free excitons at low temperatures.

2. Experimental Procedure

An experimental undoped ZnO thin film was grown on *c*-plane sapphire by MOCVD in a modified vertical injection commercial MOCVD reactor. The thickness of the film samples studied for this work was about 830 nm and their crystal properties were characterized by X-ray diffraction (XRD). XRD 2θ-scans showed the wurtzite ZnO(0002) peak at 2θ of 35° and the (0004) peak at 2θ of 73°, without other orientation peaks. The full width at half maximum (FWHM) for the (0002) peak 2θ was 0.200°.[7,8)] Temperature-dependent photoluminescence (PL) measurements were conducted under the 5 mW/cm^2 excitation of a microchip laser (266 nm). The luminescence was collected using a spectrometer (Zolix omni-λ 500) with a grating of 1200 grooves/mm and detected using a GaAs photomultiplier tube. The PL signal obtained from the photomultiplier was analyzed using a lock-in technique and recorded on a computer. In addition, Janis Research Model CCS-150 and LakeShore Model 321 temperature controller were used to measure the PL spectrum as a function of temperature.

3. Results and Discussion

The PL spectrum from a ZnO thin film taken at 10 K excited by the 266 nm line is shown in Fig. 1 and the PL intensity is displayed on a logarithmic scale. According to the previous reports,[9–12)] the significant peak at 3.360 eV can be attributed to neutral-donor-bound-exciton (D^0X) emission. The PL spectrum also exhibits a weak shoulder at about 3.370 eV and has been attributed to the free-exciton (FX) emission by comparing its position with the reported value.[9–12)] At the lower energy side of the D^0X peak, three peaks are observed clearly at the positions of 3.319, 3.246, and 3.174 eV, respectively. According to the reported literature,[9,11,12)] the 3.319 eV peak can be assigned to the recombination of the donor–acceptor pair (DAP). Further evidence supporting this assignment is the observed rapid thermal quenching (as observed in Fig. 2) of the emission at high temperatures.[13)] The peaks at 3.246 and 3.174 eV are attributed to the longitudinal optical (LO) phonon[9,11,12)] replicas of DAP emission separated with an energy of ~72 meV.

Figure 2 shows the PL spectra for several selected temperatures between 10 and 300 K. The temperature-dependent PL spectra show the redshift of the position and

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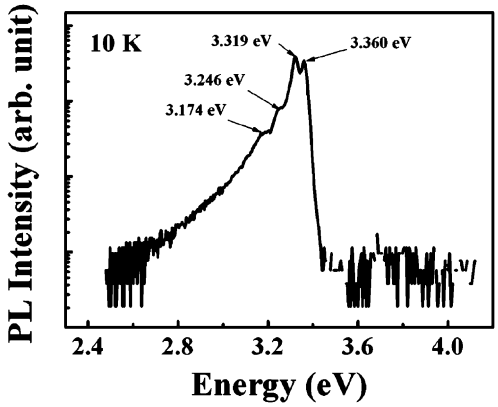

Fig. 1. 10 K PL spectrum displayed on logarithmic scale of ZnO thin films.

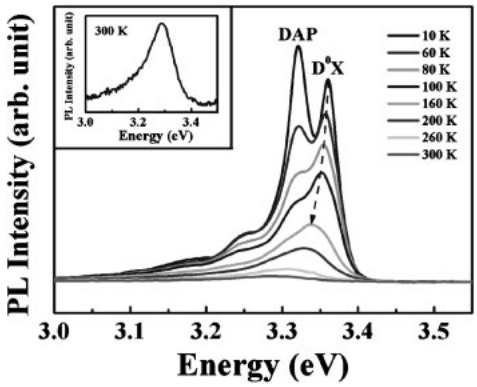

Fig. 2. Photoluminescence spectra of ZnO thin films at selected temperatures. The dashed line denotes the resolved D^0X peak position below 160 K. The inset shows the room-temperature PL spectrum of ZnO thin film.

the quenching of the intensity of the D^0X peak (3.360 eV) with increasing temperature. However, as shown in Fig. 2, at higher temperature, a clear resolution of D^0X and FX peaks may not be feasible because of spectra broadening with increasing temperature. Previous reports have indicated that at low temperatures, the FX emission is not clearly observed because the D^0X recombination dominates the PL spectrum.[13,14] With further increases in temperature, the content of FX emission becomes much stronger than that of D^0X emission and finally dominates the PL spectra up to room temperature, as shown in the inset of Fig. 2. The reason for this is that a sufficient thermal energy is acquired at higher temperature that can break the small binding energy (~14 meV) of bound excitons, resulting in the dissociation of bound excitons into free excitons.[5,11]

To clarify the behaviors of exciton emission in ZnO thin films, the emission peak positions as a function of temperature are plotted in Fig. 3. From 10 to 160 K, the position of the D^0X peak (□) can be observed clearly. As the temperature increases beyond 160 K, the D^0X feature is gradually displaced by the FX emission, and eventually the FX emission (■) becomes dominant at higher temperatures. The variation in resolved D^0X peak position in the temperature region of 10–160 K is fitted according to the Varshni empirical expression:[15]

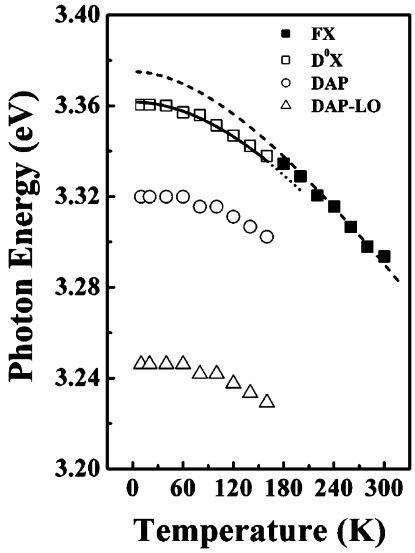

Fig. 3. Temperature dependence of PL peak position. The solid line through the position of the D^0X peak is fitted to the Varshni empirical expression and the dashed line is the theoretical simulation of the FX peak position with the temperature dependence by the Varshni empirical expression.

$$E(T) = E(0) - \frac{\alpha T^2}{T + \beta}, \tag{1}$$

where $E(0)$ is the exciton energy at $T = 0$ K, and α and β are fitting parameters. The solid line in Fig. 3 shows that the fitting curve well matches with the experimental data in the low-temperature region. When the solid line is extrapolated to higher temperature, shown by the dotted line, the fitted line deviates from the experimental data, showing a different emission at high temperatures. The observation can be satisfactorily accounted by the dominant D^0X emission at low temperatures, while at high temperatures, the FX emission dominates. To further understand the temperature dependent behavior of the FX emission, a reasonable value of β in eq. (1) should be estimated using the relation $\beta \approx$ Debye temperature, θ_D.[11,16] Thus far, different results of θ_D estimated from the values of β for ZnO have been presented in a wide range between 305 and 700 K;[16] therefore, the reasonable value of θ_D for ZnO should be discussed in depth.

Manasreh reported that the reasonable Debye temperature can be derived as a function of the elastic constants (C_{11}, C_{12}, and C_{14}) for semiconductors as[17]

$$\theta_D = C(aB/M)^{1/n}, \tag{2}$$

where C is a model parameter, a is the lattice constant, B is the bulk modulus, M is the atomic weight, and n is a constant. The parameter C used in ref. 18 was described as $C = 3.89 \times 10^{11} s^{-1/6} h/k$, where s is the number of atoms per unit cell and is taken as 4 for the wurtzite structure. h and k are Planck's and Boltzmann's constants, respectively, with $h/k = 4.80 \times 10^{-11}$ K $(\text{m·kg/N})^{1/2}$. With these numbers, the value for C is evaluated to be 14.82 K $(\text{m·kg/N})^{1/2}$. The lattice constant a in eq. (1) has been derived for several cubic material classes with a diamond or zinc-blende structure, but not for those with a hexagonal structure.[17,18] For simplicity, the lattice constant ($a = 4.62$ Å)[19] for ZnO

with a zinc-blende structure has been assumed in this work.[17] The atomic weight is taken as $M = (M_{Zn} + M_O)/2 = 41 \times 10^{-3}$ kg, and the bulk modulus is taken as $B = (C_{11} + 2C_{12})/3 = 14.75 \times 10^{10}$ Pa with the following values of the room temperature elastic constants $C_{11} = 20.70 \times 10^{10}$ Pa and $C_{12} = 11.77 \times 10^{10}$ Pa.[20] Substituting the above data and n = 1.721[18] into eq. (2), the Debye's temperature θ_D was calculated to be about 358 K, which is close to the fitted value of β for free excitons in ZnO thin films.[11]

Several works have indicated that the bound exciton recombination dominates the PL spectrum at lower temperatures (below ~150 K), while the free exciton (FE) emission can be clearly identified in the temperature range of 150–200 K.[5,11] The dashed line in Fig. 3 is theoretically calculated using eq. (1) with α taken as 6.5×10^{-4} eV/K for free excitons from ref. 21 and $\beta = 358$ K as estimated from eq. (2). The dashed line well describes the behavior of the temperature dependence of FX emission and shows the dominance of FX emission above 160 K. By extending the dashed line to 0 K, we can evaluate the 0 K band gap of FX to be 3.374 eV. This value is in good agreement with previous observations.[5,6,10,11] The exciton–donor binding energy of about 14 meV can also be derived from the difference between the bound exciton energy (3.360 eV) and the free exciton energy (3.374 eV) at low temperatures. The result implies that the onset of the bound-to-free exciton transition appears at about 162 K, which is also consistent with our experimental observation.

4. Conclusion

We have presented the excitonic luminescence of ZnO thin films as a function of temperature using the PL technique. The temperature-dependent PL spectrum shows the interplay of the bound-to-free exciton transition as the temperature is varied from 10 K to room temperature. The bound exciton transition dominates up to 160 K. Beyond 160 K, the free exciton transition dominates the PL spectrum and its emission can be observed up to room temperature. The Debye temperature of ZnO is evaluated by taking into account the elastic constants of ZnO and utilized as a parameter in the Varshni empirical expression giving an accurate description of the free exciton emission behavior up to room temperature.

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