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Intrinsic exciton transitions in high-quality ZnO thin films grown by plasma-enhanced molecular-beam epitaxy on sapphire substrates

X. Q. Zhang,^{a)} Z. G. Yao, and S. H. Huang

Key Laboratory of Luminescence and Optical Information, Ministry of Education, Institute of Optoelectronic Technology, Beijing Jiaotong University, Beijing 100044, People's Republic of China

Ikuo Suemune and H. Kumano

Research Institute for Electronic Science, Hokkaido University, Kita-21, Nishi-10, Sapporo 001-0021, Japan

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High-quality ZnO thin films have been grown by plasma-enhanced molecular-beam epitaxy on sapphire substrates. Free-exciton absorption and exciton-LO phonon absorption peaks are observed in the films at room temperature, indicating that the exciton states are stable even at room temperature. Three excitonic transitions associated with valence bands *A*, *B*, and *C* are clearly revealed in the reflectance spectrum measured at low temperatures. This result indicates that the ZnO thin films have a perfect wurtzite crystal structure. Biexciton emission is observed in the photoluminescence spectra at low temperatures, from which the biexciton binding energy is estimated to be 14.5 meV, in good agreement with previous results. Exciton-LO (Ex-LO) and exciton-2LO (Ex-2LO) photon emission peaks are observed at low temperature. The energy difference between the Ex-LO and Ex-2LO bands is about 72.5 meV, which coincides with previously reported values of the LO phonon energy for ZnO thin films. © 2006 American Institute of Physics. [DOI: 10.1063/1.2183354]

I. INTRODUCTION

Wide-band-gap semiconductors have attracted much attention due to their potential in commercial applications as short wavelength optoelectronic devices. Initially, efforts focused on ZnSe-based II-VI compound semiconductors.¹ Later, interest in GaN-based materials developed.² Both types have been employed in the fabrication of continuous wave laser diodes operating at room temperature. These achievements have stimulated the exploration of other wide-band semiconductors with distinctive properties. Recently, much interest has been attracted by ZnO, a wurtzite compound semiconductor of the II-VI family, which has a direct band gap of 3.37 eV at room temperature and so is a good candidate for optoelectronic applications that operate in the near-UV region.^{3–10} Compared with III-V nitride materials and other II-VI compound semiconductors, the most unique property of ZnO is its 60 meV exciton binding energy, which is about thrice as large as that of ZnSe and GaN. This large binding energy makes excitons stable even at room temperature. With this distinct feature ZnO will be a promising material for exciton-related optoelectronic applications, allowing in principle efficient excitonic lasting operation at room temperature or even higher. In particular, since the excitons are stable at room temperature, ZnO is a very interesting candidate for cavity coupled polariton lasers operated at room temperature.^{11,12}

To produce high-performance light-emitting devices a high-quality heteroepitaxial ZnO thin film is necessary. Recent progress in growth techniques has enabled us to obtain

ZnO samples of high optical quality and to explore the intrinsic recombination processes of excitons. It is imperative to fully characterize the excitons in ZnO thin films since not only are excitons a sensitive indicator of material quality but also they play an important role in the stimulated emission and gain processes in real device structures. Three exciton transitions have been observed in reflection measurements at low temperature.^{13,14} Photoluminescence (PL) of biexciton recombination, a result of the large biexciton binding energy (12–20 meV),^{15–20} has also been reported in ZnO bulk materials¹⁵ and thin films.^{21,22} However, the information provided in previous papers is still relatively incomplete.

In this paper we describe the use of absorption, reflectance, and photoluminescence spectroscopies to characterize the exciton transitions in ZnO thin films grown by plasma-enhanced molecular-beam epitaxy (P-MBE) on sapphire substrates. Spectral features associated with interband excitonic transitions were observed in the absorption spectra at room temperature and in reflectance spectra at various temperatures, with results indicating that the films have perfect crystalline structure. We also observed a PL band that may be attributed to the biexciton state in our high-quality ZnO thin films; so to confirm this we studied the dependence of the PL spectra on excitation intensity and temperature.

II. EXPERIMENT

High-quality ZnO thin films were grown by plasma-enhanced molecular-beam epitaxy on sapphire (0001) substrates. The background pressure in the growth chamber was less than 6×10^{-10} Torr. A rf-plasma source was used to provide reactive oxygen radicals. 5*N* oxygen gas is first purified and then through a mass flow control system is injected into

^{a)}Author to whom correspondence should be addressed; FAX: 86-10-51688018; electronic mail: xqzhang@center.njtu.edu.cn

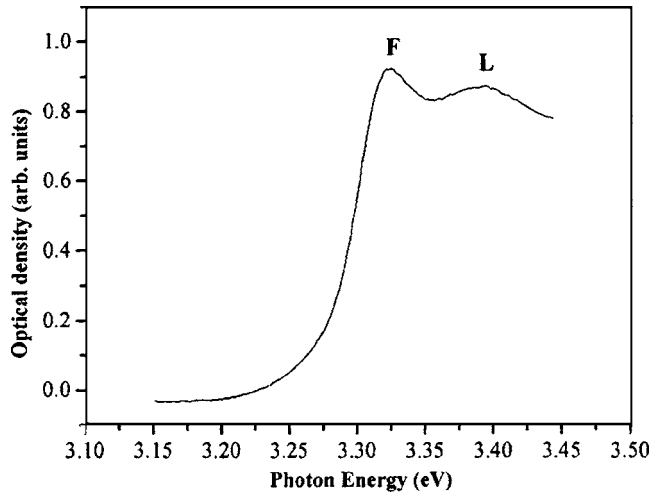


FIG. 1. Absorption spectrum in ZnO thin film at room temperature.

the plasma source. A Knudsen effusion cell was used to evaporate a 7N Zn metal source. The growth temperature was 650 °C. A reflection high energy electron diffraction pattern showed well-defined streaks at the initial growth stage, while x-ray diffraction measurements revealed that the ZnO microcrystallites have high crystallinity with *c*-axis orientation. The samples were 220 nm thick.

Investigation of the intrinsic exciton transitions was carried out using absorption, reflectance, and PL measurements. In the absorption and reflection measurements, a xenon lamp was used as the excitation source. For measurements of the temperature and excitation dependence of the PL spectra, the samples were illuminated by the 325 nm line from a He–Cd continuous wave (cw) laser, and the PL was dispersed by a monochromator and detected by a photomultiplier tube with the amplification by a lock-in amplifier.

III. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectrum of a ZnO thin film sample at room temperature. A pronounced exciton absorption peak (denoted by *F*) is found at 3.3239 eV, which can be attributed to free-exciton absorption, indicating that the exciton states are stable even at room temperature. Clearly separated from peak *F*, there is a broad absorption feature peaked at 3.3964 eV (denoted by *L*). This feature originates from the strong exciton-LO phonon coupling interaction in an indirect absorption process, which has been observed in polar materials such as CdS.^{23,24} Since the Zn–O bond is more polar than other II–VI semiconductors, a larger exciton-phonon interaction should be found in ZnO. This argument is supported by our observation of exciton-2LO phonon emission in the PL spectra, as will be discussed later. The energy difference between the *F* and *L* bands is about 72.5 meV, which is within the range of the previously reported values of 72–73 meV for the LO phonon energy of ZnO thin films.^{25,26}

In wurtzite ZnO which has C_{6v}^4 symmetry, three subbands (*A*, *B*, and *C*) are closely located near the valence band maxima (Γ_{7v}^u , Γ_{9v} , and Γ_{7v}^l), resulting in three exciton transitions. This is verified by the reflection measurements at low

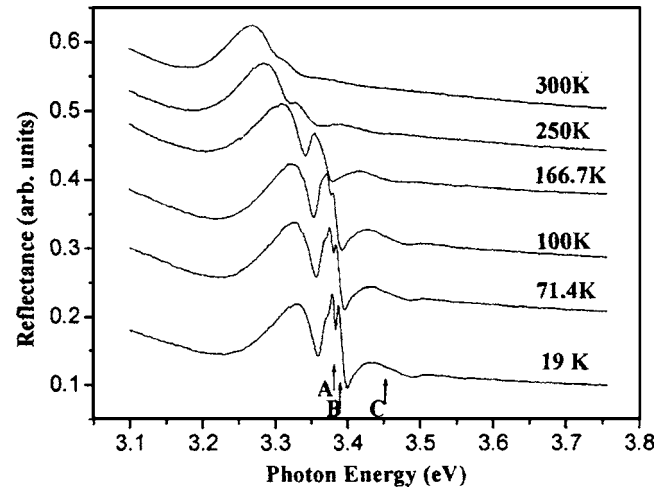


FIG. 2. Temperature dependence of the reflectance spectra in ZnO thin film.

temperatures. Figure 2 shows the temperature dependence of the normalized reflectance spectra for a 220 nm thick ZnO thin film. At a temperature below 166.7 K, three transitions labeled *A*, *B*, and *C* are found, which correspond to exciton resonance transitions from the exciton states *A*, *B*, and *C* that are formed from the conduction band (Γ_{7c}) and the three valence bands (Γ_{7v}^u , Γ_{9v} , and Γ_{7v}^l). According to the polarization selection rules, transitions *A* and *B* are allowed for light polarization perpendicular to the *c* axis, while transition *C* is allowed for light polarization parallel to the *c* axis. However, since the incident light was unpolarized and the thin ZnO crystal film strained by the lattice mismatch with the sapphire substrate, leading to relaxation of the selection rules, all the three transitions are revealed in the reflectance spectra, and the oscillator strength of the *C* exciton is found to be smaller than that of the *A* and *B* excitons.^{27,28} The well-resolved, sharp resonance peaks imply an extraordinarily low damping effect, indicating a very low concentration of residual free carriers in addition to the high optical quality of the material. As the temperature increases, the peaks gradually broaden and shift to lower energies. Peaks *A* and *B* are not clearly resolved at a temperature above 166.7 K, whereas peak *C* is still resolvable up to 300 K. For a detailed description of *A*, *B*, and *C* excitons see Refs. 11 and 12.

To obtain a better understanding of the properties of excitons in ZnO thin films, PL measurements were carried out at various temperatures. Figure 3 shows the temperature dependence of the normalized PL spectra with an excitation intensity of 80 W/cm². At 19 K, only a single peak (labeled XX) in the PL spectrum is observed. When the temperature is increased to 45.5 K, another peak (labeled FX) emerges at the higher energy side of peak XX, which, based on its energy, could be attributed to a free-exciton transition. In order to determine the origin of peak XX, the dependence of the PL spectra on excitation intensity was investigated at 77 K, as shown in Fig. 4. It can be seen that the integrated PL intensity of the XX band increases superlinearly with increasing excitation intensity. This result is quite different from that of impurity- or defect-related luminescence, which we would expect to be saturated at relatively high excitation powers, indicating that peak XX is associated with

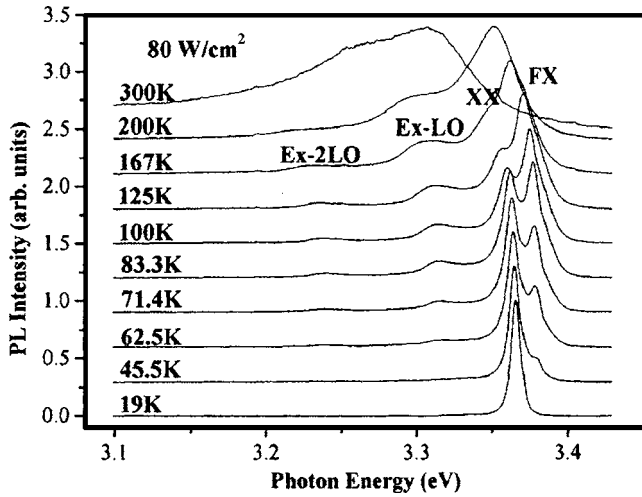


FIG. 3. Temperature dependence of PL spectra in ZnO thin film.

biexcitons^{29,30} formed by the frequent collisions in high concentration excitons. This result confirms that the films are of excellent quality, since the density of defects is so low that the excitons can avoid excessive scattering by impurities and crystalline defects before they form biexcitons. The average biexciton binding energy, 14.5 meV, can be derived from the energy separation of the two peaks, FX and XX, and is in good agreement with the reported values of 14.7 and 15 meV.^{21,22} It should be noted that the biexciton binding energy we obtained is also within the range of previously reported values for bulk crystals (12–20 meV).²¹ As the temperature increases further, peak XX decreases and submerges gradually into peak FX. This is due to the dissociation of biexcitons with temperature. As the temperature increases, the number of dissociated biexcitons increases, leading to decrease of the emission intensity. At 200 K, when the biexciton binding energy is less than the effective thermal energy kT , 17 meV, the biexciton emission peak disappears.

It is interesting to note that when the temperature increases to 62.5 K, two weak emission peaks (labeled Ex-LO and Ex-2LO, respectively) are observed in the spectra, which can be identified as being due to the radiative transitions of free excitons associated with one and two LO phonons, re-

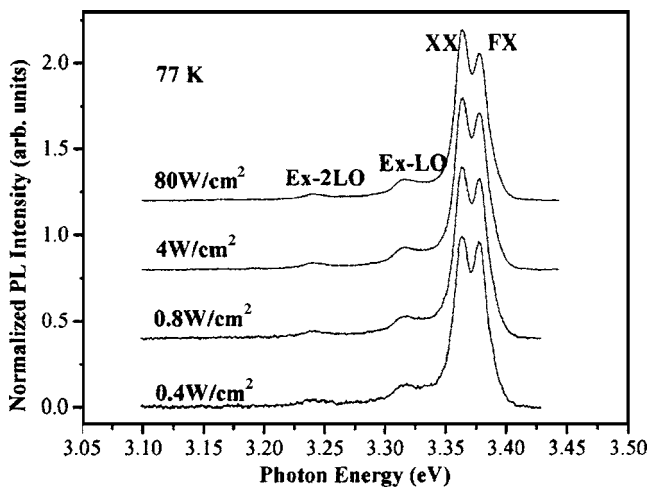


FIG. 4. Excitation intensity dependence of PL spectra in ZnO thin film.

spectively. The energy difference between the Ex-LO and Ex-2LO bands is about 72.5 meV, which coincides with previously reported values of the LO phonon energy for ZnO thin films. The observation of multiple phonon replicas in PL also indicates that ZnO is a polar material exhibiting strong exciton-LO phonon interaction.³¹ When the temperature increases to 165 K, Ex-LO and Ex-2LO emission peaks reach a maximum value. At room temperature, only free-exciton emission is observed.

IV. CONCLUSIONS

The intrinsic exciton transitions of high-quality ZnO thin films grown by P-MBE on sapphire substrates have been studied. A pronounced free-exciton absorption peak and an exciton-LO phonon absorption peak are observed at room temperature, indicating that the exciton states are stable even at room temperature because of the large exciton binding energy. Three excitons associated with valence bands *A*, *B*, and *C* are clearly observed in the reflectance spectra at low temperatures. The spectral features broaden and shift to lower energies as the temperature increases. Biexciton emission is revealed in the PL spectra at low temperatures, indicating that the films are of excellent quality and have a low defect density. The biexciton binding energy is estimated to be 14.5 meV, in good agreement with previous results. The observation of exciton-LO and exciton-2LO phonon emission peaks in the PL spectra indicates a strong exciton-phonon interaction in ZnO. The energy difference between the exciton-LO and exciton-2LO bands is about 72.5 meV, which agrees with previously reported values of the LO phonon energy for ZnO thin films.

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