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Photoluminescence of localized excitons in ZnCdO thin films grown by molecular beam epitaxy



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ABSTRACT

We have investigated the luminescence characteristics of $Zn_{1-x}Cd_xO$ thin films with different Cd contents grown by molecular beam epitaxy system. The temperature-dependent photoluminescence (PL) and excitation power-dependent PL spectra were measured to clarify the luminescence mechanisms of the $Zn_{1-x}Cd_xO$ thin films. The peak energy of the $Zn_{1-x}Cd_xO$ thin films with increasing the Cd concentration is observed as redshift and can be fitted by the quadratic function of alloy content. The broadened full-width at half-maximum (FWHM) estimated from the 15 K PL spectra as a function of Cd content shows a larger deviation between the experimental values and theoretical curve, which indicates that experimental FWHM values are affected not only by alloy compositional disorder but also by localized excitons occupying states in the tail of the density of states. The Urbach energy determined effect estimated from the temperature-induced S-shaped PL peak position described an increasing mean exciton-localization effects in ZnCdO films with increasing the Cd content. In addition, the PL intensity and peak position as a function of excitation power are carried out to clarify the types of radiative recombination and the effects of localized exciton in the ZnCdO films with different Cd contents.

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1. Introduction

Recently, ZnO-based semiconductors materials have been rapidly and widely developed for laser diodes (LDS) and lightemitting diodes (LEDs), owing to their tunable band gap by alloying with MgO to reach ultraviolet region or by alloying with CdO to achieve the visible region [1–4]. For the application in the region from ultraviolet to green light spectra, the ZnCdO alloy is useful to fabricate ZnCdO-related heterostructures or quantum well structures, which are the key elements in ZnO-based light emitters and detectors [5]. Therefore, it is quite necessary to investigate the optical characteristics in the ZnCdO alloys, such as the properties of band gap engineering, exciton behavior, and luminescence.

However, it has been known that the hexagonal wurtzite $Zn_{1-x}Cd_xO$ films with high Cd contents are difficult to be prepared, because the thermodynamic solubility limit of Cd in ZnO is 2% in thermal equilibrium condition, as well as the phase separation between wurtzite ZnO and rocksalt CdO would induce the alloy

compositional disorder in ZnCdO films with higher Cd contents [2,6–7].

In this work, we investigate the optical characteristics of ZnCdO thin films with different Cd contents grown by plasma assisted molecular beam epitaxy (PA-MBE) system by temperature-dependent photoluminescence spectrum. By analyzing the 15 K PL spectra of the ZnCdO films as a function of the Cd content, the variations in the estimated full width at half maximum (FWHM) values are not only compared to theoretical calculations but also considered with the Urbach energy. Additionally, the temperature induced S-shaped (red-blue-red) PL peak energy and excitation intensity-dependent PL intensity are carried out to explain in details for the luminescence mechanisms of the ZnCdO films.

2. Experimental procedures

The investigated $Zn_{1-x}Cd_xO$ films were grown on the *c*-plane Al_2O_3 substrates by SVT associates molecular beam epitaxy system equipped with conventional effusion cells for evaporation of elemental Zn (6N) and Cd (6N). Oxygen (5N5) was supplied via an rf-plasma source after additional gas purification. In order to reduce

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the lattice mismatch between $Zn_{1-x}Cd_xO$ and Al_2O_3 , the $Zn_{1-x}Cd_xO$ films were firstly grown at 350 °C following a 70 nm thick ZnO buffer layer grown at 650 °C. The Cd concentration of $Zn_{1-x}Cd_xO$ was controlled by adjusting the Cd/Zn beam pressure. The Cd concentrations applied for the five $Zn_{1-x}Cd_xO$ films are approximately estimated to be 0.11, 0.13, 0.16, 0.18, and 022, respectively by using the energy-dispersive X-ray spectroscopy (EDX) measurement. More details about the growth procedures have been described in the previous work [8].

The temperature-dependent photoluminescence measurements were conducted under the excitation with a 10 mW/cm² microchip laser (260 nm). The luminescence was collected by using a spectrometer (Jobin Yvon Horiba TRIAX 550) with a 1200 grooves/mm grating and detected by the high-speed GaAs photomultiplier tube (PMT). Then, the PL signal obtained from the PMT was analyzed by using the lock-in technique and recorded in a computer. Janis Research Model CCS-150 and LakeShore Model 321 temperature controller were used to carry out the temperature-dependent PL spectrum. In addition, the excitation intensity-dependent PL spectra were measured under the power density from 1 to 10 mW/cm².

3. Results and discussion

The normalized PL spectra of ZnCdO films with different Cd contents taken at 15 K and 300 K are presented in Fig. 1(a) and (b), respectively. As shown in Fig. 1(a), the peak position of the PL spectra locates at 2.85, 2.84, 2.7, 2.67, and 2.57 eV for the samples with x=0.11, 0.13, 0.16, 0.18 and 0.22, respectively. The estimated values of the PL peak energy are plotted in Fig. 2 and exhibit the redshift as increasing the Cd content. Since ZnO is a direct band gap semiconductor, the PL peak energy of ZnCdO films with different Cd contents can represent the value of band gap, which are



$$E_{g,Zn_{1-x}Cd_{x}O}(x) = (1-x)E_{g,ZnO} + xE_{g,CdO} - bx(1-x)$$
(1)

where the band-gap of ZnO ($E_{g,ZnO}$) and CdO ($E_{g,CdO}$) are 3.28 and 2.3 eV [9–10], respectively. The bowing parameter *b* is about 2.92 derived from the simulated result shown as the red solid curve in Fig. 2, which can be well throughout the experimental data. Two main factors, the compositional inhomogeneity and the carrier localization at the potential minima formed by Cd composition fluctuations, would dominate significantly the PL energy position to affect the value of bowing parameter, are further considered [11,12].

As shown in Fig. 1(b), the FWHM and lineshape of 15 K PL of the ZnCdO films exhibit more asymmetric and broader with increasing the Cd contents, respectively. The derived FWHM values are displayed as opened squares in Fig. 3, and further compared with a theoretical curve based on statistical alloy broadening by the following equation [9]:

$$\Delta(x) = 2\sqrt{2\ln 2} \left| \frac{dE_{\text{ex}}(x)}{dx} \right| \sqrt{x(1-x)\frac{V_0(x)}{V_{\text{ex}}(x)}}$$
(2)

where $E_{\text{ex}}(x)$ is excitonic transition energy depending on the alloy content x. The $V_0(x)$ and $V_{\text{ex}}(x)$ are the volume of elementary cell and the exciton, respectively. The computed relevant exciton volume is $V_{\text{ex}}(x) = \frac{4\pi}{3}[r_{\text{B}}(x)]^3$, where $r_{\text{B}}(x)$ denoted the Bohr radius of exciton. The estimated volume of the elementary cell of wurtzite ZnCdO is $V_0(x) = \frac{1}{N} \frac{3\sqrt{3}}{2} [a(x)]^2 c(x)$, where N=6 is the number of cations in the unit cell, while a(x) and c(x) are the constants of ZnCdO alloy. For this work, we assumed that the crystal structure of CdO is wurtzite and the dependency of $r_{\text{B}}(x)$ on the alloy content is a linear variation with the alloy content. The solid line shown in Fig. 3 is the simulation curve calculated by Eq. (2). However, the FWHM values estimated from the PL spectra of the ZnCdO films



Fig. 1. (Color online) PL spectra for the $Zn_{1-x}Cd_xO$ films with different Cd contents measured at (a) 15 K and (b) 300 K.



Fig. 2. (Color online) Energy band-gap of the $Zn_{1-x}Cd_xO$ films as a function of Cd content. The red solid line is the fitted curve from Eq. (1).



Fig. 3. (Color online) The variation of the 15 K PL FWHM for the $Zn_{1-x}Cd_xO$ films with different Cd contents. The solid line shows the broadening tendency of PL FWHM calculated by Eq. (2).

with different Cd contents significantly deviate from the theoretical curve. It implies that the unexpected experimental FWHM should not only be related to the alloy compositional disorder but also to the contribution of asymmetric lineshape [13–14].

It can be observed that the 15 K PL spectrum shows more asymmetric lineshape induced by extending the band tail to low energy with increasing the Cd content. Usov et al. have indicated that the low-energy side of the PL lineshape is mainly related to the localized exciton states, whose energy distribution can be described by the Urbach tail of the density of states [15–16]. Furthermore, the Urbach energy (E_U) is determined from the PL lineshape in the low-energy side by an exponential function [15,17]:

$$\rho(E) \propto \exp(h\nu/E_{\rm U}) \tag{3}$$

where E_U is the Urbach energy describing the distribution of tail states extending into the forbidden gap. The inset of Fig. 4 shows the typical linear fitting of the curve in semi-log plot by Eq. (3) for deriving the E_U from the 15 K PL spectrum of the CdZnO film with the Cd content of 0.22. The estimated value of E_U is about 70 meV for the sample with Cd=0.11, and it would be increased with increasing the incorporated Cd contents to be about 105 meV for the sample with Cd=0.22. It is noted that the symbol of star shown in Fig. 3 obtained by subtracting the $E_{\rm U}$ from the experimental FWHM would be closer to the theoretical curve describing the effects of alloy compositional disorder. However, the residual discrepancy between the experimental data and theoretical curve still presents, especially a larger deviation at higher Cd content. The phenomenon attributed to the actual value of Bohr radius in our samples should be smaller than the theoretical value due to much more alloy disorder [18]. It can be understood that the much smaller value of Bohr radius would enlarge the calculated excitonic volume in Eq. (2) to result in the much broader FWHM values [19–20].

We further consider the recombination of excitons localized within the band tail states added to the broaden PL FWHM. The effects of localized exciton in the Cd content-dependent ZnCdO films are discussed by temperature-dependent PL peak energy, which are plotted in Fig. 5. For the ZnCdO samples with Cd content of 0.11 and 0.13, the variations in their PL peak energy exhibit the typical redshift with increasing the temperature. However, by increasing the Cd content above 0.16, it observes that the PL peak redshifts slightly in the low temperature region, then blueshifts in the intermediate temperature region, and again redshifts till room temperature is reached. The anomalous luminescence peak position varying with temperatures have been described as the S-shaped shift [21-22], and become more significant with increasing the Cd contents incorporated into the ZnCdO films. We further use the Bose-Einstein empirical equation taken account of localization effect to describe the temperaturedependent PL peak energy as [21–22]:

$$E(T) = E(0) - \frac{2a_{\rm B}}{\exp(\Theta_{\rm B}/T)} - \frac{\sigma^2}{K_{\rm B}T}$$
(4)

where E(0) is the band gap energy at the T=0 K, $a_{\rm B}$ is strength of the electron/exciton-phonon interaction, $\Theta_{\rm B}$ is the Einstein characteristic temperature. The third term originates from the localization effect, in which σ indicates the degree of localization effect as well as $K_{\rm B}$ is the Boltzmann's constant [22]. By taking σ into consideration, the Eq. (4) can describe an anomalous band gap behavior at higher temperature region, which exhibits the redshifted emission peak with decreasing temperature. However, at lower temperatures, the excitons would be trapped in the local minima and no further relax due to larger localization effect of σ . It means that the luminescence peak position no longer follows Eq. (4) and can even increase with decreasing temperature [23]. The red solid lines in Fig. 5 show the results of the fit by using Eq. (4). It is noted that no observed localization effect (σ =0) for the samples with Cd=0.11 and 0.13, whereas the values of σ can be estimated to be about 11, 32, and 45 meV for the samples corresponding to Cd = 0.16, 0.18 and 0.22, respectively. The σ value increased



Fig. 4. (Color online) The values of Urbach energy E_U as a function of Cd content.



Fig. 5. (Color online) Temperature dependence of PL peak position for the $Zn_{1-x}Cd_xO$ films with different Cd contents.

as a function of Cd content indicates an increasing mean excitonlocalization energy in the ZnCdO films. In addition, it can be observed that the obtained fitting curve cannot describe the typical band gap behavior at lower temperatures because the larger value of σ would induce a sharper theoretical curve for fitting the larger degree of anomalous redshifted emission peak with increasing temperature at higher temperatures.

The power-dependent PL spectra at 15 K are carried out to characterize the type of radiative recombination in the ZnCdO films. Fig. 6 presents the log scale plot of the integrated PL intensities (I_{PL}) of the ZnCdO films with different Cd contents as a function of laser pump power (L). The relationship between I_{PL} and *L* can be mathematically expressed by the power law as $I_{\rm PL} \propto L^k$, where k is the coefficient to represent the radiative recombination mechanism [24-25]. The value of k calculated from the slope of the logarithmic representation of I_{PL} and L is about 1.19, 1.08, 1.06, 1.02, and 0.93 for the $Zn_{1-x}Cd_xO$ films with x=0.11, 0.13, 0.16, 0.18and 0.22., respectively. According to Refs. [18,19], it can be known that when the excitation energy is higher than the band gap, the value of exponent k is generally 1 < k < 2 for free- and boundexciton recombination and is less than 1 for defect-related recombination processes. The *k* value of 0.93 for the sample with Cd=0.22 implies an extra type of transition mechanism having to be considered. Moreover, the inset of Fig. 6 shows that the 15 K PL peak position of the sample with Cd=0.18 and 0.22, respectively, exhibits a constant and blueshift with increasing excitation power



Fig. 6. (Color online) Excitation power-dependent PL spectra of $Zn_{1-x}Cd_xO$ films with different Cd contents.

intensity. The phenomenon of blueshift means that the higher power excitation results in increases of the generated carriers. The generated carriers will fully fill the lowest-energy state first, and then the overgenerated carriers will overflow to the higher-energy [26]. Therefore, the result supports a larger density of states of the localized state existing in the CdZnO film with Cd content of 0.22, which corresponds to the larger tail on the low-energy side influenced by the localized state or fluctuation state from higher Cd incorporations [27].

4. Conclusion

We have reported on the temperature-dependent PL and excitation power-dependent PL of $Zn_{1-x}Cd_xO$ films with x=0.11, 0.13, 0.16, 0.18 and 0.22 grown by the MBE system. The variations in the FWHM value estimated from 15 K PL spectra of CdZnO films as a function of Cd content would be affected not only by alloy compositional disorder but also by localized excitons occupying states in the tail of the density of states. The Urbach energy (E_{II}) determined from an exponential fit to the low-energy tail in PL lineshape and the degree of localization effect (σ) derived from the temperature-induced S-shaped PL peak position can indicate an increasing mean exciton-localization effects in ZnCdO films with increasing Cd content. The excitation-power-dependent PL intensity and peak position are measured to investigate the radiative recombination mechanism in the ZnCdO films with different Cd contents, and shows the broader PL peak of the ZnCdO films with Cd = 0.22 induced by the lager localized state or fluctuation state from higher Cd incorporations.

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