

Thermal-activated carrier transfer in ZnCdO thin film grown by plasma-assisted molecular beam epitaxy

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ARTICLE INFO

Available online 9 January 2013

Keywords:

A3. Molecular beam epitaxy

B1. Oxides

B1. Zinc compounds

B2. Semiconducting II–VI materials

ABSTRACT

The thermal-activated carrier transfer processes in a Zn_{0.98}Cd_{0.02}O thin film grown by plasma-assisted molecular beam epitaxy were investigated using temperature-dependent and time-resolved photoluminescence (PL) spectroscopy. As the temperature increases from 50 to 220 K, the carriers transfer from shallow to deep localized states. Additionally, the carriers escape from the deep localized states above 220 K due to an activation energy of about 19 meV.

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1. Introduction

Zinc oxide has received considerable attention due to its promising integration into optoelectronic devices. Its large band gap of about 3.37 eV at room temperature, high exciton binding energy (60 meV), and structural compatibility with GaN are some of the properties that make this material interesting for optoelectronic applications [1]. Recently, Zn_{1-x}Cd_xO compound semiconductors have been further utilized to tailor the band gap of ZnO from ultraviolet to visible spectral range owing to the small band gap of CdO of about 2.30 eV [2]. The fabrication of ZnO/Zn_{1-x}Cd_xO heterojunctions and multiple quantum wells would provide the key elements in ZnO-based light emitting diodes and laser diodes. Therefore, it is worthwhile to understand the light emission mechanism in the Zn_{1-x}Cd_xO alloy system. However, the rock-salt structure of CdO is dissimilar to the wurtzite structure of ZnO. It results in reducing crystalline quality and causing phase separation for Zn_{1-x}Cd_xO alloys. The difficulty was solved by metal organic chemical-vapor deposition growth technique, and Cd composition can be increased up to 2.0% [3]. However, the cathode-luminescence results showed that a low energy shoulder emerges. The sample quality was further improved by Sadofev et al. using molecular beam epitaxy (MBE) to eliminate the low energy shoulder [4]. In this article, high-quality Zn_{0.98}Cd_{0.02}O thin film was grown by plasma-assisted MBE. The temperature-dependent PL and time-resolved PL

(TRPL) were used to study the thermal-activated carrier transfer dynamics of Zn_{0.98}Cd_{0.02}O.

2. Experimental procedure

ZnO and Zn_{0.98}Cd_{0.02}O thin films were grown on *c*-plane Al₂O₃ substrates by a SVT Associates MBE system equipped with conventional effusion cells for evaporation of elemental Zn (6N), Mg (5N), and Cd (6N). Oxygen (5N5) was supplied via an rf-plasma source after additional gas purification. The substrates were degreased in acetone, methanol, and then chemically etched in H₂SO₄:H₃PO₄=3:1 mixture at 160 °C for 15 min, followed by a deionized water rinse. Prior to the growth, substrates were desorbed at 850 °C and treated with oxygen plasma to produce an oxygen terminated Al₂O₃ surface. In order to reduce the lattice mismatch between Zn_{1-x}Cd_xO and Al₂O₃, the 300 nm thick Zn_{0.98}Cd_{0.02}O film was grown at 350 °C following a 70 nm thick ZnO buffer layer grown at 650 °C. The oxygen flow rate was 0.6 SCCM with plasma power 250 W. The Zn and Cd cell temperatures for the growth of Zn_{0.98}Cd_{0.02}O thin films were 290 and 180 °C, respectively. The optical characterization of the samples was analyzed by temperature-dependent PL and TRPL measurements. The 325 nm-line of a He–Cd laser was used as the excitation source for PL, and TRPL was excited using a pulsed laser (377 nm/40 MHz).

3. Results and discussion

Fig. 1 shows the PL spectra of ZnO and Zn_{0.98}Cd_{0.02}O films at 10 K. The emission peaks at 3.361 and 3.366 eV were assigned to the

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excitons bound to neutral donors (D_0X) [5]. The peak at 3.377 eV is attributed to the free A excitons (FX_A) [6]. When Cd atoms were introduced into ZnO, the PL band becomes broad and the spectral position of the PL peak shifts to 3.185 eV. According to the experimental results of Gruber et al. [7], the Cd composition herein can be estimated as 2%. Additionally, the PL emission profile of $Zn_{0.98}Cd_{0.02}O$ is not symmetry due to the existence of localized states at low energy

side. The transmittance spectrum at 10 K shown in the inset shows a strong absorption near the band edge. It can be seen that the Cd incorporation reduces the band gap energy and causes a Stokes' shift of about 100 meV. The Stokes' shift is attributed to the localization of excitons due to the Cd compositional fluctuation [8].

In order to further investigate and compare the optical properties of $Zn_{0.98}Cd_{0.02}O$ with ZnO, the temperature-dependent PL measurements of ZnO and $Zn_{0.98}Cd_{0.02}O$ were carried out. In Fig. 2(a), both D_0X and FX_A of ZnO shift to lower energies, and the line-width broadens with increasing temperature. The PL linewidth broadening is related to the carrier-phonon interaction. Additionally, because of thermally activated processes of carriers, FX dominates at high temperature. In Fig. 2(b), three PL peaks of $Zn_{0.98}Cd_{0.02}O$ labeled as P1, P2, and P3 were observed at different temperatures. The P1 emission was observed at low temperature. When $T > 140$ K, additional peaks, P2 and P3, become visible. The intensity of P2 increases and exceeds that of P1 when $T > 220$ K. Similar optical properties were also observed by Yang et al. [9] in $ZnSe_{1-x}Te_x$ ($x=0.01$) epilayers. In the case of $ZnSe_{1-x}Te_x$, at low temperature of 10 K, X/Te is not observed and the PL of the Te_n -bound excitons (X/Te_n) is very pronounced. The energy states of X/Te and X/Te clusters become observable as the temperature was increased. Thus, the PL peaks of P1, P2, and P3 can be attributed to the emissions from X/ Cd_n , X/ Cd , and X/ Cd cluster, respectively. Fig. 2(c) shows the dependence of X/ Cd_n intensity on temperature with a double-channels activation energy function: [10]

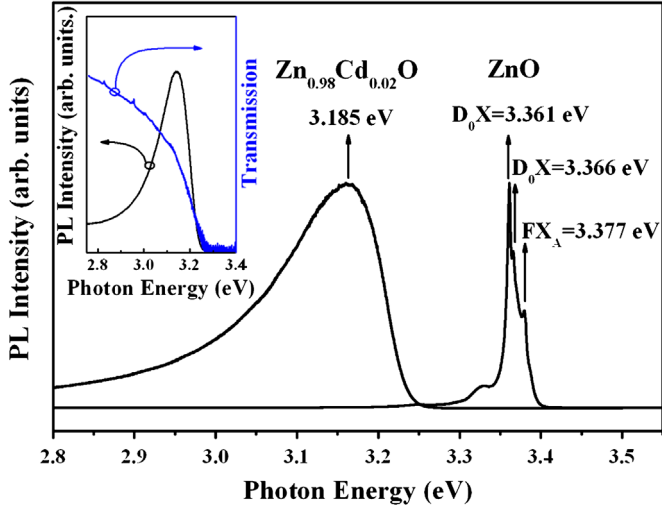


Fig. 1. (a) PL spectra of ZnO and $Zn_{0.98}Cd_{0.02}O$ films at 10 K. The inset shows the PL and transmittance spectra of $Zn_{0.98}Cd_{0.02}O$ at 10 K.

$$I_{PL}(T) = \frac{I_0}{1 + C_1 \exp(-E_{a1}/k_B T) + C_2 \exp(-E_{a2}/k_B T)} \quad (1)$$

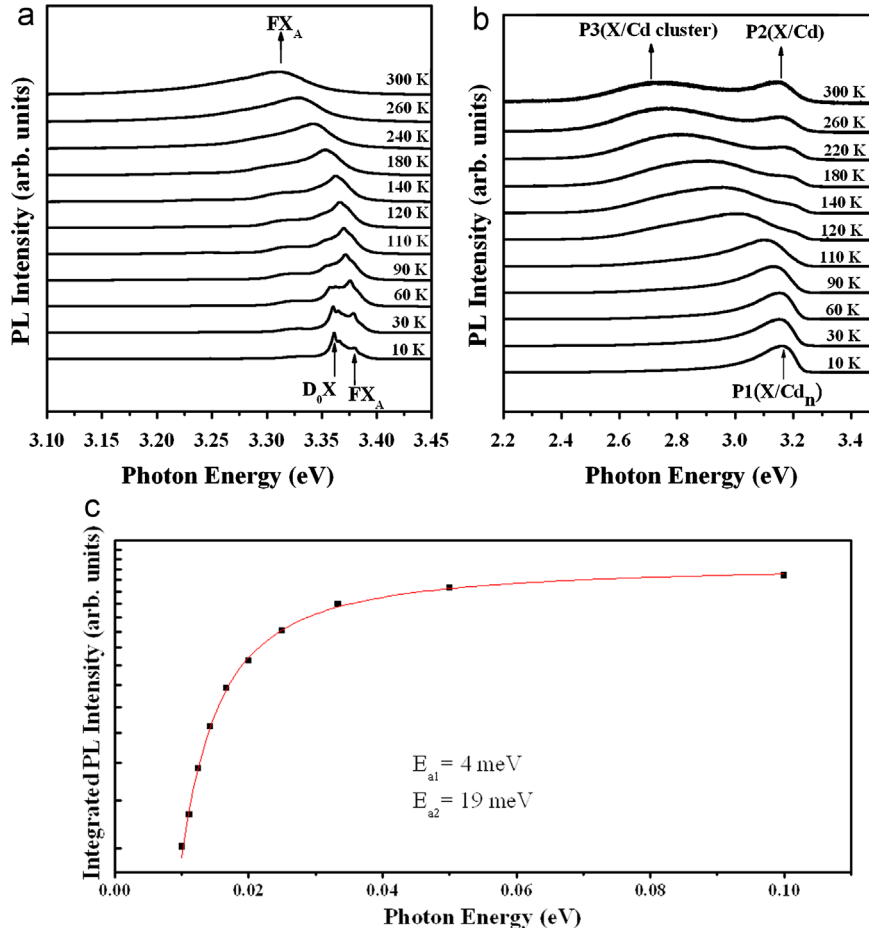


Fig. 2. PL spectra of (a) ZnO and (b) $Zn_{0.98}Cd_{0.02}O$ thin films at various temperatures. (c) Integrated PL intensity of X/ Cd_n as a function of temperature for ZnCdO. The solid line is fitted by Eq. (1).

where $I_{\text{PL}}(T)$ is the integrated PL intensity at temperature T , k_B is the Boltzmann constant, E_{a1} and E_{a2} denote the activation energy, C is a tunneling factor, and I_0 is the integrated intensity at the low temperature limit. In this study, $E_{a1}=4$ meV and $E_{a2}=19$ meV were extracted. The activation energy E_{a1} is attributed to the average localization energy of the X/Cd_n . On the other hand, the activation energy E_{a2} corresponds to thermal energy of 220 K, which is similar to the quenching temperature of X/Cd_n intensity. Therefore, we consider that the activation energy E_{a2} is the energy for carriers transferred from X/Cd_n to X/Cd .

In order to confirm the origin of the emissions from X/Cd , X/Cd_n , and X/Cd clusters, the PL peak positions of the free-exciton (FX), X/Cd , X/Cd_n , and X/Cd clusters as a function of temperature were plotted in Fig. 3(a). The FX peak positions obtained from transmittance are well fitted by the Varshni's prediction [11] which is written as

$$E_g(T) = E_g(0) - \alpha T^2 / (\beta + T) \quad (2)$$

where $E_g(0)$ is the band-gap energy at $T=0$ K, and α and β are the corresponding thermal coefficients. The fitting is labeled by solid lines in Fig. 3(a). The X/Cd peaks exhibit a similar trend. The emission energy of X/Cd is 80 meV lower than that of FX. It implies that there is not enough energy to offer the carriers transferred from X/Cd states to FX states. Therefore, X/Cd dominates the carrier recombination at 300 K. However, the X/Cd_n peak demonstrates a fast redshift at temperatures above 50 K. This phenomenon could be

attributed to continuous localized states formed with the X/Cd_n states. We proposed that excitons assisted by the scattering of LO phonons would transfer to the deep localized states, and the possibility of this re-localization process is promoted as the temperature increases because the spreading of exciton wave-function enhances the interaction with LO phonon fields. In this condition, the increased temperature only causes small parts of the carriers to delocalize from the deep localized states to the shallow ones. The X/Cd_n peak redshifts dramatically until the carriers were relocalized at the X/Cd cluster states (the deepest localized states). On the contrary, as the temperature exceeds 220 K, the thermal energy overthrows the activation barrier of 19 meV, which promotes large amount of the carriers to escape from the deep localization and the X/Cd emission dominates. Fig. 3(b) shows the power dependent PL spectra at 220 K for $\text{Zn}_{0.98}\text{Cd}_{0.02}\text{O}$. The intensity of PL emission is enhanced with increasing excitation power. Under an excitation power of 65 W/cm^2 , the emission energies of X/Cd cluster and X/Cd are at 2.782 and 3.160 eV, respectively. As the excitation power is increased, the X/Cd cluster exhibits energy blueshift and the X/Cd state dominates the spectrum. This result implies that the density of state for the X/Cd_n is much higher than that for the X/Cd cluster. The increasing excitation density saturates the lower energy states. As a result, the X/Cd_n state dominates the emission.

In order to provide further evidence to support the existence of localized states and to demonstrate the origin of the radiative

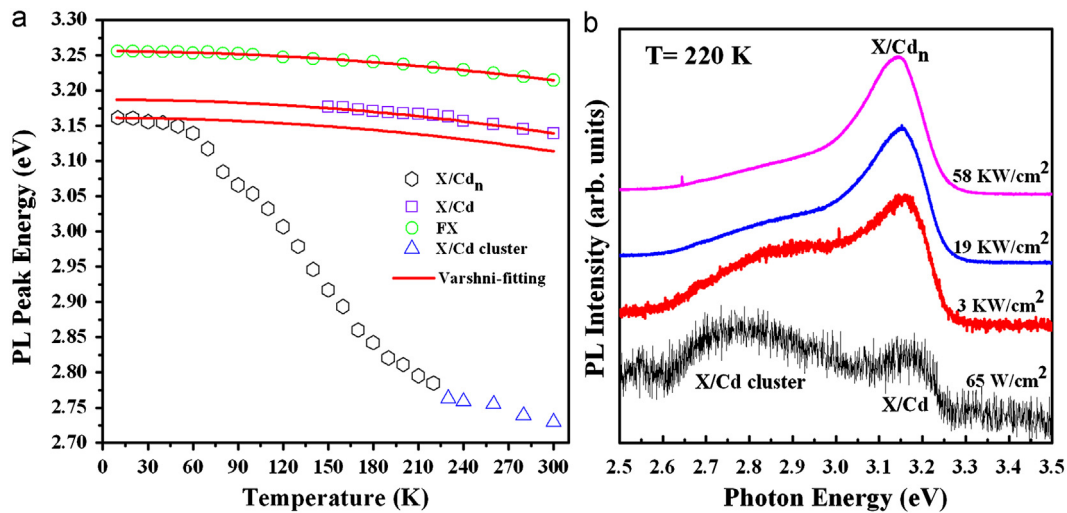


Fig. 3. (a) PL peak energy trace of X/Cd , X/Cd_n , X/Cd cluster and FX at various temperatures. The solid lines are Varshni's fits. (b) Power dependent spectra of $\text{Zn}_{0.98}\text{Cd}_{0.02}\text{O}$ at 220 K.

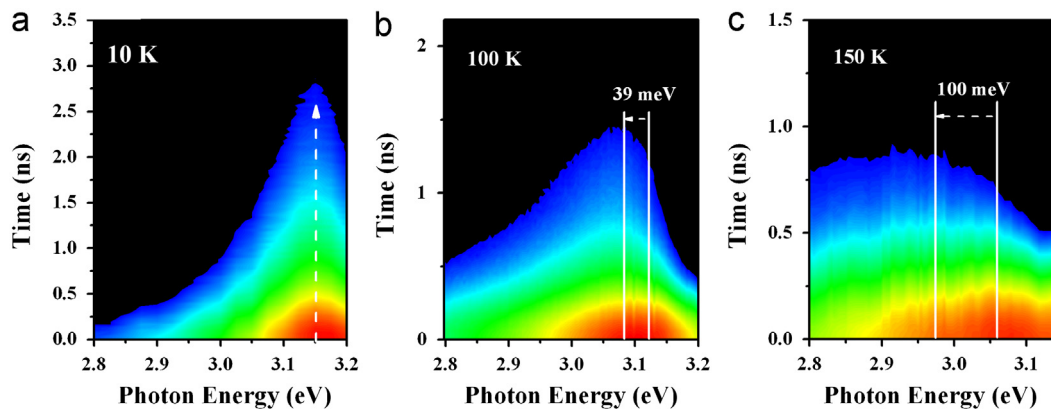


Fig. 4. Temporal evolution of the PL spectra at (a) 10 K, (b) 100 K, and (c) 150 K.

recombination, we performed TRPL measurements at 10 K, 100 K and 150 K as shown in Fig. 4. The carrier recombination time decreases with increasing temperature. It implies that the thermalized carriers could relax easily over a long distance and find a lower local-energy minimum. Besides, the main PL peak positions undergoes no obvious energy shift over time at 10 K, reflecting the main recombination of the localized state with the same concentration of Cd. However, the main peak shifts 39 meV toward the low energy side with time at 100 K. It reveals that the thermal-activated carriers transfer to the deeper localized states via the phonon scattering. As the temperature increases to 150 K, a larger redshift of 100 meV with the delay time was found, indicating more carriers can transfer to the deeper localized states. In combination with temperature-dependent PL and TRPL, we demonstrate the carrier transfer dynamics in $\text{Zn}_{0.98}\text{Cd}_{0.02}\text{O}$. The strong redshift of the X/Cd_n peak energy is caused by the carrier transfers to the deep localized states as $T < 220$ K. Moreover, a delocalization process occurs as the temperature exceeds 220 K.

4. Conclusion

Emissions of X/Cd , X/Cd_n , and X/Cd cluster from $\text{Zn}_{0.98}\text{Cd}_{0.02}\text{O}$ thin film were investigated by PL and TRPL spectroscopy. Two emission peaks, which are attributed to the carrier recombinations of X/Cd states and X/Cd cluster states, were observed at elevated temperatures. From 50 to 220 K, the carriers transfer from shallow X/Cd_n states to deep localized X/Cd_n states. Above 220 K, the carriers escape from the deep localized X/Cd_n states to X/Cd states.

Acknowledgments

This work was supported by the National Science Council and the Ministry of Education under Grant numbers NSC100-2119-M-009-003 and MOE-ATU 101W961, respectively.

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