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Optical property and Stokes' shift of $Zn_{1-x}Cd_xO$ thin films depending on Cd content

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Ternary $Zn_{1-x}Cd_xO$ films were grown on (0001) sapphire substrates by pulsed laser deposition. The energy band gap of $Zn_{1-x}Cd_xO$ films decreases with increasing Cd content. An increase of Cd content also leads to the emission broadening, absorption edge broadening, and crystallinity degradation. The absorption edge and ultraviolet emission energy shift to lower energy from 3.357 eV to 3.295 eV and 3.338 eV to 3.157 eV, respectively, with increasing Cd content from 0.3% to 3% at 4 K. The Stokes' shift between the absorption and emission is observed and that indicates the increase of exciton localization with Cd content. © 2006 American Institute of Physics. [DOI: 10.1063/1.2186372]

ZnO, a wide and direct band gap (about 3.37 eV) II-VI semiconductor, has found many applications in different fields. For example, it can be used as the material base for heterojunction laser diodes, ultraviolet (UV) lasers, UV solid-state emitters and detectors, transparent conductive contacts, thin-film gas sensors, varistors, solar cells, surface electroacoustic wave devices, and others.¹⁻³ Interest in short wavelength display devices based on ZnO has also been getting more attention recently.¹⁻³ An important step to design ZnO-based devices with high emitting efficiency is the band gap engineering in order to fabricate the quantum wells that are necessary in devices such as light emitting diode (LED) and laser diode (LD).⁴ Fabrication and characterization of alloys such as (Mg,Zn)O or (Cd,Zn)O are important from the viewpoint of band gap engineering as well as a *p-n* junction.⁵ Many results are reported related to ZnMgO.⁵⁻⁷ However, ZnCdO has not been widely studied.^{2,5,8} Moreover, the Stokes' shift in ZnCdO is rarely reported. In this paper, we report the experimental results of band gap modulation, structural characteristics, spectral broadening, and Stokes' shift in ZnCdO films as a function of Cd content.

Thin $Zn_{1-x}Cd_xO$ films were grown on (0001) sapphire substrates by pulsed-laser deposition (PLD), using a pulsed XeCl laser operating at a wavelength of 308 nm and a repetition rate of 5 Hz. The target was a ceramic pellet which consists of 80 wt % ZnO and 20 wt % CdO. The substrate temperatures during deposition were systematically varied from 200 °C to 800 °C while the oxygen pressure was maintained at 350 mTorr. Cd content in ZnO depending on deposition temperature from 200 °C to 800 °C was changed from 3% to 0.3%. Experimental details to deposit $Zn_{1-x}Cd_xO$ films and mechanism can be found elsewhere.² The structural properties of the $Zn_{1-x}Cd_xO$ films were investigated by x-ray diffraction (XRD). $Zn_{1-x}Cd_xO$ films have the thickness of

700 nm. The stoichiometry of thin films was estimated using Rutherford backscattering spectroscopy (RBS). The optical properties of the films were characterized by photoluminescence (PL) using a He-Cd laser as a light source having an excitation wavelength of 325 nm and absorption measurements, both at 4 K.

All of the films studied were preferentially oriented as indicated by the only (0002) diffraction. Figure 1 shows the full width at half-maximum (FWHM) values of the x-ray rocking curve from (0002) diffraction peaks and emission broadening from PL spectra as a function of Cd content. The FWHMs of the x-ray rocking curve from (0002) diffraction peaks and emission broadening increase with the Cd content x in $Zn_{1-x}Cd_xO$ films. This indicates the structural degradation of film and optical properties' degradation as the Cd content increases.

A comparison of photoluminescence (PL) and absorption measured at 4 K for $Zn_{1-x}Cd_xO$ films is shown in Fig. 2. The broadening of both emission energy and absorption edge in-

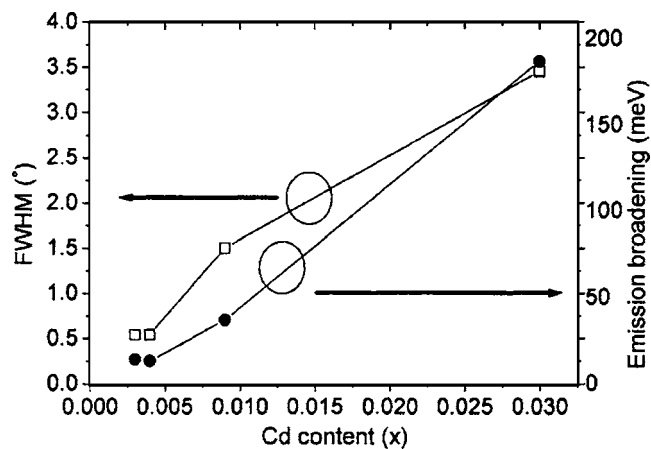


FIG. 1. The FWHM values of rocking curve from (0002) diffraction and emission broadening from PL spectra as a function of Cd content.

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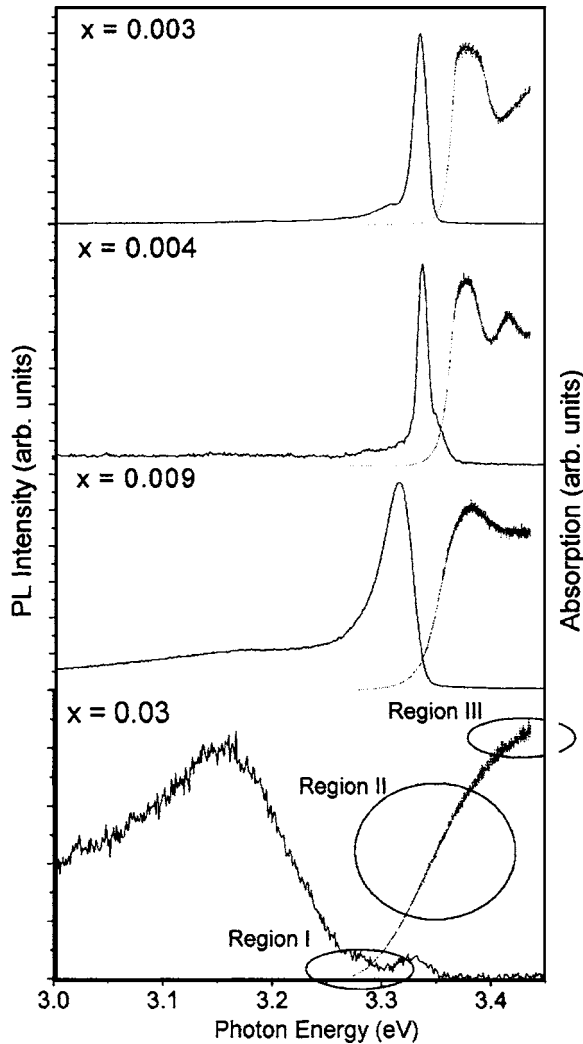


FIG. 2. Photoluminescence (solid lines) and absorption (dotted lines) spectra of $Zn_{1-x}Cd_xO$ thin films at 4 K as a function of Cd content x .

creases as the emission peak energy decreases. This increase of broadening is mainly due to the increase of disorder in the semiconductor, which leads to the appearance of localized electron and/or hole states.^{9–11} Two localization mechanisms have been suggested.¹¹ One is that exciton is localized by Coulomb interaction in very deep potential wells. The other is a case of wide potential well with dimensions larger than the excitonic Bohr radius. In this case, the exciton is localized as a whole in a wide potential well. R. W. Martin *et al.* suggested the additional mechanism.¹⁰ An additional localizing mechanism may be found in the nature of the segregated quantum dots (confinement effect) or alternatively from the large piezoelectric fields present in wurtzite semiconductors (Coulomb effect). Emission and absorption spectra are broadened due to increase of these localized states. Generally, absorption spectrum has three regions¹¹ as shown in Fig. 2. In region I, the absorption is weak and is caused by impurities in the alloy or amorphous semiconductor, i.e., atoms of a different chemical nature. The region II is where the absorption coefficient increases exponentially with photon energy. This region is also known as the “Urbach tail.”¹¹ Its origin in disordered semiconductor is, however, not the interaction with phonons, but simply the exponential tail of the

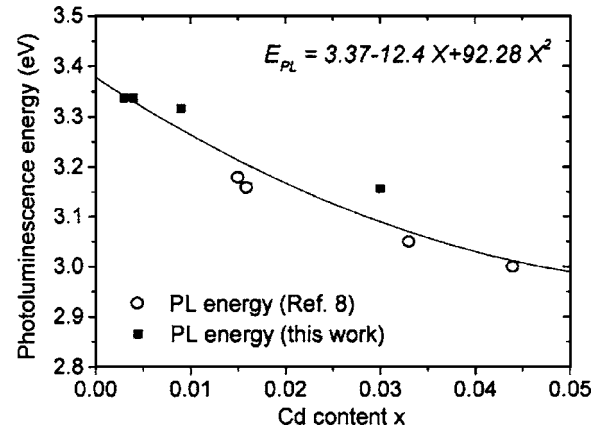


FIG. 3. Photoluminescence peak energy of $Zn_{1-x}Cd_xO$ as a function of Cd content x . Solid line shows the estimated curve of results of Ref. 8 and this work, Eq. (1).

density of states of localized excitons. Region III is related to an optical and mobility gap. The region II, which is related to the density of localized states, increases with the Cd content shown in Fig. 2. The increase of localized states in semiconductor leads to the increase of emission and absorption broadening. This, in turn, causes the Stokes’ shift.

Figure 3 shows the measured and referred values of PL peak position of $Zn_{1-x}Cd_xO$ depending on Cd content. For the comparison, the results reported by Th. Gruber *et al.*⁸ in Fig. 3 were included. The solid line shown in Fig. 3 shows the estimated curve that roughly follows a nonlinear behavior, Eq. (1).

$$E_{PL} = 3.37 - 12.4x + 92.28x^2 \text{ (eV)}. \quad (1)$$

The difference between the solid line peak and the dotted line edge in Fig. 2 exhibits the Stokes’ shift of $Zn_{1-x}Cd_xO$. The Stokes’ shift, defined as the energy difference between energy band gap and the peak of the emission spectrum,⁹ is plotted as a function of Cd content shown in Fig. 4. Theoretical results reported by Th. Gruber *et al.* were introduced in Fig. 4 to suggest the more exact Stokes’ shift data of $Zn_{1-x}Cd_xO$ depending on Cd content. Th. Gruber *et al.* reported that they performed absorption measurements to determine the Stokes’ shift, but could not be analyzed because

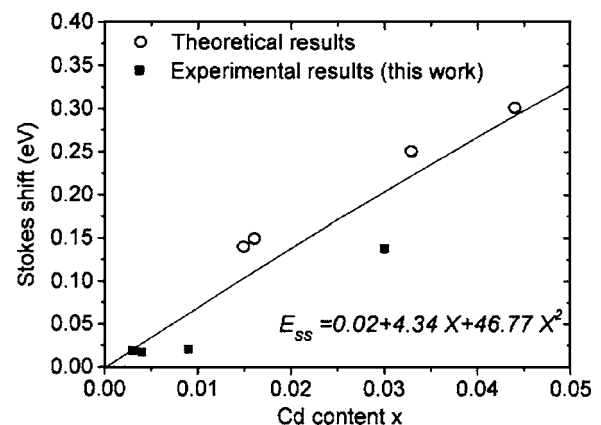


FIG. 4. Stokes’ shift plotted as a function of Cd content for $Zn_{1-x}Cd_xO$. Solid line shows the estimated curve of results of theoretical results induced by Ref. 8 and this work, Eq. (2).

of the absence of clear absorption edge from the $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ layers. However, Stokes' shift was clearly observed in this work as shown in Fig. 4. The Stokes' shift increased as Cd content increased. The solid line shown in Fig. 4 exhibits Stokes' shift curve of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ that follows a nonlinear behavior, Eq. (2). The curve of Stokes' shift of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ was represented like a linear curve as shown in Fig. 4 despite the nonlinear equation, Eq. (2).

$$E_{ss} = 0.02 + 4.34x + 46.77x^2 (\text{eV}). \quad (2)$$

The mechanism of Stokes' shift of ZnCdO in this work could be explained as follows. Disorder in ZnCdO increases with the Cd concentration. The increase of disorder in ZnCdO leads to degraded crystallinity and introduces more localized states. The increase of localized states in ZnCdO gives rise to the increase of Stokes' shift as a function of Cd content as shown in Figs. 3 and 4. The results as shown in Figs. 3 and 4 exhibit a little difference between theoretical and experimental results, results in this work and referred results. This is caused by crystallinity degradation and crystallinity difference.

Disorder and potential fluctuation generated in alloyed and heavily extrinsic dopant doped semiconductors cause the increase of localized states. This increase of localized states with increasing content of alloyed atoms and dopants leads to an increase of Stokes' shift and broadening of the emission and absorption edges.^{7,9-13} These effects are observed in various structures such as quantum well structures,¹⁴⁻²⁰ quantum dot structures in alloyed semiconductors,^{7,9,10} and heavily doped semiconductors.^{12,13} In view of the structure and experimental results, the results in this investigation are closer to quantum dot model in alloyed semiconductors.^{7,9,10} However, these models are based on ideal structure materials having high crystallinity and homogeneity. Therefore, the exact application and analysis using above mentioned model are necessary for more investigation on the homogeneity of ZnCdO , the relationship between optical properties and the crystallinity of ZnCdO , and the relationship between Stokes' shift and crystallinity degradation.

In summary, *II-VI* semiconductor alloying $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ thin films ($0.003 \leq x \leq 0.03$) were grown by PLD. A systematic increase in emission broadening with decreasing emission peak energy is observed. The investigation on emission and absorption spectra of $\text{Zn}_{1-x}\text{Cd}_x\text{O}$ has enabled the demonstration of a linear dependence of the Stokes' shift on the

emission peak energy, in which the Stokes' shift increases with Cd content caused mainly by the localized states in ZnCdO films.

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