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Localized excitons in cubic $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ lattice matched to GaAs

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Excitonic properties have been studied in cubic $\text{Zn}_{0.42}\text{Cd}_{0.58}\text{S}$ lattice matched to GaAs. At 2 K, the time-integrated photoluminescence spectrum was composed of single emission peaking at 2.863 eV and its LO-phonon replica. The linewidth of the main peak was 18.5 meV, which fairly well agreed with the theoretical value based on the disorder-induced broadening of exciton luminescence in alloys. In order to assess the emission mechanism, the transient luminescence decay was measured at various emission energies. At the high energy tail (2.883 eV), the luminescence showed exponential decay with a time constant of about 72 ps. On the other hand, the decay time increased with decreasing the detected emission energy. It was about 660 ps at the emission peak (2.863 eV). We interpret these features by means of the model of exciton localization.

I. INTRODUCTION

Currently there have been increasing requirements for the development of laser diodes (LD's) covering a shorter-wavelength region, especially for the application of optical data storage. Since the first pulsed operation of blue-green LD's at 77 K in $\text{Zn}_{1-x}\text{Cd}_x\text{Se}/\text{ZnSe}$ separate confinement structure,¹ much effort has been concentrated on the improvement of device performance. Recently, blue LD's (489.9 nm) were achieved at room temperature (RT) under a continuous wave (cw) mode, using $\text{Zn}_{1-x}\text{Mg}_x\text{S}_{1-y}\text{Se}_y$ quaternary alloys as cladding layers.²

Besides the ZnSe-based system mentioned above, another candidate for the short-wavelength optoelectronic devices is the $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ ternary alloys. This is because their band-gap energies can be varied approximately from 2.4 eV to 3.7 eV which correspond to green to ultraviolet. Particularly, cubic $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ epilayers lattice matched to GaAs ($x \sim 0.58$) have been proposed as blue emitters because they possess a wide band gap of about 2.88 eV.^{3,4} It has been shown that the full width at half maximum (FWHM) of the (400) x-ray rocking curve was as small as 70 arcsec for the closely lattice matched epilayers. Such layers exhibited strong blue photoluminescence (PL) even at RT. However, the emission mechanism has not been clarified yet in this ternary alloy system. Our interest is whether or not the model of exciton localization due to alloy disorder, which has been proposed in anion substituted alloys ($\text{CdS}_x\text{Se}_{1-x}$),⁵⁻⁷ can be applicable to cation substituted alloys ($\text{Zn}_{1-x}\text{Cd}_x\text{S}$). In this paper, we studied the dynamical behavior of excitons in $\text{Zn}_{0.42}\text{Cd}_{0.58}\text{S}$ layers by employing time-resolved luminescence spectroscopy.

II. EXPERIMENTAL PROCEDURE

$\text{Zn}_{0.42}\text{Cd}_{0.58}\text{S}$ layers were grown on semi-insulating (100)-oriented GaAs by means of organometallic va-

por phase epitaxy using diethylzinc, dimethylcadmium, and methylmercaptan. The substrate temperature was 420 °C during the growth. The layer thickness was about 0.7 μm . Detailed growth procedure has been reported elsewhere.^{3,4} The PL experiments were performed using a mode-locked titanium sapphire laser and a titanium sapphire regenerative amplifier, both of which were pumped by a cw Ar⁺ laser. The repetition rate and the pulse width of the amplified laser output were 250 kHz and 200 fs, respectively. The second harmonic light of the amplified laser output was used as an excitation source. The time-resolved luminescence was measured by means of a synchroscan streak camera in conjunction with a subtractive-dispersion double monochromator. The instrumental response of this system had an exponential decay-time constant of about 5 ps.

III. RESULTS AND DISCUSSION

Cross-sectional microstructures by transmission electron microscopy (TEM) were observed to assess the crystallinity of a $\text{Zn}_{0.42}\text{Cd}_{0.58}\text{S}$ layer on (100) GaAs. The growth of cubic (zinc blende) structured epilayer was confirmed by an electron diffraction pattern. Figure 1 shows the bright field image taken from [011] direction using a JEOL TEM instrument operated at 400 kV. Although stacking faults across the layer were seen in some area, the interface between $\text{Zn}_{0.42}\text{Cd}_{0.58}\text{S}$ and GaAs was almost coherent and the crystallinity was comparable to that of $\text{ZnS}_{0.07}\text{Se}_{0.93}$ lattice matched to GaAs. The FWHM value of the (400) x-ray rocking curve was as small as 85 arcsec indicating the uniform distribution of composition within the layer.

The effect of disorder on the broadening of exciton linewidth in II-VI wide-band-gap alloys is significant ow-



FIG. 1. Cross-sectional TEM image (bright field) of a $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ with $x = 0.58$ on a GaAs substrate.

ing to their small exciton Bohr radius. The FWHM of an exciton line ($\Delta(x)$) in $A_{1-x}B_x$ alloy due to this effect is given by the following equation:⁸

$$\Delta(x) = 2\sqrt{2 \ln 2} [dE_{\text{ex}}(x)/dx] \sqrt{x(1-x)V_0(x)/V_{\text{ex}}(x)} \quad (1)$$

if a Gaussian line shape is assumed, where $E_{\text{ex}}(x)$ is the exciton transition energy which is dependent on concentration x , $V_0(x)$ is the volume of the elementary cell, and $V_{\text{ex}}(x)$ is that of exciton. Zimmermann⁹ has derived the relevant exciton volume using a statistical theory expressed by

$$V_{\text{ex}}(x) = 8\pi r_B^3(x), \quad (2)$$

where $r_B(x)$ denote the Bohr radius of exciton. The $\Delta(x)$ values have been calculated for common cation alloys of $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ and $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ using r_B values of ZnSe, CdSe, ZnS, and CdS as 3.30 nm, 4.34 nm, 2.16 nm, and 3.00 nm, respectively. For the x dependence of r_B , a linear variation with x has been assumed. As shown in Fig. 2, $\Delta(x)$ values of $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ alloys are approximately two times larger than those of $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ due to their smaller exciton Bohr radius. It is noted that a broadening of 2.5 meV has been found for a ZnS epilayer due to exciton-acoustic-phonon interaction as well as due to strain distributed randomly within the layer. If the same offset value is assumed for the alloy, the FWHM of $\text{Zn}_{0.42}\text{Cd}_{0.58}\text{S}$ is estimated to be 17.4 meV.

The time-integrated PL spectrum taken from the sample at 2 K under weak excitation condition ($0.025 \mu\text{J}/\text{cm}^2$) is shown in Fig. 3. The excitation wavelength was 400 nm, which corresponded to band-to-band excitation. The spectrum is composed of single emission peaking at 2.863 eV (433.0 nm) and its longitudinal-optical (LO) phonon replica. It was reported that two LO modes were observed in cubic $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ by Raman scattering spectroscopy.¹⁰ Since the two modes are relatively close (39.6 meV and 42.4 meV), each peak is not clearly resolved. The FWHM of the main peak is 18.5 meV. This value fairly agrees with the theoretical one obtained by

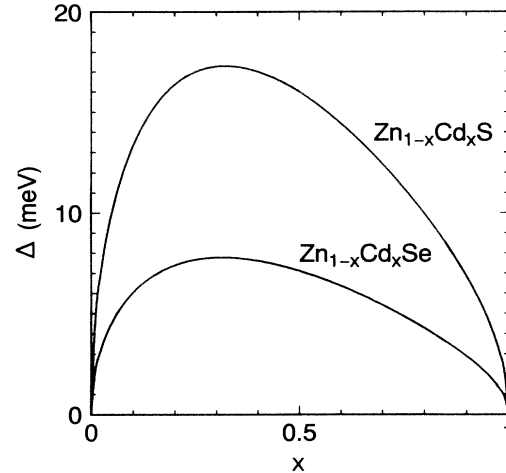


FIG. 2. Theoretical values of disorder-induced broadening of exciton linewidth in $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ and $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ alloys.

the model mentioned above. The transient luminescence decay was measured at various emission energy. At the high energy tail (2.883 eV, 430.0 nm), the luminescence shows an exponential decay with a time constant of about 72 ps. On the other hand, the decay time increases with decreasing the detected emission energy. It is about 660 ps at the emission peak (2.863 eV, 433.0 nm). The data of decay time ($T(E)$) are plotted by the closed circle in Fig. 3.

In order to account for the above results, we consider the model of exciton localization, in which the decay time $T(E)$ as a function of emission energy E is well expressed as follows,

$$T(E)^{-1} = T_r^{-1} \{1 + \exp[(E - E_{\text{me}})/E_0]\}, \quad (3)$$

where E_0 is the characteristic energy for the density of states, T_r is the radiative lifetime, and E_{me} is defined

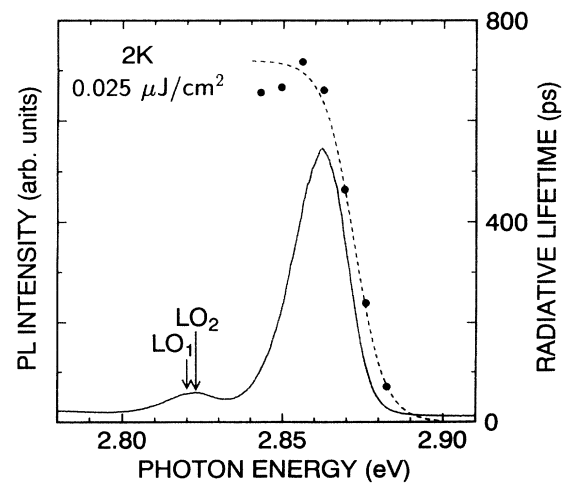


FIG. 3. Time-integrated excitonic PL at 2 K under an excitation energy density of $0.025 \mu\text{J}/\text{cm}^2$. The LO_1 - and LO_2 -phonon sidebands are indicated by arrows. Radiative lifetimes observed at various emission energies are also shown by closed circles. The dashed curve is the theoretical one which is obtained by the model described in the text.

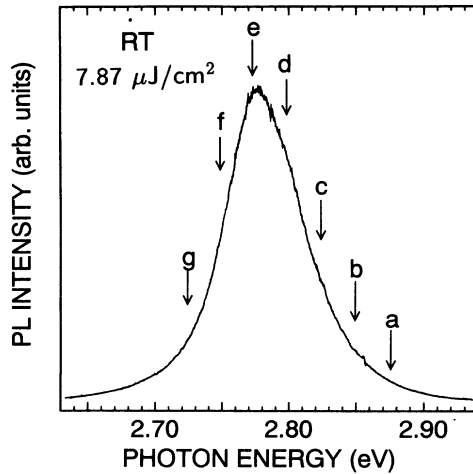


FIG. 4. Time-integrated excitonic PL at RT under an excitation energy density of $7.87 \mu\text{J}/\text{cm}^2$.

by some definite energy for which the decay time equals the transfer one.¹¹ It is reported that E_{me} plays a role analogous to a mobility edge although its value does not indicate the precise energy position between extended states and unmobile localized states.¹² This model leads to a density of tail states of the form of $\exp[-(E/E_0)]$. The best fit is obtained using the following parameters: $E_0=4.8$ meV, $T_r=720$ ps, and $E_{me}=2.8722$ eV and indicated by the dashed line in Fig. 3. It is generally recognized that the effect of exciton localization on anion substituted alloys is much larger than that on cation substituted alloys. This is because the effective mass of holes is much larger than that of electrons.⁶ However, the E_0 value in $\text{Zn}_{0.42}\text{Cd}_{0.58}\text{S}$ is 4.8 meV, which is more than two times larger than the reported one (2.2 meV) in $\text{CdS}_{0.36}\text{Se}_{0.64}$.¹¹ This is probably due to the smaller Bohr radius of excitons in $\text{Zn}_{0.42}\text{Cd}_{0.58}\text{S}$ (2.65 nm) than that in $\text{CdS}_{0.36}\text{Se}_{0.64}$ (3.86 nm).

The temperature dependence of the PL peak was found to be anomalous between 2 K and about 120 K. From 2 K to 45 K, the peak gradually shifted toward lower energy side (redshift) by about 3 meV. Above 45 K, it conversely shifted towards higher energy side (blueshift). The net blueshift from 45 K to 110 K was about 4 meV. These features can be understood that the excitons localized by alloy disorder are delocalized by the thermal energy. Above 120 K, the peak changed to the redshift again. The shift above 200 K was well fitted by Varshni's formula.¹³ Therefore, it is expected that the PL at RT mainly originates from nearly delocalized free excitons. Figure 4 shows the time-integrated PL at RT. The emission is located at 2.777 eV (446.3 nm). Owing to the exciton-LO-phonon interaction, the spectrum is homogeneously

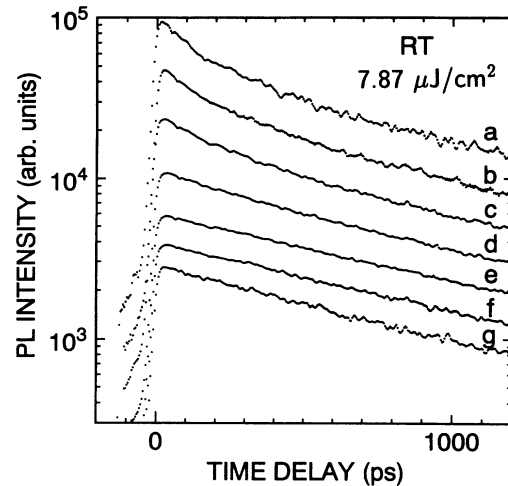


FIG. 5. Photoluminescence time decay at RT under an excitation energy density of $7.87 \mu\text{J}/\text{cm}^2$. Observation energies are at (a) 2.876 eV, (b) 2.849 eV, (c) 2.823 eV, (d) 2.798 eV, (e) 2.773 eV, (f) 2.748 eV, and (g) 2.724 eV.

broadened to about 65 meV. The time-resolved PL observed at various emission energies of (a)–(g) is shown in Fig. 5. The emission at the high energy tail (2.876 eV, 431.0 nm) shows a double-exponential decay whose time constants are estimated to be about 150 ps and 1050 ps. The fast decay component becomes less dominant with decreasing emission energy and disappears below about 2.798 eV (443.0 nm). The time constant of the slow decay component does not show the emission energy dependence. It is suggested that the fast component shows the radiative lifetime of free-carrier recombination and that the slow one corresponds to that of nearly delocalized excitons.

IV. CONCLUSIONS

Photoluminescence properties have been studied in cubic $\text{Zn}_{0.42}\text{Cd}_{0.58}\text{S}$ lattice matched to GaAs. The feature was interpreted by the model of exciton localization using the fitting parameters: $E_0=4.8$ meV, $T_r=720$ ps, and $E_{me}=2.8722$ eV at 2 K, and by the delocalized excitons homogeneously broadened by the LO-phonon scattering at RT.

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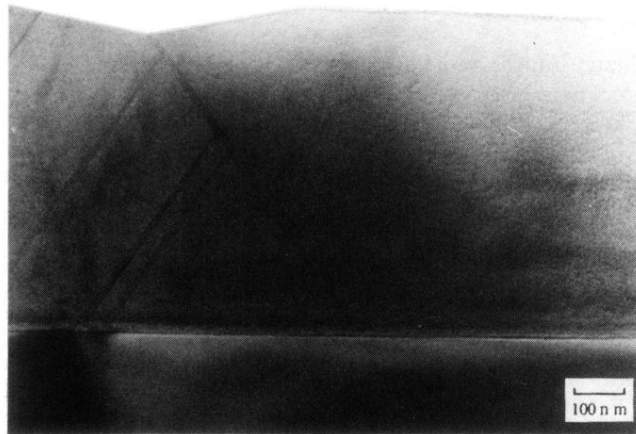


FIG. 1. Cross-sectional TEM image (bright field) of a $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ with $x = 0.58$ on a GaAs substrate.