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

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Excitonic properties have been studied in cubic Zn$_{0.42}$Cd$_{0.58}$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 Zn$_{1-x}$Cd$_x$Se/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 Zn$_{1-x}$Mg$_x$S$_{1-p}$Se$_p$ quaternary alloys as cladding layers.2

Besides the ZnSe-based system mentioned above, another candidate for the short-wavelength optoelectronic devices is the Zn$_{1-x}$Cd$_x$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 Zn$_{1-x}$Cd$_x$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 (CdS$_{2y}$Se$_{1-x}$),5–7 can be applicable to cation substituted alloys (Zn$_{1-x}$Cd$_x$S). In this paper, we studied the dynamical behavior of excitons in Zn$_{0.42}$Cd$_{0.58}$S layers by employing time-resolved luminescence spectroscopy.

II. EXPERIMENTAL PROCEDURE

Zn$_{0.42}$Cd$_{0.58}$S layers were grown on semi-insulating (100)-oriented GaAs by means of organometallic va-
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: \(^8\)

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

(1)

if a Gaussian line shape is assumed, where $E_{ex}(x)$ is the exciton transition energy which is dependent on concentration $x$, $V_0(x)$ is the volume of the elementary cell, and $V_{ex}(x)$ is that of exciton. Zimmermann\(^9\) has derived the relevant exciton volume using a statistical theory expressed by

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

(2)

where $r_B(x)$ denote the Bohr radius of exciton. The $\Delta(x)$ values have been calculated for common cation alloys of Zn$_{1-x}$Cd$_x$Se and Zn$_{1-x}$Cd$_x$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 Zn$_{1-x}$Cd$_x$S alloys are approximately two times larger than those of Zn$_{1-x}$Cd$_x$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 Zn$_{0.42}$Cd$_{0.58}$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 $\mu$J/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 Zn$_{1-x}$Cd$_x$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 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,

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

(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 $\mu$J/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.
by some definite energy for which the decay time equals the transfer one.\textsuperscript{11} It is reported that $E_{\text{me}}$ 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.\textsuperscript{12} This model leads to a density of tail states of the form of exp\{$-\rho(E/E_0)$\}.

The best fit is obtained using the following parameters: $E_0=4.8$ meV, $T_r=720$ ps, and $E_{\text{me}}=2.8722$ 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.\textsuperscript{6} However, the $E_0$ value in Zn$_{0.42}$Cd$_{0.58}$S is 4.8 meV, which is more than two times larger than the reported one (2.2 meV) in CdS$_{0.36}$Se$_{0.64}$.\textsuperscript{11} This is probably due to the smaller Bohr radius of excitons in Zn$_{0.42}$Cd$_{0.58}$S (2.65 nm) than that in CdS$_{0.36}$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 2K 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.\textsuperscript{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 broadened to about 65 meV. The time-resolved PL observed at various emission energies of (a)–(g) is shown on 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.

\textbf{IV. CONCLUSIONS}

Photoluminescence properties have been studied in cubic Zn$_{0.42}$Cd$_{0.58}$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 $E_{\text{me}}=2.8722$ eV at 2 K, and by the delocalized excitons homogeneously broadened by the LO-phonon scattering at RT.

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13 Y. P. Varshini, Physica 34, 149 (1967).
FIG. 1. Cross-sectional TEM image (bright field) of a Zn$_{1-x}$Cd$_x$S with $x = 0.58$ on a GaAs substrate.