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# Time-space-resolved photoluminescence from (Zn,Cd)Se-based quantum structures

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## Abstract

Spectroscopic technique which possesses both temporal and spacial resolution was developed by combining the pico-second pulsed laser system with the optical microscope. By using this technique, the time-resolved photoluminescence (TRPL) with micron spatial resolution was performed for the self-organized CdSe/ZnSe quantum dots (QDs) fabricated on GaAs(110) crystal surfaces. PL spectra of CdSe/ZnSe with 10 monolayer (ML) deposition thickness were composed of two emission bands peaking at 2.6 and 2.2 eV. These bands could be ascribed to the emissions from CdSe quantum wells (QWs) acting as wetting layers and QDs, respectively. With macroscopic excitation (spot size: 100 μm), temporal behavior of the emission band of QDs was characterized by multi-exponential decay. However, with microscopic excitation (spot size: 5 μm), it was found that both spectrum shapes and PL lifetimes have changed with sweeping the location of focus. Especially, the lifetimes were quite valuable and were well fitted by the single exponential decay. These results suggest that the radiative lifetime differs very much depending on the degree of exciton localization. © 2000 Published by Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Optical properties and functions of semiconductor materials are controlled by the recombination processes of excitons created by photoexcitation or electron injection. Until now, many attempts have been made to confine excitons in low-dimensional

nanostructures. Especially, quantum dot (QD) structures are expected to be effective for the achievement of the laser diode (LD) with low threshold and of the light emitting diode (LED) with high efficiency. For InAs/GaAs [1] or Ge/Si [2] materials, the self-organization method of QDs with Stranski–Krastanov (SK) mode has been well established by MBE and MOCVD. In contrast, QD structures of the wide band gap II–VI semiconductor have not so far been established in spite of the large efforts during the last few years. In order to explore the emission mechanism from QDs in II–VI materials, CdSe/ZnSe systems were often

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studied because the lattice mismatch is similar to that of the well-established InAs/GaAs systems, and also because these materials are promising for the photonics device operating at blue–green spectral region. Xin and co-workers reported for the first time that the CdSe QDs were formed if CdSe was deposited with 3 monolayer (ML) thickness on ZnSe(100), and that the broad photoluminescence (PL) peak at 2.3 eV was attributed to the recombination at QDs [3]. Since the nucleation mode is changed according to the surface condition of ZnSe, CdSe/ZnSe layers have been fabricated on substrates with different orientations. For example, Ko et al. grew CdSe/ZnSe on GaAs(011) substrates [4] and the growth of the CdSe/ZnSe on GaAs(111) [5] and the CdSe/ZnSe on CdS(0001) [6] were also reported.

The PL spectroscopy has usually been used to observe the emission from excitons localized at QDs. In many cases, spectra from QDs are inhomogeneously broadened due to random distribution of size, shape and depth of QDs [7–9]. Therefore, it is very complex and difficult to elucidate the emission dynamics of excitons in QDs whose nature may differ depending on the confinement conditions of QDs [10]. Consequently, it is desired to develop the spectroscopy possessing both spatial and temporal resolution. In this paper, we describe the system of time–space-resolved laser spectroscopy, and then assess how PL spectra and lifetimes from CdSe QDs change with the location of microscopic-excitation spot.

## 2. Experimental procedure

The self-organized CdSe/ZnSe QDs structures used in this study have been fabricated on GaAs(110) crystal surfaces obtained by cleaving GaAs wafers in ultrahigh vacuum by molecular beam epitaxy (MBE). The detailed growth condition has been described in Ref. [4]. We used the same samples as reported in Refs. [4,11], where 1, 2, 4, and 10 MLs of CdSe active layers were sandwiched between ZnSe cladding layers (100 and 50 nm in thickness of upper and lower layer, respectively). QD structures of CdSe were organized by Stranski–Krastanow growth mode, which was

monitored with the observation of in situ reflection high-energy electron diffraction (RHEED). Island structures with base diameters of 47 nm and height of 10 nm were observed on average by the atomic force microscope (AFM) image after deposition of CdSe with a 10 ML thickness without the upper cladding layers. The density of CdSe QDs were estimated to be  $1.7 \times 10^9 \text{ cm}^{-2}$ , which is much smaller than that of GaAs-based QDs.

The experimental setup of the time–space-resolved spectroscopy is schematically shown in Fig. 1 [12]. This system consists of three components: the ultrafast pulsed laser, the optical microscope and the detection apparatus. In the laser unit, the frequency-doubled beam of mode-locked  $\text{Al}_2\text{O}_3:\text{Ti}$  laser pumped by a cw  $\text{Ar}^+$  laser was used for excitation. Pulse width, wavelength, and repetition rate were 1.5 ps, 400 nm, and 80.00000 MHz, respectively. This pulsed laser was expanded by the beam expander and focused to 5  $\mu\text{m}$  diameter by the objective lens ( $\times 5$ ) on the samples. The emission images were observed by the microscope and detected by the color CCD camera with 2000000 pixels. At the same time, time-resolved photoluminescence (TRPL) spectra were measured by synchroscan streak camera in conjunction with monochromator (25 cm, 150 lines/mm grating). The temperatures of the samples were controlled at 77 K by the flow of liquid nitrogen. The space resolution along the  $X$ – $Y$  direction was achieved by the moving micro-stage. By using this method, we measured the dynamical behavior of recombination processes of CdSe/ZnSe structures.

## 3. Results and discussion

Fluorescent micro-image for each sample was observed at 77 K by the mercury lamp excitation in the optical microscope/CCD camera system. As can be seen in Fig. 2, emission color changed from blue to yellow (red shift) with increasing the number of CdSe MLs. As for CdSe/ZnSe samples with 1 ML [Fig. 2(a)] and 2 ML [Fig. 2(b)], the color image is substantially uniform except dark lines. These lines correspond to the ridge structures observed by AFM. It is probable that these structures act as nonradiative recombination centers because

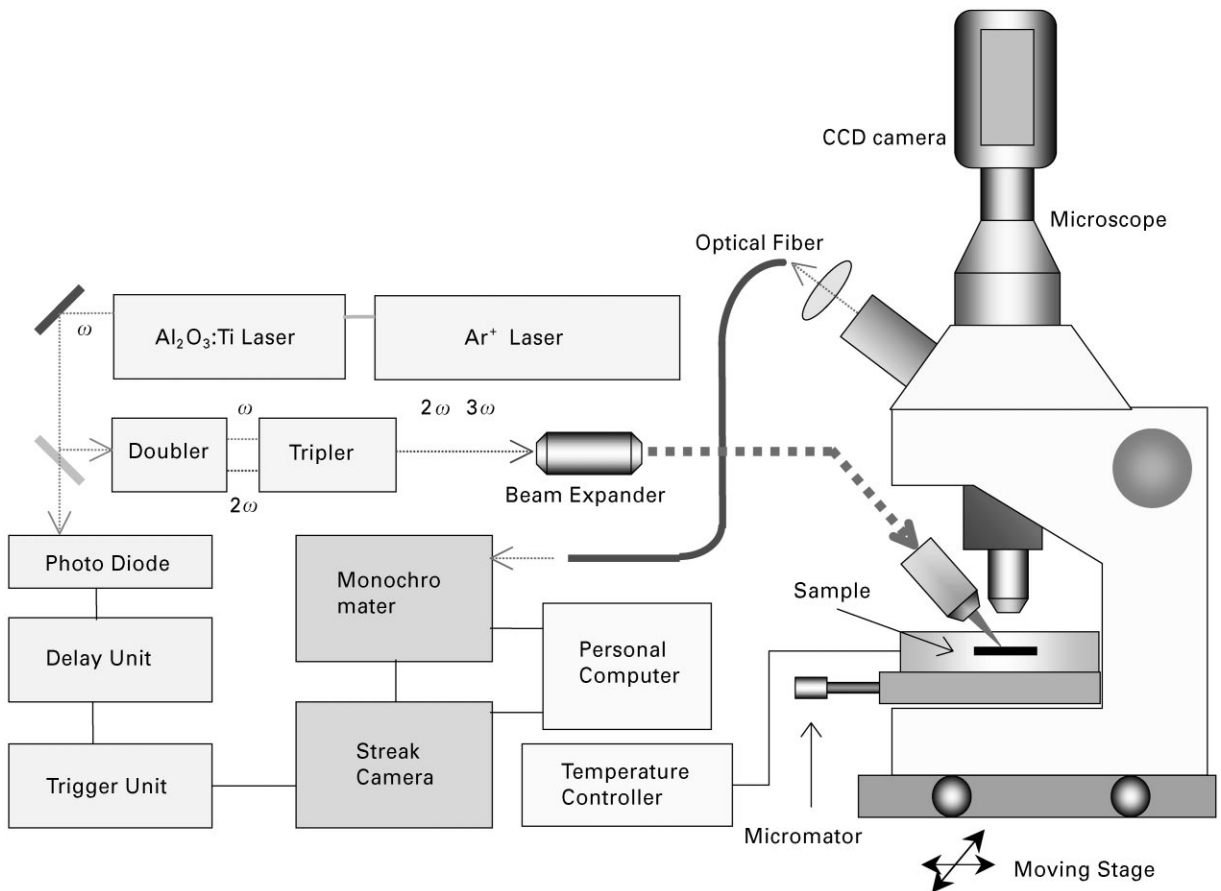


Fig. 1. Experimental setup of the time-space-resolved laser spectroscopy which is composed of the ultra short-pulsed laser, the optical microscope and the synchroscan streak camera.

transmission electron microscopy (TEM) reveals the association of misfit-dislocation at the ridge structures. On the contrary, dot-like emissions, whose observed size is limited by the spatial resolution (about  $0.6\ \mu\text{m}$ ), are observed for samples with 4 ML [Fig. 2(c)] and 10 ML [Fig. 2(d)]. As discussed later, these emissions are originating from the radiative recombination of excitons confined in self-formed CdSe QDs.

Fig. 3 shows cw-PL spectra at 77 K taken at each sample by using the He–Cd laser ( $3\ \text{mW}/\text{cm}^2$ ) excitation. The calculated transition energies of CdSe/ZnSe single quantum wells (QWs) with 1–3 MLs of active layer thickness were estimated to be 2.67, 2.61 and 2.5 eV, respectively [4]. Therefore,

the main PL peak at 2.7 eV and small sub-peak at 2.6 eV observed at the CdSe(1 ML)/ZnSe sample [Fig. 3(a)] are attributed to the emissions from QWs with 1 and 2 ML thickness, respectively. In the case of the CdSe(2 ML)/ZnSe sample, the broad peak around 2.52 eV was observed in Fig. 3(b), indicating that the emission is originating from two different CdSe QWs whose thicknesses are 2 and 3 ML, respectively. The in situ RHEED observation revealed that the three-dimensional nucleation of CdSe takes place when the nominal deposition exceeds 3 ML. In such samples, broad PL bands at the vicinity of 2.2 eV were observed besides emissions originating from CdSe QWs with 1–3 MLs thickness as shown in Fig. 3(c) [CdSe(4 ML)/ZnSe]

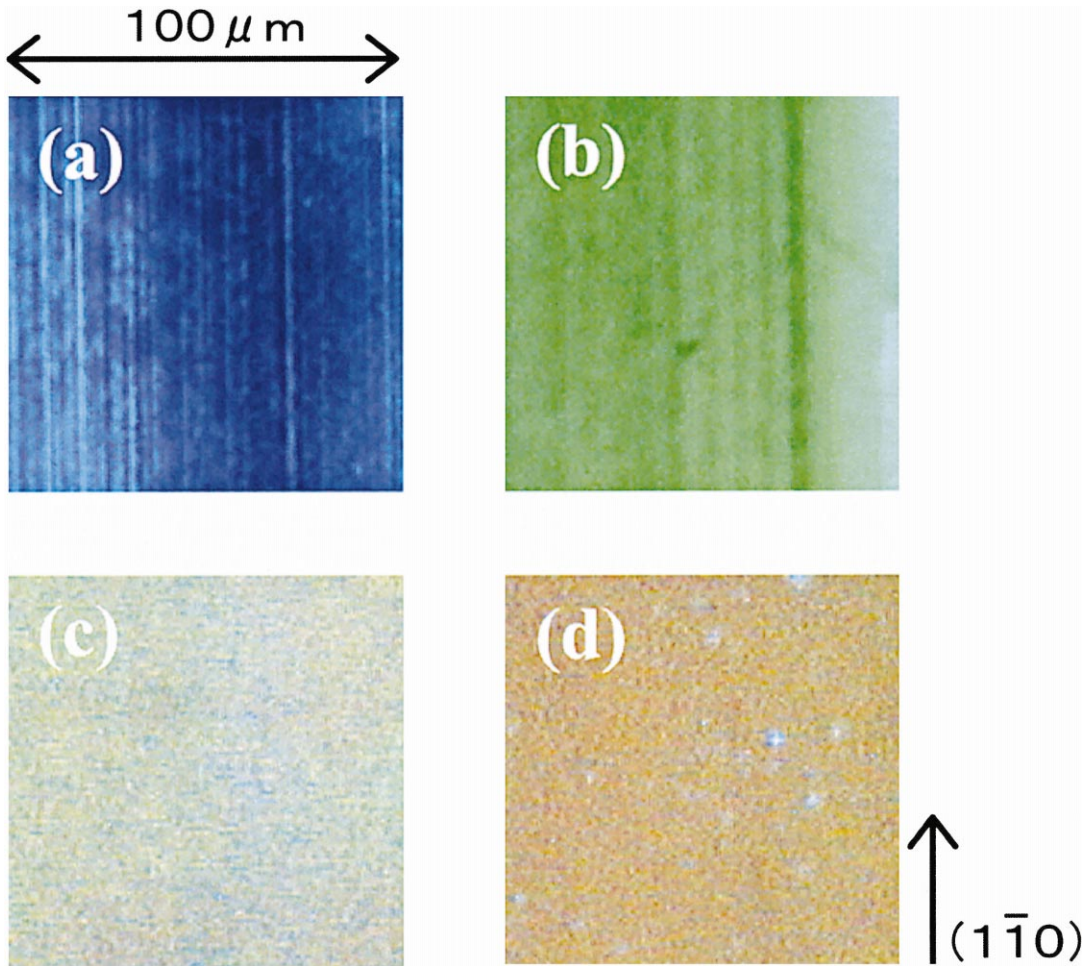


Fig. 2. The microscopic PL image by using a mercury lamp and a high-resolution color CCD camera (up) and the cw-PL spectra by using the He-Cd laser and multi-channel photo-detector (down) at 77 K taken at CdSe/ZnSe on GaAs(110) with (a) 1 ML, (b) 2 ML, (c) 4 ML and (d) 10 ML CdSe-deposition thickness.

and Fig. 3(d) [CdSe(10 ML)/ZnSe]. These bands were ascribed to the emission from exciton localized at QDs. It was also found that the broadness of PL bands is due to the inhomogeneous effect as a result of size-distribution of QDs because the microscopic-cw-PL spectroscopy has shown that the bands are composed of a number of spike-like peaks [13]. Actually, yellowish spots (emission from QDs) are randomly distributed within green background (emission from QWs) as can be seen in Figs. 2(c) and (d).

In order to assess the detailed recombination dynamics, TRPL spectroscopy was performed with both macroscopic and microscopic configurations. As for 1 and 2 ML samples, the temporal behavior of PL emissions from CdSe QWs could be fitted with single exponential decay in the case of macroscopic excitation [spot size ( $\phi_{\text{ex}}$ ) = 100 μm, excitation energy density ( $I_{\text{ex}}$ ) = 7 μJ/cm<sup>2</sup>]. In these samples, time profile taken under the microscopic excitation ( $\phi_{\text{ex}}$  = 5 μm,  $I_{\text{ex}}$  = 7 μJ/cm<sup>2</sup>) was almost same as that under macroscopic excitation.

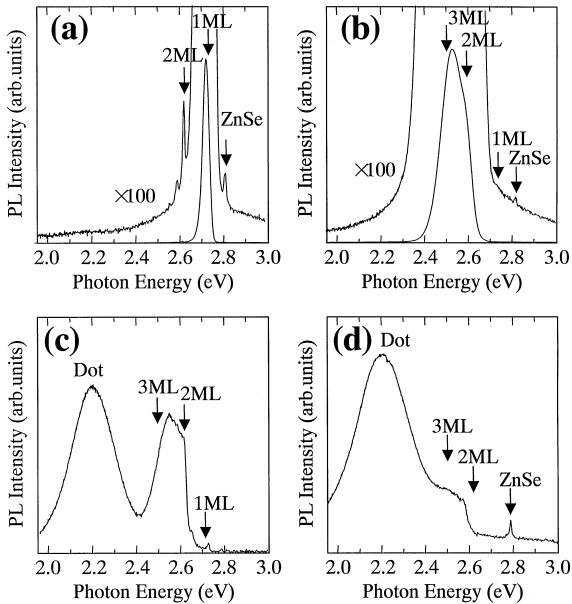


Fig. 3. The cw-PL spectra by using the He–Cd laser and multi-channel photo detector at 77 K taken at CdSe/ZnSe on GaAs (110) with (a) 1 ML, (b) 2 ML, (c) 4 ML, and (d) 10 ML CdSe-deposition thickness.

Moreover, spectral feature of PL, as well as time profile did not depend on the location of excitation focus spot. Only the PL peaks were slightly shifted with location suggesting that the strain field is distributed gradually within the epilayers. Detailed result and discussion will be described in Ref. [14]. On the other hand, remarkable difference of both PL and decay spectra was observed between macroscopic and microscopic excitation conditions for 4 and 10 ML samples.

Fig. 4 shows the PL spectra of the CdSe 10 ML sample at 77 K which are time-integrated between  $t = 0$  and 1.5 ns after the pulsed excitation, where Fig. 4(a) is the spectrum with macroscopic excitation, Figs. 4(b)–(d) are the spectra with microscopic excitation ( $\phi_{\text{ex}} = 5 \mu\text{m}$ ,  $I_{\text{ex}} = 7 \mu\text{J}/\text{cm}^2$ ) taken at dark yellow, bright yellow and bright green regions, respectively. The dark yellow region is widely distributed within the layer, while the bright yellow and bright green regions look like spots whose diameter is comparable to the focus size. At the

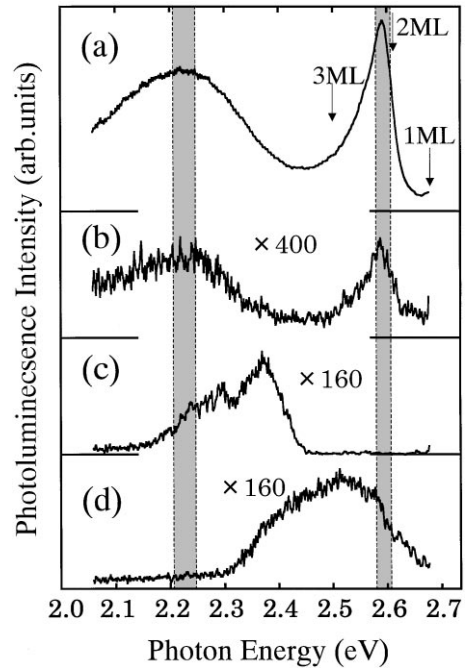


Fig. 4. Time-integrated PL spectra between  $t = 0$  and 1.5 ns after pulsed photo-excitation taken at CdSe(10 ML)/ZnSe on GaAs(110) at 77 K with (a) macroscopic excitation ( $\phi_{\text{ex}} = 100 \mu\text{m}$ ,  $I_{\text{ex}} = 7 \mu\text{J}/\text{cm}^2$ ) and microscopic excitation ( $\phi_{\text{ex}} = 5 \mu\text{m}$ ,  $I_{\text{ex}} = 7 \mu\text{J}/\text{cm}^2$ ) at the (b) dark yellow region, (c) bright yellow point, and (d) bright green point. Spectral windows used for plotting decay profiles (Figs. 5 and 6) are also shown by dotted lines.

dark yellow region [Fig. 4(b)], the spectral shape was similar to that taken under macroscopic excitation [Fig. 4(a)]. However, the feature was significantly changed for the spectra taken at bright yellow and bright green spots. As for the spectrum at the bright yellow spot [Fig. 4(c)], the emission component from QDs was enhanced and that from QWs with 2 ML was reduced in intensity. On the other hand, at the bright green spot [Fig. 4(d)], the component from QWs with 3 ML dominated the spectrum compared to that from QDs. As can be seen in Fig. 4(c), spike-like spectral feature from QDs is substantially observed compared with noise level, suggesting that the band is composed of emissions from individual QDs.

The time profiles of the emission from QWs and QDs are shown in Figs. 5 and 6, respectively. The

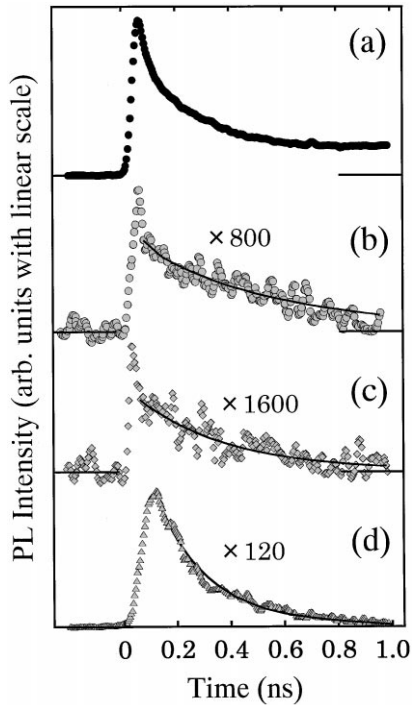


Fig. 5. Decay profiles of PL spectra of emission from QWs (at 2.6 eV) taken at CdSe(10 ML)/ZnSe on GaAs(1 1 0) at 77 K with (a) macroscopic excitation, and microscopic excitation at the (b) dark yellow region, (c) bright yellow point, and (d) bright green point. Solid curves are theoretical ones fitted with single exponential decay whose lifetimes for (b)–(d) are 538, 329 and 194 ps, respectively.

emission intensity from QWs is monitored at 2.6 eV with a collection window ( $\Delta E$ ) of 40 meV, while that from QDs is at 2.2 eV with  $\Delta E = 27$  meV. In each figure, decay profiles labeled (a)–(d) are measured with same conditions as in Fig. 4, namely (a) is taken under macroscopic excitation, while (b)–(d) are under microscopic excitation at positions of dark yellow region, bright yellow spot and bright green spot, respectively. As shown in Fig. 5(a), if the intensity is monitored with macroscopic excitation the decay profile of the emission from QWs is expressed with multi-exponential curve. However, decay profiles taken under microscopic excitation were well-fitted with double exponential curve for Figs. 5(b) and (c), and with single exponential one for Fig. 5(d). Although it is difficult to estimate the exact value of fast decay component in Figs. 5(b)

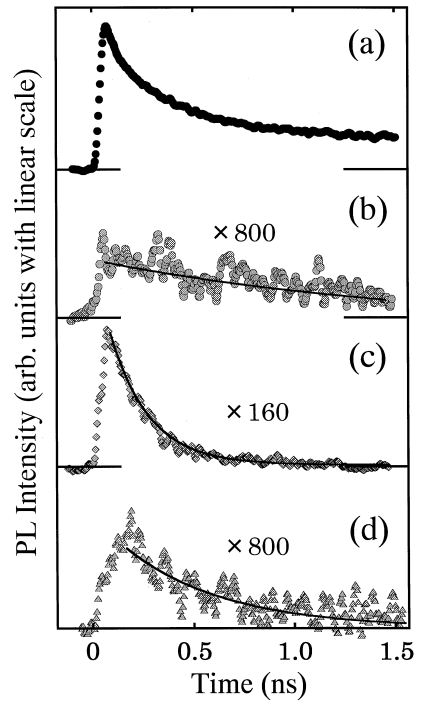


Fig. 6. Time profile of PL spectra from QDs (at 2.2 eV) taken at CdSe(10 ML)/ZnSe on GaAs(1 1 0) at 77 K with (a) macroscopic excitation and microscopic excitation at the (b) dark yellow region, (c) bright yellow point, and (d) bright green point. Solid curves are theoretical ones fitted with single exponential decay whose lifetimes for (b)–(d) are 1.6 ns, 193 ps and 706 ps, respectively.

and (c) due to the limitation from signal to noise ratio, the decay time is probably less than 20 ps. The slow decay components for Figs. 5(b) and (c), and the decay time for Fig. 5(d) are estimated to be  $538 \pm 20$ ,  $329 \pm 29$  and  $194 \pm 3$  ps, respectively. In general, the decay time of PL ( $\tau_{\text{PL}}$ ) is given by the following equation:

$$\frac{1}{\tau_{\text{PL}}} = \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{nonrad}}} + \frac{1}{\tau_{\text{trans}}}, \quad (1)$$

where  $\tau_{\text{rad}}$ ,  $\tau_{\text{nonrad}}$  and  $\tau_{\text{trans}}$  denote lifetimes representing radiative, nonradiative and transfer processes, respectively. Assuming that the nonradiative recombination channel can be omitted at this temperature (77 K), the fast decay components for (b) and (c) can be attributed to the transfer process of

excitons towards localized QD centers. It is probable that this transfer process is easily saturated because of two reasons: (i) the transfer of excitons takes place effectively without the phonon-bottleneck effect and (ii) the number of localized centers is limited. These models are also supported by the fact that almost no fast decay component is observed in (d), where the emission from QDs is suppressed at this monitoring position.

Multi-exponential decay is also observed in the decay profile of the emission from QDs [Fig. 6(a)] if the signal was monitored under macroscopic condition. On the other hand, microscopic decay profiles are in accordance with single exponential curves as shown in Figs. 6(b)–(d), whose lifetimes are  $1.6 \pm 0.6$  ns,  $193 \pm 2$  ps and  $706 \pm 34$  ps, respectively. Accordingly, it is found that PL lifetimes of the emission from QDs strongly depend on the location of the micro-focus. Three models can be applied to account for these phenomena, where (i) PL lifetimes are limited by the nonradiative processes, (ii) radiative lifetimes are changed drastically with the dimensionality of QD-centers [15] and (iii) the situation is the combined effect between (i) and (ii) models. It is therefore necessary for a detailed discussion to evaluate the internal quantum efficiency of emission bands by employing temperature dependence of TRPL measurements which are currently under progress. Nevertheless, such an approach has obviously to be performed with microscopic spectroscopy.

#### 4. Conclusion

Recombination mechanism has been assessed for CdSe/ZnSe layers grown on in situ cleaved GaAs(110) by MBE. TRPL spectroscopy was employed at the CdSe(10 ML)/ZnSe sample for emission bands from either QWs (CdSe wetting layers) or QDs (self-formed CdSe QDs) under macroscopic and microscopic excitation. It was found that excitons photo-generated at QWs are effectively transferred to QDs though the number of transfer channels strongly depends on the number of QDs

in the vicinity of microscopic-focus, and that PL lifetimes of emissions from QDs ranged from 193 ps to 1.6 ns at 77 K.

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