Cathodoluminescence and photoluminescence decay behaviors of CdSe dots embedded in ZnSe

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Abstract

We have investigated cathodoluminescence (CL) and decay dynamics of photoexcited states in CdSe/ZnSe single-fractional monolayer structures grown by molecular beam epitaxy on a GaAs(001) substrate. CL spectra measured at 10 K by scanning the focused electron beam with a diameter of 200 nm show sharp peak structures superimposed on a broad spectrum. The observed spectra are ascribed to exciton luminescence from individual CdSe-based dots in two different lateral size ranges: large dots (15–40 nm) and small ones (6–10 nm). Decay behaviors of photoluminescence measured in the picosecond time region have been interpreted in terms of exciton migration in the nanostructures. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Low-dimensional heterostructures of II–VI semiconductors have considerable current interest from the point of view of nanostructure physics and technological applications. Studies on growth and characterization of CdSe quantum dots (QDs) on ZnSe surfaces have been reported by several groups. However, conclusions about structure, morphology, size and composition are rather diverging [1–6]. Although one can expect a Stranski–Krastanov-type process for CdSe QD formation similarly to the case of InAs/GaAs, a larger ionicity and a weaker surface diffusion make a formation process complicated. Micro- and nano-probe spectroscopies are a powerful tool to investigate electronic states associated with quantum size effects in nanostructures with a large inhomogeneity in morphologies. A cathodoluminescence experiment combined with scanning electron microscope enables us to investigate both structure and electronic states on a scale of hundreds nanometer.

In this paper we report on cathodoluminescence (CL) and decay dynamics of photoexcited states in CdSe/ZnSe single-fractional monolayer (FM) structures grown by molecular beam epitaxy (MBE) on a GaAs(001) substrate. CL spectra showing sharp peak structures superimposed on a broad spectrum have been analyzed taking into account three-dimensional exciton confinement effects and compositional alloying. Decay behaviors of photoluminescence measured in the picosecond time region have been interpreted in terms of exciton migration in the nanostructure.

2. Experiments

CdSe single layers were deposited on a 50 nm ZnSe layer by using conventional MBE at 280°C and then capped with a 10 nm ZnSe layer [5]. The nominal
thickness of the CdSe layer was in the range of 1.5–3.2 monolayer (ML). The typical diameter and the density of CdSe-enriched dots spontaneously formed within the layer are 15–40 nm and \( \sim 2 \times 10^{10} \text{ cm}^{-2} \), respectively, for the sample with the 2.8 ML thickness, as measured by transmission electron microscopy (TEM) [7]. The CL system consists of a modified commercial scanning electron microscope including a continuous flow He cryostat. For the acceleration voltage of 5 kV an electron beam diameter is about 200 nm which provides a spatial resolution of about 500 nm taking into account carrier diffusion. Spectra were detected by a cooled CCD camera. We used a time-correlated photon counting method and second harmonic light of a mode-locked Ti:sapphire laser to measure photoluminescence decay behaviors with a time resolution of \( \sim 10 \text{ ps} \).

3. Results and discussion

Fig. 1 shows CL spectra measured at 10 K for a CdSe/ZnSe single fractional monolayer (FM) structure with a nominal CdSe layer thickness of 2.8 ML. The acceleration voltage and the current are 5 kV and 0.6 nA, respectively. The spectra (a)–(c) measured by scanning the focused electron beam with a diameter of 200 nm exhibit sharp peaks superimposed on the broad spectrum, and the spectral feature depends upon the region on the sample surface under investigation. The spectral width of sharp spikes is limited by a spectral resolution of 1 meV. The similar spectral features are observed for CdSe/ZnSe FM structures with nominal thicknesses of 1.5 and 3.2 ML. As shown in the inset of Fig. 2 the photoluminescence spectrum measured by the spot illumination with a diameter of about 2 \( \mu \text{m} \) has no sharp peak structure. The broad luminescence band is centered at around 2.493 eV and the width is \( \sim 38 \text{ meV} \). These results suggest that the CL spectrum consists of luminescence lines from small numbers of CdSe dots or nanostructures [8].

Here, we make a simulation of a CL spectrum assuming that the Gaussian spectrum consists of sharp luminescence lines due to excitons confined in individual CdSe dots. We take the spectral width of the sharp peak as 1 meV, and the peak energy and the width of the distribution are 2.485 and 45 meV, respectively. We show in Fig. 1(d)–(f) the simulated spectra for different dot numbers. When the dot number \( N \) is \( 1 \times 10^2 \), we see many sharp peaks which are well resolved. As the dot number increases, sharp spike structures are less resolved and the spikes are unresolved for \( N = 3 \times 10^4 \). Comparing the simulated spectrum to the observed one, the spectrum for \( N = 1 \times 10^4 \) reproduces well the experiment. Using the dot number and the spatial resolution, we estimate the dot density as \( \sim 5 \times 10^{13} \text{ cm}^{-2} \). This density is much larger than the density \( \sim 2 \times 10^{10} \text{ cm}^{-2} \) of dots visible by TEM (15–40 nm), which suggests an existence of QDs smaller than 15 nm.

We calculate optical transition energies of CdSe QDs using a quantum disk model with a finite barrier potential to discuss dot structures from the energetics. We used the effective masses of electrons and holes as 0.13\( m_0 \) and...
0.45m₀, respectively [9]. The band gaps of CdSe with a zincblende structure and ZnSe are 1.765 and 2.821 eV, respectively, and the conduction- and valence-band discontinuities are 0.826 and 0.23 eV, respectively [10]. The calculated energy for QDs with a thickness of 3 ML and a diameter of 15–40 nm for the 2.8 ML sample ranges from 2.506 to 2.535 eV. If we take into account a strain effect due to the lattice mismatch, the transition energy is increased by ~12 meV. As shown by the horizontal bar at the bottom of Fig. 1 the energy range corresponds to the higher-energy side of the CL spectrum. To reproduce the observed spectrum we have to consider QDs with a diameter smaller than 15 nm; the QDs with a thickness of 4 ML and a diameter of 6–10 nm can generate luminescence in the range corresponding to the observed spectrum. A separated study on the cross-sectional structure of the CdSe layer embedded in ZnSe layers by transmission electron microscopy has revealed the co-existence of small QDs (<10 nm) and large QDs (15–40 nm) [11]. The similar structural result has been recently reported by Kirmse et al. [6].

Here, we discuss a possibility of compositional alloying of a CdSe layer. If we take a Cd composition ratio of 0.77, CdSe-based dots with a thickness of 4 ML and a diameter of 15–40 nm give rise to a spectrum corresponding to the observed peak range, and the observed range is covered by luminescence from QDs with a thickness of 5 ML and a diameter of 6–15 nm. For the samples with nominal thicknesses smaller than 2.8 ML, we can reproduce the observed spectral range only when we take account of the alloying effect. A more definite conclusion about the alloying effect should be done on the basis of detailed analysis of the CL spectra as well as structural and chemical analysis data.

To investigate dynamical properties of CdSe-based QDs we measured decay behaviors of photoluminescence. Fig. 2 shows decay curves measured at 4.2 K for various photon energies which are indicated by the allows in the inset. The decay becomes faster with increasing photon energy, and the slow component appears for the photon energy of 2.531 eV. The decay time obtained by fitting to the single-exponential decay curve is 380 ps for 2.471 eV, while it is as short as 50 ps for 2.531 eV. It is shown in the inset of Fig. 2 together with the PL spectrum, the decay time drastically changes with the photon energy within the spectrum. Such a behavior might suggest a quantum size effect on the radiative recombination rate. However, we measured decay times for other samples with slightly different nominal thicknesses, and found that the decay curves measured at the same photon energy for different samples yield different decay times. Since there is a correspondence between the photon energy and the dot size in the QD model neglecting the alloying effect, the radiative lifetime corresponding to the size should be the same. Therefore, the observed luminescence decay is mainly determined by non-radiative recombination processes such as exciton migration between dots or between the dot and barrier layer.

4. Summary

We have investigated cathodoluminescence and decay behaviors of photoluminescence in a CdSe/ZnSe single-fractional monolayer structure with a nominal thickness of 1.5–3.2 ML. The CL spectrum measured by the focused electron beam has been well reproduced by the spectrum simulation assuming that the sharp peaks are due to individual QDs in the CdSe layer sandwiched between ZnSe layers. From these results and the calculated luminescence energies, we have found that there exist two classes of QDs: large dots (15–40 nm) and small dots (6–10 nm). The results obtained for the samples with smaller nominal thicknesses suggest a possibility of compositional alloying. The photoluminescence decay times have been measured, and the photon energy-dependent behaviors have shown exciton migration within CdSe/ZnSe nanostructures.

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References