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Quasi-Stranski–Krastanow growth mode of self-assembled CdTe quantum dots grown on ZnSe by molecular beam epitaxy

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Abstract

This study investigates the growth mode of highly lattice-mismatch (∼14%) CdTe self-assembled quantum dots grown on a ZnSe buffer-layer by molecular beam epitaxy. Two growth processes were used to prepare the samples. For the group-I samples, Te and Cd sources were alternately used to deposit a CdTe coverage layer of 0.6 to 8.0 mono-layers on a Zn-stabilized ZnSe buffer layer. The growth process of group-II samples was reversed; that is, the Cd beam was supplied first on a Se-stabilized ZnSe buffer layer. The optical spectra, including the power-dependent, time-resolved photoluminescence (PL) and PL excitation measurement, demonstrate a ZnTe-like and a CdSe-like two-dimensional precursor layer (wetting layer) in the group-I and group-II samples, respectively. Following the formation of the precursor layer, three-dimensional highly strained CdTe quantum dots were formed. Accordingly, the growth of CdTe self-assembled quantum-dot structures was attributed to the quasi-Stranski–Krastanow mode.
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1. Introduction

II–VI self-assembled quantum dots (SAQDs) have attracted much interest for their potential in opto-electronic applications in the visible and ultraviolet spectral regions. Much of the research in this area has focused on II–VI SAQDs, CdSe/ZnSe [1–5], ZnTe/ZnSe [6,7] and CdTe/ZnTe [8–10] SAQDs, whose lattice mismatches are approximately 7%. Their growth modes are confirmed to be Stranski–Krastanow (SK) growth mode, implying that a two-dimensional wetting-layer is present between the dots and the matrix. However, in the CdTe/ZnSe heterostructure, which has a large conduction band (0.58 eV) and valence band off-set (0.61 eV) [11], the lattice mismatch between CdTe and ZnSe is approximately 14.4%. The large lattice mismatch leads to the Volmer–Weber (VW) growth

mode, according to both theoretical calculation [12] and experimental data [13–15]. The carrier capture efficiency of SK dots exceeds that of VW dots. Matsumura et al. pioneered the study of CdTe/ZnSe SAQDs [13,14], and obtained similar results using an alternating supply (AS) and general molecular beam epitaxy (MBE) growth processes. No photoluminescence (PL) spectrum of a sample with a 0.5-cycle supply and the broad PL spectra of samples with a supply of 1.0 cycle or more were observed. In reference 14, the Zn-stabled buffer and Te-irradiation process was used. In other works, Cd was supplied first on the Se-stabled buffer [15]. Regardless of the growth processes, similar PL spectra were obtained. Chang et al. explained that bright and broad luminescence was associated with the compositional heterogeneity [15]. Dao et al. [16] found CdTe/ZnSe QDs have two PL decay times. The short time is attributed to the migration and tunneling of photo-excited carriers to neighboring QDs. The long time is associated with the lifetime of excitons in

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QDs. All investigations define the VW growth mode for CdTe/ZnSe SAQDs. However, in this work, a two-dimensional precursor layer formed between CdTe dots and ZnSe matrix using the AS growth method and two different growth processes. One formed an Zn-stabilized ZnSe buffer-layer and then Te was supplied. The other involves initial Cd-irradiation on the Se-stabilized buffer-layer. PL, PL excitation measurements (PLE), power-dependent PL, and time-resolved PL measurements were made to determine the optical characteristics of CdTe SAQDs.

2. Experiments

The CdTe/ZnSe SAQDs were grown on semi-insulating epi-ready GaAs(0 0 1) using Veeco-Applied EPI 620 molecular beam epitaxy. Before growth, the native oxide of the substrates was removed by chemical etching with NH_4OH and subsequent thermal desorption. The ZnSe buffer-layer included several mono-layers (MLs) grown by migration enhance epitaxy and subsequent a thickness of 50 nm which is grown by conventional MBE. Atomic force microscopy (AFM) measurements showed the average roughness of the ZnSe buffer layer was only approximately 0.5 nm, and no Se drops were found, as shown in Fig. 1(a). Two growth processes were employed herein to form the dots. In the first group, a Zn-stabilized surface was fixed on the end of an ZnSe buffer-layer. Next, Te and Cd were deposited by the AS method with various coverages. In the second group, however, after the 50 nm-thick ZnSe buffer-layer had been deposited, the Zn source was closed and the Se source continued to supply for 5 s to produce an Se-stabilized surface. After that, the Cd was supplied initially and interrupted with Te. The growth rate of CdTe was approximately 0.2 ML/s, as determined by the reflectance spectra of the thick CdTe epilayer. The CdTe coverage was varied from 0.6, through 1.0, 2.0 and 5.0, to 8.0 MLs in both groups. After the CdTe had been deposited, the samples with (without) a 50 nm-thick ZnSe capped-layer were used to make PL (AFM) measurements. Fig. 1(b) presents the AFM image of 1.0 ML CdTe QDs sample, in

which shows that the surface roughness increased from 0.5 nm (50 nm-thick ZnSe buffer-layer) to 1.2 nm. A 325 nm He–Cd laser was used as a PL pumping source. A 300 W xenon lamp with a TRIAX-180 monochromator was used as an excitation source for PLE measurement. The spectral accuracy is about 1 meV.

3. Results and discussions

Fig. 2(a) and (b) present the PL spectra of the group-I 0.6 and 5.0 MLs samples at 10 K, respectively. Fig. 2(c) and (d) shows the PL spectra of group-II 0.6 and 5.0 MLs samples, respectively. The ZnSe buffer-layer near-band-emission (NBE) was found at 2.800 eV. A broad and asymmetric peak was observed at the low energy side. This peak was attributed to the CdTe QDs emissions. However, we posit that the spectrum of the 0.6 ML sample reveals two structures, associated with an interface (or wetting layer) state and dots-related emissions. This postulation is
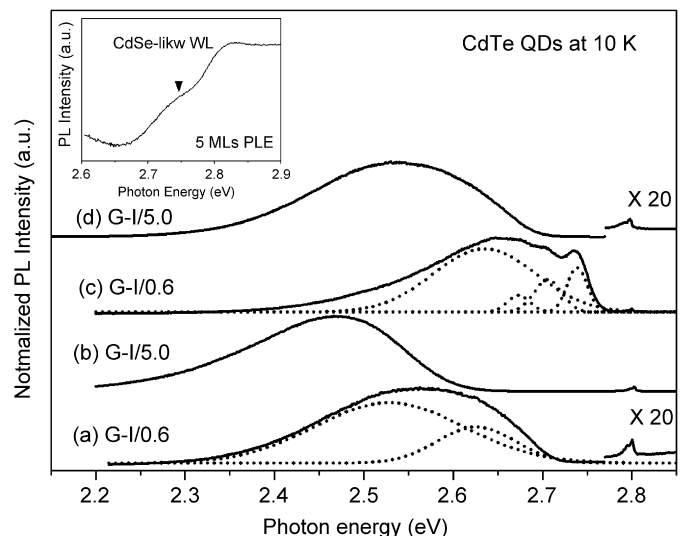
Fig. 2. PL spectra of (a) group-I 0.6 ML, (b) group-I 5.0 MLs, (c) group-II 0.6 ML, and (d) group-II 5.0 MLs samples at 10 K. The dotted-lines were from the curve-fitting of the peak. The insert shows the PL excitation spectrum of the group-II 5.0 MLs sample.
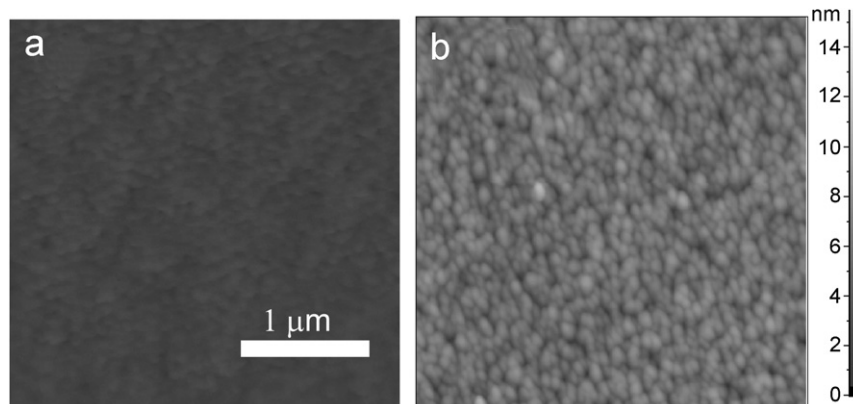
Fig. 1. AFM images of (a) 50 nm-thick ZnSe buffer layer and (b) 1.0 ML CdTe QDs sample.

based on the AS growth process, the initial supply of the Te source and the deposition on the Zn-stabilized atomic-flat ZnSe matrix. In our previous work, a two-dimensional precursor-layer (wetting layer) was formed when the ZnTe coverage was under 2.5 MLs [7]. Accordingly, when the CdTe coverage was 0.6 ML and the Te was deposited firstly, a ZnTe-like precursor layer was fabricated, and then a CdTe dots structure was present when Cd was supplied. The dotted-lines in Fig. 2(a) are from the curve fitting of the peak. One dotted line was for the ZnTe-like wetting layer, and the other was associated with CdTe QDs. The optical evidence of the ZnTe-like wetting layer is discussed below. As the CdTe coverage increased to 5.0 MLs, the CdTe dot-related emissions shifted from 2.530 to 2.469 eV. In a manner similar to that for group-I samples, a CdSe-like precursor layer was present at about 2.740 eV in the spectrum of the group-II 0.6 ML sample. Notably, the CdSe wetting layer formed as the coverage below 2.0 MLs [4,5]. Additionally, the phonon replica of the CdSe-like wetting layer was also observed. The curve fitting of the peak in Fig. 2(c) is plotted under the spectrum as dotted lines. The first and second longitudinal-optical (LO) phonon replicas are clearly defined. The energy difference adjacent pairs of 0LO-CdSe, 1LO-CdSe, and 2LO-CdSe is about 33 meV, which exceeds the LO phonon energy of bulk CdSe (25 meV) [17], because the compressive strain at the interface of CdTe and ZnSe increases the LO phonon energy [18]. However, when the coverage is increased to 5.0 MLs, the CdSe-precursor emission disappears. Nevertheless, the CdSe-like wetting layer state can be determined using PLE, as presented in the insert in Fig. 2, in which the detection photon energy (E_D) of the PL-excited spectrum was 2.535 eV. Two clear peaks at about 2.800 and 2.740 eV were associated with the ZnSe NBE and CdSe-like wetting layer, respectively.

Fig. 3 plots the PL peak energy of group-I samples as a function of CdTe coverage. The error-bar of the peak
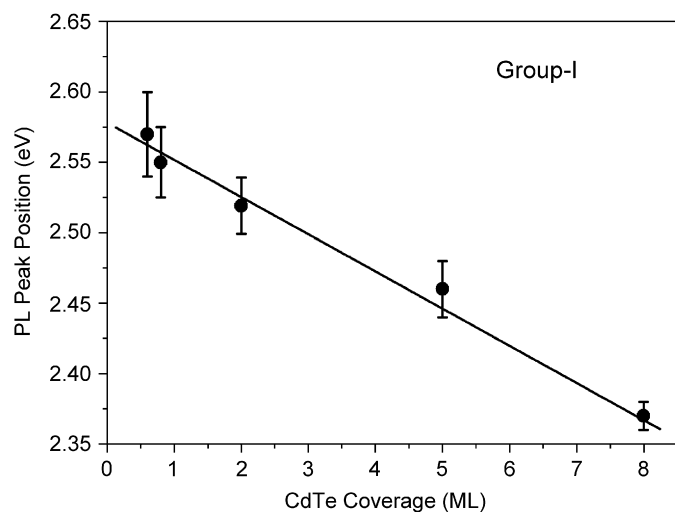
energy originates in the curve-fitting of the peak. The solid-line is a guide to the eyes. The trace of the quantum dot emissions as a function of the coverage thickness was linear. In contrast, the trace of the CdSe QDs emissions as a function of the coverage thickness in the SK growth mode has two slops [5]. Therefore, while the group-I samples have ZnTe-like wetting layers, the growth mode of CdTe QDs is the VW mode. More accurately, the AS growth mode of CdTe QDs, including the precursor layer, is a quasi-SK mode.

Fig. 4(a) and (b) schematically depicts possible band diagrams of group-I and II, respectively. The growth process and PL spectra reveal the presence of a wetting layer between CdTe QDs and the ZnSe matrix. Therefore, the band structure of the hetero-structure may include a ZnTe-like (group-I) and a CdSe-like (group-II) wetting layer. The band alignment of ZnTe/CdTe is type-I, in which the electrons and holes are confined to the same layer, and ZnSe/ZnTe is type-II, in which the electrons are confined in ZnSe and holes are confined in ZnTe [11,19], respectively. Accordingly, in group-I, the recombination process should include type-I transition for CdTe QDs and the type-II transition for the electrons confined in the conduction band of the ZnSe layer and the holes in the valence band of the ZnTe-like wetting layer. However, in group-II, the band alignment of CdTe/CdSe and CdSe/ZnSe are type-I. For both the emitting QDs and the CdSe-like wetting layer, the origin of the luminescence is type-I recombination. A power-dependent PL was adopted to confirm this suggestion. Fig. 5 plots the PL excited power as a function of the wetting layer emission energy of group-I (open square) and group-II (open circle) of the 0.6 ML sample. The solid line represents the fit to the cube root of the excitation intensity in group-I. It is characteristic of the type-II structure, because of the dipole layer formation [20]. As the excitation power is increased, the static electric filed of the dipole layers induces band-bending. This band-bending effect increases the energy level and causes the observed blue-shifted. However, in group-II, the peak

Fig. 3. PL peak position of QDs-related emission as a function of coverage thickness for group-I sample at 10 K.
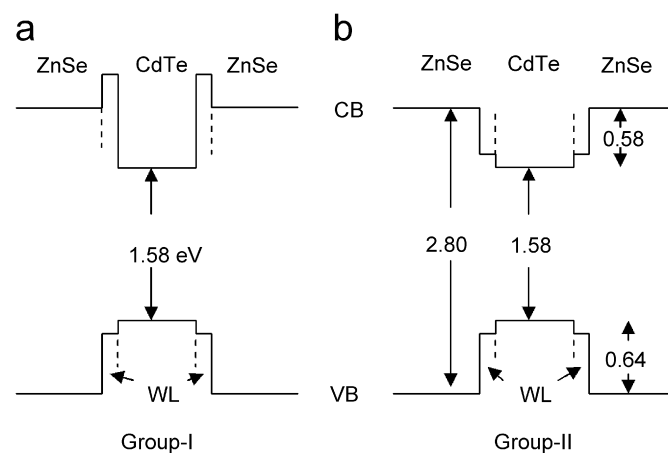

Fig. 4. Schematic possible band diagram of (a) group-I and (b) group-II samples.

energy of the CdSe-like wetting layer is independent of the excitation power.

Fig. 6(a) and (b) displays the experimental PL decay profiles of group-I and II with 0.6 ML measured at 2.633 and 2.755 eV (at 10 K), respectively. The peak energies at 2.633 and 2.755 eV for group-I and -II with 0.6 ML is close to the ZnTe-like and CdSe-like wetting layer emission energies, as presented in Fig. 2. These two curves exhibit a multi-exponential decay, comprising a fast decay and a much slower decay with a lifetime of several tens of ns. The two decay times were 8.9 and 52.8 ns in Fig. 5(a) and 2.0 and 11.8 ns in Fig. 5(b). The long luminescence decay time is perhaps related to the high luminescence intensity [21] or the high dot density [22]. The PL intensity at 2.633 eV (or 2.755 eV) includes wetting layer emission and the dots with
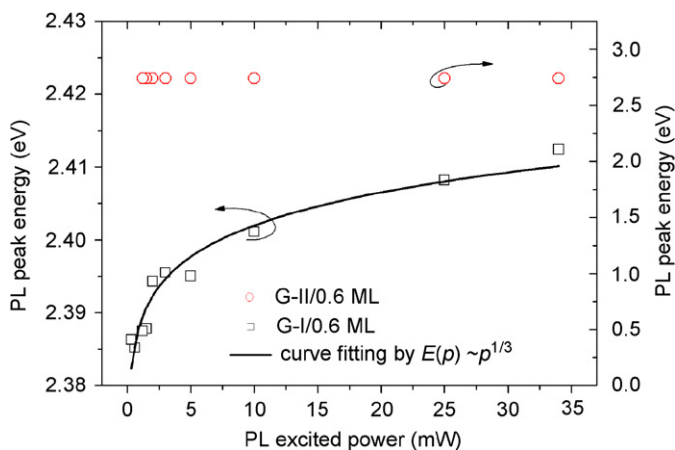
the small size. The fast decay is attributed to the wetting layer emission, and the slow decay is related to the emission from the dots [9]. The decay time is longer in group-I than in group-II because of the type-II band alignment of the ZnTe-like wetting layer, which is determined by smaller spatial overlap between the hole and electron wavefunctions.

4. Conclusion

CdTe QDs were grown in the quasi-SK growth mode by the AS method. ZnTe-like and CdSe-like precursor layers were present in the group-I and group-II samples, respectively. The ZnTe-like wetting layer leads to type-II transition. The emission energy is proportional to the cube root of the excitation intensity. The life-time of the carriers in the ZnTe-like wetting layer exceeds that of the carriers in the CdSe-like wetting layer. After the interface layer had formed, the highly-strained CdTe quantum dots were grown in the VW growth mode. Hence, the growth of CdTe self-assembled quantum-dot structures proceeded in the quasi-Stranski–Krastanow mode.

Fig. 5. PL excited power versus wetting layer emission energy of group-I (open squire) and group-II (open circle) of 0.6 ML samples at 10 K. The solid line is the curve fitted to group-I data according to $E(p) \sim p^{1/3}$, where p represents the PL excited power.
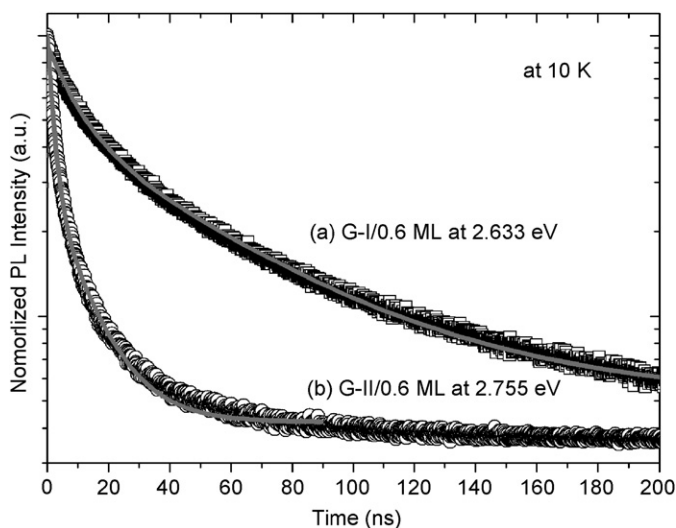

Fig. 6. Typical luminescence decay profiles of 0.6 ML CdTe/ZnSe QDs in (a) group-I (open squire) and (b) group-II (open circle) samples. The measured photon energy is at (a) 2.633 eV and (b) 2.755 eV. These photon energies are close to those of the ZnTe-like and CdSe-like wetting layer emissions.

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