Zero-dimensional excitonic properties of self-organized quantum dots of CdTe grown by molecular beam epitaxy

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The successful growth of self-organized quantum dots (QDs) of CdTe on ZnTe (100) surface by molecular beam epitaxy is reported. Atomic force microscope measurements on the uncapped samples revealed the formation of CdTe QDs with typical dot diameters of 20 ± 2 nm and heights of 2.7 ± 0.3 nm at 3.5-ML-thick CdTe deposited. The intensity of photoluminescence (PL) from the capped QDs was higher than CdTe/ZnTe single quantum wells (SQWs) by a few orders of magnitude at 4.2 K, and exhibited a thermal quenching with an activation energy of 110 meV, which is about twice as large as those in SQWs. In time-resolved PL measurements, the decay time was almost independent of temperature below 20 K. This is interpreted as due to the zero-dimensional excitonic properties in QDs. © *1998 American Institute of Physics.* [S0003-6951(98)03851-0]

Self-organized quantum dots (QDs) are creating great interest both for the basic physics related to the zero-dimensional excitons and for the application for optoelectronic devices, because they have the advantage of fabricating damage-free quantum dot structures *in situ* without the help of complicated nano-lithography processes. In III-V semiconductors such as In(Ga)As on GaAs, self-organized QDs have been fabricated with well-established technique.[1] In II-VI semiconductors, on the other hand, where several groups have just recently reported the fabrication of CdSe QDs on ZnSe,[2,3] the study of self-organized QDs is just beginning. In particular, the growth mechanism and optical properties of II-VI self-organized QDs have not been well understood compared with the III-V materials. Besides, the investigations up to the present have been limited to selenide compounds such as CdSe[4] and there have been no reports on telluride compounds except MnTe QDs.[5]

In this letter, we report the fabrication of self-organized QDs of CdTe on ZnTe (100) surface by molecular beam epitaxy (MBE) and their optical properties. In this combination, the lattice mismatch $\Delta a/a$ equals $+6.2\%$, which is nearly the same as the combination of InAs on GaAs $(+7.2\%)$. Therefore the formation of self-organized QDs in a similar mechanism could be expected.

The growth of CdTe on ZnTe (100) surface was performed in an MBE chamber equipped with elementary sources. First, ZnTe was grown on a GaAs (100) substrate. In order to relax a lattice mismatch of 8% between ZnTe and GaAs and to obtain an atomically smooth ZnTe surface, a relatively thick ($0.6-1.0$ μm) ZnTe layer was grown. The growth of CdTe was performed by an alternate deposition[5] of Cd and Te fluxes at a substrate temperature of 300 °C. It is known that at this growth condition, 1/2 ML of CdTe is grown at each cycle of the alternate deposition in an auto-regulated manner (atomic layer epitaxy—ALE).[6] With the repetition of ALE cycles, the intensity of reflection high-energy electron diffraction (RHEED) reconstructed pattern was declined and a transformation from a streak pattern to a spotty one was observed at about five ALE cycles.

The uncapped CdTe surface was examined by atomic force microscope (AFM) in the air. Figure 1 shows an AFM top view of the surface on which 3.5-ML-thick CdTe was deposited (seven ALE cycles). It can be seen that circular islands were formed on the surface in a high density. The typical size of dots was 20 ± 2 nm in diameter and 2.7 ± 0.3 nm in height. The density of dots was 8×10^{10} cm^{-2}, which is the same order of magnitude as that of InAs QDs on GaAs.[7] On the other hand, when no more than 2-ML-thick CdTe was deposited, the surface was almost flat. This result coincides with a transformation to a spotty RHEED pattern at five ALE cycles and the growth of dots looks like the Stranski-Krastanow mode. It was found that uncapped CdTe QDs on ZnTe were stable; the size and the density did not

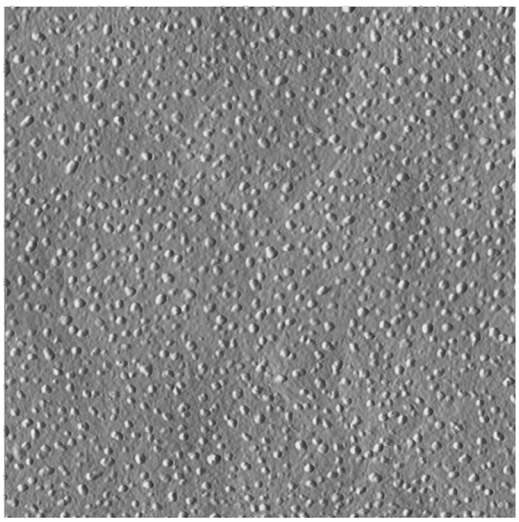

FIG. 1. AFM top view of the surface on which 3.5-ML-thick CdTe was deposited. The scanned size is 1×1 μm.

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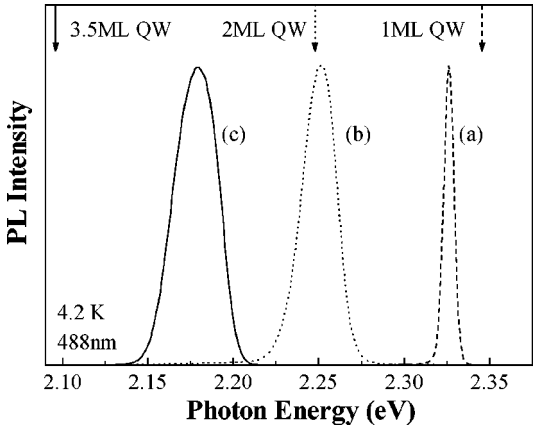

FIG. 2. Time-integrated PL spectra of samples (a)–(c) at 4.2 K. Samples (a), (b) are CdTe/ZnTe SQWs with well widths of (a) 1 ML, (b) 2 ML, respectively, and sample (c) is CdTe QDs sandwiched by ZnTe. The ordinate is normalized by the peak intensity of the respective PL lines. The arrows in the figure show the calculated optical transition energies for SQWs with 1, 2, and 3.5-ML-thick CdTe well widths, respectively.

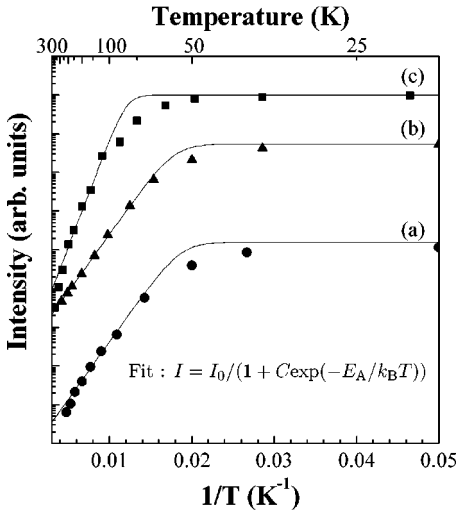

FIG. 3. The temperature dependence of the integrated PL intensity of samples (a)–(c). The solid lines show the result of fitting to the equation $I = I_0/[1 + C\ \exp(-E_A/k_BT)]$. From the fitting, we obtained the activation energy $E_A = 59$ meV for samples (a), (b) and $E_A = 110$ meV for sample (c).

change after the sample had been left in the atmosphere at room temperature for a few months. This is different from the CdSe-on-ZnSe case, in which a remarkable ripening was observed.[2]

For photoluminescence (PL) measurement, we prepared three samples with different amounts of CdTe deposited—(a) 1, (b) 2, and (c) 3.5-ML-thick CdTe—and overgrown by a 30-nm-thick ZnTe capping layer. Judging from AFM images of the uncapped surfaces, samples (a), (b) are single quantum wells (SQWs) in which a CdTe wetting layer was sandwiched by ZnTe, and sample (c) is CdTe QDs (and also a wetting layer). Figure 2 shows time-integrated PL spectra from samples (a)–(c) at 4.2 K. We calculated the optical transition energies using a simple Kronig-Penney model for SQWs with well widths which are equal to the amount of CdTe deposited in the respective samples. The calculated energies are indicated by arrows in the figure. As shown in the figure, the observed emission energies of samples (a), (b) approximately agree with the calculated ones. In sample (c), however, the calculated energy of 3.5 ML SQW is much lower than the observed one. At the same time, the optical transition energy expected from the dot size obtained by the AFM measurement for the uncapped surface deviates further to the lower energy from the observed PL line. (A rough estimate assuming a rectangular box structure with a base of 20 nm and a height of 2.7 nm gives about 1.9 eV.) This is a different case from In(Ga)As QDs, in which the observed PL energy is substantially consistent with the dot size measured by AFM.[8]

Figure 3 shows the temperature dependence of the intensity of time-integrated PL. As shown in the figure, the PL intensity of sample (c) is higher than samples (a), (b) by 2–4 orders at low temperatures. A PL quenching at elevated temperatures is attributed to the escape of carriers to a nonradiative recombination path. We fitted the temperature dependence of the intensity I using the equation $I = I_0/[1 + C\ \exp(-E_A/k_BT)]$, where I_0 and C are constants and E_A is an activation energy which corresponds to a barrier height to the nonradiative recombination path.[9] From the fitting, we obtained $E_A = 59$ meV for samples (a), (b) and $E_A = 110$ meV for sample (c). The obtained values E_A in samples (a), (b) are almost the same as reported previously in MQWs.[10] The enhancement of E_A in sample (c) by a factor of 2 could be attributed to an additional confinement of excitons in QDs.

Time-resolved PL measurements were performed using a frequency-doubled Ti-sapphire laser with a photon energy of 3.229 eV ($\lambda = 384$ nm), which is above the band gap of ZnTe. Decay times of the PL intensity at its peak energy were plotted against temperature in Fig. 4. In sample (b), the decay time increases linearly with temperature at low temperatures and then decreases above a critical temperature (~ 40 K). This behavior of the decay time is considered to be typical of excitons in the two-dimensional system; that is, the linear increase of the decay time is attributed to the thermal distribution of dark excitons away from the zone center.[11] In contrast, the decay time decreases with temperature from the lowest temperature measured in sample (a). This unusual behavior was also observed in InAs/GaAs SQW with a thin well thickness[13] and interpreted due to an enhanced nonradiative recombination rate from low tempera-

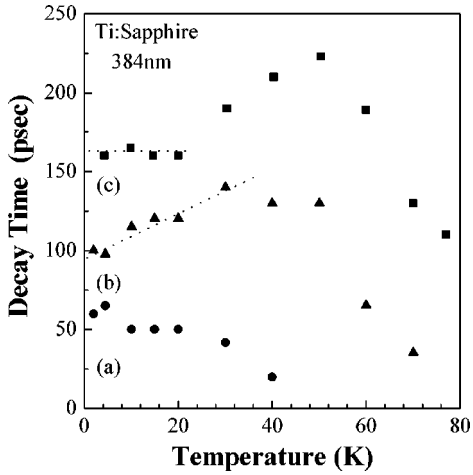

FIG. 4. The temperature dependence of the PL decay time in samples (a)–(c). The dotted lines are guides to the eye.

tures. In sample (c), on the other hand, the decay time is almost constant up to 20 K and then increases linearly with the further increase of temperature. A similar behavior of the decay time was also observed in In(Ga)As self-organized QDs.[12,13] It is considered that a temperature independent region reflects the δ-function-like density of state in the zero-dimensional confinement.[11,13] As for the increase of the decay time at higher temperatures, it was argued[11] that the thermally activated escape of carriers to the wetting layer and subsequent recapture in another dot could be an origin of a prolonged decay time at elevated temperatures.

The temperature dependence of the decay time in sample (c), particularly a temperature independent region at low temperatures, suggests the zero dimensionality of the excitons involved in the emission. This behavior of the decay time, along with a much higher PL intensity than SQWs, convinces us that the origin of luminescence in sample (c) is the zero-dimensional excitons confined in QDs. However, as mentioned earlier, the emission energy in sample (c) was higher than the energy expected from the dot size obtained by the AFM measurement. This suggests that the capped dot structure may be different from the uncapped one. In particular, the interdiffusion of Zn and Cd during the overgrowth might deteriorate the uncapped dot structure with well-defined shape—due to the diffusion of Zn into the dots, the outer part might be turned into mixed crystal (Zn,Cd)Te with a gradient of the composition and only the inner core might be left as pure CdTe. The above picture could reasonably explain the experimental results that the luminescence from the capped dot sample exhibits zero-dimensional character and a large blueshift compared to the expectation from the uncapped dot size.

As discussed previously, the increase of the activation energy E_A in comparison with SQWs is also attributed to the enhanced exciton confinement in QDs. However, it should be pointed out that the value of $E_A = 110$ meV is not far from, but does not necessarily agree with, the energy separation between the wetting layer and the QDs, which is estimated to be about 70 meV from the energy difference in the PL energy between samples (b) and (c). This might mean that a simple picture of the thermally activated escape of excitons to the wetting layer could not be applied[11] in the present case. Further studies will be necessary to clarify detailed processes of the carrier escape from QDs.

In conclusion, we have succeeded in fabricating self-organized QDs of CdTe on ZnTe (100) surface. AFM measurement revealed that the typical diameter and the height of dots is given by $D = 20 \pm 2$ nm and $h = 2.7 \pm 0.3$ nm, respectively. In contrast to CdSe QDs on ZnSe, no ripening was observed for uncapped CdTe dots. For QDs overgrown by ZnTe capping layer, an intensive luminescence was observed at 2.2 eV at 4.2 K. The temperature dependence of the integrated PL intensity indicated that the thermal activation energy E_A in QDs was enhanced by a factor of 2 compared with SQWs. The PL decay time in QDs was constant in the low temperature range up to 20 K. These experimental results were substantially interpreted as zero-dimensional character of excitons in QDs.

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