CdSe self-assembled quantum dots with ZnCdMgSe barriers emitting throughout the visible spectrum

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Self-assembled quantum dots of CdSe with ZnCdMgSe barriers have been grown by molecular beam epitaxy on InP substrates. The optical and microstructural properties were investigated using photoluminescence (PL) and atomic force microscopy (AFM) measurements. Control and reproducibility of the quantum dot (QD) size leading to light emission throughout the entire visible spectrum range has been obtained by varying the CdSe deposition time. Longer CdSe deposition times result in a redshift of the PL peaks as a consequence of an increase of QD size. AFM studies demonstrate the presence of QDs in uncapped structures. A comparison of this QD system with CdSe/ZnSe shows that not only the strain but also the chemical properties of the system play an important role in QD formation. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1834993]

Low-dimensional semiconductor heterostructures have been extensively studied because of their potential applications and the unique physical phenomena they exhibit.[1,2] Quantum dots (QDs) represent the latest innovation in the realization of these semiconductor structures with reduced dimensionality. Due to the three-dimensional confinement of the carriers or excitons, semiconductor QD structures are expected to lead to improvement in the performance of light emitting diodes and semiconductor laser diodes.[3] Although red, green, and blue (RGB) light emitters and semiconductor-based full color displays are currently manufactured, their fabrication still requires complex engineering designs and/or combinations of different materials.[4] Semiconductor systems with flexibility and simplicity in the structure design are required for these photonic applications. Light emission and intensity of semiconductor QDs are anticipated to be controllable through the size and density of the dots, offering a new possibility for the abovementioned optical device applications.

Important advances in the fabrication of these low-dimensional structures have been recently achieved using different methods.[5–7] Among these, self-assembled quantum dots (SAQDs) grown by molecular beam epitaxy (MBE) offer some advantages. The MBE technique allows the control of the alloy composition and growth rate of the QDs and in addition, permits the monitoring of the growth in real time by using reflection high-energy electron diffraction (RHEED). The SAQDs formed by the Stranski–Krastanow mode have been fabricated by MBE in group IV[8] and group III–V semiconductors.[9–11] The II–VI semiconductors, such as CdSe/ZnMnSe,[12] CdSe/Zn(Be)Se,[13–17] ZnCdSe/ZnSe,[18] CdTe/ZnTe,[19] and ZnSe/ZnS[20] have recently been extensively explored due to the higher exciton binding energy and the wide energy band gap that these materials offer.[21] However, the control and reproducibility in the size of the SAQDs

continue to be drawbacks as regards future device applications. In this letter, we present a II–VI QDs system, CdSe QDs with ZnCdMgSe barriers, grown by MBE on InP substrates. The ZnCdMgSe barrier layer can be grown lattice matched to the InP substrate offering the possibility of a wide selection of band gaps, from 2.1 to ~ 3.6 eV.[22] An interesting feature of this system with respect to other II–VI systems is that the size of CdSe/ZnCdMgSe QDs, and consequently the photoluminescence (PL) spectrum emission are easily controllable and reproducible by changing the deposition time (t_D) of CdSe.

The QDs samples were grown by MBE on InP (001) substrates in an ultrahigh vacuum system that has two Riber 2300 growth chambers, one dedicated to III–V materials and another for II–VI materials. First, the oxide layer of the InP substrate is removed by heating the substrate with an As flux impingent on the substrate surface. The complete removal of the oxide layer was determined, using the RHEED, by the transition from a (2×4) to a (4×2) surface reconstruction (495 °C). Immediately after the deoxidation temperature was reached, the substrate temperature was decreased to 470 °C to recover the (2×4) surface reconstruction and then, a 150 nm lattice-matched InGaAs buffer layer was grown in order to obtain an atomically flat surface. The substrate temperature was gradually increased to about 485 °C during the InGaAs layer growth. The RHEED showed a streaky (2×4) surface reconstruction during growth, indicating a good quality of the epilayer and the formation of an As-terminated surface, essential for a good II–VI/III–V interface.[4] After the III–V buffer layer growth, the samples were transferred into the II–VI chamber in UHV. Prior to the II-VI layers growth, Zn exposure for a duration of 40 s at 170 °C was performed to reduce defect density of the ZnCd-MgSe layer, which is related to the formation of undesired compounds between Se atoms and In or Ga atoms, such as Ga_2Se_3.[4] This was followed by ~ 60 Å ZnCdSe to promote the two-dimensional nucleation. Then the substrate temperature was increased to 250 °C and a 13 nm ZnCdMgSe layer

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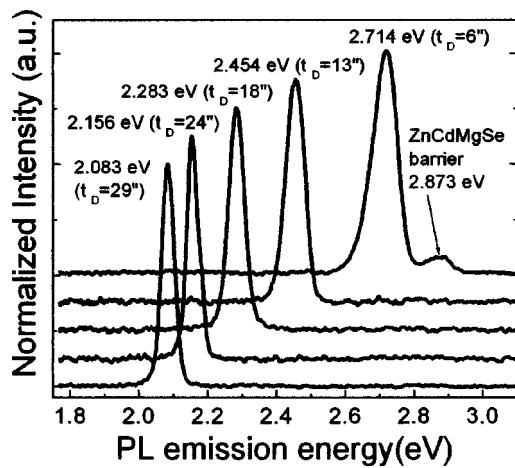[b]Electronic mail: tamar@sci.ccny.cuny.edu

FIG. 1. PL spectra of five samples grown with t_D. The PL peak emission energy and t_D for each sample is indicated in parentheses.

FIG. 2. Three-dimensional AFM image of CdSe QDs deposited on ZnCdMgSe barrier ($t_D = 10$ s). The inset shows a histogram of the QD height.

was grown. After this, the substrate temperature was set at 270 °C for the remainder of the growth. The total thickness of the quaternary is 400 nm, the RHEED showed a streaky Se-terminated (2×1) surface reconstruction indicating a good quality epilayer.[4] To initiate the CdSe deposition, the Zn and Mg shutters were closed. The different CdSe QDs were formed on the ZnCdMgSe by variation of the t_D from 6 to 36 s, followed by a growth interruption (t_{GI}) of 30 s with only the Se shutter open. The CdSe QDs were capped with a 130-nm-ZnCdMgSe barrier. A 60 Å ZnCdSe cap layer was grown to prevent the oxidation of the ZnCdMgSe top layer. The Se/Cd and VI/II ratios were kept at 7.5 and 3.9, respectively, during the entire II–VI growth.

The PL emission spectra at 77 K were obtained using a 0.3 m SPEX 1680-B spectrometer connected to a photomultiplier. The excitation source was a 325 nm-He–Cd laser.

The AFM measurements of the QDs were performed using a ThermoMicroscopes Explorer AFM of Veeco-Digital Instruments operated in the noncontact mode under ambient conditions. The AFM has a Si cantilever with a spring constant of $13-100$ N/m and a nominal resonance frequency of $240-420$ kHz. Images were recorded with a resolution of 300×300 pixels and a scan rate of 3.69 μm/s. Samples for the AFM were removed from the chamber immediately following QD formation (without the quaternary top and cap layers). To slow down a possible ripening effect,[4] the samples were immediately immersed in liquid nitrogen after growth and kept in this condition until taking the surface topography.

Figure 1 shows the PL spectra of the five samples having t_D of 6, 13, 18, 24, and 29 s, which would correspond to the deposition of layers with nominal thicknesses of 1.2, 2.5, 3.6, 4.8, and 5.8 monolayers (ML). The ZnCdMgSe barrier layers were grown with the same composition, thickness and band gap, of about 2.8 eV, for all the samples. This band gap was measured in a reference layer grown under the same conditions as the QD barrier layer. The PL peak intensities were normalized. A weak PL emission from the ZnCdMgSe barrier is observed in the sample that exhibits blue emission. As shown in Fig. 1, by appropriate choice of the CdSe t_D, the size of the QD and consequently the emission wavelength from the CdSe QDs can be adjusted to fall anywhere within the visible range. Ivanov *et al.*[16] have recently reported a similar study in the case of CdSe QDs on
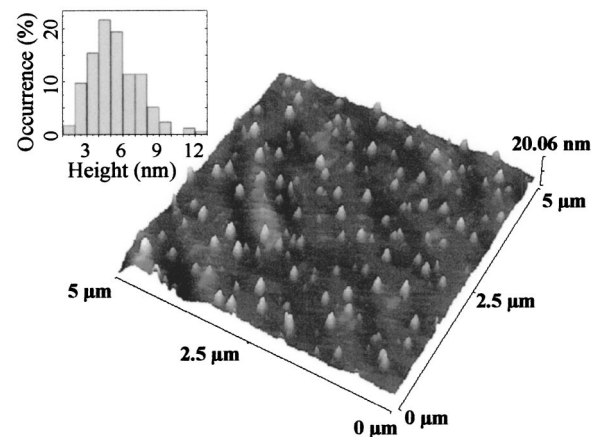
ZnSe barriers. However, in their work, they reported emission only from the blue to the green and not in the entire range of the visible spectrum as in our case. Furthermore, they observed a very dramatic decrease in the QD emission intensity for the sample with emission at about 2.29 eV which was attributed to the fact that, in that case, after deposition of 3.2 ML, the critical thickness was exceeded, and thus there was formation of defects that reduced the efficiency of the luminescence. In our system we are able to reach the red (1.964 eV) with a $t_D = 36$ s and an equivalent nominal thickness of 7.2 ML, without such a reduction of emission intensity. We attribute this result to the fact that the critical thickness of this II–VI SAQDs system is greater than in the CdSe/ZnSe system due to the much smaller lattice-mismatch (3.08%) between the ZnCdMgSe lattice matched to InP ($a = 5.869$ Å)[4] and CdSe ($a = 6.050$ Å),[4] compared to that between ZnSe, and CdSe ($a = 5.668$ Å).

A three-dimensional atomic force microscopy (AFM) image of an uncapped CdSe/ZnCdMgSe QD structure is shown in Fig. 2. The t_D for this sample was 10 s. The PL spectrum of a capped sample grown under the same conditions appeared at 2.633 eV. The inset in Fig. 2 is a representative histogram of the QDs height distribution in the sample. The histogram shows a near-Gaussian line shape, with 4.5 ± 0.5 nm being the most abundant value. The average radius of the QDs base is 47 nm. However, the radius should be cautiously considered due to the AFM tip convolution which can make the radius of the QDs base appear bigger than the real value. The average QDs density was 7 $\times 10^8$ cm^{-2}.

In Fig. 3, the PL emission peak position and full width at half maximum (FWHM) are plotted as a function of t_D. The relationship between PL peak energy and the t_D [Fig. 3(a)] is nearly linear (a line is given to guide the eye) and has been observed in several sets of samples grown on different days, indicating that good control and reproducibility in the optical properties were achieved. A similar linear relationship was obtained by Ivanov *et al.* for CdSe/ZnSe.[16] By choosing properly the t_D, light emission at any wavelength within the visible range can be obtained, which may be useful for full color (RGB) light emitters and white light sources.

Figure 3(b) shows the FWHM of the same samples represented in Fig. 3(a). The linewidth increases with increasing band gap (smaller size). By contrast, Ivanov *et al.*[17] reported
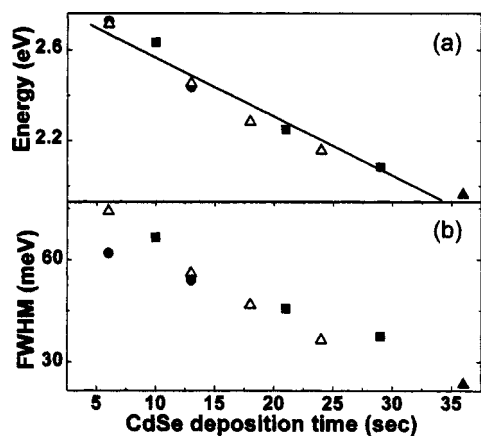
FIG. 3. (a) Variation of the PL emission energy and (b) of FWHM with t_D for several samples grown on different days. The different symbols indicate the different days the samples were grown.

a reduction of the FWHM with QD size, which he attributed to higher uniformity of QD size in the samples with smaller QDs. This comparison suggests that the dominant effect determining the linewidth variation with QD size in our case is not a change in uniformity of the QDs size, but rather that the intrinsic linewidth of the QD increases as the dot size decreases due to enhanced interface effects in the smaller dots.

The system investigated in this letter ZnCdMgSe/CdSe SAQDs provides a comparison to the well-studied system of CdSe/ZnSe. The band-gap of the ZnCdMgSe barrier ($E_g \sim 2.8$ eV) used is comparable to the band gap of ZnSe. However, the lattice-mismatch between the CdSe QD material and the ZnCdMgSe barrier material is approximately half ($\sim 3.1\%$ vs 6.7%) of the mismatch between ZnSe and CdSe. Thus we can compare directly the effects of lattice mismatch (or strain) on QDs formation. If we compare the PL emission energy for a given deposition of CdSe deposition obtained in our experiments with those reported by Ivanov, we note that the results are strikingly similar, suggesting that the CdSe QD sizes are similar. This is surprising if we assume that lattice-mismatch (or strain) is the principal mechanism controlling the QD size, and points to other factors, such as the different chemical composition of the two barrier layers, as being dominant. Chemical effects have been reported before showing that small quantities of certain elements (such as Be[15] or Mn[21]) in the ZnSe barrier cause significant change in QD size. In our case, large quantities of the Mg and/or Cd in the barrier layers are clearly affecting the dynamics of QD formation.

In summary, the formation of CdSe SAQDs on a new barrier material, ZnCdMgSe lattice-matched to InP, were reported and their optical properties investigated. The size, and consequently PL emission energy, of the QDs can be precisely tuned by the CdSe deposition time. As expected, higher emission energy is observed for smaller QDs due to the quantum confinement effect. The AFM images demonstrate the formation of CdSe QDs on ZnCdMgSe. The CdSe QD emission, covering the entire visible range, followed a simple near linear relationship with the deposition time. This

result demonstrates that this material can be an attractive alternative for optical applications in the RGB range or white-light range. A comparison of our results with those obtained in ZnSe/CdSe indicates that the chemical composition of the barrier material is an important factor in determining the growth behavior of the SAQDs.

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