Single layer and stacked CdSe self-assembled quantum dots with ZnCdMgSe barriers for visible and white light emitters

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We have grown structures with single layers of self-assembled quantum dots (SAQDs) and stacked layers of SAQDs in the II-VI materials systems CdSe/ZnCdMgSe. The structures were grown on InP substrates by molecular beam epitaxy. Good control of the quantum dot (QD) size by controlling the CdSe deposition time was obtained, giving structures whose emission can be adjusted to be at any wavelength within the visible spectrum range. Stacked QD structures consisting of three QD layers emitting in the red, green and blue (R-G-B) regions of the spectrum, respectively, were grown. Photoluminescence measurements exhibited bright white emission that could be observed by eye, at 77 K or at room temperature, as a result of the mixing of the three lines. These results indicate that this material may be an attractive alternative for optical applications in the R-G-B range and may be useful for the fabrication of white light sources. © *2005 American Vacuum Society.* [DOI: 10.1116/1.1885015]

I. INTRODUCTION

Extensive research has been carried out in the fabrication and applications of low-dimensional heterostructures such as quantum wires (QWRs),[1] quantum dots (QDs)[2] and coupled arrays of multi quantum dots (MQDs)[3] due to their potential advantages[4] (such as excellent lasing characteristics) compared to traditional semiconductor[5,6] or quantum well (QW)-based devices.[7,8] Although the advantages of low-dimensional semiconductor heterostructures were predicted about 30 years ago by Dingle and Henry[9] (wavelength tunability, lower lasing threshold, maximum material gain and reduction of temperature influence in the device performance), commercial applications of QDs and QWRs-based devices are still far from those of QWs. The reason for this is the lack of control in the size, shape, density and QD distribution that determines the optical and electrical properties of these nanostructures and, consequently, limits their device applications. Recently, we found that using a II-VI material system, CdSe QDs on ZnCdMgSe barriers, the size and photoluminescence (PL) emission are controllable and reproducible only by changing the CdSe deposition time (t_D). Furthermore, a combination of stacked CdSe/ZnCdMgSe QDs layers with emission in red, green, and blue (R-G-B) promises new possibilities for the realization of white light sources.[10]

Stacked multi-sheet arrays of coherent QDs have already been investigated to solve one of the most important weaknesses of these 0-dimensional structures, QDs spatial distribution during the self-organized process.[11] Other important advantages obtained from correlated layers of QDs were the coupling of electronic states along growth direction and the control of edge PL polarization.[12] However, few works[13,14] explored the possibility of integrating stacked QD layers each with a different emission, for example, in the red, green and blue to produce white light, since traditional QD systems do not offer such well-controlled emission throughout the visible spectrum.

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In this article, CdSe/ZnCdMgSe self-assembled quantum dots (SAQDs) were grown by molecular beam epitaxy (MBE). Single layer QDs (SQDs) and MQD structures are studied, respectively, to cover, individually, the entire visible spectrum and to explore the possibility of combining diverse QDs layers with different QD size for the fabrication of white light emission structures through the mixture of the three primary colors.

II. EXPERIMENTAL DETAILS

The SQD samples were grown by MBE on InP (001) substrates in an ultrahigh vacuum (UHV) system that has two Riber 2300 growth chambers, one dedicated to III-V materials and another to II-VI materials. First, the oxide layer of the InP substrate was removed by heating the substrate with an As flux impinging on the substrate surface. The oxide desorption of the substrate was monitored using reflection high energy electron diffraction (RHEED). The removal of the oxide layer was determined by the transition from an As-rich (2×4) to a group III-rich (4×2) surface reconstruction, which occurs at about 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 for the growth of the II-VI layers. The substrate temperature was about 485 °C during the InGaAs layer growth, the RHEED showed a streaky (2×4) surface reconstruction, indicating a good quality epilayer and the formation of an As-terminated surface, which is essential to obtain a good II-VI/III-V interface.[15] After the III-V buffer layer growth, the samples were transferred into the II-VI chamber via UHV transfer modules. Prior to the growth of II-VI layers, a Zn exposure for a period of 40 s at 170 °C was performed to reduce the stacking fault density of the ZnCdMgSe epilayer, which is related to the formation of undesired compounds between Se atoms and In or Ga atoms, such as Ga_2Se_3.[16] This Zn exposure was followed by ~60 Å of ZnCdSe at this low temperature to promote the two-dimensional nucleation and allow an ordered deposition of the ZnCdMgSe layer. Then the substrate temperature was increased to 250 °C and a 13 nm ZnCdMgSe layer was grown, after which, the substrate temperature was set to 270 °C for the remainder of the growth. The RHEED exhibited a streaky Se-terminated (2×1) surface reconstruction indicating the formation of good quality epilayer.[15] The total thickness of the quaternary barrier was 400 nm. To initiate the CdSe deposition, the Zn and Mg shutters were closed. The different CdSe QDs were formed on the ZnCdMgSe barrier by variation of the t_D from 6 to 36 s, which corresponds to the deposition of 1.2 to 7.2 ML, followed by a growth interruption time of 30 s with only the Se shutter open. To perform the PL measurements, the CdSe QDs were capped with a 130 nm ZnCdMgSe barrier. The structure was capped with a 60 Å ZnCdSe layer to prevent the oxidation of the ZnCdMgSe. Growth was ended by decreasing the temperature to 225 °C under a Se flux.

The Se/Cd, Cd/Zn and VI/II flux ratios were kept at 7.5, 1.3 and 3.9, respectively, during the entire II-VI growth. The ZnCdMgSe barrier layers were grown with the same composition, thickness and band gap (~2.8 eV), for all the samples. The ZnCdMgSe barrier band gap was measured on a reference layer grown under the same conditions as the QD barrier layer. Samples for the atomic force microscopy (AFM) images were removed from the chamber immediately following the QD formation (without the quaternary top and cap layers). To slow down a possible ripening effect,[15] the samples were immediately immersed in liquid nitrogen. They were kept like this until the moment of making the surface topography measurement.

Two stacked CdSe/ZnCdMgSe SAQD structures were grown with the same ZnCdMgSe barrier, the same ZnCdMgSe top layer, and ZnCdSe cap layer conditions as explained in the previous paragraph. These MQD structures were composed of three CdSe QD layers, each with a different t_D, separated by 33 nm ZnCdMgSe spacers. CdSe depositions were 7.2 (t_D=36 s), 3.6 (t_D=18 s), 1.2 (t_D=6 s) ML, and 7.2 (t_D=36 s), 3.6 (t_D=18 s), 0.6 (t_D=3 s) ML.

AFM images were recorded in noncontact mode using a ThermoMicroscopes Explorer™ system, operated in air and at room temperature. Silicon microfabricated cantilevers with a spring constant of 13–100 N/m and a resonance frequency of 260 kHz were used. The integral and proportional gains ranged between 0.5 and 1.2. Images were recorded in the range of 5×5 μm with a 300×300 pixel resolution and a scan rate of 3.69 μm/s. The microscope was placed on a pneumatic anti-vibration table, under a damping cover. The processing was performed using the SPMLAB software. The PL emission spectra at 77 K were obtained using a 0.3 m SPEX 1680-B spectrometer which is connected to a photomultiplier tube. The excitation source was a He–Cd laser with an emission wavelength of 325 nm.

III. RESULTS AND DISCUSSION

A three-dimensional image of an uncapped CdSe/ZnCdMgSe QD structure is shown in Fig. 1. The t_D for this sample was 10 s. The inset in Fig. 1 is a representative histogram of the QD height distribution in the sample. The histogram shows an approximately Gaussian line shape, with 4.5 ± 0.5 nm being the most abundant value. The average radius of the QD base is 47 nm. However, the radius should be cautiously considered due to the AFM tip convolution which can make the radius of the QD base appear larger than the real value. The average QD density was 7×10^8 cm^{-2}.

Figure 2 shows the normalized 77 K PL spectra of five samples each consisting of a CdSe SQD layer grown under the conditions described above and having t_D of 6, 13, 18, 24, and 29 s, respectively, which corresponds to the deposition of layers with nominal thicknesses of 1.2, 2.5, 3.6, 4.8, 5.8 MLs. A weak PL emission from the ZnCdMgSe barrier is observed in the sample that exhibits blue emission. As shown in Fig. 2, by appropriate choice of the t_D, the size of the QD and consequently the emission wavelength from the CdSe

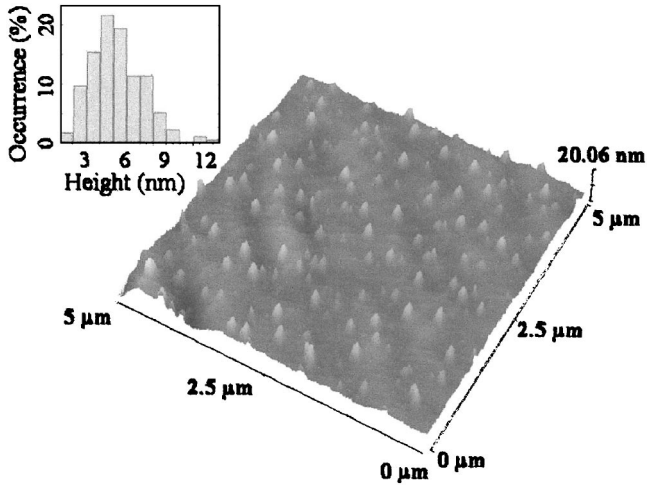

FIG. 1. (Color online) Three-dimensional AFM image of CdSe QDs deposited on ZnCdMgSe barrier (t_D=10 s). Inset shows a histogram of the QD height.

QDs can be adjusted to fall anywhere within the visible range. Ivanov *et al.*[17] have recently reported a similar result for the case of CdSe QDs with ZnSe barriers, grown on GaAs. In their work, they reported emission only from the blue to the green. Furthermore, they observed a very dramatic decrease in the QD emission intensity for the sample with emission at about 2.29 eV (green) which was attributed to the fact that, in that case, after deposition of 3.2 MLs, the critical thickness was exceeded, followed by the formation of defects that reduced the efficiency of the luminescence. In our system we are able to reach the red emission (1.964 eV) with a CdSe deposition time, 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 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)[15] and CdSe (a=6.050 Å).[15]

In Fig. 3, the PL emission peak position (the line is given to guide the eye) and full width at half maximum (FWHM)

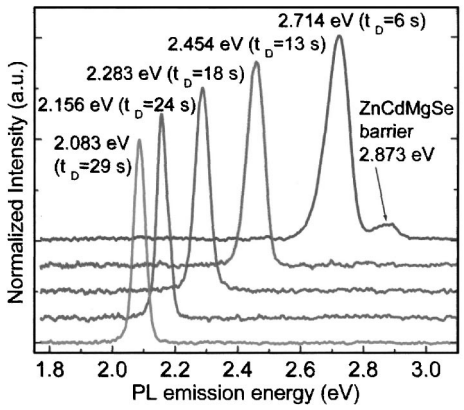

FIG. 2. (Color online) PL spectra of five samples grown with different CdSe deposition times. The PL peak emission and t_D for each sample is indicated in parenthesis.

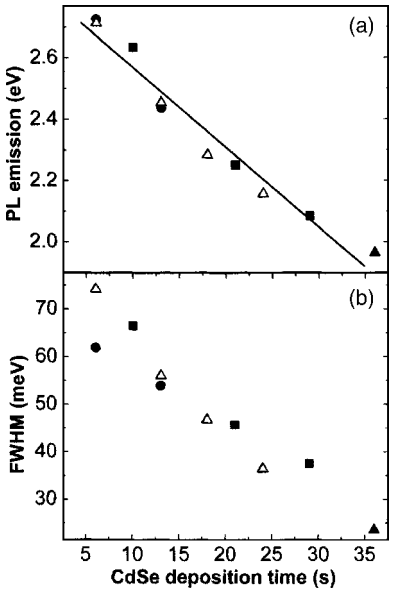

FIG. 3. (a) Variation of the PL emission energy and (b) of FWHM with t_D for several samples grown on different days. The different symbols indicate the different days the samples were grown.

are plotted as a function of t_D. The relationship between PL peak energy and the t_D [Fig. 3(a)] is nearly linear and has been observed in sets of samples grown on different days, indicating good control and reproducibility. Figure 3(b) shows the FWHM of the same samples represented in Figure 3(a). The linewidth increases with increasing band gap (smaller size). This suggests that the dominant factor determining the linewidth variation with QD size in our case is the enhanced interface effect in the smaller dots.

Figure 4 shows the PL spectrum of a MQD structure having white emission (as seen by eye) at 77 K. Three peaks corresponding to the red (1.964 eV), green (2.270 eV) and blue (2.658 eV) emissions were observed from the QD layers grown with the following deposition times: t_D=36 s, t_D=18 s and t_D=6 s, respectively. The light emitted from the

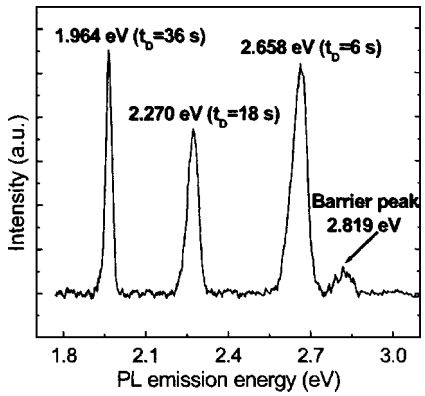

FIG. 4. PL spectrum of an R-G-B MQD sample with white emitted light color at 77 K. PL peak emissions with their corresponding t_D assignments are indicated in the figure (red QD layer t_D=36 s, green QD layer t_D =18 s, blue QD layer t_D=6 s). ZnCdMgSe barrier peak can be noticed in the figure at 2.819 eV.

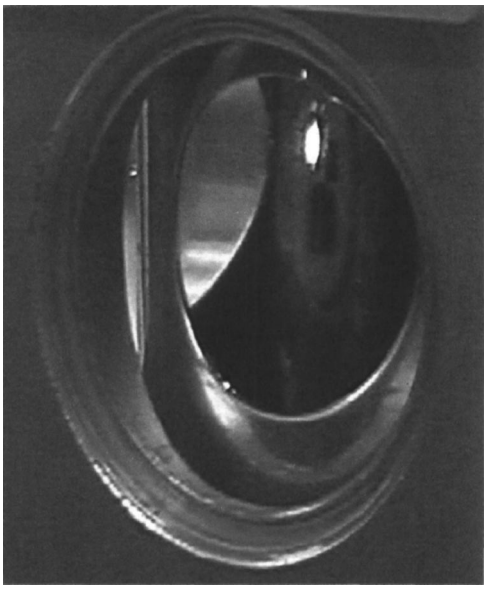

FIG. 5. (Color online) White light emitted for the R-G-B MQD structure represented in Fig. 4. The sample was mounted on the cold finger of a Janis cryostat, which can be clearly distinguished in the figure.

sample was white at 77 K as can be observed in the photograph taken during the PL measurement (Fig. 5). As the sample temperature is raised to room temperature (RT), the emission appears greenish as a result of the slight shift of the QD PL emission towards longer wavelengths with temperature. This shift is about 50 meV. To overcome this effect, another sample was grown with a different CdSe deposition time for the blue layer (t_D=3 s). In this case white emission was achieved at RT. The FWHM for the 77 K PL emission lines of Fig. 4 are 23.6 meV for the red, 40.2 meV for the green, and 53.1 meV for the blue emission. Both the PL emission energy and the FWHM of the three QDs layers in the MQD structure follow the same trend with t_D as the samples represented in Fig. 3, which indicates that there is not any disruption of the growth due to a correlation between layers of QDs.

IV. SUMMARY

In summary, the formation of CdSe SAQDs on a barrier material, ZnCdMgSe lattice matched to InP, was reported and their optical properties were investigated. The size, and consequently the PL emission of the QDs, can be precisely tuned by the CdSe deposition time. As expected, higher emission peak energy is observed for smaller QDs due to the quantum confinement effect. The AFM images demonstrate the formation of uncapped CdSe QDs on ZnCdMgSe. Combinations of three stacked QD layers with Cd deposition time corresponding to the red, green and blue emission were used to obtain white light. The CdSe QD emission, covering the entire visible range, followed a simple near linear relationship with the t_D, not only between different samples of SQDs, but also within the white MQD structure. These results indicate that this material may be an attractive alternative for optical applications in the R-G-B range and may be useful for the fabrication of white light sources.

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