

CdSe quantum dots grown on a $\text{Zn}_{0.2}\text{Mg}_{0.8}\text{S}_{0.64}\text{Se}_{0.36}$ barrier: MBE growth and μ -PL characterisation

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ABSTRACT

We report the growth and characterisation of CdSe quantum dots grown by MBE with $\text{Zn}_{0.2}\text{Mg}_{0.8}\text{S}_{0.64}\text{Se}_{0.36}$ barriers and their subsequent characterisation by 77 K PL and 4 K μ -PL. The 4 K μ -PL spectra showed numerous peaks having spectral diffusion on a timescale of < 25 ms. By correlating the variation in peak energies and intensities we are able to assign which transitions arise from individual dots and hence count the number of distinguishable dots within the resolved spot of the microscope system. This is found to be consistent with a dot density of $4 \pm 1 \times 10^{10} \text{ cm}^{-2}$.

We also discuss the possible mechanism behind the spectral diffusion seen in these measurements. Correlation of emission intensity from single-dot emission lines was also observed over much longer time periods (~ 200 s). These results will be compared with previous results from CdSe dots grown on ZnSe barriers.

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1. Introduction

The necessity of growing wide bandgap II–VI semiconductors on commercially available III–V substrates often poses problems for a range of experiments, as the III–V substrates typically have bandgaps that are smaller than those of the II–VI layers and therefore absorb in the region where II–VI material is optically active. For ZnSe based structures grown on GaAs, we have recently developed an epitaxial lift-off process utilizing MgS as a sacrificial layer [1]. This lift-off process allows the epitaxial layers to be transferred to a range of new functional substrates, allowing the substrate's properties to be tailored exclusively to the experiment without considering whether the substrate is suitable for the growth of II–VI material. This is of particular use in micro-cavity experiments, as it allows for the use of highly reflective dielectric mirrors, resulting in very high Q cavities [2].

MgS is an excellent barrier material with a bandgap of ~ 4.8 eV and we have previously shown that it can be used as a barrier for both ZnSe quantum wells and CdSe dots [3,4]. It cannot however be used as such in structures where lift-off is also required. Consequently, we have developed a wide bandgap alloy, $\text{Zn}_{0.2}\text{Mg}_{0.8}\text{S}_{0.64}\text{Se}_{0.36}$, which provides both the required confinement and also resists our standard etching solution [5].

In this paper we report MBE growth of a series of CdSe quantum dot samples utilizing ZnMgSse barriers and their subsequent characterisation by PL and μ -PL. Our motivation in developing this material system is to eventually integrate CdSe dots with ZnMgSse barriers into a micro-cavity setup to allow their optical behaviour to be fully investigated as a step toward creating a possible room-temperature polariton source [2].

2. Growth

All of the samples were grown in a VG V80H MBE system using 6 N elemental sources of Zn, Cd, Mg and Se, with a 6 N ZnS source as the only source of sulphur. All the layers, except the QDs, were grown by conventional MBE [2] at 300 °C. The QDs were grown by atomic layer epitaxy (ALE) using alternate deposition cycles of Cd and Se at 300 °C, and were then annealed for 4 min at 350 °C to thermally activate the dot formation process [6].

A series of samples were grown with the same basic structure—GaAs/34 nm ZnSe (buffer)/10–15 nm ZnMgSse (barrier)/CdSe QD layer/10–15 nm ZnMgSse (barrier). None of the samples received an additional ZnSe capping layer, as the ZnMgSse alloy has been found to resist oxidation sufficiently, to protect them [3].

The structures were monitored by RHEED throughout the growth. The ZnSe buffer layer showed a strong and streaky 2×1 pattern, as expected. During the growth of the first ZnMgSse barrier layer both $c(2 \times 2)$ and 2×1 RHEED patterns were seen, which is

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usual for all our growths of this material [7]. The CdSe dot layers show an initially weak 2×1 pattern, which is converted into a series of spots during thermal activation. The final upper ZnMgSSe barrier initially showed a spotty pattern, but after a short time (~ 1 min) both $c(2 \times 2)$ and 2×1 RHEED patterns were again seen.

Double crystal rocking curve and X-ray interference measurements of ZnMgSSe samples [8] show well-resolved diffraction features with interference fringes, indicating that they are pseudomorphic and are of high crystalline quality with no evidence of segregation or conversion to the rocksalt phase [9]. Samples have also been analysed using TEM and again show excellent crystallinity [9].

3. Ensemble PL

Ensemble PL measurements were made at 77 K using the 351 nm line of an argon ion laser as the excitation source. Spectra obtained from these measurements are shown in Fig. 1 and show a broad peak centered around ~ 2.5 eV from the CdSe QDs similar to those grown on ZnSe or MgS barriers [10,11] and a smaller peak at ~ 2.79 eV arising from emission from the ZnSe buffer layer.

The intensity of the PL emission from these samples is significantly lower than that seen with CdSe dots grown on ZnSe barriers by a factor of approximately 500. This is most likely due to the reduction in the absorption cross-section of the samples, as the ZnMgSSe barrier has a bandgap far larger than the incident photon energy and hence only the CdSe containing layer (and the substrate) will be able to absorb incident photons. This reduction in the number of photo-carriers generated therefore results in the relatively low emission intensity.

The significant reduction in emission intensity in the 2 samples (5.5 ML vs. 4.5 ML) is most likely brought about by the introduction of dislocations due to the thicker CdSe layer; a similar effect in CdSe dots grown on MgS has been seen previously [12]. There is also a small shift of peak emission energy of the broad QD emission band between the 2 samples of ~ 35 meV, which is likely to have been brought about by a change in size, distribution or composition of the dots, and is currently under investigation.

4. Micro-PL

Two samples were selected for μ -PL study with 9 and 11 ALE cycles giving 4.5 and 5.5 ML of CdSe, respectively. The μ -PL measurements were made at 4 K using a diffraction limited confocal microscope system utilizing either a 0.85 NA microscope objective or a combination of an aspheric and solid-immersion lens, with an effective NA of 1.3. The samples were excited using a 40 mW 405 nm laser diode mounted on a TEC cooler and driven at roughly 90% of its maximum drive current, so as to ensure that it produces a highly stable output. The beam was then collimated and the fibre coupled to the microscope head, mounted directly about the liquid helium cryostat in which the samples were placed [13]. The excitation density for all our measurements was kept constant at relatively high ~ 220 kW cm $^{-2}$, to compensate for the low emission intensity of the samples. The emitted light was dispersed using either 300 or 1800 line gratings onto an LN2 cooled CCD giving energy resolutions of 0.95 meV and 90 μ eV, respectively.

Figs. 2 and 3 show a μ -PL spectrum from each of the samples obtained by averaging the emission of the samples over 30 s, to

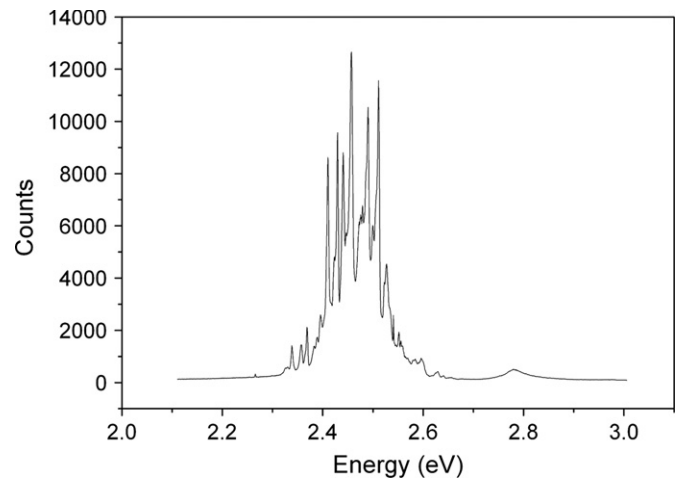


Fig. 2. μ -PL spectra for the 5.5 ML sample at 4 K.

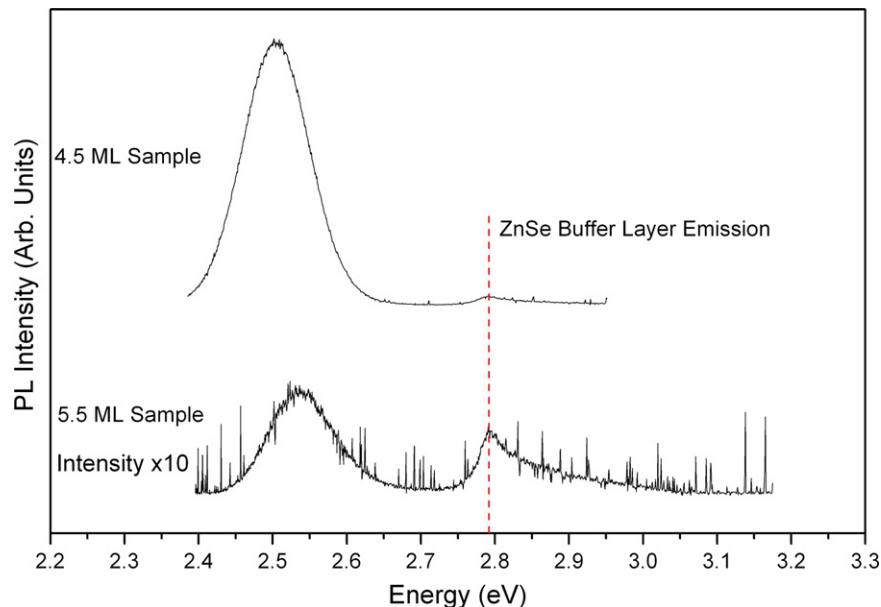


Fig. 1. Ensemble 77 K PL measurements of CdSe/ZnMgSSe QD samples.

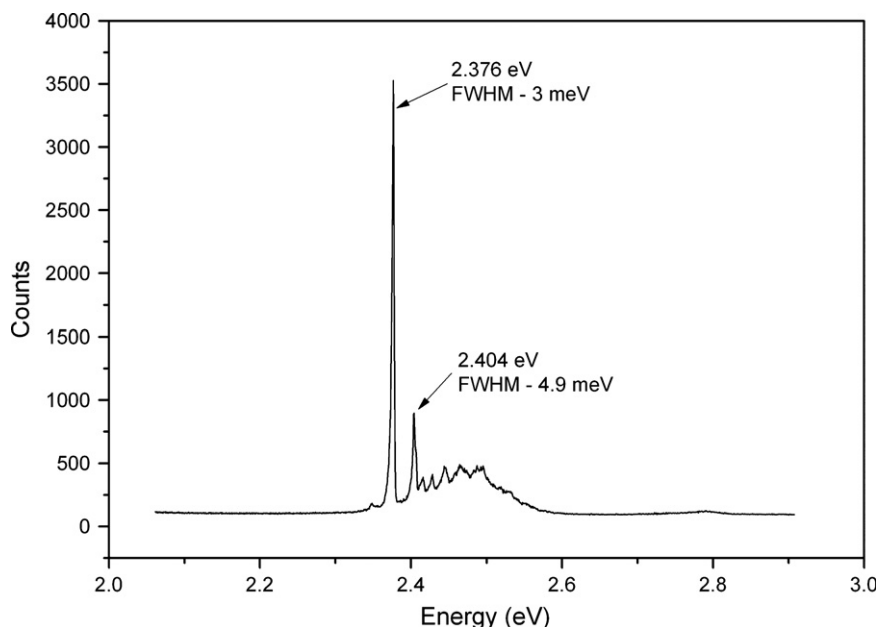


Fig. 3. μ -PL spectra for the 4.5 ML sample at 4 K, the first frame (10 s) of Fig. 4.

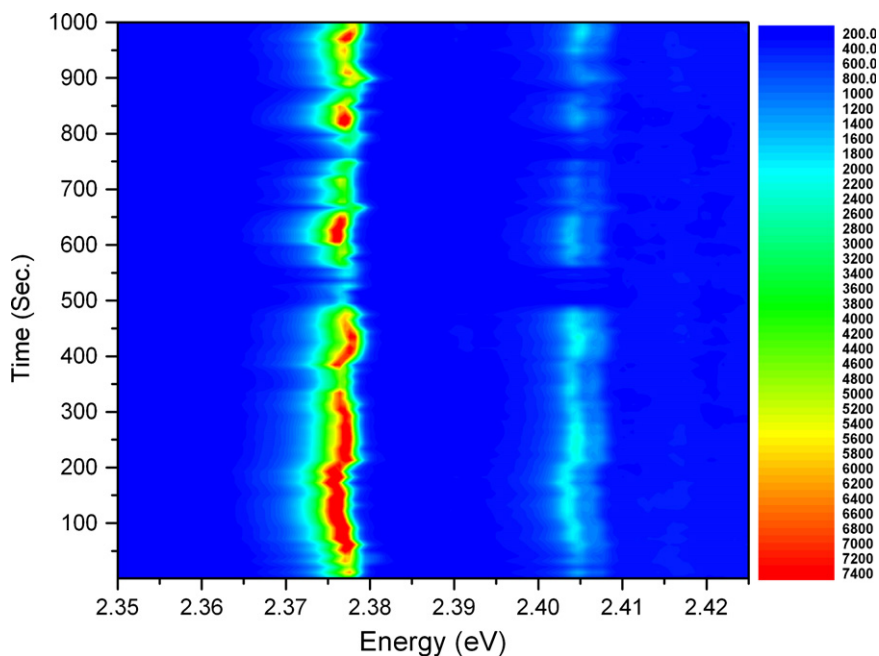


Fig. 4. Time evolution of the 4.5 ML samples spectra at 4 K (10 s integration time \times 100 frames).

compensate for the low emission intensity. Both samples show a series of closely spaced, relatively narrow features at 4 K centered around 2.5 eV, representing emission from individual dots. An additional smaller feature is seen at \sim 2.8 eV, representing emission from the ZnSe buffer layer, as in Fig. 1. By translating the sample using sub-nm positioning stages, it is possible to find spatially isolated individual dots that are sufficiently separated from the main ensemble in emission energy to investigate their behaviour. An example of this can be seen in Fig. 3. The sharpest features observed with these samples have FWHM in the region of 3 ± 0.95 meV.

Fig. 4 shows the time evolution of the spectra observed from the dot shown in Fig. 3. Over a period of time both intensity and peak emission energy of the dot fluctuate. It should be noted that

although it appears in the figure that emission intensity periodically falls to zero (for example at times 500–550 s and around 750 s) this is not actually the case; in reality the intensity has just dropped to a level where it is not well-resolved from the background in this colour map. It is also apparent that the large FWHM of the lines obtained in the integrated traces arises from fluctuations in the peak position.

The graph also shows a second feature, whose emission energy is roughly centered on 2.475 eV. The fluctuations in intensity and energy of this feature are highly correlated to that of the lower energy line, with coefficients 0.958 and 0.716, respectively, indicating that they arise from the same dot, as has previously been observed in ZnSe/CdSe QD emission [14].

From the correlations of energies of individual lines it is possible to deduce whether lines within the spot the microscope resolves probably arise from the same or different dots and hence estimate the number of dots within the spot. After repeating this process at different positions values for the dots, densities for these samples can be obtained

Fig. 5 shows the temporal evolution for a representative spectrum containing 15 well-resolved peaks. From an analysis of the correlation of peak energies and intensities we can determine that of these 15 peaks, 6 (3 pairs, indicated by the coloured arrows) of them show a strong correlation (greater than 0.5), suggesting that within the resolved spot of the system there are 12 distinguishable dots. Repeated over several spectra this is consistent with a dot density of $4 \pm 1 \times 10^{10}$ dots/cm², which is similar to the densities seen with CdSe dots grown on ZnSe and MgS [10].

The 3 pairs of spectral lines in Fig. 5, which are highly correlated in terms of both energy and intensity, all share common features; the peaks are separated by $\sim 26 \pm 2$ meV and lower energy peak of the pair is the most intense. Because of these features we believe that it is most likely that the 2 peaks are due to the 1s and 2s level emissions from the dots. However we have not been able to perform any additional measurements to fully confirm this.

Fluctuations in both energy and intensity of QD emission have previously been observed for CdSe dots grown on both ZnSe and MgS barriers [10,15], and for samples grown on ZnSe it has been demonstrated that these fluctuations arise from the Quantum Confined Stark Effect (QCSD) produced by fluctuating charge close to the dots, either located at the sample surface [10] or at dislocations originating at stacking faults [15]. We observe typical fluctuation (spectral diffusion) in the dot energy of 2–3 meV. Assuming our dots are roughly similar in size and polarizability to the CdSe dots grown on ZnSe [16], this could arise from single charges located approximately 10 nm from the dot, which is compatible with the charge being located at the surface of the sample.

QCSD produced by a fluctuating electric field will cause energy of the emission line to decrease together with emission intensity. Consequently, there should be a strong correlation between these

two effects produced by the fluctuating electric field, as has been previously observed for ZnSe/CdSe dots [15–17]. However, the weaker emission from the ZnMgSSe/CdSe samples means that although we are able to identify both energy and intensity fluctuations from all dots we have examined so far, we have thus far not been able to observe any statistical correlation between the two quantities for an individual emission line.

If the quantities are indeed correlated, then our inability to resolve them signifies that the fluctuations are occurring on timescales shorter than the smallest integration time we have used in these experiments, which is 25 ms.

For the brightest isolated dots observed, as shown in Fig. 4, emission intensity shows a characteristic long period oscillation, with a strong correlation in intensity occurring on a timescale of 200 s. This effect has also been observed on ZnSe/CdSe dots by other groups, where correlation times of 160 s [15] and 220 s [17] have been obtained. We have thus far been unable to determine a cause for this.

5. Conclusion

We have investigated the behaviour of CdSe QDs grown on a MgS-rich ZnMgSSe alloy barrier and found the alloy to provide good carrier confinement; however, many of the individual lines observed showed significant spectral diffusion, giving peak FWHM of ~ 3 meV. Energy and intensity of all the QDs within the field of view was also observed to fluctuate on a timescale of < 25 ms, which is compatible with QCSD arising from isolated charges located close to individual dots.

On analysing the correlations of the various well defined peaks seen in the spectra from the samples we have been able to count the number of individual dots seen within the resolved spot of the microscope system. This has allowed us to calculate a dot density for the sample of $4 \pm 1 \times 10^{10}$ cm⁻². It also suggests a 1–2 s exciton binding energy separation of 26 ± 2 meV, which is comparable to that seen with other II–VI material systems [18–20].

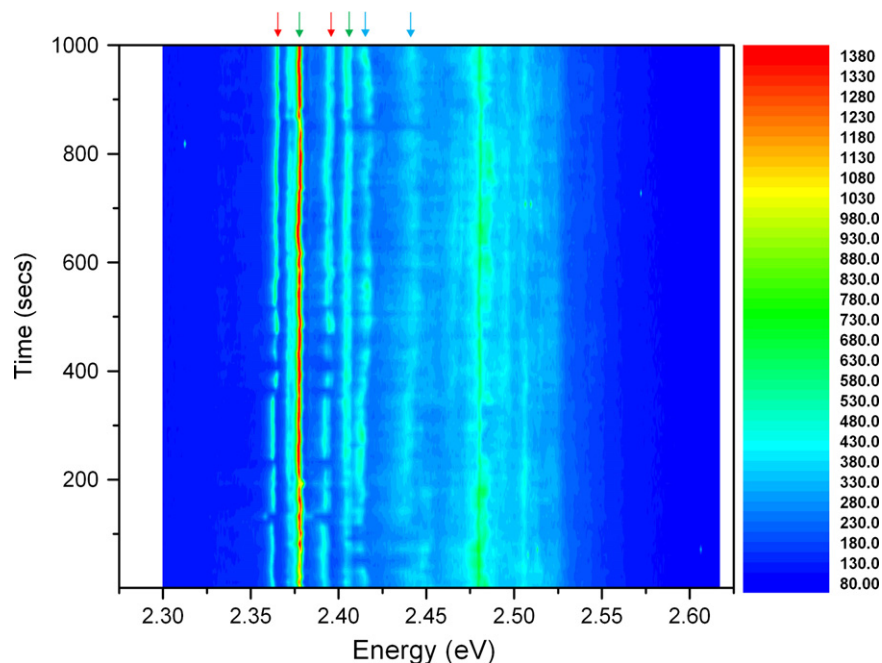


Fig. 5. Time evolution of a representative spectra at 4 K (10 s integration time \times 100 frames).

A characteristic timescale of ~ 200 s has been determined by statistical analysis for variation in emission intensity and energy for some of the dots examined.

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