Measurement and control of size and density of type-II ZnTe/ZnSe submonolayer quantum dots grown by migration enhanced epitaxy

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Abstract

For practical applications of self-assembled semiconductor quantum dots (QDs), it is important to control their densities and sizes, however these parameters are difficult to quantify. This is particularly challenging in case of submonolayer QDs, in spite of their remarkable features including absence of wetting layers and significantly small dimensions that are advantageous for many device application. We report here the investigation of submonolayer type-II ZnTe/ZnSe QDs grown via migration enhanced epitaxy (MEE) with varying Te content. The employment of MEE assists in the formation of QDs and facilitates improvement in overall material quality. The structural and optical properties of these QD structures were investigated using a variety of characterization tools. Low temperature photoluminescence measurement allowed for a good estimate of QD thicknesses, while observation of robust Aharonov-Bohm-oscillations in magneto-PL spectra was used to precisely determine diameters of these disc-shaped QDs. These results, in conjunction with high resolution x-ray diffraction and secondary ion mass spectrometry data of the Te concentration, were then used to evaluate the QD density. It is evident from the results that the dot density increases much faster than the QD size with respect to the increase in overall Te content. Most importantly, this study provides the dependence of average QD size and density as a function of Te flux and Te MEE cycles, and shows that these are the key parameters to control the QD dimension and distribution.

Keywords

A1. Growth models

A1. Nanostructures

B1. Migration enhanced epitaxy

B2. Zinc compounds

B3. Semiconducting II-VI materials

B3. Magneto-optic materials

Introduction

Semiconductor quantum dots (QDs) have revolutionized the field of electronic and photonic devices and have exposed a vast range of new physical phenomena [1]. For practical applications of these novel materials, it is essential to control their sizes and distribution; parameters that remain elusive in many cases. Two important new results are presented here. First, we obtain estimates of the dot densities and their size as we vary the Te flux and the number of Te cycles during their growth via migration enhanced epitaxy (MEE). Secondly, we obtain a relationship that allows us to control the size and densities of the type-II QDs.

The vast majority of the QD systems in use today are the so-called type-I QDs, in which both electrons and holes are confined within the QD region. There is an increasing interest in type-II quantum structures due to the expectation that, by taking advantage of the type-II band alignment and quantum confinement effects, their optical and electrical properties can be tuned in unique ways [2]. Type-II ZnTe QDs embedded in a ZnSe matrix (or ZnTe/ZnSe QDs) are particularly interesting because of their relatively large valence band and conduction band offsets [3]. Specifically, a slightly modified system made out of type-II ZnCdTe/ZnCdSe submonolayer QDs has been shown to be one of the best candidates for efficient intermediate band solar cells [4,5]. Furthermore, since ZnTe can be readily p-doped, submonolayer ZnTe/ZnSe QDs and related multilayer structures have been implemented for improving p-type doping in ZnSe, which otherwise is difficult to achieve [6]. Additionally, submonolayer QDs grown via MEE, form without the formation of wetting layers, an advantageous feature for practical applications. However, in order to obtain high-quality, controlled growth of QDs with uniform size distribution and adequate densities, it is important to understand the growth habits of these materials. Here we use high resolution x-ray diffraction (HRXRD), secondary ion mass spectrometry (SIMS), low-temperature photoluminescence (PL), and magneto-PL to measure the size and density of the QDs and to analyze how the variations of the growth conditions contributes towards controlling these important parameters. The experimental results also demonstrate that the dot density increases much faster than the QD size as a

function of increasing Te flux and/or the number of Te MEE cycles, providing better control over dot properties.

Experimental details

I. Growth

All samples presented here were grown in a Riber 2300P molecular beam epitaxy system on (001) semi-insulating GaAs substrates. The system includes both III-V and II-VI chambers connected by a transfer module under ultrahigh vacuum (UHV). Before transferring the samples to the II-VI chamber, oxide removal was done by standard procedures, and a GaAs buffer layer was grown to ensure a smooth Arsenic terminated GaAs surface. Prior to the growth of the II-VI epilayers, the substrate temperature was set to 200 °C and the surface was exposed to a Zn flux for 30s. Subsequently a buffer layer (<10 nm) of ZnSe was grown at this low temperature. The temperature was raised to the optimum growth temperature of 300 °C at which a buffer layer of ZnSe was grown under Se-rich conditions. Subsequently, the QD multilayers were grown following the shutter sequence shown in figure 1(a). Reflection high energy electron diffraction (RHEED) exhibited a typical (2×1) reconstruction pattern during the growth of ZnSe spacers. A clear change in the RHEED pattern from (2×1) to $C(2 \times 2)$ was observed prior to and during the formation of QDs, indicating the presence of Zn-rich surface throughout the MEE cycle. Six samples labeled A through F were grown with different Te content obtained through variations of the growth process. A summary of important parameters of the investigated samples is presented in Table 1. The samples are organized in order of increasing Te concentration as measured by SIMS and HRXRD. This was achieved by changing Te cell temperature, and therefore the Te flux, as well as by varying number of Te MEE cycles during the shutter sequence.

II. Characterization

HRXRD measurements were performed using a Bruker D8 Discover x-ray diffractometer with a Cu source ($\lambda = 1.54056 \text{ \AA}$). PL measurements were made using the 351 nm emission line from an Ar^+ laser for

excitation. The PL emission was detected by a TriVista SP2 500i triple monochromator coupled to a thermoelectrically cooled photomultiplier tube (PMT) and a photon counting system. A temperature-variable closed-cycle refrigerating system with a helium compressor was used for low-temperature measurements. The SIMS measurements were performed by Evans Analytical Group.

Results and discussion

The structural characterization was performed using HRXRD measurements (see Fig. 2) in order to calculate strain and compositions in each of the samples. The out-of-plane and in-plane lattice parameters for the superlattices were calculated by performing 2θ - ω scans along (004) and (224) orientations respectively and using Bragg's law. It was assumed that the cubical unit cell is deformed to tetragonal due to equal biaxial in-plane strain components. Consequently, these lattice parameters allowed us to calculate average strain and compositions; the results obtained are shown in Table 1. Weak satellite SL peaks were also observed in the HRXRD scans (not shown here), which were then used to calculate the SL period.

This analysis also led us to confirm a rather interesting observation that in these samples, MEE and consequently the formation of submonolayer QDs suppressed rapid relaxation that usually occurs due to the natural lattice mismatch between the GaAs substrate and the ZnSe matrix. The strain calculated from HRXRD measurements were plotted with respect to the sample thicknesses (see Fig. 3) for the samples with very low Te concentrations (sample A through E). This allowed estimation of the critical thickness of ZnSe with a slight inclusion of Te grown on GaAs. This value was estimated to be ~225 nm, considerably larger than the previously reported values (~ 100 to 150 nm) for bulk ZnSe on GaAs. [7,8] MEE has been shown to be very useful to grow high quality atomically flat heterostructures [9] as well as to grow QDs with enhanced size uniformity [10,11] due to the enhancement in the surface migration of adatoms. Here, we have applied this technique to grow self-assembled submonolayer QDs. This growth process results in the formation of QDs essentially without the formation of wetting layers, analogous to the so called Volmer-Weber growth mode. The results show that the formation of submonolayer QDs via MEE leads to high structural quality of the samples.

SIMS analysis was performed on all the samples to measure average Te concentration and the results are shown in Figure 4. Although Te was only incorporated in the QD regions, the SIMS analysis does not spatially resolve the thin spacer regions (<10 monolayers), and an approximately flat Te concentration trace, indicative of the value of the average Te concentration within the structure, is obtained. The SIMS data was also used to calculate the composition of the superlattice structures by using the known values of volumetric atomic densities of ZnTe and ZnSe. The Te concentration values as well as the percentage Te content for each sample are summarized in Table 1. The results show that if the spacer thickness is kept constant, Te concentration in the samples increases with Te cell temperature and with the number of Te cycles. To further examine the effect of varying growth conditions on the formation of the type-II QD structures, a new parameter ‘ τ ’ was introduced, which is a better measure of actual Te content in the samples.

$$\tau = flux_{Te} \times MEE_{Te} \quad \dots \text{Eq. (1)}$$

where, $flux_{Te}$ is the actual Te flux (beam equivalence pressure) measured prior to the growth of the sample and MEE_{Te} is the time for which Te shutters were kept open during an MEE shutter sequence (see Table 1).

The optical characterization was done by performing PL as well as magneto-PL experiments at 10 K. The normalized PL spectra at 10 K for all the samples are shown in Figure 5(a). The PL spectra, consistent with our previous reports, are typically broadband consisting of a ‘*blue band (BB)*’ (>2.7 eV) which is attributed mostly to the emission from Te isoelectronic centers (ICs) in ZnSe spacers and a ‘*green band (GB)*’ (<2.7 eV) that originates from the QD-related emissions [12]. Near band-edge sharp emission lines are observed in the PL spectra of samples with lowest Te content (samples A and B) which are known to be due to small concentration of ICs in the spacer regions. Presence of up to four phonon replicas also point toward a large electron-phonon interaction. Thus, in spite of some distribution in QD sizes, the biggest contributor to the broad PL line widths is the electron-phonon interaction, as in bulk ZnSeTe, due to the hole trapping at Te ICs [13] (similar results have been obtained for ZnMgTe/ZnSe QDs [14]).

Firstly, excitation intensity dependent PL analysis was performed to confirm the presence of type-II band alignment (not shown here). We observed the expected blue shift in PL peak position with an increase in excitation intensity for all the samples [15], which is a signature of type-II behavior [12,16].

For detailed spectral analysis of the PL data, the spectra were fitted with four Gaussian lineshapes (see Fig. 5(a)). The near band edge BB mostly originates from the emission from Te ICs, while the contribution from QDs dominates in all the other GBs as discussed earlier in this section. It is observed that as τ increases, the contribution from the GBs goes up with a small red shift in PL peak positions (see Fig. 5(b)), indicating rise in QD density along with a slight increase in QD dimensions with τ . Thus, the peak positions of all the three GBs associated with the QD emissions were used to estimate the average QD size, specifically the thickness, by simply solving 1-D Schrödinger equation. Note that there is a considerably large electron-phonon interaction accounting for most of the width of these lineshapes as discussed earlier whereas the contribution to the confinement due to radial dot sizes is negligible as will be discussed in the following sections. Figure 6(a) shows the band alignment in this heterostructure while Fig. 6(b) shows the dependence of hole confinement energies on various QD thicknesses, both calculated using previously reported parameters [3,17].

Magneto-PL is a way to obtain an accurate estimation of the radial sizes of these submonolayer QDs due to their type-II nature. As we have previously shown, the vertical correlation in these submonolayer QDs separated by a thin spacer causes them to form vertical stacks [18] resulting in a cylindrically symmetric type-II QD structure, a favorable geometry for an observation of excitonic Aharonov-Bohm (AB) effect [19]. In the presence of external magnetic field applied in a Faraday geometry, the angular momentum of a type-II exciton makes a discrete transition from a zero to a non-zero angular momentum state [20–23]. The magnetic field value of the AB transition is dependent on the trajectories of electrons and holes, and consequently on the radial size of the QDs as discussed in Ref. [15]. The average QD radii for the samples in this study are estimated to be about 13 to 20 nm, justifying the claim that most of the confinement in these disc-shaped QDs is along the growth direction i.e. due to the QD thicknesses.

Moreover, accurate estimates of the distributions of QD radii can be obtained with the help of high resolution spectral analysis of the magneto-PL spectra [15,24]. Through this analysis, it was observed that the lateral QD size changes more or less discretely and is related to the average lateral size of the stack of the QDs. The combined result of the calculated QD thicknesses and radii over the complete PL spectrum is shown in Fig. 8. The discrete changes in the lateral QD sizes appear to coincide with the specific energy values where different lineshapes start to overlap each other. Furthermore, sample F shows continuous change in QD radii with relatively large lateral size dispersion as indicated by the observation of a broad peak in magneto-PL spectrum, whereas, the QD radius in sample A does not vary over the entire PL spectrum resulting in a very narrow peak in magneto-PL spectrum [15].

Upon obtaining the spectral distribution of QD radii and the thicknesses, the intensities of the GBs were used to estimate weighted QD volume over the full PL spectrum for each of the sample (see Fig. 8).

The density of QDs was then estimated from this calculated QD volume as follows. Considering that all the Te is concentrated within the QDs, the areal density of QDs, n_{QD} , can be calculated as:

$$n_{QD} = \frac{N_{SIMS}}{N_{Te}} \left(\frac{L}{V_{QD}} \right) \quad \dots \text{Eq. (2)}$$

where N_{SIMS} is the average Te concentration provided by the SIMS measurements, N_{Te} is the volumetric atomic density of Te in Zn(Se)Te QDs, V_{QD} is the average volume of the QDs, and L is the average superlattice period obtained from HRXRD as well as from SIMS (see Table 1).

We plot average QD radii and thicknesses (Fig. 9(a)) as well as areal QD density (Fig. 9(b)) vs. corresponding values of τ (see Table 1) for samples A through F. Although the values of QD radii were accurately calculated there might be an error of about 10% in the estimates of QD thicknesses. Also, we show even larger error bars (~20%) in case of the dot density estimates as the small contribution from the Te ICs has not been included in the calculations. Thus, the errors in the absolute value of the QD areal density obtained in this analysis may be significant, but the qualitative conclusions central to this study can be derived.

Two important conclusions are reached. Firstly, we note that concentrations at least one order of magnitude higher would be required to form a full ZnTe-rich monolayer (i.e. for the QDs to physically coalesce into a continuous layer). In this investigation, during each MEE cycle, the amount of Te is supplied in such a way that there is less than a monolayer of ZnTe formed, i.e. less than is needed to form a wetting layer. Thus, no wetting layer forms in this regime and such a growth mode is analogous to Volmer-Weber growth. Although this is not surprising from the growth perspective, we make a special note of this as, for certain applications of QD structures, the absence of a wetting layer is critical.

Secondly, the observed dependence of average QD size and density as a function of Te flux as well as number of Te MEE cycles shows that these are the key parameters to control QD dimensions and distribution. The other variables such as the substrate temperature as well as the interruption time during the MEE cycles may introduce more subtle changes in the formation mechanism of the QDs.

The data also appears to indicate that the thickness of these QDs starts to vary prior to the variation in the lateral QD size (see Fig. 7). Sample A has a sharp AB peak in the magneto-PL spectrum and position of which shows no change when we perform the spectral analysis, indicating the presence of dots with almost zero lateral size variation. Nonetheless, there is a significant thickness distribution in this sample. Also, sample F with comparatively larger QDs shows only about 20% variation in the dot radius with the lowest thickness distribution. This is most probably due to the stacked nature of the QDs as the vertical QD correlation is supposed to enhance QD size uniformity [18]. This also leads to the observation of a small increase in the radial dot size ($\sim 46\%$) as opposed to about 150% increase in the average QD thickness as values of τ vary from sample A through F. Moreover, the increase in density from sample A through F is about 670%, much larger than that of the QD size.

Conclusions

We have investigated submonolayer ZnTe/ZnSe type-II submonolayer QDs using various characterization tools in order to develop an understanding of the parameters that control the size and density of these nanostructures. HRXRD analysis shows that the samples have high crystalline quality owing to the

implementation of MEE technique. Spectrally analyzed PL and magneto-PL data has been employed for an accurate determination of QD sizes, while QD densities have been calculated using the Te concentration data obtained from the SIMS analysis. We show that the dimensions and the distribution of the QDs can be controlled by varying Te flux and the number of Te MEE cycles during the sample growth. The results also demonstrate that the areal dot density increases much faster than that of the QD dimensions providing, in principle, a better control over their distribution. This study provides us a practical way of estimating and controlling the size and density of these hard-to-image type-II QDs which is of critical importance in applications of these composite nanomaterials.

Acknowledgements:

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Award No. DE- SC003739.

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Figure Captions

Figure 1. (a) A typical shutter sequence for growth of a QD sample with three consecutive MEE cycles. (b) A schematic diagram of a multilayered structure with embedded submonolayer QDs; here Z denotes the growth direction.

Figure 2. HRXRD 2θ - ω curves for all the samples along (a) (004) and (b) (224) reflections.

Figure 3. A plot showing strain along the growth direction in samples with low Te content with respect to their individual thicknesses. The dotted line is for eye guidance only.

Figure 4. SIMS data for all the samples showing average Te concentration as a function of depth.

Figure 5. (a) PL spectra of all the samples at 10K along with the fitted Gaussian lineshapes. (b) The change in the peak position as a function of τ for each of the line shapes.

Figure 6. (a) Schematic band line-up of Zn(Se)Te/ZnSe QD system. (b) Calculated hole energy levels (HH and LH correspond to heavy and light holes respectively) inside the submonolayer QDs as a function of their thicknesses, here ML denotes the thickness of a monolayer.

Figure 7. Combined diagram of the spectral dependence of QD radii and thicknesses in all the samples overlaid on the corresponding PL spectra, the GBs are specifically highlighted as they correspond to QD-related emissions.

Figure 8. A plot showing spectrally resolved, normalized weighted QD volume as a function of PL energy, overlaid with the PL spectra of individual samples.

Figure 9. (a) Plot showing average QD radii and thicknesses as a function of τ . (b) Plot showing the dependence of areal QD density on τ ; dashed lines are for eye guidance only.

Table Caption

Table 1. Important parameters of the samples under investigation

Table 1.

Table

Samples	A	B	C	D	E	F
Te flux in 10^{-7} torr	2	1.2	1.3	1.9	2	8
Number of Te MEE cycles	1	3	3	3	3	2
τ in 10^{-7} torr.s	2	3.6	3.9	5.7	6	16
SL period in nm	1.7	2.5	1.7	2.5	1.7	2.8
Number of periods	100	100	100	250	100	120
Te concentration from SIMS (XRD) in %	0.1 (-)	0.2 (-)	0.3 (0.1)	0.3 (0.2)	0.5 (0.3)	3.2 (2.6)

Figure 1.
(a)

Figure 2.

Norm. Intensity (arb. units)

(a)

(b)

Norm. Intensity (arb. units)

Figure 3.

Figure 4.

Figure 5.

Figure 6
(a)

(b)

Figure 7.

Figure 8.

Figure 9.