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Self-organized CdSe/ZnSe quantum dots on a ZnSe (1 1 1)A surface

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Abstract

Self-organized CdSe quantum dots (SQDs) were grown by atomic layer epitaxy (ALE). As a buffer layer we used the nearly atomically flat surface of thin (1 1 1)A ZnSe layers grown on (1 1 1)A GaAs. In this special system we find, due to the enhanced surface diffusion, formation of coherently strained islands (coherent Stranski–Krastanow islanding) already well below the critical thickness (~ 3 monolayers) of CdSe on ZnSe. An increase in the material deposition leads to an increase in the density of the dots rather than a change in average base diameter (47 ± 5 nm). The strongly blue shifted emission energy of typically 2.3 eV corresponds to an ZnCdSe alloy with approximately 50% of Zn. Micro-Auger measurements were used to determine the wetting layer thickness.

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1. Introduction

For an optimized fabrication of zero dimensional devices for future optoelectronic applications it is vital to find ways for a self-organized, defect free growth to obtain high quality structures. In the case of InAs on GaAs, growth of self-assembled low dimensional structures is well established by now [1] and the first quantum dot (QD) laser structures have already been fabricated.

One system closely related to InAs/GaAs in view of lattice mismatch and band gap difference is CdSe/ZnSe, which would be the ideal material to cover the green–blue visible spectral range. In the first report about this material system Xin et al. [2] observed that CdSe islands formed at a deposition close to the critical thickness of CdSe on (1 0 0) ZnSe (~3 monolayers (ML)) at increased substrate temperatures of 350°C. At low temperatures a broad luminescence peak was observed at 2.3 eV and a much smaller feature was initially attributed to the wetting layer. This has been revised to come from the Y-transition commonly observed in ZnSe [3]. However, an emission from the wetting layer has been observed in CdSe QD samples grown

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on the (1 1 0) surface [4]. QDs were formed at a nominal deposition of more than 3 ML on top of the relaxing layer (wetting layer ~3 ML) at a substrate temperature as low as 250°C (conventional Stranski–Krastanow growth).

In our study we have grown CdSe QDs onto (1 1 1)A ZnSe buffer layers. This system was chosen since for buffer layers in the thickness range of 30–50 nm a nearly atomically smooth surface could be achieved (see Ref. [5]), giving a rather high surface diffusion length of adatoms of more than 1 μm. We will show that in this system dots of similar size, shape and properties as in the above cited cases are formed with only a thin wetting layer. The dot formation occurs already well below the nominal critical thickness as compared to the coherent Stranski–Krastanow (SK) growth mode, which is observed in the semiconductor system Ge on Si [6] and InAs on GaAs [1].

2. Experimental procedure

Thin (30–50 nm) ZnSe buffer layers were directly deposited onto thermally deoxidized, epi-ready GaAs (1 1 1)A substrates by molecular beam epitaxy (MBE). The substrate temperature was 300°C. Directly after the ZnSe growth start, the RHEED (Reflection High Energy Electron Diffraction) was streaky two dimensional (2D) and the brightness of the specular spot increased indicating a smoothing of the surface immediately after the growth start. The Zn/Se flux was chosen to be stoichiometric, giving a mixed $(2\times1)/c(2\times2)$ RHEED pattern on (1 0 0) oriented substrates and a low growth rate of 150 nm/h, which corresponds to 50 nm/h for the (1 1 1)A orientation due to the reduced bond density on the surface.

The buffer thickness was chosen to be 30 nm since on thicker layers the formation of ZnSe pyramid and dot like structures was observed (details are given elsewhere [5]). However, the surface could be prepared nearly atomically flat over a long range for thin buffer layers. Unlike the standard (1 0 0)-surface which tends to have a surface undulation of typically 2 nm with a frequency in the range of 1/50–1/100 nm (compare also Ref. [7]), the surface of the (1 1 1)A ZnSe buffer layer shows a much slower modulation corresponding to less than 1 nm per 0.5–1 μm.

The CdSe SQDs were deposited by means of atomic layer epitaxy (ALE) at 300°C substrate temperature by exposing the substrate alternately to Cd and Se with a 10 s interruption after each half cycle. The dwell time was chosen to be 2 min to give adatoms sufficient time to occupy favorable sites.

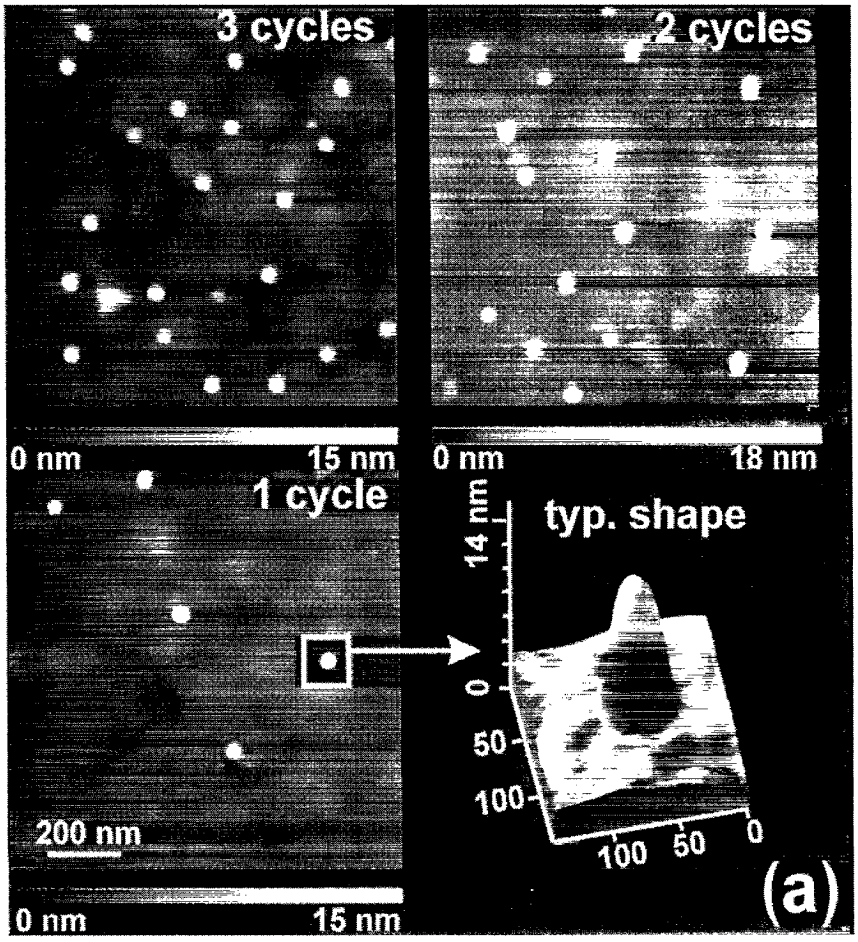
Uncapped samples were measured immediately after growth (< 1 h) in an ex situ atomic force microscope (AFM). Capped and uncapped samples were examined within one day by photoluminescence (PL) (325 nm HeCd excitation). Strong degradation occurs due to Ostwald ripening in uncapped dots [2] and, as we found, a thin capping of 10–12 nm only slows the ripening process by a factor of about 4. To prevent this ripening some samples were stored at −2°C [3]. No difference in the ripening was observed for storage in air and under vacuum.

Micro-Auger electron spectroscopy (AES) measurements were performed ex situ using an emission current of 6×10^{-8} A and an acceleration voltage of 5 kV. To prevent charge-up, the non-conducting samples were studied at an incidence angle of 30°. The system resolution is of the order of 100 nm and a typical 2×2 μm^2 area scan takes 2 h.

3. Results

The (1 1 1)A oriented surface has the lowest possible surface bond density of all orientations and corresponds to the least reactive surface. Together with the reduced density of surface nucleation centers on the nearly atomically smooth surface, the diffusion of adatoms could be strongly enhanced. In this system we observe coherently strained island formation already at a deposition well below the nominal critical thickness of CdSe on ZnSe (~3 ML).

To study the dot formation, we have fabricated samples with 1–5 ALE cycles of CdSe deposition. It is known from RHEED oscillations that for (1 0 0) oriented CdTe, one ALE cycle corresponds to the growth of 1/2 ML [8]. We have observed a similar behaviour of the RHEED when growing CdSe on (1 0 0) ZnSe, pointing to the same deposition rate.



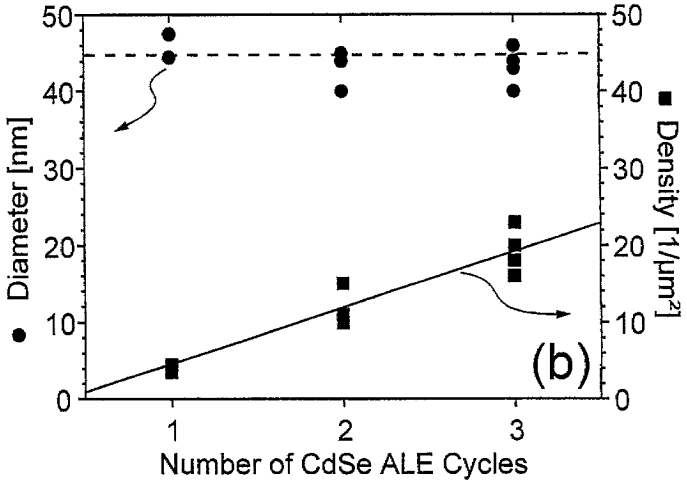


Fig. 1. (a) AFM scans for varying nominal CdSe layer thicknesses. (b) Plot of dot sizes and densities vs. number of ALE cycles.

Since in the case of the (1 1 1)A surface no pronounced RHEED oscillations were observed, the deposition rate is not known.

For a deposition of 3 ALE cycles of CdSe, we observed reproducibly the formation of rather uniform round shaped dots with a density of about 20 μm^{-2}. Their average base diameter is 47 ± 5 nm and the height is typically 19 ± 1% of that value. These properties are quite similar to the dots grown by Xin et al. [2] on (1 0 0) substrates using conventional MBE deposition of about 2.5 ML of CdSe. What is quite striking in our system is that by reducing the number of applied ALE cycles not the size but only the density of the dots changes. This is a direct indication of the coherent Stranski-Krastanow islanding, see Fig. 1a and Fig. 1b.

Opposite to the conventional SK growth mode where above a critical thickness the total energy is minimized by forming isolated thick islands in which the strain is relaxed by interfacial misfit dislocations, in the coherent SK mode coherently strained, dislocation free islands are formed, for some systems already below the critical thickness. Coherently strained islanding is based on the fact that prior to dislocation introduction the energy minimization can occur through a finite elastic deformation of the underlying interface. Previously, this has been directly observed in the semiconductor systems: Ge/Si [6] and InAs/GaAs [1].

In the case of only one cycle deposited, we observed a density of approx. 4–5 dots/μm^2, which implies that the surface mean free path should be of the order of 1 μm. The density for deposition below a critical coverage is linearly correlated with the number of applied ALE cycles, Fig. 1b, indicating a homogeneous nucleation of the islands corresponding to the average mean free path of surface adatoms. The critical coverage should be of the order of the nominal critical thickness (i.e. ~3 ML for CdSe/ZnSe) and in fact we have not yet succeeded in the growth of similar types of dots for 4 or 5 ALE cycles.

A statistic for the dot formation is given in Fig. 2. Dots are stable under growth conditions, however, under storage at room temperature a strong Ostwald ripening occurs and the distributions are broadened and the PL emission from the dots is quenched (results given elsewhere [5]).

In Fig. 3 the generally observed PL emission energies are plotted versus the number of applied ALE cycles. For the 2 and 3 ALE cycles the emission energy is in the vicinity of 2.3 eV. The typical line width varies between 150 and 300 meV for different samples. It has been pointed out [2,9] that alloying with ZnSe may be responsible for the rather blue shifted and broadened emission of the CdSe QDs. In fact, the emission energies suggest a Zn concentration of the order of 50%.

For a 3 ALE cycle sample with an average dot density of 17 μm^{-2} we have measured space resolved Micro-AES, which is given in Fig. 4. Fig. 4a shows the averaged AES spectrum. Considering the varying system sensitivity for the different elements and a penetration depth of about 3 MLs (molecular) [10], the observed Cd signal corresponds rather well to a surface coverage by dots of 2–3% as observed by AFM, indicating that the wetting layer

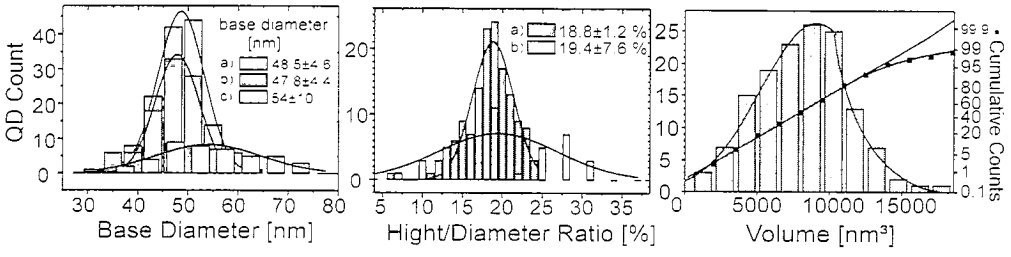


Fig. 2. Statistics for CdSe dot structures: *left*: base diameter (a) sum of 5 different samples with 1–3 ALE cycles deposited, (b) single 3 cycle sample, (c) after storage for 3 days at room temperature; *center*: height/diameter ratio for (a) fresh and (b) 3 days old samples; *right*: distribution of volumes: the left side follows a Gaussian distribution, while the right side corresponding to larger volumes declines more rapidly.

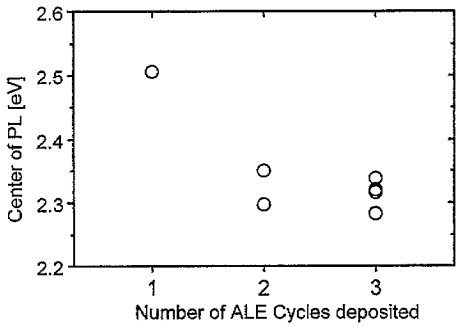


Fig. 3. Typically observed center of PL emission for CdSe QDs on (1 1 1)A ZnSe.

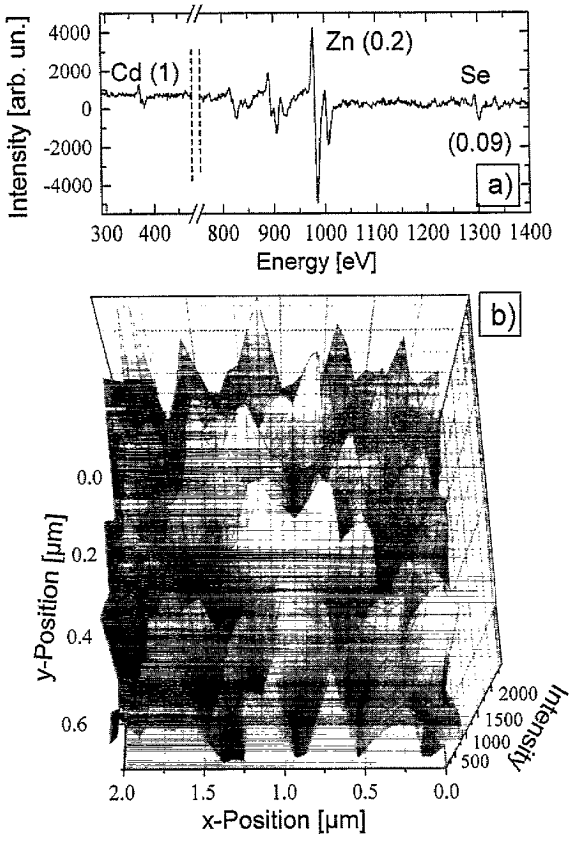


Fig. 4. Auger electron measurements for a 17 dots/μm^2 sample: (a) space averaged signal, the sensitivity factors for the AES system are given in brackets and (b) space resolved scan of the peak–peak intensity of the Cd-signal showing a strong modulation due to a higher Cd-signal from the QDs.

formed must be rather thin. In fact, the space resolved measurements clearly show a strong variation of the Cd signal and the wetting layer can be estimated to be 1 ML with a Cd concentration of approx. 30%. However, one has to be careful about this result, since the electron beam interaction with the sample surface leads to a faster ripening of the QDs and the sample measured in this case showed a reduced density of dots of 7 μm^{-2} and a broadened size distribution after 6 h of measurement. The Cd signal shown was obtained from the fresh sample.

4. Conclusion

We have demonstrated that the formation of CdSe based QDs on a (1 1 1)A ZnSe surface occurs in the coherent Stranski–Krastanow growth mode already well below the nominal critical thickness (~3 ML) of CdSe on ZnSe due to a strongly enhanced surface diffusion length. The optical properties of the dots point to alloy formation with ZnSe. The wetting layer observed from our structures seems to consist of only 1 ML with a Cd concentration of about 30%.

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