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Properties and self-organization of CdSe:S quantum islands grown with a cadmium sulfide compound source

E. Kurtz[a,*], M. Schmidt[a], M. Baldauf[a], S. Wachter[a], M. Grün[a], D. Litvinov[b], S.K. Hong[c], J.X. Shen[d], T. Yao[c], D. Gerthsen[b], H. Kalt[a], C. Klingshirn[a]

[a]*Institut für Angewandte Physik, Universität Karlsruhe, D-76128 Karlsruhe, Germany*
[b]*Labor für Elektronenmikroskopie, Universität Karlsruhe, D-76128 Karlsruhe, Germany*
[c]*Institute of Materials Research, Tohoku University, 980-77 Sendai, Japan*
[d]*RISM, Tohoku University, 980-77 Sendai, Japan*

Abstract

We demonstrate a new technique to grow high-quality CdSe quantum films and islands with a very small sulfur contamination by using a cadmium sulfide compound source as Cd supply and additional Se flux. By monitoring the lattice constant with reflection high-energy electron diffraction, it is shown that the sulfur is almost completely substituted by Se and CdSe with a contamination below 5% sulfur is formed. The quantum structures obtained by the new method are generally of higher quality than those obtained by more conventional growth methods using elemental sources, even if migration enhanced methods were employed. With a brief growth interruption or post-growth annealing step the initially smooth CdSe layer can be reorganized into islands. The duration of this step as well as the initial amount of deposition allows a rather good control over the island formation. A strongly enhanced growth rate is observed for the first few monolayers of the ZnSe capping layer, which indicates a partial dissolution of the islands in the ZnSe growth front and Cd segregation.

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Keywords: II–VI; CdSe; CdS; Self-organized Quantum Dots; MBE; Micro-Photoluminescence; RHEED; TEM

1. Introduction

Despite the confusion, which early results of atomic force microscopy on open CdSe quantum structures caused (see comments in Ref. [1]), the existance of coherently strained CdSe quantum islands has been proved using transmission electron microscopy (TEM) by various groups [2–4]. However, the formation process as well as a reliable control over the island formation is still an important issue in the II–VI related research, since it differs from the standard Stranski–Krastanow islanding observed in the system InAs/GaAs. In this paper we introduce a novel technique to obtain CdSe quantum islands with a very low sulfide contamination using a CdS compound source instead of the commonly applied Cd elemental source.

* Corresponding author. Tel.: + 49-7216086476; fax: + 49-7216087031.

E-mail address: kurtz@ap-pc513b.physik.uni-karlsruhe.de (E. Kurtz).

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2. Experiment and results

Additionally to the more traditional way of growing CdSe with Cd and Se elemental sources (see Ref. [4]), we have also explored the possibility of using a cadmium sulfide compound as Cd source. Exposure of the growing surface to CdS and additional Se flux leads to an exchange reaction between the sulfide and the selenium at the given growth conditions. Monitoring the RHEED (reflection high-energy electron diffraction) rod positions during growth we can obtain the relaxation of the lattice parameter, which approaches that of CdSe rather than CdS, Fig. 1a. From the data the sulfur contamination can be estimated to be well below 5%. Further evidence is given by photoluminescence (PL) and reflectance measurements which indicate a band edge at around 1.77 eV, corresponding to $\sim 1\%$ S. A more detailed chemical analysis is under way.

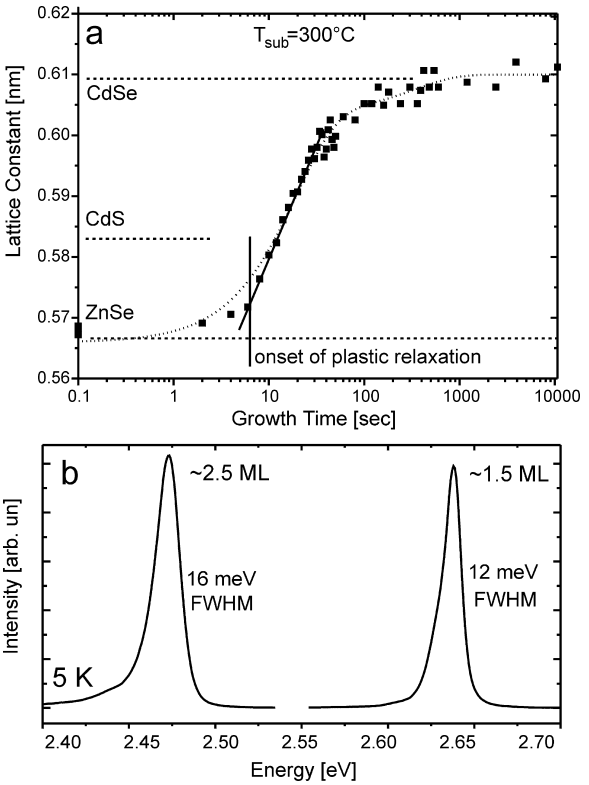

Fig. 1. (a) Relaxation of the lattice constant for growth of CdSe:S using CdS compound and Se at a growth rate of approx. 0.5 monolayers/s. The lattice constant approaches the value expected for CdSe at the given growth temperature. (b) Photoluminescence spectra at 5 K for two QWs grown with CdS and Se. The QW thicknesses were obtained from RHEED intensity oscillations.

In ZnSe embedded quantum structures obtained with this method are of high optical quality and the observation of pronounced RHEED oscillations allows a very accurate determination of the deposited layer thickness. Furthermore, regarding the high band gap difference the quantum wells exhibit a very narrow PL line width, as shown in Fig. 1b. This is an indication of the superb homogeneity of the QWs as in both cases depicted the avarage thickness fluctuation should be about or even less than $\frac{1}{20}$ monolayer. Our structures also do not show the typical behavior of laterally strong localized excitons, i.e. a pronounced blue shift of the PL in the temperature range 30–120 K, which is usually observed in the temperature-dependent PL of rough quantum wells [5].

Submission of such CdSe:S layers with thicknesses (typ. 1.5–4 monolayers) below or slightly above the critical thickness of CdSe (~ 3 monolayers) to either a growth interrupt under Se flux or a brief annealing step initiates the reconfiguration of the surface. The CdSe:S draws together to form coherently strained islands, thus relaxing the strain caused by the lattice misfit ($\sim 7\%$) to the ZnSe buffer. The average size of the islands strongly depends on the initial deposition and the duration of the annealing step. Small, completely defect-free islands are obtained for very short growth interrupts of 10–20 s after CdSe deposition. Under annealing, the RHEED specular spot intensity is almost not reduced while with increasing annealing time very pronounced 3D transmission spots indicate the island formation on an otherwise smooth surface. The lattice constant approaches gradually 0.61 ± 0.01 nm which corresponds to fully relaxed CdSe at 300°C. This also demonstrates that during the annealing step very little intermixing occurs. However, intermixing is known to occur in capped structures [6] and has been suggested by various groups to explain their optical findings, e.g. [7,8].

As we have previously shown [4,7], the capping of the island structures with ZnSe leads to a very quick recovery of a more two dimensional, streaky

RHEED pattern. A careful monitoring of the RHEED intensity oscillations at the onset of the cap growth, Fig. 2, reveals a considerably increased growth rate of the ZnSe cap ($\sim$350 nm/h instead of 250 nm/h). Typically, within 5–15 monolayers it approaches the growth rate of the buffer layer, depending on the island structure and total thickness of the underlying CdSe. A material burst after shutter opening can be excluded and a pure filling in of the space between the islands cannot account for such a large increase as the island density is too low. Thus, this behavior combined with the quick recovery of the streaky RHEED pattern is a strong evidence that the CdSe islands previously formed partially dissolve in the growing ZnSe cap and Cd atoms are carried along the growth front adding to the growth rate observed by RHEED. The presence of a segregation effect in CdSe-based quantum structures was previously shown by Rosenauer et al. [6]. This implies that the capped CdSe islands that are observed in the TEM are considerably different from the initially deposited ones. The lateral shape of the islands always appears non-faceted and rounded, while the strain field usually has a squarish shape in the growth plane with the diagonals pointing along the various $\langle 1\,1\,0\rangle$ directions (see also Ref. [4]), depending on the observation conditions. The plan view TEM pictures of an area of $200 \times 200\,\mathrm{nm}^2$ for two island structures are shown in Fig. 3, the samples will be referred to as A, Fig. 3a, and B, Fig. 3b.

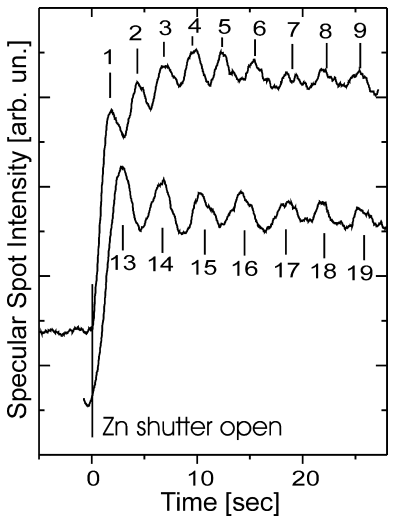

Fig. 2. RHEED oscillation observed at the beginning of the ZnSe cap growth. The initially enhanced growth rate of 350 nm/h reaches after about 15 monolayers the intended growth rate of 250 nm/h. The monolayers deposited are sequentially numbered. After 12 monolayers a brief growth interrupt was introduced to recover the RHEED intensity oscillations, the curves have been shifted for clarity.

Sample A was submitted only to a brief growth interrupt of a few seconds after the CdSe deposition. The structure shows small, very evenly sized quantum islands with a maximum diameter of approximately $\sim$5 nm and a density of the order of $10^{10}\,\mathrm{cm}^{-2}$, the nominal deposition was 2 monolayers CdSe:S. In the case of sample B, a similar layer was deposited, however, it was annealed prior to cap growth at 320°C for 5 min. The total procedure considering warming and cooling periods lasted about 10 min. The structure contains a few small islands similar to those in sample A. Otherwise coalesced, plastically relaxed and possibly alloyed structures appear. The uniformity is strongly inferior to that of sample A which had only a brief growth interrupt. The larger amount of material stored in the large islands of sample B implies a reduced wetting layer thickness as compared to sample A. In any case, the annealing leads to an increasing red shift of the PL emission with annealing duration, cf. Fig. 4 and Ref. [4]. The average island size which contributes to the radiative emission increases while the size distribution broadens with annealing time. For samples with a very long annealing time, typ. 10 min, the majority of island structures are relaxed by misfit dislocations and the PL intensity is considerably reduced by defect related non-radiative recombination centers.

The insets of Fig. 4a and b show the results of micro-PL for samples A and B, respectively.

The samples were homogeneously illuminated using the 351 nm line of an Argon ion laser with an intensity of approx. $8\,\mathrm{mW/mm}^2$. The spatial resolution was approximately 1 μm. Both samples show clearly resolved single-dot emission lines. Furthermore, because of the on the on average larger island size, the PL emission of the longer annealed sample B, Fig. 4b, is considerably broadened and red-shifted compared to the more homogeneous distribution of the unannealed sample A, Fig. 4a. In

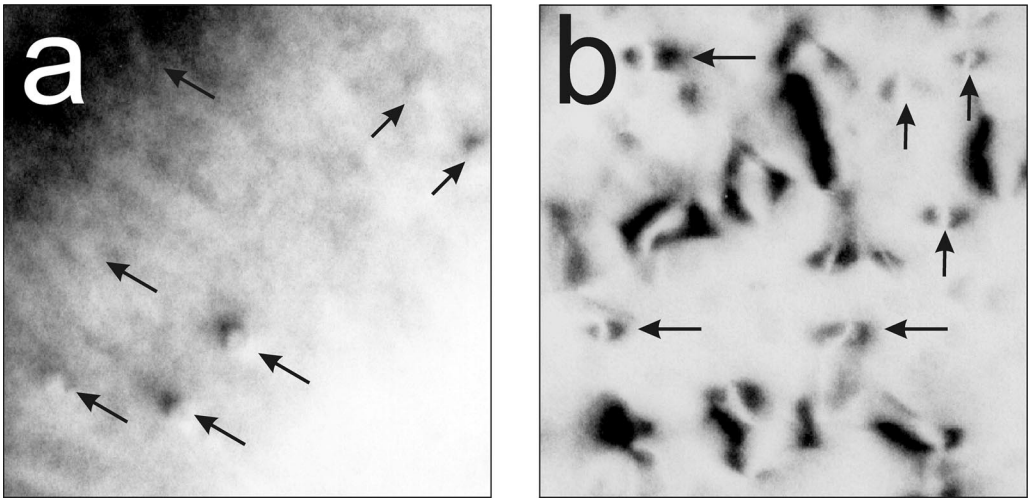

Fig. 3. (2 2 0) bright field plan view TEM images taken of an area of $200 \times 200\,nm^2$ of: (a) sample A grown with CdS compound, nominal deposition 2 monolayers, with a brief growth interrupt under Se flux; (b) sample B grown similar to sample A but annealed for 5 min at $\sim 320^{\circ}C$.

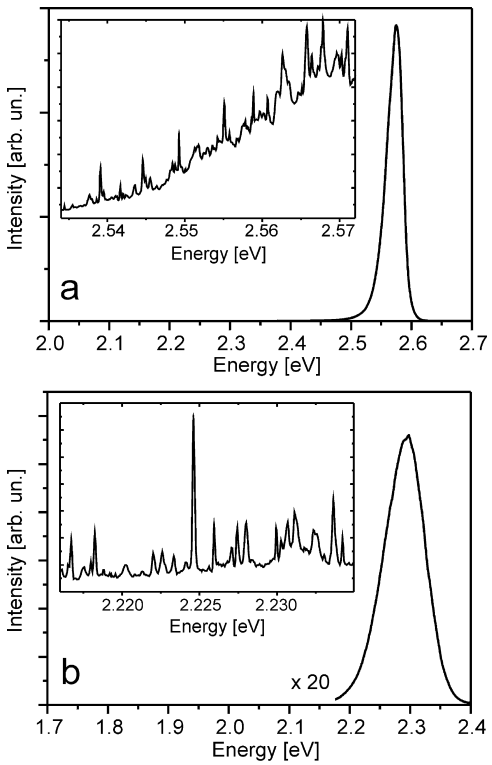

Fig. 4. (a) Macro-PL of sample A, the inset shows resolved single-dot emission lines from micro-PL. (b) macro-PL of sample B. The inset shows resolved lines from micro-PL ($\sim 1\,\mu m$ resolution).

case of sample A, the islands are small enough ($< 5\,nm$) to show sufficient 3D confinement and the single-dot emission lines appear on the low-energy side of the wetting layer emission. In case of sample B no evidence of a wetting layer was found in the PL spectra.

In conclusion, growing CdSe-related quantum structures using a cadmium sulfide compound source provides a good tool to improve the optical and structural properties of deep quantum wells. The rather controlled way in which quantum island formation can be initiated allows a more detailed study of the process in the future.

Acknowledgements

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