Investigations on the Stranski–Krastanow growth of CdSe quantum dots

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We have investigated the growth kinetics of the self-assembled formation of coherently strained CdSe islands. We have found that two distinctly different types of islands are formed in succession. Analyzing the density distribution function of the two dominating size classes of islands, we show that islands of an average diameter of about 16 nm (type B islands) are correlated with a phase transition via a Stranski–Krastanow growth process. The other islands with a diameter of less than 10 nm (type A islands) is formed during the growth of the first 2 ML. At a coverage of about 3.1 ML CdSe stacking faults appear, indicating the beginning of the plastic relaxation of the quantum dot structure. © *2000 American Institute of Physics.* [S0003-6951(00)00804-4]

The growth of self-assembled quantum dots (QDs) using molecular beam epitaxy (MBE) or metalorganic chemical vapor deposition is of considerable current interest as it offers the possibility for low-threshold current optoelectronic devices. Self-assembled growth of CdSe islands has been reported recently.[1,2] A wide range of substrate temperatures between 315[3] and 450 °C [1] was used depositing between 1.5[4] and 10 ML[5] CdSe on ZnSe. However, reliable data necessary for a controlled formation of CdSe QD structures are not fully available presently. This concerns, besides others, the evidence for a Stranski–Krastanow growth mechanism and information about the structural and chemical evolution of the CdSe–ZnSe QD structure. The focus of our letter is to investigate the kinetic reasons for the formation of different size classes of islands, analyzing the island density p_i as a function of the CdSe coverage Θ. Related to this analysis, the stability range for the formation of dislocation free QD structures is determined.

Our experiments were performed in a two-chamber MBE system, equipped with elemental sources of Zn, Cd, and Se in the II–VI chamber and Ga and As in the III–V chamber. The growth process was continuously controlled by reflection high energy electron diffraction (RHEED). The ZnSe buffer layers of 45 nm thickness were grown on exactly (001) oriented GaAs substrates at a substrate temperature of about 305 °C. The CdSe growth was performed at 260 and 340 °C, respectively. Recording clear resolved RHEED oscillations in combination with phase-locked epitaxy, the CdSe coverage could be reproduced with an accuracy of about 0.2 ML. The ZnSe cap layers were grown at 260 °C with a thickness of about 45 nm, to ensure that the complete structure is pseudomorphically grown. The transmission electron microscopy (TEM) investigations were performed with a Philips CM 200 FEG/ST microscope with an electron energy of 200 keV. The island density was analyzed using plan-view samples. High-resolution cross-section TEM combined with the chemical evaluation of lattice fringe images (CELFA)[6,7] techniques were carried out to determine the Cd distribution at the ZnSe–CdSe–ZnSe interface. The photoluminescence (PL) investigations were performed using the 325 nm line of a continuous wave He–Cd laser with an output power of about 15 mW as excitation source.

The CdSe QD samples grown in this study show typical structural features, which are depicted in Fig. 1. The figure illustrates a plan-view image (a) of a sample consisting of 3.1 ML CdSe embedded between 45 nm ZnSe. Two different types of islands can clearly be distinguished, large islands
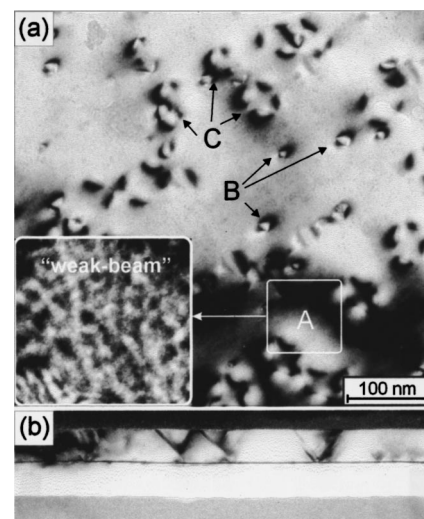

FIG. 1. TEM plan-view image (a) and TEM cross-section image (b) of a sample containing 3.1 ML CdSe. Large B islands are marked by arrows. The C features represent coalesced islands of the B type. The small-scale speckle contrast in the inset of (a) which appears under weak-beam conditions, is induced by A islands with sizes below 10 nm. The dark-field TEM cross-section image (b) shows some stacking faults, which extend through the ZnSe capping layer.

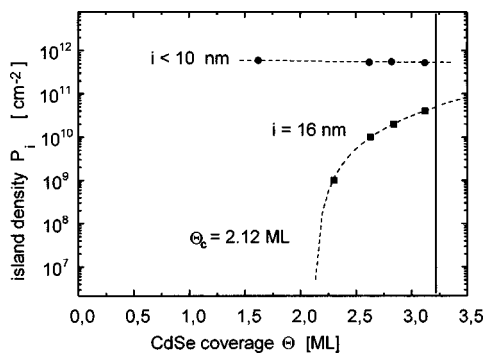[a]Electronic mail: schikora@uni-paderborn.de

FIG. 2. Density (p_i) dependence of two different size classes ($i<10$ nm, $i\cong16$ nm) of CdSe islands plotted vs the total coverage (Θ) of CdSe. Both selected size classes are dominating the island distribution obtained from plane-view high resolution TEM experiments.
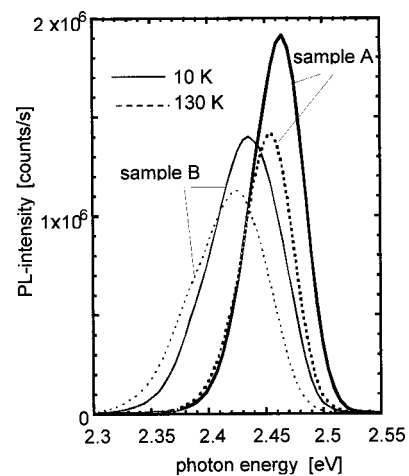

FIG. 3. PL spectra of two QD samples each containing 2.8 ML CdSe deposited at 260 °C and capped with 45 nm ZnSe. The CdSe layer in sample A was grown with MEE, whereas the CdSe overlayer in sample B was grown using MBE with a growth rate of about 0.1 ML/s. The dotted lines denote the PL spectra measured at 130 K.

(examples indicated by arrows) with a diameter of about 16 nm$\pm$5 nm (type B islands), and small islands with diameters below 10 nm (type A islands). The diameters of the type B islands were determined by a precise measurement of the extension of the strain-contrast feature perpendicular to the imaging vector $\vec{g}=(220)$, which implies that the actual size of the appropriate islands is somewhat smaller. The type A islands are identified by a typical small-scale speckle contrast, which is clearly visible under weak-beam conditions, as shown in the inset of Fig. 1(a). The extended dark/bright C features in Fig. 1(a) correspond to coalesced B islands. Figure 1(b) shows a dark-field cross-section image of the sample of 3.1 ML CdSe coverage. Obviously no misfit dislocations were formed at this CdSe thickness, but some stacking faults can be observed, which extend through the cap layer. However, the stacking fault density is too low to provide a significant misfit relaxation. To compare this data with the relaxation of a CdSe quantum well layer, the damping of the RHEED oscillations was studied in dependence on the growth temperature. The RHEED oscillations were recorded during the growth of CdSe on ZnSe (001), at substrate temperatures of about 260 and 340 °C, respectively. In both cases we have observed a rapid damping of the RHEED intensity after the third maximum, which we attribute to the onset of plastic relaxation in the layer structure. In the low temperature regime the damping occurs at $h_c=3.7+/-0.1$ ML, whereas at 340 °C substrate temperature the RHEED oscillations disappear already at $h_c=3.1+/-0.1$ ML. We explain the delayed oscillation damping in the low temperature growth by a hindered movement of partial dislocations and misfit dislocations due to the lower thermal energy in the system. This confirms the results of the TEM cross-section analysis of the QD structure shown in Fig. 1(b) and indicates that coherently strained CdSe islands can be grown at least to a CdSe coverage of about 3.1 ML.

To study the origin of the two dominating size classes observed, different samples with CdSe coverages of 1.6, 2.2, 2.6, 2.8, and 3.1 ML were grown under identical conditions. The island density and size distribution were determined by plane-view TEM investigations. The results are shown in Fig. 2. It is obvious that the density of the type B islands strongly depends on the CdSe coverage Θ. The steep increase of the island density of the type B islands over many orders of magnitude, when a threshold value is exceeded, is one of the

characteristic features of the Stranski–Krastanow (SK) growth process. Furthermore, we have found that a saturation size exists for the type B islands which is of about 16 $+/-5$ nm, independent of the amount of excess CdSe deposited. This is an additional indication for the SK nature of these clusters. Therefore, we assign the type B islands to a SK growth process. In contrast to that, the top curve in Fig. 2 shows that the type A island density is almost invariant with respect to the CdSe coverage. The formation of this island type starts already when the first monolayer is deposited. Our CELFA investigations reveal that the type A islands are located within the wetting layer. We have found that the composition of the type A islands and the surrounding wetting layer show a correlated dependence on the amount of CdSe deposited. The ratio between the Cd concentration in the type A islands and in the wetting layer is of about two for all CdSe coverages varied. From these facts, we conclude that type A clusters are formed during the wetting layer growth most probably due to strain-driven surface kinetics near the island edges. The analysis of the island density distribution function $p_i(\Theta)$ is well suited to extract also information about critical parameters of a phase transition. The data of the B islands were fitted by a function of the form $p_i=p_0(\Theta-\Theta_{\mathrm{crit}})^\alpha$ where Θ_{crit} is the critical wetting layer thickness. Using a p_0 value of 6×10^{10} cm^{-2} and an exponent of $\alpha=2.08$ we extrapolate a critical wetting layer thickness of CdSe on ZnSe of about 2.1 ML. A similar approach was reported earlier for InAs–GaAs,[8] experimentally confirmed by atomic force microscopy studies.[9]

To get more information about the origin of the type A islands, PL investigations were performed. In Fig. 3 the PL spectra of two QD samples are compared, each of them containing 2.8 ML CdSe deposited at 260 °C and capped after a short growth interruption with 45 nm ZnSe. The CdSe layer in sample A was grown using migration enhanced epitaxy (MEE), whereas the CdSe overlayer in sample B was grown by conventional MBE with a growth rate of about 0.1 ML/s. It can be recognized from Fig. 3 that by varying the growth mode alone, the size of the QDs and their size distribution is significantly changed. The spectral halfwidth of sample A is

of about 46.3 meV, whereas the halfwidth of sample B is of about 62.5 meV, indicating a change of the size distribution of the QDs in the structure. The peak emission energy is shifted from 2.46 eV (sample A) to 2.43 eV (sample B) due to the variation of the QD size. The temperature dependence of the PL of both samples is characteristic for the behavior of localized excitons. That properties indicate additionally that the small A clusters cannot be correlated with a SK process, which is obviously suppressed at the low growth temperature selected. The saturation size of SK islands is mainly determined by strain and cannot be influenced by a variation of the growth mode alone. We have found that the A islands are acting as QDs having a high quantization and exhibiting an emission energy of about 2.4–2.7 eV, which is significantly blueshifted with respect to the emission of the B islands of about 2.3 eV.[10]

In conclusion we have investigated the stability range for the formation of dislocation free CdSe islands. We have found that at a coverage of about 3.1 ML CdSe stacking faults appear, indicating the beginning of the plastic relaxation of the structure. We have studied the kinetic reasons for the formation of different size classes of islands, analyzing the island density distribution function $p_i(\Theta)$. This analysis clearly shows that type B islands of an average diameter of about $16+/-5$ nm are correlated with the SK growth. The A islands with a diameter of less than 10 nm and a density of about 10^{11} cm^{-2}, which are generating a bimodal QD-size distribution, are formed during the growth of the first 2 ML most probably due to strain driven surface kinetics near the island edges. The A islands are influencing the optical properties of the CdSe QD structure and may act as precursor seeds for the growth of the B islands because they appear before type B islands are formed.

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