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Journal of Crystal Growth 214/215 (2000) 698–702

JOURNAL OF CRYSTAL GROWTH

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Investigations on the formation kinetics of CdSe quantum dots

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Abstract

High- resolution TEM investigations reveal that CdSe quantum dot samples are often characterised by the existence of two different types of islands, which form a bimodal size distribution. Analysing the density distribution function of the two dominating size classes of islands, we show that islands of an average size of about 16 nm (type B islands) are clearly correlated with a phase transition via a Stranski–Krastanow growth process. The smaller clusters with a size of less than 10 nm (type A islands) are formed during the growth of the wetting layer, bevor the critical wetting layer thickness is reached. The stability range for the formation of dislocation-free SK islands was experimentally determined. We discuss gain measurements and stimulated emission of vertically stacked CdSe–ZnSe quantum dot structures which were grown on tilted GaAs substrates.

PACS: 73.20.D; 68.55.B; 61.14.H; 78.66.Hf; 71.35

Keywords: CdSe; Self-assembled quantum dots; MBE; RHEED; TEM; Gain

1. Introduction

The growth of self-assembled quantum dots (QDs) using molecular-beam epitaxy (MBE) or metal-organic chemical vapour deposition (MOCVD) is of considerable current interest as it offers the possibility for low-threshold current opto-electronic devices. Self-assembled growth of CdSe islands has been reported [1,2] for a wide range of substrate temperatures between 315°C [3,4] and 450°C [1] depositing between 1.5 [5] and 10 ML [6] CdSe on ZnSe. However, reliable data necessary for a controlled formation of CdSe quantum dot structures are difficult to obtain and not fully available presently. This concerns, besides others, in particular, the evidence for a Stranski–Krastanow growth mechanism, data about the critical wetting layer thickness and informations about the structural and chemical evolution of the CdSe–ZnSe QD structure. The focus of our paper is to investigate the kinetic reasons for the formation of different size classes of islands, analysing the island density p_i and the island composition x_i as a function of the CdSe coverage Θ. Related to this analysis, the influence of the interdiffusion on the quantum dot structures is discussed.

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0022-0248/00/$ - see front matter
PII: S0022-0248(00)00181-0

2. Experimental setup

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 were grown on exactly (0 0 1) oriented GaAs substrates at a substrate temperature of about 305°C. The CdSe was grown at 265°C and 340°C, respectively. 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 analysed using plan-view samples. Conventional and high-resolution cross-section TEM combined with the chemical evaluation of lattice fringe images (CELFA) techniques [7,8] were carried out to determine the Cd-distribution at the ZnSe–CdSe–ZnSe interface. The investigations of the optical gain have been performed in the edge geometry using a pulsed dye laser pumped by an excimer laser. The gain spectra were evaluated using the variable-stripe-length method [9].

3. Results and discussion

The CdSe quantum dot samples grown 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 (examples indicated by arrows) with extensions of 16 nm $\pm$ 5 nm (type B islands), and small islands with sizes below 10 nm (type A islands). 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 the Figs. 1(a) correspond to coalesced B-islands. Fig. 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

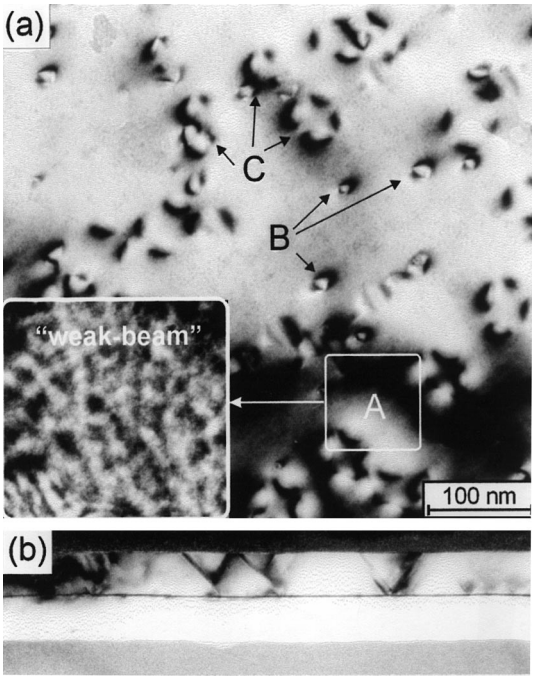

Fig. 1. TEM plan-view image (a) and TEM cross-section image (b) of a sample containing 3.1 ML CdSe.

stacking fault density is too low to provide a significant misfit relaxation. This 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 the size distribution were determined by plan-view TEM investigations. The results are shown in Fig. 2. We have found that the density of type B islands strongly depends on the CdSe coverage Θ. The steep increase of the island density of type B islands over many orders of magnitude, when the critical wetting layer thickness is exceeded, is one of the characteristic features of the Stranski–Krastanow growth process. Furthermore, we have found that a saturation size exists for type B islands which is of about 16 $\pm$ 5 nm, independent on the amount of excess CdSe deposited. This is an additional indication for the SK nature of these clusters. Therefore, we assign type B islands to a Stranski–Krastanow growth process. In contrast

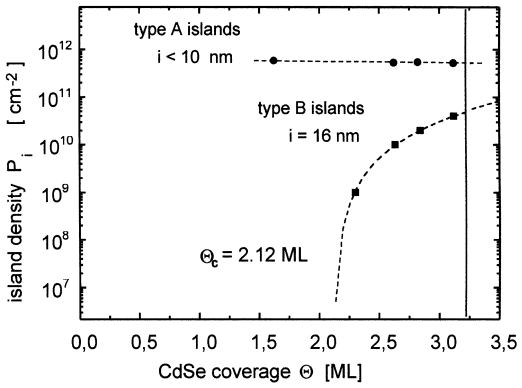

Fig. 2. Density (p_i) dependence of two different size classes (type A: $i < 10$ nm, type B: $i \cong 16$ nm) of CdSe islands plotted versus the total coverage (Θ) of CdSe.

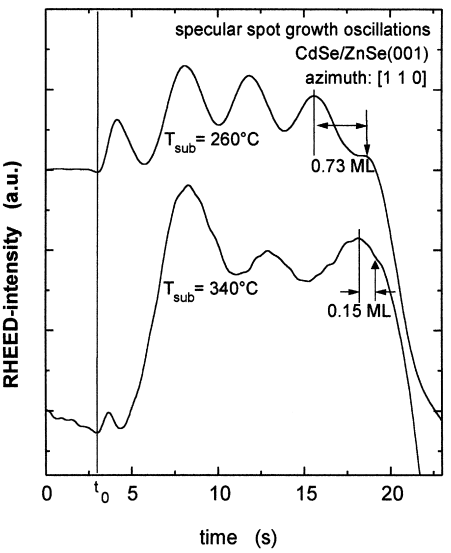

Fig. 3. RHEED intensity oscillations recorded at the specular spot position during the MBE growth of CdSe on ZnSe/GaAs substrates at different substrate temperatures.

to that, the top curve in Fig. 2 shows that type A island density is almost invariant with respect to the CdSe coverage. The formation of this island type starts alredy when the first monolayer is deposited. This clearly indicates another kinetic origin of the formation of these particular islands. Our CELFA-investigations reveal that type A islands are located within the wetting layer. We have found that the composition of type A islands and of the wetting layer shows a correlated dependence on the amount of CdSe deposited. The ratio between the Cd-concentration in type A islands and in the wetting layer is of about 2 for all CdSe coverages varied. From this facts, we conclude that type A clusters are formed during the wetting layer growth on top of large, flat 2D islands most probably due to strain-driven surface kinetics near the island edges. The resulting composite structure, consisting of large, flat 2D islands and small clusters on it, exhibits a rather specific exciton localisation potential. Similar features are well known in fractional-monolayer structures [10].

The data about the critical wetting layer thickness in CdSe–ZnSe reported so far are based entirely on PL measurements [1,3]. The analysis of the island distribution function $p_i(\Theta)$ is well suited to extract also informations about critical parameters of a phase transition. The data of the B-islands were fitted by a function of the form $p_i = p_0(\Theta - \Theta_{crit})^{\alpha}$ where Θ_{crit} is the critical wetting layer thickness. Using a p_0-value of $6 \times 10^{10}\,cm^{-2}$ 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 [11]. Fig. 3 shows RHEED oscillations of CdSe quantum wells grown on ZnSe (0 0 1), which were recorded at substrate temperatures of about 260°C (top curve) and 340°C, respectively (bottom curve). In both the cases we have observed a rapid damping of the RHEED intensity after the third maximum, which mainly indicates the onset of plastic relaxation in the layer structure. In the low-temperature regime the damping occurs at $h_c = 3.73 \pm 0.1$ ML whereas at 340°C substrate temperature the RHEED oscillations disappear already at $h_c = 3.15 \pm 0.1$ ML. We can conclude that at least up to the h_c-value of 3.15 ML coherently strained islands can be grown. Furthermore, the RHEED-oscillation damping reveals informations about the interdiffusion between CdSe and ZnSe. It is obvious, that no significant interdiffusion occurs during the growth stage recorded. An influence of interdiffusion would lead to a shift of the critical thickness to higher values, when the growth temperature is increased. Therefore, we assume that the strong interdiffusion observed in our quantum dot structures, which broadens the wetting layer

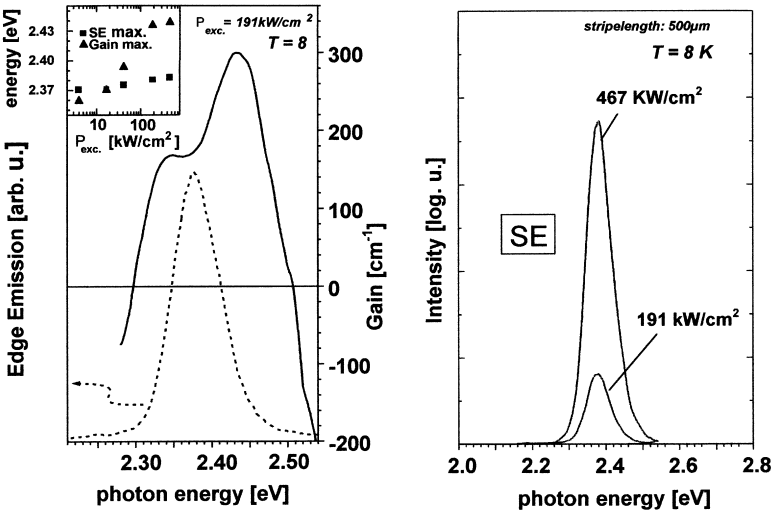

Fig. 4. Gain spectrum and stimulated emission (SE) obtained from a sample with a 10-fold stack of Stranski–Krastanow grown CdSe islands. The spectra were recorded for an excitation density well above the threshold.

from 2 up to 9 ML, must occur during the growth of the ZnSe cap-layer. Although the temperature selected for the ZnSe cap-layer growth of about 265°C was comparable low, the composition of the wetting layer and type A islands drastically changes. It is not clear at the moment, to what extent the morphology of the coherently strained SK islands is influenced by the capping process.

Considering the specific formation kinetics of types A and B islands, stacked quantum dot structures were grown on vicinal surfaces. The samples consist of a sequence of 2.8 ML CdSe capped with 12 nm ZnSe, which was 10 times stacked and overgrown finally with 45 nm ZnSe. A typically gain spectrum and the stimulated emission (SE) obtained from a sample with a 10-fold stack of CdSe islands is shown in Fig. 4. The most significant result is the appearance of a broad gain curve with a maximum value of $300\,cm^{-1}$. For highest applied excitation densities ($467\,kW/cm^2$) the gain maximum reached up to a value of $465\,cm^{-1}$. To reveal the gain mechanisms a comparison with the SE is necessary. Since the maximum of the gain was observed on the high-energy tail of the SE band and the density of type B islands is same in the $10^{10}\,cm^{-3}$ volume [4], the filling of states remains as the most reliable process contributing to the gain. This explanation was confirmed by the excitation density dependence of the gain and the SE (see inset in Fig. 4). Whereas at the threshold the gain was observed in the resonance of the SE, an increase of the excitation density lead to a slight blue shift of the SE accompanied by a broadening of the high-energy tail, and to an even more pronounced blue shift of the gain maximum.

4. Conclusions

We have investigated the kinetic reasons for the formation of different size classes of islands, analysing the island density distribution function $p_i(\Theta)$ and the island composition x_i as a function of the CdSe coverage Θ. This analysis clearly shows that type B islands of an average size of about 16 ± 5 nm are correlated with the Stranski–Krastanow growth. Type A islands are formed below the critical wetting layer thickness during the growth of the first monolayer on top of large, flat 2D islands most probably due to strain-driven surface kinetics near the island edges. We have shown that the quantum dot structure is significantly modified during the growth of the ZnSe cap layer. The gain spectrum and the stimulated emission (SE) obtained from a sample with a 10-fold stack of SK-grown CdSe islands on tilted GaAs substrates,

shows a gain curve with a maximum value of $300\,cm^{-1}$.

References

[1] F. Flack, N. Samarth, V. Nikitin, P.A. Crowell, J. Shin, D.D. Awschalom, Phys. Rev. B 54 (24) (1996) R17312.
[2] M. Strassburg, V. Kutzer, U.W. Pohl, A. Hoffmann, I. Broser, N.N. Ledentsov, D. Bimberg, A. Rosenauer, U. Fischer, D. Gerthsen, I.L. Krestnikov, M.V. Maximov, P.S. Krèpv, Zh.I. Alferov, Appl. Phys. Lett. 72 (8) (1998) 942.
[3] M. Rabe, M. Lowisch, F. Henneberger, J. Crystal Growth 184/185 (1998) 248.
[4] D. Schikora, S. Schwedhelm, D.J. As, K. Lischka, D. Litvinov, A. Rosenauer, D. Gerthsen, M. Strassburg, A. Hoffmann, D. Bimberg, Appl. Phys. Lett., 1999, in preparation.
[5] S.H. Xin, P.D. Wang, A. Yin, C. Kim, M. Dobrowolska, J.L. Merz, K. Furdyna, Appl. Phys. Lett. 69 (25) (1996) 3884.
[6] H.-C. Ko, Y. Kawakami, Sz. Fujita, Sg. Fujita, J. Crystal Growth 184/185 (1998) 283.
[7] A. Rosenauer, T. Remmele, D. Gerthsen, K. Tillmann, A. Förster, Optik 105 (1996) 99.
[8] A. Rosenauer, U. Fischer, D. Gerthsen, A. Förster, Ultramicroscopy 72 (1998) 121.
[9] C. Benoit a la Guillaume, J.M. Denber, F. Salvan, Phys. Rev. 177 (1969) 567.
[10] S. Ivanov, A.A. Toropov, S.V. Shubina, I.V. Sedova, A.A. Sitnikova, P.S. Kopev, Zh.I. Alferov, H.J. Lugauer, G. Reuscher, M. Keim, F. Fischer, A. Waag, G. Landwehr, Appl. Phys. Lett. 74 (4) (1999) 498.
[11] D. Leonhard, K. Pond, P.M. Petroff, Proceedings of the 22nd ICPS, Vancouver, Vol. 1, 1994, p. 648.