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Analysis of Quantum Dot Formation and Exciton Localisation in the (Zn, Cd) (S, Se) System

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The formation process and exciton localisation properties of CdSe/ZnSe quantum dot structures were studied. Pseudomorphically strained structures were exposed to a stationary sulphur vapour after the formation process of three-dimensional (3D) islands. Temperature dependent photoluminescence investigations confirm the increasing 2D-like character with increasing sulphur exposure times. The sulphur exposure had no impact on the island formation in partially relaxed structures.

Introduction The growth of self-assembled quantum dots (QDs) using molecular beam epitaxy (MBE) or metal-organic chemical vapour deposition (MOCVD) is of considerable interest as it offers the possibility for low-threshold-current opto-electronic devices for the green spectral range. Furthermore, such structures have the potential to study basic phenomena of quantum information processing. However, reliable data necessary for a controlled formation of well ordered arrays of CdSe QDs are difficult to obtain and not fully available presently.

As reported earlier [1], two distinctly different types of CdSe islands are formed in succession during the deposition of about 3 monolayers (ML) CdSe on ZnSe (001). From kinetic analysis we have concluded that above a critical threshold of about 2.1 ML the islands are formed by the Stranski-Krastanov (SK) growth process, which is thermodynamically controlled. To proof that, in this paper, we demonstrate for the first time the reversible nature of this particular growth mode transition. A similar approach has been reported earlier for the behaviour of InAs islands on GaAs [2]. The presence of deep localisation sites as provided by e.g. SK grown islands lead to a pronounced redshift of the emission wavelength with increasing temperature. As it was shown by temperature dependent and time delayed photoluminescence (PL) spectroscopy [3, 4], this redshift is caused by a lateral redistribution of excitons to deeper localisation sites.

Experimental Starting with a deposition of about 3 ML CdSe on 45 nm ZnSe, the formation of the 3D CdSe islands was controlled by reflection of high-energy electron diffraction (RHEED) measurements. After CdSe island formation the RHEED shows

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a spotty 3D reflection pattern, which is stable under a stationary overpressure of Se of about 3.6×10^{-7} mbar. Than the CdSe islands were exposed abruptly to a stationary sulphur vapour of about 3×10^{-7} mbar. After sulphur treatment the surface was capped with 45 nm ZnSe at 260 °C. The optical properties of the QDs were investigated by temperature dependent PL spectroscopy at temperatures between 5 and 200 K. The luminescence was excited by the 325 nm line of a HeCd laser and detected by a LN_2-cooled CCD camera attached to a 0.3 m single-grating spectrograph with a spectral resolution of 0.4 nm.

Results and Discussion Figure 1a shows the RHEED pattern of the initial structure of CdSe-3D islands, formed after deposition of about 3 ML CdSe and stabilised in a Se overpressure. After exchanging the Se vapour by the sulphur vapour, the RHEED pattern changes qualitatively with time, as shown in Figs. 1b and c. Already, after 15 s S exposure the specular spot appears again, indicating the reversible formation of a two-dimensional flat surface. After a reproducible time period of about 30 s, the RHEED pattern is complete streaky, the surface is fully re-developed to a flat morphology. In contrast to that, the RHEED sequence of Fig. 2, which was obtained after a deposition of about 3.5 ML CdSe does not show any change of the surface morphology after an S exposure time of about 30 s and even after 90 s. As reported in [5], the CdSe islands formed after a deposition of more than 3.2 ML are partially relaxed. From these results we conclude that the reversible transformation obviously can only occur on strained surfaces and is related to a significant strain reduction due to the interdiffusion of sulphur atoms from the vapour into the CdSe islands and into the CdSe wetting layer.

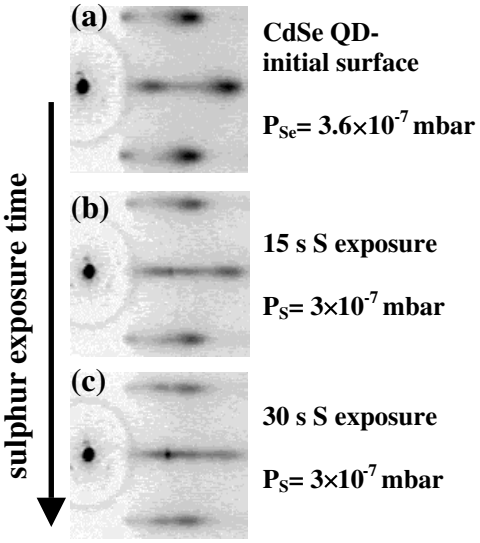

Fig. 1

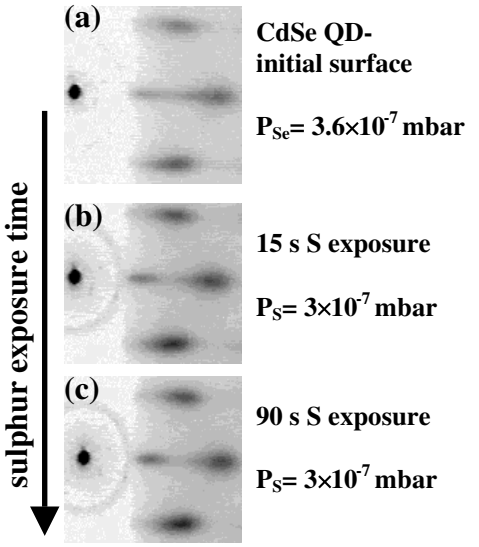

Fig. 2

Fig. 1. RHEED sequence of the reversible CdSe quantum dot formation after deposition of 3.0 ML CdSe on ZnSe (001) (strained surface)

Fig. 2. RHEED sequence of the irreversible CdSe quantum dot formation after deposition of 3.5 ML CdSe on ZnSe (001) (partially relaxed surface)

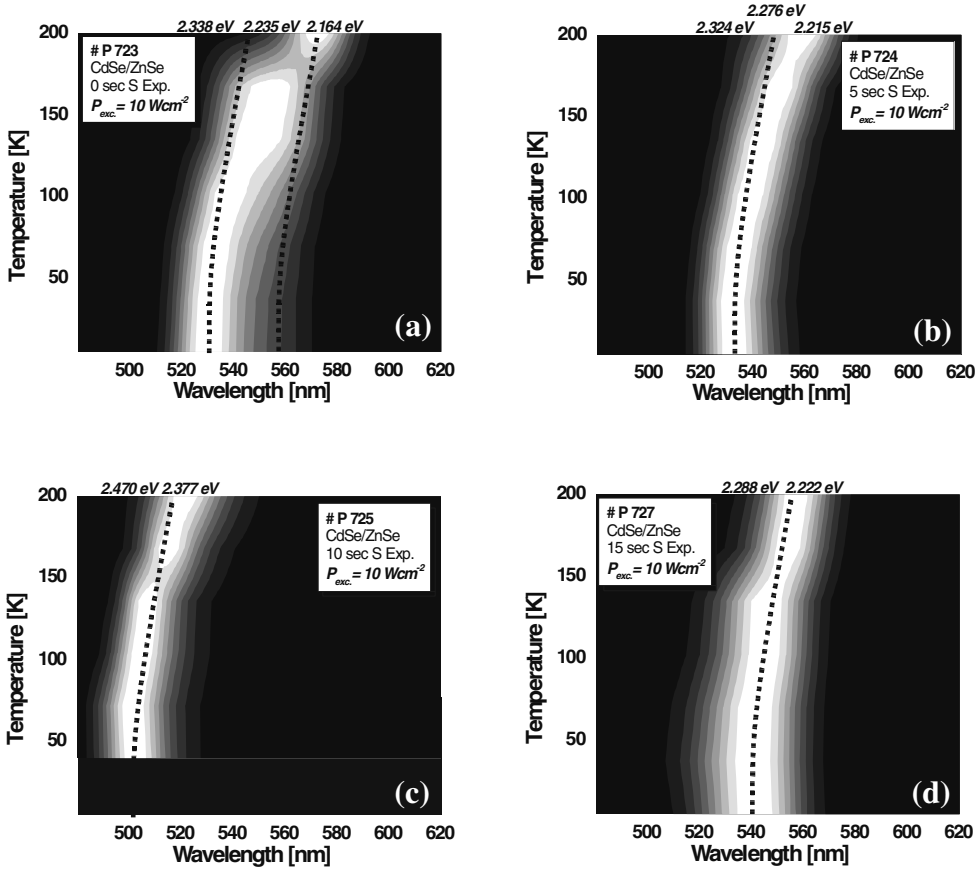

Fig. 3. Normalised greyscale-coded photoluminescence (PL) spectra as a function of temperature for structures with sulphur exposure times between 0 and 15 s after the island formation. Bright light indicates high intensities. The dotted lines show the temperature dependence of the ZnSe barriers [6] shifted to the respective energies at 5 K. The energies on the top of the figures denote the PL maxima either at 5 or 200 K

In addition to that, it was found that the re-development of the CdSe QD is accompanied by a shift of the PL maximum of the QD emission of about 200 meV after a stationary S exposure of about 10 s (see Fig. 3c). The observed shift is most probably the result of a complex interplay between the size reduction of the QDs, the mixed crystal formation in the dots and in the wetting layer and strain reduction processes. To get a more clear understanding of the reversible QD formation, optical investigations were performed. Temperature dependent PL confirmed the re-development of the CdSe QDs (strained-surface samples) as it is displayed in Fig. 3. With increasing temperature, the PL maxima of the QD emission band are shifted to longer wavelength. This behaviour is caused by the redshift of the ZnSe-matrix bandgap and by a lateral redistribution of localised excitons. A strong correlation of the observed energy shift with the S exposure time during the growth was found. For the sample without S exposure an energy shift of $\Delta E \sim 170$ meV between the PL maxima at 5 and 200 K was

observed. This behaviour is typical of structures containing islands formed by Cd fluctuations and islands grown in a SK-like process [3, 4]. With increasing S exposure time the strength of the PL maximum redshift is reduced (see Figs. 3b to d). An S exposure time of 15 s leads already to a temperature dependence of the emission band which follows the bandgap behaviour of the ZnSe matrix ($\Delta E \sim 60$ meV) [6]. This can be attributed to an inhibited lateral redistribution of excitons and therefore, to a reduction of deep localisation sites (e.g., 3D-like islands). Hence, the size and/or the density of larger QDs are decreased. Furthermore, due to the S exposure, the QD structures became more homogeneous as it is indicated by the half widths (FWHM) of the QD emission bands. Excitation density dependent PL investigations (not shown here) and the evolution of the FWHM of the emission bands confirm the reduction of deep localisation sites and the rise in the homogeneity of the QD ensemble with increasing S exposure time.

Conclusions The reversibility of the three-dimensional (3D) CdSe quantum dot (QD) formation is enabled by a stationary S vapour exposure after the formation of the QDs. RHEED and PL investigations confirm the reduction in size and/or the density of the 3D QDs and an enhancement of the homogeneity of the remained QD ensemble. The present results demonstrate a possibility to control and reproduce the properties of a QD ensemble. Hence a new degree of freedom for the tuning of the optical properties of QD based opto-electronic devices is enabled.

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