

Coexistence of planar and three-dimensional quantum dots in CdSe/ZnSe structures

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Two well distinguishable classes of nanoscale islands were identified in CdSe/ZnSe quantum dot structures by optical spectroscopy and transmission electron microscopy. For 2.1 to 3.1 monolayer CdSe deposition, coherent three-dimensional (3D) islands, formed in the Stranski–Krastanow (SK) mode, are found with typical diameters of ~ 16 nm and a coverage-dependent density of up to $3 \times 10^{10} \text{ cm}^{-2}$. Simultaneously, small islands with lateral extensions below 10 nm and a density of $\sim 5 \times 10^{11} \text{ cm}^{-2}$ are formed by strain-modified island growth. Whereas the 3D SK islands dominate the emission properties at room temperature, the latter smaller islands determine the optical properties at temperatures below 120 K. © 2000 American Institute of Physics.
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Quantum dot (QD) structures based on II–VI compounds are promising candidates for laser diodes in the green and blue-green spectral range. In order to fabricate dense arrays of islands uniform in size and shape, self-organized formation either in the Stranski–Krastanow (SK) growth mode^{1–3} or by strain-modified island growth [formed by fractional monolayer (FM) and submonolayer deposition]^{4–8} was investigated. Recently, we have investigated the CdSe-coverage dependence of large (~ 16 nm lateral size) SK grown islands and small (< 10 nm lateral size) FM islands⁹ to identify the kinetic origin of the two size classes of coherently strained islands.

In the present letter, the consequences of the coexistence of the two size classes on the optical properties of such QD samples are demonstrated. To clarify and understand the emission properties of these structures a clear distinction of the observed types of islands [type A: FM islands formed by strain-modified island growth and type B: three dimensional (3D) islands grown in the SK mode] is necessary.

The samples were grown by molecular beam epitaxy (MBE) as described in detail in Ref. 9. The investigated structures consist of pseudomorphically strained ZnSe-buffer layers of 45 nm thickness grown on GaAs (001) substrates, the CdSe layer, and a 45 nm ZnSe cap layer. The CdSe deposition was varied from 2.1 monolayer (ML) up to 3.1 ML. The formation of 3D islands was confirmed by the characteristic reflection high-energy electron diffraction (RHEED) pattern change. The structural properties were investigated by plan-view and cross-sectional transmission electron microscopy (TEM) studies. The Cd distribution was determined by the method composition evaluation of lattice fringe analyses (CELFA)¹⁰ applied to high-resolution (HR) TEM images. The optical properties of the CdSe QDs were

investigated by photoluminescence (PL) and PL excitation (PLE) spectroscopy at temperatures between 1.8 and 300 K. The PL was excited using a continuous-wave (cw) He–Cd laser. PLE was recorded by dispersing the light of a tungsten lamp with a monochromator.

CdSe depositions above the critical thickness for the transition of the two-dimensional to the three-dimensional growth in the CdSe/ZnSe system, which is about 2.1 ML,⁹ leads to the formation of (3D) islands (type B). In contrast, the formation and the density of type A islands is found to be independent of this critical value and of the total coverage of CdSe.⁹ TEM and HRTEM were performed to reveal the types A and B islands, and to investigate their structural properties. Figure 1(a) shows a plan-view TEM image of a sample with 2.8 ML CdSe deposition supporting the coexistence of both island types (labeled A and B). Furthermore, large island clusters with a diameter of about 50 nm were observed (labeled C). Such islands are most likely formed by the coalescence of type B islands and contain structural defects. Therefore, the latter islands do not contribute to the PL spectra and will be neglected below. The formation of the type B islands in the SK mode implies a wetting layer. More details about such a wetting layer and the type A islands are revealed by cross-sectional TEM and HRTEM lattice fringe images combined with the CELFA evaluation method which show the Cd distribution on an atomic scale. Cross-sectional TEM images [Fig. 1(b)] reveal a significant broadening of the wetting layer. An filtered image is displayed in Fig. 1(c) where the local Cd concentration is visualized in a color-coded map. The wetting layer, which is broadened to a thickness of 3 nm, exhibits an inhomogeneous Cd concentration between 13% and 25%. The Cd-rich regions with lateral sizes of about 10 nm are associated with type A islands which appear as small-scale speckle contrast in Fig. 1(a). We found an approximately linear increase of the Cd content of

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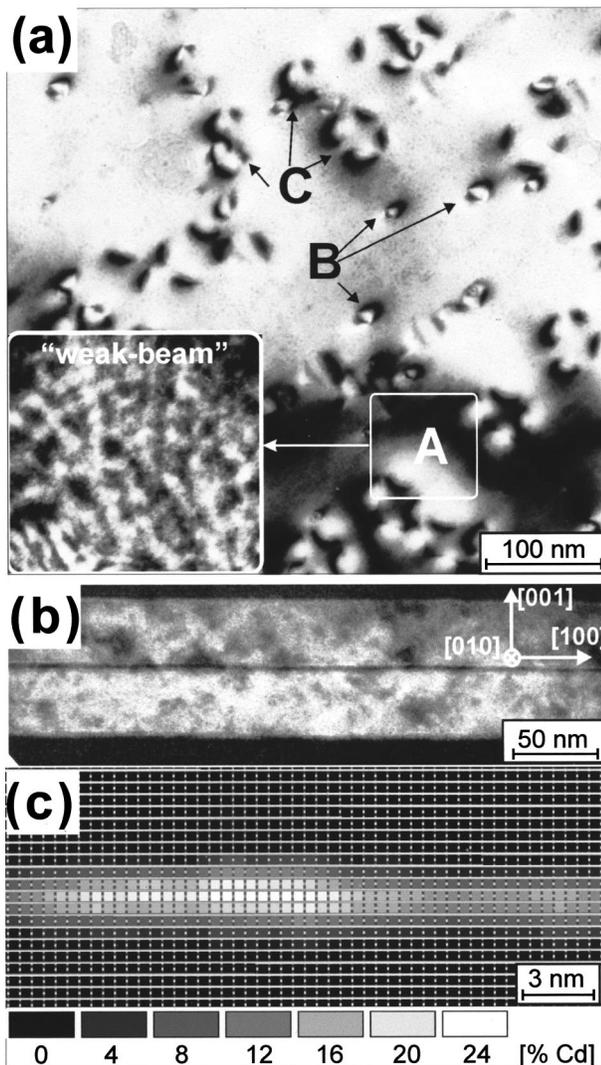


FIG. 1. (a) Plan-view (220) bright-field TEM image of the sample with 2.8 ML CdSe deposition. The insert shows a (220) weak-beam image of the marked area with a magnification of three to reveal the type A islands. (b) Cross-section TEM image [(200) dark-field with a (010) zone axis] of the 2.3 ML sample. (c) Cross-section HRTEM lattice fringe image of the 2.3 ML sample evaluated with the CELFA technique displaying the Cd distribution of the broadened wetting layer in a color-coded map. A Cd-rich region (white area) is embedded in the wetting layer with a Cd content twice as high as in the alloy quantum well.

the wetting layer and the type A islands with the CdSe deposition reaching 18% and 35%, respectively, for 3.1 ML CdSe deposition. The analysis of the Cd-concentration profile in the wetting layer along the growth direction revealed an asymmetric shape suggesting that segregation contributes to the broadening of the wetting layer.¹¹

The impact of the structural properties on the PL properties of the samples with 2.3–3.1 ML CdSe deposition is shown in Fig. 2. The broad emission band around 2.5 eV are originated by excitons localized in both types of QDs. Although two different types of QDs appear in the investigated samples, only one PL band was detected. This behavior can be understood, if there is an overlap of the QD states and/or one of the island types (A or B) dominates the emission properties. As a first approximation, due to the observed island sizes, it can be assumed that the low energy tail is governed by type B islands. The emission maximum above

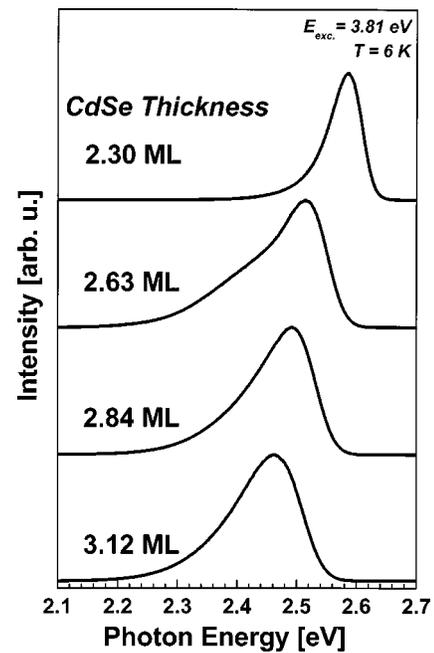


FIG. 2. Photoluminescence spectra of samples with 2.3–3.12 ML CdSe coverage. The broad emission band originates from radiative transitions of zero-dimensional excitons.

2.5 eV is attributed to the stronger quantization of the carriers in the type A islands and their lower Cd content. The comparison of the PL spectra for different CdSe depositions reveals two significant effects. First, a shift of the luminescence maximum to lower energies with increasing CdSe deposition. HRTEM and PLE investigations (see Figs. 1 and 4) show the Cd content in the wetting layer (ZnCdSe-alloy quantum well) and in the type A islands to increase with the deposited CdSe amount. This effect dominates the red-shift of the PL maximum. A second effect becomes evident from a comparison of the full widths at half maximum (FWHM) of the PL emission band. The increasing FWHM with increasing CdSe deposition is attributed to the increasing contribution of type B islands to the low energy tail of the PL emission band. In accordance with plan-view TEM for the investigated samples⁹ we attribute this behavior to the increase of type B island density with increasing CdSe deposition.

A more detailed investigation of the type B islands is carried out by temperature-dependent PL spectroscopy. The shift of the peak maximum of the emission band as a function of the sample temperature is displayed in Fig. 3. While up to 100 K the temperature dependence follows the behavior of the matrix material, a further increase of the sample temperature reveals a significantly stronger shift of the emission peaks to lower energies as it would be expected for a ZnSe- or CdSe-like behavior.¹² This behavior can be explained by the delocalization of the excitons from the type A islands due to the thermal activation and their redistribution to larger islands (e.g., type B islands) providing stronger localized energy states for carriers. Thus, excitons localized in type B islands dominate the PL spectra at elevated temperatures (see inset of Fig. 3). The absence of type B islands in the reference sample influences the temperature-dependent PL dramatically, as it is shown in Fig. 3. Up to temperatures of 150 K the PL-peak maximum is similar to the behavior of

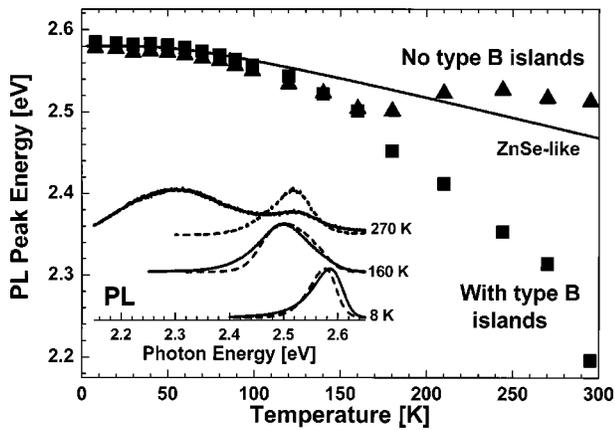


FIG. 3. Temperature dependent shift of photoluminescence maximum of samples containing both types of islands (squares, solid lines in inset) and type A islands only (triangles, dash lines in inset). The temperature dependence of the ZnSe matrix (Ref. 12) is shifted for clarity (solid line). The inset shows the PL spectra of these samples at selected temperatures.

the samples containing both type of islands. A further increase of the sample temperature leads to a blue-shift of the emission maximum attributed to the appearance of a new emission band on the high energy tail (see inset in Fig. 3). The energy position and its temperature dependence suggest that the origin of this emission band is the radiative transition of excitons in a quantum well suggesting delocalization of excitons from type A islands.

PLE spectroscopy was applied to identify the influence of the wetting layer on the observed redshift of the PL maximum in the case of thicker CdSe depositions and on the Cd content in the planar islands. In Fig. 4 the PLE spectra of the type A as well as the type B islands are depicted for the sample with 2.3 ML CdSe deposition. The two island classes exhibit a completely different excitation behavior. The most efficient excitation mechanism for the type B islands was found to be the generation of excitons in the ZnSe matrix, for which a strain-induced splitting of the light- and heavy-hole free exciton was observed. In contrast, the type A islands are excited predominantly via hot exciton relaxation in the wetting layer. This excitation channel was identified by the pronounced phonon replica starting from the detection position. The phonon energy was determined to be 31 meV close to the ZnSe LO phonon energy. The influence of other excitation mechanisms is about one order of magnitude weaker than the described channels for both island classes. In the case of the type B islands an excitation via phonon assisted processes was observed. The phonon energy (28 meV) differs strongly from the bulk value in ZnSe (31.8 meV). The reduction of the phonon energy might be explained by the confinement of phonon modes in quantum dot structures.¹³ Nevertheless, a common excitation mechanism was observed for the types A and B islands: In both cases a broad excitation band was found originating by the generation of excitons in the ZnCdSe-alloy quantum well. The absorption edge of the quantum well clearly depends on the CdSe deposition (see insert of Fig. 4), almost matching the shift of the PL maximum. An increased amount of CdSe results in a higher Cd content in the ZnCdSe-alloy quantum well. This effect underlines that the PL-emission energy at low temperatures

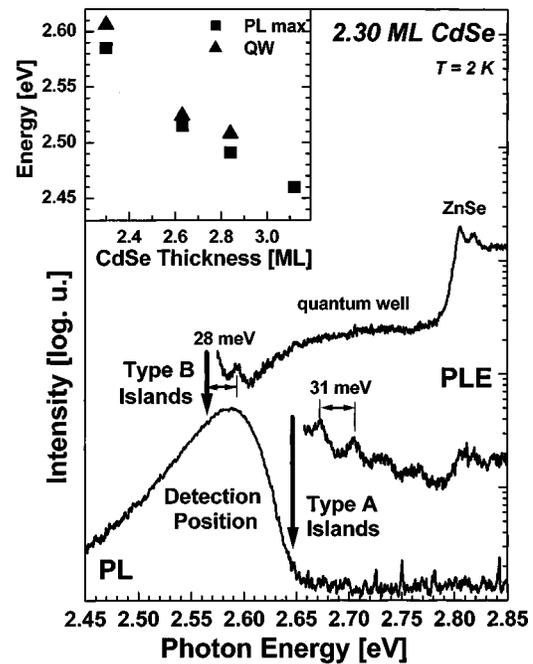


FIG. 4. PL excitation spectra for types A and B islands recorded for the sample with 2.84 ML CdSe coverage. The detection positions are marked by arrows in the PL spectrum. The insert shows the position of the absorption edge of the wetting layer and of the PL maximum of the samples with 2.3–3.12 ML CdSe coverage.

was mostly determined by the Cd content in the alloy quantum well and not by the type B islands.

In conclusion, we have shown the coexistence of two classes of islands, formed by strain-modified island growth and in the SK growth mode, respectively. The distinction of these both classes was enabled by optical spectroscopy and confirmed by structural investigations. Interdiffusion processes at the ZnSe/CdSe interfaces and segregation lead to the formation of a ZnCdSe-alloy layer. Therefore, we note that the interpretation of the optical properties of II–VI QD structures requires a careful examination of the island nature.

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