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# Quantum island formation in CdS/ZnS heterostructures grown by MOVPE

C. Meyne[a,*], U.W. Pohl[a], W. Richter[a], M. Straßburg[a], A. Hoffmann[a], V. Türck[a], S. Rodt[a], D. Bimberg[a], D. Gerthsen[b]

[a]*Institut für Festkörperphysik, Technische Universität Berlin, Sekr. PN 6-1, Hardenbergstr. 36, 10623 Berlin, Germany*
[b]*Laboratorium für Elektronenmikroskopie der Universität Karlsruhe, Kaiserstr. 12, 76128 Karlsruhe, Germany*

**Abstract**

Formation of coherently strained CdS quantum islands, embedded in ZnS, was achieved by metalorganic vapor-phase epitaxy (MOVPE). A lateral island of size 15 nm and height 2.5 nm is found by transmission electron microscopy. The three-dimensional confinement of excitons in the islands is proven by localized and resolution-limited cathodoluminescence in the deep-blue to near-UV spectral range. Optical gain as high as 225 $cm^{-1}$ at 265 $kW/cm^2$ and up to 420 $cm^{-1}$ at 3 $MW/cm^2$ assigned to a state filling process is achieved at a photon energy of 3.49 eV. 

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## 1. Introduction

Quantum dot (QD) structures have enhanced linear and nonlinear optical properties compared to systems of higher dimensionality. Growth of highly strained heteroepitaxial structures has gained increasing interest due to a self-organized formation of quantum dots by the Stranski–Krastanow mode. Previous investigations of II–V materials with a high lattice mismatch demonstrated Stranski–Krastanow-grown large islands (several 10 nm) [1,2], or in the case of submonolayer or monolayer deposition in the (Zn, Cd)Se system flat 2D nanoscaled islands [3,4]. Nevertheless in the (Zn, Cd)S system no island formation was observed yet. Quite the reverse, exciton localization was only achieved by monolayer fluctuations of quantum wells [5]. However, the individual energies show a large energy spread.

In this work we present the formation of coherently strained CdS quantum islands embedded in ZnS, which will act as localization centers for excitons up to high excitation densities.

## 2. Sample structures and experimental procedure

The studied samples were grown by metalorganic vapor-phase epitaxy (MOVPE) on GaP

* Corresponding author. Tel.: + 49-30-314-24926; fax: + 49-30-314-21769.
*E-mail address:* pello@physik.tu-berlin.de (C. Meyne).

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(0 0 1) substrates at 350°C and 100 mbar total pressure using DMZn-TEN, DMCd, $Cp_2Mg$, DTBS (because of gas-phase reactions between tBSH and $Cp_2Mg$) and tBSH precursors. TMGa and tBP were used during substrate deoxidation and for GaP buffer growth prior to II–VI deposition. Results of two kinds of sample structures are presented. Type A samples consist of a single CdS layer of 2–3 monolayers (ML) thickness, deposited on a 25 nm thick ZnS buffer layer with a 10 nm nearly lattice matched ZnMgS barrier, all embedded by 5 nm ZnS. These samples were used for low-temperature photoluminescence (PL) and transmission electron microscopy (TEM). Type B samples had threefold stacked 2–3 ML thick CdS layers, separated by 3 nm ZnS, embedded by 30 nm ZnS, 10 nm ZnMgS and 5 nm ZnS. We grew these samples for cathodoluminescence (CL) and optical gain measurements. The growth rate for the stacked CdS layers was varied from about 1 Å/s, referred to as slow in the following, up to 4 Å/s (fast).

The distribution of the embedded CdS was studied by TEM with a PHILIPS CM 200 FEG/ST electron microscope with a Scherzer resolution of 0.24 nm using $\langle 1\,1\,0\rangle$ cross-section samples. The optical properties of the samples were investigated by low-temperature PL and CL. PL at a low power density of about 1 W/cm$^2$ was excited by an HeCd laser at 3.81 eV. High-excitation surface and edge emissions were investigated using an XeCl excimer laser with $\sim$ 20 ns pulse duration, providing a maximum pulse power of 3 MW/cm$^2$ at 4.03 eV. The luminescence was analyzed by a 0.85 m Czerny–Turner double monochromator. Gain studies were performed in the edge geometry using the variable-stripe-length method [6].

CL was performed in a Jeol 840 scanning electron microscope. The luminescence light was dispersed in a 0.3 m spectrometer and detected by a 512 channel Si-diode array. For 3 kV acceleration voltage a spatial resolution of about 300 nm was achieved. The wavelength resolution was better than 1.4 meV. Mounting the sample on an He flow cryostat enables temperatures between 5 and 300 K. A detailed description of the setup is given in Ref. [7].

## 3. Results and discussion

The structural properties of a type A sample with a CdS layer of 3 ML deposition thickness and a growth interruption (GRI) of 1 s after the deposition, are shown in the bright-field cross-sectional TEM image (Fig. 1) taken with a $g = (0, 0, 2)$ imaging vector. One can clearly distinguish between CdS (black) and the embedding ZnS (grey). The deposited CdS has formed flat islands with a lateral size of about 15 nm and a height of 2.5 nm. The island density, estimated by the one-dimensional density in the TEM image, is of the order of $10^{11}\,cm^{-2}$, thus providing a dense array of islands. High-resolution images (not shown) prove that the islands are coherently strained. We did not find misfit dislocations at CdS islands or at the ZnS/GaP interface, although the critical layer thickness of 2.7–4 ML [8–10] is significantly exceeded at the islands. This is assigned to an elastic strain relaxation in the islands. We did not find evidence for the existence of a wetting layer, in contrast to results on III–V QDs fabricated by the Stranski–Krastanow growth mode [11,12].

The samples show a strong photoluminescence in the deep-blue to near-UV spectral range. PL spectra of type A structures with about 3 ML CdS deposition are shown in Fig. 2. In the preparation of those samples, growth interruptions (GRI) of different durations were applied after the deposition of CdS and prior to the subsequent growth of the upper ZnS layer. Furthermore, the effect of different growth rates is shown. Variation of the GRI after a slow CdS deposition from 1 s up to 5 s leads to a strong red shift in the PL spectra (black curves). The peak shifts from 3.35 to 3.15 eV and the full-width at half-maximum (FWHM) increases

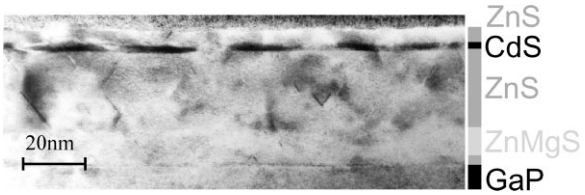


Fig. 1. Cross-section bright-field TEM image of a sample with 3 ML CdS embedded in ZnS (type A). The layer structure is marked at the right.

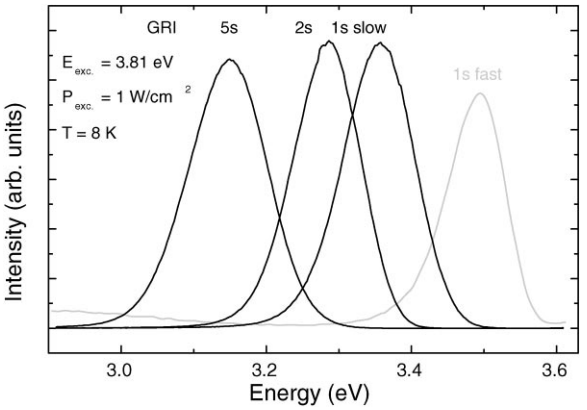


Fig. 2. Photoluminescence spectra of different samples which have always identical amounts of deposited CdS in one single layer (type A). The black curves represent the change of the PL energy, induced by different growth interruptions (GRI) during sample preparation after the CdS deposition. The grey curve shows the spectrum of a sample with a fourfold increased CdS growth rate.

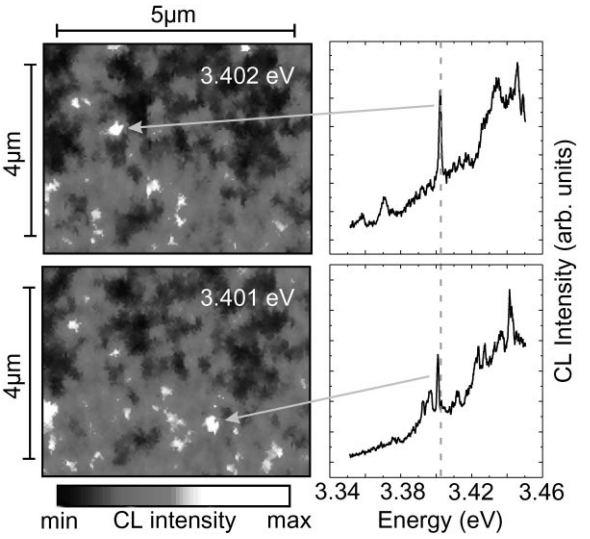


Fig. 3. Monochromatic cathodoluminescence images (left), recorded at the identical area of $4\,\mu m \times 5\,\mu m$, at two different energies, of a fast-grown type B sample. On the right side the local spectra of the points which are marked by arrows, are given. The luminescence was recorded at 8 K.

from 100 to 130 meV. At 5 s GRI the PL intensity slightly drops. Exceeding a GRI of 5 s, the luminescence decreases drastically. We interpret this behavior in terms of an Ostwald ripening process [13]. The CdS islands grow during GRI until they get too large for elastic strain relaxation and misfit dislocations are introduced. Increasing the growth rate up to 4 Å/s, the same amount of CdS leads to smaller islands. This results in a blue shift of the PL to 3.5 eV (grey curve). Simultaneously, the FWHM decreases to 85 meV. This indicates a smaller size distribution of the islands.

For site-selective measurements CL was performed. Fig. 3 shows two monochromatic CL images and two local spectra of a type B sample. The CL images cover an identical sample area of about $5\,\mu m \times 4\,\mu m$ and show the spatial origin of the luminescence at a distinct energy of 3.402 and 3.401 eV, respectively. The extension of the spots that are marked by arrows is that of the carrier generation volume of the CL setup. The local spectra from the excitation at the spot positions show sharp lines with 1.4 meV FWHM on a broad background. The line width is limited by the resolution of the setup. Varying the detection energy in the order of the resolution limit switches off one spot and brightens another, clearly demonstrating the formation of recombination centers with 3D confinement. This result, the observation of the ripening behavior and the structural investigations prove the formation of quantum islands.

Quantum islands are interesting for the fabrication of novel semiconductor lasers [14,15]. Therefore, we studied the optical gain of the CdS/ZnS quantum island samples. The gain spectrum of a type B sample is depicted in Fig. 4 for an excitation density well above the threshold for stimulated emission. A broad gain curve was detected between 3.445 and 3.517 eV. A maximum gain as high as $225\,cm^{-1}$ was found at a photon energy of 3.492 eV and an excitation density of $265\,kW/cm^2$. Since the gain maximum exhibits a significant shift only at very high excitation densities of about $3\,MW/cm^2$, the high gain is assigned to the zero-dimensional excitons which are localized in the nanoscaled islands. The gain shown in Fig. 4 is significantly higher than that of the sample with larger islands shown in Fig. 1 ($\sim 70\,cm^{-1}$). We attribute this effect to the stronger localization of the excitons in smaller islands, leading to a larger overlap of the carrier wave functions. In the case of the highest applied

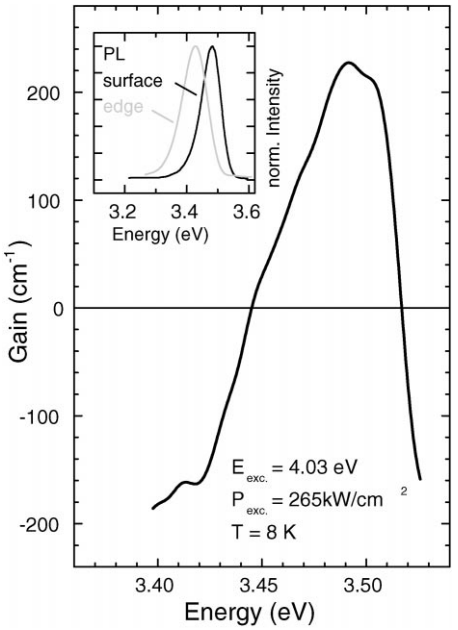


Fig. 4. Optical gain spectrum of a threefold stacked, fast-grown CdS sample (type B). A maximum gain of 225 $cm^{-1}$ is obtained for an excitation power of 265 $kW/cm^2$, at a stripe length of 65 μm. In the inset the normalized photoluminescence from the surface (black) and the stimulated emission from the edge (grey) is shown.

excitation densities of 3 $MW/cm^2$ the maximum gain value rised up to 420 $cm^{-1}$, accompanied by a further blueshift of 8 meV (not shown here). We note that this value is significantly higher than the values reported till now for CdS/ZnS structures [16]. To learn more about the gain mechanism, a comparison with the stimulated emission and the high-excitation PL is shown in the inset of Fig. 4. The most significant feature is the shift of the stimulated emission to lower energies by 55 meV. Since the maximum of the gain was observed on the high-energy tail of the stimulated emission band, and the density of the islands is of the order of $10^{11}$ $cm^{-2}$ (compare Fig. 1), a filling of states appears as the most likely process contributing to the gain. Due to the high excitation densities, the lower energy levels became filled and the smaller islands providing free states at higher energies were populated. The gain is thus strongly affected by the size distribution and the total amount of the islands acting as localization centers for carriers up to highest excitation densities.

## 4. Conclusion

Coherently strained CdS quantum islands embedded in ZnS were fabricated. Growth interruptions after the CdS deposition and slow growth rates induce a ripening which leads to larger islands and an increased size distribution. Localized and resolution-limited excitonic luminescence in the deep-blue to near-UV spectral range was observed proving 3D confinement. Optical gain of 225 $cm^{-1}$ at 265 $kW/cm^2$ and up to 420 $cm^{-1}$ at 3 $MW/cm^2$ was achieved in threefold stacked samples.

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