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Quantum dots formed by ultrathin CdSe-ZnSe insertions

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Abstract. We review on experimental and theoretical studies on a new type of quantum-dot (QD) structures obtained growing ultrathin, i.e. below the critical thickness for 2D-3D transition, strained narrow gap insertions. The formation of dense arrays (up to 10^{12} cm^{-2}) of nanoscale two-dimensional islands formed by submonolayer (SML) or slightly above-1 ML CdSe insertions in a wide gap II-VI matrices is revealed in processed high-resolution transmission electron microscopy images. In the case of stacked sheets of SML insertions, the islands in the neighboring sheets are formed predominantly in correlated or anticorrelated way for thinner and thicker spacer layers, respectively. By monitoring of sharp lines due to single QDs using cathodoluminescence the 3D confinement is confirmed. We manifest significant squeezing of the QD exciton wavefunction due to lateral confinement in magneto-optical experiments. Different polarization of photoluminescence (PL) emission recorded in edge geometry for vertically-uncoupled and coupled QDs confirms the QD nature of excitons. We show complete suppression of lateral motion of excitons bound to islands in case of wide-gap (ZnMgSSe) matrices.
A resonant (0-phonon) lasing is observed in ultrathin CdSe insertions and proves the lifting of the **k**-selection rule for QD excitons. Lack of exciton screening in QDs up to high excitation densities enables strong resonant modulation of the refractive index in stacked ultrathin insertions and allows realization of resonant (excitonic) waveguiding and lasing. This enables the realization of a new type of heterostructure laser operating without external optical confinement by layers having lower average refractive indices or a new type of a surface-emitting laser.

1 Introduction

Quantum dot heterostructures [1, 2], i.e. semiconductor structures providing confinement in all three dimensions, present an ultimate limit of size quantization in solids and result in the strongest possible modification of electronic properties as compared to quantum wells and wires. The recent breakthrough in device application of QDs is mostly related to Stranski–Krastanow growth, resulting in the formation of 3D islands on top of a wetting layer [1]. 1.3 μm-emitting GaAs-based lasers with parameters, superior to those in InP-based quantum well (QW) lasers are created [3]. With regard to this progress, there are many attempts to apply similar concept to widegap lasers based on II–VI material systems and group-III nitrides [4, 5]. The CdSe/ZnMgSSe system represents the best choice to study physical mechanisms of lasing in wide-gap compounds and, with regard to the extended history of investigations [6], can be considered as a model system. For fabrication of CdSe/ZnSe QDs two principally different growth modes have been introduced. The Stranski–Krastanow mode results for the CdSe/ZnSe system in the formation of islands with a diameter being typically larger than 30 nm [7]. Such II–VI islands are too large as

compared to Bohr-diameter in ZnSe (9 nm [8]) to provide significant quantization. Another way to fabricate quantum wires and QDs has been proposed by using submonolayer (SML) narrow gap insertions [9–11]. It was shown that such islands having a height of 1 ML are providing a uniform size (width of about 4 nm for InAs elongated islands on GaAs (100) surface) [10]. The increased exciton binding energy [12] and oscillator strength [13] have been demonstrated. An island of such a size can be used very effectively to localize ZnSe excitons, which have Bohr-radii of about 4.5 nm [8].

The proposal for formation of such islands in case of II–VI SML insertions as well as demonstration of high exciton oscillator strength and lifting of **k**-selection rule for such structures has been given in [14]. This idea, however, was met with criticism, as the mechanisms used for III–V growth were believed to be hardly possible for II–VI materials [15]. However, high-resolution transmission electron microscopy images and studies of the influence of deposition conditions on SML luminescence confirmed formation of nanoscale islands having a lateral size of 4–5 nm [16]. These islands have been revealed both in case of MBE [17] and MOCVD [18] growth. Similar CdSe islands having two-dimensional shape and a size of about 5 nm have been recently reported for MBE growth using migration-enhanced MBE mode [19]. Formation of uniform nano-islands can be explained by kinetic [20] or equilibrium models [21, 22].

A different interpretation of the CdSe-ZnSe SML growth was given by Toropov *et al.* [23], who proposed that uniform quasi-alloy coverage is formed for CdSe SML depositions for average thickness below 0.7 ML. As opposite, for deposition above 0.7 ML formation of large mesoscopic islands with dimensions much larger than exciton Bohr-radii is proposed. The density and the size of these islands has believed to be about 3×10^9 cm^{-2} and 20–60 nm, respectively [4].

2 Self-organization of two-dimensional islands

Spontaneous formation of ordered arrays of islands has been long studied theoretically and experimentally (see e.g. review in: [24]). The formation of ordered ("parquet") structures on crystal surfaces has been shown to occur when two phases with different values of intrinsic surface stress (τ_{ij}) are coexisting on the surface [25]. For strained above-monolayer-high 2D islands the total energy minimum for particular island size always exists [26].

In case of stacked arrays of 2D nano-islands it was predicted, that correlated growth prevails at small spacer layer thicknesses, while anticorrelated growth occurs for thicker spacers [27]. This effect has been observed experimentally using processed high-resolution transmission electron microscopy [28]. As opposite, in publications by Toropov et al. [23, 29] anticorrelated growth of mesoscopic islands has been claimed for small spacer layer thicknesses.

3 Structural characterization of ultrathin insertions

Processed high-resolution transmission electron microscopy (HRTEM) arises as a powerful tool to reveal the structural properties of structures with ultrasmall QDs. In Fig. 1 we show a processed HRTEM images obtained using DALI procedure [30] for a stacked SML-CdSe/ZnMgSSe structure with 30 Å spacer thickness. The image was taken by a projection of a relatively thick foil of 12–20 nm, where many islands are captured. This may also contribute to the smaller contrast in comparison to a SML-CdSe/ZnSe structure with the same spacer thickness [17]. A color-coded map corresponding to the local lattice parameter in growth direction is shown. The DALI processing allows clear visualization of QDs as

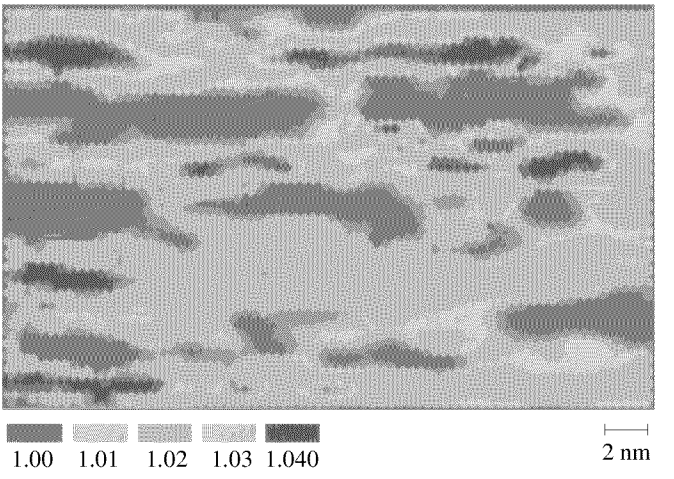

Fig. 1. The color-coded map of the local lattice parameter (LLP) in growth direction digitally processed from a HRTEM image of a stacked submonolayer-CdSe/ZnMgSSe structure.

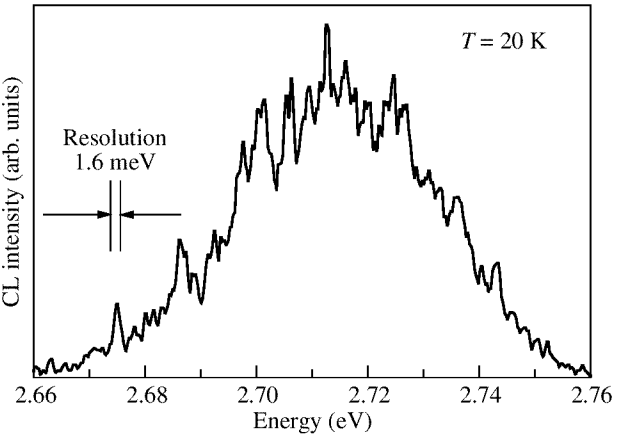

Fig. 2. Cathodoluminescence (CL) spectra of single 1 ML CdSe insertion in a ZnSSe at $T = 20$ K. The sharp luminescence lines in the spectra originate from single QDs.

local regions with increased local lattice parameter. The image reveals planar islands with a lateral size of only a few nanometers. According to the larger island size distribution in the case of quaternary spacer, the FWHM of the PL band is much broader [31] than observed for ZnSe spacers [17].

Similar conclusions can be deduced from the color-coded maps of the total local lattice displacement with respect to the lattice of the buffer layer [17]. In the case of CdSe/ZnSe structures HRTEM investigations were performed for samples with different spacer thicknesses [28, 32, 33]. Here, a correlated growth of islands was observed for spacer layer thickness < 3 nm, while anticorrelated growth occurs for spacers thicker than 3 nm. The lateral size of the QDs is about 4–5 nm in the case of ZnSe matrix. Essentially the same size of the CdSe island has been revealed in [19]. For MOCVD-grown QDs the lateral size varies between 2 and 6 nm and, thus, the PL emission from ultrathin (0.5–2 ML) insertions is broader [34].

4 Emission of individual QDs

0D confinement of excitons at 2D nano-islands must produce an atom-like energy spectrum of excitons [35] leading to the appearance of discrete energy levels of QDs. In the case of a very dense array of QDs, e.g., as formed by ultrathin insertions, it is very difficult to resolve luminescence lines corresponding to individual QDs. Such a result has been achieved in spot-focus CL studies. The luminescence spectrum of a MOVPE-grown sample [34] with a $\sim$ 1 ML CdSe insertion in a ZnSSe matrix is depicted in Fig. 3. The FWHM of the sharp emission lines, corresponding to spatially resolved luminescent areas, are limited by the spectral resolution of the setup. Ultrasharp luminsescence lines due to single QDs and a high density of nanoscale QDs formed by 1–2 ML CdSe deposition in a ZnSe matrix using MBE-growth has been proven in [19].

5 Polarization of edge emission and symmetry of the heavy hole wavefunction in QDs

Polarization of the luminescence in edge geometry enables a clear distinction between the QW and QD cases. According to Kane's selection rule, the heavy hole exciton luminescence in QWs must be completely TE polarized. As opposite to the QW case, a significant contribution of TM emission has been observed (Fig. 3), pointing to a significant role of exciton lateral confinement. The most remarkable observation has been done for polarization of edge emission in case of vertically-coupled QD states (see Fig. 3(c)). This emission is predominantly TM polarized. This indicates that the heavy-hole wavefunction is more extended in the growth direction and a has cylindrical shape. A similar effect has been observed in case of vertically-coupled InGaAs-GaAs Stranski–Krastanow QDs [36].

The extension of the exciton wavefunction in uncoupled and coupled QD structures was estimated from the Zeeman behavior with B applied parallel to the growth direction [37]. Following Ref. [38], the lateral extension of the exciton wavefunctions was estimated from the diamagnetic shifts to be $\sim$ 5.5 nm and $<$ 3 nm for uncoupled and coupled QDs, respectively, being smaller then the bulk Bohr-diameter (9 nm) [8]. These results are in good agreement with the lateral dimensions of the 2D islands observed in cross-sectional HRTEM images [28], supporting the corresponding localization of the excitons.

6 Matrix effects: lack of QD exciton transport in the case of wide gap matrix

Despite of the observation of luminescence lines due to single QDs, energy transfer processes can still be very pronounced. This results in a faster tunneling to neighboring larger QDs, having lower exciton transition energy, similar to the case of neighboring thicker and thinner quantum wells. Thus, ground state transitions can be revealed in PLE spectra [32]. This is very different from the case of InAs-GaAs Stranski–Krastanow QDs, where ground state transition is not resolved in PLE spectra, while it is observed in absorption and luminescence spectra [39]. It was observed, however, that by cladding QDs by a wider-gap ZnMgSSe matrix, one can suppress tunneling of excitons and thus realize a true QD-like PLE spectrum [31]. In this case the first peak in PLE spectrum coincides with the first excited state in QD.

7 Lasing mechanism in II–VI QDs

In bulk material direct radiative recombination of excitons with finite **k**-vector, which dominates at high temperatures and high excitation densities, is forbidden. Another particle, e.g. a LO-phonon is necessary to accommodate the exciton **k**-vector [40]. Thus, exciton-phonon scattering processes dominate the gain mechanism in II–I materials, where exciton

Bohr radii are small and densities necessary to screen excitons are higher than the excitation density at gain threshold [41]. At even higher excitation densities, exciton-exciton and exciton-electron scattering processes dominate. These processes shift the lasing wavelength typically by one or two LO-phonon energies towards longer wavelength as compared to exciton energy revealed in absorption spectrum. In QDs, however, the lasing mechanism must have principally excitonic (or biexcitonic) character, as excitons can not be screened in QDs and the **k**-selection rule is not appropriate.

8 Waveguiding and lasing

High exciton oscillator strength in case of stacked dense arrays of QDs and the experimentally proven resonant character of lasing up to room temperature [31] stimulated an idea of creating a new type of a laser based on the concept of resonant waveguiding and lasing. It was shown that a significant enhancement of the refractive index originates on the low energy side of the absorption spectrum in accordance with Kramers–Kronig relations [42]. This fact enables waveguiding in a small spectral window without external waveguides. Absorption measurements [43] demonstrated maximum absorption coefficients of the order of 10^5 cm^{-1} in the case of stacked SML QDs. This fact agrees with the estimation of the

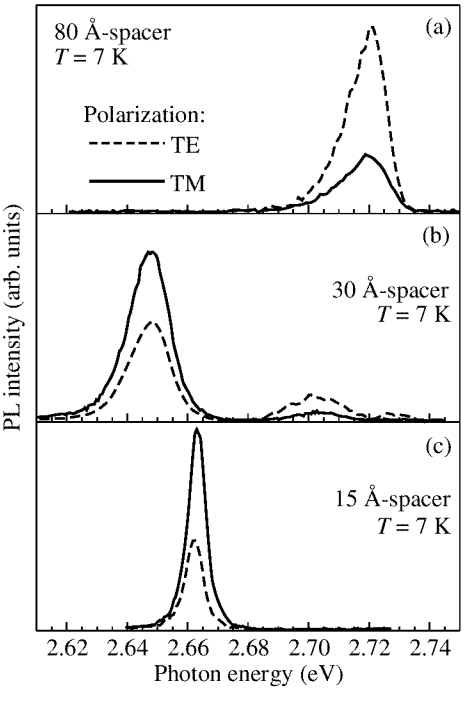

Fig. 3. Linearly polarized photoluminescence (PL) of structures with 80 Å, 30 Å and 15 Å spacers measured in edge geometry. The polarization changes from mostly TE for uncoupled islands (80 Å spacers) to mostly TM (accompanied by a red shift) for vertically coupled islands (15 Å spacers). The 30 Å spacer sample shows emission from both types of islands.

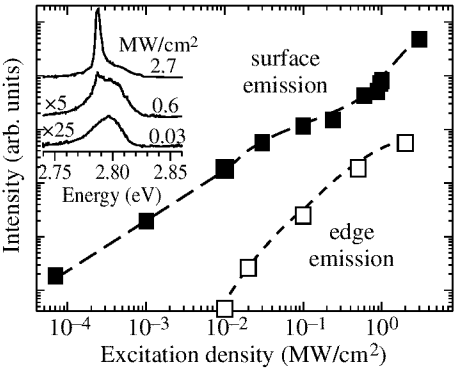

Fig. 4. Surface and edge emission of a stacked SML-CdSe structure with ZnMgSSe barriers as a function of the excitation density. The spectra are vertically displaced for clarity. The superlinear growth and the narrowing of the surface emission occurs, when edge emission saturates. The inset shows the surface emission.

exciton oscillator strength from the optical reflectance spectra and correspond to the values of the refractive index enhancement of about 0.2–0.3. Lasers based on the resonant waveguiding were demonstrated to be exceptionally promising both for II–VI [31] and III–V [44] SML structures.

9 Surface lasing without Bragg mirrors and self-adjustment of cavity

High exciton absorption coefficients in arrays of QDs allow to achieve lasing in case of very short cavity lengths in edge geometry, or realize surface lasing in vertical geometry when no highly-reflecting Bragg mirrors is used. E.g., just ZnSe/GaAs and ZnSe/air interfaces allowing to achieve about 30% reflectivity each made it possible to have surface lasing in structures with 20-fold stacked CdSe SML insertions [32]. The surface emission in dependence of the excitation density is depicted in Fig. 4.

In the case when the gain in the active medium is small, the modulation of refractive index, caused by changing gain with increase in the excitation density (chirp) is small. If the gain is high, then the shift of the cavity modes with the excitation density increase can be very significant [32]. This allows to achieve self-adjustment effect between the cavity mode and the gain spectrum. In this case the cavity mode wavelength tunes with excitation density rise, until it reaches the spectral region, where gain is able to overcome external losses.

Currently photopumped GaN-based surface emitting laser, emitting in the blue spectral range, is realized using similar concept [45]. Using of low reflectivity lower AlGaN/GaN Bragg reflector allowed to achieve room temperature surface lasing [46].

10 Conclusion

To conclude, we discussed optical properties of ultrathin CdSe insertions in a ZnSe matrix. These insertions represent dense arrays of two-dimensional nano-islands with a size comparable to the exciton Bohr-radius. The QD nature is proven by direct observation of luminescence lines from single QDs, by resonant character of gain and by lateral squeezing of excitons revealed in magneto-optical studies. New effects led to fabrication of unique devices such as resonantly-waveguiding lasers and cavity-self-adjusted surface-emitting lasers without Bragg reflectors.

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