Be-induced island formation in CdSe/ZnSe heterostructures: Ensemble versus single dot studies

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(Received 5 July 2000)

We present photoluminescence (PL) studies on quantum islands formed below the critical thickness for Stranski-Krastanow growth by a well-defined incorporation of Be nucleation centers in CdSe/ZnSe heterostructures. The occurrence of spectrally narrow, individual photoluminescence peaks in spatially resolved PL spectra and a significant enhancement of the recombination lifetime clearly indicate the presence of zero-dimensional states. A direct comparison of temperature-dependent single dot measurements with optical studies on quantum dot (QD) ensembles demonstrates an efficient coupling between individual QD's at elevated temperatures.

Low-dimensional semiconductor structures have attracted a lot of interest stemming from both the fact that a variety of physical properties like electron-hole-interaction, recombination rate, or exciton-phonon interaction, can be manipulated by reducing the dimensionality of the system, and the large application potential of semiconductor nanostructures.[1–4] Currently, research is strongly focused on self-assembled quantum dots (QD's) being ideal candidates for realizing quasi-zero-dimensional systems with high quantum efficiency.[5–9] While above a critical thickness the formation of self-organized QD's occurs via Stranski-Krastanow growth,[10–14] a distinct island formation takes place even for sub-ML insertions of CdSe in ZnSe.[15] However, it is still rather challenging to control or even to manipulate the dot formation, the size dispersion, the density, or the lateral ordering of single-layered epitaxially grown QD's. Current approaches towards the goal of laterally ordered dot ensembles include self-ordering in stacked dot layers,[16,17] as well as induced nucleation on crystal defect sites,[18] or selective growth on patterned substrates.[19,20]

Such a long-range lateral ordering is of particular interest, as from the application point of view, not only the properties of individual dots, but also the interaction between the dots, especially at elevated temperatures, is of fundamental importance. Indeed, experimental studies on InAs/GaAs dot ensembles reveal a significant transfer of electron-hole pairs between the dots, resulting in an anomalous temperature dependence of both the photoluminescence (PL) energy and the PL linewidth.[21] However, a direct comparision between single dots and dot ensembles is still missing. Such a comparison gives us the chance to understand the photoluminescence properties of a QD ensemble in more detail by separating the involved interaction processes from intrinsic dot properties.

In this paper we investigate Be-induced CdSe islands by using time-resolved and spatially resolved PL measurements. In order to demonstrate the manipulation of QD formation, nominally identical samples grown with and without the incorporation of Be sites are studied. By comparing temperature-dependent PL measurements of individual QD's and of QD ensembles, a thermally activated transfer between the dots is clearly proved.

The samples under investigation consist of CdSe submonolayers (nominal thickness 0.4 ML) sandwiched between a 100-nm ZnSe buffer and a 20-nm ZnSe capping layer. Prior to the growth of CdSe by migration-enhanced epitaxy, the ZnSe starting surface has been exposed to Be and a subsequent delay under Se flux leads to a formation of BeSe centers, which are expected to act as nucleation sites for the following CdSe deposition (sample *A*). As a reference, a nominally identical sample was grown without Be exposure (sample *B*) and in addition, a sample with a nominal CdSe layer thickness of 3 ML, i.e., above the critical thickness for self-assembled growth, was prepared for comparison (sample *C*). Details about the growth are reported elsewhere.[22]

In order to get experimental access to individual dots, square mesas with lateral extensions L_x down to 50 nm were realized by electron-beam lithography and wet-chemical etching.[23] For cw PL studies, the samples were excited by an uv-Ar^+-ion laser, focussed to a spot size of about 25 μm. The PL emission was dispersed by a 0.32-m Jobin-Yvon monochromator with an 1800-mm^{-1} grating and detected by a charge coupled device (CCD) camera. The spectral resolution of the setup is about 0.15 meV. For the time-resolved experiments, the samples were excited by a frequency-doubled titanium-sapphire laser with a pulse length of 1.5 ps. After spectral dispersion in a monochromator, the PL signal was recorded using a streak camera with a subsequent CCD camera. An overall time resolution of the system of about 10 ps is obtained.

Figure 1 presents PL measurements for the sub-ML samples (nominal thickness=0.4 ML) without (left) and with (center) Be treatment in comparison to a CdSe/ZnSe reference structure with $d_{nominal}=3$ ML (right). Various degrees of spatial resolution as defined by different mesa sizes are indicated in the figure. The shape of the PL signal of the structure grown without Be is virtually independent on the spatial resolution, i.e., there are no signs for the formation of

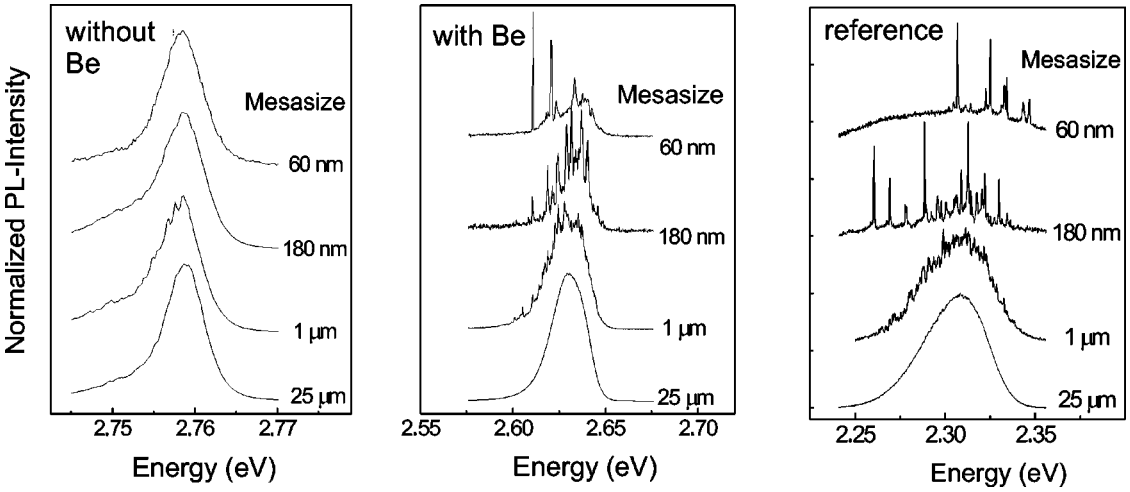

FIG. 1. Sequence of spatially resolved PL spectra for nominally 0.4 ML CdSe embedded in ZnSe barriers without (left) and with (center) Be exposure before CdSe growth. For comparison, the PL spectra of a reference structure with a nominal CdSe thickness of 3 ML is shown on the right part of the figure. The mesa size, corresponding to the degree of spatial resolution, is indicated in the figure.

QD islands. This suggests an almost homogeneous two-dimensional morphology of the Cd(Zn)Se layer with a corresponding quantum-well-like density of states.[24] This is supported by the relatively small full-width at half-maximum (FWHM) (≈ 5 meV) of the PL signal. Due to the fact that the excitonic Bohr radius in these structures is small as compared to the extension of the smallest mesa, no significant lateral quantization is expected, unlike what is observed in etched III-V nanostructures of similar size.[25] In contrast, the sample exposed to Be before the CdSe growth reveals a significantly enhanced inhomogeneous broadening (FWHM ≈ 20 meV) for the 25 μm mesa, shifted by about 140 meV to the red. Moreover, the broad emission line of the large mesa breaks up into distinct single lines with a typical FWHM of about 150 μeV, limited by the spectral resolution of our setup. These narrow features can be attributed to the recombination of single, quasi-zero-dimensional excitons in individual QD's. An analogous dependence of the PL signal on the mesa size is found for the sample with $d_{nominal} = 3$ ML (right). This comparison is strong evidence for the Be-induced formation of QD islands, although the detailed shape and composition of the islands is not yet clear. Our conclusions are further supported by x-ray-diffraction measurements on similar structures.[22]

The influence of Be-nucleation sites on the formation of QD islands becomes also evident in time-resolved PL measurements. Figure 2 shows the spectrally integrated transient behavior of the PL emission of the submonolayer structures with (diamonds) and without (circles) Be nucleation centers. While the rise time of about 20 ps is identical for both samples, indicating an efficient carrier relaxation into the luminescent QD ground state, the decay times differ strongly. We observe a significantly enhanced radiative lifetime for the Be-exposed sample A ($\tau = 205$ ps) as compared to the reference sample B ($\tau = 100$ ps). This further supports the formation of QD islands, as can be understood by the following arguments: If the excitons are three-dimensionally confined in real space, the excitonic wave function in k space is delocalized. This significant contribution of optically forbidden k components reduces the radiative recombination rate with increasing spatial confinement.[26]

The three-dimensional exciton confinement in sample A is further supported by the temperature dependence of the excitonic lifetime (see inset of Fig. 2). While thermal escape of carriers leads to a decrease of the lifetime at high temperatures ($T > 120$ K) a constant lifetime up to $T \approx 120$ K is obtained. In addition, no decrease of the PL intensity is found up to 120 K, i.e., the experimentally obtained lifetime directly reflects the radiative recombination rate in the QD's. This temperature-independent regime of the radiative lifetime again supports the presence of a δ-like density of states, i.e., the existence of zero-dimensional excitons.[23,27–29] It may be an interesting point that in the case of InAs/GaAs QD's an exciton lifetime independent on temperature is typically only obtained for temperatures below about 50 K. At elevated temperatures, an increase of the lifetime is found, indicating a significant occupation of higher dot states.[30,32]

It is therefore necessary to study transfer processes of excitons within a QD ensemble in more detail by comparing temperature-dependent PL measurements of QD ensembles with experimental data obtained for an individual QD. Figure 3 shows the PL emission energy of sample C as a function of

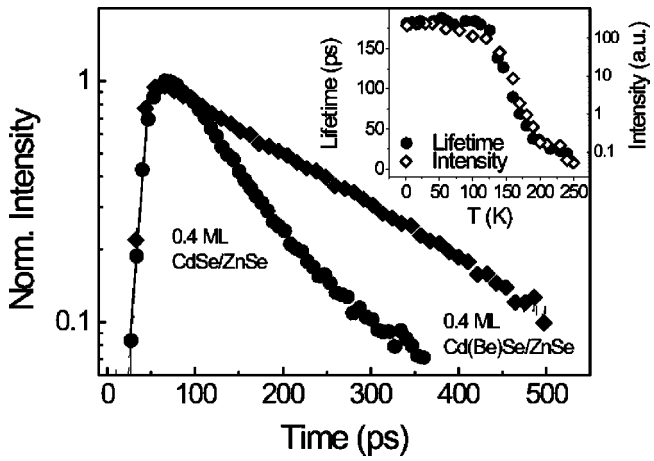

FIG. 2. Spectrally integrated PL signal of samples A and B versus time. The temperature dependence of the lifetime and intensity of sample B is depicted in the inset.

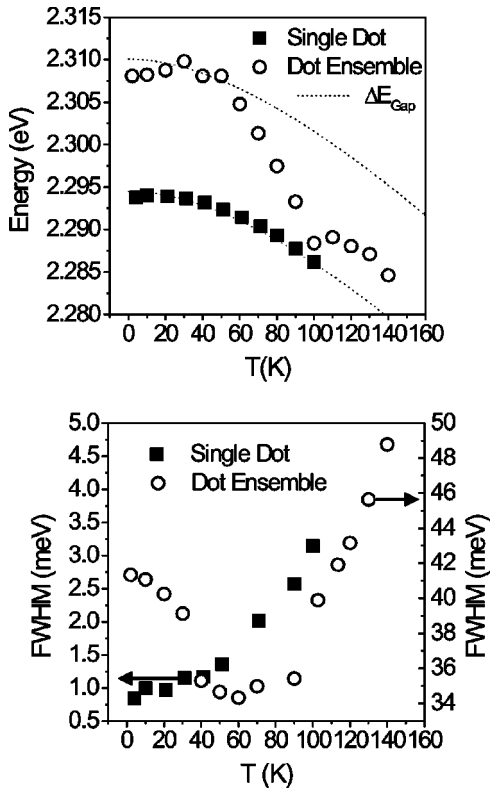

FIG. 3. PL energy (top) and full-width half-maximum (bottom) of PL signal for an ensemble of CdSe QD's (open circles) in comparison to a single QD (full squares) as a function of temperature.

temperature. The dotted line indicates the temperature-induced redshift of the band gap as expected by Varshni's law.[31] In contrast to the single QD, where the energy shift of the PL signal virtually follows Varshni's relation, the redshift of the PL energy of the QD ensemble is at moderate temperatures ($T \approx 50-100$ K) much stronger than expected by a simple fit with Varshni's equation. Similar findings, although not yet reported for II-VI QD's, have been obtained for InAs/GaAs QD's and explained in terms of exciton transfer processes between the QD's within the ensemble:[21] At low temperatures, the QD's are occupied homogeneously after the laser excitation,[33] while at elevated temperatures, electron-hole pairs from relatively small QD's (i.e., at the high-energy side of the PL signal) are able to escape the QD thermally, and after a transfer process via wetting layer or barrier states, the carriers are captured in neighboring QD's with lower effective band gap, i.e. dots that are larger or contain more Cd. This exchange process leads to a reduction of the PL energy of the exciton ensemble (in addition to the redshift of the band gap) with temperature. It has to be emphasized here that this temperature behavior is completely different than what is usually observed for quantum wells containing localization centers due to size or composition fluctuations (''natural dots''). There, the temperature shift of the PL energy at low temperature is expected to be smaller than Varshni's law, a consequence of a successive occupation of free-exciton states with increasing temperature.

The FWHM of the PL signal of both the dot ensemble (open circles) and the single QD (filled squares) is plotted for various temperatures in the bottom part of Fig. 3. Starting from a FWHM of 41 meV at $T=2$ K, the FWHM of the ensemble signal decreases up to about 60 K. This is in agreement with the interpretation discussed above: A transfer of electron-hole pairs to QD's with lower energy should result in a distinct linewidth narrowing because only a part of the dot ensemble contributes to the PL signal. Increasing the temperature further, phonon scattering and redistribution come into play, causing an increase of the FWHM. The observation of a pronounced minimum in the FWHM can be explained in the same way as the additional redshift of the QD ensemble as a function of temperature. Note, that up to $T=120$ K, both recombination lifetime and PL intensity remain constant, indicating negligible nonradiative recombination, i.e., the transfer of electron-hole pairs between individual dots does not affect the quantum efficiency of the dot ensemble.

The temperature dependence of a single QD, on the other hand, is completely different as shown in Fig. 3. Unlike the dot ensemble, the FWHM of the single QD PL signal exhibits a monotonic increase with temperature due to exciton-phonon scattering. Comparing the data to the temperature-dependent PL linewidth of the quasi-two-dimensional reference (sample *B*), no significant difference was found within the experimental resolution, i.e., there is no indication of a change in the exciton-phonon coupling in self-assembled QD's as compared to reference quantum wells.

In summary we have shown that Be sites deposited on ZnSe prior to the growth of CdSe submonolayers can act as nucleation centers for CdSe islanding. This was confirmed by spatially resolved and time-resolved photoluminescence spectroscopy. Temperature-dependent measurements on an ensemble of QD's in comparison to experiments on single QD's clearly demonstrate that the energy and the linewidth of the photoluminescence signal is governed by a transfer of excitons between neighboring QD's. Thus, despite the discrete density of states and the temperature-independent lifetime below 120 K, excitons in neighboring individual QD's can interact. This results in an anomalous behavior of the PL energy and PL linewidth of the dot ensemble with increasing temperature in contrast to a phonon-induced broadening of the FWHM in a single QD.

We gratefully acknowledge the expert technical assistance of M. Emmerling and the financial support of the Deutsche Forschungsgemeinschaft in the frame of the Sonderforschungsbereich 410.

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