Excitonic emission of colloidal nano-crystals embedded in Molecular Beam Epitaxy grown ZnSe

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Abstract. We combine ZnSe layers grown by molecular beam epitaxy with colloidal CdSe core, CdSe/ZnSe and CdSe/ZnS core/shell nano-crystals (NCs) to achieve monolithic NC-semiconductor heterostructures. The NCs are prepared in solution and deposited by spray-coating on ZnSe buffer layers and subsequently overgrown by ZnSe. We find a blue shift of the photoluminescence of core/shell dots when they are overgrown by ZnSe. Rapid thermal annealing is used to improve the interface region between the NCs and the ZnSe matrix. The effect of different annealing temperatures on the optical properties of CdSe core, CdSe/ZnSe and CdSe/ZnS core/shell NCs overgrown with a cap layer of ZnSe is investigated. After annealing at 673 K the photoluminescence of these samples is red-shifted as compared to unprocessed samples. All photoluminescence results are explained by a model calculation with the following assumption about the 3D confining potential of the NCs: (i) the shell of core/shell NCs dissolves during ZnSe overgrowth, (ii) after overgrowth NCs are separated from the ZnSe matrix by an interface barrier, (iii) the height of this barrier is significantly reduced by annealing. For all three types of NCs we find an excellent quantitative agreement between the experimental and calculated NC transition energies. The absence of the barrier after annealing is further demonstrated by low temperature photoluminescence data of annealed samples which show enhanced diffusion of electron-hole pairs from ZnSe into the NCs.

1. Introduction
Wet chemically prepared colloidal nanoparticles of numerous shapes, sizes, and compositions have been reported over the past two decades and continue to exhibit exciting optical and electrical characteristics [1]. Further, such colloidal NCs exhibit an enormous potential regarding the tuning of their optical and structural properties [2]. As free parameters, the size, shape, material composition and NCs density can be varied and exactly matched to the requirements of specific devices. Alternatively, different types of NC which emit light at several wavelengths can be combined in the same device to achieve multi-color or white light emission from a single chip. In addition, wet-chemically prepared core and core-shell nanocrystals (NCs) can be deposited on different materials with very low concentrations. However, NCs show a relatively fast photodegradation and photoluminescence intermittency [3]. To overcome this effect, colloidal NCs can be capped with a larger band gap material and/or organic ligands to increase the confinement and passivate the surface states [4]. Our unique approach is the integration of the NCs in an epitaxial grown semiconductor matrix to stabilize their optical properties. In this paper we present the investigation of the photoluminescence
(PL) of different types of colloidal NCs which were deposited on ZnSe/GaAs substrates and overgrown with ZnSe layers. Finally these samples were rapid thermal annealed at different temperatures. The peak energy of the NC-related luminescence of overgrown and annealed samples showed a pronounced shift relative to the emission of the NCs in solution. This shift is well reproduced by a model calculation which assumes a variation of the confining potential of the NCs due to overgrowth and annealing.

2. Experimental

Three types of NCs, CdSe core, CdSe (ZnSe) and CdSe (ZnS) core (shell) NCs with a shell thickness of 2 monolayers were synthesized by standard high-temperature reaction of organometallic precursors in strongly coordinating solvents, (see ref. [5]). We used 0.2 milliliters of the colloidal solution with a volume concentration of $10^{16}$ NCs/l. These colloidal solutions of NCs were sprayed on the surface of a 50 nm ZnSe buffer layer which was grown by molecular beam epitaxy on GaAs substrates. Then, the sample was transferred back to the MBE chamber and overgrown with a 30 nm thick ZnSe cap layer, for details see ref. [6]. The photoluminescence (PL) was measured using both the 325 nm emission line of a continuous wave He-Cd laser and the 405 nm emission line of a semiconductor laser diode in a µ-PL setup with a spectral resolution of 0.1 nm. The PL emission was detected with a N$_2$ cooled CCD detector. Annealing of the samples was performed in an AnnealSys AS-One rapid thermal annealing (RTA) system in N$_2$ gas. The RTA was accomplished isochronic with an annealing time of 30 sec.

3. Results and discussion

The room temperature PL spectra of the three different types of NCs mentioned in the experimental part were measured in solution, after overgrowth and after annealing at temperatures of 598 K, 623 K and 673 K for 30 sec. As an example fig. 1 shows the room temperature PL intensity versus photon energy of CdSe/ZnSe NCs. The black curve (a) is the PL spectrum of the NCs in solution, while the red curve (b) is referring to the PL of the NCs after overgrowth with ZnSe. The PL spectra after RTA treatment at three different temperatures are the curves (c). We find a blue shift between the PL emission of the NCs in solution and of the overgrown NCs. In contrast, a red shift is observed between the PL emission of the overgrown NCs and the annealed sample.

The blue shift was explained by a model presented in Ref. [6]. This model is based on two assumptions: (i) during the overgrowth process, the shell of the core/shell NCs is dissolved, and (ii) after overgrowth the NCs are separated from the ZnSe matrix by a thin barrier of yet unidentified origin which prevents excess electron-hole pairs generated in ZnSe to recombine within the NCs. The red shift after annealing may be explained also in the framework of this model, if we assumed that the

![Figure 1](image_url). Room temperature PL spectra of CdSe/ZnSe NCs in solution (a), overgrown with a 30 nm ZnSe cap layer (b) and after rapid thermal annealing at 598 K, 623 K and 673 K for 30 s (c).
barrier is reduced during the RTA process and after annealing at 673 K the barrier is completely extirpated. A similar trend regarding the red shift of the PL spectra after annealing was also observed for CdSe core and CdSe/ZnS core/shell NCs.

Figure 2. Confinement potential used in the calculation of excitonic energy of CdSe/ZnSe NCs in solution (a), overgrown in a ZnSe matrix (b) and after rapid thermal annealing at 673 K/30 sec (c).

Fig.2 illustrates the band structures used in our model calculations for ZnSe/CdSe core-shell NCs (a) in solution, (b) after overgrowth and (c) after annealing at 673K. We used an electron affinity of 3.92 eV [7] for CdSe and 3.5 eV for ZnSe [8]. The 0.5 nm thick ZnSe shell around the CdSe core is marked as (s) in fig. (2a). The barrier which is formed during the overgrowth process is marked (b) in fig. (2b). We set its width to 1 nm. Furthermore, we assume that during the annealing process the barrier is reduced. After annealing, the barrier height is zero and the ZnSe matrix is directly connected to the NCs shown in fig. (2c). Therefore, the carrier transfer between the ZnSe matrix and the NCs has high probability to occur.

Figure 3. The PL peak energy (open symbols) and the calculated transition energies (filled symbols) for NCs in solution (a), overgrown in a ZnSe matrix (b) and after rapid thermal annealing at 673 K (c). Cases (c) and (d) indicated the experimental data annealed at 589 K and 623 K, respectively.

Figure 4. Low temperature PL spectra of CdSe/ZnSe NCs before and after 30sec rapid thermal annealing at 673 K.
The calculated exciton transition energies of three types of NCs (full symbols) together with PL peak energies (open marks) measured with NCs in solution, after overgrowth and after annealing at 673 K are shown Fig. 3. We find quantitative agreement between experimental and calculated data which we consider a strong support of the assumptions made, especially that the barrier between NCs and ZnSe matrix can be removed by RTA treatment.

Fig. 4 shows the low temperature PL spectra of CdSe/ZnSe NCs as overgrown (gray curve) and after annealing at 673 K (black curve). Two peaks can be identified in these spectra. The peak at 2.8 eV is due to recombination of excitons in the ZnSe matrix [9] and the emission band at about 2.5 eV is the PL of the CdSe/ZnSe NCs. The relative intensities of these emission lines are inverted after annealing of the sample. The spectrum before annealing (gray curve) exhibits a strong PL due to the recombination of excitons in ZnSe while the emission from the NCs is relatively week. In contrast, after annealing the ZnSe PL is strongly reduced while the emission from the NCs is substantial enhanced. This behavior can be explained by an enhanced diffusion of excess e-h pairs from ZnSe into NCs when the barrier between NCs and ZnSe matrix is annihilated by annealing in excellent agreement with our model.

4. Conclusion
We have combined wet-chemical growth of colloidal NCs and molecular beam epitaxy to create complex semiconductor structures with NCs as the optical active material. After overgrowth of various core-shell NCs a distinct blue shift is observed which is not present in samples of CdSe core NCs overgrown with ZnSe. PL measurements indicate that the overgrown NCs are predominantly directly excited and a barrier layer prevents the diffusion of excited carriers from the ZnSe into NCs. Rapid thermal annealing of these heterostructures leads to a pronounced red-shift of the NC-related emission. Using a numerical model which contains distinctive assumptions about the confining potential of the NCs we can explain the measured PL peak energy of NCs in solution, after overgrowth and after annealing. One essential result of our investigation is that annealing reduces the barrier between NCs and the ZnSe matrix. This is supported by low temperature PL data which show an increase of the NC emission of annealed samples. Thus annealing of NCs-semiconductor heterostructures can pave the way towards applications of NCs in photonic and optoelectronic devices.

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