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TITLE: Nanostructures: Physics and Technology International Symposium [9th], St. Petersburg, Russia, June 18-22, 2001 Proceedings

9th Int. Symp. “Nanostructures: Physics and Technology”
St Petersburg, Russia, June 18–22, 2001

Optical properties of CdS nanostructures crystallized in the pores of insulating template

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Abstract. The characteristic features of the luminescence spectra obtained at different polarization of the exciting light beam and time-resolved luminescence spectra of CdS nanocrystals crystallized in 8–10 nm diameter hollow channels of a dielectric Al_2O_3 template have been explained in terms of exciton transitions in semiconductor-dielectric quantum wires. In these structures the dielectric confinement effect leads to a considerable increase of the exciton binding energy — the Coulomb attraction between electron and hole is considerably enhanced as a result of the difference between the permittivities of the semiconductor and insulator.

In semiconductor quantum wires (QWRs) — nanostructures in which carriers and excitons move freely in one direction but are localized in two others, the electron-hole attraction is intensified and excitonic transitions dominate in the absorption and luminescence spectra. Quantum confinement results in prominent exciton features such as large binding energies and oscillator strengths. The binding energy and oscillator strength of an exciton transition can be substantially increased by replacing the semiconductor barriers with insulators having much lower permittivities than the semiconductor [1, 2, 3].

For semiconductor-dielectric (S–D) QWRs the enhancement of exciton binding energy (dielectric confinement), predicted in Ref. [4], can be explained by the fact that although electron and hole are located in the thin semiconductor filament, the Coulomb interaction energy is concentrated in the insulator because of the large difference of the permittivities. The electric field lines connecting electron and hole partially or, for thin wires mainly, pass through the dielectric. The binding energy and oscillator strength of excitons in S–D QWRs can be varied over wide limits (the binding energy may exceed 100 meV) by choosing semiconductor and dielectric with different permittivities — realizing “Coulomb interaction engineering” [3].

We report the results of optical properties’ investigation of CdS nanostructures crystallized in the pores of Al_2O_3 insulating template. We show that in these nanostructures the role of dielectric confinement effect is of paramount importance that leads to large values of the exciton binding energies ($>$ 100 meV). Large oscillator strengths of exciton transitions make it possible to observe different physical processes determined by excitons in the samples with substantial size (diameter) dispersion of QWRs.

CdS nanostructures have been made by crystallization of the semiconductor in insulating template [5] prepared by anodic oxidation of an aluminum substrate. CdS was formed in the resulting pores of about 8–10 nm in diameter (the atomic force microscope have been used to measure the diameters of pores) and several microns long by cathodic electrodeposition. The formation of CdS nanocrystals was confirmed by their phonon spectra (IR Fourier spectroscopy method have been used) measured by A. I. and L. I. Belogorokhov.

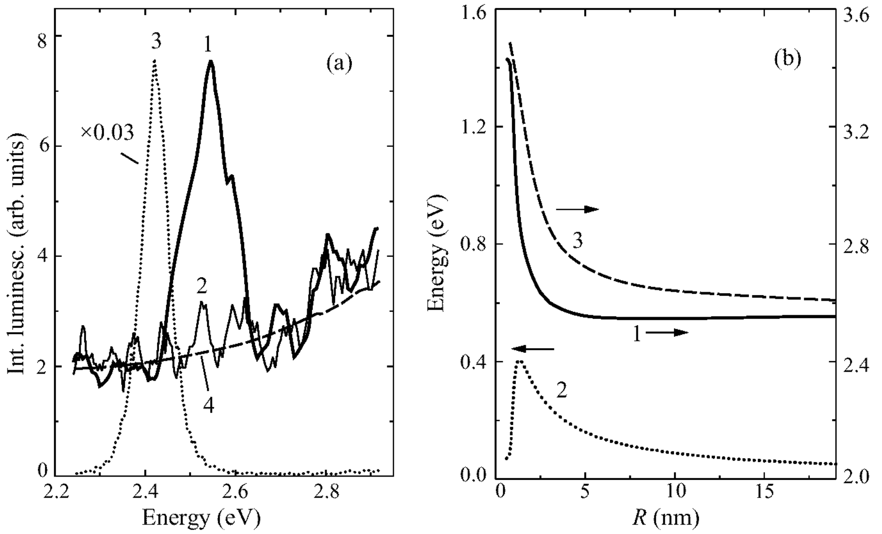

Fig. 1. (a) PL spectra of CdS nanocrystals crystallized in hollow channels of insulating matrix measured with pumping beam polarized at angles 45 (1) and 90 (2) degrees with respect to the direction of the channels of the matrix, as well as the spectra of bulk CdS (3) and matrix (4). (b) Theoretically computed exciton transition energy (1), exciton binding energy (2), renormalized band gap (3) as a function of radius of a cylindrical quantum wire surrounded by Al_2O_3.

Figure 1(a) shows the photoluminescence (PL) spectra of the sample A containing CdS nanocrystals ($T = 300\,K$) for different polarization of the exciting light of a Hg-lamp. For comparison, the luminescence spectra of bulk CdS (a single crystal grown from the vapour phase) and of the insulating Al_2O_3 matrix are presented in the same figure. Comparing the spectra, we can conclude that the luminescence band with maximum at 2.54 eV and a half-width of about 150 meV arises due to CdS nanocrystals. It can be attributed either to the lowest electron–hole transition in quantum dots (QDs), or to excitonic transitions in QWRs, or to transitions in nanostructures of both types. However, the well-expressed luminescence band of CdS nanocrystals arises only if the excitation radiation contains a field component parallel to the axis of the channels. This allows us to suggest that nanostructures have been crystallized primarily as QWRs. Inside thin nanometer size parallel wires surrounded by an insulator the field component of the exciting radiation perpendicular to the axis of the wire is substantially weakened as a result of the boundary conditions, which decreases the absorption (and the luminescence intensity) of light with such polarization [6]. Thus, we attribute the characteristic features of the spectra of CdS structures to the dominant luminescence of excitons in S–D QWRs.

The theoretically computed exciton transition energy, the renormalized band gap and the exciton binding energy of CdS S–D QWRs as a function of the wire radius are presented in Fig. 1(b). Comparing the experimentally determined exciton transition energy 2.54 eV with the computed values (Fig. 1), we find that the QWR radius can lie in the range from 5 nm to 15 nm. In this region (Fig. 1(b)) the changes in the energy of a free transition are compensated by the changes in the binding energy. As a result, the exciton transition energy is independent of the wire's radius over a wide range of its values that largely suppresses the

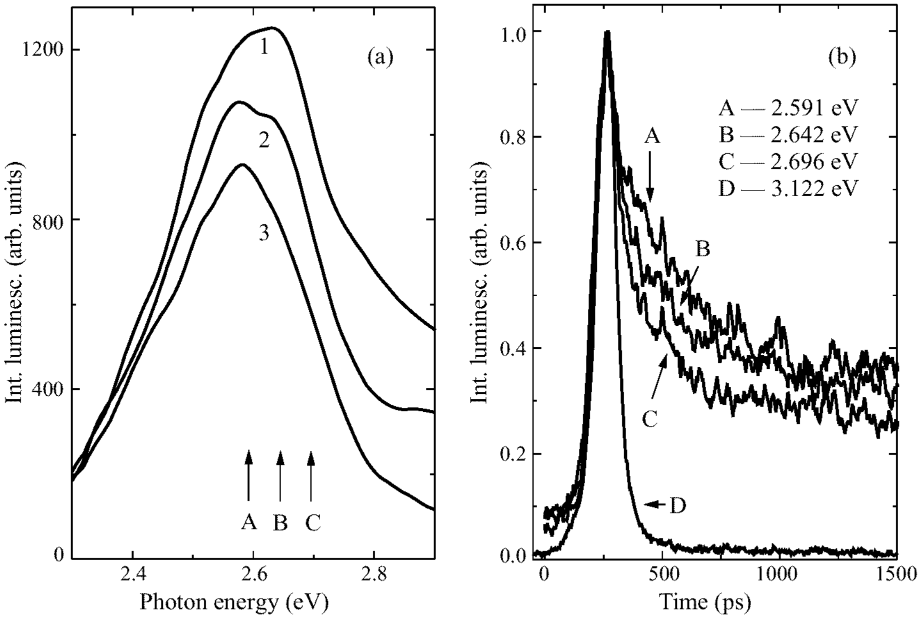

Fig. 2. (a) PL spectra registered at different delays after excitation: 100 ps (1), 200 ps (2), 300 ps (3); (b) The kinetics of PL for different parts of the spectrum are shown by arrows in Fig. 2(a). (D) is the kinetic of matrix PL.

inhomogeneous broadening of the exciton absorption and luminescence bands in samples with large QWR's size variance.

The time-resolved PL spectra were registered using a Ritsu MC-12N polychromator and Hamamatsu C1587 synchroscan streak camera with a two-dimensional detector. The focused beam (0.2 μJ/cm^2) of the second harmonic of the Argon–ion laser pumped Ti–sapphire laser ($\hbar\omega = 3.3$ eV, pulse duration 1.5 ps, repetition rate 82 MHz) was used for excitation of nanostructures. The time resolution was less than 50 ps and the spectral resolution about 1 meV. The time-resolved luminescence spectra of sample B ($T = 2$ K) are presented in Fig. 2(a). The maxima of the broad luminescence spectra (we assume that the inhomogeneous broadening arises due to the size dispersion of QWRs) are shifted with time to the low energy side. It may be explained by the difference in relaxation of excitons in QWRs with different lateral dimensions. In the inhomogeneously broadened spectrum the high energy part (it belongs to the wires of lesser diameter) decays faster than that of the low energy part. The latter is confirmed by the kinetic profiles of the different parts of the spectrum (Fig. 2(b)). The relaxation time may be associated with the nonradiative recombination. In the wires of lesser diameter it is more effective probably due to the more essential role of surface states.

In summary, the peculiarities of the luminescence and time-resolved luminescece spectra of CdS nanostructures crystallized in hollow channels of Al_2O_3 dielectric matrix show that exciton transitions dominate in quantum wires of approximately 10 nm in diameter. The great binding energies of excitons (about 170 meV) arise both due to quantum and dielectric confinement.

Acknowledgments

The research described in this publication was made possible in part by Grant 99-02-18327 from the Russian Foundation for Basic Research and by the Grant 97-1083 of the "Physics of Nanostructures" program.

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