ABSORPTION AND PHOTOLUMINESCENCE STUDY OF CdS QUANTUM DOTS: THE ROLE OF HOST MATRIX AND NANOCRYSTAL SIZE AND DENSITY

Yu.P. RAKOVICH[*,♦], A.G. ROLO[*], M.V. STEPIKHOVA[#,*], M.I. VASILEVSKIY[*], M.J.M. GOMES[*], M.V. ARTEMYEV[‡], W. JANTSCH[**], W. HEISS[**], G. PRECHTL[**]

[*]Departamento de Física, Universidade do Minho, 4709-320 Braga, Portugal,
E-mail: arolo@fisica.uminho.pt
[♦]Department of Physics, Brest Polytechnic Institute, Brest, Belarus
[#] Institute for Physics of Microstructures, RAS, Nizhni Novgorod, Russia
[‡]Physico-Chemical Research Institute, Belarussian State University, Minsk, Belarus
[**]Institute for Semiconductor & Solid State Physics, J. Kepler University, Linz, Austria

ABSTRACT

In this paper we present results of the absorption and photoluminescence (PL) of CdS-doped SiO_2 films fabricated by RF co-sputtering (semiconductor volume fraction f=1-15%, nano-crystallite's mean size 5-7nm) and matrix-free films of close-packed CdS nano-crystallites (f~30%, size 2-5nm) produced by an original chemical method. The absorption spectra have been modelled using the modified Maxwell-Garnett model. This gives the e-h pair state energies and evidence of a strong absorption in the glass matrix containing CdS. The temperature dependence of the spectral position and broadening of the PL peak is analysed. It is concluded that a photo-generated hole is captured on an acceptor-type trap before the radiative recombination with a confined electron. The excitation of this 'band-edge' PL occurs through some states in the matrix and directly in the CdS crystallites for the two kinds of samples, respectively. The temperature coefficients of the optical transition energies for the nearly matrix-free films are similar to those of bulk CdS, while for the CdS/glass films they are smaller. This may be because of the different boundary conditions for the thermal expansion of CdS crystallites.

INTRODUCTION

Since the first works of Ekimov and co-authors [1] and Brus [2], CdS nano-crystallites (NC) have been extensively studied by many groups as an example of semiconductor quantum dots (QD). The experimental studies, however, suffered from an inability to separate quantum size effects from the effects, for example, of the chemical bonding at the semiconductor-matrix interface or changes in the stoichiometry of the NC. As a result, the mechanism of the 'band-edge' photoluminescence from CdS QD has not been definitely established as yet [3,4]. Another question, which has no clear answer yet, is to what extent CdS NC's can be thought of as small pieces of the bulk material. Do they possess bulk parameters, such as the characteristic electronic structure energies with their dependence on temperature, phonon frequencies or electron-phonon interaction constant?

In this work, we studied the temperature dependence of the absorption, PL and PL excitation (PLE) spectra of two kinds of CdS QD composites: CdS - doped glass films and matrix-free films of close-packed (CP) CdS nanocrystals. This paper is devoted to comparison of their properties. We discuss the origin of the 'band-edge' PL and temperature dependence of the parameters extracted from the spectra.

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EXPERIMENTAL

CdS-doped glass films were produced by a conventional rf-magnetron co-sputtering method using an Alcatel SCM650 apparatus. Details of the rf-sputtering deposition procedure have been previously published [5]. The NC size, as determined from the X-ray spectrum, was typically 5-10nm for these samples, with a cubic structure resolved for larger NC.

CP CdS NC were prepared by mixing at room temperature two equimolar (10^{-2}M) solutions of 1-thioglicerol cadmium salt and sodium sulfide. Both were dissolved in dimethylsulfoxide (DMSO). Two parts of the colloid solution of CdS NC were heated to 170^0C under nitrogen with an excess of cadmium ions. To remove the residual components, the resulting NC colloid solutions were precipitated using acetone and re-dissolved in fresh portions of DMSO. Thin solid films of matrix-free CdS nanocrystals on quartz, glass or Si substrates were then prepared by spin-coating using the colloid solutions. After drying, CdS NC's formed a random CP structure of nearly spherical particles separated by surface monolayers of thioglicerole. The NC size was 2-5nm, as determined from the absorption peak for different samples of this kind.

Optical absorption spectra were measured using a double-beam Shimadzu model UV-3101 PC. A Spex 1680 spectrometer was used for photoluminescence (PL) measurements in the spectral range 380 to 800nm. The PL spectra were obtained by exciting the samples with either an Ar^+ laser (λ=350nm and 457.9nm, output power 50mW and spot size 2mm) or a Xenon lamp (output power 0.5-2mW, depending on the wavelength, and spot area 10mm^2). The luminescence signal was recorded using a 1402 Spex double spectrometer equipped with an R943 Hamamatsu photomultiplier. The Xenon lamp was used also for the study of the PLE spectra.

RESULTS AND DISCUSSION

In the absorption spectra (Fig.1), quantised e-h transitions are clearly seen only for the CP samples. We modelled these spectra in the following way. First, the energies of the confined e-h pair states were determined. Within the effective mass approximation and assuming an infinitely high potential barrier at the interface, the dependence of these energies on the QD radius R is given by the simple formulas of ref. [6]. The rigorous calculation of the hole confinement energies is rather complicated because of the small spin-split energy in CdS [7], However, these values are small (few meV for QD larger then 2nm [7]) and were therefore ignored. We also took into account the bulk E_1 transition, which presumably is little affected by the spatial confinement and responsible for the strong NC absorption below 300nm [2].

Given the transition energies, the QD susceptibility χ can be defined [8] and its polarisability calculated according to:

$$\alpha = R^3 \left\{ \frac{\varepsilon_\infty^{(1)} - \varepsilon_\infty^{(2)}}{\varepsilon_\infty^{(1)} + 2\varepsilon_\infty^{(2)}} + \frac{4\pi\chi}{\varepsilon_\infty^{(1)} + 2\varepsilon_\infty^{(2)}} \right\}, \qquad (1)$$

where $\varepsilon_\infty^{(1)}$ and $\varepsilon_\infty^{(2)}$ are the high-frequency dielectric constants of the QD and matrix, respectively. In the low QD concentration limit, this quantity (averaged over the sizes) gives the optical response of a QD ensemble. However, for dense composites like the CP NC films, collective effects (multipole interaction of the QD) should be important. We took into account the dipole-dipole interaction effects by introducing the renormalised polarisability, simultaneously including the distribution of sphere's sizes, as proposed in [9]. The effective

dielectric function of a composite film was then calculated from the renormalised polarisability using the Maxwell-Garnett equation.

Using the bulk CdS parameters (m_e=0.2m_0, E_g=2.5eV and the Kane energy E_P=15.5eV [10]) and calculating the oscillator strength [8], the first absorption peak (designated ($1S_e1S_{3/2}$)) was fitted quite well with the nominal values of the film thickness and semiconductor volume fraction. The rest of the curve was fitted adjusting the parameters of three more transitions (Fig.1). However, the absorption spectra of CdS-doped glasses could be only modelled assuming a strong resonance in glass, centred at 4.75eV. Normally SiO_2 glasses do not absorb at this energy, but those with semiconductor NC inside do [8]. We think this may be due to some residual ions of the semiconductor constituents, which stay in the glass instead of forming NC. Another remark concerning this fitting is that the *log-normal* distribution of sizes used does not reproduce accurately the probability of QD larger than the average (and the Gaussian is even worse).

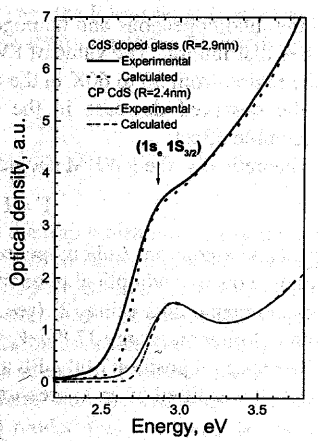

Fig.1. Absorption spectra of a CP CdS NC film (left) and a CdS-doped glass film (right). Theoretical curves were calculated using the modified Maxwell-Garnett theory (NC volume fraction f=0.3 and 0.13 for the CP and CdS/glass films, respectively).

Some representative PL and PLE spectra for the two kinds of samples are presented in Fig.2. They show a broad band in the visible range and a pronounced high-energy (HE) peak, whose intensity (relative to that of the band) increases as the temperature decreases.

PLE spectra collected at this HE peak for each sample also show a peak at a slightly higher energy. We notice that, for all the samples studied, the HE PL peak lies at an energy slightly less than that of the ($1s_e1S_{3/2}$) transition seen in the absorption. In order to investigate if one is really related to the other, we studied the temperature dependence of the position, intensity and broadening of the PL peak. A Gaussian fit of the peak lineshape was used for the estimation of its full width at half-maximum (FWHM) for each temperature. In such a manner, the luminescence linewidth of the CdS doped SiO_2 film was determined to be, for example, 126meV and 131meV at T=4.2K and 60K, respectively. The FWHM value for a CP NC film was estimated to be 125meV at 77K. This broadening includes

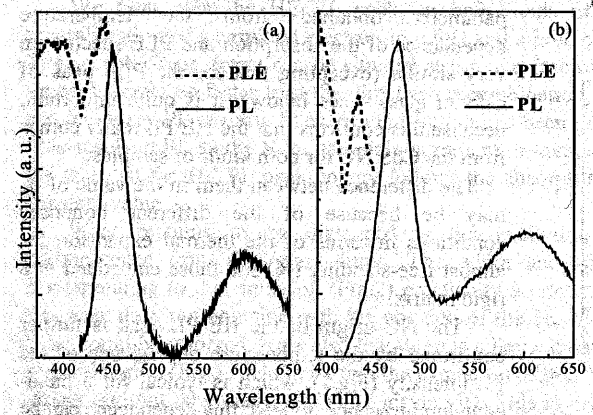

Fig. 2. Room temperature PL (solid line) and PLE (dashed line) spectra of films of close-packed CdS nanocrystals (a) and CdS nanocrystals in glass matrix (b).

both the inhomogeneous and homogeneous contributions, the former is mainly because of the NC size distribution. The value of FWHM increases relatively rapidly with temperature, except for the region from 30 to 60K in the case of CdS-doped SiO_2 samples. It should be emphasised that the observed decrease in the width of the PL peak in this temperature region is a reproducible effect.

Theoretically, the FWHM should vary with temperature according to:

$$\Gamma = \Gamma_0 + \beta \cdot T + \gamma \cdot N(\hbar\omega_{LO}) \,, \qquad (2)$$

where Γ_0 is a constant (inhomogeneous broadening), the second and third terms represent the effect of acoustic and optical phonons, respectively, and N is the Bose-Einstein factor. A fit to the experimental data using (2) (see Fig.3) gave Γ_0=128meV, β=7.6·10^{-2}meV/K, γ=143.1meV and an LO-phonon energy 37.8*meV*, which are typical for CdS NC [4].

The spectral position of the PL and absorption peaks for different temperatures is presented in Fig.4. It was fitted by an expression: proposed by Varshni [11]:

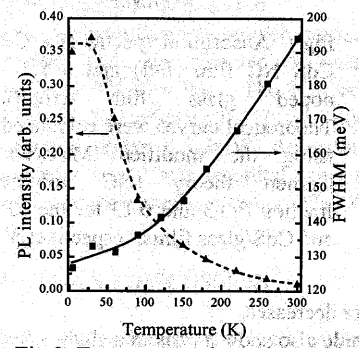

Fig.3. Temperature dependence of the FWHM and the integrated intensity of the HE PL peak for CdS NC's in glass (R≈.30A°)

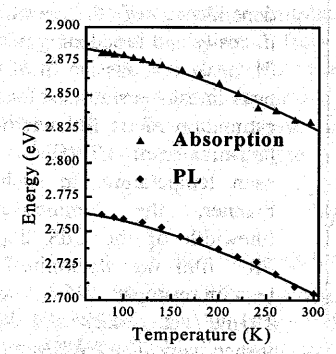

Fig.4.Temperature dependence of the absorption and HE PL energies for the CP CdS NC film (R≈.25A°)

$$E(T) = E_0 - \frac{\alpha_g \cdot T^2}{T + \Theta} \,, \qquad (3)$$

where E_0 is the band gap energy at 0K and α_g and Θ are constants. The values of E_0 obtained for CdS NC in glass and CP film presented in Fig.4 are 2.65eV and 2.77eV, respectively. For the absorption and PLE peaks, the values of E_0 were estimated as 2.89eV (CP NC) and 2.88eV (CdS-doped glass). The values of α_g obtained for the HE PL peak for both samples, namely, 3.61·10^{-4}eV/K for CdS/glass and 6.6·10^{-4}eV/K for CP NC, agree with those reported in the literature for CdS NC in glass [5], and are slightly less than for bulk CdS (α_g=7.7·10^{-4}eV/K [12]). The values of this parameter obtained from the temperature dependence of the absorption and PLE spectra are very similar (excepting that for the PLE peak of CdS in glass – see below). It is quite important, because this confirms that the HE PL really comes from the CdS NC for both kinds of samples.

The difference between them in the value of α_g may be because of the different boundary conditions in terms of the thermal expansion for almost free-standing NC and those embedded in a rigid matrix.

The NC origin of the HE PL peak is further confirmed by the temperature dependence of the PL intensity (Fig.3), which is typical for a band-edge luminescence. Indeed, this dependence can be modelled considering, apart from the radiative recombination channel, a non-radiative recombination mechanism (via traps). Assuming

both the inhomogeneous and homogeneous contributions, the former is mainly because of the NC size distribution. The value of FWHM increases relatively rapidly with temperature, except for the region from 30 to 60K in the case of CdS-doped SiO_2 samples. It should be emphasised that the observed decrease in the width of the PL peak in this temperature region is a reproducible effect.

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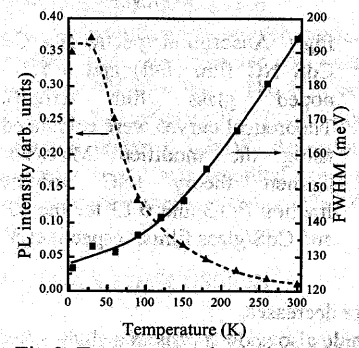

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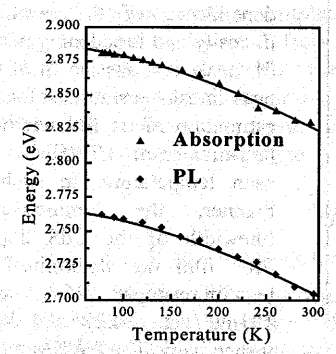

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The NC origin of the HE PL peak is further confirmed by the temperature dependence of the PL intensity (Fig.3), which is typical for a band-edge luminescence. Indeed, this dependence can be modelled considering, apart from the radiative recombination channel, a non-radiative recombination mechanism (via traps). Assuming

that the trap level lies in the upper part of the CdS band gap, the Fermi level is somewhere in the middle, and using the Schockley-Reed formula, we can approximate the PL intensity by the following expression:

$$I_{PL}(T) = \frac{I_0}{1 + B \cdot \left(1 + g^{-1} \cdot \exp\left(\frac{E_t - E_F}{kT}\right)\right)^{-1}}, \qquad (4)$$

where I_0 and B are constant, g is the degeneracy factor, E_t the trap ionisation energy and E_F the Fermi level. As one can see from Fig.3, (4) provides a good fit to the experimental dependence. The activation energy (i.e., the difference between the trap depth and the Fermi level) was found to be rather small (e.g., 25meV for CdS/glass). A better fit can be achieved if we assume two kinds of traps, the second one is shallower and its contribution to the non-radiative lifetime is smaller. We would like to draw attention to the increase in the PL intensity at approximately 30K. This effect has been reported before [13] and correlates with the decrease in the FWHM of the PL peak mentioned above. In terms of the present model, this can be explained by the crossing of the trap level and the Fermi energy at $T \approx 30$K. However, a detailed study of this effect will be the subject of the future work.

Thus, it looks plausible that the HE PL peak originates from CdS NC. However, if we admit this, we have to explain the Stokes shift between the absorption and emission (about 100meV for CP films). Such large Stokes shifts have been observed before for CdS/glass [14] and CdSe/glass systems [15]. Sometimes they were explained by the strongly enhanced electron-LO-phonon coupling in QD [14]. This requires unrealistic values of the Huang-Rhys parameter and would be very unlikely. Another explanation [15] stresses the effect of a broad QD size distribution. Larger QD (with smaller confinement effect) contribute more to the emission ($\sim R^3$) when the whole ensemble is excited (non-selective excitation). On the contrary, all QD contribute to the absorption according to the distribution of their sizes. Finally, there is an explanation of the Stokes shift in terms of the 'dark' (ground) and 'bright' exciton states [15,16]. The splitting between them can be as large as several tens of meV [16]. However, any of these effects can hardly explain such a shift of 100meV for moderate size NC in our case.

We think that the HE PL peak, in both kinds of samples, is due to the radiative recombination of a confined electron in a QD and a hole captured at a shallow acceptor level. The acceptor-type defect can be situated at the interface or even outside the QD. The capture process should be faster than the direct e-h recombination, this is why the latter is not seen in the stationary PL spectra. Such an explanation has been proposed in ref. [3] on the basis of a time-resolved PL study. Here, the main argument in favour of this PL mechanism comes from the fact that the HE PL peak energy follows the absorption peak, shifted from it by almost a constant value.

What remains to be discussed is the excitation mechanism of the 'band-edge' luminescence from CdS/glass films. The width and spectral position of the PLE peak corresponding to this emission (Fig.2) practically do not change with temperature. Moreover, this peak does not coincide with the position of the $1s_e$-$1S_{3/2}$ transition for samples where the latter could be resolved. Note also that there is a large absorption due to the matrix in the same spectral region (Fig.1). We think that the excitation of this PL occurs through these states in the matrix and not by creating e-h pairs inside QD. This is confirmed by the fact that PL spectra excited with the λ=457.9nm line of the Ar laser (that is, size-selectively) practically coincide with those obtained with λ=350nm (non-selective excitation).

CONCLUSIONS

It follows from our studies of the temperature dependence of the absorption, PL and PLE spectra of two kinds of CdS nano-crystalline samples, that the intense PL peak in the ultra-violet spectral range most likely originates from the recombination of an electron confined in a QD ($1s_e$ state) and a hole trapped on a shallow acceptor state. The excitation mechanism of this PL is different for the CP and CdS/glass films. The glass matrix absorbs the light strongly, probably because only some part of the Cd and S atoms form crystallites, while the rest of them stay dissolved in the glass. The excitation of the NC-related PL probably occurs through these light-absorbing states in the glass matrix.

From the temperature dependence of the optical transition energies we can conclude that nearly free-standing NC have parameters similar to those of bulk CdS, while for NC embedded in the matrix the temperature coefficient of the band gap energy is smaller. This may be because of the thermal expansion dictated by the matrix, not the crystallite itself.

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