TEMPERATURE AND SHELL THICKNESS EFFECTS ON THE OPTICAL PROPERTIES OF II-VI SEMICONDUCTOR CORE-SHELL ENSEMBLES

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Abstract

We have investigated the temperature and shell thickness effects on the extinction and photoluminescence (PL) optical properties in II-VI semiconductor core-shells of type I. To this purpose, we used Maxwell-Garnett (M-G) effective theory by defining appropriate dielectric functions for the constitutive materials of the core-shells. We have obtained one sharp resonant peak which can be related to the $1S_h \rightarrow 1S_e$ optical transition, which is red-shifted with the increase of shell thickness. This peak is also red-shifted with increasing temperature due to core shrinking band gap described by Varshni´s law. For the PL spectra, we have considered radiative and non-radiative decay rates as the main processes that can lead to the carrier relaxation. The Stokes shift between the absorption- and PL- peaks is of the order of a few meV. Finally, our findings are similar to that reported in the literature in absorption and PL experimental spectra.

Keywords: Semiconductor nanostructures, Maxwell-Garnett theory, optical properties

1. INTRODUCTION

In recent years, II-VI semiconductor core-shell type composite quantum dots (QDs) exhibit novel properties making them very attractive from both experimental and practical point of view. It has been shown that overcoating nanocrystallites improve the photoluminescence quantum yields by passivation of surface nonabsorbing recombination sites [1,2].

Baranov et al. [3] and Dzhagan et al. [4] reported interesting features in the Raman, absorption and PL experimental spectra of II-VI semiconductor core-shell nanocrystals (NCs) due to the effects of shell thickness. Valerini et al. [5] reported the temperature dependence of the PL spectra and PL relaxation dynamics for CdSe/ZnS core-shell QDs. On the other hand, we have investigated the optical properties of isolated II-VI semiconductor core-shell in IR and VIS spectra [6], where we have reported the effects of core-shell size, embedding medium and phonon contribution in optical spectra. However, the effects of temperature and shell thickness are not considered.

Therefore, the aim of this work is to investigate the absorbance along with the PL of II-VI semiconductor ensembles taking into account the effects of shell thickness and temperature in order to extend our previous work and to compare it to the experimental research.

2. SYSTEM UNDER INVESTIGATION AND THEORETICAL MODEL

The core-shells of type I (electrons and holes confined in the core) are characterized by a total radius R_s and a core of radius R_c with their respective core and shell frequency-dependent dielectric functions ε_e and ε_s. We assume that ε_c has two terms: the first one, obtained from the electric-dipole approximation, describes the QD polarization due to the ground-state exciton as described in references [7,8] and the second one, due to the bulk phonons contribution [9]. For the shell material, we use the bulk-like semiconductor dielectric, with its plasmons and phonons contributions as described in ref. [9], while the insulating medium has a non-frequency dependent dielectric function ε_e. On the other hand, the exciton energy is written as

$$E_c = E_{g,c} + E(e) + E(h) + E(Coulomb) \quad (1)$$

where $E_{g,c}$ is the intrinsic core band energy, whose temperature dependence is described by Varshni´s law [10]. We calculated the electron and hole energies (E(e) and E(h)) using Effective Mass Approximation (EMA) in a finite barrier potential, while the Coulomb interaction (E(Coulomb)) is treated as a perturbative correction to the confinement energies [11].

Once the ε_c and ε_s are well established, the effective core-shell dielectric function ε_{ns} can be expressed within the framework of the electrostatic dipole approximation such as [12]

$$\frac{\varepsilon_{ns} - \varepsilon_e}{\varepsilon_{ns} + 2\varepsilon_e} = \frac{(\varepsilon_s - \varepsilon_e)(\varepsilon_c + 2\varepsilon_s) + (R_c / R_s)^3 (\varepsilon_c - \varepsilon_s)(\varepsilon_e + 2\varepsilon_s)}{(\varepsilon_s + 2\,\varepsilon_e)(\varepsilon_c + 2\varepsilon_s) + 2(R_c / R_s)^3 (\varepsilon_c - \varepsilon_s)(\varepsilon_s - \varepsilon_e)}. \quad (2)$$

Considering the core-shell NCs as polarizable point dipoles, the effective dielectric function of the composite medium is described using M-G effective approach; i.e.,

$$\frac{\varepsilon_{eff} - \varepsilon_e}{\varepsilon_{eff} + 2\varepsilon_e} = f\,\frac{\varepsilon_{ns} - \varepsilon_e}{\varepsilon_{ns} + 2\varepsilon_e} = Q. \quad (3)$$

By solving the above eq. for ε_{eff}, being f the volume fraction of the distribution, we find that

$$\varepsilon_{eff} = \frac{\varepsilon_e (1 + 2Q)}{1 - Q}. \quad (4)$$

Then, the extinction coefficient is given by [13]

$$\alpha\left(cm^{-1}\right) = \frac{8.88\times10^7}{\lambda(nm)}\sqrt{-\varepsilon'_{eff} + \sqrt{\left(\varepsilon'_{eff}\right)^2 + \left(\varepsilon''_{eff}\right)^2}} \quad (5)$$

where ε'_{eff} and ε''_{eff} are, respectively, the real and imaginary parts of ε_{eff}.

Regarding to the PL spectra, we follow the model proposed by Valerini et al. [5], where we consider two approximations. First, the possible processes that can lead to carrier relaxation in core-shell ensembles will be radiative relaxation, thermal escape from the core-shells assisted by LO phonons and thermally activated carrier localization in surface states processes. We neglect Auger non-radiative relaxation, and Förster energy transfer. Second, the radiative decay will be independent of the core-shell size. Then, the rate equation for the carriers population n is given by

$$\frac{dn}{dt} = g(t) - \frac{n}{\tau_{rad}} - \frac{n}{\tau_{act}} - \frac{n}{\tau_{esc}} \quad (6)$$

where g(t) is the generation term, $1/\tau_{rad}$ is the radiative recombination rate, $1/\tau_{esc}$ the thermal escape rate and $1/\tau_{act}$ the thermally activated process rate. Then, the integrated PL intensity at a temperature T is given by [5]

$$I_{PL}(T) = \int_0^\infty I_{PL}(t)\,dt = \frac{n_0}{1 + \tau_{rad}/\tau_{act} + \tau_{rad}/\tau_{esc}}. \quad (7)$$

In the above eq, n_0, the initial carrier population, is considered to be $j_p.\sigma_0$, where σ_0 is the extinction cross section, which is equal to the extinction coefficient multiplied to the volume of the core-shell NC, and j_p is the photon fluence fixed to a value of 3×10^{11} photons.cm^{-2} in this work. For our PL simulated spectra, we will take the same decay parameters values than those considered as the best fitted for the PL spectra in ref. [5].

3. RESULTS AND DISCUSSION

We apply Maxwell-Garnett effective theory in typical II-VI semiconductor core-shell nanocrystals (NCs) such as CdSe/ZnS, where the effects of the temperature and shell thickness are investigated on the absorbance and PL simulated optical spectra. In order to compare our theoretical results with those obtained in the literature, we take similar shell thickness 2, 3 and 4 ML than those reported in refs. [3, 4]. As the NCs have

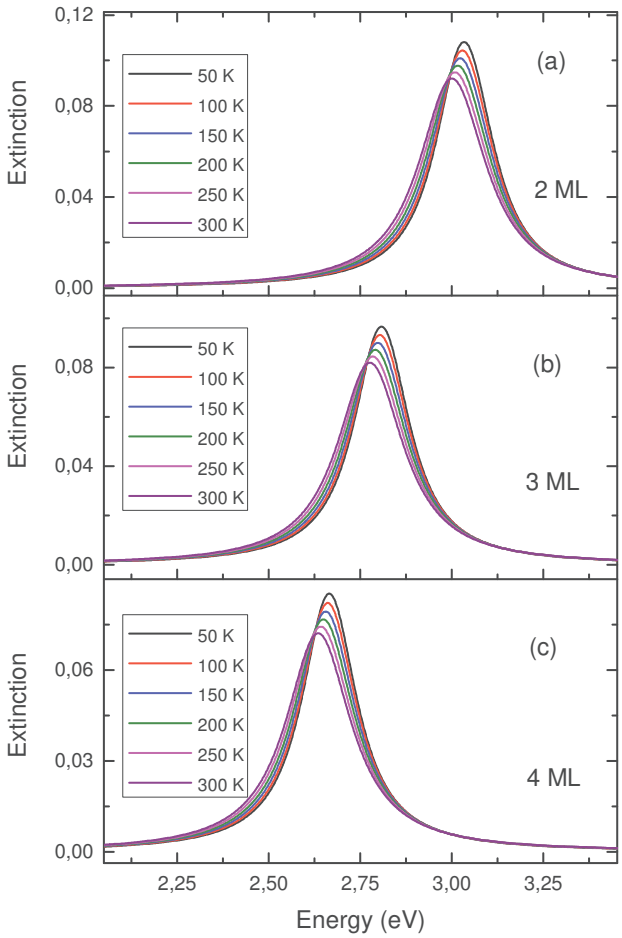

Figure 1 Extinction spectra for CdSe/ZnS/gelatine as a funtion of the temperature with shell thicknesses equal to 2 ML (a), 3 ML (b) and 4 ML (c)

nanometric size, the extinction is mainly due to absorption processes, accordingly to the optical properties in low-dimensional systems [14]. Indeed, the extinction (extinction coefficient multiplied by the nanocrystal thickness) [6] and the integrated PL signal will be shown as a function of energy for temperatures ranging in the interval 50-300 K and with an excitation wavelength λ_{exc} = 380 nm. This value is greater than the exciton energy in these NCs. Values of the different constants for CdSe, ZnS and insulating media are reported in refs. [15,16]. **Figure 1** shows the extinction spectra for CdSe/ZnS/gelatine core-shells as a function of the energy with f = 0.1, core radius R_c = 2 nm and shell thicknesses equal to 2, 3 and 4 ML, respectively in the interval of temperatures 50-300 K. For each shell thickness, we obtain a sharp resonant band located

approximately at 3 eV (2 ML), 2.8 eV (3 ML) and 2.6 eV (4 ML), respectively. We can attribute these peaks to the $1S_h \rightarrow 1S_e$ optical transition in CdSe cores of radius 2 nm and different thicknesses. We found a blue-shift of this band if it is compared to refs. [3, 5]. This could be explained by means of the complex weighting terms in the MG formalism. The red-shift of the peaks due to shell thickness enlargement can be attributed to the partial tunneling of the carriers wave functions into the ZnS shell. A qualitative similar behavior of absorption spectra with increase of the shell thickness is reported in refs. [3, 4] for CdSe/ZnS core-shell NCs. As can be observed in **Figure 1**, for each investigated shell thickness, there is a red-shift of the core peak as the temperature increases from 50 K to 300 K, along with a decreasing of its peak intensity and an increasing of the Full Width at Half Maximum (HWHM) peak. This red-shift of the resonant peaks is consequence of the shrinking band gap, which is taken into account by means of Varshini´s law [10], being

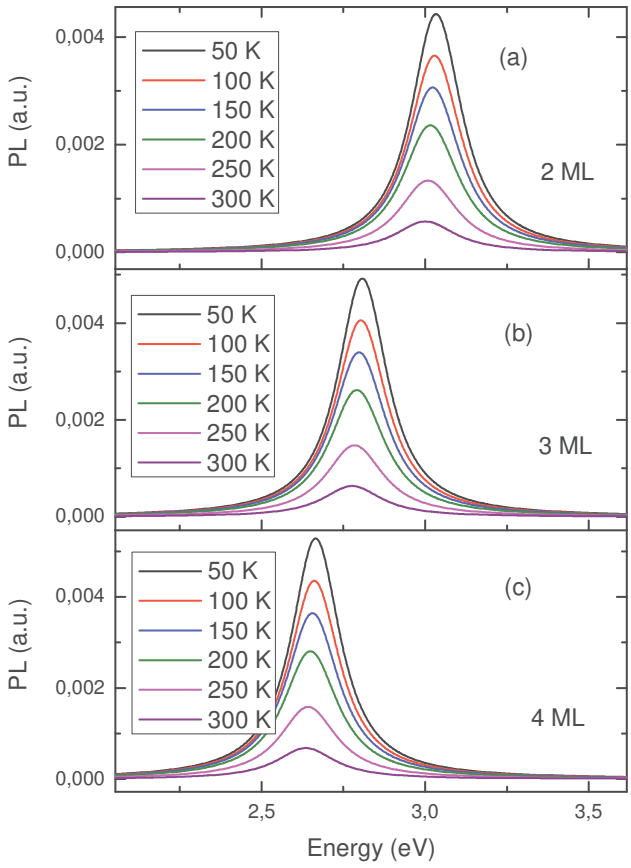

Figure 2 PL spectra for CdSe/ZnS/gelatine as a function of the temperature with shell thickness equal to 2 ML (a), 3 ML (b) and 4 ML (c)

the thermal expansion in the overall temperature range neglected, as this effect is very small compared to the former [5, 11]. The increasing of the FWHM peak is consequence of the excitonic peak broadening due to different charge carrier-phonon scattering processes. We obtain that the red-shift of the resonant peak is greater for increasing shell thickness than for increasing temperature in the range of 50-300 K. On the other hand, a similar temperature dependence of the intensity is obtained in a previous work [11] for the imaginary part of the dielectric function in CdSe/ZnS core-shell distributions. Besides, the decrease in intensity is greater for shell thickness increase than temperature increase. In the light of the above results, we can conclude that the confinement effect is greater than the temperature effect on the extinction spectra of II-VI NCs ensembles. We show in **Figure 2** the PL integrated spectra for CdSe/ZnS/gelatine core-shell ensembles for volume fraction f = 0.1, core radius R_c = 2 nm and shell thicknesses equal to 2, 3 and 4 ML, respectively in the interval of temperatures 50-300 K. For each shell thickness, we obtain a sharp resonant band located approximately at

3 eV (2 ML), 2.8 eV (3 ML) and 2.6 eV (4 ML), respectively. Then, the Stokes shift between the extinction- and the PL- peaks is of the order of a few meV for the three shell thicknesse and for the temperature range investigated. This Stokes shift is a typical value in II-VI core-shell NCs [17]. A qualitative similar behavior of PL spectra with increasing of the shell thickness is reported in refs. [3,4] for CdSe/ZnS core-shell NCs. In order to look more closely at the evolution of the PL peaks as the temperature is varied, we show in **Figure 3** their peaks position as a funtion of temperature. We obtain that the red-shift of the resonant band is greater for increasing shell thickness than for increasing temperature in all temperature range investigated. Besides, the energy peak temperature dependence shows slightly three different regions between 50-125 K, 125-225 K and 225-300 K, which could be related to the three relaxation decay processes considered in this work; i.e., radiative relaxation, thermal escape assisted by LO phonons and thermally activated carrier localization in surface states processes.

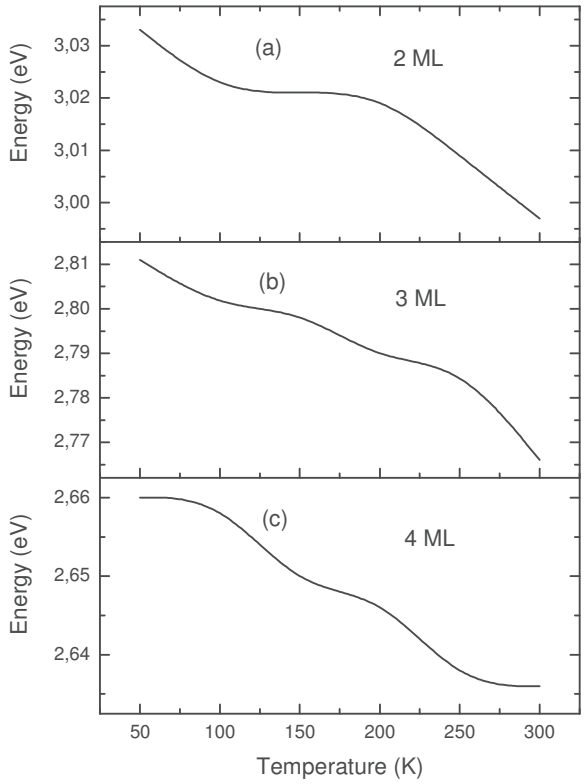

Figure 3 PL peak energy as a function of temperature for CdSe/ZnS/gelatine with shell thickness of 2 ML (a), 3 ML (b) and 4 ML (c)

4. CONCLUSION

Temperature and thickness effects on the simulated extinction and PL spectra of II-VI semiconductor core-shells of type I have been investigated by means of M-G effective theory by defining appropriate dielectric functions for the constitutive materials of core-shells. A very sharp peak is related to the $1S_h \rightarrow 1S_e$ optical transition in CdSe core. This peak is red-shifted for thicker shells, feature that can be ascribed to the partial tunneling of the carriers wave functions into the ZnS shell. When the temperature is increased, this peak is also red-shifted due to core shrinking band gap described by Varshni´s law. For the PL integrated spectra, we have considered three relaxation decay processes consisting of radiative relaxation, thermal escape assisted by LO phonons and thermally activated carrier localization in surface states processes. Finally, we can conclude that the confinement effect is greater than the temperature effect in optical spectra of II-VI NCs distributions.

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