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Temperature dependence of photoluminescence in CdS nanocrystals prepared by the sol–gel method

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Abstract

The temperature-dependent photoluminescence spectra of CdS semiconductor nanocrystals-doped glasses prepared by a sol–gel method were measured at different excitation intensities. Based on the temperature dependence of the peak energy, linewidth and intensity of the luminescence, the characteristics and origins of the band-edge luminescence were discussed.

1. Introduction

The recombination processes of photogenerated carriers in semiconductor nanocrystals are important to their applications in optoelectronic devices. It was found that the recombination time decreased with increasing laser excitation intensity and was in the range from milliseconds to several picoseconds, corresponding to different recombination processes. The photoluminescence (PL) technique is widely used to investigate both radiative and nonradiative transitions of carriers in nanocrystals. The PL spectra observed in CdS nanocrystals, embedded in colloids, glasses, polymers and zeolites, were strongly dependent on the sample preparation techniques. The band edge PL emissions were attributed to various recombination mechanisms such as the donor-acceptor pair emission [1] and the recombination luminescence of shallow traps [2,3] and electron–hole pairs (excitons) [3,4].

In this work, we report a study of the temperature-dependent PL spectra of CdS semiconductor nanocrystals doped in sodium borosilicate glasses prepared by a sol–gel method, for different excitation intensities and discuss the characteristics and origins of the band-edge luminescence.

2. Experimental

CdS nanocrystal-doped glasses were obtained by a sol-gel technique. Sodium borosilicate system gels containing $Cd(NO_3)_2 \cdot 4H_2O$ and $SC(NH_2)_2$ were prepared by using tetraethyl orthosilicate, boric acid, sodium alkaxide as precursors, ethanol, glycolic methyl, ether, ethanol as precursor solvents, and hydrochloric acid as a catalyst. After isothermal heat-treatment at 100°C for 10 h, the stiff gels were first heated up to around 350–450°C for 24 h in a silica tube with flowing oxygen gas. The CdO-containing gels, were then cooled to 150°C and exposed to dry H_2S gas for 2 h in a silica

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tube previously evacuated of N_2, to convert CdO to CdS. They were then heated to the temperature region of 550–650°C under vacuum, for various treatment times for consolidating into pore-free glasses. The CdS nanocrystal-doped glasses used in these experiments were obtained for a heat-treatment time of 14 h at 590°C. The average size of the nanocrystals was determined to be 8–10 nm by a transmission electron microscope.

The temperature-dependent PL spectra of samples were obtained with a Spex 1403 double grating monochromator and detected with a photomultiplier tube. The samples were mounted in a closed-cycle cryostat with sample temperatures variable between 20 and 300 K. The luminescence was excited with frequency-tripled light (355 nm) from a *Q*-switched Nd:YAG laser with pulse duration of 10 ns and 10Hz repetition rate.

3. Results and discussion

The temperature-dependent PL spectra of CdS nanocrystals were measured for different excitation intensities. The spectra at 30 K exhibit two emission bands: a strong one at about 2.5 eV and a weak broad band in the range of 1.7 to 2.0 eV. The higher energy band, which is referred to as band-edge luminescence because its energy is close to that of the absorption band edge of the sample, was related to various radiative mechanisms [1–6]. The low-energy band was possibly related to surface defects or surface states [4, 5]. Increasing the excitation intensity results in a blue shift and a broadening of the band-edge luminescence perhaps due to band filling. The peak energies and full widths at half maximum (FWHM) are 2.507 eV, 156 meV and 2.525 eV, 224 meV, respectively, for excitation intensities of $0.1I_0$ and I_0, where I_0 is about 10^6 W cm^{-2}.

The temperature dependence of the peak energies for the band-edge luminescence at different excitation intensities is shown in Fig. 1. In general, the variation in the energy gap with temperature is believed to result from the following two mechanisms: (1) lattice dilation, which causes a linear effect with temperature, and (2) temperature-dependent electron–phonon interactions. Varshni proposed the following empirical relation for the temperature dependence of the energy gap for semiconductors:

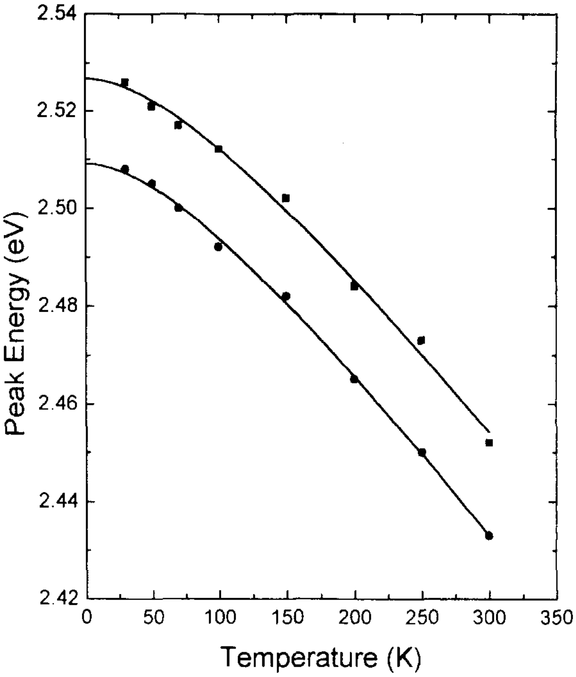

Fig. 1. Temperature dependence of the peak energies for the band-edge luminescence at excitation intensities of $0.1I_0$ (circles) and I_0 (squares).

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta} \tag{1}$$

where $E_g(0)$ is the value of the energy gap at 0 K, and α and β are constants. The fits to this equation, as shown in Fig. 1, are excellent. The parameters obtained were as follows:

$E_{g1}(0) = 2.509\,\text{eV}, \quad \alpha_1 = 3.8 \times 10^{-4}\,\text{eV/K},$

$\beta_1 = 149.9\,\text{K},$

$E_{g2}(0) = 2.527\,\text{eV}, \quad \alpha_2 = 3.6 \times 10^{-4}\,\text{eV/K},$

$\beta_2 = 150\,\text{K},$

for excitation intensities of $0.1I_0$ and I_0, respectively. The values of α_1 and α_2 agree with those of CdS single crystals, for which $\alpha = 5 \times 10^{-4}$ eV/K. Thus the temperature dependence of the peak energy of the band-edge luminescence in CdS nanocrystals is similar to the behavior of the band gaps of the bulk material and of quantum dots in glasses [5].

Fig. 2 shows the variation of the FWHM as a function of temperature for the band-edge luminescence of CdS nanocrystals. The FWHMs of the band-edge luminescence decrease somewhat from 30 to 70 K, and then increase rapidly. Taking the interaction of excitons with optical phonons (LO) into account, the temperature dependence of the FWHM can be expressed [5]:

$$\Gamma = \Gamma_0 + \frac{\Gamma_{\mathrm{ph}}}{\exp(\hbar\omega_{\mathrm{LO}}/kT) - 1}, \qquad (2)$$

where Γ_0 is a constant term, $\hbar\omega_{\mathrm{LO}}$ the LO phonon energy and Γ_{ph} a phonon-broadening coefficient. For CdS nanocrystals, $\hbar\omega_{\mathrm{LO}} = 37.8$ meV. The solid curves in Fig. 2 are fits of Eq. (2) to the experimental data with $\Gamma_{01} = 150.7$ meV, $\Gamma_{\mathrm{ph1}} = 154.3$ meV, and $\Gamma_{02} = 213$ meV, $\Gamma_{\mathrm{ph2}} = 157.1$ meV for low and high excitation intensities, respectively. This implies that the phonon-broadening coefficient Γ_{ph} is independent of the excitation intensity. The luminescence linewidth of CdS nanocrystals was determined to be 139 meV at 30 K and at very weak laser intensity. Recently, Blanton et al. [6] determined the luminescence linewidth of single CdS nanocrystallites to be 15 meV by two-photon excitation microscopy. The PL linewidth obtained in that work mainly originates from the size distribution of nanocrystals at weak laser intensity and significantly broadens with increase of the excitation intensity.

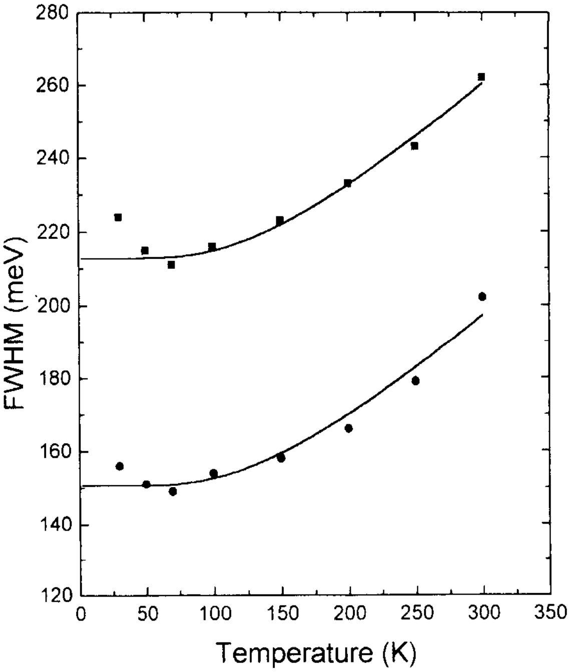

Fig. 2. Temperature dependence of the FWHMs for the band-edge luminescence at excitation intensities of $0.1I_0$ (circles) and I_0 (squares).

The temperature dependence of the exciton emission energy is expected to follow the bandgap of the bulk material. The similar dependence may also be observed in the recombination processes of the shallow traps. Thus it is difficult to distinguish whether the band edge luminescence originates from the recombination of excitons or shallow traps. However, it is clearly different for the temperature dependence of the PL intensities of excitons and shallow traps. Furthermore there must exist a different excitation intensity dependence for the recombination of excitons and shallow traps. The recombination of shallow traps is dominant at weak excitation intensities and saturates at higher excitation intensities, where the luminescence of excitons becomes dominant. The temperature dependence of the PL intensity for the CdS nanocrystals is shown in Fig. 3. The PL intensities of the band-edge luminescence at different excitation intensities decrease rapidly with increasing temperature. The temperature variation of the PL intensity at low excitation intensities is clearly larger than at high intensities, particularly over the temperature range of 30–100 K. On the basis of two thermally activated nonradiative recombination mechanisms, the PL emission efficiency can simply be described by

$$\eta = \frac{P_{\mathrm{r}}}{P_{\mathrm{r}} + {}^{\mathrm{A}}P_{\mathrm{nr}} + {}^{\mathrm{B}}P_{\mathrm{nr}}}, \qquad (3)$$

where P_{r} is the probability for a radiative transition. ${}^{\mathrm{A}}P_{\mathrm{nr}}$ and ${}^{\mathrm{B}}P_{\mathrm{nr}}$ are the nonradiative recombination rates of centers A and B, and are assumed to have the following temperature dependences:

$${}^{\mathrm{A}}P_{\mathrm{nr}} = {}^{\mathrm{A}}P_{\mathrm{nr0}} \exp\left(-\frac{E_{\mathrm{A}}}{kT}\right)$$

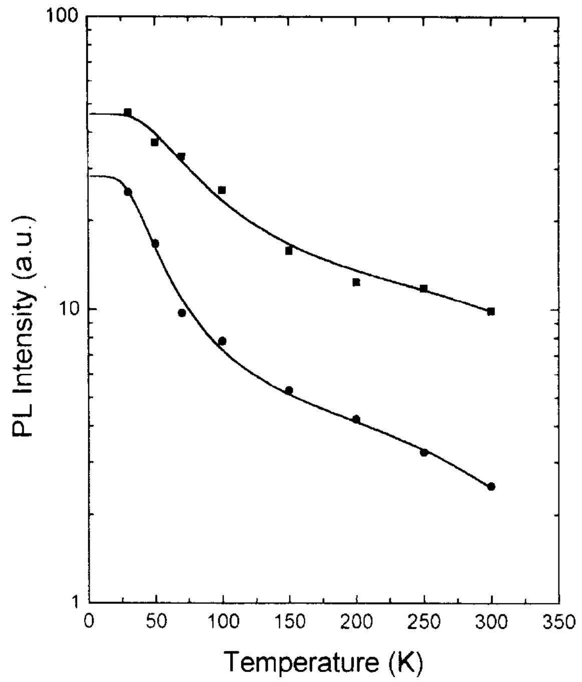

Fig. 3. Temperature dependence of the integrated intensities for the band-edge luminescence at excitation intensities of $0.1I_0$ (circles) and I_0 (squares).

and

$$^{\mathrm{B}}P_{\mathrm{nr}} = {}^{\mathrm{B}}P_{\mathrm{nr0}} \exp\left(-\frac{E_{\mathrm{B}}}{kT}\right),$$

where E_{A} and E_{B} are thermal activation energies and $^{\mathrm{A}}P_{\mathrm{nr0}}$ and $^{\mathrm{B}}P_{\mathrm{nr0}}$ are temperature-independent factors. The temperature dependence of the luminescence intensity is therefore given by

$$I(T) = \frac{I(0)}{1 + C_{\mathrm{A}} \exp(-E_{\mathrm{A}}/kT) + C_{\mathrm{B}} \exp(-E_{\mathrm{B}}/kT)}, \tag{4}$$

where $C_{\mathrm{A}} = {}^{\mathrm{A}}P_{\mathrm{nr0}}/P_{\mathrm{r}}$ and $C_{\mathrm{B}} = {}^{\mathrm{B}}P_{\mathrm{nr0}}/P_{\mathrm{r}}$. Using Eq. (4), we obtained the best-fit parameters:

$C_{\mathrm{A1}} = 1024$, $E_{\mathrm{A1}} = 147.7\,\mathrm{meV}$,

$C_{\mathrm{B1}} = 11$, $E_{\mathrm{B1}} = 11.6\,\mathrm{meV}$

and

$C_{\mathrm{A2}} = 996$, $E_{\mathrm{A2}} = 197.6\,\mathrm{meV}$,

$C_{\mathrm{B2}} = 6$, $E_{\mathrm{B2}} = 15.5\,\mathrm{meV}$

for the excitation intensities of $0.1I_0$ and I_0, respectively. This simple model determines the activation energies from the temperature dependence of the PL intensity, but the nature of the thermally activated mechanisms remains a matter of conjecture. The activation energies E_{A1} and E_{A2} are perhaps associated with a dominant deep trap as a nonradiative recombination center. The activation energies E_{B1} and E_{B2} which are smaller than 20 meV are likely to be related to the ionization of shallow surface traps or excitons localized at surface defects and surface fluctuations [2, 7], and they are not the exciton binding energies (which are larger than 30 meV in CdS nanocrystals). The thermal quenching of the luminescence and the decrease of its linewidth perhaps originate from the thermal ionization of electrons or holes trapped on surface defects or shallow surface traps. On the other hand, the thermal activation of excitons localized at the surface of nanocrystals with surface fluctuations of ~10 meV [7] clearly leads to a decrease of the PL intensity. At higher excitation intensities the probability of intrinsic excitons through direct recombination effectively rises, which causes a difference in the temperature dependence of the band-edge luminescence intensity. Therefore, the band-edge luminescence of the CdS nanocrystals is possibly composed of recombination luminescence of shallow traps or surface defects, localized excitons and intrinsic excitons.

Acknowledgements

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