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Photoluminescence of CdS semiconductor nanocrystals in sodium borosilicate glasses

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Semiconductor nanocrystals as a state of matter in the transition region between molecules and solids have received much attention because of their potential applications in optoelectronics. The relationship between the optical absorption and the size of nanocrystals is well established [1–3]. With decreasing radius, the absorption bandgap of the nanocrystals, for a favourite example, CdS nanocrystals including colloidal particles [4, 5], gas-evaporated particles [6] and those embedded in glasses [7–9], polymers [10, 11] and zeolite cages [12], shifts to higher energy due to quantum size effects. However, the luminescence spectra observed in the nanocrystals are strongly dependent not only on the sample preparation technique, but also on the conditions of measurement. The origins of the luminescence bands are far from being well interpreted. Thus it is worth investigating the characteristics of the luminescence bands in CdS nanocrystals.

In the work reported here, we studied the temperature- and excitation intensity-dependent photoluminescence (PL) spectra of CdS semiconductor nanocrystals in sodium borosilicate glasses prepared by a sol–gel method and discussed the carrier recombination mechanisms. On the basis of the dependence of peak energy, half width and intensity of the PL band on temperature and excitation intensity, we identified that the band-edge luminescence dominantly originates from the direct recombination of electrons and holes (excitons).

CdS nanocrystal-doped glasses were prepared by a sol–gel technique. The composition of the glasses was $5Na_2O–23B_2O_3–72SiO_2 + x\mathrm{CdS}$ ($x = 0.1$, 1, 2) (wt %). The densification temperature of the gels to give the glasses of that composition was in the range 550–650 °C.

Sodium borosilicate system gels containing $Cd(NO_3)_2 \cdot 4H_2O$ and $SC(NH_2)_2$ were prepared by using tetraethyl orthosilicate (TEOS), boric acid and sodium alkaxide as precursor, ethanol, glycolic methyl, ether, ethanol as precursor solvents, and hydrochloric acid as catalyst. First, TEOS was added to methanol solution, and deionized water (pH 2) was added to the mixture, which was hydrolysed by stirring for 1 h at 20 °C. Next, H_3BO_3 solution was added to the mixture, mixed and stirred for 1 h. The mixture was poured into a plastic container for further drying treatment. The molar ration of $Si(OEt)_4$, HOEt, H_2O, HCl, H_3BO_3, NaOEt was maintained at 1:2:2:0.0027:0.69:0.18. After the isothermal heat treatment at 100 °C for 10 h, stiff gels were first heat treated up to 350–450 °C for 24 h in a silica tube with flowing oxygen gas. The CdO containing gels, after being cooled to 150 °C, were exposed to dry H_2S gas to convert CdO to CdS at 150 °C for 2 h in a silica tube previously evacuated of N_2 by a retiary pump. The gels were then heated to the temperature region of 550–650 °C in vacuum at various treatment times for densification into pore-free glasses. The CdS nanocrystal-doped glass used in the experiment was obtained with a heat treatment time of 14 h at 590 °C.

The temperature- and excitation intensity-dependent PL spectra of samples were obtained with a Spex 1403 double monochromator and recorded with a photomultiplier tube. The samples were mounted in an He gas-flow cryostat. The temperature was varied from 20 to 300 K. The luminescence was excited with a frequency-tripled light (355 nm) of a Q-switched Nd:YAG laser with a duration of 10 ns and a repetition rate of 10 Hz. The laser was focused onto the samples by a 10 cm focal lens with a spot size of ~0.5 mm. The laser intensity was adjusted with neutral filters from 10^4 to $10^6\ \mathrm{W\,cm^{-2}}$.

Fig. 1 shows the temperature-dependent luminescence spectra of CdS nanocrystals with an average size of 8–10 nm determined by a transmission electron microscope (TEM) at an excitation intensity of $1 \times 10^5\ \mathrm{W\,cm^{-2}}$. The spectrum at 30 K exhibits two emission bands, a strong one with a peak at 2.507 eV and a weak broad band in the range of 1.7–2.0 eV. The high energy band is referred to as the band-edge luminescence because its energy is in agreement with that of the absorption band edge of the sample and slightly larger than the bandgap of the bulk. The band-edge luminescence of CdS nanocrystals prepared by the sol–gel method shifts to the blue due to quantum size effects with decreasing the size of nanocrystals by controlling the heat treatment time of samples. The low energy band was possibly related to the surface defects or

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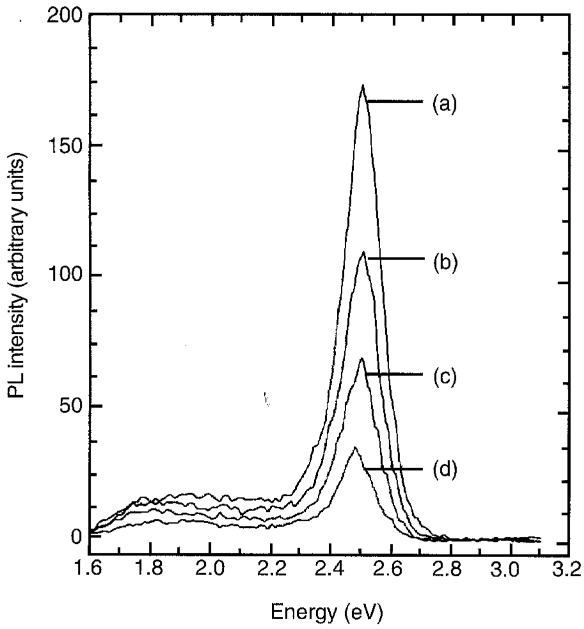

Figure 1 Luminescence spectra of CdS nanocrystals at (a) 30 K, (b) 50 K, (c) 70 K and (d) 150 K.

surface states [4–8, 10–12]. As can be seen in Fig. 1, the spectra do not change greatly in the temperature region of 30–300 K. The luminescence intensities of both the high and low energy bands decrease as the temperature increases.

The temperature dependence of peak energy for the band-edge luminescence is shown in Fig. 2. The variation in the energy gap with temperature is believed to result from the following two mechanisms: (i) A shift in the relative position of the conduction and valence bands as a result of the temperature-dependent dilatation of the lattice. This effect is linear with temperature at high temperatures. (ii) A shift in the relative position of the conduction and valence band as a result of the temperature-dependent electron–phonon interactions. Varshni [13] proposed the following empirical relation for the temperature dependence of the energy gap:

$$E_g(T) = E_g(0) - \alpha T^2/(T + \beta) \qquad (1)$$

where $E_g(0)$ is the value of the energy gap at 0 K, and α and β are constants. The experimental data are fitted with Equation 1, as shown in Fig. 2. The fit using Equation 1 is excellent. The parameters were obtained as follows: $E_g(0) = 2.509$ eV, $\alpha = 3.79 \times 10^{-4}$ eV K^{-1} and $\beta = 149.9$ K. The value of α agrees with that of CdS single crystals, for which $\alpha = 5 \times 10^{-4}$ eV K^{-1}. The temperature dependence of peak energy of the band-edge luminescence in the CdS nanocrystals is similar to those of the bandgaps of the bulk and the quantum dots in glasses [14].

Fig. 3 shows the variation of the full width at half maximum (FWHM) as a function of temperature for the band-edge luminescence of the CdS nanocrystals. The FWHM does not change significantly between 30 and 70 K, and then increases rapidly. Taking into account the interaction of excitons with optical phonons (LO), the temperature dependence of the FWHM can be expressed as [15]:

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

where Γ_0 is the constant inhomogeneous term, $\hbar\omega_{LO}$ the LO phonon energy and Γ_{ph} the phonon-broadening coefficient. For CdS nanocrystals [16], $\hbar\omega_{LO} = 37.8$ meV. The solid curve in Fig. 3 is the fit of Equation 2 to experimental data with $\Gamma_0 = 150.7$ meV and $\Gamma_{ph} = 154.3$ meV. As can be seen, the fit is satisfactory. The inhomogeneous linewidth broadening is mainly attributed to the size distribution of nanocrystals.

Fig. 4 shows the luminescence spectra at various laser intensities. At low intensity (7×10^4 W cm^{-2}), the peak energy and the FWHM of the band-edge luminescence band are 2.505 and 0.139 eV, respec-

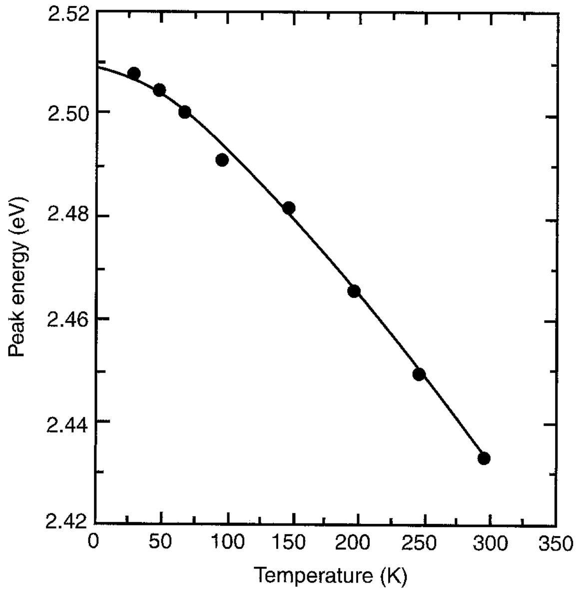

Figure 2 Peak energy of the band-edge luminescence as a function of temperature.

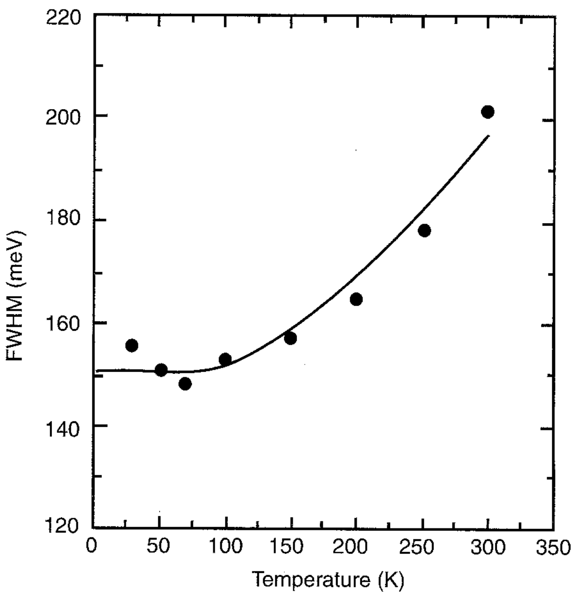

Figure 3 Temperature dependence of the FWHM for the band-edge luminescence.

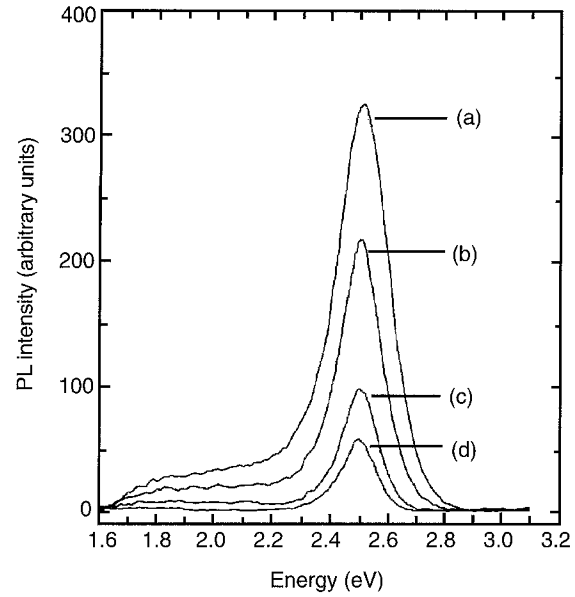

Figure 4 Luminescence spectra of CdS nanocrystals at (a) 0.7 I_0, (b) 0.3 I_0, (c) 0.1 I_0 and (d) 0.07 I_0. $I_0 = 1.0 \times 10^6$ W cm^{-2}.

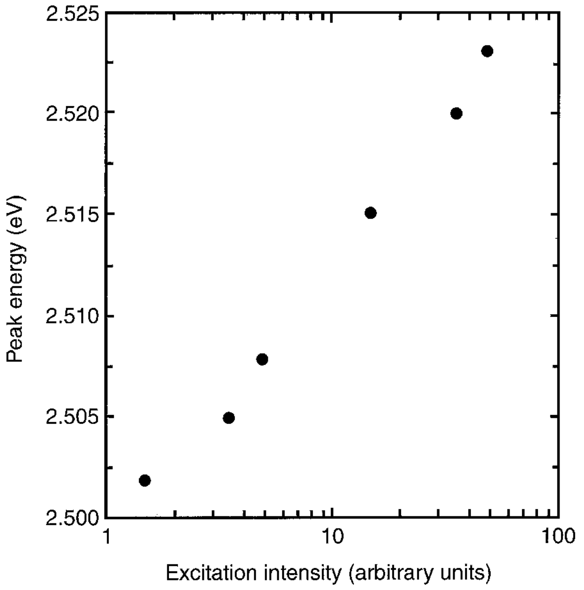

Figure 5 Peak energy of the band-edge luminescence as a function of excitation intensity.

tively. Increasing the excitation intensity results in a blue shift, as shown in Fig. 5, and a broadening of the luminescence band, which is a typical feature of band filling.

The excitation intensity-dependence of the band-edge luminescence at 30 K is shown in Fig. 6, which can be expressed as:

$$I_{\mathrm{PL}} = C I_{\mathrm{ex}}^{\nu} \tag{3}$$

where I_{PL} is the measured PL intensity, C is a constant, I_{ex} is the excitation intensity and ν is a coefficient. The solid line is shown in Fig. 6 as the coefficient $\nu = 1.04$. The similar dependence of the PL intensity on the laser intensity was observed in CdSSe-doped glasses [17].

In conclusion, the recombination processes of the carriers in the CdS nanocrystals were characterized

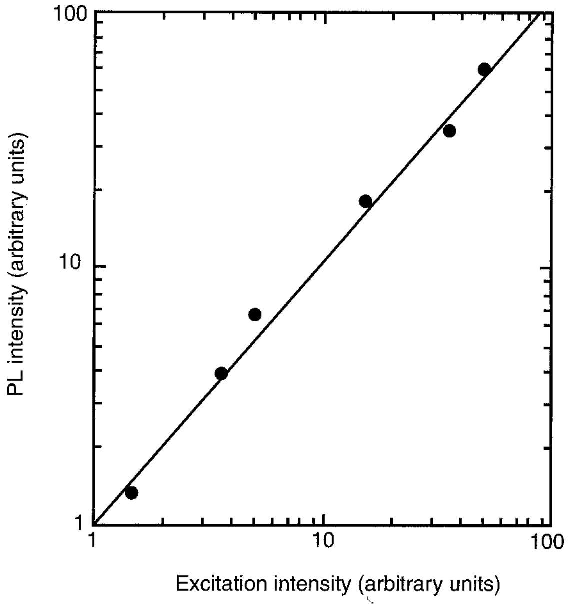

Figure 6 Excitation intensity-dependence of the band-edge luminescence intensity.

by the temperature- and excitation intensity-dependent PL spectra. The results show that the recombination luminescence of electrons and holes (excitons) dominates in the radiative recombination processes of the CdS nanocrystals in the range of excitation intensity 10^4–10^6 W cm^{-2}.

Acknowledgements

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