

Size-dependent photo-induced shift of the first exciton band in CdTe quantum dots in glass prepared by a two-stage heat-treatment process

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Received 23 June 2007; received in revised form 4 October 2007; accepted 11 October 2007

Available online 22 October 2007

Abstract

CdTe nanocrystals were grown from commercially available RG850 Schott filter glass by two-step heat-treatment process which almost doubles the particle to matrix volume fraction. A calculation shows that a quantized-state effective mass model in the strong confinement regime might be used to deduce the average radius for the nanocrystals larger than 2 nm in radius from the energetic position of the first exciton peak in optical absorption spectrum. Size-induced shift of ~ 360 meV in the first exciton peak position was observed. The steady state photoluminescence spectra exhibit a broad band red shifted relative to the first exciton band, which indicates the existence of shallow trap states. The non-linear optical properties of CdTe nanocrystals were studied by room temperature resonant photoabsorption spectroscopy. The differential absorption spectra had three-lobed structure whose size-dependent evolution was explained by bleaching of the absorption, red shift and broadening in the Gaussian absorption band used to fit the first exciton peak. A maximum red shift of 2.32 meV for the average nanocrystal radius of 4.65 nm was estimated by fitting the photomodulation spectra with a combination of first and second derivative Gaussian absorption bands. We presume that the red shift is induced by the electric field of trapped charges in surface states. Internal electric field strengths of 23 and 65 kV/cm were predicted for the average nanocrystal radii of 3.95 and 4.65 nm, respectively, with the help of second-order perturbation theory in the strong confinement limit.

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PACS: 78.67.Bf; 78.67.-n; 68.65.Hb

Keywords: Quantum dots; Photomodulation spectroscopy; CdTe nanocrystals; Diffusion-limited growth

1. Introduction

The first observation of quantum size effect in zero dimension by Ekimov and Onushchenko in 1981 [1], who reported a blue-shift in the optical absorption edge of nanometer sized CuCl semiconductors, marked the beginning of an era for new physics, called today nanophysics or nanotechnology. These tiny crystals or quantum dots have since possessed versatile potential applications for non-linear optical devices [2,3], fluorescent labels in biomedical systems [4] and solar cells [5]. The photoabsorption (PA) has been one of the powerful techniques to study the non-linearity in $\text{CdS}_x\text{Se}_{1-x}$ nanoparticles in glass by using pulsed and continuous wave (cw) laser excitation. The

wavy shape of the differential absorption spectrum was explained by various mechanisms such as bleaching of the absorption caused by state filling and red shift in the exciton band induced by quantum-confined Franz–Keldysh effect due to photodarkening or trap states [6,7]. $\text{CdS}_x\text{Se}_{1-x}$ nanoparticles in glass have been most widely studied a model system for quantum confinement effect. However, CdTe nanocrystals in glass have not been studied extensively. The preparation of CdTe nanoparticles in glass is quite involved due to the difficulties associated with the possible oxidation of Te during the crystal growth. A two-step heat-treatment process is required to increase the particle to matrix volume fraction and thus to optimize the optical properties of the structure [8]. Esch et al. [9] were the first to study photomodulation in a single glass sample within which an ensemble of CdTe quantum dots of an average radius of 3.6 nm were embedded. They

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employed micro-, nano- and femto-second (fs) optical pulses and observed long radiative lifetimes for pump generated carriers which are trapped at the surface between the glass and the crystal or at the outside of the nanocrystal in glass. In a recent work by Padilha et al. [10], recombination processes such as carrier trapping in surface states with a time constant of 360 fs, Auger recombination, trapped electron–hole recombination and recombination from deep trap states with milli- or micro-second time constants in CdTe nanocrystals of an average radius of 7.2 nm embedded in glass were identified by fs pump- and probe-measurements.

In this work, we first evaluate the validity of *particle in a box* model to determine the average radius of nanocrystals from the energetic position of the first exciton band in the optical absorption spectrum and then discuss the growth kinetics of CdTe nanocrystals in glass prepared by a two-stage heat-treatment process. We then briefly discuss the evolution of trap states with size through photoluminescence (PL) spectroscopy. We finally present a systematic study based on the photo-modulation spectroscopy to understand the origin of photo-induced modulations in the optical absorption and address different size CdTe nanoparticles in glass by using cw laser excitation above the exciton resonance.

2. Validity of particle in a box model to determine the average nanocrystal radius

In the absence of direct structural measurements such as TEM, the validity of particle in a box model to determine the average nanocrystal radius is to be evaluated. In this study, the glass is the dielectric material within which CdTe nanoparticles are embedded. The band gap is about 5 eV for glass and about 1.6 eV for bulk CdTe. A schematic of the energy band diagram is shown in Fig. 1. The height of potential well confining the charged particles (electrons and holes) is finite and may vary depending on the dielectric

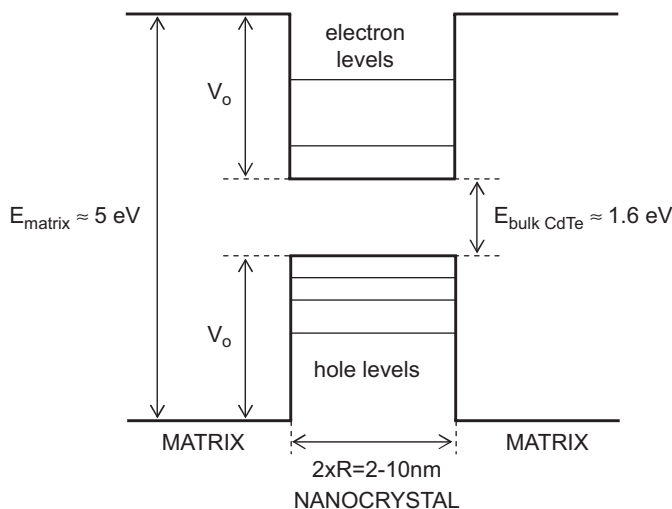


Fig. 1. A schematic of the energy band diagram of CdTe nanocrystal in glass matrix.

host. We first discuss the confinement of charged particles in a finite potential well. In other words, the penetration of the wave function of the charged particles into the glass host is taken into account in the following calculation. The energy levels for a particle in a one-dimensional finite potential well are given by the following transcendental expressions [11]:

$$\left| \cos\left(\frac{kR}{2}\right) \right| = \frac{k}{k_0}, \quad \tan\left(\frac{kR}{2}\right) > 0, \quad (1a)$$

$$\left| \sin\left(\frac{kR}{2}\right) \right| = \frac{k}{k_0}, \quad \tan\left(\frac{kR}{2}\right) < 0, \quad (1b)$$

where $k = \sqrt{2m_{e(h)}E_{1s1s}/\hbar^2}$, $k_0 = \sqrt{2m_{e(h)}V_0/\hbar^2}$ and V_0 is the potential well height. R is the average radius of nanoparticles. The band gap of the dielectric material is $E_{\text{matrix}} = E_g + 2V_0$. In Fig. 2, by using Eqs. (1a) and (1b) we calculated the first exciton peak position (E_{1s1s}) as a function of the inverse square of the radius for various potential well heights. The straight lines are the linear fits to E_{1s1s} against $1/R^2$ data for the nanoparticles of radius greater than 2 nm. The slope of a least-squares straight line fit increases with increasing potential well height as shown in the figure. The calculation presented here in one dimension can be extended to three dimensions. The behavior in three dimensions is in agreement with the results in Fig. 2 [12].

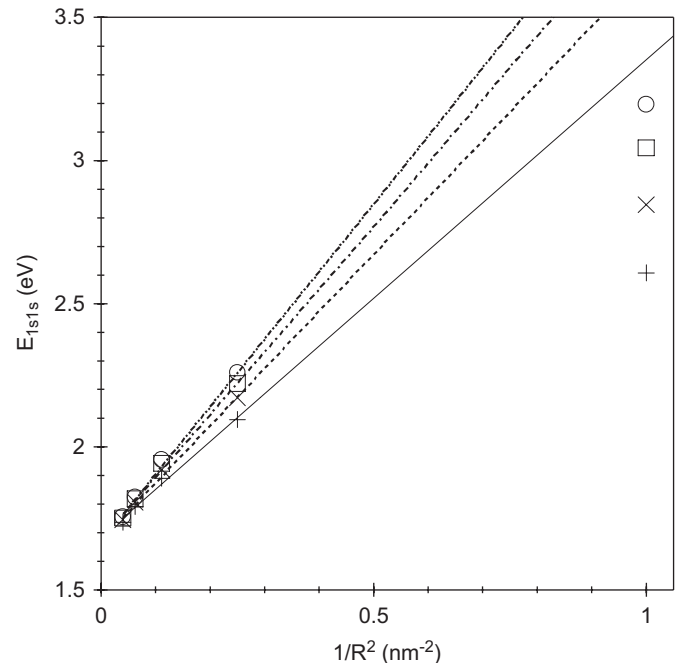


Fig. 2. A calculation of first exciton energy levels (E_{1s1s}) of charged particles as a function of reciprocal average nanocrystal radius squared, confined in a finite one-dimensional square potential well of height V_0 within a dielectric matrix of band gap $E_{\text{matrix}} = E_g + 2V_0$: (O) $V_0 = 2.5 \text{ eV} - E_{\text{matrix}} = 6.6 \text{ eV}$, (□) $V_0 = 2.0 \text{ eV} - E_{\text{matrix}} = 5.6 \text{ eV}$, (×) $V_0 = 1.5 \text{ eV} - E_{\text{matrix}} = 4.6 \text{ eV}$ and (+) $V_0 = 1.0 \text{ eV} - E_{\text{matrix}} = 3.6 \text{ eV}$. The straight lines are the linear fits for the nanocrystals larger than 2 nm in radius.

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