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Thermal diffusivity and photoacoustic spectroscopy measurements in CdTe quantum dots borosilicate glasses

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Abstract. In this paper we describe the results of photoacoustic spectroscopy and thermal diffusivity measurements in borosilicate glass matrix with CdTe quantum dots. Samples treated at the temperature of 540^0C for different periods were studied. The photoacoustic spectra show the absorption band of CdTe quantum dots, which shifts as a function of the thermal treatment time, revealing the evolution of the average radius of the nanocrystals. Thermal lens measurements provide the thermal diffusivity of the treated samples and give the behavior of the temperature coefficient of the refractive index, dn/dT, which is correlated to the transmittance spectra.

1. INTRODUCTION

Semiconductor doped glasses (quantum dots in glass) have been of great interest as fast non-linear optical materials, and intensive studies on their quantum confinement and optical non-linearity have been carried out [1,2]. However, besides the great interest in the optical properties of these materials, thermal and opto-thermal data are still rare scarce.

In this paper we use the photoacoustic and the thermal lens techniques to investigate both thermal and opto-thermal parameters of borosilicate glasses doped with CdTe. The samples were annealed to produce CdTe nanocrystals embedded in the glass matrix. These nanocrystals present quantum confinement, thus shifting the band edge of the bulk semiconductor to higher frequencies. The ability of tuning the absorption band wavelength is the key of potential applications of these materials.

As discussed below, the photoacoustic measurements were used to obtain the absorption spectra in the visible range. Conventional reflectance and transmittance measurements were also performed as a complementary optical characterization of the samples. The importance of the photoacoustic measurements is related to the fact that the photoacoustic signal accounts for the fraction of absorbed energy that is converted into heat, which means that the re-emitted fraction (luminescence) is not involved. Therefore, it can be used to normalize the thermal lens signal, allowing the determination of the behavior of the temperature coefficient of the refractive index, dn/dT. From the thermal lens measurements the thermal diffusivity is also determined, providing information about the influence of the nanocrystals on the heat propagation.

2. EXPERIMENTAL

The glass used in the present study was obtained by quenching appropriately a doped melt. The matrix glass composition was SiO_2:ZnO:B_2O_3:Na_2O, which was doped with 2.0 wt % of CdTe. The glass was prepared by melting in a furnace at 1400 ^{0}C under reducing conditions, and then cast as discs. The discs were cut to suitable sizes and isothermally treated in a muffle furnace at the temperature of 540 ^{0}C for time periods of 20 min, 65 min, 150 min, 255 min, 300 min, 360 min or 480 min (8 hours) to cause the controlled precipitation of the semiconductor particles.

The photoacoustic spectra were obtained in a homemade spectrometer, which uses a Xenon arc lamp (Oriel, mod.6128, 1000 W), a mechanical chopper (PAR, mod. 192) and a monochromator operating in the 400-700 nm range (Oriel, mod. 77250). The modulation frequencies were chosen to guarantee the thermally thick sample condition.

The thermal diffusivity of the samples was measured at ambient temperature using the thermal lens technique in the mismatched-mode. The experimental setup used an Argon ion laser as the excitation beam (514.5nm, 200-300 mW output power) and a He-Ne laser (632.8 nm and a few milliwats at the sample) as the probe beam. A shutter controlled the exposure of the sample to the excitation beam. The output of a fast probe photodiode was coupled to a digital recorder, which was triggered by a second photodiode, and stored the thermal lens signal as a function of time (30 ms range). The thermal diffusivity values were obtained from the data fitting to the aberrant model [3].

3. RESULTS AND DISCUSSION

Figure 1 shows the photoacoustic spectra of the seven studied samples in the range from 400 to 700 nm. As one can see, the samples treated for 20 and 65 min are quite transparent in the visible range, presenting the tail of the UV absorption bands characteristic of dielectrics such as glasses. Samples treated for 150 min or more present an additional band located in the visible, which shifts to long wavelengths as the time of annealing increases. This band is a consequence of electron quantum confinement effects associated with the existence of extremely small CdTe crystals embedded in the glass. The band gap energy of bulk CdTe is 1.52 eV (818 nm), and the quantum confinement causes a "blueshift" of the transition energy. Calculated energy of a 3 nm radius nanocrystal of CdTe is about 2.2 eV (565 nm). As the time of annealing increases, the radii of the nanocrystals augments through mechanisms of nucleation and coalescence, and the energy of the fundamental level of the tri-dimensional quantum-well diminishes towards the bulk band value, as observed in the photoacoustic spectra.

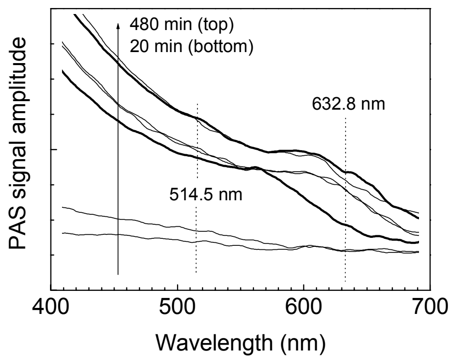

Figure 1. Photoacoustic spectra of the samples treated at 540 ^{0}C for 20 (bottom curve), 65, 150, 255, 300, 360 and 480 min (top curve).

In order to determine the thermal diffusivity of the samples, thermal lens measurements in the time-domain were carried out. Data of the thermal lens time-evolution were fitted to the theoretical model [3], and from the adjusted parameters the thermal diffusivity, α, and the magnitude of the thermal lens, θ, were obtained. The values of the thermal diffusivity are plotted against the annealing time in Fig. 2(a). These values are quite close to thermal diffusivity of silicate glasses reported in the literature [4], and show a small decrease in the thermal parameter for the samples annealed for long periods. This effect could be caused by the perturbation in the heat propagation introduced by the aggregates above a critical size.

The magnitude of the thermal lens, θ, is given by: $\theta = (\eta\ \beta\ P\ l / \lambda_p\ k)\ (dn/dT)$, where η is the fraction of absorbed energy that is converted into heat, β is the optical absorption coefficient, P is the excitation beam incident power, l is the sample thickness, k is the sample thermal conductivity, and dn/dT is the temperature coefficient of the sample refractive index at the probe beam wavelength, λ_p.

On the other hand, the photoacoustic spectroscopy signal is proportional to the sample surface temperature, T(0), and is given by: PAS Signal = cnt T(0) = cnt $(\eta\ \beta\ I_0 / k\ \sigma^2$, where I_0 is the incident beam intensity and σ is the complex coefficient of thermal diffusion ($\sigma^2 = j\ \pi\ f / \alpha$, f being the modulation frequency). Therefore, normalizing the values of θ (obtained from the thermal lens data fitting) by the photoacoustic signal, the incident power and the thickness, one has: (θ / P l PAS Signal) = (cnt / α) dn/dT. Using the values of α from Fig. 2(a) one can get a quantity that is proportional to dn/dT at the probe wavelength, ($\theta\ \alpha$ / P l PAS Signal) = cnt (dn/dT), which is shown in Fig. 2(b) (left axis) for the different samples (black circles). From this figure one can see that dn/dT slightly increases for samples treated for 20-150 min, followed by a strong augmentation for samples annealed during 255 and 300 min, and finally dropping back for samples treated for 360 and 480 min.

The observed behavior for the temperature coefficient of the refractive index at 632.8 nm is connected to the position of the quantum dot absorption band. Indeed, the quantity dn/dT is fairly related to $dn/d\lambda$ for dielectrics (bonded charges) far from the resonance or in the cases of broad resonance. Furthermore, when the imaginary part of the refractive index is much smaller than the real one, as in this case, the derivative of the refractive index is proportional to the derivative of the transmittance, i.e., $dn/d\lambda$ = cnt $dT/d\lambda$ (the constant is a function of the wavelength itself). The transmittance and reflectance spectra of the samples were obtained using a Lambda 9 conventional spectrometer, and from these data the derivatives of T with respect to λ were calculated at the probe beam wavelength, 632.8 nm. They are displayed in Fig. 2(b) (right axis), and reveal a quite good correspondence with those obtained from thermal lens measurements, as expected.

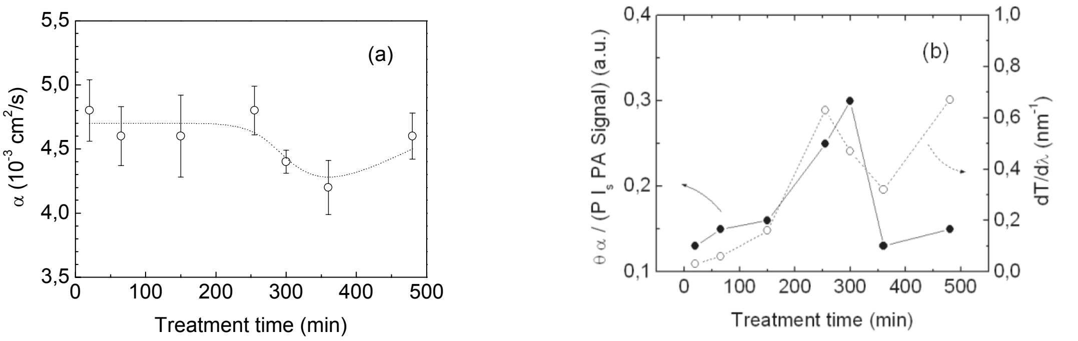

Figure 2. (a) Thermal diffusivity of the samples as a function of the period of thermal treatment at 540 ^{0}C, as obtained from thermal lens measurements; (b) Normalized values of θ and the derivative of the transmittance T with respect to the wavelength as a function of the period of thermal treatment at 540 ^{0}C.

4. CONCLUSIONS

In this paper we reported results obtained using the photoacoustic spectroscopy and the thermal lens technique in the determination of thermal and opto-thermal parameters (thermal diffusivity and dn/dT) of borosilicate glasses doped with CdTe. The use of the two techniques, one as a complement of the other, is clearly important since it permits the non-equivocal determination of the opto-thermal parameter through a proper procedure of data normalization.

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