Synthesis and Characterization of PbS Quantum Dots Embedded in Oxide Glass

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The fusion method was used to produce PbS quantum dots (QDs) embedded in S-doped glass matrix (SiO_2-Na_2CO_3-Al_2O_3-PbO_2-B_2O_3:S). Measurements of optical absorption (OA), photoluminescence (PL) and atomic force microscopy (AFM) have been carried out in order to characterize the produced QDs. A strong red-shift observed in the optical features with an increase of the annealing time indicates an increase in QD-size. The QD sizes predicted by **k.p** theoretical results were confirmed by AFM observation.

Keywords: Synthesis and characterization; Oxide glass; PbS quantum dots

I. INTRODUCTION

Semiconductor quantum dots (QDs) have attracted a lot of attention due to their technologically promising optical and electronic properties. QDs show for instance discrete optical transition that can be manipulated through their sizes. Based on these properties QDs can be used in light emitting devices such as lasers for telecommunications [1-4]. In the last few years, there has been considerable attention towards material and device research for 1.3 to 1.55 μm wavelength laser structures for optical communications and single processing. One simple way to realize 1.3 μm laser emission is to use semiconductor quantum dot doped glasses, which can be easily synthesized by means of fusion method [4]. Such materials are inexpensive and robust for photonic applications. However, useful devices based on PbS quantum dots doped glasses have not been fully developed. This is mostly attributed to the obtained broad size dot distribution, high concentration of many vacancies, substitution defects, and low dot concentrations. Thus, further improvements on the fabrication of QDs embedded in glass matrices are required. In this study a systematic investigation of the effects of the thermal treatment upon the fabrication of PbS dots in S-doped glass matrix was realized.

II. EXPERIMENTAL

The sulphur doped oxide glass matrix (SiO_2-Na_2CO_3-Al_2O_3-PbO_2-B_2O_3:S) used in this study was prepared from high purity powders using SiO_2 as glass former and Na_2CO_3 to reduce the melting point. The mixture was melted in alumina crucible at 1200^oC for 30 min, cooling down to room temperature afterwards. Further thermal treatment of the glass matrix was performed at 500^oC to enhance the diffusion of Pb^{2+} and S^{2-} ions. As a result of the thermal treatment PbS quantum dots were formed in the glass matrix. In this samples quoted as SG_1, SG_2, SG_3 and SG_4, corresponding to annealing times of 2, 3, 4 and 5 hours, were selected for optical investigation. Room-temperature photoluminescence (PL) measurements were recorded using a SPEX-750M monochromator equipped with a Jobin-Yvon CCD 2000×800-3. Samples were optically excited by the 514.5 nm line of an Argon-ion laser. The optical absorption (OA) spectra were obtained using a spectrophotometer Varian-500 operating between 175-3300 nm. AFM images were recorded for samples SG_2 and SG_4.

III. RESULTS AND DISCUSSIONS

Room-temperature PL and optical absorption spectra of samples SG_1, SG_2, SG_3 and SG_4, with different annealing process are shown in Fig. 1. Quantum confinement effects are clearly observed in Fig. 1 (a) and (b) as shown by the red-shift of the quoted. The appearance of well-defined subband peaks in both absorption and photoluminescence spectra demonstrates the high quality of the synthesized samples and the relatively small size distribution of the PbS QDs. The average estimated sizes for the PbS QDs are 3.3 nm, 4.0 nm, 4.4 nm and 4.5 nm for samples SG_1, SG_2, SG_3 and SG_4respectively. Note that the measured Stokes shifts between corresponding OA and PL peak positions are 250 meV (SG_1), 140 meV (SG_2), 90 meV (SG_3) and 82 meV (SG_4). Size dispersion for the QDs are around 6%, as estimated by the method of Wu *et al*. [5]. The dispersion is described by $\xi = W/4(\nu - E_g)$, where W, ν, and $E_g$are the full width at half maximum of the OA peak, the photon energy peak, and the bulk semiconductor gap, respectively.

Comparing the numerical simulations of the energy levels and the observed OA peaks, we were able to estimate the average sizes for the PbS QDs. Neglecting anisotropy effects, energy level calculations were realized using the envelope function formalism of four bands (**k.p** 4x4) in a bulk Hamiltonian, within the spherical approximation [3]. The energy transitions as a function of the PbS QD size are shown in Fig. 2. Autovalues result from the **k.p** method corresponding to the total momentum angular quantum number (j) and parity (π). For instance the calculated value for the first optical transition of a 4.0 nm PbS QD is 1.1514 eV, which is very much close to the optical feature (1.1534 eV) of sample SG_2. Thus, the average PbS QD size in sample SG_2 is about 4.0 nm. Likewise, it is possible to estimate the average sizes of PbS QD in samples

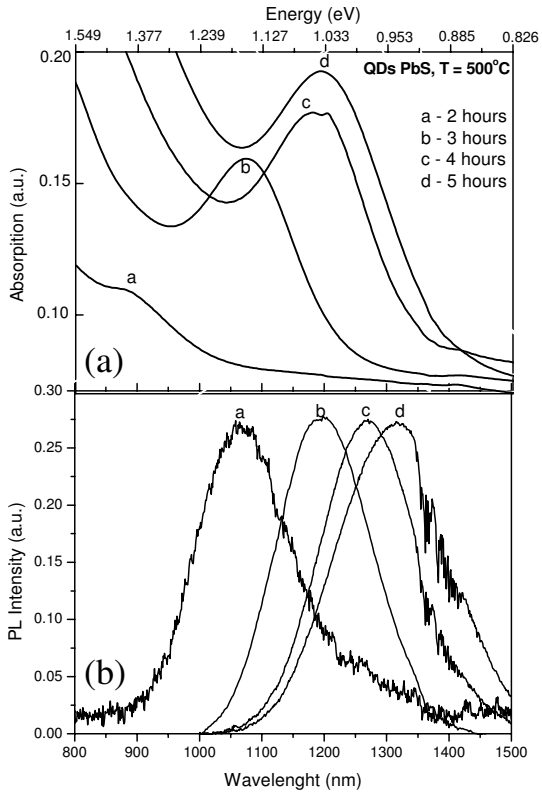

FIG. 1: Room-temperature (a) optical absorption and (b) photoluminescence spectra for samples SG_1, SG_2, SG_3 and SG_4.

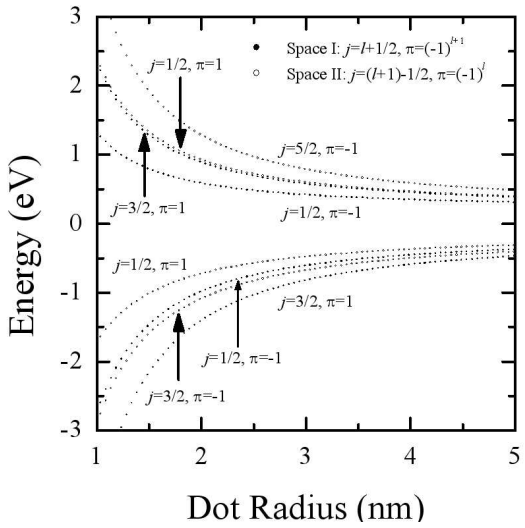

FIG. 2: Energy calculations as a function of the PbS QD sizes using the k.p 4x4 method. Autovalues resulting from this method corresponds to the total momentum angular j and parity π, where l represents the orbital angular momentum.

SG_1, SG_3, and SG_4 as 3.3 nm, 4.4 nm, and 4.5 nm, respectively.

In order to directly observe the QD formation and distribution, AFM images were obtained as shown in Fig. 3. Figures 3(a) and 3(b) show AFM images of individual PbS QDs in samples SG_2 and SG_4, respectively. AFM data obtained from samples SG_2 (SG_4) showed an average QD-size of about 4.3 nm (4.8 nm). The PbS QD sizes obtained from the AFM pictures are very much close to the values estimated by **k.p** theory. The average QD size observed for SG_4 sample is larger than the size observed for SG_2 sample, as expected from the difference of annealing times.

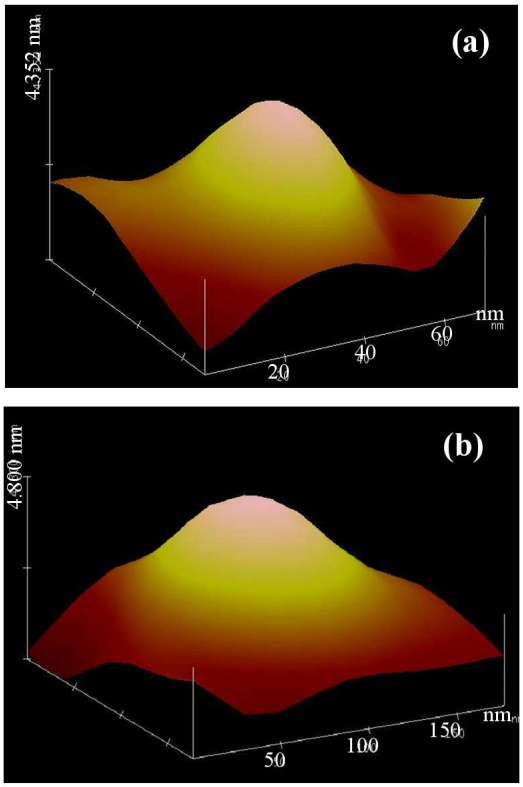

FIG. 3: AFM image illustrates the morphology of PbS nanocrystals in samples (a) SG_2 and (b) SG_4.

IV. CONCLUSION

Four sulphur-doped glass samples (SiO_2-Na_2CO_3-Al_2O_3-PbO_2-B_2O_3) were synthesized via different thermal treatment process at 500°C, using the fusion method. We found that the thermal treatment of the investigated samples allows the growth of PbS quantum dots whose size increases with increasing annealing time. The PbS QD sizes, as predicted by theoretical analysis, are in very good agreement with the optical features observed in the absorption and photoluminescence measurements and with the images obtained from

atomic force microscopy.

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