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Structural and optical properties of silica single-layer films doped with ZnS quantum dots: Photoluminescence monitoring of annealing-induced defects

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ABSTRACT

Zinc Sulfide (ZnS) quantum dots (QDs) embedded in sol-gel silica single-layer films were synthesized by dip-coating and thermal treatment. Nucleation and growth of these QDs occurred during annealing. The effect of annealing temperature on morphological, structural and optical properties of the films was considered in the range (200–500 °C). Scanning electron microscopy (SEM), atomic force microscopy (AFM), grazing incident angle X-ray diffraction (GIXD), UV–Visible spectroscopy (UV–Vis) and photoluminescence (PL) were used to characterize the films. The band gap values of the ZnS QDs ranged from 3.83 to 4.03 eV corresponding to average radii in the range 1.5–2.1 nm. PL revealed different annealing-induced defects in the ZnS QDs. Zn interstices dominate at 400 and 500 °C annealing temperatures by the appearance of two excitation bands at 395 nm and 404 nm respectively. Corresponding emission bands were recorded at 402 nm and 408 nm. An emission peak (457 nm) and an excitation peak (437 nm) were also observed at 500 °C. These peaks were attributed to S vacancies which might be created by the transformation of ZnS to ZnO. Finally, an overall energy-level diagram showing all the defect states in the gap of ZnS was proposed.

1. Introduction

The synthesis and characterization of semiconductor quantum dots (QDs) have been intensively investigated during the past three decades for applications in various devices such as lasers [1], solar cells [2–4], biological labels [5,6] and light emitting diodes [7–9]. When the size of the crystals is reduced, a blue shift in the band gap is observed [10]. Zinc sulfide (ZnS) is a promising II-VI semiconductor with a wide direct band gap of 3.66 eV in the bulk, an exciton binding energy of 34 meV and a good transparency in the visible region. ZnS is particularly suitable in optoelectronic devices operating in the UV, violet and blue regions [11]. In order to avoid the use of toxic cadmium compounds, ZnS is also a potential candidate to replace CdSe and CdS in biological imaging [12] and solar cells [13], respectively.

ZnS nanoparticles are synthesized by a variety of methods including, hydrothermal synthesis [14], wet chemistry [15–17], sol-gel [18–20] and solid state route [21]. In practice, these quantum dots are coated by a shell material or dispersed in a matrix to ensure the passivation of the particle surface. Silica is chosen as a matrix due to its low cost, chemical stability and transparency in the visible region.

The optical properties of ZnS QDs depend on two major factors: particle size due to quantum confinement of carriers and defects. It is then important to control the radii of the ZnS nanoparticles and the concentration of defects in the material. Particle size control is well achieved in the case of colloidal micro-emulsion [17] in the liquid phase. A second step is necessary to incorporate these nanoparticles into the glass matrix as, for example, in the case of PbS [22]. However, inserting controlled-size and surface-passivated ZnS nanoparticles in a solid matrix using a one-step process is still challenging. A possible route is to form and grow the nanocrystals in the pores of a matrix by thermal treatment. The later has an effect on the formation and growth of the nanoparticles as well as on the densification of the matrix.

The literature survey shows that few authors reported optical and structural properties of ZnS nanoparticles dispersed in sol-gel silica prepared from thiourea as a sulfur precursor under acidic conditions [18–20]. Bhattacharjee et al. [19] obtained spin-coated films of ZnS nanoparticles confined in silica with molar ratios Zn/Si = 3/7 and Zn/S = 1 in the initial solution. They reported average nanoparticle sizes in

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the range 2.5–7 nm for 30 min flush heating from 200 to 400 °C. Tiwari et al. [20] reported structural and optical characterization of copper doped ZnS nanoparticles in silica and obtained an average particle size of 7.5 nm for powders dried between 100 and 150 °C. In all the above mentioned studies, the pH value of the initial solution was not specified and a detailed study of defects has not been reported.

On the other hand, the PL of ZnS nanoparticles is sensitive to the synthetic conditions, crystal size and the surrounding medium. In particular, the luminescence bands are influenced by both intrinsic and extrinsic defects. Several studies have been devoted to photoluminescence of doped and un-doped ZnS nanoparticles prepared by using different techniques [19,23–28]. The reported results regarding wavelength emissions and attributions are various and different. For example, Denzler et al. [24] reported four blue emission peaks in the range (416 nm, 438 nm) in the case of colloidal ZnS nanocrystals. These peaks were attributed to vacancy and interstitial sites for both sulfur and zinc atoms. A Study carried out by Bhattacharjee et al. [19] has shown UV bands at around 380 nm and a red emission centered at 636 nm for ZnS nanoparticles dispersed in silica. The authors ascribed these emissions to respectively Zn^{+2} vacancy and the formation of ZnS (O_2^-) on the surface layers of the ZnS particles. In the case of ZnO, Samavati et al. reported the influence of thickness [29] and temperature growth [30] on structural and optical properties of ZnO QDs imbedded in silica and fabricated by radio-frequency magnetron sputtering. Therefore, an overall study of intrinsic defects in ZnS QDs by PL is needed for a better understanding of the involved optical transitions in the gap.

In this work, we used a one step sol-gel method and thermal treatment to synthesize ZnS QDs embedded in low porosity silica films deposited by dip-coating. This cost-effective technique is attractive due to the possibility of large-area deposition of uniform thin films. This is of crucial importance in the photovoltaic field where both large surface and low cost are highly needed. Thiourea has been chosen as a sulfur precursor at pH ≈ 2.5 (near the isoelectric point of silica) due to its stability without any release of sulfur ions at ambient temperature [31]. Another advantage of the acidic medium is the very low concentration of zinc hydroxide ($Zn(OH)_2$) that avoids the formation of zinc oxide (ZnO) during annealing [32]. At the above considered pH, the formation of ZnS occurs during thermal treatment by decomposition of thiourea in the solid-state phase [33]. The kinetics of semiconductor nanocrystals formation and growth in silica has been investigated by Ekimov and Lublinskaya et al. [34,35] in oversaturated solid solutions. Different point defects may appear during the nucleation and growth as the later processes are thermally activated. Our system offers an opportunity to study the annealing-induced intrinsic defects in ZnS QDs. In order to avoid possible interface defects, only single-layer films were considered in the present study. The structural, morphological and optical properties of dip-coated thin films were studied for various annealing temperatures from 200 to 500 °C. The characterization techniques include scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and UV–visible spectroscopy (UV–vis). Also, a PL study was carried out in both excitation and emission modes to monitor the appearance of different intrinsic defects in ZnS QDs.

2. Experimental methods

2.1. Synthesis

All reagents were analytically pure and used as received without any further purification. Double-distilled water was prepared in our laboratory. Tetraethyl orthosilicate (TEOS-$Si(OC_2H_5)_4$) was provided by Fluka. Hydrochloric acid 2 M (HCl) was purchased from Riedel-de Haën. Zinc nitrate hexahydrate ($Zn(NO_3)_2{\cdot}6H_2O$), thiourea (NH_2CSNH_2), ethanol (C_2H_6O) and methanol (CH_4O) were from Biochem Chemopharma.

A silica sol containing Zn and S precursors was prepared using TEOS, zinc nitrate hexahydrate and thiourea as described in our previous work [33]. The composition of the solution is given by the following molar ratios: Zn/S = 1/2, H_2O/Si = 6 and Zn/Si = 1/5. These ratios were optimized for an effective formation of ZnS QDs in a low porosity silica matrix. Double-distilled water, ethanol and methanol were used as solvents. The pH was adjusted to approximately 2.5 by addition of 1 M HCl. The final sol was filtered and aged for 72 h.

The films were deposited on glass slides (15 mm × 45 mm) using a KSV DC computer -controlled and user-programmable dip coater. To deposit single-layer films, only one dipping has been performed at a withdrawal speed of 120 mm/min. Before deposition, the substrates were washed with detergent in an ultrasonic container followed by rinsing in water. The slides were then etched in HCl, cleaned with double distilled water and ethanol and finally dried in air.

ZnS QDs were synthesized via thermal decomposition of zinc nitrate and thiourea in silica at temperatures of 200–500 °C. Annealing was achieved in a tubular furnace under ambient air during one hour at different temperatures: 200 °C, 300 °C, 400 °C and 500 °C. A rate of 10 °C/min was programmed for both heating and cooling steps.

2.2. Characterization

Scanning electron microscopy (SEM) micrographs were taken at room temperature using a Quanta 200 scanning electron microscope. Surface roughness was investigated by Multimode-8 (Bruker) atomic force microscope (AFM). The AFM scans were carried out using a silicon tip in amplitude-modulation (tapping) mode. The thickness of the films was determined by using a Veeco Dektak 150 profilometer. Scratched lines were made on the films and depth profiles were measured across these lines. The maximum depth was taken as the film thickness. Glancing angle X-ray diffraction (GIXD) studies were carried out using an automated Panalytical X'pert Pro diffractometer working at (30 mA, 40 kV) with Cu K_α radiation over the range 2Θ between 20° and 80°. This apparatus is equipped with a monochromator and a divergence slit. The absorbance measurements were taken on a Safas Monaco instrument in the wavelength range (300–800 nm). Photoluminescence (PL) spectra were recorded in both emission and excitation modes on a Horiba FluoroMax-4 Spectrofluorometer.

3. Results and discussion

3.1. Morphological and structural properties

3.1.1. Scanning electron microscopy

The single-layers were found to be well adherent to the substrate after annealing. Fig. 1 shows SEM micrographs of the deposited films annealed at different temperatures. It can be observed that the films are uniform and cover well the glass substrate. The surfaces of the films are also smooth and pinhole-free without any agglomerated species. The samples obtained at 200 and 300 °C are slightly porous compared to others which show a relatively dense and compact structure at the micrometer level.

3.1.2. Atomic force microscopy

The AFM surface roughness scans (3 μm × 3 μm) of single layers annealed at various temperatures are shown in Fig. 2. It is revealed that the films have granular structure with typical silica grain size ranging about 100 nm down to 30 nm. Note that the apparent lateral size of Nano-features results from the convolution between particle size and tip radius apex (about 30 nm). Accordingly, the actual size of nanoparticles could be lower than 30 nm, and the quantum dots could not be identified.

The quantitative data on surface roughness have been carried out using Nanoscope Analysis software. The roughness is evaluated in terms of arithmetic average height Ra and root mean square average height