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CdS/ZnS-doped silico-phosphate films prepared by sol-gel synthesis

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ABSTRACT

Silico-phosphate films doped with CdS/ZnS quantum dots (QDs) for luminescence temperature sensing devices, were deposited on silicon substrate by sol-gel method, spin coating technique. Optical absorption and photoluminescence emission of CdS/ZnS-doped silico-phosphate films were investigated. CdS/ZnS nano-crystalline particles were put into evidence by X-Ray Diffraction (XRD) spectroscopy. The specific vibration modes of the constituents were evidenced by structural analysis carried out by Raman and Fourier Transform Infrared spectroscopy (FTIR). The characteristic fluorescence emission of CdS/ZnS nanoparticles was noticed in the visible domain. The morphology of the films was investigated by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). Clusters of hexagonal crystalline CdS/ZnS QDs were put into evidence.

1. Introduction

In recent years, II-VI binary semiconducting compounds, belonging to cadmium chalcogenide family have been intensively investigated mainly due to their quantum confinement effect with potential use in optoelectronics devices [1–3]. CdS quantum dots (QDs) have many applications, which, sometimes, require to embed the nanocrystals into a solid matrix host, allowing optical information or signals to be transmitted with high propagation efficiency [4]. The host material plays the important role of providing a stable matrix, preventing the agglomeration of the dopant nanoparticles and, in the context of optical properties, it should be transparent in the region of interest.

Several approaches have been developed for producing bulk or thin films materials doped with semiconductor QDs: melt glasses, [5,6] polymers [7,8] and sol-gel glasses [9].

Optical and structural characterization of CdS QDs for solar concentrators was reported in [10] and luminescent down-shifting layer for crystalline Si solar cells was presented in [11].

The sol-gel method, as compared to the classical solid-state synthetic routes offers advantages, such as: the mild synthetic conditions, versatility, high homogeneity of dopants and purity of the final material, which are fundamental for the development of new advanced materials [12].

The paper presents the preparation as well as optical and structural characterization of luminescent silico-phosphate films doped with CdS/ZnS quantum dots QDs.

2. Experimental

Silico-phosphate films doped with CdS/ZnS quantum dots (QDs) have been deposited on silicon substrate, by sol-gel method, spin coating technique. The following regents were used as precursors: tetraethyl ortho-silicate (TEOS), phosphoric acid (H_3PO_4) and ethanol (EtOH), with the molar ratio 1.5/0.82/1.04. CdS/ZnS (QDs) have been previously prepared by chemical synthesis of CdS core nanoparticles followed by growth of ZnS shell [13]. The final solution was prepared by using 0.5 ml of precursor silico-phosphate solution and 3 ml of CdS/ZnS QDs alcoholic solution, under continuous magnetically stirring, for two hours. The final solution was deposited in 10 successive layers on silicon substrate. Each layer was dried at 200 °C, for 2 min on electric plate and the 10 layers stack was annealed at 100 °C, for 30 min, in oven, aiming at growing of dopant nanocrystals within the films. In order to characterize both silico-phosphate matrix and CdS/ZnS dopant, the below mentioned analysis techniques were applied and

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complementary results were evidenced. Optical absorption was investigated by UV–Vis ellipsometry using a Perkin Elmer Lambda 1050 spectrophotometer. X-Ray Diffraction (XRD) spectra were recorded with a Bruker D8 Advance device, (CuKα, $\lambda = 1.54056$ Å). Photoluminescence emission of CdS/ZnS-doped silico-phosphate films was recorded with a Horiba Jobin-Yvon Nanolog 3 spectrofluorometer. Structural investigations were carried out by Fourier Transform Infrared (FTIR) (Perkin Elmer Spectrophotometer-Spectrum 100) and Raman (micro-Raman LabRAM HR 800, Horiba Jobin-Yvon) spectroscopy, showing in evidence specific vibration modes of the constituents from the deposited films. The morphology and elemental composition of the films were investigated using an EVO 50XVP Carl Zeiss Scanning Electron Microscope (SEM) and TECNAI F30 G^2 Transmission Electron Microscope (HRTEM), linear resolution 1 Å and punctual resolution 1.4 Å. Qualitative microanalysis X-Ray Energy Dispersive (EDX) was performed with a detector of 133 eV resolution. The roughness and homogeneity of the films were investigated by Atomic Force Microscopy (AFM), XE100 Park System.

3. Results and discussion

3.1. Optical absorption and X-ray diffraction analysis

The ellipsometry modeling of the absorption spectra of CdS/ZnS-doped sol-gel films used the Bruggeman Effective Medium Approximation (BEMA) [14], considering that the precursor solution for each deposited layer has the following molar composition: 31.26% SiO_2, 19.38% P_2O_5 and 49.35% CdS/ZnS (QDs). The model takes into consideration nine similar layers deposited successively on silicon substrate, the last upper layer being in contact with atmosphere (Fig. 1). The interface between those nine layers, on one side, and between the first layer and the silicon substrate, on the other side, is considered to be a very thin layer of SiO_2, which is formed by an oxidizing process. It is assumed that those nine layers have a chemical composition slightly different from the upper deposited layer and the voids concentration is considered similar.

The fit of the experimental data is satisfactory and indicates a thickness of 90.409 nm for the package formed by those ten layers.

Fig. 2 shows the ellipsometric absorption coefficient variation in dependency on wavelength in the UV–Vis domain, for the CdS/ZnS-doped films.

It is noticed a significant decrease of absorption in the 300–500 nm range that continues to remain at low value in the visible range. This behavior is assigned to semiconductor dopant CdS/ZnS. The variation of $(\alpha h\upsilon)^2$ in dependency of $(h\upsilon)$ is presented in Fig. 3. The band gap of the semiconductor dopant was graphically determined, according to Tauc's law [15], defined as:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \tag{1}$$

where, E_g is the effective band gap of the semiconductor particle dopant, α is the absorption coefficient, h is the Planck's constant, ν is the frequency of vibration and A is the proportionality constant. The linear branch of the plot $(\lambda h\nu)^2$ versus photon energy $(h\nu)$ extrapolated for

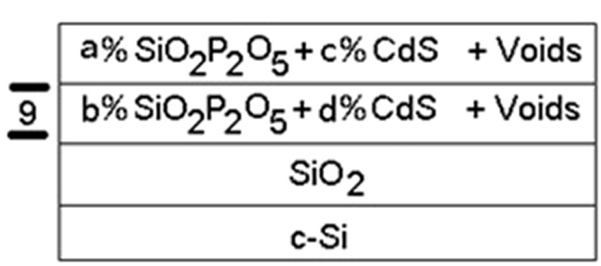

Fig. 1. The model of 10-layered structure of CdS/ZnS-doped sol-gel films, were a < b and c > d.

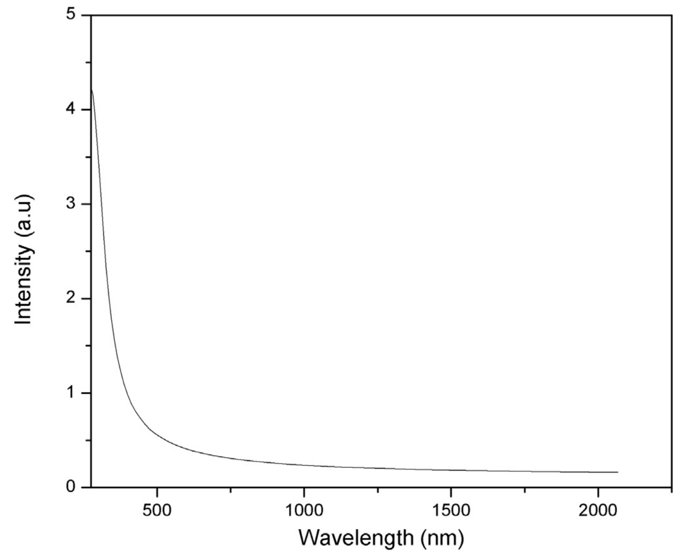

Fig. 2. Absorption spectrum of CdS/ZnS-doped sol-gel films.

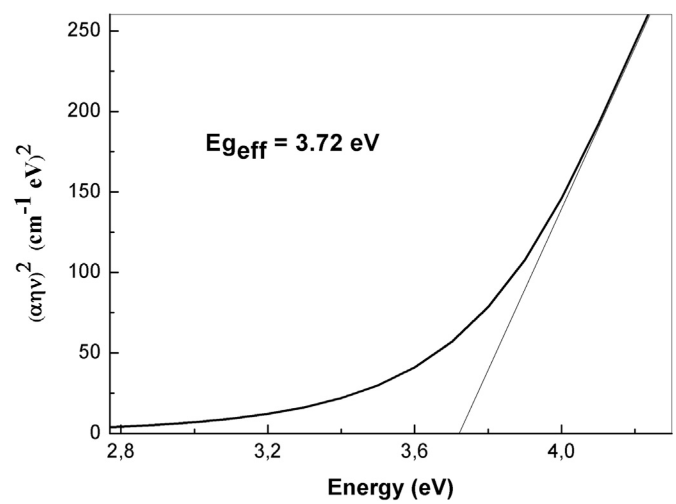

Fig. 3. $(\alpha h\nu)^2$ versus hν of CdS/ZnS-doped sol-gel films.

$(\lambda h\nu)^2 = 0$ gives a band gap value of 3.72 eV. The band gap is found to decrease due to an increase of the cluster size or grain size (R). This is known as the quantum size effect, enabling both strong and weak confinements, when $R \ll a_e$ and $R \gg a_e$, respectively, where a_e is the effective Bohr radius, being 3.5 nm for CdS [16].

Further on, the approximate dimension d of the nanoparticle, CdS/ZnS, is determined from the energy band gap dependency on the size of semiconductor dopant, using Eq. (2): where, $E_g^{(bulk)}$ is the energy band gap of a bulk semiconductor, m* is the reduced mass of exciton [17], calculated based on the effective mass of electrons and holes (0.19 m_o and 0.8 m_o respectively, where m_o is the free electron mass) [18], d is the nanocrystal dimension, the energy band gap of the bulk semiconductor, $E_g^{(bulk)} = 2.42$ eV.

$$E_g^{(eff)} = E_g^{(bulk)} + \frac{h^2}{2m^* d^2} \tag{2}$$

It was found that the dimension of the semiconductor nanoparticles is about 2.75 nm.

The XRD spectrum shown in Fig. 4 confirms the presence of CdS/ZnS hexagonal (ASTM file-00-041-1049) together with ZnS face-centered cubic (ASTM file-01-079-0043) and Si base-centered orthorhombic (ASTM file-01-089-9056) from the substrate. Phase identification was performed using Rigaku's PDXL software connected to ICDD