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PROPERTIES OF Por.Si-ZnSTe:Cr NANOCRYSTALLINE THIN FILMS

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Thin films of ZnSTe and Cr doped ZnSTe have been deposited on glass and Por-Si substrates by electrochemical deposition method taking ammonia as complexing agent. The pH of the solution was maintained at 8−9 at a temperature of 70^0C. Characterization of the ZnSTe and Cr-doped ZnSTe films were carried out using X-ray diffraction (XRD) and Atomic force microscopy (AFM). Structural properties and optical absorption has been observed for both doped and undoped films. Studies show that there is an increase of crystallite size and good optical properties in visible region from 420 nm in Cr-doped ZnSTe thin film.

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1. Introduction

Studying the size quantum phenomena in the little-studied and promising semiconductors of the type A^2B^6 opens up many prospects for the elaboration of new devices on their basis with different functional abilities. Among the wide range of nanomaterials, nanostructure materials for nanoelectronics occupy a special place. Nanostructuring allows one to tune the physicochemical properties of the substance. It caused the emergence of the definition “programmable matter” in the literature, which can strictly be understood as the elaboration of materials with a defined set of characteristics via nanostructuration.

Interest in the synthesis of small particles and nanocrystals of various substances has noticeably increased when a decrease in the crystallite size below a certain threshold value is found to cause a pronounced change in the crystal structure and the emergence of quantum properties. The quantum effects are manifested at a particle size below 10 nm. The spherical shape of nanocrystals is also of great importance to attain the optimum discrete spectrum of the energy levels of quantum dots. Chemical deposition from aqueous solutions allows the acquisition of semiconductor nanocrystals with much smaller dimensions in contrast to molecular-beam epitaxion and lithography. The incipience of nuclei and their growth upon chemical deposition results in a quasi-spherical shape of the nanocrystallites, whereas the synthesis of films via molecular-beam epitation or electrochemical deposition leads to a nonspherical shape. On the other hand, a small amount of the broken bounds on the cleavage surface (below 10^{10} cm^{-2}) allows the layered semiconductors to be used as solid substrates for quantum-dot formation [1], growing fullerenes, and the acquisition of van der Waals epitaxy [2–4] in the production of solar elements [5]. The X-ray detectors [6], optical converters [7], and luminophores [8], as well as photodetectors operating in the UV–visible–near-IR spectrum range of the electromagnetic radiation on the basis of A^2B^6 compounds are favorably different from the others by high radiaiton resistance and photosensibility. The ZnS-based luminophores exhibit high brightness and light output in the visible spectrum range. Doping ZnS with the activators results in blue luminescence for ZnS:Ag crystals, while it is green for ZnS:Cu and orange for ZnS:Mn. In this work we report the experimental results for nanoparticles synthesized on the basis of ZnSTe:Cr at por-Si combined with an analysis of their structure and optical, and photoluminescent characteristics.

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2. Experimental

The ZnSTe:Cr nanoparticles were obtained via electrochemical deposition. The preparation of substrates and compounds, as well as the synthesis, play important role. To manufacture the heterojunctions, p-type *c*-Si wafers (2.5 Ohm· cm resistivity and 0.2 ÷ 0.3 mm thickness) of (100) orientation were used as a substrate. Before anodization, the surface of the *c*-Si substrates were etched in an aqueous solution of HF and further washed in distilled water (at temperature of 80°C) and ethyl alcohol and then dried in air. The anodization of *c*-Si substrate surface was carried out in Teflon chamber with Pt cathode. HF: ethanol solution (1:1) were used for the porous silicon formation. The anodization voltage, current density and anodization time were 30V, 40-70 mA/cm^2 and 30–1800 sec, correspondingly. Depending on the anodization current and time porous-Si with porous size of 7 – 50 nm were prepared on the surface of *c*-Si.

In order to fabricate the heterojunctions, an ohmic In electrode, in reticulose form was evaporated on the CdS films with an area of ~0.82-1cm^2. An ohmic contact was performed on the side of *c*-Si wafers by evaporating an Al electrode.

The glass (İTO) substrates were previously cleaned in the potassium dichromate/sulfuric acid solution. Deposition of ZnSTe films was based on the reaction between zinc chloride ($ZnCl_2$) as the source of Zn^{2+}, $Te0_2$ and $Na_2S_2O_3$ providing S^{2+} and ammonium (NH_4OH) that was used as the complex-forming agent varying pH in the solution and enabling us to control the Zn^{2+} concentration.

After wards the mixed solution was stirred for 15 minutes. To improve homogeneity and the growth rate 15 ml of 1M hydrazine hydrate $\{(NH_2)_2\}$ was used. Then ammonia solution was added drop wise to form the complex and to raise the pH of the solution. The pH value was maintained between 8-9; keeping the temperature constant at 70 °C. For the Cr doping ZnSTe thin film, 0.05 M and 0.1 M solutions of CrO_3 were prepared separately. 20 ml of CrO_3 of each molarity was mixed in two separate beakers containing chemical solution of zinc acetate, thiourea and hydrazine hydrate of same molarities as described above in the deposition of pure ZnS thin film and then the CrO_3 mixed solution was stirred for 45 minutes. After some chemical reaction, deposition of films started slowly on the substrates. Keeping bath temperature maintained for 30−45 minutes, the whole solutions were kept undisturbed at room temperature for further deposition of the films. All the films were kept deposited for 24 hours. Then the glass slides covered with a white layer were taken out, washed with distilled water and dried out in air. However Cr-doped films were yellowish white in colour. Thus we prepared three different types of thin films namely undoped ZnSTe, 0.05M CrO_3 doped ZnSTe (Cr-ZnSTe1) and 0.1 M CrO_3 doped ZnSTe (Cr-ZnSTe2) separately. Some films were covered in both sides of the substrates. One side of these substrates was then cleaned by nitric acid. These films were kept to study the optical absorption. Other deposited films were kept “as it were” for the other characterization like XRD, AFM and XRF. Thickness of the films was measured by gravity method. Thickness for ZnSTe, Cr-ZnSTe films was varied from 84 – 85.26 nm.

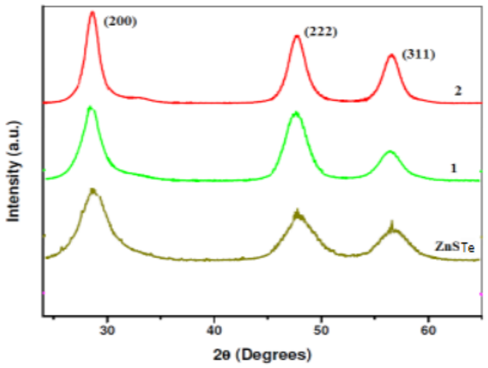

Fig. 1. XRD spectra of ZnSTe and Cr-doped ZnSTe films at Por-Si substrate.
1- Cr-ZnSTe1,2- Cr-ZnSTe$_2$.

Atomic force microscopy (AFM) is one of the effective ways for the surface analysis of thin films due to its high resolution and powerful analysis software. The ZnSTe and Cr-ZnSTe thin films were morphologically characterized using AFM technique. Fig. 2 shows the 2D and 3D image of undoped and doped ZnSTe film (Cr-ZnSTe2) in scanned area of 5 × 5 and 10 × 10 µm2. In both the films the surface is rough and fully covered in the substrate. Clusters of particles are observed over the surface in undoped ZnSTe film. While formation of unregulated grains of different sizes are observed clearly with pinhole free in Cr-ZnSTe2 film. From the AFM images average grain size in Cr-ZnSTe2 film is found to be 250 nm and the RMS (Root Mean Square) roughness is 210 nm as obtained by using the software WSxM 4.0 Beta7.0 version (14). RMS roughness is larger in doped film than that obtained from the undoped ZnSTe film which is 145 nm. Again we have found that grain size obtained from AFM image is quit larger than the crystallite size obtained from XRD. This may be because of small crystallites combine to form larger grain.

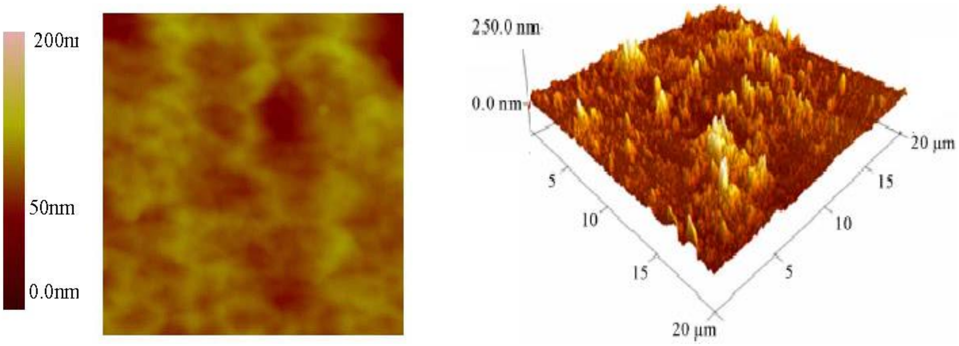

Fig. 2. The 2D and 3D image of undoped and doped ZnSTe film (Cr-ZnSTe$_2$).

Optical absorption of ZnS and Cr-ZnS films at glass substrate have been studied in the wave length range 340-800 nm. Optical absorption studies of semiconducting materials give some information related to band structure. Optical absorption spectra of typical undoped ZnSTe and Cr-ZnSTe thin films have been shown in Fig. 3a. At higher wavelength i.e. at lower energy side, absorption is low towards visible region. However, an increase of absorption is seen in lower wave length (higher energy) side for both types of films. Higher absorbance has been observed in Cr doped ZnSTe films. This may due to the presence of extra states created by Cr impurity in the doped films that absorbs more photon energy than that of the undoped film.

For direct transition the n value is ½ whereas for indirect transition the n value is 2.

Fig. 3b shows a typical plot of $(\alpha h\nu)^2$ versus $h\nu$ for doped and undoped ZnSTe film from which extrapolation of data to the $(\alpha h\nu)^2 \rightarrow 0$ axis gives the band gap energy Eg= 3.64 eV and for Cr- ZnSTe1 and Cr- ZnSTe2 film, this value is 3.84 eV and 3.87 eV respectively. Thus band gap decreases in case of Cr doped ZnSTe film. This is due to the extra electronic states associated with Cr located below the conduction band.

Fig. 4 shows the PL spectra and absorption spectra of a series of samples with different doping concentration. The PL spectra (Fig. 4a) of the nanocrystal samples show three peaks, at 478, 550 and 655 nm, which are attributed to the band edge, shallow and deep traps, respectively. We see that undoped nanocrystals have a narrower size distribution than the 5% and 10% doping nanocrystals.

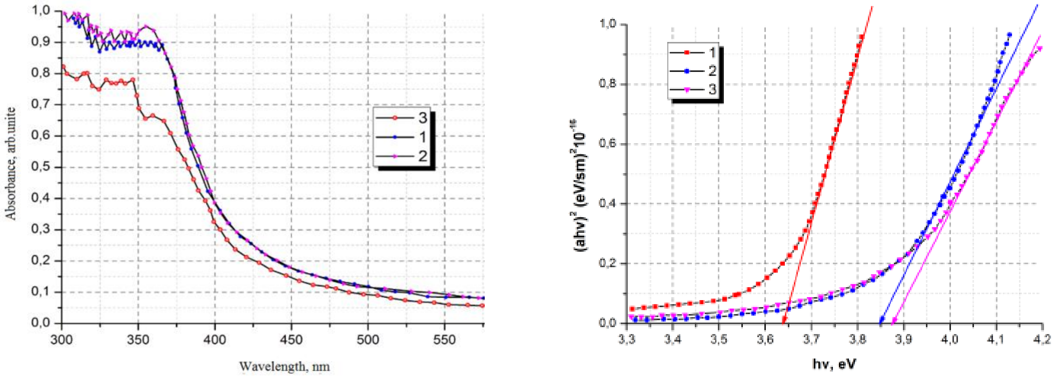

Fig. 3. Absorbance spectra of ZnSTe thin films and Cr-doped ZnSTe nanocrystalline films at glass substrate.

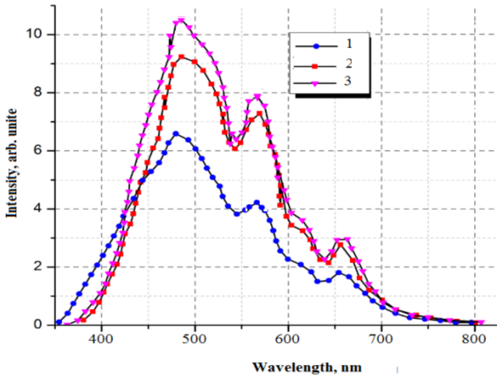

Fig. 4. Luminescence spectra of nanocrystalline ZnSTe:Cr, 1- ZnSTe, 2- Cr- ZnSTe1 and 3-Cr- ZnSTe2 films at por-Si substrate.

From the comparison it is seen that value of extinction coefficient is higher in Cr-ZnSTe films than that of the undoped ZnSTe film which indicates more efficiency of Cr-ZnSTe film in electrical conduction than ZnSTe film.

As is known the photoluminescence intensity from the point defects can be enhanced by increasing their volume density or decreasing the nanocrystallite size. An increase in the impurity content is however limited by their dissolution, whereas with a decrease in the nanoparticle size the luminescence efficiency depends on two rival process. On the one hand, an increase in the nanoparticle dimensions leads to the overlap of the electron and hall wave functions, which increases the emitting recombination probability and, on the other hand, increases the role of radiation-deficient recombination channels. Obviously, during low-temperature decomposition, a large amount of nonequilibrium defects is formed in ZnSTe films, which define the wide state spectrum. Cr in ZnSTe is an effective luminescence center, substituting Zn in the cation sublattice, and the introduction process is more efficient with the zinc vacancy.

3. Conclusions

Thin films of ZnSTe and Cr-doped ZnSTe have been prepared on glass and Por-Si substrates by the electrochemical method. XRD results reveal the polycrystalline nature of the films with preferred orientation along (200) plane. Different structural parameters such as crystallite size, lattice constant, internal strain and dislocation density were calculated from their XRD spectra.

AFM images show the rough surface of the films with increasing grain size and RMS roughness with doping. Optical studies confirm the direct band gap nature of the films and also the decrease of band gap energy in case of doped films. Higher value of extinction coefficient in Cr-ZnSTe films may enhance the efficiency of Cr-ZnSTe film in electrical conduction than that of ZnSTe film.

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