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Original research article

Optical constants and dispersion parameters of La-doped ZnS nanocrystalline films prepared by sol–gel technique

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ABSTRACT

The structure, morphology and particle size of La-doped ZnS nanocrystalline films were investigated by XRD, SEM and FTIR. XRD showed that the obtained films are nanocrystalline corresponding to the hexagonal ZnS phase with the particle size 3.44–15.13 nm. Optical properties of La-doped ZnS nanocrystalline films were investigated by UV–vis absorption technique. The band gap energy of nanocrystalline films was found to be 2.93 to 2.77 eV. Wemple – Didomenico single effective oscillator model was used to study the dispersion of nanocrystalline films refractive index. The red shift in the absorption band edge of the La-doped ZnS samples provides possibility for improving the solar energy application of ZnS.

1. Introduction

Recently, among II—VI semiconductors, ZnS is a significant semiconductor in photonics research and optoelectronic applications such as light emitting diodes, laser diodes and photodetectors. ZnS has two stable phases at 300 K, cubic zinc-blende (ZB) and hexagonal wurtzite (WZ) crystal structures. Both structures have large direct energy band gap with values of 3.65 eV and 3.77 eV for ZB and the WZ structures, respectively [1]. It is a promising material in several applications such as window layers of solar cells and coatings due to its wide band gap [2]. It is a superior host material for electroluminescent phosphors applications [3] and it is being commercially used for electroluminescent (EL) displays. Also, it is suitable for blue light-emitting diodes [4], multilayer dielectrics filters [5] and a buffer layer in thin film solar cells [6]. Furthermore, owing to the non-centrosymmetric properties of wurtzite ZnS superior piezoelectric "nanogenrator" sensitivity makes it one of the most suitable semiconducting-based mechanical energy harvesting materials [7]. Doped with transition-metal or rare-earth elements, ZnS can also be used to synthesis effective phosphor materials [8] or enhancing ZnS visible-light photoactivity [9,10]. Various techniques, such as spray pyrolysis [11], chemical bath deposition [12], electrodeposition [13] sputtering [14], successive ionic adsorption and reaction [15], chemical vapor deposition [16], and sol gel were used to prepare ZnS [17]

In this paper, we prepare $La_xZn_{1-x}S$ (x = 2, 3,4and 5 mol %) nanocrystalline films by sol–gel technique. The structural, morphological and optical properties of the these films were studied using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Fourier Transformer Infrared (FTIR) spectra and UV–vis-Near IR Spectroscopy measurements. The structural and

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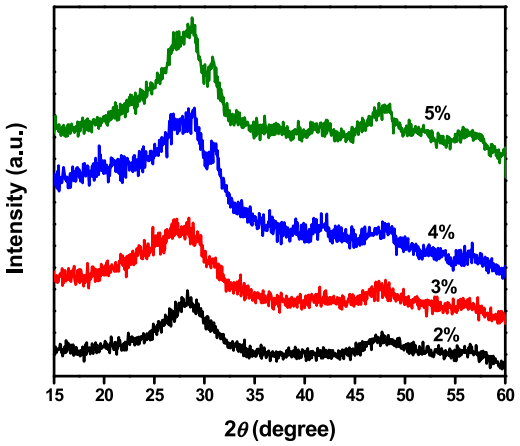

Fig. 1. X-ray diffraction pattern for Zn_{1-x} La_x S nanocrystalline films at room temperature.

Table 1
grain size, lattice parameters, bond length and density of Zn_{1-x} La_x S nanocrystalline films.

x (mol%)	*D* (nm)	*a* (Å)	C (Å)	L_B (Å)	ρ (g/cm^3)
2	3.44	3.809	6.319	5.04	4.14
3	4.5	3.790	6.280	5.01	4.18
4	9.48	3.843	6.177	4.95	4.22
5	15.13	3.766	6.231	4.97	4.39

optical properties studies reveal significant variations in these properties of the films with respect to La-doping at different concentrations.

2. Experimental

$La_xZn_{1-x}S$ (x = 2, 3, 4 and 5 mol%) nanocrystalline films were deposited on glass substrate using sol–gel technique. Two stock solutions were prepared by dissolving 0.01 M Zn $(OOCH_3)_2$ and 0.03 M CH_4N_2S separately in methanol at 303 K (room temperature). La $(OOCH_3)_3$ was added to the first precursor solution during stirring with the mentioned ratios. The two precursor solutions were mixed in the same flask with molar ratio 1:3. After 20 min, Triethanolamine (TEA) was added drop by drop to the mixed solution during stirring. The final solution was stirred (at 250 rpm) for 36 h at 303 K with final ph 8. Before the deposition the substrates were etched by boiling HCl for 30 min and rinsed in distilled water using ultrasonic bath for 20 min. After deposition, all nanocrystalline films were dried at 250 C for 20 min and then annealed at 450 C in air for 1 h [18]. The thickness of nanocrystalline films was measured using ZYGO Maxim-GP 200 profilometer. The crystal structure of samples was investigated using X-ray diffraction (PANalytical Empyrean diffractometer). The thickness of films was measured using ZYGO Maxim-GP 200 profilometer. The film thickness varied from 400 to 600 nm. A Quanta 250 FEG (Field Emission Gun), FEI Company, Netherlands scanning electron microscope was used to investigate nanocrystalline films morphology. A double beam Shimadzu 5000 UV–vis spectrometer was used to measure the transmittance, absorption and reflectance of the La doped ZnS nanocrystalline films. For FTIR investigation Jasco-FT/IR4100 type A was used.

3. Results and discussion

3.1. Structural and morphological characteristic of $Zn_{1-x}La_xS$ nanocrystalline films

3.1.1. X-ray diffraction (XRD)

Fig. 1 shows the X-ray diffraction (XRD) spectrum of $Zn_{1-x}La_xS$ where (x = 2, 3, 4 and 5 mol%) nanocrystalline films at room temperature. The XRD spectrum shows four main peaks at approximately 26.93, 48.5 and 31.07 which corresponding to (100), (101) and (110) planes of hexagonal ZnS phase [19]. The peak at 28.85 can be attributed either to (111) plane of the cubic phase or to the reflection of the hexagonal structure (002) plane. It is hard to distinguish between $(111)_{cubic}$ and $(002)_{hexagonal}$ planes because their similar angles position [20]. However, when La-doping ratio is much more than 3% (4 and 5 mol%), the new peaks were observed and the crystalline quality greatly improved as opposed to the host (Table 1). This is probably due to the creation of new nucleating centers from the dopant atoms that is favorable for the growth of the ZnS crystals phase. Also from the fact that the characteristics planes (100), (101) and (110) of hexagonal ZnS were observed in