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Structural and optical properties of PVA doped zinc sulphide thin films

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ABSTRACT

Zinc sulphide (ZnS) nanostructured thin films have been prepared using CBD method on glass substrate at room temperature under three different concentrations of PVA. The structural and optical properties of the films have been studied. The XRD pattern suggests wurtzite structure with lattice constant 5.3876 Å and average particle size of 4 nm which is confirmed by TEM micrographs. The bandgap of the synthesized ZnS nanoparticles are found to decrease with increase of PVA concentration. The Raman spectra of ZnS nanoparticles are also reported.

1. Introduction

Zinc sulphide, with large direct bandgap of 3.5 – 3.7 eV in the UV range [1], is found in both cubic as well as hexagonal forms. The less dense hexagonal phase (wurtzite), stable above 1020 °C at atmospheric pressure [2], is more attractive for device applications [3]. The optical and electrical properties of CuS and ZnS films deposited on glass microscope slides using improved CBD method shows variation with PH [4] while a strong absorption near 360 nm has been observed with increasing film thickness in ZnS thin films [5]. A transmittance of 96% has been observed in the ZnS films synthesized on Ge substrate using ionized cluster beam method [6] whereas transmittance more than 60% above 400 nm has been observed in ZnS films grown on polyester foils [7]. ZnS films exhibit bulk values of refractive index deposited at high rates and low pressures [8] and it has been also observed that the refractive indices varies with the thickness of the films as well as with wavelength of the incident light [5,9]. Using SILAR technique, polycrystalline and cubic ZnS films have been synthesized on different substrates and it is found that refractive indices varies for different substrates [10]. The bandgap of ZnS has been estimated using different processes and is found to be 3.67 eV and 3.58 eV, respectively [11]. Wurtzite ZnS nanocrystals, of size about 1.54 nm, have been synthesized in PVA capping agent [12] and it has been observed that particle size varies with PVA concentration as well as inter band transition of optical absorption. ZnS – PVA nanocomposite films synthesized using CBD method shows significant changes in their various properties with Zn source concentration [13].

In the present study, wurtzite ZnS nanostructured thin films in presence of polyvinyl alcohol (PVA, as a capping agent) have been deposited on glass substrates using CBD method. The structural, morphological and optical properties have been investigated along with Raman study.

2. Materials and methods

The starting materials were zinc acetate [$Zn(CH_3COO)_2$], sodium sulphide (Na_2S), polyvinyl alcohol (PVA) as capping and dispersing agent, NH_3 as reducing agent and deionized water as medium. ZnS nanostructured thin films have been synthesized on glass substrates using chemical bath deposition (CBD) method as reported previously [13] because due to low capital expense and appropriate for the production of devices. The samples were prepared under three different concentration of PVA (5, 10 and 20 ml) at room temperature. The synthesized films were dried under vacuum for 48 h and kept there for different studies. The films were characterized by X-ray diffractometer (Rikagu Miniflex, CuKα line) for structural and

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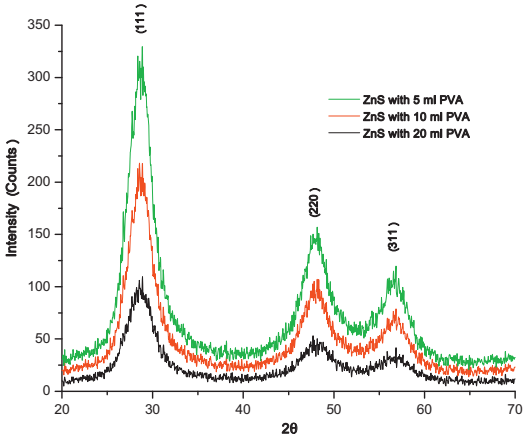

Fig. 1. X-ray diffraction pattern ZnS thin films in different PVA concentrations.

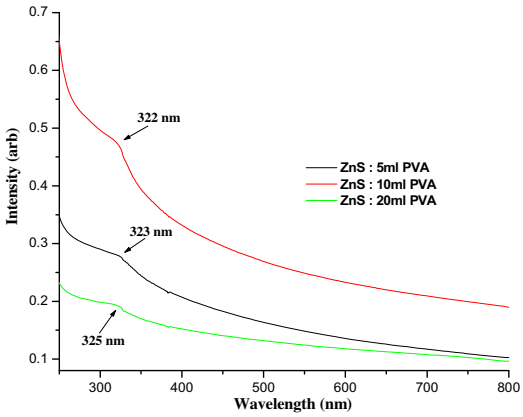

Fig. 3. Absorption spectra of ZnS thin films different PVA concentrations.

Table 1
Lattice parameters, particle size and bandgap of ZnS nanoparticles.

PVA Concentration (ml)	Lattice parameters (A°)	Bandgap (eV)	Average particle size (nm)		
			From XRD	From TEM	From bandgap
5	5.3876	4.9	3.2	3.9	2.2
10	5.4023	4.5	3.7	4.2	2.6
20	5.4187	4.1	4.1	4.8	3.2

Transmission electron microscope (JEOL, Japan) for morphological studied. The optical properties of the films were studied using UV – visible spectrometer (Perkin Elmer, USA), photoluminescence (PL) at room temperature at an excitation wavelength of 325 nm and Raman scattering.

3. Result and analysis

3.1. Structural and morphological properties

The X-ray diffraction patterns of ZnS nanostructured thin films synthesized with different concentrations of PVA are shown in Fig. 1. The observed XRD patterns show diffraction peaks at $2\theta = 28{\cdot}62^\circ$, 48.08° and $56{\cdot}87^\circ$ with lattice parameter $a = 5.3876$ Å and are in agreement with reported previously [12]. The highest intensity reflection peak observed at $28{\cdot}62^\circ$ corresponds to (1 1 1) plane which indicates that (1 1 1) is the preferred direction. The peak positions tally with wurtzite structure of ZnS crystals. The particle size has been calculated using the Scherer formula [14],

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where, D is the particle size, λ is the wavelength of the radiation used, θ is the Bragg's angle and β is the FWHM measured in radian. The calculated average particle size of ZnS is 4 nm and is given in Table 1. TEM micrographs of ZnS thin films with 5 ml, 10 ml and 20 ml PVA have been shown in Fig. 2(a – c), respectively. From micrographs, it is clear that the grains of ZnS nanoparticle are uniformly distributed with grain size (3 – 5 nm). The XRD and TEM analysis indicates that with increase of PVA concentration, particle size of ZnS nanoparticles increases because PVA acts as a surfactant and capping agent and prevent the growth of the particles.

4. Optical properties

Fig. 3 shows the UV – visible spectra of ZnS thin films with different concentrations of PVA at room temperature. The recorded absorption spectra show blue shifted absorption peaks as compared to bulk ZnS (336 nm) [15,16] which indicates the increase of bandgap as compared to bulk (3.7 eV) owing to quantum confinement effect [17–19]. The spectra of ZnS nanoparticles with 5, 10 and 20 ml PVA have the absorption peak at 322, 323 and 325, respectively, which are slightly red shifted with increase of PVA concentration. Absorption coefficient (α) associated with the films was calculated from absorbance (A) and the film thickness (t) using the relation [20]:

$$\alpha = 2.3026A/t \quad (2)$$

The absorption coefficient (α) was analyzed using the following expression for near-edge optical absorption of semiconductors $(\alpha h\upsilon) = K(h\upsilon - E_g)^{n/2}$, where K is constant, E_g is the separation between the valence and conduction bands and n is a constant that is equal to 1 for direct bandgap semiconductors. The bandgap values were determined from the intercept of the straight-line portion

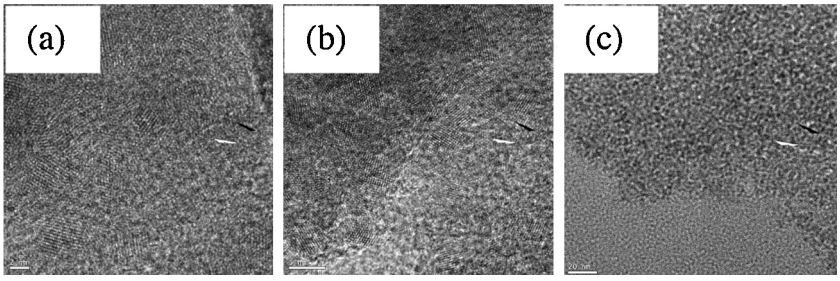

Fig. 2. (a – c): TEM micrographs of ZnS thin films in different PVA concentrations.