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ZnS Dendrites – Optical, Electrical and Structural Properties

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ABSTRACT

ZnS dendrites have resulted in use of the simple wet chemical route of sol-gel. Zinc acetate and thiourea were used as zinc and sulphur sources respectively, whereas ethanol was used as solvent. 10% diluted HNO_3 was used to maintain the pH at a value of 6. Transparent and stable ZnS sol was spin coated onto glass substrates at 3000rpm for 30 seconds. X-ray diffraction results confirm the formation of hexagonal wurtizite phase with preferred orientation of (1 0 1) after annealing at 300^{o}C for 60 minutes. ZnS dendrites with dimensions in the range of 100 – 300 nm were observed by scanning electron microscopy. Direct band gap ~3.52 eV is calculated through transmission measurements. It is important to mention here that these dendrites have been prepared without the use of any complexing agent or surfactant. These optical results are comparable with the reported values where ZnS was prepared in the presence of Na_2EDTA and Na_3-citrate.

1. INTRODUCTION

Most recently, great attention is being paid to nanostructured materials owing to their novel/unique properties which are impossible to observe at the bulk level. These nanostructured materials have great impact on the economy of modern electronics industry. Quantum size effects and surface effects are the two phenomena because of which materials at the nano level exhibit innovative properties including optical, electrical, magnetic, chemical and structural that might find many technological applications (Borah 2008).

In optoelectronic devices, semiconducting nanostructures play a vital role due their exceptional size dependent properties. Most importantly, the optical band gap of semiconductors can be easily tuned by reducing the particle size, and the semiconductors with modified optical properties can have applications in many optoelectronic devices, such as in solar cells (Huynh 2003), light emitting diodes (Zhao 2006), flat panel displays (Liu 2001), infrared windows, lasers, bio-devices, electroluminescence (Hirabayashi 1987), electro-optic modulators, photoconductors, optical sensors, phosphors etc. (Fang 2011). ZnS can be used for the cathode ray tube, field emission display, and the scintillator as one of the most frequently used phosphors (Saravanan 2010).

ZnS is one of the important II–VI compound semiconductors having band gap of 3.7 eV. In view of incorporation of ZnS (wide band gap semiconductor) in optoelectronics,

especially fluorescence, infrared transparency, blue light photoluminescence and electroluminescence (Ma 2011), it has acquired lot of interest of researchers. In the bulk form, ZnS exists in two polymorphs, hexagonal wurtizite and cubic sphalerite. ZnS has a phase transition temperature of 1020˚C from cubic zinc-blende to hexagonal in bulk. However, the transition occurs at relatively low temperature in nanocrystals due to high surface energy (Radhu 2011).

In the past, many techniques have been employed to synthesize ZnS nanostructures such as sol-gel (Saravanan 2010), mechano-chemical (Pathak, 2012), reverse micelles method (Murugadoss 2011), hydrothermal process (Hoa 2009), chemical co-precipitation reaction method (Reddy 2011). Among these deposition techniques, sol-gel (wet chemical route) has been extensively used due to several advantages such as: low cost, large-scale production, low-temperature process and no catalyst assistance (Su-fen 2008).

The objective of the present work is to optimize ZnS synthesis conditions for the preparation of ZnS dendrites by using sol-gel technique. Dependence and variation in optical properties as a function of the change in structural and morphological properties are also investigated.

2. EXPERIMENT

ZnS thin films were synthesized by wet chemical method (sol-gel). Zinc acetate di-hydrated and thiourea were used as source materials for zinc and sulphur respectively, while ethanol was used as a solvent. Appropriate amounts of zinc acetate and thiourea were separately dissolved in ethanol. Solution of thiourea was then added drop-wise to zinc acetate solution under vigorous stirring at 40˚C to avoid precipitation. Initially, several ZnS sols were prepared at room temperatures and at relatively lower temperatures but precipitation and incomplete dissolution of precursors were observed. Final precipitate-free ZnS sol was achieved at 40^{o}C without the addition of any surfactant. Lee et al. (2002) have also prepared ZnS sol by sol-gel but at relatively higher temperature of ~80^{o}C. Few drops of diluted nitric acid were added into the mixture in order to maintain the pH ~6 of final sol (Navaneethan 2010). The prepared sols were left for aging at room temperature prior to deposition. Glass substrates were ultrasonically cleaned with acetone and IPA for 15 minutes respectively to have contamination free substrate surface. Optimized ZnS sol was deposited on glass substrates by spin coating. Samples were prepared in two intervals with different spinning speeds and time. First coat was obtained at the spinning speed of 500 rpm for 5 seconds while second coat was deposited at 1500 rpm for 10 seconds. As-prepared samples were dried for 24 hours at room temperature and then subjected to annealing in vacuum for 1 h at 300^{o}C.

Samples were characterized structurally with Rigaku D/MAX-IIA X-ray diffractometer (XRD) using Cukα (Ni filtered) radiations (λ=1.5404Å). Surface morphology of the samples was observed by Hitachi S-3400N Scanning Electron Microscope (SEM). Optical characterization of ZnS thin films was performed by JA Woolam's variable angle spectroscopic ellipsometer (VASE).

3. RESULTS AND DISCUSSION

3a. Surface Morphology of ZnS Thin Films

The surface morphology of the prepared ZnS samples was observed through scanning electron microscopy. SEM micrographs clearly show the formation of dendrites in the first three samples as shown in Fig. 1 (a, b and c).

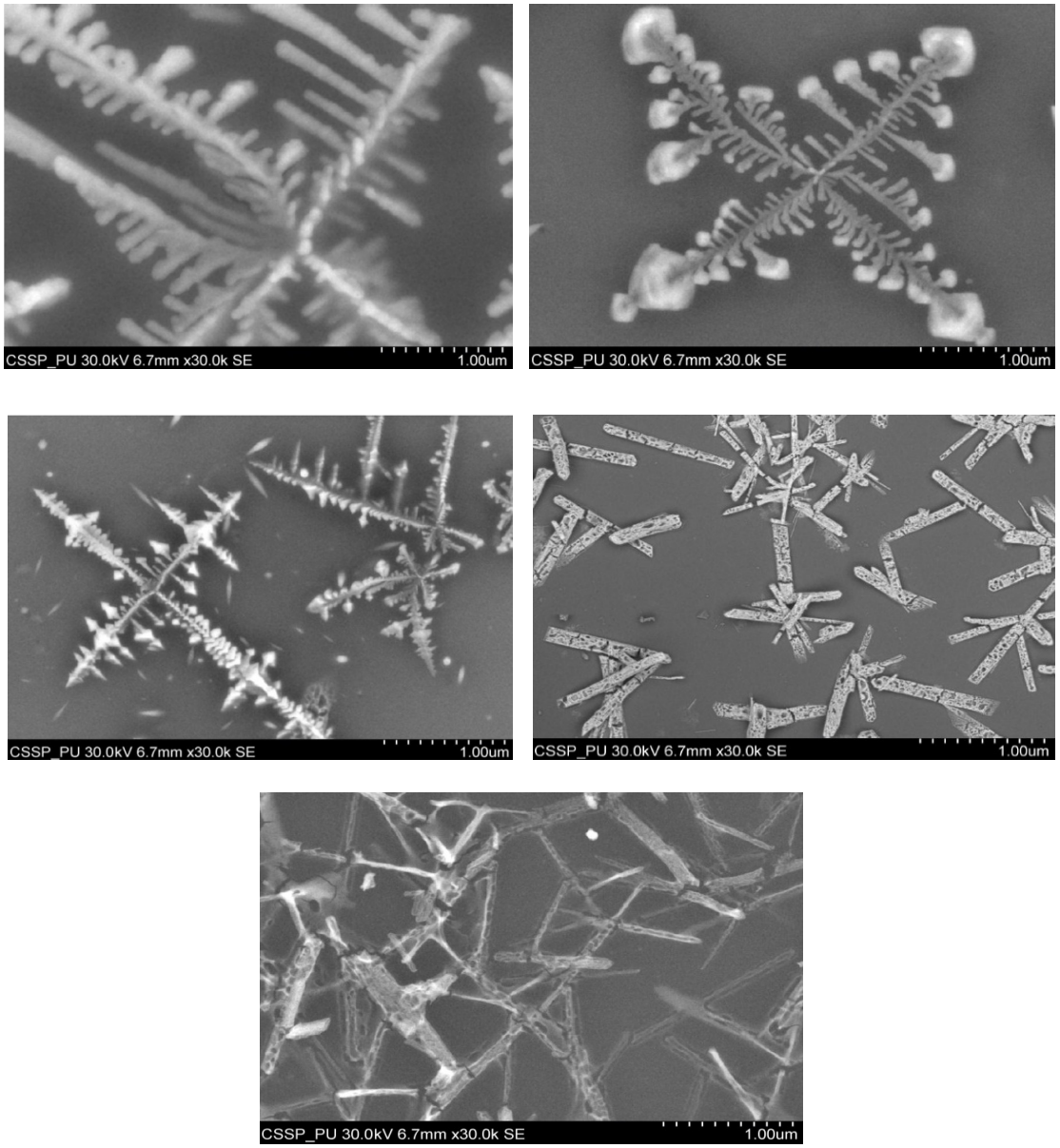

Fig. 1: (a-e) SEM micrographs showing formation ZnS-dendrite

From SEM micrographs it can be clearly observed that the synthesized ZnS dendritic nanostructures [Fig. 1 (a-c)] have stems with branches having several leaf-like

structures attached. In the present work the effect of thickness and annealing on the formation of ZnS dendrites is observed. As the thicknesses increases from 110 nm 119 nm the structure of the ZnS dendrites have slight variation in dimensions and particularly in angle between stems and branches. In Fig. 1(a) the angle between the leaves of the dendrite is ~ 75˚ for 110 nm which increases slightly towards 90˚ and lies exactly at 90˚ for the 119 nm as shown in Fig. 1(b-c) respectively. When the samples with slight increase in thickness (i.e. from 124 – 129 nm) were annealed under the same conditions distorted dendritic structure was observed [Fig. 1(c-d)]. Dendrites have attractive applications in sensors, optical and electronic systems, and fluorescence–enhancement materials (Lu 2006). Average diameters of the formed structure is in between 170-350nm.

3b. Structural Analysis of ZnS Thin films

Fig. 2 shows the XRD patterns of ZnS annealed at 300^{o}C. The XRD pattern confirms the hexagonal phase of ZnS with the characteristic peak at 29.985˚ in (1 0 1) plane. The observed diffraction peaks are well matched with reported data (JCPDS No.10-434). However, it can be seen that the material is more amorphous-like rather than crystalline. The reason for this observation could be that XRD was performed on the as-prepared samples rather than taking the materials off the substrate.

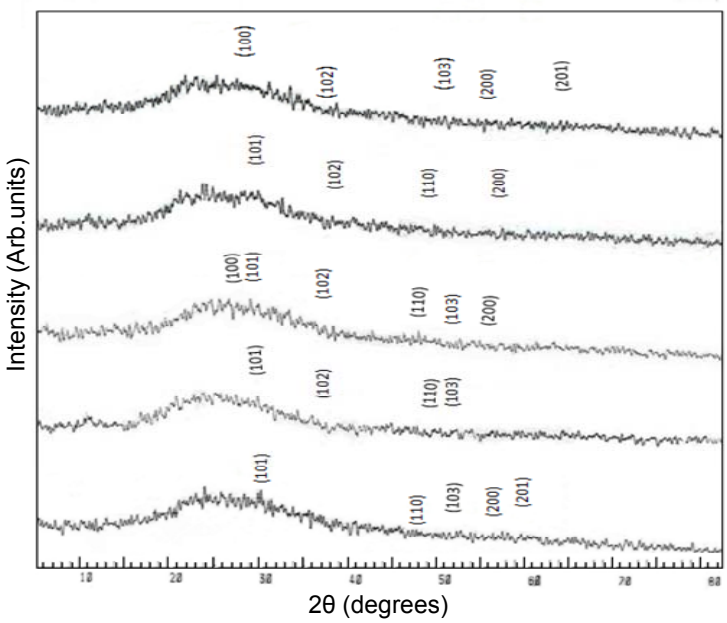

Fig. 2: *XRD patterns of ZnS Dendrites*

The first layer deposited plays the role of seed for the growth of material on the amorphous substrate. These results are in agreement with the report presented earlier for the growth of ZnS thin films. Reduction in the effect of substrate with increasing

thickness of the film has also been reported earlier by depositing ZnS thin films on glass substrate by thermal evaporation method (Prathap 2008).

Microstrain of the deposited ZnS thin films can be calculated by differentiating the Bragg's law as:

$$b = \Delta 2\theta = -2\left(\frac{\Delta d}{d}\right)\tan\theta$$

where, 'b' represents the broadening introduced by the strain effect. This broadening is attributed to the fractional change occurred in plane spacing of deposited thin films and is given by Δd/d (Cullity 1978). Thin films show a uniform strain [Fig. 3] which is apparent from the shapes and shifts of peaks corresponding to reflection planes when compared with standard data as observed in XRD patterns.

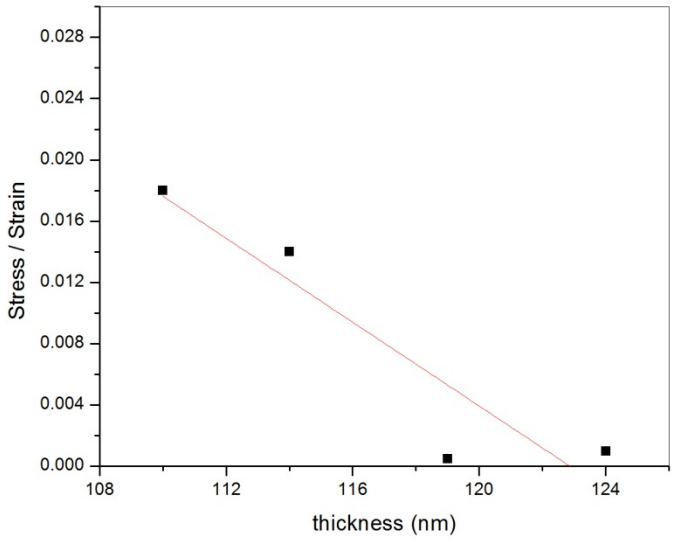

Fig. 3 *Variation in stress/strain of ZnS dendrites for different thicknesses*

3b. Optical Analysis of ZnS Thin Films

Fig. 4 shows transmission spectra of annealed ZnS samples at 300^{o}C obtained from variable angle spectroscopic ellipsometer. Variation in transmission as a function of wavelength for ZnS thin films with different thicknesses is observed. Transmission was observed to decrease as thickness of the film increased from 119 to 129 nm, as reported earlier (Salim 2012). The maximum transmission of the film observed in our work was found to be 83% for ZnS thin film having thickness of 114 nm which is in agreement with the report presented earlier (Goudarzi 2007).

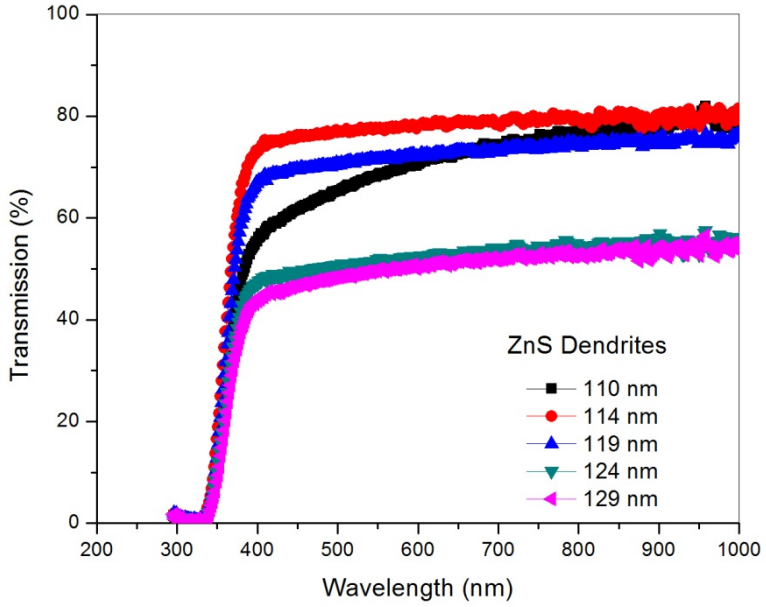

Fig. 4 Transmission spectra of ZnS Dendrites on glass substrate

Refractive index of ZnS thin films was observed to be in the range of 2.20 to 2.32, in the visible region, as shown in Fig. 5.

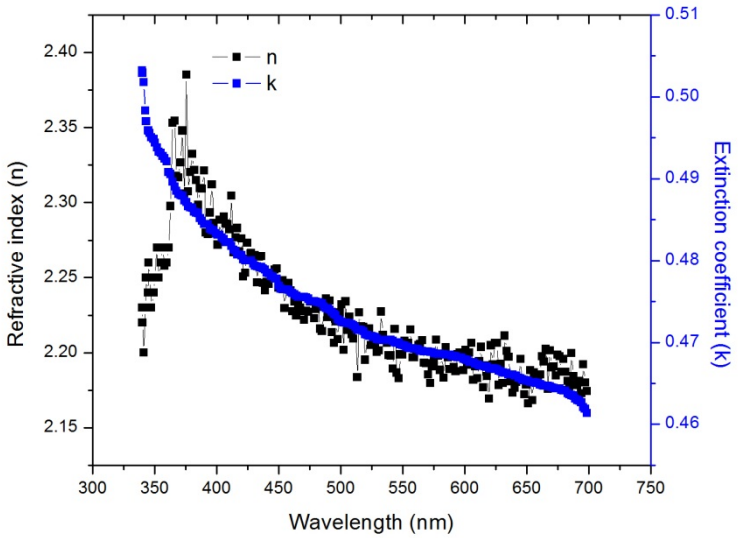

Fig. 5 Variation in refractive index (n) and extinction coefficient (k) of ZnS Dendrites

The extinction coefficient obtained from ellipsometric data lies in the range of 0.47 – 0.485, in the visible region, as shown in Fig. 5 above.

The band gap is calculated by extrapolating the linear portion of α^2 versus photon energy E(eV) towards the energy axis. The value of bandgap was observed to increase as the number of coatings increased. The values of energy bandgap are found to be in the range of 3.52 - 3.54 (Fig. 6). These results are in agreement with previously reported values of energy band gap (Bhargava 1994, Dutta 2008)

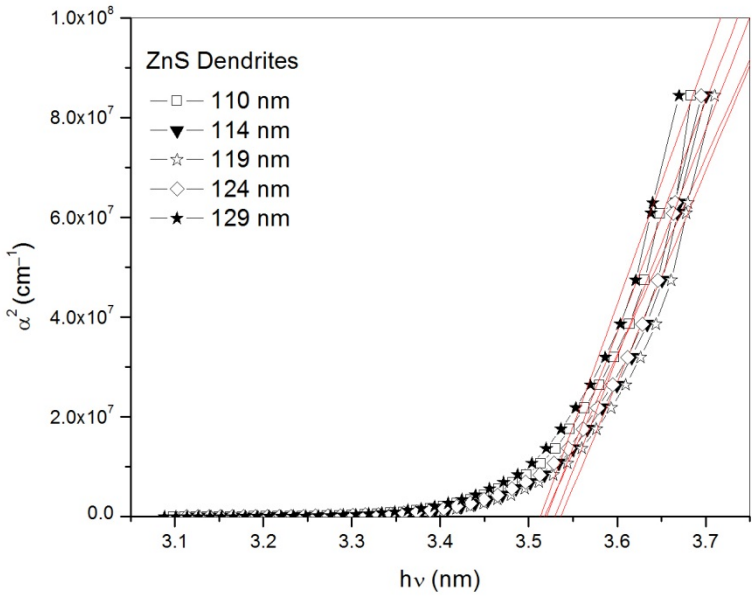

Fig. 6 Band gap of ZnS Dendrites on glass substrate

CONCLUSION:

ZnS dendrites have been observed when its sol was spun onto glass substrates. These structures were observed using scanning electron microscope. Optical and structural properties of these dendrites were checked, and the main results from these characterization techniques are summarized in Table 1. In conclusion, very well defined dendrites can be observed using simple sol-gel technique.

Table.1: Structural and optical properties of ZnS Dentrites

Sample	Structure	XRD (101) Peak	Dimension (nm)		Angle (degrees)	Transmission (%)	Band Gap (eV)
			Leaves	Stems	Between Leaves and Stems		
1	Dendrites	√	150	235	75	79.02	3.519
2	Dendrites	√	100-300	250	83	82.31	3.519
3	Dendrites	√	100	210	90	76.94	3.533
4	Dendrites (distorted)	√	-	-	-	56.63	3.537
5	Dendrites (distorted)	-	-	-	-	54.17	3.513

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