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Nanostructurred $ZnS_{1-x}Se_x$ (x =0.4) Thin Film Prepared by Chemical Bath Deposition for Solar cell applications

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Abstract: **Ternary nanostructurred zinc selenosulphide ($ZnS_{0.6}Se_{0.4}$) thin film was grown on glass substrate using chemical bath deposition technique employing ammonia free precursors at 80 °C. As deposited thin film exhibits nanostructurred polycrystalline nature confirmed by X-ray diffraction pattern (XRD). The optical band gap (Eg) was calculated from the observed transmittance spectra by Urbach method and found to be 3.29 eV. The optical and electrical properties' study revealed that $ZnS_{0.6}Se_{0.4}$ thin film is useful in optoelectronic device fabrication and applications, and as an environment friendly alternative to the commonly used toxic material such as CdS.**

Index Terms: **semiconductor, thin films, chemical synthesis,**

I. Introduction

Wide-energy band-gap II–VI compounds are attractive because of their potential applications for nanostructured electronic and optoelectronic devices. The bulk, single crystal and polycrystalline thin films have been growth and characterized for these applications (Kontos, G.et al.,2003; Jung, J. H., et al.,2007; Li F., et al.,2008; Zhu X. L., et al.,2007)**.** Polycrystalline thin films of $ZnS_{1-x}Se_x$ have been reported for different optoelectronic applications such as blue lasers and blue laser diodes (Patil D. et al.,2004), heterojunction nontoxic solar cells (Subbaiah Y., et al.,2007; Subbaiah, Y., et al.,2008) etc. Now a days, growth and characterization of nanostructure $ZnS_{1-x}Se_x$ composite thin films have wide scope for optoelectronic device applications. Moreover, on considering the industrial production and environmental protection issues, the nanostructure $ZnS_{1-x}Se_x$ composite materials are the promising alternatives to the presently explored toxic materials such as CdS window layer in photovoltaic applications. Earlier, thin films of $ZnS_{1-x}Se_x$ have been prepared using atomic layer epitaxy **(**Hsu C., et al.,1999), high pressure sputtering (Ganguly, S., et al.,2001), metal organic vapor epitaxy (Lovergin, N., et al.,2000), MOCVD (Song J. H., et al.,2000), laser ablation (Ambrico A., et al.,1998), close space evaporation, spray pyrolysis (Ganesha K.,2020), epitaxial growth Lee M. K., et al.,2003), soft chemical route technique (Agawane G. L., et al.,2014). Among the galore of thin film deposition techniques, soft chemical route technique is low cost, low temperature and no special instrumentation is required. In this technique, substrates are immersed in an alkaline solution containing the chalcogenide source, the metal ion, added base and complexing agent. Furthermore, in soft chemical route technique, controlled chemical reactions play an important role during the deposition of thin film and the rate of deposition can be controlled by adjusting the parameters like bath temperature, pH of solution, stirring rate and relative concentration of solutions in the bath.

In the present investigation, we report a simple and economic soft chemical route technique for the growth of $ZnS_{1-x}Se_x$ (x=0.4) thin films using ammonia free precursors. Typically, the $ZnS_{0.6}Se_{0.4}$ thin films were deposited using mixture of aqueous solutions of zinc sulphate, thiourea, selenium powder, sodium sulphite, trisodium citrate, triethanolamine (TEA), hydrazine hydrate, and sodium hydroxide (NaOH), where triethanolamine was used as the complexing agent and sodium hydroxide for adjusting the pH.

II. Experimental Details

A. Thin film preparation

Thin films of $ZnS_{0.6}Se_{0.4}$ were grown by soft chemical route using precursors of zinc (zinc suphate), sulfur (thiourea), selenium (sodium selenosulphate) and suitable complexing agents.

The substrates used for the deposition of $ZnS_{0.6}Se_{0.4}$ thin film were commercial microscope glass slides (Blue Star) with the size

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of 75 x 25 x 1.35 mm. Before deposition, the substrates were degreased in HNO_3 solution for 24 h, cleaned by commercial detergent and finally rinsed with de-ionized water and dried in air. This process is to ensure clean surface, which is essential for formation of nucleation centers, required for thin film deposition. All chemicals used in the present investigations were Loba Chem AR grade. Aqueous solutions of 0.25 M zinc sulphate ($ZnSO_4$), 0.25 M sodium selenosulphate (Na_2SeSO_3), 0.25 M thiourea, 0.2 M trisodium citrate, triethanolamine (TEA), 80 % hydrazine hydrate and 4 M sodium hydroxide (NaOH) were used to prepare thin films. Sodium selenosulphate was prepared (sadekar H.K., et al.,2013). Typically, 20 mL zinc sulphate solution was taken in a 50 mL glass beaker. Under continuous stirring, 30 drops of TEA, 5 mL NaOH and 5 drops of hydrazine hydrate solutions were added slowly. Initially, the solution was milky and turbid due to the formation of $Zn(OH)_2$ suspension. Addition of excess NaOH led to the dissolution of turbidity and made the solution clear and transparent. Then 5 mL trisodium citrate and 8 mL freshly obtained sodium selenosulphate and 12 ml thiourea solutions were added slowly with constant stirring and the pH of final mixture was adjusted to ~ 13.

Pre-cleaned glass substrates were inserted into the reaction mixture in the beaker standing parallel with the walls of the beaker, which was kept in constant temperature bath for 1 h at 80 ºC. Thereafter, the substrate coated with $ZnS_{0.6}Se_{0.4}$ was removed, rinsed with distilled water, and dried in open air

B Characterization Techniques

Thickness was measured by weight difference method. Glancing incidence angle X-ray diffraction (GIXRD) pattern of the film was recorded on a Bruker AXS, Germany (D8 Advanced) diffractometer in the scanning range 20–70o (2θ) using Cu-Kα1 radiations with wavelength 1.5405 Å at 0.5° glancing angle. Transmittance and absorbance spectra were recorded in the range 300–900 nm by means of Jasco V630 spectrophotometer.

III. Results and Discussions

A. Structural Studies

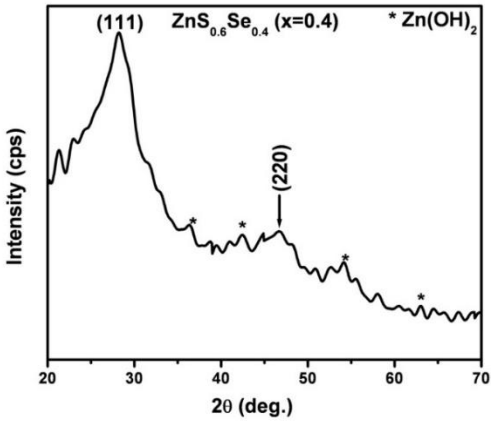

Figure. 1. GIXRD pattern obtained from the as-deposited ZnS0.6Se0.4 thin film.

The 2θ peaks at 27.45°, and 45.57° corresponds to reflections from (111), (220) planes, respectively. The (111) plane is the preferred orientation, and it is the close-packing direction of the zinc-blende structure of cubic phase (JCPDS card No 80-0021). Crystallite size (D) of the film was calculated using Scherrer's formula from the full width at half maximum (β) of the peaks expressed in radians,

$$D = \frac{K\lambda}{\beta Cos\theta}$$

where 'K' is constant dependent on crystallite shape (0.89), 'λ' is wavelength of $CuK_{\alpha 1}$ radiation, and 'θ' is angle between the incident and scattered X-rays. The average crystallite size (derived from Fig. 2) is found to be < 10 nm.

B. Optical Studies

Figures 2 show absorbance and transmittance spectra of as-deposited $ZnS_{0.6}Se_{0.4}$ thin film. The optical transmittance and absorbance spectra were used to study the optical transition in the films, which were studied at room temperature in the wavelength range of 300-900 nm.

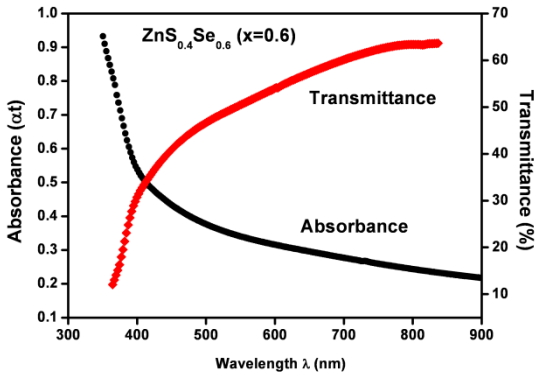

Fig.2. Plot of absorbance and transmittance versus wavelength

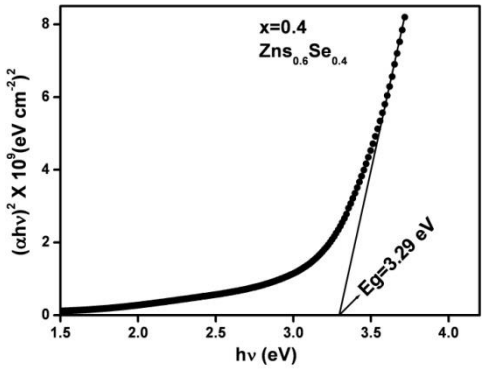

Fig.3 Plot of $(\alpha h\nu)^2$ versus (hν) obtained from as-deposited ZnSe thin film

The result shows optical transmittance over 60% in the visible region for all the compositions. The relation between the absorption coefficient α and the incident photon energy (hν) can be expressed as [16],

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (2)$$

where 'A' is constant, n= ½ for direct allowed transition, 'Eg' is optical band gap of the material. Figure 3 shows the variation of $(\alpha h\nu)^2$ against $(h\nu)$. Extrapolating the straight-line portion of the plot of $(\alpha h\nu)^2$ vs $(h\nu)$ for zero absorption coefficient value gives the band gap, which is found to 3.29 eV

CONCLUSION

It is possible to grow $ZnS_{1-x}Se_x$(x=0.4) thin films from ammonia free precursor solutions using soft chemical route by appropriate selection of the growth parameters. The as grown films present excellent adherence, uniform deposition smooth morphological and nanostructure properties, confirmed from XRD analysis. The physical, optical and electrical property studies reveal that the nanostructure $ZnS_{0.6}Se_{0.4}$ thin film can be suitably employed in photosensor and/or opto-electronic applications, especially as a photovoltaic solar cell window layer, with the advantage of being a best alternative to conventionally used toxic CdS window material

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