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Research Article

Synthesis, Characterization of CdZnS Thinfilms and SnS Nanoparticles

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Abstract. The replacement of CdS with its ternary alloy $Cd_{1-x}Zn_xS$ has been attempted for improvement of the $(Cd, Zn)S/Cu(In,Ga)Se_2$ solar cell performance; this has resulted in a higher efficiency of 16.9%. Moreover, the replacement of CdS with the higher energy gap ternary $Cd_{1-x}Zn_xS$ has also led to a decrease in window absorption loss and has resulted in an increase in the short circuit current in the solar cell. In this work, the Zn-CdS thin films were fabricated on glass substrates under optimized chemical bath conditions and its structural, surface and optical properties were investigated and the results of the optimized sample are presented and discussed. Among them, the solvent growth technique is very effective in yielding a desirable size distribution and optimization of the physical properties. For investigation the materials are synthesized using chemical bath deposition technique.The ternary compound CdZnS were deposited by various methods such as *metal organic chemical vapor deposition* (MOCVD), spray pyrolysis, vacuum evaporation, chemical bath deposition, *successive ionic layer absorption and reaction* (SILAR). Among these, the *chemical bath deposition* (CBD) method is a cost effective, simpler and more reliable method and gives the more precise possibility of obtaining films with required and suitable properties for optoelectronic applications and also applicable to large area deposition. Due to the incorporation of Zn^{2+} in to CdS thin films enhances the open-circuit voltage and short-circuit current in hetero-junction devices which results the decrease in the window absorption losses. The growth of SnS materials in single crystal, polycrystal-line, thin films and other forms has been carried out by various well known chemical, mechanical and physical methods.

Keywords. Cds, Chemical Bath, SnS, Nano-particle, XRD, SEM Analysis

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1. Introduction

The cadmium zinc sulfide (CdZnS) thin film is one of the promising materials in sensors, short wavelength laser diodes and optoelectronic applications. Some recent research reports on CBD CdZnS thin films mainly focused the tailorability of the structural, surface texture, optical, morphological and photoluminescence emission characteristics by imposing the post and preprocesses such as annealing temperature, changing precursor concentration, different substrate surface influence and addition of complexing agent on the chemical bath deposited chalcogenide thin films. The wide band-gap CdZnS thin films have been widely used as a buffer and window material in hetero-junction solar cells and in photoconductive devices.

O'Regan *et al*. [9] electrodeposited nonporous Zn-CdS films on transparent conductive supports using an electrolyte of $LiNO_3$ and $ZnCl_2$ in *propylene carbonate* (PC). The morphology and porosity of the films variation with salt concentration, water content and voltage were studied. The morphology of developed films was proven to be useful in constructing solid-state dye sensitized solar cells. Karuppuchamy *et al*. [4] deposited zinc oxide and titanium dioxide thin film cathodic electro-deposition methods. They aimed to develope cost effective alternative rules to the photo-electrode materials for *dye sensitized solar cells* (DSSCs). They have also developed a sandwich cell using the electro deposited Zn-CdS/N^2 film photoelectrode measured Isc = 0.61 mA/cm^2, Voc = 0.46 V, F.F = 0.46 and n = 0.13% under illumination by an artificial light source, being the first example of a real working DSSC fabricated without any heat treatment.

Natsume *et al*. [8] prepared doped and un-doped Zn-CdS thin films by sol gel method. The un-doped films were post annealed in hydrogen at 350 °C for three hours followed by annealing from 500 °C - 575 °C. The chemical and optical properties were investigated and presented the following values were given film resistivity 0.22 Ω, optical band gap value Eg = 3.20 – 3.21 eV and wide of the localized state Ee = 0.08 – 0.09 eV. Jeyakrishnan *et al*. [3] electrodeposited Zn-CdS films from a dimethyl sulfoxide bath containing dissolved gaseous oxygen. Variation in deposition parameters and their effects on the structural (crystal size, growth direction) optical (band gap variations, photoluminescence) and electrical (conductivity) properties were studied.

Yoshida *et al*. [12] reported that electrode position of Zn-CdS/eosin y hybrid thin films from aqueous mixed solutions of zinc chloride and eosin y as promoted by the reduction of oxygen. Highly oriented crystalline hybrid films with two distinctive structures were obtained depending on the redox state of eosin y Deposition at potentials more positive than that of eosin y reduction resulted in the formation of compact Zn-CdS crystals into which eosin y molecules were entrapped while that accompanied with the reduction of eosin gave a film consisting of sponge structure of Zn-CdS crystals with internal nonporous structure to which eosin y molecules were absorbed. The addition of eosin y accelerated the film growth both in oxidized and reduced forms due to its catalysis toward the reduction of oxygen.

Lee *et al*. [5] reported the effect of drying conditions and the first and second heat treatments on the structural electrical and optical properties of Zn-CdS thin films prepared by the sol gel spin coating method on silica glass substrates. Zinc acetate di-hydrate, 2-methoxyethanal and mono-ethylamine were used as a starting material, solvent and stabilizer, respectively.

The films had (002) plane as more preferment orientation. Optical transmittance was higher than 85% in the visible region and the resistivity value was $0.0\lambda\ \Omega$cm.

Yoshida *et al*. [11] studied the mechanism of electro-deposition of zinc oxide (Zn-CdS) thin films from aqueous solution of zinc nitrate under controlled mass transport. Lisco *et al*. [7] reported the *Cadmium Sulphide* (CdS) thin films were deposited by two different processes, *chemical bath deposition* (CBD), and *pulsed DC magnetron sputtering* (PDCMS) on fluorine doped-tin oxide coated glass to assess the potential advantages of the pulsed DC magnetron sputtering process. Barzilai *et al*. [1] reported the effects of ammonium sulfate on the CdS film produced by CBD using cadmium sulfate as the cadmium source. The concentration of ammonium sulfate was varied from 0 M up to 0.006 M.

SnS is one of the binary compound belongs to IV-VI group. It is a layer-structured compound like *germanium sulfide* (GeS), *germanium selenide* (GeSe) and *tin selenide* (SnSe), etc. Owing to their layered structures, SnS also exhibits strong anisotropic vibrational properties and therefore these structures show significant differences in their physical properties when measurements are made along their crystallographic axes. Further, the layers in SnS compound are coupled with weak van der Waals forces. The presence of week forces in SnS provides intrinsically a chemical inert surface without dangling bonds and surface density states [6]. As a result, the surface of SnS becomes free from Fermi level pinning. This fact makes SnS to be chemically and environmentally inert [10]. At *normal temperature and pressure* (NTP), the SnS compound usually possesses orthorhombic disorder crystal-structure with a space group of Pbmn. Dittrich *et al*. [2] surveyed many materials in view of their possible PV applications and suggested that the sulfosalts are more promising candidates for future solar cell devices .

2. Results and Discussion

2.1 Characterization of CdZnS

Experimental

The deposition took place, at 80 °C for 1 hour, on slide glass substrates, well cleaned with acetone, ethanol and distilled water in an ultrasonic bath. 0.005 M portion of $CdCl_2$, 0.02 M portion of $ZnCl_2$, NH_4Cl and 0.4 mol of $CS(NH_2)_2$ were dissolved into 100 ml double distilled water in a round bottom flask. The pH was adjusted by the addition of 0.2 M of NH_4OH solution to raise the pH with constant stirring. All the substrates were placed vertically inside the chemical bath and the deposition was carried out for 45 min. Finally, the obtained films were sonicated for 2 min and rinsed by double distilled water and dried in air atmosphere.

X-ray Diffraction Analysis

The XRD pattern as shown in Figure 1, Zn-CdS deposited on glass substrate from CBD technique shows broad peaks indicating that the film made up of Nano-crystallites. All the peaks in the diffraction pattern are in good agreement with the previous reported values. The XRD peaks in the pattern Figure 1 suggest that the nanoparticles are in the Wurtzite form and are in good agreement with the reported data on CdZnS. Particle size (D) was calculated by using the Scherer's relation as shown below. The estimated average Particle size (D) of Zn-CdS film deposited on glass substrate shows <10 nm. The observed crystallographic details on many

deposition conditions done by using the present optimized condition results the Zn-CdS thin films grown on glass substrate show better structural properties than the film deposited from other conditions.

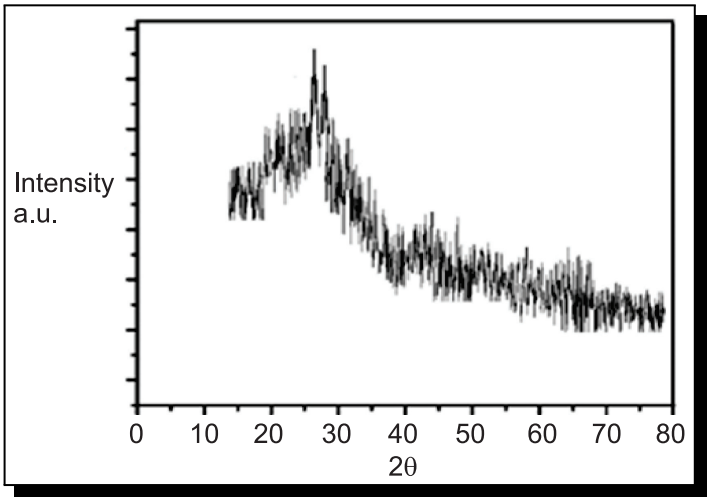

Figure 1. X-ray diffraction spectra of Zn-CdS thin film deposited on glass substrate <10 nm under optimized condition and maximum peak at 25 nm

Surface Morphology

The surface morphology of the deposited Zn-CdS thin film under optimized condition was analyzed by SEM analysis. Figure 2 shows the SEM image of the Zn-CdS thin film deposited on glass substrate. The investigated result showed the granular like surface morphology from present optimized condition and it showed densely packed surface morphology and more number of grains was observed in small area. Our other samples deposited from different bath conditions showed poor surface morphology than the present optimized conditions. Other bath conditions showed the poor surface morphology with the presence of powdery like deposits and more pinholes and voids.

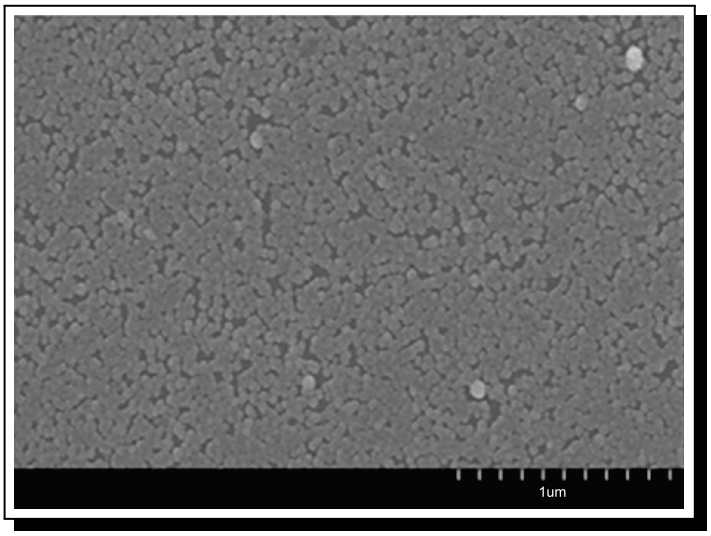

Figure 2. SEM image of the deposited Zn-CdS thin film under optimized condition

2.2 Characterization of SnS

Experimental

In the present experimental 0.2 M of Tin Chloride di-hydrate ($SnCl_2.2H_2O$), 0.5 M of Acetic acid were mixed together IN 700 rpm for several seconds to get a clear and homogenous solution and 0.8 M of thiourea ($(NH_2)_2CS$) were mixed and 50 ml water was added to make the final chemical bath volume of 100 ml. Prior to the precipitation reaction the chemical bath temperature was set at 80 °C. Duration of deposition was three hours and the final product was washed by using distilled water several time to remove the other impurities and dried in air atmosphere.

XRD and SEM Analysis

The structural properties of synthesized nanoparticles were investigated using powder *X-raydiffraction* (XRD) analysis with minimum scan steps of 0.001 ° per minute. The wavelength of the X-ray source utilized for XRD measurement was Cu-Kα:1.5406 Å. Figure 3 shows the XRD pattern of tin sulphide nanoparticles with 2.0 M acetic acid concentration. The pattern shows good crystalline property compared to lower acetic acid concentration mean that the acetic acid plays a vital role in improving the structural property and exhibit mixed phase of hexagonal and orthorhombic. Characteristic peak for other impurity has not found in the XRD pattern resembles the purity of the particle. Figure 4 shows the capping agent of acetic acid concentration shows rod like structure morphology.

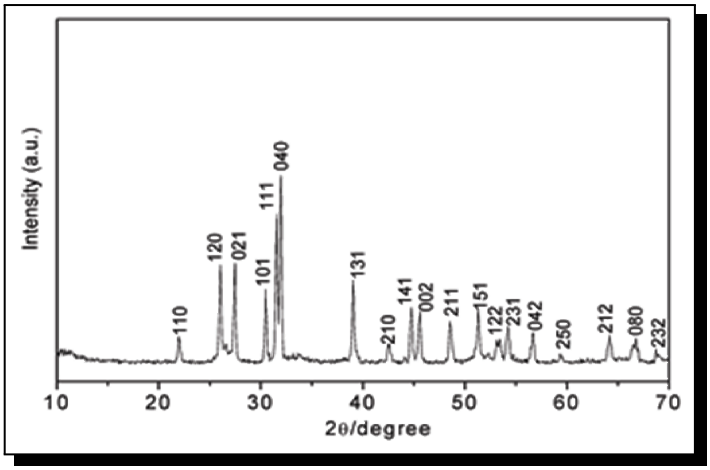

Figure 3. XRD pattern of the SnS Nano particle

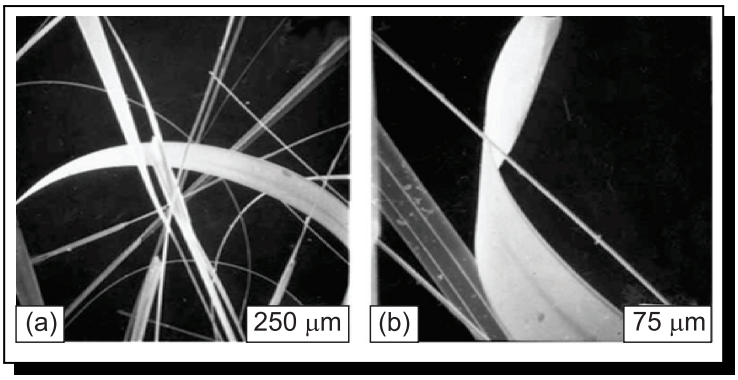

Figure 4. Image (a) and (b) shows the SEM micrograph for the acetic acid concentration rod like morphology 250 μm and 75 μm observed

3. Conclusion

Zn-CdS thin films were deposited on the glass substrate by CBD technique under our optimized conditions. From the several attempts made on the fabrication of Zn-CdS thin films, the present optimized chemical bath conditions showed better structural and surface characteristics. SnS can be synthesized in any form including single crystals (amorphous or polycrystalline) by using all most all well-established techniques starting from low-cost and low temperature methods to higher cost capital intensive techniques. The quality of SnS structures can also be easily tuned by changing the growth or deposition conditions of the associated technique. Moreover, without disturbing the crystal structure, the optical and electrical properties of SnS can be tailored through various external post-treatments including thermal, chemical and plasma ions routes. Even though there have been good progress in the synthesis and characterization SnS structures, further investigation is ongoing to scale up the process.

Competing Interests

The author declares that he has no competing interests.

Authors' Contributions

The author wrote, read and approved the final manuscript.

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