Preparation and Optical Characterization of Tin Doped Zinc Sulfide Thin Film

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Abstract

Zinc sulfide (ZnS) is a wide band gap semiconductor wich has found extensive use as a thin film coating in the optical and microelectronic industries. It has high refractive index and high effective dielectric constant. High band gap of ZnS (3.5 eV – 3.8 eV) makes it a potential candidate for solar cell applications. Tin Doped Zinc Sulfide (ZnS:Sn) thin films exhibit electrical conductivity and high transmittance in visible region making it more suitable for Solar Cell applications. This work aims to study the effect of Sn doping on optical and electrical properties of ZnS thin films. ZnS:Sn thin films were deposited on glass substrate from a bath containing Zinc Chloride ($ZnCl_2$), Tin Chloride ($SnCl_2$), thiourea ($SC\ (NH_2)_2$), Tri Ethanol Amine (TEA) and ammonium solution. Films with different amounts of dopant were prepared and their optical and electrical characterizations were done using UV-VIS-NIR spectrophotometer and Keithley Tektronix source meter respectively. The structural characterization was carried out using XRD technique.

Keywords: Tin doped Zinc Sulfide (ZnS:Sn) , Chemical Bath Deposition (CBD), Optical bandgap study.

Introduction

Zinc sulfide (ZnS) is a wide band gap semiconductor with a direct wide band gap of 3.37 eV and a large exciton binding energy of 60 MeV at room temperature. Zinc sulfide has high effective dielectric constant, wide wavelength pass band and reasonable work function. It has high refractive index and high optical absorption coefficient, which makes it a potential material for solar cell applications [1]. The optical properties of the prepared film depend strongly on the manufacturing technique. ZnS is a less toxic, efficient, low-cost material and has good transparency.

ZnS has attracted considerable attention due to its excellent electrical and optical properties with its distinct properties has become the potential candidate for many applications such as, electroluminescence devices, field emission devices and solar cells [2]. Due to non-toxicity, it is considered an ideal candidate for fabrication of high-performance sensors and is important for applications in infrared windows and lasers.

Various growth techniques such as chemical bath deposition, sputtering, pulsed laser deposition, sol-gel techniques, chemical vapour deposition etc. have been used to prepare nano ZnS [3,4,5,6]. Among these, chemical bath deposition (CBD) is promising because of its low cost, arbitrary substrate shapes, simplicity, and capability of large area preparation.

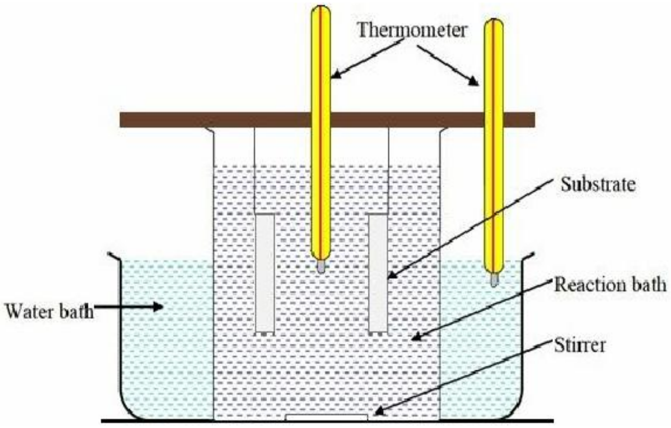
Tin Doped Zinc Sulfide (ZnS:Sn) thin films are a special kind of material that exhibit electrical conductivity and at the same time, high transmittance in visible region making it suitable for Solar Cell applications. In the present work, to study the effect of Sn doping on optical and electrical properties of ZnS thin films, a series of investigations were made. Thin films were deposited on glass substrate using Zinc Chloride ($ZnCl_2$), Tin Chloride ($SnCl_2$), thiourea ($SC(NH_2)_2$), Tri Ethanol Amine (TEA) and ammonium solution, with different tin concentration, utilizing chemical bath deposition technique. Optical and electrical characterization of the films with different amounts of dopant was carried out using UV-VIS-NIR spectrophotometer and keithley source meter. The samples were also characterized using XRD technique.

Experimental Details

The basic principle of CBD technique consists in the controlled generation of the metal and chalcogenide ions in an alkaline medium and their ion-by-ion deposition on the substrate in order to form a film. In our CBD experiment, the deposition of ZnS:Sn film was based on the reaction between zinc chloride($Zncl_2$) as a source of Zn^{2+},thiourea ($SC(NH_2)_2$) as a source of s^{2-} and tin chloride as a source of Sn^{2+} ions with ammonia(NH_4OH) that used as a complexing agent to vary the pH of the reaction bath and to control the Zn^{2+}concentration.The addition of TEA can significantly improve the quality of the thin films obtained. When the ionic product of Zn^{2+}, S^{2-} and Sn^{2+} exceeds the solubility product of ZnS, the precipitation of ZnS can occur either in solution or on the surface of the substrates. For doping the samples, $SnCl_2$ solution was added to the chemical bath.

ZnS thin film is coated on a glass substrate by chemical bath deposition technique. Prior to deposition, the substrate was washed well using soap solution , followed by ultrasonic cleaning with double distilled water for 10 minutes. They were rinsed in de-ionized water and finally dried in the air. The deposition of ZnS thin film is achieved by mixing solutions of zinc chloride, tin chloride and thiourea with ammonia as buffer solution. 10 ml of 0.1molar (0.1M) Zinc chloride solution is mixed with 1ml of triethanolamine (TEA). TEA acts as the capping agent. Tin chloride solution is added to it. Then the complexing agent and 0.1M ammonia solution was added slowly to this mixture, after stirring for several minutes the solution becomes colorless and homogeneous, and thereafter 0.1M thiourea solution was added. The reaction solution is placed in 50 ml beaker in a water bath. glass substrates were then immersed vertically inside the beaker and supported against the wall of the beaker. A hotplate is used to provide the required heat for reaction inside the chemical bath. A stirrer is used to enhance the reaction as well as to get uniform coating on the substrate. The schematic diagram of the experimental set up is shown in figure 1 [7] .

Figure1: Experimental setup for chemical bath deposition of ZnS:Sn thin film



Thin films were deposited by keeping water bath temperature at T_b=92ºC, for different durations, and varying time of deposition and amount of $SnCl_2$ in the bath. After completion of film deposition, each sample was removed from the beaker and was cleaned with de-ionized water to remove the white, loosely, adherent powder precipitate in the solution during the deposition. These samples were used for optical, structural and electrical characterization.

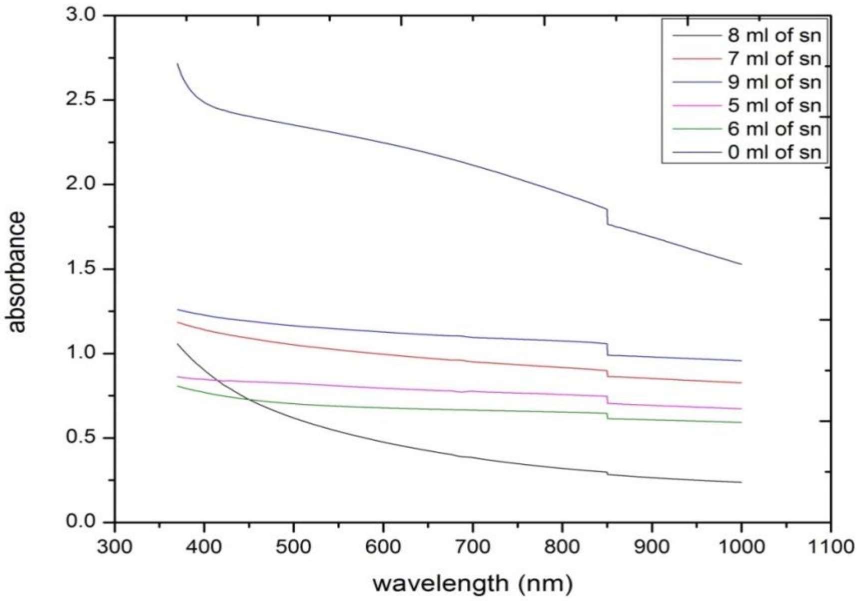
Results and Discussions

1. Optical studies of ZnS:Sn

The study of optic al absorption is important to understand the behavior of semiconductor ZnS. The optical absorption measurements were carried out using a Schimatzu dual beam UV-Vis spectrophotometer (Model No: UV-1800). The evolution of the optical properties of the prepared ZnS:Sn thin films were studied after obtaining the absorbance and transmittance spectrum. The spectrum was recorded by using a similar glass slide as reference and hence the absorption due to the film only (α) was obtained. The band gap of the films were calculated from the Tauc's plot.

The absorption spectrum of ZnS:Sn films prepared by varying the amount of tin chloride in the bath is shown in figure 2.

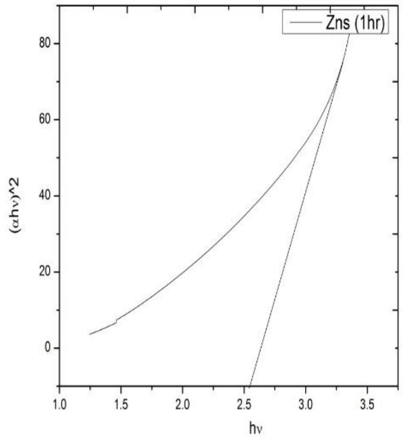
Figure 2 : Absorption spectrum of ZnS:Sn films prepared with different amount of tin chloride

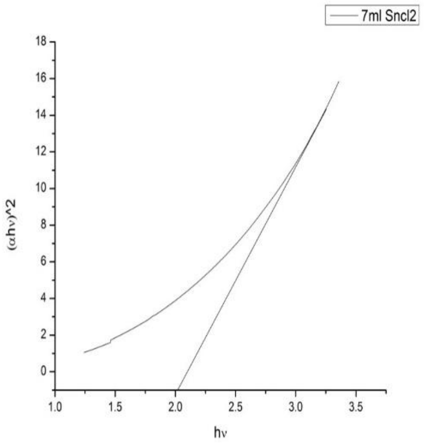


The bandgaps were obtained by plotting (hν) against $(\alpha h\nu)^2$ and extrapolating the linear part. By extrapolating the linear portions of the plots of $(\alpha h\nu)^2$ versus (hν) to the point where $(\alpha h\nu)^2 = 0$, the intercept on the energy axis (hν) axis gives the bandgap energy value. $(\alpha h\nu)^2$ versus (hν) plot of undoped and ZnS:Sn samples doped using 7 ml $SnCl_2$ are shown in figure 3.1 and 3.2. The value of bandgap obtained for undoped ZnS is 2.54 eV and that of ZnS:Sn is 2.01 eV respectively.

The bandgap values of all the doped samples were determined and Figure 4 shows the variation in bandgap value of the samples with doping concentration of $SnCl_2$ in the chemical bath. It was observed that the energy bandgap of ZnS:Sn films decreased with increase of doping concentration to the minimum bandgap value of 2.01 eV for doping concentration (7 ml). Decrease in optical bandgap energy can be attributed to the creation of new donor levels in the forbidden zone and a shift in the Fermi level in the band structure of the films [8].

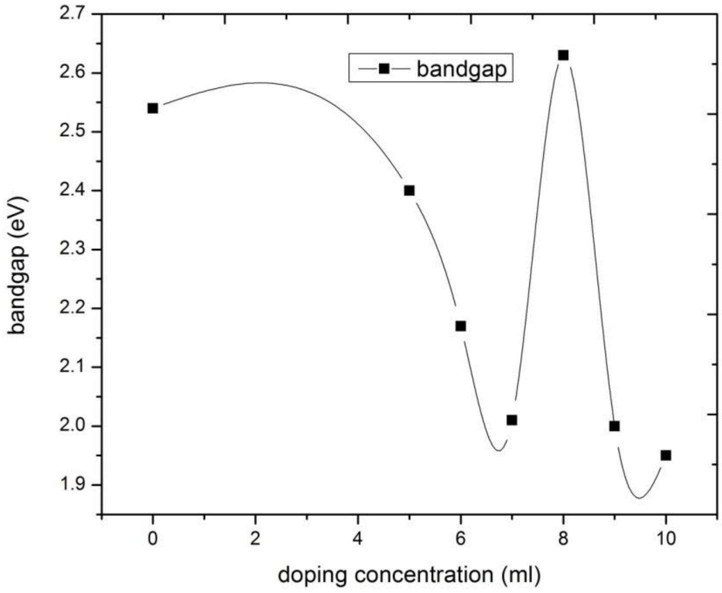
Figure 3.1: Bandgap of undoped ZnS Figure 3.2: Bandgap of ZnS:Sn sample





Further increase in doping concentration resulted in increase of bandgap with highest one at 2.63 eV for tin concentration (8 ml). This may be attributed to Moss-Burstein effect , in which the bandgap is increased as the absorption edge is pushed to higher energies as a result of some states close to the conduction band. As doping concentration is further increased, again there is decrease in the band gap which may be due to change in chemical composition of the sample.

Figure 4: Bandgap versus doping concentration of ZnS:Sn



2. XRD analysis

The phase identification and crystalline properties of undoped and doped samples were studied by X-ray diffraction (XRD)method employing a Bruker (D8 advance) x-ray diffractometer with Ni-filtered Cu-Kα radiation (λ=1.5418 Å).
Figure 5 shows the XRD pattern of ZnS:Sn thin films prepared from a bath containing 7 ml of $SnCl_2$. The typical sharpening of the diffraction peaks was observed, implying that the size of the ZnS:Sn thin film particles are of the order of micrometer. The different peaks of the sample match very well with the hexagonal wurtzite structure of ZnS (JCPDS card number 80-0007) [9]. The high intensity and sharpness of the peaks indicate perfect crystallization of the particles. The size of the thin film particles has been calculated using Debye - Scherrer for particle size determination,

$$D = \frac{0.94\lambda}{\beta \cos \theta} \qquad (1)$$

where, D is the particle size of the material, λ is the wavelength of Cu-k α source, β is full width at half maxima, θ is angle corresponding to peaks. Calculated particle sizes lie in the range 5.5 to 8.3 micrometer and are shown in table 1 .
Figure 5: XRD spectrum of ZnS:Sn sample.

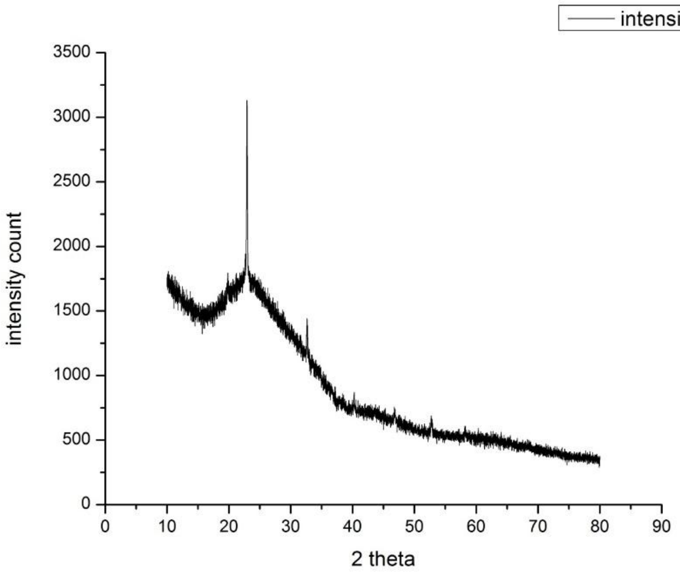


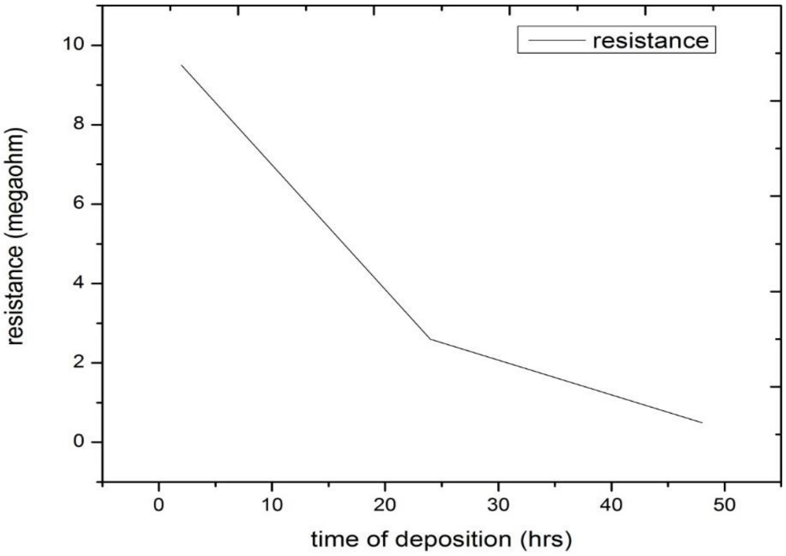
Table 1: XRD data of ZnS:Sn sample

Angle 2θ (de-gree)	**Interplanar distance d_{hkl}**	**FWHM(β)**	**Plane h k l**	**Particle size D(µm)**
22.89	3.88	0.15	1 0 0	5.5
32.65	2.74	0.10	1 0 1	8.3

3. Resistance measurement

Resistance of the ZnS:Sn samples prepared from a bath containing 7 ml of $SnCl_2$ were measured at room temperature using Keithley 2450 source meter (Tektronix). Variation of the resistance with time of deposition is shown in figure 6. It was found that as the time of deposition increases, resistance of the sample decreases. For the samples with time of deposition 2 hours, the resistance value measured is 9.5 MΩ and it decreases to 490 KΩ as the time deposition is increased to 48 hours. This may be due to the increase in thickness of the film with the increase in the time of deposition.

Figure 6: Resistance versus time of deposition of ZnS:S



As the time of deposition increases, resistance of the sample decreases. For the samples with time of deposition 2 hours the resistance value measured is 9.5 MΩ and it decreases to 490 KΩ as the time deposition is increased to 48 hours. This may be due to the increase in thickness of the film.

Conclusion

ZnS:Sn thin films were prepared by varying parameters like time of deposition and amount of $SnCl_2$, using chemical bath deposition technique. Optical properties of the sample were studied. Energy bandgap of ZnS:Sn films decreased with increase of doping concentration and the minimum bandgap of 2.01eV was obtained for the sample prepared from a bath containing 7 ml of $SnCl_2$. Decrease in optical bandgap energy can be attributed to the creation of new donor levels in the forbidden zone and a shift in the Fermi level in the band structure of the films. The high intensity and sharp peaks observed in XRD spectrum indicated perfect crystallization of the particles. The electrical resistance of the doped samples was found to decrease with increase in deposition time.

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References

1. U. Sarute , I. Yingyot , “A comprehensive review on ZnS: From synthesis to an approach on solar

cell", Renewable and Sustainable Energy Reviews, 2016, 55, 17-24.

2. A. Goudarzi, G.M. Aval, R. Sahraei, H. Ahmadpoor, "Ammonia-free Chemical Bath Deposition of
3. Nanocrystalline ZnS Thin Film Buffer Layer for Solar Cells", Thin Solid Films, 2008, 516(15),4953-4957.
4. M.S. Shinde, P.B. Ahirrao, R.S. Patil, "Structural, Optical and Electrical Properties of Nanocrystalline ZnS Thin Films Deposited by Novel Chemical Route", 2011, Archives of Applied Science Research, 3(2), 311-317.
5. F. Ghribi, L. E.l. Mir , K. Omri , K. Djessas , "Sputtered ZnS Thin Film from Nanoparticles Synthesized by Hydrothermal Route", Optik, April 2016, 127(7), 3688-3692.
6. A. Al-Zahra, M. A. Abdul Karim, Al-Sammarraie, "Synthesis and Characterization of Zinc Sulfide Nano Structure by Sol Gel Method", Chemical Methodologies, January 2022, 6(1),67-73.
7. E.Y.M. Lee, N. H. Tran, R.N. Lamb, "Growth of ZnS Films by Chemical Vapor Deposition of $Zn[S_2CN(CH_3)_2]_2$ Precursor", Applied Surface Science, March 2005, 241, (3-4), 493-496.
8. R. Zein, I. Alghoraibi, "Effect of Deposition Time on Structural and Optical Properties of ZnS," International Journal of Chem Tech Research, 2014, 6 (5), 3220-3227.
9. K. S. Wanjala1, W. K. Njoroge1, J. M. Ngaruiya, "Optical and Electrical Characterization of CuO Thin Films as Absorber Material for Solar Cell Applications", International Journal of Energy Engineering 2016, 6(1), 1-6.
10. T.B. Nasr, N. Kamou` 1n, M. Kanzari , R. Bennaceur, "Effect of pH on the Properties of ZnS Thin Films grown by Chemical Bath Deposition", Thin Solid Films, 2006, 500(1-2), 4-8.