Effect of pH on the optical and structural properties of SnS prepared by chemical bath deposition method

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Abstract: In this work we study the influence of pH on the optical and structural properties of SnS thin films. The films were grown on the glass substrate using chemical bath deposition method. Hydrous tin chloride and thioacetamide were used as cationic and anionic precursors respectively. The pH of the solution was changed using Ammonia. The film was prepared at five different pH values 9.2, 9.3, 9.4, 9.5 and 9.6. The optical and structural properties were studied using UV Visible spectrophotometer and XRD. From optical characterisation it was found that the band gap decreases as the pH increases from 9.2 to 9.5. The crystallinity of the film increased as the pH value increased.

1. INTRODUCTION

Nowadays thin film semiconducting materials are extensively used in the fabrication inexpensive opto electronic materials. Among them metal chalcogenides have attracted huge attention due to their application in solar cells, photo electrochemical cells, polarisers etc. Here we have chosen tin sulphide as it has high theoretical photoelectron conversion efficiency (24%), less toxicity, good chemical stability and due to the abundance of its constituents. All of these make SnS as a promising layer for optoelectronic devices especially for solar cells. It is a p type semiconducting material. It show both direct and indirect band gap. The reported optical band gap of SnS varies between 1.1eV to 2.1eV [1].

There are several methods to grow SnS thin film. It include spray pyrolysis, thermal evaporated, radio-frequency sputtering (RF sputtering) and plasma-enhanced chemical vapour deposition (PECVD) techniques, chemical bath deposition (CBD) and successive ionic layer adsorption reaction. In this paper we have chosen chemical bath deposition method. It is less expensive, simple, requires no sophisticated instruments, can be used for large area deposition and there is no handling of poisonous gases [3]. In CBD method, pre cleaned substrate is made in contact with dilute chemical baths containing cationic and anionic solutions and the film is formed on the substrate when ionic product exceeds solubility product.

The SnS thin film was prepared with four different pH values. The prepared films were characterized optically structurally and electrically using UV spectroscope, XRD and four probe respectively. The effect of pH of the solution on the prepared thin films was studied.

2. METHODS AND MATERIALS

We have used ordinary glass slide of dimension 5.5 cm × 2.5 cm × 2 mm as the substrate. It was
ultrasonically cleaned and dried. The SnS thin films were prepared from the aqueous solutions of hydrous tin chloride, SnCl$_2$.2H$_2$O (source of Sn$^{2+}$) and thioacetamide (source of S$^{2-}$). Here we used 5ml of 0.1M stannous chloride, 5ml of 1M thioacetamide, 10ml 3.75 M triethanolamine [N(CH$_2$CH$_2$OH)$_3$] (TEA), 5ml 0.66 M of tri sodium citrate. TEA was used to optimize the speed of the reaction In order to obtain high quality thin films by CBD, the reaction must be very slow. Triethanolamine (TEA) is used to help tin ion come into existence in solution by reducing the reaction speed [2], [6]. When TEA was not in the solution, the precipitation was very rapid and the film did not form on the substrate.

The pH of the solution was optimized and varied using Ammonia solution. 2.5 ml, 3ml, 3.6ml and 4ml of Ammonia was added to the solution to get 9.2, 9.3, 9.4, 9.5 and 9.6 respectively. For a solution with pH less than 9.2 film was not formed even after 24 hours and for pH greater 9.6 the solution turned chocolate brown and then into brown precipitated solution within five minutes. So the effect of pH on the properties on the film was studied between 9.2 and 9.6. The pH of the solution was measured using pH meter. All the solution was mixed well using a magnetic stirrer. The whole solution was made up to 100ml using deionized water.

The colour of the solution in which the SnS thin film was formed was first white in colour then it changed into yellow and then to chocolate brown. The obtained films were chocolate brown in colour. One side of the film was wiped and the other side is dried and characterized optically and chemically.

3. RESULTS AND DISCUSSIONS

3.1. Optical Characterization

The as prepared films were optically characterized using UV spectrophotometer. The wavelength used was for the characterization was in the range 190nm to 1190nm. Tungsten was used as the source for UV and Helium for visible radiation. The absorption graph was drawn and from that Tauc plot was plotted with $h\nu$ on x axis and $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ on the y axis for direct and indirect band gap respectively.

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

Where, A is a constant, $h\nu$ is photon energy, $E_g$ is the allowed energy gap, $n = \frac{1}{2}$ for allowed direct transition and $n = 2$ for allowed indirect transition. The band gap is called direct if the crystal momentum of electrons and holes is the same in both the conduction band and the valence band; an electron can directly emit a photon and if it is different in conduction and valence band and the transition is assisted by a phonon then the energy gap is called indirect band gap. SnS exhibits both direct and indirect band gap. Both the energy gap was obtained using the above relation.
Figure 1. Tauc plot for direct band gap for pH 9.2, 9.3, 9.4 and 9.6.

The energy gap both direct and indirect decreased as the pH value increased. This can be explained as the thickness of the thin film may be increased. The increase in the energy gap may be due to the existence of grain boundaries in the polycrystalline structures which results in free carrier concentrations and existence of potentials in the boundaries [4]. Therefore an electric field was formed and the band gap increases. So as band gap decreases crystallinity increases so as pH of the solution increase the crystallinity increases.

The tauc plot for SnS thin as prepared for the direct and indirect band gap were plotted figure 1 and figure 2.
3.2. Structural Characterization

Structural characterization was done using XRD. The obtained peaks were compared with JCPDS data. The crystalline size was calculated using Scherrer equation

\[ \tau = \frac{K\lambda}{\beta \cos \theta} \]

Where \( \tau \) is the mean size of the ordered domains, \( K \) is the shape factor which is dimensionless has a typical value of about 0.9, \( \lambda \) is the wavelength of X ray (0.15418nm) and \( \beta \) is the full width half maximum of the intensity peak and \( \theta \) is the Bragg’s angle [5]. The XRD pattern of the film formed with five different pH values were plotted in figure 3 and the corresponding 2 theta peaks and crystalline size calculated using Scherrer’s equation were tabulated in the table 1.
Figure 3. The XRD pattern of SnS thin film with pH 9.3, 9.4, 9.5 and 9.6.

| hkl planes | 2θ (P) pH=9.3 | 2θ (O) pH=9.4 | 2θ (P) pH=9.5 | 2θ (O) pH=9.6 | hkl planes |
|------------|---------------|---------------|---------------|---------------|------------|
| 012        | 25.761        | 26.643        | 26.465        | 26.567        | 012        |
| 102        | 28.010        | 28.045        | 28.945        | 28.055        | 102        |
| 022        | 44.539        | 44.481        | 44.039        | 022          |

The standard 2 theta values of JCPDS data and the observed 2 theta values were plotted in table 1. The peaks are matched with orthorhombic planes of SnS. The crystalline size was calculated using Scherrer’s equation. It was found to be 25nm, 26nm, 27nm and 33nm for the pH 9.3, 9.4, 9.5 and 9.6 respectively. It was found that as the pH increase the peaks become more and more sharp and intense that can means the crystallinity increases as pH of the solution increases. This happens because as pH increases more and more OH⁻ brings the tin ion into the solution and makes the thin film formation uniform and crystalline.

4. CONCLUSION

The SnS thin film was prepared using chemical bath deposition in five different pH values. The films was characterized optically and structurally characterized. It was found that the energy gap decreases with the increase in the pH value for both direct and indirect band gap. The crystalline size increases with the pH value of the solution. So the pH of the solution plays an important role in the optical and structural properties of the SnS thin film prepared by Chemical bath deposition method.

REFERENCES

[1]. Meriem Reghima, Anis Akkari, Cathy Guasch, and Najoua Turki-Kamoun. 2014 Journal of Electronic Materials. S11664-014-3269-0
[2]. Guneri, F. Gode, C. Ulutas, F. Kirmizigul, G. Altindemir and C. Gumus. 2010 Chalcogenide Letters. Vol. 7, No. 12, 685-694
[3]. M.H Selma and Al-Jawad. 2017 Materials Science in Semiconductor Processing. 67, 75–83.
[4]. H.M. Pathan and C.D Lokhande. 2004 Bulletin of material science. 27, 85-111.
[5]. P. sateesh and P. Madhusudhanarao, International Journal of Latest Trends in Engineering and technology. Vol.(8)Issue(1), pp.413-422.
[6]. Sunil H. Chaki, Mahesh D. Chaudhary, and M. P. Deshpande. 2016 Journal of Semiconductors. Vol. 37, No. 5