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SnS thin films grown by successive layer adsorption and reaction method

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Abstract

Tin monosulphide (SnS) is a relatively new material, and has attracted considerable interest for use in low-cost thin- film photovoltaic because of its earth abundant constituents, optimal band gap, high absorption coefficient and its potential for large-scale power generation. The current study deals with the fabrication of SnS thin films using a new modified chemical method, Successive Layer Adsorption and Reaction (SLAR), which facilitated the growth by chemical method at room temperature. Primarily, the experiment deals with optimizing the deposition parameters for SLAR at room temperature. The technique involves multiple dipping of a substrate in cationic and anionic precursors. The films were prepared using $SnCl_2$ as tin (Sn) source and Na_2S as sulphur (S) source. This paper summarizes the first results obtained in the growth of SnS thin films at room temperature using a very simple and cost effective procedure, taking onlyshorter time spans for film deposition. The result is very important for industry, where tin sulphide has enormous applications. The characterization using XRD confirms the presence of polycrystalline SnS thin films. SEM images show uniform film formation. Optical studies suggest a band gap around 1.7 eV. Resistance measurements suggest a resistance in the Mega Ohm range.

1. Introduction

Tin mono-sulfide (SnS) is a potentially promising candidate for photovoltaic cells in today's world comprised of earth abundant elements, yet relatively less studied. The performance of solar cell critically depends on properties of light absorber.High absorption in the visible region, p-type conductivity, low resistivity, high mobility and minimum defects are some of the important features of an ideal solar energy absorber. SnS has high absorption coefficient ($>10^4$ cm^{-1})near the absorption edge similar to that of CdTe (Yue *et al.*, 2009). Its band-gap (1.3 ~ 1.4 eV) is near the optimum value of 1.5 eV, theband gap required for an efficient light absorption (Biswajit Ghosh *et al.*, 2008). Generally the material shows a p-type electrical conductivity and its conductivity can be increased to several orders of magnitude by suitable dopants like Al, Cu, Cl etc. (Parenteau M.et al,1990 and ZainalZ et al,1997). Also, high conversion efficiency (24%) is reported(YueG H et al, 2009 and). All these conditions make tin sulfide a valuable candidate for solar cell applications(Loferski, J.J., 1956).In addition to this favourable properties, non-toxicity and availability of raw

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materials, environment friendliness, and lower production costs are some another advantages. Moreover, due to its simple stoichiometry, it may a possible substitute for CdTe, with simplicity to control. SnS is found to be a brown colored powder whose crystal type is orthorhombic. (a = 4.329A˚, b= 11.193A˚ and c = 3.98A˚). SnS belongs to IV-VI semiconductors in which layers of Sn and S are bound by van der waals forces (Hofmann, 1935.).

It has been found that the bandgap greatly depends on the deposition techniques, and so does the S to Sn ratio. A variety of methods for depositing of SnSthin layers were developed as spin coating on soda lime glass substrates (Welatta *et al.*, 2018), co-evaporation on glass substrates (Cifuentes *et al.*, 2006), atomic layer deposition (Sinsermsuksakul, Prasert, *et al.*, 2011), SILAR on glass (Mukherjee & Mitra, 2015) and ITO coated glass substrates (BiswajitGhosh et al, 2008),thermal Evaporation (Hegdea et al., 2018), dip coating (Sunil H. Chaki *et al.*, 2016), chemical bath deposition (CBD) (Sunil H. Chaki et al, 2016), chemical spray pyrolysis (Thierno Sall *et al.*, 2016), electro-deposition (Mariappan *et al.*, 2011), physical vapour deposition (Ganchev *et al.*, 2016), RF sputtering (Katy Hartman *et al.*, 2016 and Rona Banai *et al.*, 2013) etc. Each deposition technique has its own merits and demerits. But the development of simple, rapid and economical methods for preparing materials with good reproducibility and with controllable deposition parameters is still a great challenge.

SILAR is a chemical method of thin film deposition invented by Ristov in 1985. It is actually new version of CBD and is often called modified CBD. It is a simple, inexpensive, low time consumingmethod which can be used for large area thin film deposition (Mukherjee & Mitra, 2015).In this method substrate will be dipped in cationic and anionic precursor solutions with rinsing in distilled water between every immersion in cationic and anionic precursors.The current study utilizes the method of SLAR, which is a modified method of SILAR. A single SLAR cycle consists of dipping the cleaned substrate in cationic and anionic solutions successively. The thickness of thin film can be controlled by the number of dipping.This method is particularly useful as a highly cost effective one for the synthesis of films at room temperature on substrates of any shape or size.

In industrial point of view, budget fitting is easier if process steps are conducted at lower temperatures and in shorter time spans. The solution-phase deposition of inorganic semiconductors is a promising, scalable method for the manufacture of thin film photovoltaic. But high temperature, long duration process steps are common in thin film deposition. When using sol-gel and other wet or ceramic methods, the synthesis of membrane films involves some heating stages to remove solvents. If the substrate is a polymer or any heat-sensitive material, heating steps may have to be avoided. In this work we highlight that room temperature deposition is possible for

SnS thin films, which was an unattainable goal using SILAR and CBD.In the present work, we report on structural, morphological, electrical and optical properties of SnS thin film prepared by a new method SLAR, which is a modified method of SILAR. A single SLAR cycle consists of dipping the cleaned substrate in cationic and anionic solutions successively. Parameters like dip duration, dry duration, dip velocity etc. can be programmed and controlled. As the synthesis of films is at room temperature, fabrication is possible on even thermally sensitive substrates of any shape or size. The room temperature deposition avoids high temperature effects such as inter-diffusion, contamination and dopant redistribution. Another attractive point is that one complete SLAR cycle took just 35mints and 15 seconds for thin film deposition. In addition to its simplicity and economy SLAR can be used for large area thin film deposition and the thickness can be controlled by the number of dipping. SLAR is a very promising method for industrial scale production.

2. Experiment

2.1. Method description

Single SLAR deposition cycle involves the immersion of the substrate alternately in cationic and anionic precursor solutions. Figure1 represents the basis of SLAR growth.

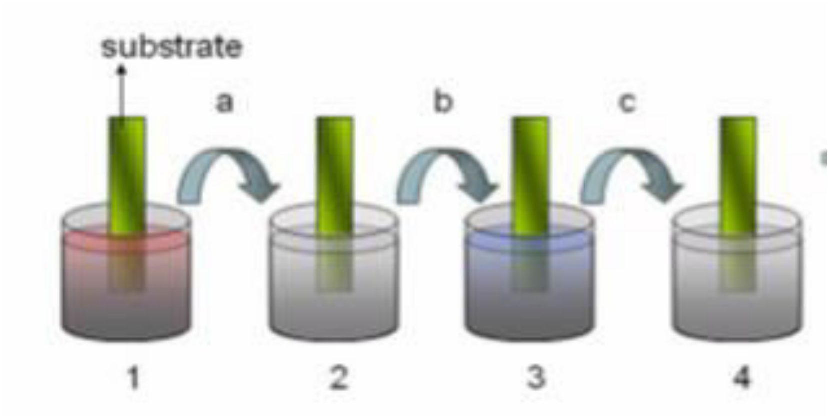

Fig 1: Schematic diagram of SLAR growth (1) Adsorption, (2) Reaction,(3) Adsorption and (4) Reaction.

It consists of two different steps; 1) Adsorption, 2) Reaction

1) **Adsorption**

In this first step of SLAR process, the cations present in the precursor solution are adsorbed on the surface of the substrate and form the Helmholtz electric double layer. This layer is composed of two layers: first, the inner (positively charged) and outer (negatively charged) layers. The positive layer consists of the cations and the negative form the counter ions of the cations(Pathan H. M. and Lokhande C. D.,2004).

2) **Reaction**

In this reaction step, the anions from anionic precursor solution are introduced to the system. Due to the low stability of ions reaction between cation and anion takes place leading to formation of solid phase over substrate (Lindroos *et al.*, 2000).

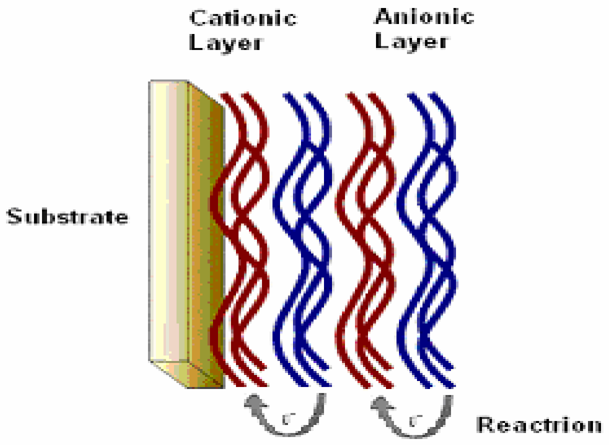

Fig. 2: Schematic diagram of reaction between newly adsorbed anions with pre-adsorbed cations forms the thin films of desired material.

The factors like temperature and concentration of solution, nature of the substrate, pH of solution, area of the substrate, immersion time in respective precursor solution etc. affect the deposition process (Pathan & Lokhande, 2004).

Among these thin film deposition methods, successive layer adsorption and reaction (SLAR) method is relatively simple and offers wide range of advantages over other expensive methods of thin film deposition. It is a process in which the deposition rate and thickness of the film can be easily controlled over a wide range by changing the deposition cycles. Relatively uniform films can be obtained on substrates of any shape; there is no restriction on substrate material, dimensions or its surface profile. Unlike vacuum based deposition method, SLAR method does not require any expensive and sophisticated instruments. No need of vacuum at any stage is a great advantage in the context of an industrial application.SLAR method saves material cost due to non-formation of precipitate in solution. This method can be used for the deposition from aqueous or non-aqueous baths and it can be employed in the preparation of polymers, semiconductors or oxides. The SLAR method usually requires low operating temperature. Apart from the obvious advantages in terms of energy saving, low deposition temperature avoids many adverse high temperature effects (Pathan & Lokhande, 2004; Lindroos et al., 2000; Nicolau et al., 1990). In this work we were able to deposit SnS thin film at room temperature.

2.2 SnS film fabrication

Prior to deposition glass substrate were carefully cleaned. Surface cleaning has a predominant effect on SLAR growth as it enhances the active center as well increase the wettability and hydrophilicity of the substrate (Biswajit Ghosh *et al.*, 2008). Glass slides of dimensions 75mm*25mm*1mm were first washed using detergent in running water, followed by rinsing in dilute chromic acid. Again washed in distilled water, dipped in dilute nitric acid for 10 minutes, followed by acetone for 20 minutes. Finally the substrate is placed in an oven or hot plate at 100^0C for 1 hour for drying.The cationic and anionic precursor solutions were prepared using $SnCl_2.2H_2O$ and $Na_2S.xH_2O$ respectively by calculating the required weights and weighing them in an electronic balance accurate up to three decimal points. Both anionic and cationic precursors were kept at room temperature. The prepared Sn^{2+} precursor solution beaker was placed first, followed by a beaker of S^{2-} precursor solution, again Sn^{2+} precursor solution beaker and finally the S^{2-} precursor solution holder of the SILAR coater(Prompt). The reaction between pre-adsorbed cations (Sn^{2+}) and newly absorbed anions (S^{2-}) forms the thin films of desired material of optimum thickness. The reaction on the substrate leading to the formation of tin sulphide can be represented as :

$$\mathbf{Sn^{2+} + S^{2-} \rightarrow SnS}$$

After several trials the concentration of cationic and anionic precursor solutions, the respective immersion time were finalized for the optimal growth of SnS films at room temperature. The parameters for SnS thin films deposition by the SLAR method was found to be15 s dip duration and 5 sec dry duration. A pre-dipping in the cationic solution for 5 minutes was introduced .A curing time between cycles was also introduced as it was found to improve film formation. After imposing these conditions, a very uniform film was observed. One experimental cycle consists of the following steps:

- Immersion of the cleaned substrate in cationic precursor solution ($SnCl_2$) for 15 seconds (Tin ions were absorbed on the surface of the substrate).
- Drying for 5 seconds.
- Dipping the same substrate in the anionic precursor (Na_2S) for 5 seconds (The sulphide ions reacted with adsorbed tin ions on the active center of the substrate).
- Drying for 5 seconds.
- Another dip in the cationic and anionic precursors completes the cycle.

By varying molarity, it was found that precursor molarities of 0.05M and a 30 cycle experiment yielded SnS thin films at room temperature with good properties.The deposited SnS thin films were dark brown in colour.

With the same conditions Chemical Bath Deposition (CBD) was also tried simultaneously with SLAR to make a film. This yielded no results. The substrates were examined after 12, 20 and 24 hours and showed no film formation. As the timespan increased, the film adhesion to the substrate decreased and the films were found to wear off. This proves the advantage of the method of Successive Layer Adsorption Reaction (SLAR) over other chemical methods.

2.3. Characterization of SnS films

X-ray diffraction(XRD) using Bruker AXS D8-Advance X-Ray Diffractometer ($2\theta=20\text{-}80^o$) with copper CuK_α radiation was made for structural characterization of the deposited thin films. The phase identification and crystalline properties were studied from the XRD pattern and compared with standard JCPDS files. Transmission spectrum was recorded using UV-Visible spectrophotometer (Shimadzu corporation UV-1800). Scanning electron microscope (JEOL model JSM-6930 L)was used to study the surface morphology of the film as well as the size and shape of particles. Resistance measurements were done using Digital Multimeter Agilent 34405A.

3.Characterization

3.1 Structural Studies using XRD

Diffraction pattern with **2θ** in the range of $20\text{-}70^0$ contain many diffraction peaks indicating that these film is polycrystalline in nature .There is a prominent peak at 32.10^0 that corresponds to the preferential orientation along the (0 4 0) plane. Other peaks are seen at 27.98^0 for the (0 2 1) plane and 45.41^0 for the (0 0 2) plane(Mariappan R. et al, 2011). These results are in good agreement with the standard Joint Committee on Powder Diffraction Standard (JCPDS)card No 39-0354. data for orthorhombic SnS.

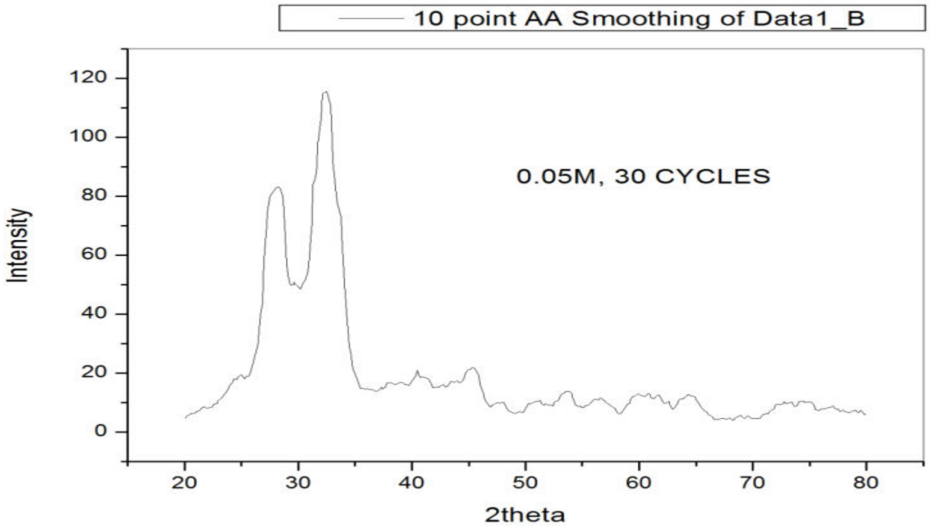

Fig 3: XRD image of the sample at 0.05M, 30 cycles

S.No	Peak - 2Θ Degrees	d value	(h,k,l) plane	Crystal structure
1.	32.106401	2.78846	(0 4 0)	Orthorhombic
2.	27.98875	3.19369	(0 2 1)	Orthorhombic
3.	45.413062	1.99245	(0 0 2)	Orthorhombic

Table 2: XRD data of sample with 0.05M

3.2. Morphological Studies using SEM

Scanning electron microscopy (SEM) is a method for high-resolution imaging of surfaces with much higher magnification (>X1,00,000) and greater depth of field up to 100 times than that of optical microscopy (Hanke L.D.,2001). The images show grains falling in the nanometer range. There are no voids or cracks to be seen. The sample also shows uniform grain distribution which is suitable for photovoltaic applications.

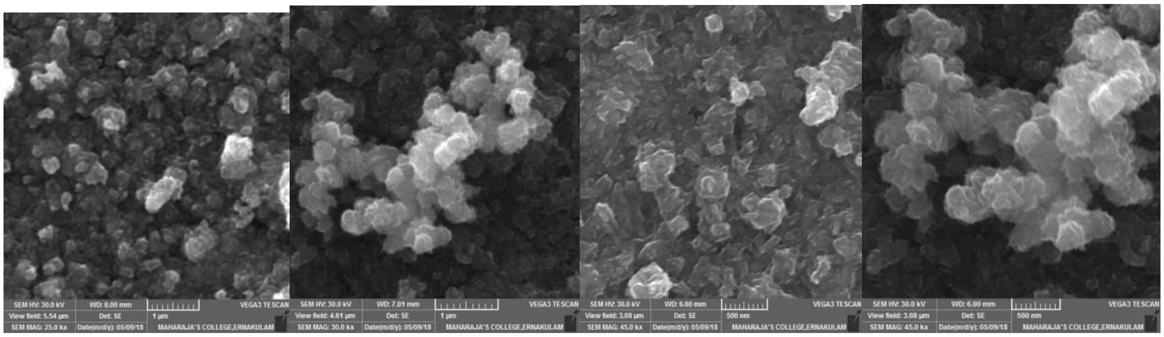

Fig 4,5,6,7: SEM images of the sample prepared at 0.05M at magnifications of 25kx, 30kx, 45kx respectively.

3.3. Optical Studies

The optical band gap (E_g) was evaluated from the plot of $(\alpha h\nu)^2$against photon energy ($h\nu$). This plot should be linear near absorption edge in the case of direct band gap semiconductors. The optical gap is obtained by extrapolating the linear region of the plot to $h\nu=0$. The sample shows a band gap of 1.799 electron Volt. The reported optical band-gap of SnS films varies between 1.1 and 2.1 eV depending on their fabrication process (Gao C. et al, 2011 and Sohila S. et al, 2011).

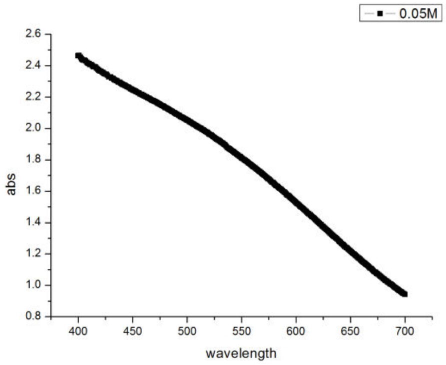

Fig 8: Plot of absorbance Vs. Wavelength(nm)

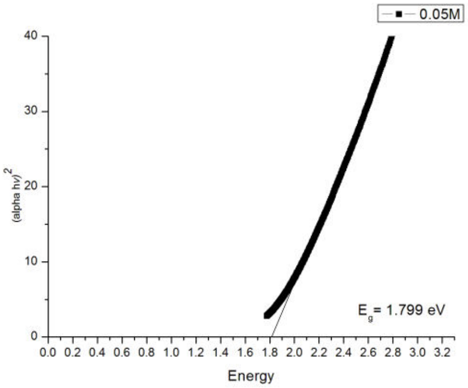

Fig 9: Plot of (alpha hv)^2 Vs. Energy for BG for the sample 0.05M, 30 cycles.

3.4. Electrical Studies.

The samples were studied for resistance using Digital Multimeter Agilent 34405A. The result has been summarized in tabular form.

S.No.	Sample	Molarity (M)	Resistance (M ohm)
1.	A1	0.05	10.2

Table 3: Resistance measurements of the sample using digital multimeter.

The resistance of the sample is 10.2 Megaohm

3. Results and discussion

SnS semiconductor thin films were successfully prepared by SLAR method at room temperature. The method of Sucessive Layer Adsorption and Reaction (SLAR) proves to be an effitient, cost effective and easy method to create SnS thin films. The film obtained shows good adhesion and has all the required properties to make it a promising candidate for future solar cell materials.It seems that the SLAR technique can be extended for other metal sulphides as well. As the room temperature, short duration deposition is possible; it is an easily scalable alternative to industrial level.

The structural, morphological, optical and electrical properties of the SnS thin films were investigated. The Structureal study using X-ray Diffraction (XRD) shows prominent peaks corresponding to the (0 4 0) and (0 2 1) planes that confirm orthorhombic structure. SEM images showed nano-meter sized particles well covered on the surface of the substrate and had almost no voids. Electrical property study indicated resistance in the Mega Ohm range. The optical band gap was obtained as 1.7 eV from UV-vis spectrophotometry which is slightly higher than the bulk band gap value.

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