Annexure –VII

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002.

PROFORMA FOR SUBMISSION OF INORMATION AT THE TIME OF SENDING THE FINAL REPORT OF THE WORK DONE ON THE PROJECT.

1.	TITLE OF THE PROJECT	Chemical Synthesis and Characterization of Tin Sulfide Thin Films.
2.	NAME AND ADDRSS OF THE PRINCIPAL INVESTIGATOR	Dr. T. H. Patel Physics Department, Viththalbhai Patel & Rajratna P. T. Patel Science College, Vallabh Vidyanagar-388120. Dist. Anand, Gujarat.
3.	NAME AND ADDRSS OF THE INSTITUTION	Viththalbhai Patel & Rajratna P. T. Patel Science College, Vallabh Vidyanagar-388120. Dist. Anand, Gujarat.
4.	UGC APPROVAL LETTER NO. AND DATE	47-1340/10(WRO) 20-09-2010.
5.	DATE OF IMPLIMEMTATION	20-10-2010.
6.	TENURE OF THE PROJECT	From 20-10-2010 to 19-10-2012.
7.	TOTAL GRANT ALLOCATED	Rs. 92,500/-
8.	TOTAL GRANT RECEIVED	**Rs. 85,465/-**
9.	FINAL EXPENDITURE	**Rs. 73,964/-** (Rs. 85465 – Rs. 73964 =11,501) Amount of Rs. 11501/- returned through DD No. 855323, dated 30/11/2012 of UCO Bank, in favor of Secretary, UGC (WRO) Pune.
10.	TITLE OF THE PROJECT	Chemical Synthesis and Characterization of Tin Sulfide Thin Films.
11.	OBJECTIVES OF THE PROJECT	• To deposit thin films of SnS using chemical method. • To characterize structural, electrical and optical properties of the deposited SnS films. • To study the effect of deposition conditions on properties of the deposited SnS films. • To see the SnS thin films suitability for device applications. • To publish the results of the work done.
12.	WHETHER OBJECTIVES WERE ACHIEVED (GIVE DETAILS)	YES • Thin films of SnS were successfully deposited on glass substrate using chemical method. • SnS films were deposited at different bath

		temperature and deposition time. • The structural, electrical and optical properties of the deposited films were determined. • The effect of deposition conditions on properties of the deposited SnS films was studied. • The suitability of the deposited SnS thin films for any device applications was studied. • The results o the work done are published.
13.	ACHIEVEMENTS FROM THE PROJECT	Under this project, good quality SnS thin films were deposited using chemical method. • The chemical bath deposition method used in this project is relatively simple, economic, fast, hazard-free and use non-toxic materials for deposition of good quality SnS thin films. • The structural, electrical and optical properties of the deposited films were determined. • The study of effect of deposition conditions like temperature and deposition time on structural, electrical and optical properties of the deposited thin films suggest a way to successfully deposit good quality SnS thin films with desired properties for any device applications.
14.	SUMMARY OF THE FINDINGS (IN 500 WORS)	***Deposition:*** Using Chemical Bath deposition (CBD) method thin films of tin sulfide have been deposited at room temperature (27 ^{0}C) and at near room temperature up to 50 ^{0}C with deposition time ranging from 8h to 72h on well cleaned amorphous glass substrate (76mm x 26mm x 1mm). For the synthesis of SnS thin films, AR grade chemicals were used. The Sn salt $SnCl_2$ $2H_2O$, thioacetamide (TA),triethanolamine (TEA) were used for the deposition. ***Characterization :*** The X- ray diffractograms of the films were obtained using Philips Xpert MPD diffractometer (employing CuKα radiation with $\lambda = 15406$ nm in 2θ range from 20^0 to 70^0) at Sophisticated Instrumentation Centre for Applied Research and Training (SICART), Vallabh Vidyanagar and at Dr. K. C. Patel Research and Development Centre, Charotar University of Science and Technology (CHARUSAT), Changa. For surface morphology, scanning electron microscopy (SEM) pictures were taken using computer controlled digital scanning electron microscope model

Philips XL30 ESEM at SICART, Vallabh Vidyanagar and at Facilitation Centre for Industrial Plasma Technologies (FCIPT), Institute for Plasma Research, Gandhinagar.

The chemical compositions of the films were determined from the energy dispersive analysis of X-rays (EDAX) spectra obtained using the system attached with Philips XL30 ESEM at SICART, Vallabh Vidyanagar.

For the optical analysis, the optical spectra of the films were obtained using Perkin Elmer Lambda 19 UV-VIS-NIR spectrometer in the wavelength range 200 nm to 1200 nm at SICART, Vallabh Vidyanagar and also at Dr. K. C. Patel Research and Development Centre, Charotar University of Science and Technology (CHARUSAT), Changa.

The electrical parameter measurements were performed on the films at room temperature using Lakeshore 7504 Hall measurement set up system at Physics Department of S.P. University, Vallabh Vidyanagar .

In order to see the photo response of the films,samples were prepared with ohmic contacts of silver paste of ~ 3mm diameter on the two ends of the film with 7~8 mm gap in between. The film side of the sample was illuminated with a halogen lamp (white) with intensity of 60 mW/cm^2 and at a bias voltage of 10V. The thermoelectric power (TEP) measurements were carried out using the set-up developed by Physics Department of S.P. University, Vallabh Vidyanagar.

Results Achieved:

The effect of deposition time on properties of the Sns thin films was studied. The SnS films with different deposition time of 24h, 48h and 72h at room temperature were deposited.

The XRD of these films exhibited polycrystalline nature with orthorhombic phase of SnS with preferred orientations along (111) direction. It was found that with increase in deposition time particle size increases from ~ 13 nm to ~ 27 nm.The EDAX analysis exhibited Sn/S ratio from 0.99 to 1.19. The SEM shows that films deposited in form of spherical grains in homogeneous manner without any pin hole or crake. However, initially, in some deposition we found pin holes and crakes depending on bath parameters. With increase in deposition time optical band gap found to decrease from 2.03 eV to 1.79 eV. During hall measurements films found highly resistive with resistivity in the range 1.6 x

10^3 Ω-cm to 1.1 x 10^3 Ω-cm. The films exhibited weak photo response under photoconductivity measurements. The Thermoelectric measurements show p-type conductivity in the films.

The effect of deposition temperature on properties of the Sns thin films was studied. The SnS films were deposited at 27 ^{0}C, 35 ^{0}C and 45 ^{0}C.

The XRD of these films exhibited polycrystalline nature with orthorhombic phase of SnS with preferred orientations along (111) direction. It was found that with increase in deposition temperature particle size increases frm ~ 13 nm to ~ 36 nm. The EDAX analysis exhibited Sn/S ratio from 0.99 to 1.18. The SEM shows that films deposited in form of spherical grains in homogeneous manner. No pin hole or crake were observed. With increase in bath temperature optical band gap found to decrease from ~2.05 eV to ~1.8 eV. During hall measurements films found highly resistive with resistivity ~ 1.9 to 1.5 x 10^3 Ω-cm, mobility ~20 $cm^2V^2s^{-1}$ and carrier concentration ~8 x 10^{13}.

The films exhibited weak photo response when illuminated with halogen lamp for photoconductivity measurements. However, thermoelectric probe measurements show p-type conductivity in the films.

A novel route was attempted using methanol solvent. The SnS films were deposited at ~ 50 ^{o}C. The XRD of the films reveals orthorhombic phase of SnS as dominant one with preferred orientation along (111) direction. The thickness of the film was estimated ~300 nm from cross-section SEM image. In this case SEM show that the film deposited in form of needle shaped highly dense grains analogous to nanowires. The film exhibited a direct band gap of ~ 2 eV. For this film resistivity of 1.1 x 10^3 Ω-cm, mobility ~27 $cm^2V^2s^{-1}$ and carrier concentration ~2 x 10^{14} were determined. During photo conductivity measurement dark conductivity of the order ~ 9 x 10^{-4} $(\Omega\text{-cm})^{-1}$ and photo conductivity of the order ~ 1.05 x 10^{-3} $(\Omega\text{-cm})^{-1}$ were observed.

Hence, the stoichiometric orthorhombic p–type SnS semiconductor films were successfully deposited at room as well as at above room temperature using chemical bath deposition. The influence of the deposition time and temperature on the properties of the deposited films has been investigated. The outcomes are published in relavent journals. **The results can be seen in detail in the reprints of the published papers attached herewith.**

15.	CONTRIBUTION TO THE SOCIETY (GIVE DETAILS)	A relatively simple, economic and environment friendly chemical method for stoichiometric deposition of good quality SnS thin films have been successfully characterized. The study carried out on influence of the deposition time and temperature on the properties of the SnS thin films enhances many researchers in various fields to prepare the SnS films with desired characteristics. Four research papers are published from the work done under the project which are listed and attached herewith.
16.	WHETHER ANY PH.D. ENROLLED/PRODUCED OUT OF THE PROJECT	**NO** **(IT'S A MINOR RESEARCH PROJECT**)
17.	NO. OF PUBLICATIONS OUT OF THE PROJECT (PLEASE ATTACH)	**4** (FOUR) *(Listed Below & Attached.)*

Publications:

1. Title : A Novel Route To Nanocrystalline Semiconducting SnS Thin Films Suitable For Photovoltaic Structures
   Journal: American Institute of Physics (AIP) Conference Proceedings.
   AIP Conf. Proc.Vol.1536,1127(2013); American Institute of Physics Publ.
   https://doi.org/10.1063/1.4810633
2. Title : Effect Of Temperature On Structural And Optical Properties Of Chemically Deposited Tin Sulfide Thin Films Suitable For Photovoltaic Structures
   Journal: Advanced Materials Research Vol. 665 (2013) pp 93-100 2013)
   Trans Tech Publications, Switzerland
   https://doi.org/10.4028/www.scientific.net/AMR.665.93
3. Title : Low Temperature Chemical Synthesis of p-type SnS Thin Films Suitable for Photovoltaic Structures
   Journal: Solid State Phenomena Vol. 209 (2014) pp 82-85
   Trans Tech Publications, Switzerland
   https://doi.org/10.4028/www.scientific.net/SSP.209.82
4. Title : Influence of Deposition Time on Structural and Optical Properties of ChemicallyDeposited SnS Thin Films
   Journal: The Open Surface Science Journal 2012,ISSN: 1876-5319 Pp 6-13.
   DOI: 10.2174/1876531901204010006

Dr. T. H. PATEL
Principal Investigator

Principal
(SEAL)

PRINCIPAL
V. P. & R. P. T. P. SCI. COLLEGE
VALLABH VIDYANAGAR-388120.

Vitthalbhai Patel & Rajratna P.T.Patel SCIENCE College,

Vallabh Vidyanagar - 388120

SUBJECT: MINOR RESEARCH PROJECTS **(Dr.T.H.Patel)**

MRP 47 – 1340/10 (WRO) Date 20/09/2010

UNIVERSITY GRANTS COMMISSION

ACCESSION CERTIFICATE

It is certified that the books purchased from MRP grant are handed over to the college central department library. Their accession number is from 48431 to 48433 & 48458 to 48460.

Signature____________________
(Principal Investigator)

Signature ____________________
(Librarian)
Seal

LIBRARIAN
V. P. & R. P. T. P. Science College
Vallabh Vidyanagar

LIBRARY

Signature ____________________
(PRINCIPAL)
Seal

PRINCIPAL
V. P & R. P T. P. SC. COLLEGE
VALLABH VIDYANAGAR

ज्ञान-विज्ञान विमुक्तये

Annexure - IV

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002.

Minor Research Project

UTILIZATION CERTIFICATE

It is certified that the grant of **Rs. 92,500 (Rupees Ninety-two thousands five hundred only)** sanctioned to **Dr. T. H. Patel** by University Grants Commission wide their letter **No. 47-1340/10 (WRO)** dated **September 20, 2010** towards **Minor Research Project** and **Rs. 85,465(Rupees Eighty-five thousands four hundred sixty-five only)** has been received. The total actual expenditure incurred for this project is of **Rs. 73,964(Rupees Seventy-three thousand nine hundred sixty-four only)** and it has been fully utilized for the purpose for which it has been sanctioned and in accordance with the terms and condition laid down by the commission. The balance amount of **Rs. 11,501(Rupees Eleven thousand five hundred one only)** is returned to the UGC office.

If as a result of check or audit objection, some irregularity is noticed at a later stage action will be taken to refund or regularize the objected amount.

Signature of the Principal Investigator
(Minor Research Project)

Signature of the Principal
With seal of the college

V.P. & R.P.T.P. Science College
V.V. Nagar
388120

P. D. PARIKH & CO.
CHARTERED ACCOUNTANTS
C. A. P. D. PARIKH
M. NO. 13247

Chartered Accountant

ज्ञान-विज्ञान विमुक्तये

Annexure-V

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

STATEMENT OF EXPENDITURE IN RESPECT OF MINOR RESEARCH PROJECT

Name of Investigator: **Dr. T. H. Patel**
College Name: **V. P. & R. P. T. P. Science College, Vidyanagar – 388 120**
Title of the Project: **Chemical Synthesis and Characterization of Tin Sulfide Thin Films**
UGC Approval No. & Date: **No. 47-1340/10 (WRO) dated September 20, 2010.**
Effective Date of Starting of Project: **October 20, 2010.**
Date of Completion of Project: **October 19, 2012. (Two Years)**
Period of Expenditure: **From 20-10-2010 to 19-10-2012**

Details of Expenditure:

Budget Head		Amount sectioned Rs.	Amount received 1st Inst. Rs.	Amount received 2nd Inst. Rs.	Total Amount received Rs.	Expenditure Rs.	Balance
Non-Recurring Grant	Equipments	12,150	12,150	-	12,150	12,150	0
	Books & Journals	10,000	10,000	-	10,000	9,821	179
Recurring Grant	Contingency	20,000	10,000	8,000	18,000	21,343	-3,343
	Special Needs	20,000	10,000	8,000	18,000	5,859	12,141
	Travel/Field Work	10,350	5,175	4,140	9,315	4,382	4,933
	Chemicals & Glassware	20,000	10,000	8,000	18,000	20,409	-2,409
Total Amount Rs.		**92,500**	**57,325**	**28,140**	**85,465**	**73,964**	**11,501**
Amount Utilized Rupees Seventy-three thousand nine hundred sixty-four only							
Amount Not Utilized Rupees Eleven thousand five-hundred one only							

Sanctioned Amount: **Rs. 92,500/-** (47-1340/10 (WRO) dated September 20, 2010)
Rs. 57,325/- received as first installment on 20th October, 2010.
Rs. 28,140/- received as second installment on 18th October, 2012.

P. D. PARIKH & CO.
CHARTERED ACCOUNTANTS
C.A. P. D. PARIKH
M. NO. 13247

Signature of the Principal Investigator
(Minor Research Project)

Signature of the Principal
With seal of the college

V. V.
Nagar
388120

Chartered Accountant

T. H. Patil (7)

OK

VRSC/2012/510

From: Dr. T. H. PATEL
Associate Professor in Physics,
V. P. & R. P. T. P. Science College,
Vallabh Vidyanagar – 388 120
Email: pateltarunh@yahoo.com
10th December, 2012

To,
The Secretary,
University Grants Commission,
Western Regional Office, Ganeshkhind Pune - 411 007

Sub: Submission of Final progress report and utilization statement under UGC Minor Research Project No. **47-1340/10** (WRO) dated September 20, 2010, of Dr. T. H. Patel.

Dear Sir,

I have received the UGC Minor Research Project No. **47-1340/10** (WRO) dated September 20, 2010 entitled: **"Chemical Synthesis and Characterization of Tin Sulfide Thin Films"**. Under this project I have published **Three Research Papers** in the **International journals, One is under review** and presented research papers at **One International** and **Three National conferences.**

I am pleased to submit the final progress report of the research activity including publication, participation in seminar and conferences as well as the utilization of grant under various heads under the above said minor research project.

The amount sanctioned to this project is Rs. 92,500/-(Rupees ninety-two thousands five-hundred only) wide letter No. 47-1340/10 (WRO) dated September, 2010 and an amount Rs. 85465/-(Rupees eighty-five thousands four-hundred sixty-five only) has been received. As the actual expenditure incurred for this project is Rs. 73964/-(Rupees Seventy-three thousands nine-hundred sixty-for only), the balance amount is of Rs. 11501/-(Rupees eleven thousands five-hundred one only). **Herewith I am returning this amount to your UGC office through DD No. 855323, dated 30/11/2012 of UCO Bank, in favor of Secretary, UGC (WRO) Pune. We request you to acknowledge us by sending the receipt of the above DD for our account records. The amount of Rs. 7035/-(Rupees seven thousands thirty-five only) as 10% of non-recurring grant, hence need not required by us.**

I have attached all the necessary documents and certificates as per the guidelines to complete the project.

I request you to do needful in order to complete this project. I sincerely thank UGC for giving me this important opportunity.

With thank and regards.

Forwarded through;

(Dr. Bhavesh D. Patel)
Principal

PRINCIPAL
V.P & R.P.T.P SC COLLEGE
VALLABH VIDYANAGAR-388 120

Sincerely Yours,

(Dr. T. H. Patel)
Principal Investigator

Date: 03-11-2012

Assets Certificate

It is certified that the following Equipments purchased under UGC Minor Research Project [47-1340/10(WR0)] of Dr. T. H. Patel have been handed over to the college:

1. Temperature Controlled hot air electrical Owen
2. Magnetic Stirrer with hot plate and temperature control

Dr. T. H. Patel
Principal Investigator

Dr. Bhavesh D Patel
Principal

ज्ञान-विज्ञान विमुक्तये

Annexure - VI

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

STATEMENT OF EXPENDITURE INCURRED ON FIELD WORK

Name of the Principal Investigator:**Dr. T. H. Patel MRP 47-1340/10(WRO)**

Name of the Place visited	**Duration of the Visit**		**Mode of Journey**	**Expenditure Incurred (Rs.)**
	From	**To**		
Dr. K.C. Patel Research and Development Centre Charotar University of Science and Technology(Charusat) Changa, Post: Anand Gujarat	13/04/2011 8.30am V.Vidyanagar - 13/04/2011 4.00pm Changa	13/04/2011 9.15am Changa - 13/04/2011 4.45pm V.Vidyanagar	Car	Rs. 278/-
Facilitation centre for Industrial Plasma Technology (FCIPT), IPR, Gandhinagar Gujarat.	18/06/2012 7.00am V.Vidyanagar - 18/06/2012 4.00pm Gandhinagar	18/06/2012 9.30am Gandhinagar - 18/06/2012 7.30pm V.Vidyanagar	Car	Rs. 2,052/-
Facilitation centre for Industrial Plasma Technology (FCIPT), IPR, Gandhinagar Gujarat.	04/09/2012 7.00am V.Vidyanagar - 04/09/2012 4.00pm Gandhinagar	04/09/2012 9.30am Gandhinagar - 04/09/2012 7.30pm V.Vidyanagar	Car	Rs. 2,052/-
	Total Rs.			**Rs. 4,382/-**

Certified that the above expenditure is in accordance with the UGC norms for Minor Research Projects.

[T. H. PATEL]
Principal Investigator

V.P. & R.P.T.P. Science College
V. V. Nagar 388120

[Dr. Bhavesh D. Patel]
Principal

6 *The Open Surface Science Journal*, 2012, *4*, 6-13

Open Access

Influence of Deposition Time on Structural and Optical Properties of Chemically Deposited SnS Thin Films

T.H. Patel*

V.P. & R.P.T.P. Science College, Sardar Patel University, Vallabh Vidyanagar Pin: 388120 Gujarat, India

Abstract: Using chemical bath deposition (CBD) technique SnS thin films have been deposited at room temperature with different deposition times. The deposited films have been investigated through X- ray diffraction measurements to determine structural properties. The deposited SnS films found amorphous and polycrystalline with an orthorhombic herzenbergite structure. The grain size found to increase with deposition time. The surface morphology of the films has been examined using scanning electron microscopy (SEM). The chemical compositions of the films have been determined using energy dispersive analysis of x-rays (EDAX). The optical absorption spectra of the films in the wavelength range of 200-1200 nm have been investigated to determine the optical band gap and types of transitions involved in the absorption process. The direct allowed transitions found to be dominant and the corresponding band gap found to decrease with increase in deposition time. In order to evaluate the electrical parameters, thermoelectric power measurements have been performed. The films exhibited p-type electrical conductivity. A systematic study on the influence of deposition time on the properties of SnS thin films deposited by CBD at room temperature has been reported.

Keywords: Band gap, chemical bath deposition, lattice parameters, optical absorption, tin sulfide electron microscopy, X-ray diffractogram,

INTRODUCTION

The search for thin film materials for solar energy conversion and other related applications has been recently identified. Many efforts have been geared towards using metal chalcogenides as this class of materials had shown somewhat superior performance when compared to others. Among the important binary semiconductors of IV-VI group, the chalcogenides formed with Sn, especially SnS have attracted considerable attention in recent years. The lattice structure of SnS is closely related to the black phosphorous structure and can be considered either as a distortion of the NaCl structure or as a binary analog of the layered arsenic structure. The tin sulfide (SnS) is having orthorhombic crystal structure with eight atoms per unit cell. The cation (Sn) and anion (S) atoms form double layers made up of two planes of zigzag cation-anion chains perpendicular to the longest crystallographic axis. The double layers are stacked to each other through a weak van der Wall's interaction whereas a relatively strong covalent bonding between the cation and anion atoms exists within the layers [1]. The compound SnS is a semiconductor with a band gap of 1.3 eV [2] and hence with the potential to become a versatile solar energy material. The high conversion efficiency obtainable from it in photovoltaic devices, according to Prince-Loferski diagrams and its acceptability from the point of view of cost, availability, toxicity and stability ascribe to SnS a unique position among the metal sulfides. The narrow band gap and the interesting structural properties of SnS satisfy most of the criterion to make them potential candidate in photoelectrochemical solar cells, as solar absorbers in thin film solar cells, near infrared detectors, as photovoltaic materials and in other optoelectronic systems. The SnS films show both direct and indirect absorptions at room temperature. It exhibits p-type conduction and high absorption coefficient of the order of 10^4 to 10^5 cm^{-1} [3]. The most extensively studied thin film solar cells are based on CdTe and Cu(In,Ga)Se_2 (CIGS). However, there are concerns existing with respect to the use of Cd and In in this type of applications due to cost, toxicity, abundance and environmental issues. SnS is one of the promising materials for low cost thin film solar cell technology, due to its optimum energy gap, a high fundamental absorption coefficient, non toxicity and abundance.

For the deposition of thin films of SnS various methods like spray pyrolysis [4-10], electrodeposition [11-17], chemical vapor deposition [18-20], magnetron sputtering [21], successive ionic layer adsorption and reaction (SILAR) [22], vacuum evaporation [23-34], brush plating [35-36], microwave assisted chemical deposition [37] and chemical bath deposition (CBD) [38-53] have been employed. Among these methods CBD is relatively simple, more rapid and inexpensive method suitable for deposition on large substrates irrespective of the shape and morphology of substrates nearly at room temperature. Mainly, it is a technique for thin film deposition on a substrate from a diluted solution comprising of a source of metal, hydroxide and sulfide or selenide ions. In CBD control of reaction rate and pH of the bath is very necessary to deposit a good quality film. For this, use of appropriate buffer solutions in the bath has been seen many times [38-39]. Most of the CBD deposited SnS films used stannous chloride salt as a tin ion source and thioacetamide [38-39] or sodium thiosulphate pentahydrate [42,47] or sodium sulphate [54] as a sulphur

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*Address correspondence to this author at the V.P. & R.P.T.P. Science College, Sardar Patel University, Vallabh Vidyanagar Pin: 388120 Gujarat, India; Tel: +91 2692 230011 235207; Fax: +91 2692 235207;
E-mail: pateltarunh@yahoo.com

1876-5319/12 2012 Bentham Open

ion source in the bath. To slowdown the immediate precipitation of the precursors in the bath buffer solutions are used. At the same time, increase in temperature increases the rate of reaction in the bath leading to an early deficit of the ions in the bath with may lead to a reverse reaction exhibiting pilling off of the deposited film. At low temperature the rate of reaction becomes low as compared to that at higher temperature which can be monitored and then optimized for better deposition of the film. Hence low temperature deposition of the film is interesting and challenging. Recently, the effect of deposition time on the properties of SnS thin films deposited by CBD using a buffer solution (ammonia/ammonium chloride) at 60 ^{0}C has been reported [38]. Such study on SnS thin films deposited at room temperature by CBD has not been found in literature survey. The temperature of the bath strongly influence the reaction mechanism and hence the formation of the film. Also at room temperature, the particle do not have enough kinetic energy and hence less probability to reach the substrate with a greater momentum to form a quick film. Under such condition the formation of SnS from the anion and cations preferably governs by the chemistry of the reactants only. In this context, a systematic study on the effect of deposition time on the structural and optical properties of SnS thin films at room temperature has been reported in the present work.

EXPERIMENTAL

Deposition of SnS Films

For the synthesis of SnS thin films using CBD, AR grade $SnCl_2$ $2H_2O$ and thioacetamide (TA) were used as Sn and S source respectively. The deposition bath was prepared first by mixing the 5 ml of 1M $SnCl_2$ $2H_2O$ with 10 ml of 3.75 M triethanolamine (TEA) (as supplied diluted to 50%) under a vigorous stirring. 2ml NH_3 was added drop-wise with constant stirring followed by addition of 5 ml of 1M TA. Finally distilled water added to make a total of 100 ml. The pH of the bath was kept 9.70 using ammonia. The solution was transferred to another thoroughly cleaned glass beaker with well cleaned amorphous glass substrate (76mm x 26mm x 1mm) placed inclined and rested on beaker wall. Before deposition process glass substrates were thoroughly cleaned using detergent, chromic acid and isopropyl alcohol in a systematic manner. The films were deposited at room temperature (27 ^{0}C) with deposition time of 24h, 48h and 72h. Each deposited film was sprayed with distilled water immediately after it was taken out of the beaker, allowed to dry and then kept in a desiccator to avoid any unwanted atmospheric effects.

Characterization of SnS thin Films

The X- ray diffractograms of the films were obtained using Philips Xpert MPD diffractometer employing CuKα radiation with λ=0.15406 nm in 2θ range from 20^0 to 70^0. For surface morphology scanning electron microscopy (SEM) pictures were taken using computer controlled digital scanning electron microscope model Philips XL30 ESEM. The chemical compositions of the films were determined from the energy dispersive analysis of X-rays (EDAX) spectra obtained using the system attached with Philips XL30 ESEM. For the optical analysis, the optical spectra of the films were obtained using Perkin Elmer Lambda 19 UV-VIS-NIR spectrometer in the wavelength range 200 nm to 1200 nm. The Hall effect measurements were attempted on the films using Lakeshore 7504 Hall measurement set up system at room temperature. The thermoelectric power (TEP) measurements were carried out using the set-up available at and developed by Physics Department of S.P. University, Vallabh Vidyanagar, India.

RESULTS AND DISCUSSION

Mechanism of SnS Thin Film Deposition in CBD

Chemical bath deposition (CBD) refers to the deposition of films on a solid substrate from reaction occurring in a solution, almost always aqueous. Although CBD has been in use for long time involving quite simple reactions, the mechanism of the CBD process is often unclear. There are several mechanisms of CBD which can be divided into four fundamentally different types as; the simple ion-by-ion mechanism, simple cluster (hydroxide) mechanism, complex decomposition ion-by-ion mechanism and complex decomposition cluster mechanism as long as formation of metal chalcogenide films are concerned [44]. The first two mechanisms involve free chalcogen ion while the last two do not involve formation of free chalcogen ion. In simple ion-by-ion mechanism, first ions diffuse over the substrate which serve as a catalyst and facilitate the nucleation. The nucleation grows as a result of absorption of ions in the solution and nucleation of new crystals occurs. At further stage the crystals bonds with one another by the van der Walls forces forming a film. In simple cluster mechanism, hydroxide colloidal particles diffuse to substrate and adhere to it. These hydroxide colloidal particles adsorbed to substrate react with free ions in the solution resulting in displacement of hydroxide by the free ions. Such displacement reaction can occur both on the substrate and in the solution and continues until most of the hydroxide converts into sulfide. The primary particles occurring by reaction adhere to each other to make up an aggregated film on the substrate and other nonadsorbed particles also aggregate and precipitate out of the solution. In last two complex decomposition mechanisms, the complex (Sn-S-L, where L is ligand or part of the S forming species) decomposes to SnS on the substrate and to a greater or lesser extent also homogeneously in the solution. The SnS nuclei formed grow by adsorption and decomposition of more complex species until a film of aggregated crystal is formed in a similar manner as for the first two mechanisms.

While using CBD method, to deposit a good quality thin film on the substrate it is very important and essential that the reaction process in the bath leading to film formation must be sufficient slow enough. In the deposition process of SnS films when TEA was not used, the precipitation of solid elements like [$Sn(OH)_2$] occurs very rapidly in the solution and a proper film was not obtained on the substrate. In order to form a good quality film on the substrate, formation of such elements should be prevented and the rate of reaction must also be slowed down. To ensure these conditions TEA was used in the synthesis process as it acts as a good complexing agent with metal ions. The basic chemical reaction that leads to formation of SnS thin films is considered as follows [45].

$[Sn(TEA)]^{2+} + CH_3CSNH_2 + 2OH^- \rightarrow SnS + TEA + CH_3CONH_2 + H_2O$

The Sn^{2+} ion complexes with TEA initially to form $[Sn(TEA)]^{2+}$ during the deposition preventing the rapid formation of solid materials like $[Sn(OH)_2]$ and later this complex decomposes and releases Sn^{2+} ions to make bonds with S^{2-} ion present in the solution to form SnS.

During the deposition time the color of the solution in the bath was observed to change from initially milky white to light yellowish brown in couple of hours then to chocolate brown and with further increase in time to deep brown. The films obtained after deposition time of 24h were found to be light brown with yellowish transmission in daylight and reflecting multicolor whereas the films obtained after deposition time of 48h and 72h were found to be deep brown-blackish with deep reddish transmission and reflecting like mirror. The change in appearing color of the film is mainly attributed to the increase in thickness of the film with the increase in deposition time since Sn/S ratio is not much affected in the films as per the EDAX results. The SnS films of deep brown or chocolate color have been reported recently [10,39,55]. Very recently, color dependence of the SnS film on the film thickness has been reported revealing that color of SnS film changes from pale yellow to brown with increase in film thickness [56]. It should be noted that films deposited on the lower side of the substrate facing the bottom of the beaker only found well adherent and taken for studies while that on the upper side found to washed off easily with spray of distilled water.

Structural Analysis

The x-ray diffraction patterns of the films deposited at different deposition times of 24h, 48h and 72h at room temperature are shown in Fig. (**1**). For all films, the observed peaks have been analyzed and indexed using standard pattern for the mineral herzenbergite with orthorhombic structured SnS (JCPDS PDF Card # 39-0354). The analysis of the XRD pattern of film deposited after 24h indicates formation of a poorly crystalline film. Except for compounds that are commonly amorphous, CBD semiconductor films are rarely truly amorphous. Most of these films are classified as "amorphous" or "poorly crystalline" either on the basis of lake of any XRD peak or because the peak(s) are very broad [44] as it happens in this case also. The peaks observed in Fig. (**1**) at 2θ values of 26.34^0, 31.88^0 and 42.80^0 were found to match with reflections from (120), (040) and (210) crystallographic planes of orthorhombic phase of SnS respectively. The peak seen at 26.34^0 is found also to contributing through reflections of maximum intensity from (110) plane of mineral cassiterite (SnO_2) (JCPDS PDF Card # 41-1445) from the glass substrate as observed earlier too [43].

The XRD patterns of films deposited after 48h and 72h shown in Fig. (**1**) exhibits sharp peaks at 2θ values of 31.48^0 and 31.42^0 respectively corresponding to (111) planes of orthorhombic structured SnS (PDF Card # 39-0354). There are some less intense peaks revealing good quality polycrystalline films with preferred orientation from (111) plane. In the XRD pattern of film with deposition time of 48h, a peak at 2θ values of 35.06^0 and in the XRD pattern of film with deposition time of 72h peak at 2θ values of 34.86^0 are identifies as originating from (101) plane of Sn (PDF#18-1380). It should be noted that peaks corresponding to other phases of SnS (SnS_2 or Sn_2S_3) have not been found during the XRD analysis.

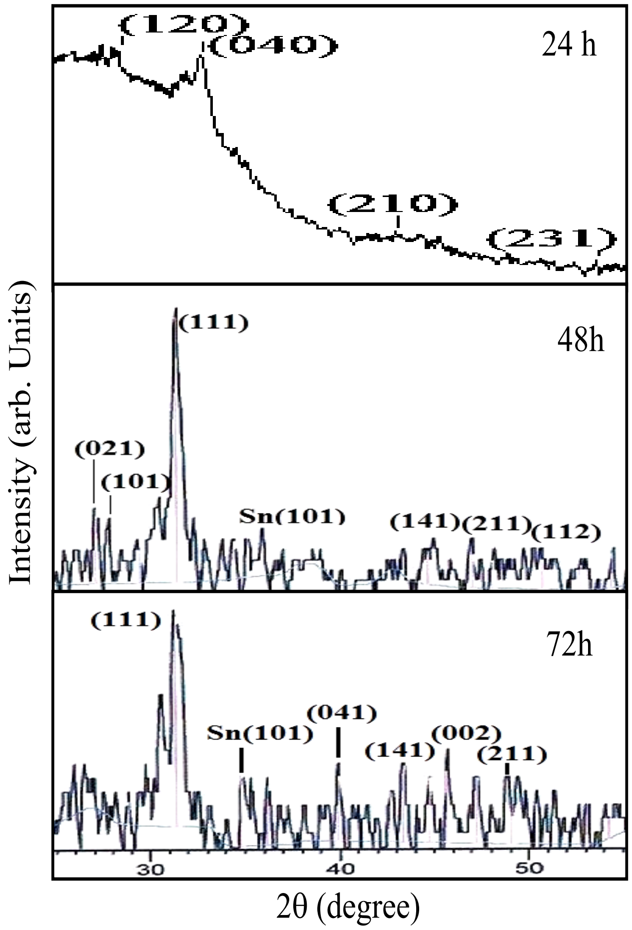

Fig. (1). XRD spectra of SnS films deposited using CBD with different deposition times.

The lattice parameters of the deposited films have been calculated from the observed values of $2\theta^0$ and using *d*-values (interplaner spacing) for the orthorhombic structure, which is given by [57]:

$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \tag{1}$$

where (*hkl*) are the Miller Indices of the plane concerned and *a, b* and *c* are lattice parameters. The values of lattice parameters so obtained are shown in Table **1**. The values of the lattice parameters have been found in good agreement when compared with the standard values taken from JCPDS Card # 39-0354. The crystallite or grain sizes were estimated using the Scherrer's formula [57]:

$$D = \frac{0.9\lambda}{\beta_c \cos\theta} \tag{2}$$

where D is the crystallite size, λ is the wavelength of the CuKα radiation, β_c is the experimentally observed diffraction peak width at half maximum intensity (FWHM) and $\boldsymbol{\theta}$ is the

Bragg angle. The values of the crystallite size determined using above relation are 13.06 nm, 26.9 nm and 27.05 nm for the films with deposition time of 24h, 48h and 72h respectively. When compared to XRD patterns of bulk SnS, the XRD patterns of the deposited films show the broadening of the peaks. Such effects are mainly arising due to small crystalline size and strain. Both crystalline size and strain effects are interconnected in the line broadening of the peaks which makes it difficult to separate. Williamson-Hall technique [58] is one of the many methods for the evaluation and separation of size and strain parameters from the occurring line broadening. In this method which is adopted in present work, grain size D and strain ε are related as

$$\frac{\beta_c \cos\theta}{\lambda} = \frac{1}{D} + \varepsilon\left(\frac{\sin\theta}{\lambda}\right) \tag{3}$$

where β_c is the instrumental effect corrected full width at half maximum of the peak measured, θ is the diffraction angle and λ is the wavelength of X-ray. The slope of the plot between $\beta_c \cos\theta/\lambda$ and $\sin\theta/\lambda$ (Williamson –Hall plot) gives micro strain ε and the inverse of intercept on y axis gives average grain size value. The variation of grain size and strain of SnS films deposited at room temperature at different deposition time are shown in Fig. (**2**). The results of the Williamson –Hall plots shown in Table **1** indicates that grain size increased from 12.65 nm to 28.57 nm as the deposition time increased from 24h to72h. These values are in good agreement with those obtained from Scherrer formula as shown in Table **1**. It is obvious to expect that with increase in deposition more ions released from the reaction contribute to the film formation process leading to an increase in grain size until deficit of either Sn or S ion occurs in the bath solution. Also, with increase in deposition time from 24h to 42h strain value decreased from 43 x10^{-4} to 3.6 x10^{-4}. Similar behavior has been observed on SnS films deposited with spray pyrolysis at increasing substrate temperature [5]. However, with further increase in deposition time to 72h strain value found to increase to 28 x10^{-4} but still decreased from that for film with deposition time of 24h. This may seems to be plausible due to sufficient time available for growth of defects as the films remains in the bath for a longer time.

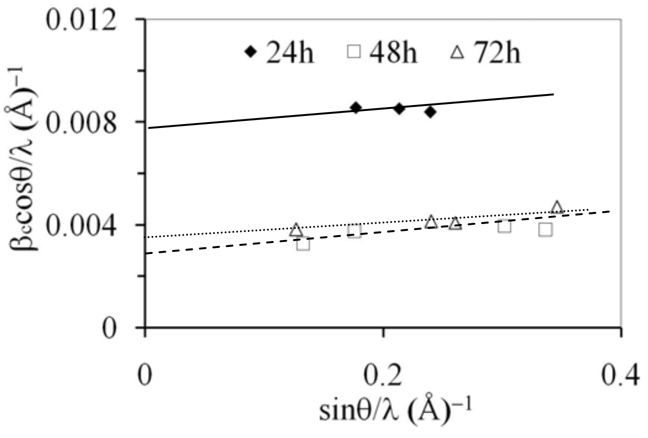

Fig. (2). Williamson-Hall Plots of SnS films with different deposition times.

Surface Morphology

The surface morphology of the films deposited at room temperature with different deposition times are shown in Fig. (**3**). The SEM images show homogeneous surfaces of the films free from any pinhole or cracks with presence of large spherical crystallites surrounded with small crystallites. The SEM images indicate that with increase in deposition time the number of crystallites increases leading to formation of more homogeneous film. The presence of more number of small grains as compared to larger ones can be attributed due to deposition at room temperature at which ions in the bath generally do not posses enough mobility to form a grain with larger size. The Fig. (**3c**) is the SEM image of the film deposited after 72 hour. In CBD, after a sufficient time when reaction of formation of SnS from the respective ions in the bath is saturated the reverse reaction starts which leads to pilling off of the films from the substrate. This effect can be seen just in its initial state to occur in Fig. (**3c**) in some directions.

Table 1. Results of XRD Analysis of SnS Films Deposited with Different Deposition Times

Dep. Time (h)	Lattice Parameter			Grain Size		Strain x 10^{-4}
	(Å)			(nm)		
	a	*b*	*c*	Sherrer Formula	W-H Plot	
24	4.38	11.20	3.99	13.06	12.65	43
48	4.28	11.29	3.90	26.9	26.31	3.6
72	4.32	11.13	3.97	27.05	28.57	28
	4.33[a]	11.19[a]	3.98[a]			

[a] JCPDS PDF # 39-0354.

EDAX Analysis

Fig. (**4**) shows the EDAX spectrum of the film with deposition time of 72h. The EDAX analysis of the films with deposition time of 24h,48h and 72h exhibited atomic ratio of Sn/S of ~ 0.99, 1.19 and 1.18 respectively. This has been indicating that deposited films are almost stochiometric. It is evident that films with deposition time of 48h and 72h has presence of small excess amount of tin. This may be due to the fact that at longer deposition time the release of Sn ion is not counterbalanced by availability of S ions in the bath as concentration of S ions in the bath had been utilized fully. The results of XRD analysis of the corresponding films justify the presence of Sn. The Na, Mg, Si, O and Ca elemental peaks have resulted due to the elements in glass substrates and distilled water.

Optical Analysis

The optical absorption technique was employed to determine the values of band gap and type of optical transitions involved in the absorption process in the films. The absorption spectra of the films obtained in the wavelength range of 200-1200 nm are shown in Fig. (**5**). The absorption edges have been found broad and pronounced around 800 nm for film with deposition time of 24h and around 850 nm for films with that of 48h and 72h. It can be seen from the Fig. (**5**) that absorption edge tends to be sharpening as the deposition time of the film increases. This can be attributed to the increase in thickness of the films with increase in deposition time.

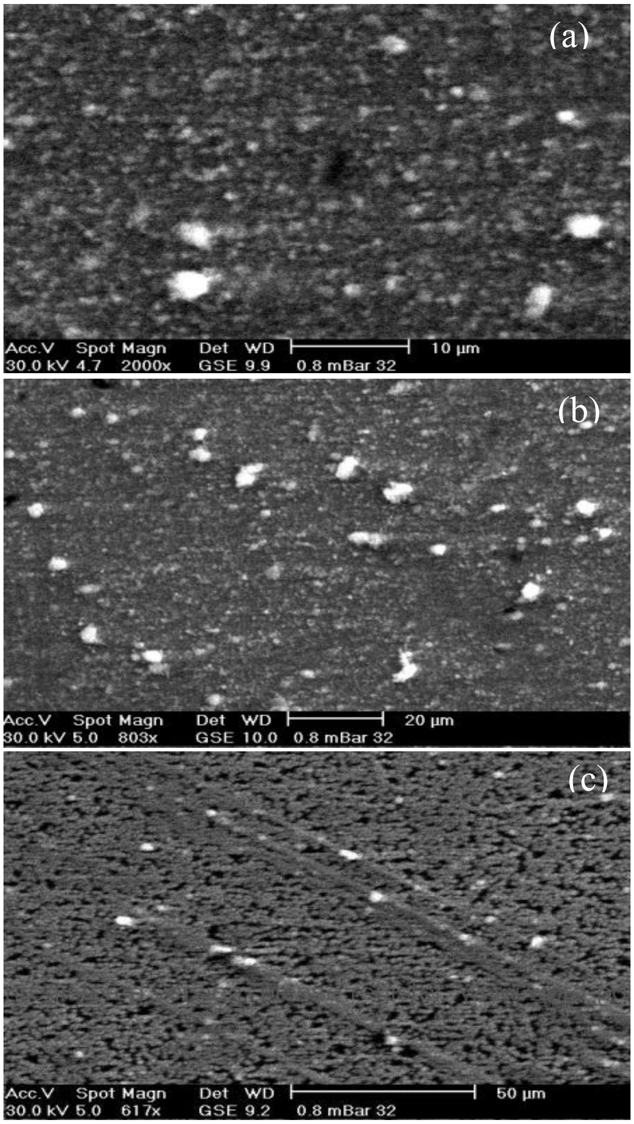

Fig. (3). SEM images of SnS films deposited by CBD at deposition time of (**a**) 24h (**b**) 48h and (**c**) 72h.

The optical band gaps E_g of the films were evaluated using the relation [59]:

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \quad (4)$$

where A is the parameter that depends on the transition probability, α is the absorption coefficient and n is the index that has value equal to 1/2 for the direct allowed transitions, 2 for the indirect allowed transitions, 3/2 for direct forbidden transitions and 3 for indirect forbidden transitions. The SnS thin films prepared by CBD has exhibited both direct [10,15, 38-39,41-42,47-48,50-51] as well as indirect [11,38-39,45,49,51] transitions. However to investigate the types of optical transitions involved with the value of corresponding optical band gap, the spectral variations of $(\alpha h\nu)^{1/2}$, $(\alpha h\nu)^2$, $(\alpha h\nu)^{2/3}$ and $(\alpha h\nu)^{1/3}$ were plotted as a function of photon energy $h\nu$ as shown in Fig. (**6**) for the SnS films deposited with different deposition times. The value of intercept on the x-axis obtained by extrapolation of the straight-line portion of the curve at $\alpha = 0$ has been used to estimate the optical band gap of the corresponding film [11,13, 38-40,42,47,49,51]. Also to determine optical band gap many researchers [40] use the Tauc-relation [60] which is consistent with equation (1).

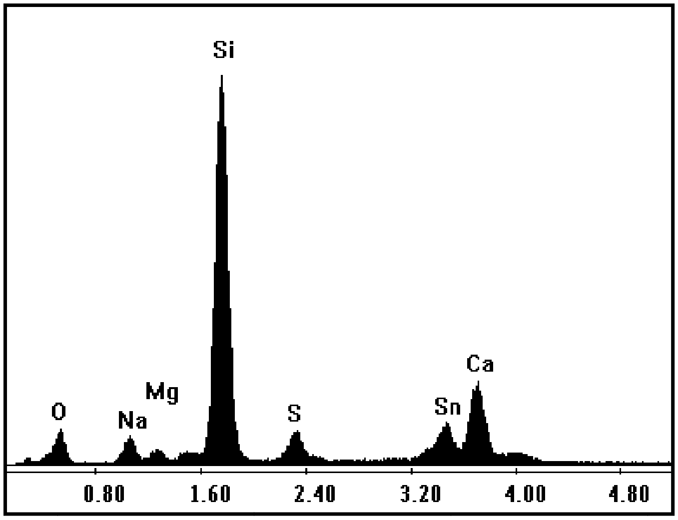

Fig. (4). EDAX spectrum of SnS film deposited by CBD with deposition time of 72h.

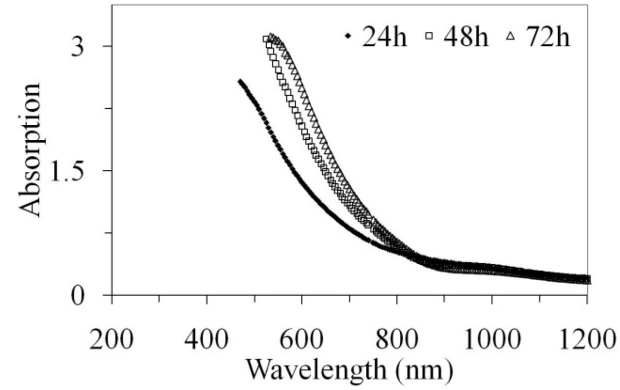

Fig. (5). Optical absorption spectra of SnS thin films deposited by CBD with different deposition times.

Fig. (**6**) show that for the deposited films the straight line portion best fits for allowed direct transitions with lesser probability for other transitions. However, the variations of band gap values with deposition time for the deposited films are shown in Fig. (**7**) for all types of transitions.

The value of indirect allowed band gap found to be not much influenced by deposition time as it decreased fractionally from 1.18 eV to 1.14 eV. The values are in the agreement with those reported for SnS films prepared by CBD [11,38-39,49]. With increase in deposition time the direct forbidden band gap found to decrease from 1.44 eV to 1.32 eV. These values are in the range observed earlier [43]

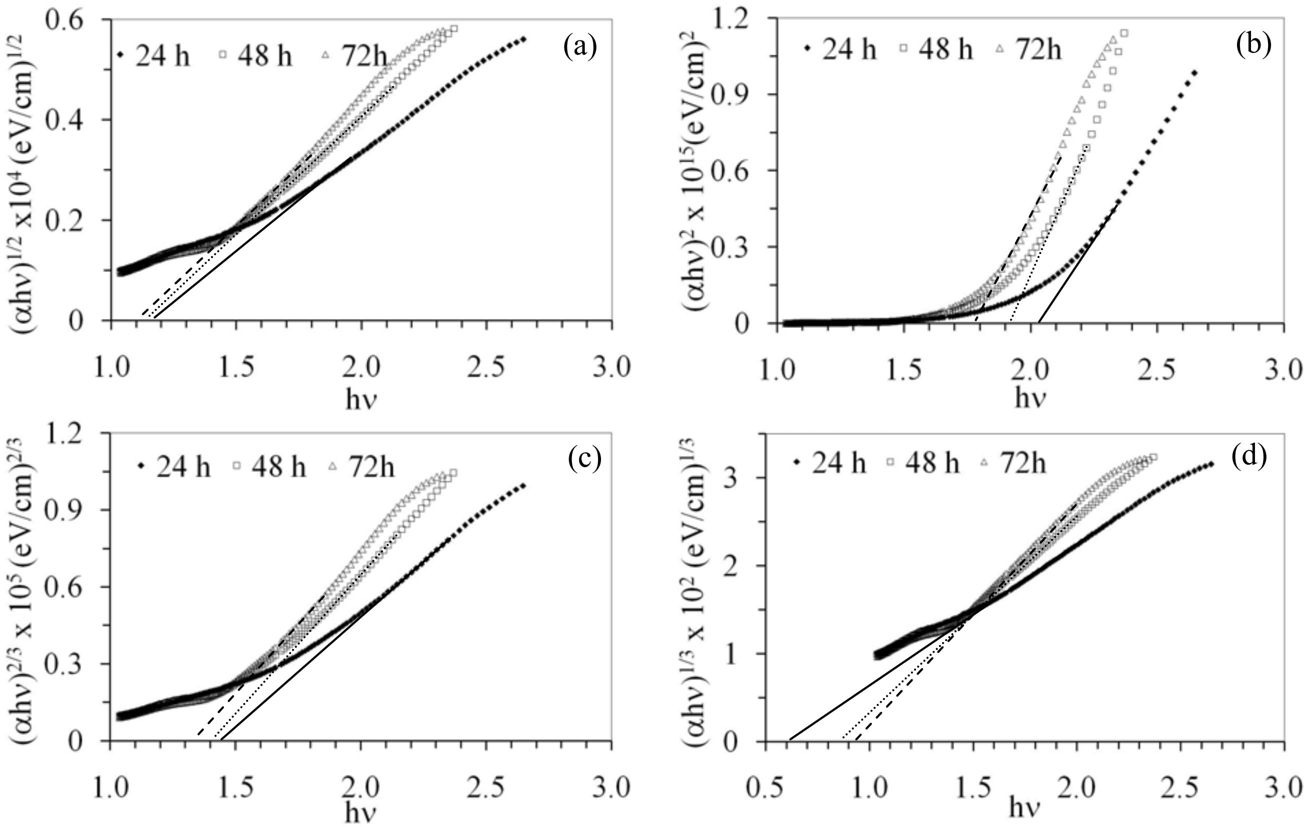

Fig. (6). Spectral variations of (**a**) $(\alpha h\nu)^{1/2}$, (**b**) $(\alpha h\nu)^2$, (**c**) $(\alpha h\nu)^{2/3}$ and (**d**) $(\alpha h\nu)^{1/3}$ with hν for the SnS films deposited with different deposition times.

but higher than those observed by other researchers [11,49,52] for SnS films deposited by CBD. The direct forbidden gap of the order of 1.7 eV have been reported for SnS films prepared by CBD with orthorhombic [49] and zinc blende structures [11,40,46] and also for SnS films prepared by successive ionic layer adsorption and reaction (SILAR) method [61]. The nature of the variations of $(\alpha h\nu)^{1/3}$ as a function of photon energy (hν) as shown in Fig. (**6d**) indicates that indirect forbidden transitions are less probable in films under investigations. However, indirect forbidden band gap estimated to increase from 0.6 eV to 0.82 eV.

The straight line portions of the curves in Fig. (**6b**) indicate that direct allowed transitions are dominant in the deposited SnS films. The direct band gap decreased from 2.03 eV to 1.79 eV with increase in deposition time. These values are higher than those reported earlier [37,39,41-42,47,50-51] but are within the range as observed in SnS films deposited by CBD [38] at room temperature and SnS films deposited by thermal evaporation [23-24]. The increase in deposition time improves the crystallnity as well as enhances the film thickness with growth of crystallites of larger size till enough Sn and S ions exist in the solution to support the growth mechanism of the film to continue. This mainly affects the optical absorption which eventually affects the optical band gap of the film. The analysis of the XRD patterns of the films showed a better crystallinity and increase in grain size in the films with increase in deposition time. The difference in crystalline structure of the films deposited at room temperature as compared to those mostly prepared at increased temperature may be the reason for higher values of the direct band gap. It should be noted that presence of other phases of tin sulfide i.e. SnS_2 (E_g = 2.44 eV) and Sn_2S_3 (E_g = 2.0 eV) is not found in the deposited films. So the decrease in bandgap in these films with increase in deposition time can be attributed mainly to increase in both the grain size and the film thickness with increase in deposition time. For SnS thin films, decrease in band gap with increase in film thickness has been observed several times for films deposited at near room temperature [23-24,38,62]. Use of SnS thin films with the band gap of the order of 1.7 eV as absorber layer deposited by CBD have been reported recently [43]. The CBD films are often nanocrystalline and the most apparent effect of very small crystal size is the increasing band gap due to size quantization. This effect is quite visible to eye if the band gap is in the visible region of the spectrum. The optical spectroscopy is fast and simple pointer to crystal size, since band gap-size correlations have been made for a number of colloids and films [44]. Also with decrease in deposition time the film thickness also decreases. Since thinner film thickness results in larger transmission in the shorter wavelength, the absorption edge shifts to shorter wavelength, thereby leading to larger bandgap as seen in this study too.

CONCLUSIONS

Using CBD amorphous and polycrystalline thin films of SnS are deposited at room temperature without using a buffer solution. The influence of different deposition times on thin films of SnS deposited using CBD at room temperature has been studied first time. The XRD analysis of the films indicates that films deposited at 24h are poorly crystalline (almost amorphous) and the films deposited at 48h and 74h are polycrystalline with orthorhombic SnS structure. The XRD analysis indicates that increase in deposition time has improved the crystallinity of the films. The average grain size is found to increase from ~13 nm to ~28nm with increase in deposition time with film color changes form light yellowish brown to deep chocolate drown. The SEM images show that deposited films are homogeneous and free form any pinholes or cracks with increase in number of crystallites with increase in deposition time. The EDAX report show atomic ration of Sn/S in the range from 0.99 to 1.19 suggesting that films deposited are almost stoichiometric. The optical absorption spectra of the films show that direct allowed transitions are dominant in the films. The allowed direct band gap is found to decrease from 2.03 eV to 1.79 eV with increase in deposition time and is mainly attributed to increase in film thickness with increase deposition time. The higher values of the band gap are attributed to small grain size and to the room temperature deposition as other phases of SnS are not found in the film. The SnS films deposited by CBD with the values of band gap obtained are suitable for absorber layers in solar cells. Work is in progress to investigate in detail the electrical properties of the films. The crystalline and optical property of the films seems to be influenced by the deposition time. The SnS films suitable for photovoltaic structures can be prepared using a cheap, safe simple CBD technique at room temperature.

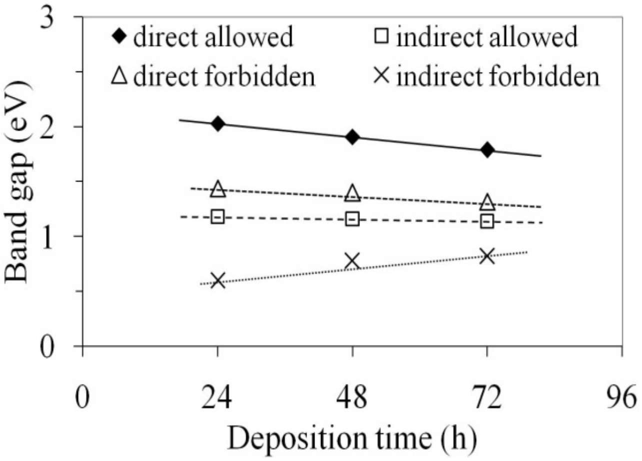

Fig. (7). The variations of band gap with deposition time.

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CONFLICT OF INTEREST

None declared.

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A novel route to nanocrystalline semiconducting SnS thin films suitable for photovoltaic structures

T. H. Patel

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A Novel Route To Nanocrystalline Semiconducting SnS Thin Films Suitable For Photovoltaic Structures

T. H. Patel

Physics Department, V.P. and R.P.T.P. Science College Vallabh Vidyanagar Gujarat India Pin-388120
E mail: pateltarunh@yahoo.com

Abstract. The chemical bath deposition (CBD) is relatively simple, more rapid and inexpensive method suitable for deposition on large substrates irrespective of the shape and morphology of substrates at room temperature. We have successfully used the CBD method at elevated temperature of ~ 50^0C to deposit SnS thin film of thickness ~ 350 nm on a glass substrate. The X- ray diffraction investigations of the film reveals polycrystalline orthorhombic phase of herzenbergite SnS structure with average grain size of ~ 12 nm. The surface morphology of the film examined using scanning electron microscopy (SEM) shows uniform deposition of the needle shaped grains. The analysis of the optical absorption spectra of the film suggests dominance of direct allowed transitions with band gap of ~ 2 eV exhibiting quantum size effect at the observed grain size in the film. The thermoelectric power measurements exhibited p-type electrical conductivity. The properties of the deposited film seems promising for use as absorption layer in photovoltaic structures like solar cells.

Keywords: thin film; XRD; polycrystalline; orthorhombic; band gap; p-type.
PACS: 78.20.-e, 68.55.-a, 61.05.cp,68.37Hk, 81.07Bc

INTRODUCTION

Recently, in the field of photovoltaic, investigations are directed towards development of cost effective and non-toxic materials that can be synthesized by a simple technology for solar cell fabrication. Tin monoselenide received considerable attention as a promising solar cell material due to its high absorption coefficient of ~10^4-10^5 cm^{-1} and near optimal direct bandgap of 1.3eV. Normally, the chemical bath deposition (CBD) is method suitable at room temperature but we have used the CBD method successfully at elevated temperature of ~ 50^0C. A systematic study on the deposition and properties of nanocrystalline SnS thin film has been reported.

EXPERIMENTAL

For the synthesis of SnS thin films, $SnCl_2$ $2H_2O$ was dissolved in methanol in a glass beaker. In another glass beaker thioacetamide solution was prepared in methanol. Both these solutions were mixed under vigorous stirring. Ammonia was used to control the pH of the bath at 9.70. The solution was transferred to another thoroughly cleaned 150 ml glass beaker in which well cleaned amorphous glass substrate was placed inclined and rested on beaker wall.The bath was placed in a temperature controlled electrical owen at ~ 50 ^{0}C for 8 hours. The X- ray diffractograms of the films were obtained using Philips Xpert MPD diffractometer employing CuKα radiation with $\lambda = 0.15406$ nm in 2θ range from 20^0 to 70^0. For surface morphology Scanning Electron Microscopy (SEM) images were taken Philips XL30 ESEM. The chemical compositions of the films were determined from the energy dispersive analysis of X-rays (EDAX) spectra obtained using the system attached with Philips XL30 ESEM. The optical spectra of the films were obtained using Perkin Elmer Lambda 19 UV-VIS-NIR spectrometer in the wavelength range 200 nm to 1200 nm. The thermoelectric power (TEP) measurements were carried out using the set-up available at and developed by Physics Department of S. P. University, Vallabh Vidyanagar, India.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the films deposited at ~ 50^0C is shown in Fig.1. The peaks observed in Fig. 1 at 2θ value of 31.64^0 found to match with reflections from (111) crystallographic planes of orthorhombic phase of SnS (JCPDS PDF Card # 39-0354).The presence of few less intense peaks reveals good quality polycrystalline film. When compared to XRD patterns of bulk SnS, the deposited films show the broadening of the peaks. Such effects are mainly arising due to small crystalline size and strain. The lattice parameters calculated for the orthorhombic structure [1] are presented in table 1. The other parameters determined from Scherer formula [1] and Williamson-Hall method [2] are shown in table 1.

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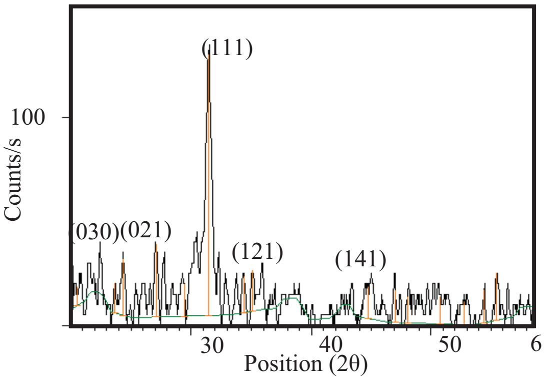

FIGURE 1. The XRD of the deposited SnS film.

TABLE 1. The parameters of the SnS film.

Parameter		Value
Lattice Constant (nm)	*a*	0.437
	b	1.120
	c	0.399
Particle Size (nm)	Scherer	10.95
	W-H Plot	12.65
Dislocation density $(10^2\ \text{nm})^{-2}$	Scherer	0.83
Strain (10^{-4})	W-H Plot	43.00

The surface morphology of the film shown in Fig. 2 indicates homogeneous deposition of needle shaped grains uniformly grown over the entire surface. The thickness of deposited film was estimated ~ 350 nm from the cross-section SEM image shown in Fig. 2.

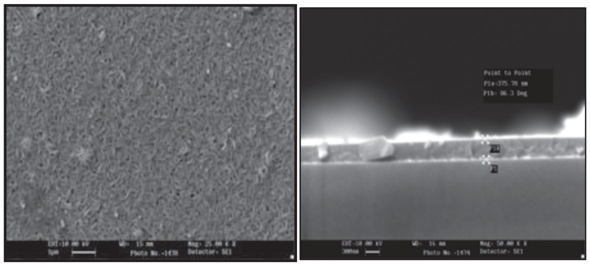

FIGURE 2. The SEM images of the SnS film.

The analysis of the EDAX spectrum of the film exhibited atomic ratio of Sn/S of ~ 1.14. The optical band gap E_g of the films was evaluated using the relation [3]:

$$\alpha h\upsilon = A\left(h\nu - E_g\right)^n \qquad (1)$$

where A is the parameter that depends on the transition probability, α is the absorption coefficient and n is the index that has value equal to 1/2 for the direct allowed transitions and 2 for the indirect allowed transitions. The extrapolation of straight line portions of curves in Fig. 3 indicates direct allowed transition as dominant one with band gap ~ 2.05 eV.

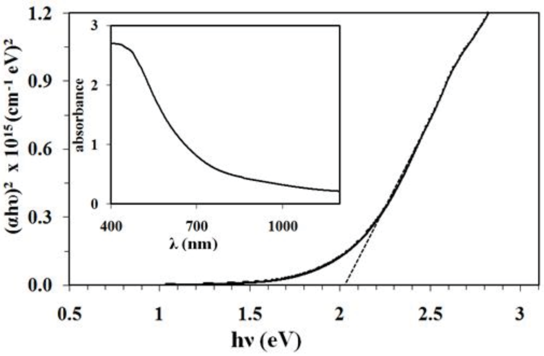

FIGURE 3. The spectral response of SnS film.

This value is higher than those reported earlier [4]. Since the presence of other phases of tin sulfide i.e. SnS_2 (E_g = 2.44 eV) and Sn_2S_3 (E_g = 2.0 eV) is not found in the deposited films, the higher values of the bandgap in these films can be attributed mainly due to quantum size effect at observed grain size and film thickness. Recently, CBD deposited SnS thin films with band gap of the order of 1.7 eV have been reported as absorber layer [5].The TEP measurements performed on deposited film show p-type conductivity.

CONCLUSIONS

Using low cost, non-toxic CBD with new approach, single phase dominated orthorhombic p-type SnS thin film with thickness ~ 350 nm has been deposited. The deposited film is homogeneous with needle shaped grains. The film exhibit quantum size effect through higher value of band gap ~ 2.05 eV. Recently SnS films with properties observed in this study are found suitable as absorber layer in photovoltaic structures like solar cells.

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Effect Of Temperature On Structural And Optical Properties Of Chemically Deposited Tin Sulfide Thin Films Suitable For Photovoltaic Structures

T. H. PATEL

VP & RPTP Science College, Vallabh Vidyamagar-388120

pateltarunh@yahoo.com

Keywords: SnS, thin film, XRD, SEM, grain size, optical band gap

Abstract. SnS (tin sulphide) is of interest for use as an absorber layer and the wider energy band gap phases e.g. SnS_2, Sn_2S_3 and Sn/S/O alloys of interest as Cd-free buffer layers for use in thin film solar cells. Thin films of tin sulphide have been deposited using CBD at three different bath temperatures (27, 35 and 45 ^{0}C) onto microscope glass substrates. The X ray diffraction (XRD) analysis of the deposited films reveled that all films has orthorhombic SnS phase as dominant one with preferred orientations along (111) direction. The temperature influence on the crystalline nature and the presence of other phases of SnS has been observed. The average grain size in the films determined from Scherer's formula as well as from Williamson-Hall-plot method agrees well with each other. Energy dispersive X-ray (EDAX) analysis used to determine the film composition suggested that films are almost stoichiometric. The scanning electron microscopy (SEM) reveals that deposited films are pinhole free and consists of uniformly distributed spherical grains. The optical analysis in the 200-1200 nm range suggests that direct allowed transitions are dominant in the absorption process in the films with variation in the band gap (~1.79 to ~2.05 eV) due to variation in deposition temperature.

Introduction

The binary semiconductors are considered as important technological materials because of their potential applications in optoelectronic devices, solar cells and IR detectors [1-3]. Recently, in the field of photovoltaic, investigations are directed towards development of cost effective and non-toxic materials that can be synthesized by a simple technology for solar cell fabrication. Tin monoselenide received considerable attention as a promising solar cell material due to its high absorption coefficient [4] of $\sim 10^4$-10^5 cm^{-1} and near optimal direct bandgap [5] of 1.3eV. The high natural abundance of tin and sulfur could potentially enable scaling of SnS photovoltaic manufacturing to higher levels. The current record efficiency of a SnS photovoltaic device is only [5] 1.3% which is substantially less than the theoretical maximum efficiency [6] of 32%. Sincere efforts towards fundamental research are necessary to explore the reasons for this low performance and to determine the ultimate potential of this material. For the deposition of thin films of SnS various methods like spray pyrolysis [7], electrodeposition [8], vacuum evaporation [9-12], chemical bath deposition [13-25] and recently successive ionic layer adsorption and reaction (SILAR) method [26] have been employed. CBD is relatively simple, more rapid and inexpensive method suitable for deposition on large substrates irrespective of the shape and morphology of substrates nearly at room temperature [27]. The properties of the deposited films are strongly influenced by the bath parameters like concentration, reaction rate, deposition time, pH and temperature. In literature, the effect of deposition temperature on the properties of SnS thin films deposited by CBD has not been reported. In this context, a systematic study on the effect of deposition temperature on the properties of SnS thin films has been carried out and reported in this paper.

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Experimental:

For the synthesis of SnS thin films each deposition bath was prepared by mixing the $SnCl_2$ $2H_2O$ with triethanolamine under a vigorous stirring followed by addition of thioacetamide. Ammonia was added drop-wise to control the pH of the bath with constant stirring. The distilled water added to make a total of 100 ml. The final pH of the solution was 9.70. The solution was transferred to another thoroughly cleaned 150 ml glass beaker in which well cleaned amorphous glass substrate (76mm x 26mm x 1mm) was placed inclined and rested on beaker wall. The glass substrates used were sequentially cleaned with detergent, hot chromic acid, isopropyl alcohol and finally with distilled water. The films were deposited at bath temperature of 27 ^{0}C, 35 ^{0}C and 45 ^{0}C with with a deposition time of 10 h. The X- ray diffractograms of the films were obtained using Philips Xpert MPD diffractometer employing CuKα radiation with $\lambda = 0.15406$ nm in 2θ range from 20^0 to 70^0. For surface morphology Scanning Electron Microscopy (SEM) images were taken using Philips XL30 ESEM. The chemical compositions of the films were determined from the energy dispersive analysis of X-rays (EDAX) spectra obtained using the system attached with Philips XL30 ESEM. For optical analysis, the optical spectra of the films were obtained using Perkin Elmer Lambda 19 UV-VIS-NIR spectrometer in the wavelength range 200 nm to 1200 nm.

Results and Discussion:

The X-ray diffraction patterns of the films deposited at different temperatures are shown in Fig.1. The observed peaks have been analyzed and indexed using standard pattern for the mineral herzenbergite with orthorhombic structured SnS phase (JCPDS PDF Card # 39-0354). The peaks observed in Fig. 1(a), 1(b) and 1(c) at 2θ values of 31.64^0, 31.48^0 and 31.60^0 respectively found to match with reflections from (111) crystallographic planes of orthorhombic phase of SnS. Fig. 1 shows that with increase in temperature upto 45^0C has not much influence on the presence of phase of SnS in the films. However, the crystallinity of the films seems to be little bit affected by the increase in temperature. The peak corresponding to reflections from (021), (140) and (041) planes disappears with increase in bath temperature. It should be noted that peaks corresponding to other phases of SnS (SnS_2 or Sn_2S_3) have not been found during the XRD analysis.

The lattice parameters of the deposited films, calculated from the observed values of $2\theta^0$ and using *d*-values for the orthorhombic structure [28] are shown in table 1. The crystallite or grain sizes were estimated from Scherer formula [28]

$$D = (0.9\lambda)/(\beta_c \cos\theta) \tag{1}$$

where D is the crystallite size, λ is the wavelength of the CuKα radiation, β_c is the experimentally observed diffraction peak width at half maximum intensity and θ is the Bragg angle. The values of the crystallite size determined using Eq. 1 are presented in table 1.

When compared to XRD patterns of bulk SnS, the XRD patterns of the deposited films show the broadening of the peaks. Such effects are mainly arising due to small crystalline size and strain. Both crystalline size D and strain ε effects are interconnected in the line broadening of the peaks which makes it difficult to separate. Williamson-Hall technique [29] is one of the many methods for the evaluation and separation of size and strain parameters from the occurring line broadening. In this method which is adopted in present work, grain size D and strain ε are related as:

$$(\beta_c/\lambda) = (1/D) + \varepsilon(\sin\theta/\lambda) \tag{2}$$

where β_c is the instrumental effect corrected full width at half maximum of the peak measured, θ is the diffraction angle and λ is the wavelength of X-ray.

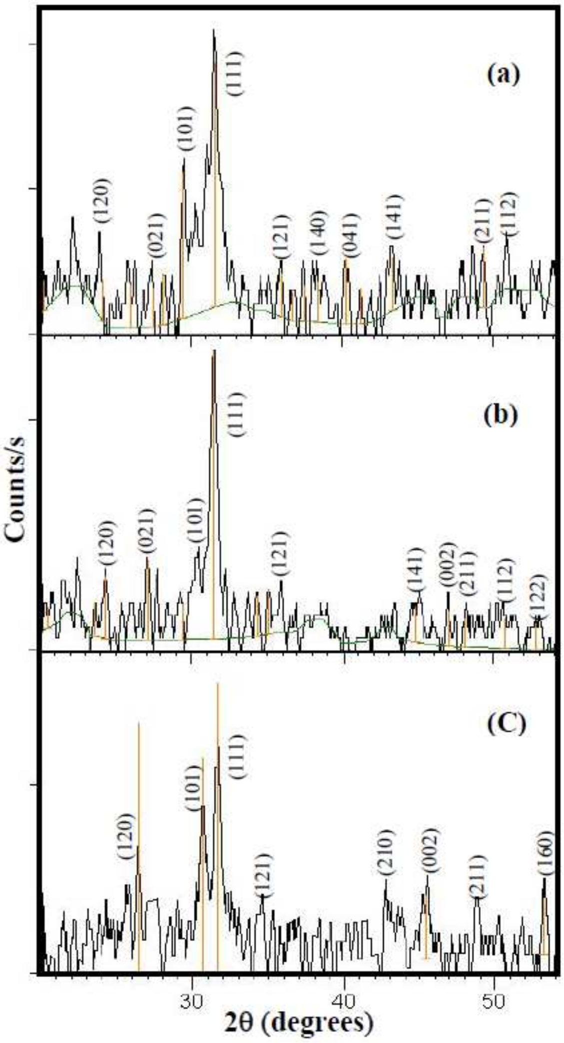

Fig. 1 XRDs of SnS films at (a) 27 ^{0}C (b) 35 ^{0}C (c) 45 ^{0}C

Table 1 Various Parameters of SnS films.

Parameter	Bath Temp.(^{0}C)		
	27	35	45
Lattice Const. *a* (nm)	0.437	0.428	0.425
Lattice Const. *b* (nm)	1.120	1.129	1.124
Lattice Const. *c* (nm)	0.399	0.390	0.389
D (nm) (Scherer)	13.06	26.90	35.55
D (nm) (W-H plot)	12.65	26.31	36.31
ε (x 10^{-4})	43	3.6	27
E_g (eV)	2.05	1.92	1.79

The slope of the plot (Williamson–Hall plot) of Eq. 2 gives micro strain ε and the inverse of intercept on y axis gives average grain size value. Fig. 2 shows Williamson–Hall plot for SnS films. The values of grain size and strain obtained from this plot, presented in table 1, indicates that grain size increased from ~13 nm to ~36 nm as the deposition temperature increased from 27 ^{0}C to 45 ^{0}C. It is obvious to expect that with increase in bath temperature reaction rate increases and more ions released which eventually results into an increase in thickness of the film and grain size until a deficit of either Sn or S ion occurs in the bath solution.

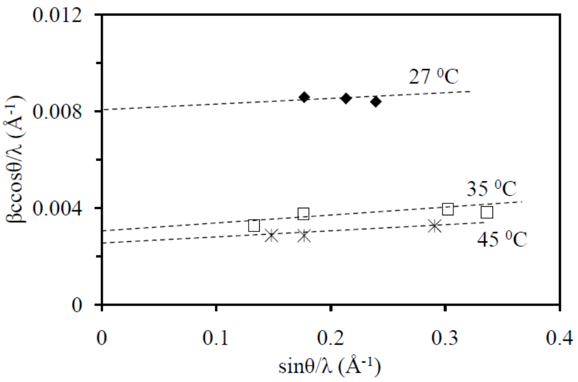

Fig. 2 W-H plots of SnS films deposited at different temperatures.

The value of strain decreased. with increase in deposition temperature from 27 ^{0}C to 35 ^{0}C. Similar behavior has been observed [7] in SnS films deposited with spray pyrolysis at increasing substrate temperature. However, with further increase in deposition temperature to 45 ^{0}C strain value found to increase but still lower than that that for film with deposition at 27 ^{0}C.

The surface morphology of the films are shown in Fig. 3. The SEM images show homogeneous surfaces of the films free from any pinhole or cracks with presence of large spherical crystallites surrounded with small crystallites. The SEM images indicate that with increase in deposition temperature the number of crystallites increases leading to formation of more homogeneous film.

The analysis of the EDAX spectrum of the films with deposition temperature of 27 ^{0}C, 35 ^{0}C and 45 ^{0}C exhibited atomic ratio of Sn/S of ~ 0.99, 1.19 and 1.18 respectively. This has been indicating that deposited films are almost stoichiometric. It is evident that films depositited at 35 ^{0}C and 45 ^{0}C has presence of small excess amount of tin. This may be due to the fact that at increased temperature the release of Sn ion is not counterbalanced by availability of S ions in the bath as concentration of S ions in the bath had been utilized fully.

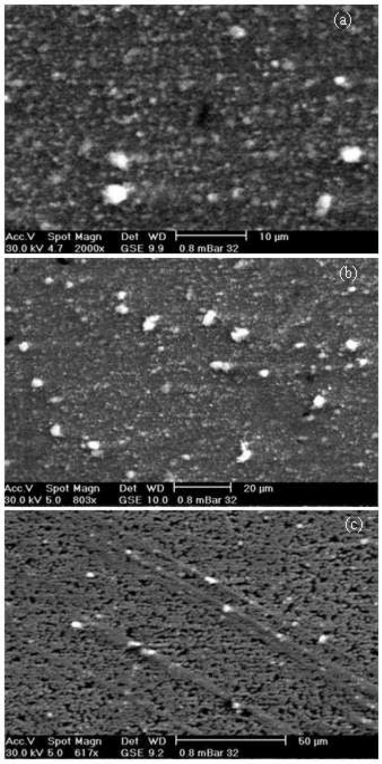

Fig. 3 SEM images of SnS films deposited at (a) 27 ^{0}C (b) 35 ^{0}C and (c) 45 ^{0}C.

The optical absorption spectra of the films obtained in the wavelength range of 200-1200 nm shown in Fig. 4 indicate that absorption edge tends to be sharpening as the deposition temperature increases which eventually increases the thickness of the films.

The optical band gap E_g of the films were evaluated using the relation [30]

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (3)$$

where A is the parameter that depends on the transition probability, α is the absorption coefficient and n is the index that has value equal to 1/2 for the direct allowed transitions, 2 for the indirect allowed transitions, 3/2 for direct forbidden transitions and 3 for indirect forbidden transitions. The SnS thin films prepared by CBD has exhibited both direct [13-16,18-21] and indirect [13,14,21,22] transitions. However to investigate the types of optical transitions involved with the value of corresponding optical band gap, the spectral variations of ($\alpha h\nu$) for n = 1/2, 2, 3/2 and 3 in Eq. 3 were plotted as a function of hν. It was found that, for the deposited films the straight line portion best fits for allowed direct transitions with lesser probability for other transitions.

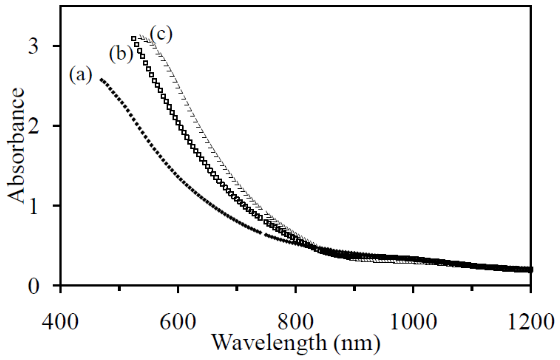

Fig. 4 Optical absorption spectra of SnS films deposited at (a) 27 ^{0}C (b) 35 ^{0}C and (c) 45 ^{0}C.

Fig. 5 shows spectral variations of $(\alpha h\nu)^2$ with hν. The value of intercept on the x-axis obtained by extrapolation of the straight-line portion of the curve at $\alpha = 0$ has been used to estimate the optical band gap of the corresponding film.

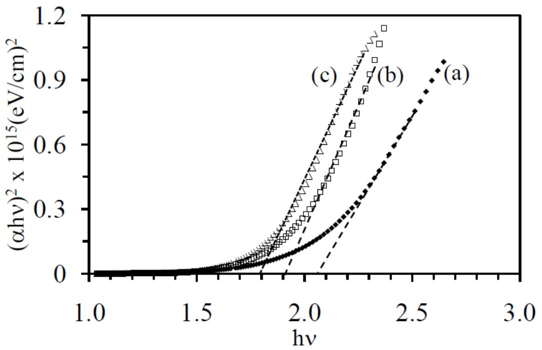

Fig. 5 The variation of $(\alpha h\nu)^2$ with hν for SnS films deposited at (a) 27 ^{0}C (b) 35 ^{0}C and (c) 45 ^{0}C.

The straight line portions of the curves in Fig. 5 indicate that direct allowed transitions are dominant in the deposited SnS films. The direct band gap decreased from 2.05 eV to 1.79 eV with increase in deposition temperature from 27 ^{0}C to 45 ^{0}C. These values are higher than those reported earlier [14-16,18,20,21] but are within the range as observed in SnS films deposited by CBD [13] at room temperature and SnS films deposited by thermal evaporation [9-10]. The increase in deposition temperature improves the crystallnity as well as enhances the film thickness with growth of crystallites of larger size till enough Sn and S ions exist in the solution to support the growth mechanism of the film to continue. This mainly affects the optical absorption which eventually affects the optical band gap of the film.

The analysis of the XRD patterns of the deposited films showed a better crystallinity and increase in grain size in the films with increase in deposition time. The difference in crystalline structure of the films deposited at room temperature as compared to those mostly prepared at increased temperature may be the reason for higher values of the direct band gap. It should be noted that presence of other phases of tin sulfide i.e. SnS_2 ($E_g = 2.44$ eV) and Sn_2S_3 ($E_g = 2.0$ eV) is not found in the deposited films. So the decrease in bandwidth in these films with increase in deposition temperature can be attributed mainly to increase in grain size and film thickness due to increase in reaction rate. For SnS thin films, decrease in band gap with increase in film thickness has been observed recently for films deposited at near room temperature[9,10,13]. The CBD films are often nanocrystalline and the most apparent effect of very small crystal size is the increasing band gap due to size quantization [27]. This effect is quite visible to eye if the band gap is in the visible region of the spectrum. The optical spectroscopy is fast and simple pointer to crystal size, since band gap-size correlations have been made for a number of colloids and films [27]. Recently, CBD deposited SnS thin films with band gap of ~1.7 eV have been reported as absorber layer [17].

Conclusions:

Using CBD single orthorhombic phase polycrystalline SnS thin films have been deposited on microscope glass substrates at 27^0C, 35^0C and 45^0C. The influence of bath temperature on structural and optical properties of these films has been investigated. The XRD analysis of the films indicates that suitable increase in deposition time up to a limit improves the crystallanity of the films. The average grain size is found to increase with increase in deposition temperature. The SEM images shows that deposited films are homogeneous and free form any pinholes or cracks with increase in number of crystallites with increase in deposition temperature. The EDAX report suggests that films deposited are almost stoichiometric. The optical absorption spectra of the films show that direct allowed transitions are dominant in the films. The allowed direct band gap is found to decrease with increase in bath temperature. The higher values of the band gap of the films are attributed to presence of smaller grain size and to the polycrystalline nature. The single phase SnS films deposited by CBD with the values of band gap obtained are suitable for absorber layers in solar cells. Work is in progress to investigate in detail the electrical properties of the films and to incorporate them in a suitable photovoltaic device.

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Low Temperature Chemical Synthesis of p-type SnS Thin Films Suitable for Photovoltaic Structures

T. H. Patel

VP and RPTP Science College, Vallabh Vidyanagar-388120, Gujarat, India

email pateltarunh@yahoo.com

Keywords: Chemical bath deposition, thin film, SnS, XRD, orthorhombic, grain size, band gap.

Abstract. SnS thin film has been deposited on glass substrate at room temperature using low cost, environmental friendly chemical bath deposition (CBD) technique. The structural parameters of the deposited film have been investigated through X- ray diffraction measurements. The deposited SnS film found almost crystalline with preferred orientations along (111) planes revealing an orthorhombic phase of herzenbergite SnS structure. The lattice parameters and dislocation density were determined. The average grain size estimated to be ~ 25 nm. The surface morphology of the film examined using scanning electron microscopy (SEM) show uniform granular deposition of the film. The energy dispersive analysis of x-rays (EDAX) confirmed stoichiometric deposition. The analysis of the optical absorption spectra of the deposited film in the wavelength range of 200-1200 nm indicate direct allowed transitions as dominant one in the film. The direct band gap determined to be ~ 1.92 eV which is higher than those reported earlier for bulk or single crystal SnS, exhibiting quantum size effect at the observed grain size in the film. This value of band gap is promising for possible use of the deposited film as absorption layer in photovoltaic structures like solar cells. The thermoelectric power measurements indicate p-type electrical conductivity of the deposited films

Introduction:

Recently, the search for thin film materials using metal chalcogenides for solar energy conversion and other photovoltaic applications has been intensely identified as this class of materials had shown somewhat superior performance when compared to others. So far CdTe and Cu(In,Ga)Se_2 based solar cells are most extensively studied. However, there are concerns existing with respect to the use of Cd and In in this type of applications due to cost, toxicity, abundance and environmental issues. On the other hand, SnS is one of the promising materials for low cost thin film solar cell technology, due to its optimum energy gap, a high fundamental absorption coefficient, non toxicity and abundance. For the deposition of thin films of SnS various basic methods like spray pyrolysis[1], electrodeposition[2], vacuum evaporation[3] and chemical bath deposition (CBD) [4] have been employed. The chemical bath deposition (CBD) is relatively simple, more rapid and inexpensive method suitable for deposition on large substrates. In this paper study on preparation and characterization of SnS thin films at room temperature using CBD has been reported.

Experimental:

The deposition bath was prepared from 5 ml of 1M $SnCl_2$ $2H_2O$, 10 ml of 3.75 M triethanolamine and 1M thioacetamide mixed in a systematic manner. NH_3 was added to control the pH (= 9.7) of the bath. Finally distilled water added to the bath to make a total of 100 ml. This solution was transferred to another thoroughly cleaned 150 ml glass beaker in which well cleaned amorphous glass substrate (76mm x 26mm x 1mm) was placed inclined and rested on beaker wall. The deposition was done at room temperature (27 ^{0}C) with deposition time of 48h. The X-ray diffractogram (XRD) of the film was obtained using Philips MPD diffractometer (CuKα radiation) in 2θ range from 20^0 to 70^0. The SEM images and EDAX spectrum were taken using Philips XL30 ESEM. The optical absorption spectrum of the film obtained using Perkin Elmer Lambda-19 UV-VIS-NIR spectrometer in the wavelength range 200 nm to 1200 nm. The thermoelectric power (TEP) measurements confirm the electrical conductivity of the deposited film.

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Results and Discussion:

The XRD pattern of the deposited film shown in Fig. 1 exhibits a sharp peak at 2θ values of 31.48^0 corresponding to (111) plane of orthorhombic structured SnS (PDF Card # 39-0354). The presence of few less intense peaks reveals good quality polycrystalline film. A peak at 2θ value of 35.06^0 was found to originate from (121) of SnS and also contributed through reflections from (101) of Sn (PDF Card # 18-1380).

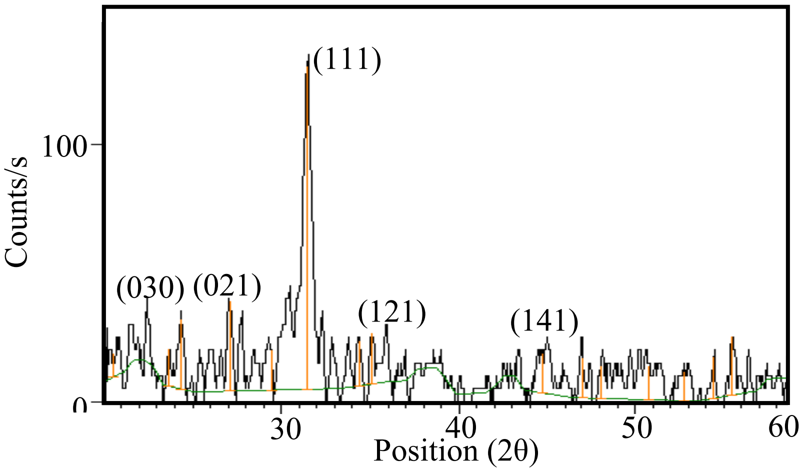

Fig. 1 XRD of SnS film

The lattice parameters of the deposited film have been calculated from the observed values of 2θ and d-values (interplaner spacing) for the orthorhombic structure, which is given by Eq. (1) [5].

$$(1 / d^2_{hkl}) = (h^2 / a^2) + (k^2 / b^2) + (l^2 / c^2) . \quad (1)$$

In Eq. (1), (hkl) are Miller indices of the plane concerned and a, b and c are lattice parameters. The crystallite or grain sizes were estimated using the Scherer's formula [5] given by Eq. (2)

$$D = 0.9 \lambda / \beta c COS\theta . \quad (2)$$

In Eq. (2), D is the crystallite size, λ is the wavelength of the CuKα radiation, β_c is the experimentally observed diffraction peak width at half maximum intensity (FWHM) and θ is the Bragg angle. When compared to XRD patterns of bulk SnS [6], the XRD patterns of the deposited films show the broadening of the peaks. Such effects are mainly arising due to small crystalline size and strain. Both crystalline size and strain effects are interconnected in the line broadening of the peaks which makes it difficult to separate. Williamson-Hall technique [7] is one of the many methods for the evaluation and separation of size and strain parameters from the occurring line broadening. In this method which is adopted in present work, grain size D and strain ε are related as

$$(\beta c \cos\theta / \lambda) = (1/ D) + \varepsilon (\sin\theta / \lambda) . \quad (3)$$

Here β_c, θ and λ are as defined ealier. The slope of the Williamson-Hall plot (W–H plot) as shown in Fig. 2 gives value of micro strain ε and the inverse of intercept on y axis gives value of average grain size. The values of various structural parameters are shown in Table 1. The SEM image shown in Fig. 3 reveals that the film surface is smooth and uniformly deposited in form of small spherical grains surrounded by large grains. The presence of small grains can be attributed to deposition at room temperature at which ions in the bath generally do not posses enough mobility to form a grain with larger size.

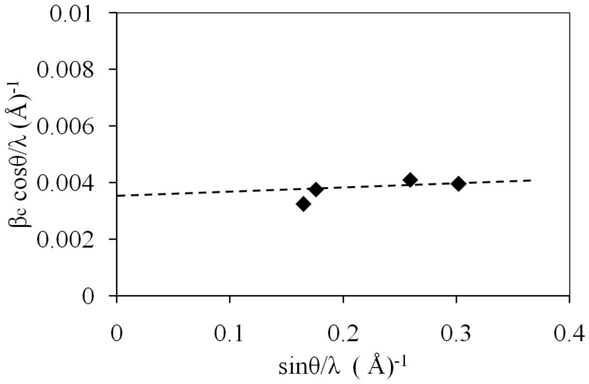

Fig. 2 Williamson-Hall Plot

Table 1 Structural parameters of SnS films.

Parameter		Value
Lattice Constants (nm)	*a*	4.2833
	b	11.2943
	c	3.909
Particle Size (nm)	Scherer	25.55
	W-H Plot	26.31
Dislocation density $(10^2 \text{ nm})^{-2}$	Scherer	0.155
Strain (10^{-4})	W-H Plot	3.6

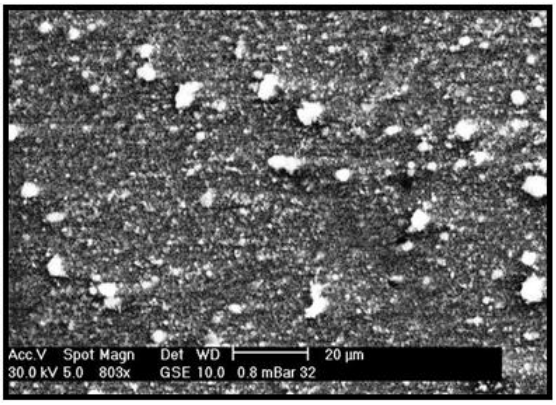

Fig. 3 SEM image of the SnS film

The analysis of the EDAX spectrum show that atomic ratio of Sn to S in the deposited film is of 1.17 indicating that the films contains very little excess amount of Sn ions as reflected in XRD analysis of the film. The absorption spectrum of the film is shown inserted in Fig. 4. The optical band gaps E_g of the film has been evaluated using the relation given by Eq. (4) [8].

$$\alpha h\nu = A(h\nu - E_g)^n . \qquad (4)$$

In Eq. (4), A is the parameter that depends on the transition probability, α is the absorption coefficient and n is the index that has value equal to 1/2 for the direct allowed, 2 for the indirect allowed, 3/2 for direct forbidden and 3 for indirect forbidden transitions. Accordingly, the spectral variations of $(\alpha h\nu)^n$ were plotted against hν for different values of n and it was observed that plot of $(\alpha h\nu)^2$ against photon energy hν exhibits a straight-line portion as shown in Fig. 4. The extrapolation of the straight-line portion of the curve at $\alpha = 0$ gives optical band gap of 1.92 eV, which is higher than that for bulk SnS semiconductor [6] and close to that reported earlier [4]. The higher value of band gap is attributed to the quantum size effect at the observed average grain size in the deposited film. Recently, the shift in optical absorption edge and hence in energy band gap has been observed in SnS films prepared using other method [3]. The thermoelectric power (TEP probe) measurements confirmed p-type electrical conduction in the film.

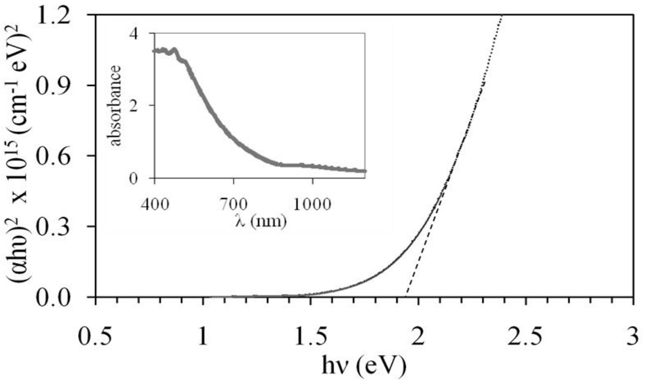

Fig. 4 Spectral variation of $(\alpha h\nu)^2$ with $h\nu$

Conclusions:

The SnS film grown on glass substrate at room temperature using CBD showed (111) peak as a dominant with near nanocrystalline orthorhombic structure with average grain size ~25 nm. The SEM images show film is homogeneous and free from any pinholes or cracks. The EDAX reveals that deposited film is almost stoichiometric. The optical analysis of the film exhibits direct allowed transitions as dominant one. The direct band gap energy is found to be 1.92 eV which is higher than that for bulk SnS semiconductor. Since the other phases of the SnS (SnS_2 or Sn_2S_3) were not found in the film, the higher value of the bandgap attributed mainly due to quantum size effect. The film with obtained band gap is suitable as absorber layer in solar cells and other photovoltaic devices. The thermoelectric power (TEP) probe confirms the p-type electrical conduction.

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