# POST ANNEALING EFFECTS ON THE OPTICAL AND STRUCTURAL PROPERTIES OF SULPHURIZED Sn-Bi THIN FILMS

A. MEHMOOD<sup>a</sup>, G. H. TARIQ<sup>b</sup>, Z. WAZIR<sup>a</sup>, M. F. NASIR<sup>a\*</sup>, A. MEHMOOD<sup>a</sup> <sup>a</sup>Department of Physics, Riphah International University, Islamabad 44000, Pakistan

<sup>b</sup>Applied Thermal Physics Laboratory, Department of Physics, COMSATS Institute of Information Technology, Islamabad 44000, Pakistan

Sn-Bi-S system based thin film layers have been studied. These thin films were deposited on glass substrates by using magnetron sputtering. Sn-Bi thin films were deposited at chamber ambient temperature by co-sputtering of Sn and Bi and then sulphurized by encapsulating deposited Sn-Bi thin films in evacuated glass tubes by placing some amount of S in the tube to produce Sn-Bi-S system thin films. These glass tubes were annealed at different temperatures. From Raman spectroscopy SnS, Bi<sub>2</sub>S<sub>3</sub>, Sn<sub>2</sub>S<sub>3</sub> peaks were observed. Using Energy Dispersive X-ray spectroscopy (EDX) elemental analysis was done. Optical properties were studied by analyzing the transmission spectra of prepared samples using UV-Vis-NIR spectrophotometer. The optical results showed that these materials have bandgap around 1.4eV. Photoconductivity response for 530 nm wavelength was studied and showed that materials have better photoconductivity around bandgap energy. Conductivity type determination showed that these Sn-Bi-S system thin films have p-type conductivity.

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# 1. Introduction

In recent age, the main objective for both basic and industrial research is to develop new low cost and less toxic materials for optoelectronics and photovoltaic solar modules. Special interest is shown in thin film materials, which have low fabrication cost than photovoltaic technology based on the Si wafers [1]. Various aspects including abundance in nature, deposition possibility, fabrication cost and toxicity in nature are considered in developing these materials [2].

Materials used in PV industry should have band gap between 1 to 1.6 with low electrical resistivity and high absorption coefficient. Different materials including binary, ternary and quaternary compounds like CdTe, PbS, MoBi<sub>2</sub>Se<sub>5</sub>, Cu(In,Ga)Se<sub>2</sub> having band gap depending upon their composition, are used [3-6]. Materials to be used as window layer include CdS [7-8], ZnS [9] and CdS(Se) [10].

Tin sulfide (SnS) and Bismuth sulfide (Bi<sub>2</sub>S<sub>3</sub>) are both very emerging materials that are being used in scientific research areas due to their suitable optoelectronic and PV properties. Tin sulfide and Bismuth sulfide belong to IV-VI and V-VI group and have band gap ~1.3 and ~1.7 eV which includes ideal value of 1.5 eV. They have direct band gap which results in high absorption coefficient [11,12] that make them a better alternative for light absorption in active layer. Different synthesis techniques have been reported SnS-Bi<sub>2</sub>S<sub>3</sub> thin films like sulfurization of metallic precursors [13,14,15], physical vapour deposition PVD [16], reaction of pure elements [17], RF magnetron sputtering [18]. Last two methods are widely used for (SnS)<sub>x</sub>-(Bi<sub>2</sub>S<sub>3</sub>)<sub>1-x</sub> thin films. SnS and Bi<sub>2</sub>S<sub>3</sub> have melting point of 879 °C and 760 °C respectively. Optoelectrical properties of PV structures depend upon defects, interfaces, absorption coefficient, synthesis techniques as well as composition and annealing temperature.

<sup>\*</sup>Corresponding author: farooq.nasir@riphah.edu.pk

Herein, we present the synthesis of multiphase Sn-Bi-S system thin films by RF magnetron sputtering and discussion about the post annealing effect on the optical and structural properties of Sn-Bi-S system thin films for photovoltaic applications.

## 2. Experimental details

The Sn-Bi-S system thin films were deposited on the clean glass substrate by co-sputtering of Sn and Bi metal circular shaped targets. The prepared samples were post annealed in the sulphur environment. Substrates were cleaned by using cleaning laboratory Decon 90 and then washed in a flow of distilled water. Further, substrates were cleaned in an ultrasonic bath with isopropyl alcohol and then dried in hot compressed air flow. For deposition of desired materials the vacuum of 10<sup>-3</sup> mbar was created by rotary pump in vacuum chamber. The sputtering power for both targets was kept at 50 watt and source to substrate distance was kept at 10 cm. Films of thickness 1000 nm were deposited. The thicknesses of films were monitored by quartz crystal microbalance fitted near substrate.

For I-V characteristics, photoconductivity and conductivity type determination, molybdenum metal contacts were deposited on the surface of prepared samples by DC magnetron sputtering. The sputtering power for Mo contacts was 200 Watts and deposited at same pressure. The circular metal contact having area 3.14 mm<sup>2</sup> each and 3 mm separation between them are shown in the Fig. 1.

All prepared samples were then placed in evacuated  $(10^{-2} \text{ mbar})$  Pyrex glass tube shown in Fig. 1, having small amount of S. Vacuum annealing was done to avoid any type of contamination. The Pyrex glass tubes were placed in the tube furnace for annealing in temperature range of 200-500 °C with a window of 100 °C for 2 hours. One sample is also annealed at 350 °C for same time.



Fig. 1. Pyrex glass tube having sample and amount of 'S'

The compositional analysis of prepared Sn-Bi-S system thin films was done using energy dispersive X-ray spectroscopy (EDX) attached with SEM (LEO 435 VP SEM with EDAX Genesis EDS system), coupled with silicon drift detector SDD. The X-ray analysis shows the microstructure of prepared sample qualitatively and quantitatively. Crystal structure was analyzed by X-ray diffraction (XRD) using CuK<sub>a</sub> radiation with  $\lambda$ = 1.5406 Å. Measurements were taken in the range of 21° to 56° for values of 20. To determine phases, Raman analysis of prepared samples obtained by using Raman spectrometer with laser light of 530 nm at room temperature. Other optical parameters like optical band gap, absorption coefficient obtained from transmission spectra recorded with wavelength range of 300 to 2500 nm using UV-Vis-NIR spectrophotometer (Perkin Elmer Lamda 950). The photoconductive response of prepared Sn-Bi-S system thin films was determined using a system that consists of monochromatic light source (100-W tungsten halogen lamp that is directed to a 1/8m monochromator, having slits equal to 15 nm bandwidth) a Si reference diode, a locking amplifier and light chopper (Stand ford Research SR 510). A quartz fiber bundle is used to focus the light on the specimen and reference diode at same time. The electrical conductivity was analyzed by using hot probe technique.

# 3. Results and discussions

#### **3.1.** Compositional analysis

The compositional analysis of Sn-Bi-S system prepared samples was carried out by using energy dispersive X-ray spectroscopy (EDX). The obtained compositional analysis data is tabulated as follows in table 1.

Sr.No.	Sample	Annealing Temperature	Sn%	Bi%	S%
1	TTB-20	300°C	16	30	54
2	TTB-21	350°C	17	24	59
3	TTB-22	$400^{\circ}$ C	16	22	62
4	TTB-23	500°C	16	23	61

Table 1. Compositional analysis of prepared Sn-Bi-S system thin films

In the present research we have taken the concentration constant and discuss the effect of temperature on physical and structural properties for photovoltaic applications.

## 3.2. Structural analysis

For investigation of crystal structure and phases, Raman analysis was done at ambient temperature of prepared samples. A laser beam of wavelength of 530 nm is used to excite the samples. The Raman spectrum of vacuum annealed samples at temperature range for 200  $^{\circ}$ C to 400  $^{\circ}$ C are shown in the Fig. 2. The presence of different peaks for the SnS, Bi<sub>2</sub>S<sub>3</sub> and Sn<sub>2</sub>S<sub>3</sub> phases at (93cm<sup>-1</sup>, 221cm<sup>-1</sup>), 100cm<sup>-1</sup>, (238cm<sup>-1</sup>, 311cm<sup>-1</sup>) were observed respectively. These are well matched with the literature [19,20].



Fig. 2. Raman shift of Sn-Bi-S thin films sulphurized at different temperatures

## 3.3. Transmission spectrum

The optical transmission (%T) of the prepared samples is shown the Fig. 3. The spectra show that, the films annealed at 350 °C, 400 °C and 500 °C have their abruption edge at 915 nm while films annealed at 200 °C and 300 °C does not show photo response. In the weak absorption region better interference patterns were observed that reveals the formation of smooth and uniform films with air/layer and glass /layer surface interfaces are smooth [21]. The absorption edge is shifted in all the annealed samples, which may be due to formation of new phases. From these spectra, the observed average optical transmittance found to be dependent upon annealing temperature. The vacuum annealing effect on optical properties showed absorption edge at 915 nm, which may be due to increase in concentration of free charge carriers. This may be due improved crystal structure.



Fig. 3. Transmission spectra of Sn-Bi-S thin films sulfurized at different temperatures

## 3.4. Band gap analysis

The optical band gap was measured by plotting of ( $\alpha$ hu) vs. hu. (Fig. 4) In this relation " $\alpha$ " is the absorption coefficient and " h" is Plank's constant and  $\nu$  is the frequency of incident light. Samples annealed at 350 °C have band gap at 1.36eV, 400 °C with band gap 1.30 eV and 500 °C have band gap at 1.43eV. First at 350°C to 400°C it decreases while at 500 °C it again increases, that may be due to development of new phases.



Fig. 4: Band gap of Sn-Bi-S thin films sulfurized at different temperatures

For material to be used in photovoltaic applications, one important parameter is the photoconductivity. The films annealed at 200 °C and 300 °C did not show any photoconductive response, while those annealed at 300 °C – 500 °C show photoconductive response as shown in the Fig. 5 below. It is revealed that photoconductive response is much pronounced and strong for samples annealed at 400 °C, which may be due to good crystallinity.



Fig. 5: Photoconductive response at different temperatures

# 3.5. I-V analysis

I-V characteristic curves were recorded at room temperature and are shown in Fig. 6. For all temperatures, these curves showed linear behavior and line crossed through the origin for both positive and negative characteristics. This verifies their ohmic behavior. The resistivity values are given in the table 2 and their dependence on annealing temperature is given in the graph shown in Fig. 7. This graph shows that the films annealed at  $350^{\circ}$ C have much less resistivity, which increases for 400 °C and for 500 °C it further increases to very high value.



Fig. 6. I-V of Sn-Bi-S thin films sulfurized at 350 °C,400 °C,500 °C

Table 2. Shows the resistivity values at different temperatures

Sr.No.	Temperature	Resistivity (Ωm)
1	350 °C	9161
2	400 °C	20258
3	500 °C	598.45×10 <sup>3</sup>



Fig. 7. Resistivity of Sn-Bi-S thin films sulfurized at 350°C, 400°C and 500°C

# **3.6.** Conductivity type determination

The conductivity type determination of prepared samples was done by using DC two probe technique also known as hot probe technique. The n-type Silicon substrate was used as reference. One probe was heated and other was kept at room temperature on the reference sample, and potential difference was obtained by voltmeter. Then the same procedure was used for all the prepared samples. All the samples showed opposite response to that of reference sample. So, these have p-type conductivity.



Fig. 8. Conductivity type determination of Sn-Bi-S thin films

#### 4. Conclusions

In the present work, Sn-Bi-S based thin layers were successfully deposited. In the first step Sn and Bi were co-sputtered and deposited on glass substrates, and in second step these Sn-Bi thin films were sulphurized by encapsulating deposited Sn-Bi thin films in evacuated glass tubes by placing some amount of S in the tube. Further these glass tubes were placed in furnace and annealed at different temperatures. These prepared thin films structurally characterized by using Raman spectroscopy that showed that these thin films have SnS, Bi<sub>2</sub>S<sub>3</sub>, and Sn<sub>2</sub>S<sub>3</sub> phases. The photoconductivity response was studied by using monochromatic light of 530 nm wavelength that confirmed that the materials are photosensitive. The optical properties like bandgap were studied from transmission spectra showed that these materials have bandgap around 1.4eV. Furthermore conductivity type was determined by using hot probe technique that was fond p-type.

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