Braz J Phys (2011) 41:15–20
DOI 10.1007/s13538-011-0013-6

SOCIEDADE BRASILEIRA DE FÍSICA

CONDENSED MATTER

Preparation and Characterization of SnS:Bi Thin Films

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Received: 21 October 2010 / Published online: 13 April 2011

Abstract Thin films based on Sn-S compounds are currently of great interest because of their potential applications in optoelectronic devices including solar cells. In this work, SnS:Bi thin films are prepared using a novel procedure based on sulfurization of their metallic precursors, varying the Bi content. The effect of the synthesis conditions on the optical properties, phase, and chemical composition of the SnS:Bi thin films was studied through spectral transmittance, X-ray diffraction, and X-ray photoelectron spectroscopy. It was established from transmittance measurements that the optical gap of the deposited films varies between 1.27 and 1.37 eV depending on the Bi content. The analysis revealed that the SnS:Bi thin films grow with a mixture of several phases which include SnS, Sn_2S_3 SnS_2, and Bi_2S_3, depending on the Bi concentration. The studies also revealed that the conductivity type of the SnS:Bi films depends on the Bi content in the SnS lattice.

Keywords SnS · Thin films · Solar cells · XPS

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1 Introduction

Currently in the world, new low-cost, abundant in nature, and non-toxic materials are investigated to develop devices. The compounds based on the Sn-S system fulfill these characteristics and are also attractive from the point of view of their potential technological applications in optoelectronic devices including solar cells with p–n or p–i–n structure. In addition to their photovoltaic properties, the chalcogenide materials such as SnS, SnS_2, Sn_2S_3, Sn_3S_4, and Bi_2S_3 are of great interest due to its applications in the fabrication of optoelectronic and thermoelectric devices and as a holographic recording medium.

Particularly, the SnS presents suitable properties to perform as absorbent layer in solar cells, thanks to its optimum energy band gap (≈1.3 eV), its high fundamental absorption coefficient ($>10^4$ cm^{-1}), and that usually exhibits p-type conduction. Theoretically, the conversion efficiency of a solar cell based on SnS thin films can be up to 25% [1].

SnS has been synthesized by different techniques such as chemical bath deposition [2], two-step processes [3], electrochemical deposition [4], and thermal evaporation [5]. In this work is presented a novel method based on sulfurization of the precursor species to synthesized SnS:Bi thin films; the effect of the concentration of Bi on its optical, structural properties, and chemical composition is studied. The substitution of Sn atoms for Bi atoms generates free electrons in the SnS lattice, and hence, a change of conductivity type from p to n in the SnS can be induced. This is important because it opens the possibility of in situ fabricating p-SnS/n-SnS:Bi solar cells, which would reduce the

photocurrent losses due to recombination at the interface, as well as the manufacturing cost of the device.

2 Experimental

The SnS:Bi thin films were grown by sulfurization of the metallic precursors, which are sequentially evaporated keeping the substrate temperature at 350°C; in a second stage, the layer containing the metallic precursors is annealed in an S environment at the same substrate temperature. During the process, Sn is evaporated with a flux of about 3 Å/s, the flux of Bi is kept around 2 Å/s, and the evaporation temperature of S is kept at 140°C. The evaporated metal flows and the substrate temperature profile used to fabricate the SnS:Bi thin films are shown in Fig 1. The deposition of the SnS:Bi films was accomplished using a system constituted by an evaporation chamber connected to a vacuum system working at pressures of about 10^{-5} Torr, two tungsten boats (used to evaporate Sn and Bi, respectively), a tantalum effusion cell to evaporate S, and a thickness monitor (Maxtec TM-400) with a quartz crystal as sensor, used to measure the evaporated metallic elements flow. The substrate temperature and the evaporation temperature of S were controlled with a programmable PID controller (Eurotherm 900C). The Bi concentration (x) in the SnS:Bi films was varied between 0 and 1 according to the relation:

$$x = \frac{\text{mols of Bi}}{\text{mols of Sn} + \text{mols of Bi}} \quad (1)$$

The optical and structural properties were studied using a VIS-IR Oriel spectrophotometer and an X-ray diffractometer Shimadzu 6000, respectively. The X-ray photoelectron spectroscopy (XPS) measurements were performed using a Perkin-Elmer ESCA/SAM system, model 560. The conductivity type was determined from thermoelectric power measurements, and the film thickness was measured with a Veeco Dektak 150 surface profiler.

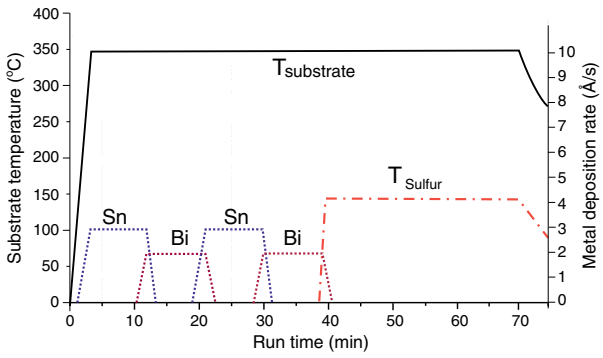

Fig. 1 Metal flows and substrate temperature profile used to fabricate SnS:Bi thin films by sulfurization

3 Results and Discussion

3.1 Optical and Structural Characterization

Transmittance and X-ray diffraction (XRD) measurements were used as an initial diagnostic method to prepare SnS:Bi thin films with suitable properties for photovoltaic applications. Figure 2 shows typical transmission spectra of SnS:Bi films deposited with Bi concentrations varying between $x = 0$ and $x = 1$. Curves of absorption coefficient α vs. λ and $(\alpha h\nu)^2$ vs. $h\nu$ are also depicted in Fig. 2. The results of Fig. 2 show that the optical properties of the SnS:Bi thin films are affected by the Bi content. The cutoff wavelength λ_c of the SnS:Bi films is smaller when the Bi content increases and therefore its optical gap increases. The optical gap was determined using curves of $(\alpha h\nu)^2$ vs. $h\nu$, from the intercept with the $h\nu$ axis at the linear part of the graph, taking into account the equation $(\alpha h\nu)^2 = A(h\nu - E_g)$ for allowed transitions in a direct-gap semiconductor. The optical gap (E_g) varies between 1.27 eV for SnS ($x = 0$) and 1.37 eV for Bi_2S_3 ($x = 1$). The absorption coefficient was calculated using experimental data obtained from spectral transmittance measurements, thickness of the films (between 800 nm and 1 μm), and a procedure described in [6]. Figure 2c shows that the absorption coefficient of the SnS:Bi films is of the order of 10^4 cm^{-1} (at values corresponding to the fundamental absorption). These results indicate that these types of compounds are suitable for solar cells fabrication.

The deposited SnS:Bi films were characterized through XRD measurements in order to get information regarding the phase, crystalline structure, and lattice parameters. Figure 3 shows typical XRD spectra of SnS:Bi films deposited varying the atomic content of Bi between $x = 0$ and $x = 1$. Theoretical simulations of the XRD spectra of Fig. 3 were also performed, in order to improve the confidence degree of the analysis on these spectra. In Table 1 are listed the crystalline structures and phases identified in the studied SnS:Bi compounds; the values for the corresponding lattice constants are also shown, which are in very close agreement with the data reported in JCPDS cards (# 039-0354 for SnS, # 014-0619 for Sn_2S_3, # 023-0677 for SnS_2 and # 017-0320 for Bi_2S_3). It was found that the SnS films ($x = 0$) grow in the orthorhombic phase, while the films synthesized by sulfurization of a Sn and Bi ($x = 0.3$, $x = 0.5$, and $x = 0.7$) grow with a mixture of several phases

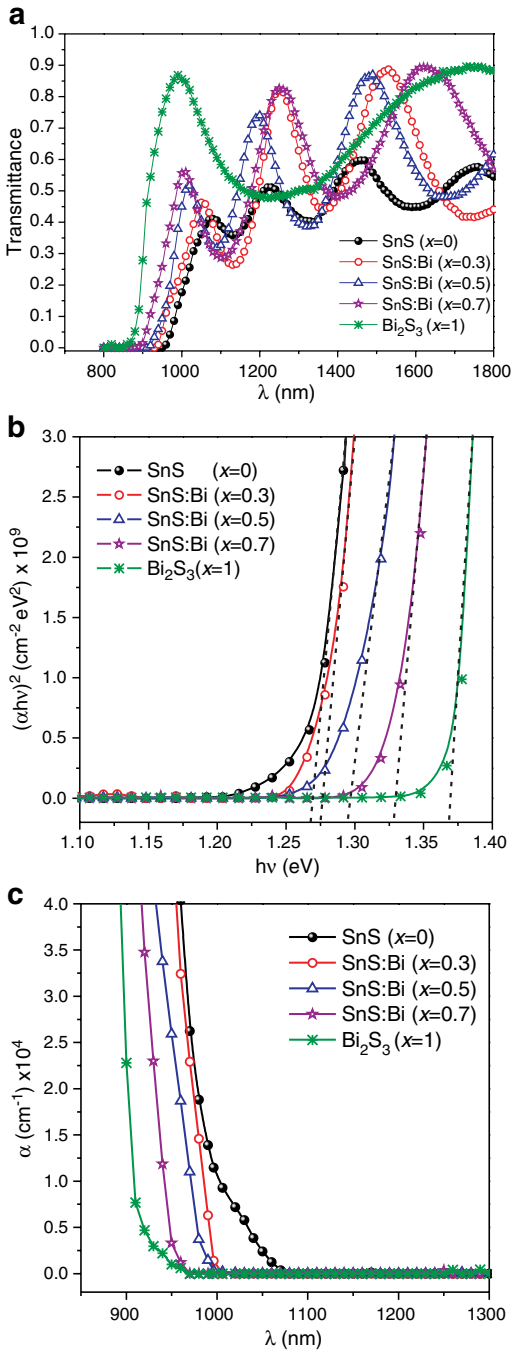

Fig. 2 Effect of the Bi-concentration in the SnS:Bi thin films on **a** the transmittance, **b** optical gap calculated from curves of $(\alpha h\nu)^2$ vs. $h\nu$, and **c** absorption coefficient

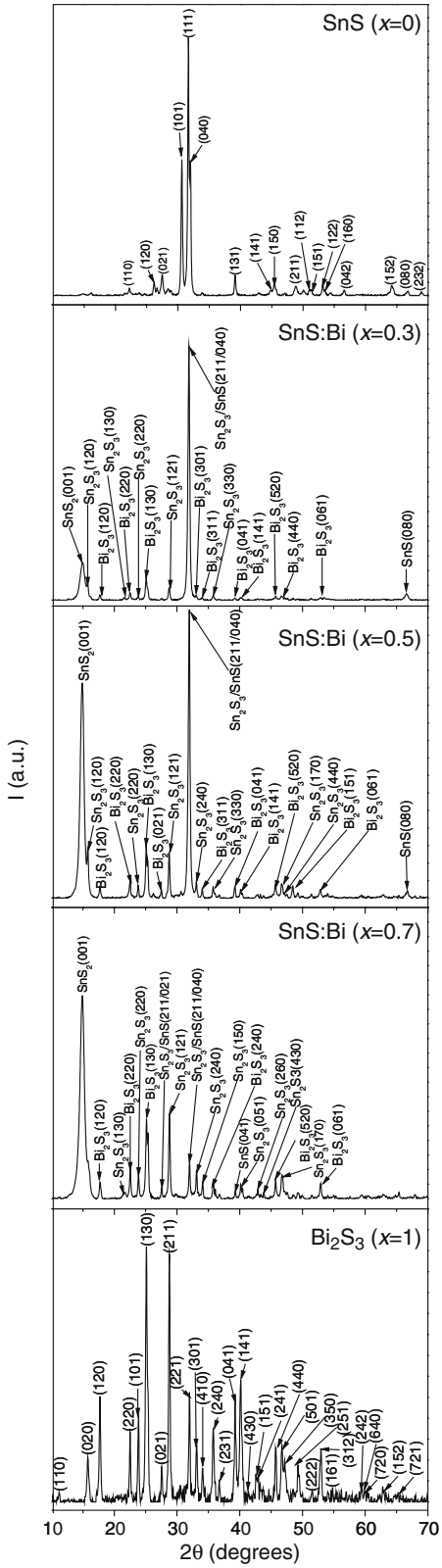

Fig. 3 XRD spectra of SnS:Bi thin films with Bi concentrations varying between $x = 0$ and $x = 1$

including the orthorhombic Sn_2S_3, SnS, and Bi_2S_3 and the hexagonal SnS_2; when $x = 1$, the Bi_2S_3 compound is formed in the orthorhombic phase. Obtaining the compound Bi_2S_3 when $x = 1$ is very important because

Table 1 Influence of the Bi concentration on the crystalline structure and phases of the SnS:Bi thin films

The lattice constants are also shown

Bi-concentration (x)	Phase	Structure	Lattice constant (Å)		
			a	b	c
0	SnS	Orthorhombic	4.201	11.201	3.961
0.3, 0.5, 0.7	Sn_2S_3	Orthorhombic	8.864	14.020	3.747
0.3, 0.5, 0.7	SnS	Orthorhombic	4.201	11.201	3.961
0.3, 0.5, 0.7	Bi_2S_3	Orthorhombic	11.149	11.304	3.981
0.3, 0.5, 0.7	SnS_2	Hexagonal	3.648		5.899
1	Bi_2S_3	Orthorhombic	11.175	11.236	3.979

it is one member of the metal chalcogenides group $A_2^V B_3^{VI}$, which begins to be widely studied because of their physical and chemical properties, suitable for the development of solar cells, luminescent devices, pigments, IR detectors, and thermoelectric devices [7, 8].

Thermoelectric power measurements showed that it is possible to grow SnS:Bi films with p or n conductivity controlling adequately the Bi content in the films. Samples with Bi content less than or equal to 50% ($0 \leq x \leq 0.5$) are p-type conductivity, and samples with Bi content greater than 50% ($0.5 < x \leq 1$) are type n. This behavior is possibly caused by the presence of Bi donor impurities in SnS:Bi films, which compensates the p-type conductivity of the SnS films. This is an important result because it indicates possible to fabricate p-SnS/n-SnS:Bi solar cells in situ, which facilitates the industrial production.

3.2 XPS Measurements Analysis

XPS measurements were performed using a Perkin-Elmer ESCA/SAM system, with a base pressure of $\approx 2 \times 10^{-9}$ Torr. Binding energy calibration was based on C 1s at 284.6 eV. The SnS:Bi thin films were eroded using the ion gun during 30 and 90 min at a rate of about 60 Å/min, which corresponds to depths of 180 and 540 nm, approximately. Figure 4 shows typical XPS spectra of SnS:Bi films deposited with different Bi contents ($x = 0$, $x = 0.5$, and $x = 1$), and the main peaks have been identified. Apart from C 1s peak, the Sn, S, and Bi peaks are identified in the spectra. The presence of C may be due to ambient contamination. Figure 5 shows a high-resolution scan of the peaks corresponding to Sn 3d, S 2p, and Bi 4f (Bi 4f overlaps with the S 2p peak) measured at different depths in SnS:Bi thin films prepared varying the Bi content ($x = 0$, $x = 0.5$, and $x = 1$).

The XPS measurements revealed that the SnS films ($x = 0$) contain only the SnS compound, the Bi_2S_3 films ($x = 1$) contain only the Bi_2S_3 compound, and the samples grown with Bi content $x = 0.5$ contain Sn sulfides additionally to the SnS and Bi_2S_3 compounds. The XRD measurements confirm those results found from XPS measurements.

Figure 5a confirms the presence of the SnS phase at binding energy of 485.8 eV [9] in the films of SnS, while the SnS:Bi films with Bi content $x = 0.5$ show

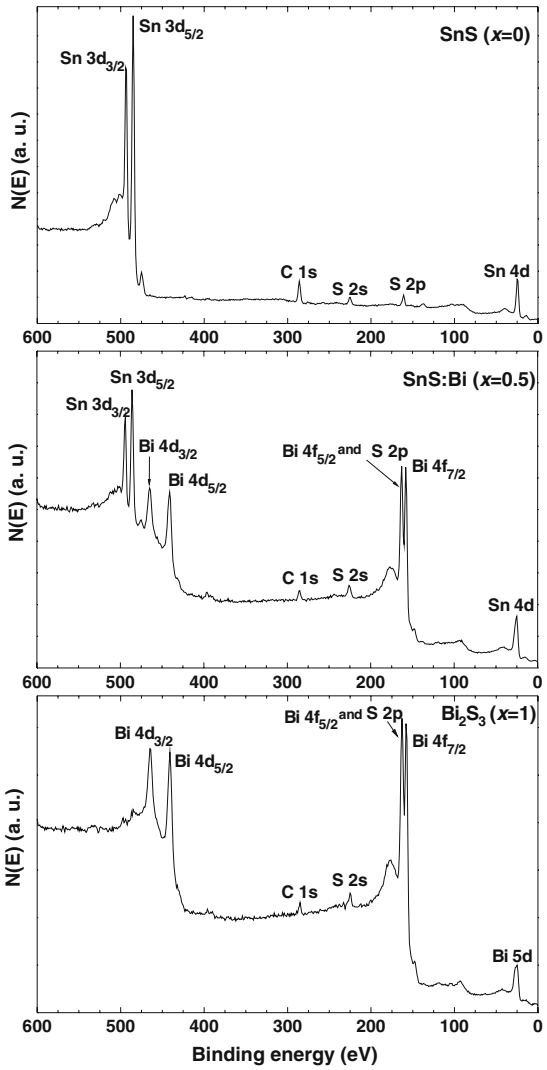

Fig. 4 XPS spectra of SnS:Bi thin films deposited with different Bi concentrations ($x = 0$, $x = 0.5$, and $x = 1$)

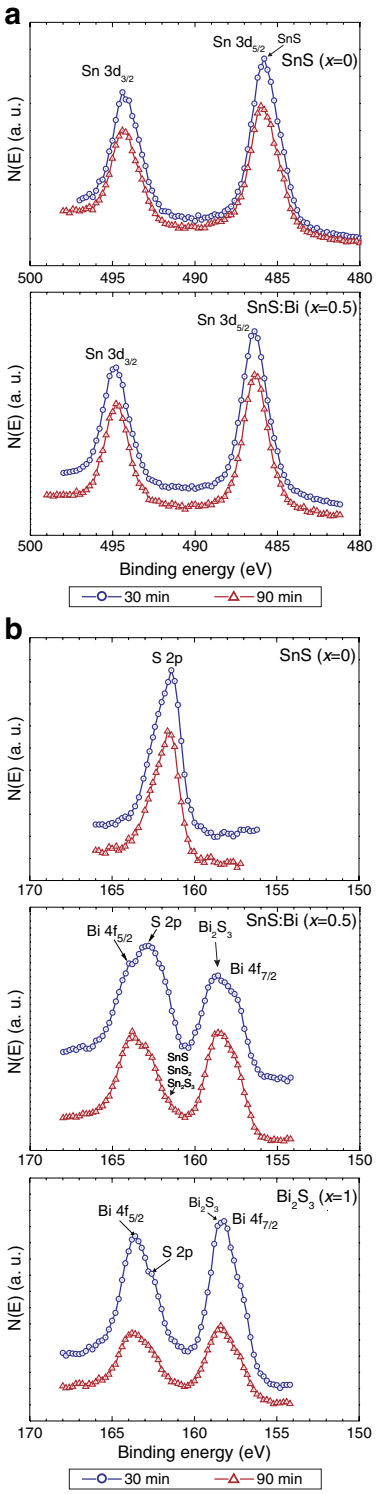

Fig. 5 **a** XPS high-resolution scans of the Sn 3d peaks measured at different depths in SnS:Bi films prepared with different Bi contents ($x = 0$, $x = 0.5$, and $x = 1$). **b** XPS high-resolution scans of the S 2p and Bi 4f peaks measured at different depths in SnS:Bi films prepared with different Bi content ($x = 0$, $x = 0.5$, and $x = 1$)

a slight shift of the Sn $3d_{5/2}$ peak (486.5 eV) which could indicate the presence of other sulfides such as SnS_2 and Sn_2S_3 present at binding energies of 486.3 and 486.6 eV, respectively [10]. Figure 5a also shows that these films are homogeneous in their chemical composition in depth. Figure 5b reveals that the S 2p peak of the sample SnS:Bi, with Bi content $x = 0.5$, presents a greater amplitude with respect to the same peak in the Bi_2S_3 and SnS films, suggesting that in this peak several phases might be present. Also a slight shift of the S 2p peak (at 161.4 eV in the SnS film) toward higher binding energies (163 eV) is observed when the Bi_2S_3 compound is formed (like in the films with Bi content $x = 0.5$ and Bi_2S_3). The XPS spectrum of SnS:Bi with Bi content $x = 0.5$ film was compared with those corresponding to Sn sulfides, and it was found that the peak of the S 2p presents several phases fitting well to Sn_2S_3, SnS_2, and SnS (presented at a binding energy of about 161.7 eV) [10]. The Bi_2S_3 phase in the SnS:Bi ($x = 0.5$) and Bi_2S_3 ($x = 1$) films was identified in the Bi 4f peak to a binding energy of 158.6 eV [9].

4 Conclusions

SnS:Bi thin films were synthesized varying the Bi concentration, using a novel procedure based on sulfurization of the metallic precursors, which are sequentially evaporated on a glass substrate. It was found that the SnS:Bi thin films present a high absorption coefficient ($>1 \times 10^4$ cm^{-1}) regardless of the Bi content and an energy band gap between 1.27 eV for SnS (Bi concentration $x = 0$) and 1.37 eV for Bi_2S_3 ($x = 1$). It was possible to increase the optical gap of SnS:Bi thin films to 1.33 eV (a value closer to the theoretical ideal of 1.4 eV for absorber layers in solar cells) by increasing the Bi content ($x = 0.5$), keeping their p-type conductivity. These results indicate that this compound has good properties to perform as absorber layer in thin film solar cells.

The studies also revealed that the conductivity type of the SnS:Bi films depends on the Bi content in the SnS lattice; this result implies that it is possible to fabricate p-SnS:Bi/n-Bi_2S_3 solar cells in situ, which has advantages for industrial production.

It was established from XPS and XRD studies that the SnS:Bi thin films grow with a mixture of several phases, including the orthorhombic SnS, Sn_2S_3 and Bi_2S_3, and the hexagonal SnS_2, when the Bi-content is $0 < x < 1$; the films grow only in the SnS phase when $x = 0$ and in the Bi_2S_3 phase when $x = 1$.

In this work was also achieved growing the Bi_2S_3 compound by a new method. This result is important

because this material is useful in the fabrication of optoelectronic and photovoltaic devices.

Acknowledgements We acknowledge the financial support of this work by the DIB-Universidad Nacional de Colombia and Conacyt (Project No. 59998). The authors thank Wilian Cauich for his help with the XPS measurements.

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