Morphological and electrical properties of SnS:Bi thin films

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Abstract. This work presents results regarding the influence of the Bi content on the morphology and electrical transport properties of SnS:Bi thin films grown by sulfurization of the metallic precursors on a soda-lime glass substrate. The SnS:Bi films were characterized through atomic force microscopy and electrical conductivity measurements. The results showed that the Bi content affects the grain size and roughness of the SnS:Bi films. The grain size affects the carrier mobility and therefore the electrical conductivity at room temperature. Measurements of conductivity as a function of temperature, carried out in the range between 90K and 630K, revealed the electrical transport in SnS:Bi thin films is affected by two different mechanisms: at temperatures greater than 350K, the conductivity is predominantly affected by free carrier transport in extended states of the conduction/valence band, whereas at temperatures below 350K the conductivity is mainly determined by the variable range hopping transport mechanism.

1. Introduction
The chalcogenide materials such as SnS, SnS2, Sn2S3 and Bi2S3 are currently of great interest due to its applications in the fabrication of optoelectronic, thermoelectric and photovoltaic devices, and as a holographic recording medium. Much of this interest is due to S and Sn being inexpensive, abundant in nature and less toxic than most of the materials used in the industry for manufacturing these types of devices. Particularly, the SnS presents suitable properties for an absorbent layer in solar cells, with conversion efficiencies of up to 25% theoretically [1], thanks to its properties: energy band gap of 1.3 eV, fundamental absorption coefficient greater than 10^4 cm^-1 and p-type electrical conduction. The Bi2S3 is widely studied because of their physical and chemical properties, suitable for the development of solar cells, luminescent devices, pigments, IR detectors, and thermoelectric devices [2, 3].

SnS compound has been synthesized by different techniques such as chemical bath deposition [4], two step processes [5], electrochemical deposition [6] and thermal evaporation [7]. In this work the SnS:Bi thin films were grown by sulfurization of the metallic precursors, which is a novel method for synthesizing thin films based on SnS. The influence of the concentration of Bi on the electrical transport properties and on the morphology of the SnS:Bi was investigated by electrical conductivity and Atomic Force Microscope (AFM) measurements. The substitution of Sn atoms by 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 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 SnS:Bi thin films were grown by sulfurization of the metallic precursors, which are sequentially evaporated on a glass substrate keeping the substrate temperature at 350 ºC; in a second stage the layer containing the metallic precursors is annealed in a S environment at the same substrate temperature, the evaporation temperature of S is kept at 140 ºC. Details of the growth routine of the films are presented in Ref. [8]. The Bi concentration ($x$) in the SnS:Bi films was varied between 0 and 1 according to the relation:

$$x = \frac{\text{mols of Bi}}{\text{mols of Sn} + \text{mols of Bi}}$$

In particular, when $x=0$ SnS films were obtained, and Bi$_2$S$_3$ films when $x=1$.

The SnS:Bi thin films were electrical and morphologically characterized to study the effect of the content of Bi on the electric conductivity, and on the grain size and average roughness. Morphological characterization of the deposited films was performed using an Atomic Force Microscope; the AFM measurements were done with a 0100 model PSI Auto-probe CP microscope. The conductivity type was determined from thermoelectric power measurements. The film thicknesses were measured with a Veeco Dektak 150 surface profiler and their values fell in the range between 800 nm and 1 μm.

3. Results and discussion
3.1. Morphological characterization
Figure 1 shows typical AFM images of SnS:Bi thin films deposited varying the Bi concentration ($x = 0, 0.3, 0.5, 0.7$ and $1$). From the results of figure 1 it is clear that the Bi content significantly affects the films’ morphology. In general, the increase of the Bi concentration ($x$) leads to a decrease of both the grain size and roughness. The curves depicted in figure 2 show the variation of the average roughness and of the average grain size as functions of $x$.

![Figure 1](image-url)  
**Figure 1.** Typical AFM images of SnS:Bi films deposited with different Bi concentrations: a) $x=0$, b) $x=0.3$, c) $x=0.5$, d) $x=0.7$ and e) $x=1$. 


Decreasing the roughness causes a decrease in light absorption, which in turn leads to an increased transmittance [8], while decreasing grain size causes an increase in the density of grain boundaries which results in a decreased mobility of the carriers and thus the electrical conductivity (\(\sigma\)). The SnS films (\(x=0\)) present higher grain size and electrical resistivity of the order of 1.1x10^2 \(\Omega\)cm, while films of SnS:Bi with high concentrations of Bi (\(x=1\) corresponding to Bi_2S_3) present lower size grain and resistivity of the order of 1.2x10^4 \(\Omega\)cm.

It must be realized that although the grain size influences the mobility (\(\mu\)) of the charge carriers and this one in turn on the resistivity (\(\rho\)), the charge carrier concentration (\(n\)) also affects the behavior of the electrical resistivity of the films; particularly for the films deposited, values of \(\mu\) between 26.14 and 4.11 cm^2/Vs and values of \(n\) between 2.04x10^{15} and 1.26x10^{14} cm^{-3} (at room temperature) were obtained for SnS and Bi_2S_3 films, respectively. Both the mobility and carrier concentration at a determined temperature depend on the compound; SnS:Bi thin films deposited in this work have different phases, in accordance to previous studies [8]: 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 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, therefore the increase in electrical resistivity observed when the Bi concentration raises is caused by the increase of Bi_2S_3 in the SnS:Bi samples, since, in general, the Bi_2S_3 phase has greater resistivity than the other phases present in the compound.

It was also found from thermoelectric power measurements that the SnS:Bi thin films with Bi content less than or equal to 0.5 have \(p\) type conductivity and films with Bi content greater than 0.5 have type \(n\).

### 3.2. Electrical properties

Electric conductivity measurements as a function of temperature in a range between 90K and 630K were used to identify the scattering processes affecting electrical transport. The conductivity was measured using electrical contacts of Ag deposited by sputtering DC. Figure 3 shows typical curves of electric conductivity as a function of temperature, for SnS:Bi films deposited with different content of Bi (\(x=0, 0.5, 1\)). The increase in conductivity with increasing temperature indicates the semiconducting nature of the films.

The \(\sigma\) vs. \(T\) curves show two different slopes, indicating that the conductivity is affected by two different transport mechanisms predominating at different temperature ranges. The results of figure 3 were analyzed assuming predominance of one mechanism at a given temperature range in an attempt to identify the mechanisms affecting the electrical transport of the SnS:Bi thin films. We found that at temperatures above 350K, the conductivity can be expressed by

\[
\sigma = \sigma_0 \exp\left[-\left(E_C - E_F\right)/(kT)\right]
\]  

(1)
indicating in this range of temperatures the conductivity is predominantly affected by free carrier transport in extended states of the conduction/valence band. Since the factor $\sigma_0$ (given by $qNC\mu(T)$) varies slowly with temperature and the term $\exp[-(E_C-E_F)/kT]$ depends strongly on $T$, $\sigma_0$ can be assumed as approximately constant. Under this approximation, the slope of the graph $ln\sigma$ vs. $1/T$ gives the activation energy $E_\sigma = E_C - E_F$, the calculated values of the corresponding activations energies are 0.22 eV for $x=0$, 0.24 eV for SnS:Bi $x=0.5$ and 0.43 eV for $x=1$.

In figure 4 are depicted curves of $ln\sigma$ vs. $1000/T$ using the experimental data of figure 3, measured between 350K and 630K. The linear behavior of the $ln\sigma$ vs. $1000/T$ curves demonstrates that, in the high temperature range, the SnS:Bi film conductivity is dominated by free carrier transport in extended states of the conduction/valence band (for $n/p$ type conductivity respectively).

\[ \sigma = \sigma_0(T) \exp\left(-\frac{A}{T^{1/4}}\right) \]  

This behavior of $\sigma$ vs. $T$ indicates in this range of temperature the conductivity is predominantly affected by transport in a band of localized states as predicted by the Davis-Mott model, where the carriers can move between states via a phonon-assisted tunneling process [9]. This transport mechanism is known as Variable Range Hopping (VRH). 

In Mott’s derivation:

\[ \sigma_0 = \frac{e^2}{2(8\pi)^{1/2}V_{ph}}\frac{N(E_F)}{\beta kT} \]  

and \[ A = \left[\frac{\beta^3}{kN(E_F)}\right]^{1/4} \]

where $N(E_F)$ is the density of localized states, and $\beta$ a quantity representing the fall-off of the wave function on the site. In principle the two parameters $\beta$ and $N(E_F)$ can be evaluated from the slope of a plot of $ln[\sigma(T)T^{1/2}]$ vs $T^{-1/4}$ and from the intercept at $T^{-1/4} = 0$, respectively.

Figure 5 shows plots of $ln[\sigma(T)T^{1/2}]$ vs $T^{-1/4}$ performed with the experimental data of figure 3, measured between 90K and 350K. The linearity of the $ln[\sigma(T)T^{1/2}]$ vs $T^{-1/4}$ curves confirms that the
conductivity of the SnS:Bi films in the low temperature range is dominated by the VRH transport mechanism.

**Figure 5.** Curves of $\ln[\sigma(T)T^{1/2}] vs T^{-1/4}$ corresponding to SnS:Bi films deposited with different content of Bi.

4. Conclusions
SnS:Bi thin films were deposited using a novel procedure based on sulfurization of the metallic precursors. The Bi concentration in the films was varied between $x=0$ and $x=1$.

AFM measurements indicated that the morphology of the SnS:Bi films is affected by Bi concentration: the increase of the Bi concentration leads to a decrease of both the grain size and roughness. The decrease of grain size leads to a decrease of the mobility of free carriers when the Bi concentration in the SnS:Bi films increases, probably due to grain boundary effect.

Measurements of conductivity as a function of temperature revealed that the electrical transport in SnS:Bi films is affected by two different mechanisms: in the range of temperatures above 350K, the conductivity is predominantly affected by carrier transport in extended states of the conduction/valence band, whereas in the range of temperatures below 350K, the conductivity is dominated by the Variable Range Hopping transport mechanism.

Thermoelectric power measurements revealed that it is possible to grow SnS:Bi films with $p$ or $n$ conductivity controlling adequately the Bi content in the films. This result indicates it is possible to fabricate $p$-SnS/$n$-SnS:Bi solar cells in-situ, which facilitates industrial production.

Acknowledgments
We acknowledge the financial support of this work by the DIB-Universidad Nacional de Colombia.

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