Nuclear Instruments and Methods in Physics Research B 272 (2012) 351–356

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

# Modifications in SnS thin films by plasma treatments

H. Martínez [a,*], D. Avellaneda [b]

[a] Instituto de Ciencias Físicas, Universidad Nacional Autónoma de México, Apartado Postal 48-3, 62210 Cuernavaca, Morelos, Mexico
[b] Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León, Mexico

ARTICLE INFO

*Article history:*
Available online 2 February 2011

*Keywords:*
Thin films
Tin sulfide
Plasma treatment
Glow discharge

ABSTRACT

The present study shows modifications of structural, optical and electrical characteristics that occur in tin sulfide (SnS) thin films treated in air and nitrogen plasma at different pressure conditions. Films were obtained by the chemical bath deposition method, which results in SnS thin films with an orthorhombic crystalline structure, band gap ($E_g$) of 1.1–1.2 eV, and electrical conductivities ($\sigma$) in the order of $10^{-6}\,\Omega^{-1}\mathrm{cm}^{-1}$. The films treated with air plasma at pressures between 1 and 4 Torr, showed the presence of $SnS_2$, $Sn_2S_3$, and $SnO_2$ phases, within band gap values ranging from 0.9 to 1.5 eV. On the other hand, films treated with nitrogen plasma presented the same phases, but showed a significant modification in the electrical conductivity, it increasing from $10^{-6}\,\Omega^{-1}\mathrm{cm}^{-1}$ (as-deposited) up to $10^{-2}$–$10^{-3}\,\Omega^{-1}\mathrm{cm}^{-1}$ (plasma treated). This result is a suitable range of conductivity for the improvement of the solar cells with SnS as an absorber material. Also, emission spectroscopy measurements were carried out in both air and nitrogen plasma treatments.



## 1. Introduction

Tin(II) sulfide is an IV–VI semiconducting material which crystallizes in an orthorhombic crystal structure ($a = 0.399$ nm, $b = 0.434$ nm, $c = 1.12$ nm), where the unit cell spans two layers that stack along the $c$ axis of the crystal [1,2]. However, an exception to the orthorhombic structure for SnS thin films is the zinc-blende structure with a lattice constant ($a$) in the range of 0.57–0.6 Å [3,4]. The SnS films have some attractive features: (a) there are a layered semiconductors with some inert surface-free dangling bonds [5]; (b) they show both direct and indirect band gaps ($E_g$) with values reported in the range of 1–1.6 eV with direct and indirect transitions, depending on the method of preparation [1,6]. The SnS thin films show p-type conductivities and large absorption coefficients ($\alpha$) in the order of $10^4$–$10^5\,\mathrm{cm}^{-1}$ [7,8], which enables the absorption of most incident sunlight. The above characteristics of SnS, along with their abundance of about 2 ppm of Sn in the earth's crust may be considers reasonable proposal for developing photovoltaic technologies in which thin films of this semiconductor plays an important role.

Several deposition techniques have been employed to obtain thin films of tin(II) sulfide, SnS: vacuum evaporation [9,10], spray pyrolysis [11], chemical vapor deposition [12], chemical bath deposition (CBD) [13–15], and electrochemical methods [16]. On the other hand, post-deposition treatment (annealing) is the most common method used to improve the characteristics of thin films. However, the gas plasma treatments have been probed as a suitable technology for the modification on the structural, optical and electrical characteristics of the films [17,18]. In this paper, we examine the changes in the structural, optical and electrical characteristics of tin sulfide SnS thin films, obtained by CBD method, with post-deposition gas plasma treatments in air and nitrogen at different pressures.

## 2. Experimental

### 2.1. Deposition of SnS thin films

The thin films of SnS were prepared by the CBD method, using the deposition solution reported previously [4,15]. Such films were deposited from the deposition solution that was prepared as follows: 1 g of $SnCl_2\ H_2O$, dissolved in 5 ml of acetone were mixed in 12 ml of 3.7 M of triethanolamine solution were mixed. Then 8 ml of 1 M thioacetamid solution was added and pH was adjusted to 6.0 by addition of 10 ml of 4 M $NH_3$ solution, and then, de-ionized water was added to the solution to make a total volume of 100 ml. Glass substrates (microscope slides of $1.25 \times 4$ cm) were placed in glass container with the deposition solution, previously the glass substrates were degreased, rinsed thoroughly on distilled water, and dried. Deposition temperature for the films was set of 60 °C, and the duration of depositions was 6 h. After deposition the SnS films were washed with de-ionized water and dried in the air at room temperature.

* Corresponding author. Tel.: +52 777 3291759; fax: +52 777 3291753.
*E-mail address:* hm@fis.unam.mx (H. Martínez).

0168-583X/$ - see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.nimb.2011.01.099

### 2.2. Characterization

Direct transmittance ($T$) and total (near normal specular) reflectance ($R$) measurements were made over a wavelength range of 250–2500 nm using a Shimadzu UV-1601 spectrophotometer. The measurements were calibrated using air and mirror-aluminized as reference surfaces. The X-ray diffraction (XRD) patterns were recorded to characterize the phase and structure of the SnS films using a Rigaku D MAX-2000 powder diffractometer with CuK$\alpha$ radiation angle $2\theta$ ranging from 20° to 80°.

The electrical conductivity at room temperature was determined using a Keithley 6487/Picoammeter/Voltage source. The films were colored in the planar configuration using two silver paint electrodes 5 mm long at 5 mm separation. A voltage of 100 V was applied across the electrodes and the photocurrent response was measured. Data acquisition and analysis were performed using a personal computer.

### 2.3. Plasma treatment

The post-deposition treatments in nitrogen and air plasmas were carried out in the SnS thin films at pressures between 1 and 4 Torr. The experimental arrangement used to generate the pulse plasma was described on detail elsewhere [18]. The plasma system has two stainless steel circular plate electrodes. The electrodes are positioned horizontally at the center of the reaction chamber, with 5 mm of separation between them. Samples were placed in the bottom electrode, and the gas was injected into the reaction chamber through the front flange. The same gas connection was used for the pressure sensor. The base pressure of the plasmas was maintained using a mechanical pump (*Varian SD-301*) and purged with the working gas at $\sim 2 \times 10^{-2}$ Torr for several times in order to remove the background gases. The discharge power supply was 300 V, and the discharge current was 0.12 A (36 W). The plasma treatment was performed for 1 h in all (nitrogen and air) samples. The optical spectroscopy measurements (OES) were carried out by using a high-resolution Ocean Optics Inc. Spectrometer *HR2000CG-UV-NIR* and a *UV2/OFLV-5* detector, the fiber optic was placed in the aperture entrance. The grating response has a spectral response in the range of 200–1100 nm.

## 3. Results and discussion

### 3.1. OES analysis

The emission spectroscopy measurements performed for $N_2$ and air glow discharge plasmas are shown in Fig. 1. The analysis of the most luminous area that corresponds to the negative glow near the cathode dark space can be accomplished. In the present work, it has been subtracted the intensities of the bands and lines, from the $N_2$ and air plasmas respectively. The identified species removed from the thin films into the plasma are displayed in Table 1. Only the most intense spectral lines and bands are quoted [8,9]. Most of the species are vibrationally excited at a fundamental level. Part of the flux of material into the plasma can be deposited somewhere in the chamber and other part return to the surface in a modified form. The difference between the two spectra is the relative intensity and the presence of O lines in the air treatment.

By using OES and observing the species formed in the plasma-SnS thin film, it is possible to assume that there are two possible mechanisms by which SnS thin film ionization occurs in plasma treatment: 1 and 2 reactions correspond to electron impact excitation and dissociation-ionization mechanism respectively, and 3 and 4 reactions correspond to recombination mechanism:

$$SnS + e \Rightarrow SnS + e \quad (1)$$

$$SnS + e \Rightarrow S^+ + Sn + 2e \quad (2)$$

$$SnS + e \Rightarrow S + Sn^+ + 2e \Rightarrow S + S \Rightarrow S_2 \quad (3)$$

$$SnS + N_2 \Rightarrow NS + Sn + N \quad (4)$$

There is a flux of material into the plasma that can be deposited somewhere in the chamber and some back on the surface from which it came (in a modified form). In addition, the formation of

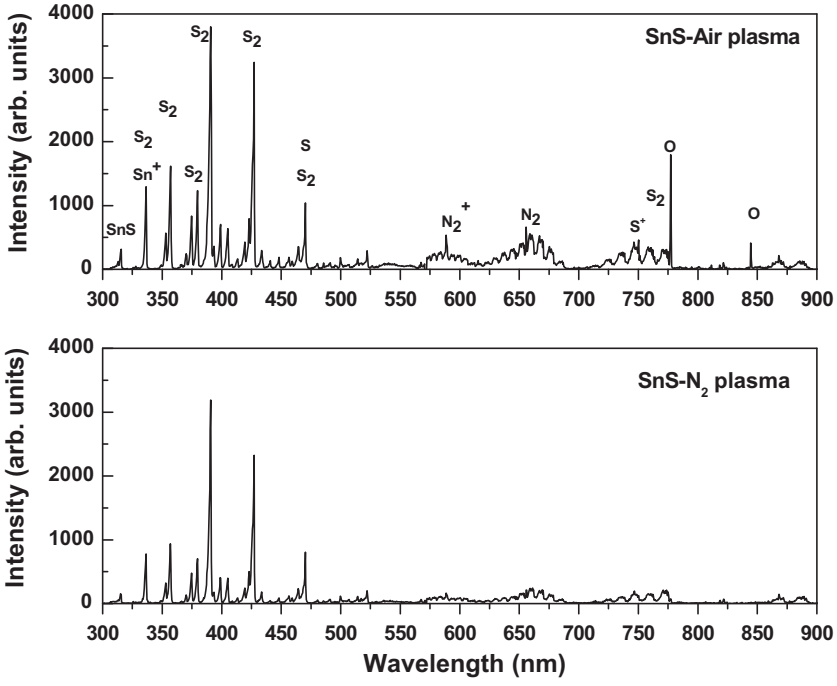


**Fig. 1.** Typical OES spectrum for $N_2$ and air plasma.