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Fabrication of SnS_2/SnS heterojunction thin film diodes by plasma-enhanced chemical vapor deposition

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Abstract

Heterojunction based on Sn–S compounds, SnS and SnS_2, have been prepared by plasma-enhanced chemical vapor deposition (PECVD). The semiconductor materials SnS and SnS_2 were obtained by the decomposition of the gas precursors $SnCl_4$ and H_2S in a capacitive-coupled RF plasma-deposition chamber. Corning glass with a transparent conductor oxide (TCO) thin film was used as substrate. The structure of the diode was glass/TCO/n-type SnS_2/p-type SnS/Al. The contact between the n-type and p-type Sn–S compounds was found to be rectifying. The estimate reverse saturation density current was 1.2×10^{-5} A/cm^2. The ratio of forward-to-reverse current exceeded 300 within the range of applied voltages of -1.0 to 1.0 V and the estimated diode factor was 2.7. A photovoltaic effect was observed under illumination giving an open circuit voltage of 0.35 V and a small short circuit current density with a value of 1.5 mA/cm^2.

Keywords: SnS_2/SnS heterojunction thin film diodes; Plasma-enhanced chemical vapor deposition; Transparent conductor oxide

1. Introduction

Binary compounds based on the Sn–S system have a high potential use in optoelectronic devices [1–5]. From the technological point of view, tin sulfide (SnS), tin disulfide (SnS_2) and the compound Sn_2S_3 are among the most interesting materials. Single crystals and polycrystalline thin films of SnS have shown indirect optical transitions with an optical band gap of about 1.3 eV, and p-type electrical conductivity whose dark value can be increased by doping with Ag, Al, N and Cl [6–8]. Since its optical band gap lies in the optimum range in which absorber materials can be used in solar cell applications [9], the SnS compound, with an optimized thickness, could be use in photovoltaic structures. Single crystal and polycrystalline thin films of SnS_2 have shown optical band gaps in the range of 2.12–2.44 eV [10–13], and n-type electrical conductivity with magnitude depending on the preparation technique. Both characteristics make this compound suitable for a window material in a heterojunction structure. On the other hand, the Sn_2S_3 compound is classified as a mixed valence compound with semiconductor behavior [14]. Single crystals of Sn_2S_3 show direct optical band gap of 0.95 eV, n-type electrical conductivity whose values are around 10^{-5} $(\Omega\ \mathrm{cm})^{-1}$ and energy activation of 0.85 eV [15]. It has been found that the optoelectronic properties are dependent on its crystalline structure and stoichiometry [14–16]. Therefore, these compounds could be used to build photovoltaic p–n or p–i–n structures with conversion efficiencies of about 25% [9]. Since the materials involved in the proposed structure are inexpensive, non-strategic and abundant in nature, it is expected that the fabrication cost will be low compared with similar structures fabricated with other materials.

Thin films of SnS, SnS_2 and Sn_2S_3 compounds have been prepared by different techniques [1–8,10–18]. Among these, plasma-enhanced chemical vapor deposition (PECVD) is a

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process that meets the requirements of controllable, simple and inexpensive large-area thin film deposition to produce a low cost materials and devices. In our previous works [17,18] we reported on the preparation and properties of Sn_XS_Y thin films prepared by PECVD. In this paper, we report the preliminary results on the preparation and properties of SnS_2/SnS heterojunction thin film diodes fabricated by plasma-enhanced chemical vapor deposition.

2. Experimental details

SnS and SnS_2 thin films were deposited onto selected substrates by the decomposition of vapor mixtures of H_2S and $SnCl_4$ in a capacitive-coupled 13.56-MHz radio frequency glow discharge chamber with a radially symmetric flow pattern. The flow rates for the H_2S and $SnCl_4$ are indicated by $Q_{H_2}S$ and Q_{SnCl_4}, respectively, and its relative concentration ratio, g, has been defined by the relation $g=Q_{SnCl_4}/(Q_{SnCl_4}+Q_{H_2}S)$. Details on the deposition chamber have been reported elsewhere [17]. Since the structural, optical and electrical properties of the Sn_XS_Y thin films deposited by PECVD depend on the process parameter depositions [17,18], we selected a set of parameters deposition values that let the formation of SnS_2 and SnS thin films, respectively, with optoelectronic properties suitable to fabricate a photovoltaic device.

Corning glass with 1.5×2.5 cm^2 dimensions was used as substrate witness to deposit SnS and SnS_2 for characterization purpose. Tin disulfide, SnS_2, thin films were obtained at substrate temperature (T_s) of 150 °C, radio frequency power density (W_p) applied to electrodes equal to 25 mW/cm^2, relative concentration of the precursor vapors (g), around 0.12, and an absolute process pressure (p) of 6.6 Pa (50 mTorr). Meanwhile, tin sulfide, SnS, thin films were obtained at T_s=200 °C, W_p=250 mW/cm^2, g=0.4 and an absolute pressure p=4.3 Pa (32 mTorr). Both materials deposited onto the Corning glass substrates were structural, optical and electrical characterized, following the experimental details reported elsewhere [17,18]. Four indium and aluminum bars of 1 mm wide, 1 mm of separation, 12.5 mm long and a thickness of 0.5 μm were deposited by thermal evaporation onto the Sn_2S and SnS thin films, respectively, for electrical characterization.

Commercial Corning glass with a transparent conductor oxide (TCO) thin film was used as substrate to build the diodes. It was chosen commercial SnO_2/Sb with a sheet resistance of 10 Ω/ to be the TCO substrate and the frontal electrical contact for the diode. The diodes were built as follow. The substrates (glass witness and glass/TCO) were cleaned using standard procedures (soap solution, acetone and methanol, all three steps in ultrasonic bath and drying with nitrogen gas). They where put inside the reaction chamber on the heater plate. The substrates were heated to the temperature process at the same time that the chamber was pumped out. After that, they were etched using an H_2/Ar plasma for cleaning the TCO substrates surface. Then, a thin film of SnS_2 was deposited onto the TCO surface using the parameters mentioned above. The deposition time was selected to grow SnS_2 layers with thickness of 0.15 μm. Without breaking the vacuum in the process chamber and by adjusting the controllers to have the parameters to let the formation of the SnS compound, a thin layer with a thickness of 0.35 μm of tin sulfide were deposited onto the SnS_2 layer. Since the electrical contact between aluminum and tin sulfide has been reported with Ohmic behavior [4], this metal was chose as the back electrical contact for the fabricated diode. Therefore, by the use of a vacuum evaporation system, aluminum (Al) circles with a 0.2-cm of diameter and 0.8 μm thick were deposited onto the SnS layer by thermal evaporation. Thus, the structure for the diodes was glass/TCO/n-type SnS_2/p-type SnS/Al (see Fig. 1).

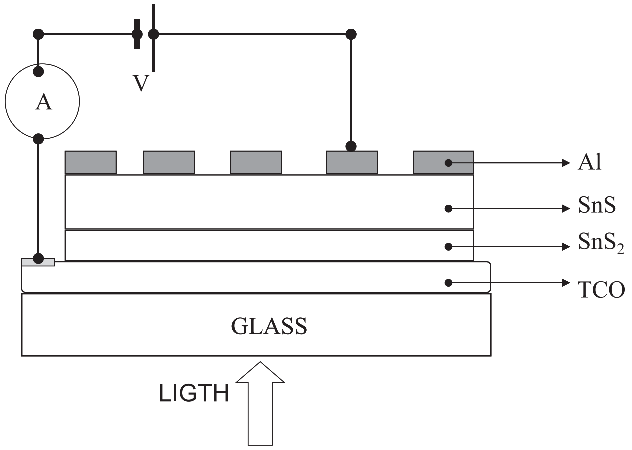

Fig. 1. Schematic diagram of the structure for the fabricated diodes.

$I–V$ characteristics in dark between the metal-semiconductor contacts and for the diodes were obtained using an automatically data acquisition system in the bias voltage range of −1 to 1 V, which was supplied by a HP4140B picoammeter/*dc* voltage source. For the $I–V$ characteristic under illumination, a tungsten–halogen lamp with an intensity of 70 mW/cm^2 was used to supply white light to the diodes. A 10-cm column of water between the lamp and the diodes was used to avoid the heating of the devices under study.

3. Results and discussion

The optical, electrical and structural characterization of the SnS and SnS_2 deposited thin films onto the glass substrates gave the optoelectronic properties listed below.

The deposited SnS_2 thin film onto glass substrates has a hexagonal crystal structure with a preferential growth along the [001] direction as is evident from the XRD pattern shown in Fig. 2(a). The average dimensions of the crystallites size, determined by the well-known Scherrer

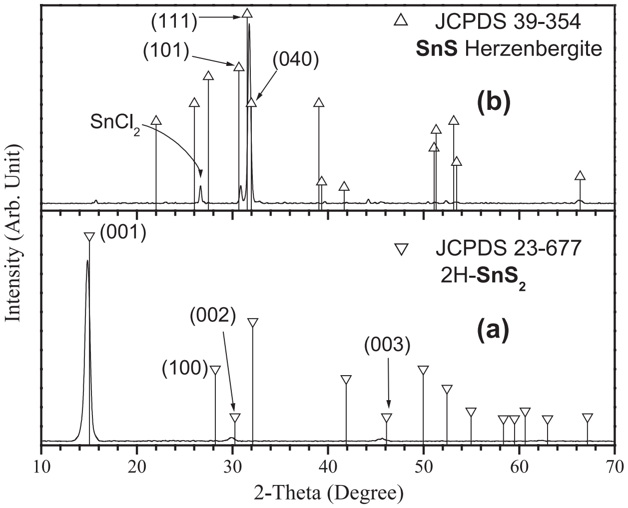

Fig. 2. XRD patterns for the deposited SnS_2 (a) and SnS (b) thin film compounds onto glass substrates.

method (uncorrected for experimental broadening) [19], was around 15 nm. The optical transmittance $T(\lambda)$ and specular reflectance $R(\lambda)$ for a typical sample is shown in Fig. 3(a). It can bee seen that the deposited SnS_2 thin films have transmittance values around 70% and reflectance values around 30%. The optical band gap was determined based on the theory of Bardeen et al. [20] for indirect transitions. The best fit of the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ and its extrapolation to $(\alpha h\nu)^{1/2}$=0 given a band gap of 2.167 eV with a phonon energy assistance of 0.074 eV (see Fig. 3(b)). The "hot point" probe [21] had shown that SnS_2 thin films are an n-type semiconductor material. A simple I–V analysis in the In-SnS_2 contacts, bias voltage range of ±1 V, had shown that the In-SnS_2 contact is Ohmic. This behavior has been expected because the electron affinity value for the semiconductor (χ=4.2 eV [22]) is bigger than the work function value for the metal (ϕ_{In}=4.12 eV [23]), in regards of the Ohmic behavior in a metal-semiconductor junction [24]. The deposited SnS_2 thin films on both substrates (glass and TCO) have a dark electrical conductivity of the order of 1.0×10^{-2} $(\Omega\ \text{cm})^{-1}$ with activation energy of 0.13 eV. It was found also that the electrical behavior phenomenon at the contact junction TCO/SnS_2 is Ohmic.

XRD diffraction pattern for the deposited SnS thin films onto glass show that the material has a preferential growth along the [111] direction as it can see in Fig. 2(b). The deposited material has an orthorhombic crystal structure with an average dimension of the crystallites size about 20 nm. There are some diffractions peaks in Fig. 2(b) that do not correspond to the SnS system. These peaks can be assignment to the $SnCl_X$ compounds as has been discussed by Ortiz et al. [4]. The chlorine incorporation into the SnS thin film like a $SnCl_X$ compound could affect the electrical properties of the material. Following the same procedure mentioned above for calculating the optical band gap from transmittance and reflectance data (see Fig. 4(a)), optical indirect transitions were confirmed with band gap of 1.25 eV (see Fig. 4(b)). I–V characteristics between the aluminum bars deposited by thermal evaporation on the surface of the SnS tin films had shown Ohmic behavior in the ±1 V applied bias voltage confirming the behavior reported elsewhere [4]. The deposited material has shown p-type electrical conductivity

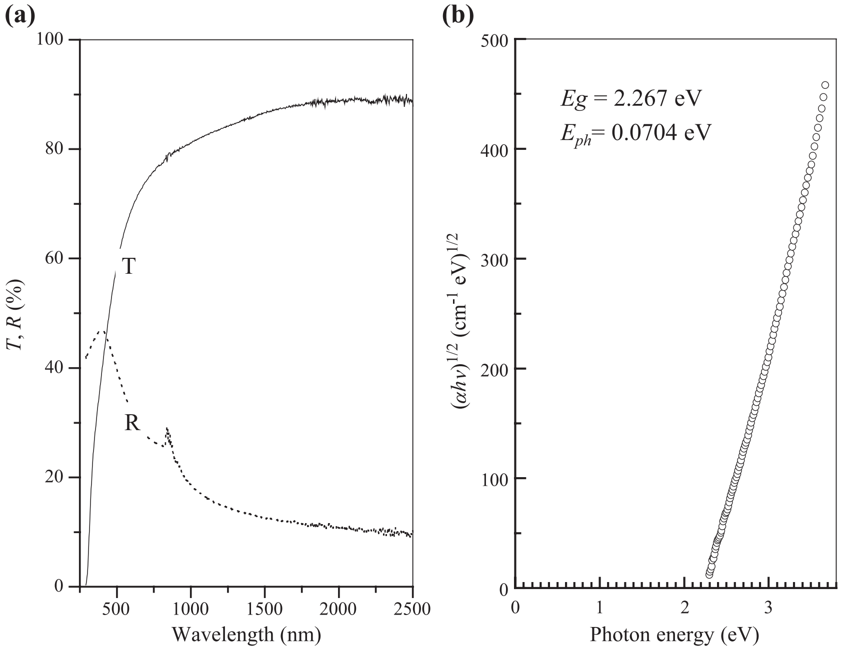

Fig. 3. Optical characteristics for the deposited SnS_2 thin film onto glass substrates with a thickness of 0.15 µm. Spectrum (a) shows the optical transmittance (solid line) and specular reflectance (dotted line), and spectrum (b) shows the variation of $(\alpha h\nu)^{1/2}$ vs. $h\nu$.

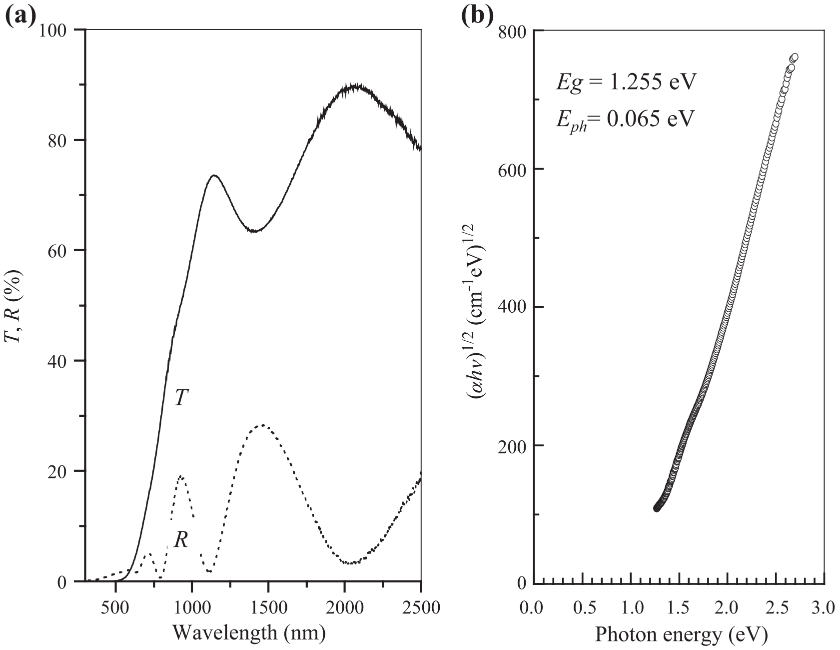

Fig. 4. Optical characteristics for the deposited SnS thin film onto glass substrates with a thickness of 0.35 μm. Spectrum (a) shows the optical transmittance (solid line) and specular reflectance (dotted line), and spectrum (b) shows the variation of $(\alpha h\nu)^{1/2}$ vs. $h\nu$.

with a dark value of 3.0×10^{-3} $(\Omega\ \mathrm{cm})^{-1}$ and activation energy of 0.31 eV.

The diodes with the structure shows in Fig. 1 were electrical characterized for applying a bias voltage, in forward and reverse direction, in order to know I vs. V junction characteristics in dark and under illumination. Fig. 5 shows I vs. V behavior for such structure. It can be seen that a typical rectification behavior is presented under dark conditions. The ratio of forward-to-reverse current exceeded 300 within the range of applied voltages of ±1.0 V.

Since the electric transport in heterojunctions devices may be slowly varying functions on temperature and applied voltage as it is predicted by the Anderson model [25], it is possible to suppose that the relationship between I and V could be used to know the junction electrical parameters. That relationship can be expressed as

$$J = J_0[\exp(qV/AkT) - 1], \tag{1}$$

In Eq. (1), J_0 is the reverse saturation density current, V the applied voltage, A the diode quality factor, k de Boltzmann constant and T the absolute temperature. The values of J_0 and A can be obtained by extrapolation of log J vs. V curve to V=0. A typical plot of log I vs. V for the fabricated diodes is shown in Fig. 6. From this graph, the reverse saturation current has a value around 3.7×10^{-7} A, given a reverse saturation density current about 1.2×10^{-5} A/cm^2. The estimated diode factor was 2.7. When the diodes were illuminated, a small photovoltaic effect was observed as it can be seen in the inset of Fig. 5. It was

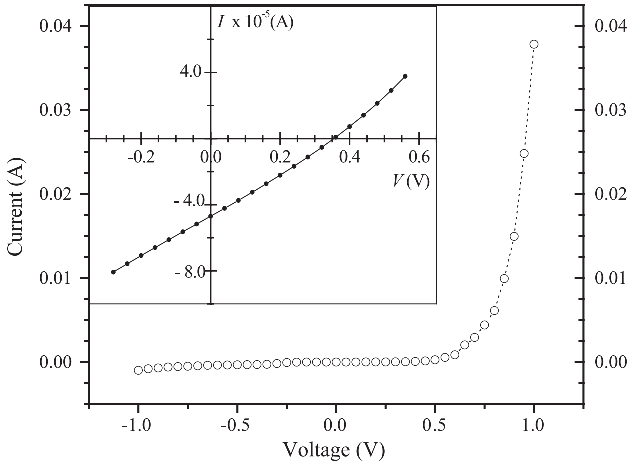

Fig. 5. Dark electrical characteristics I vs. V for the junctions. The inset shows the I vs. V characteristics under illumination.

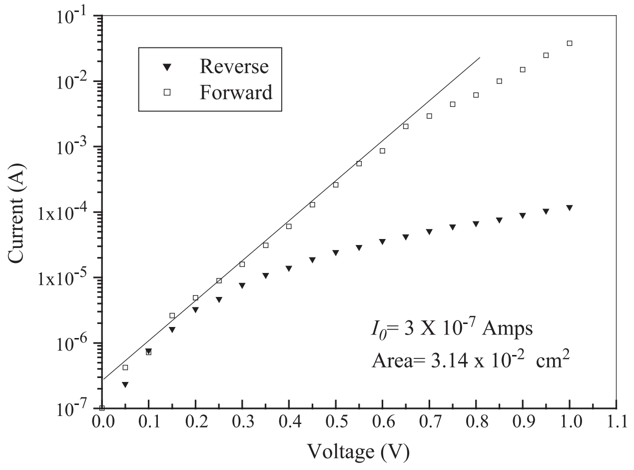

Fig. 6. Plot of log I vs. V forward and reversed bias at room temperature.

detected an open circuit voltage of around 0.35 V and a small short circuit current density with a value of 1.5 mA/cm^2. For the inset of Fig. 5, a strong effect of shunt resistance and series resistance were detected in the fabricated devices. Since there is not any report about heterojunctions formed by thin films of SnS_2 and SnS, it is not possible to compare our results. However, these results obtained here open the opportunity to study this kind of junctions. More detailed analysis must be done in order to understand the electrical transport trough the device and, at the same time, to improve the quality of these diodes and the photovoltaic effect.

4. Conclusions

Heterojunctions based on Sn–S compounds were fabricated by the PECVD process. Using SnS_2 as a window material and SnS as absorber material, the structure device glass/TCO/SnS_2–SnS/Al was electrically characterized. *I* vs. *V* characteristic showed that the device has a rectification behavior in the range of the bias voltage studied. A small photovoltaic effect was observed in this kind of structure with an open circuit voltage of around 0.35 V and a short circuit current density of 1.5 mA/cm^2. The result presented here demonstrates the possibility to build solar cells with these chalcogenide materials.

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