

Películas delgadas de SnS dopadas con Cu,Se para aplicaciones fotovoltaicas

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Resumen

En esta investigación se prepararon películas delgadas de SnS dopadas con Cu,Se, utilizando las técnicas de deposición por baño químico y evaporación térmica. Las películas delgadas fueron caracterizadas por medio de la técnica de difracción de rayos X, en donde se confirmó la presencia de la fase ortorrómbica de SnS con carta pdf#39-0354. La composición química de las muestras fue analizada a partir de un espectro general utilizando la técnica de fotoelectrones emitidos por rayos X, en donde se confirmó la presencia de los elementos Cu, Se, Sn y S. Las propiedades ópticas de las películas delgadas fueron medidas utilizando un espectrofotómetro UV-Vis-IR en el rango de 250 – 2500 nm. Las películas delgadas presentaron un coeficiente de absorción en rango de 10^{-4} – 10^{-5} (cm^{-1}), y brechas de energía de entre 1.1 y 1.3 eV para las muestras sin dopar y 0.9 eV para las muestras dopadas. Las propiedades eléctricas fueron determinadas utilizando un arreglo eléctrico, las muestras sin dopar presentaron conductividades en el rango de 9.66×10^{-7} – 3.82×10^{-4} ($\square\text{cm}^{-1}$), mientras que las muestras dopadas presentaron conductividades en el rango de 8.93×10^{-3} - 1.18×10^{-2} ($\square\text{cm}^{-1}$).

Sulfuro de Estaño, evaporación térmica, deposición por baño químico

Abstract

In this work we prepared Cu,Se doped SnS thin films by an hybrid method of chemical bath deposition and thermal evaporation. SnS thin films were characterized by X-Ray diffraction to determine the structural characteristics. The results showed the formation of orthorhombic SnS (pdf#39-0354). Chemical composition of the samples was measured by XPS, the general spectra showed the presence of Cu, Se, Sn and S elements on the samples. Optical properties of the samples were measured by using an UV-Vis-IR spectrophotometer in the range of 250 – 2500 nm. All thin films showed absorption coefficients in the range of 10^{-4} – 10^{-5} (cm^{-1}), also undoped SnS thin films showed band gaps of 1.1 to 1.3 eV, while Cu,Se SnS doped thin films showed band gaps near 0.9 eV. Electrical properties were measured by using an electrical array, undoped SnS thin films showed conductivities of 9.66×10^{-7} – 3.82×10^{-4} ($\square\text{cm}^{-1}$), while Cu,Se doped SnS thin films showed conductivities in the range of 8.93×10^{-3} - 1.18×10^{-2} ($\square\text{cm}^{-1}$).

Tin sulphide, thermal evaporation, chemical bath deposition

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Introducción

Second generation solar cells have attracted much attention due to the early success of CdTe, GaAs and $\text{CuIn}_x\text{Ga}_{(1-x)}\text{Se}_2$ as absorber materials in photovoltaic applications (Heriche, Rouabah, & Bouarissa, 2016; Ojo & Dharmadasa, 2016; Saravanan, Krishna Teja, Dubey, & Kalainathan, 2016). However, the main problems with these absorber materials are the scarcity of the constituent elements and high toxicity. Also, the deposition techniques used to prepare these materials, such as chemical vapor deposition, are expensive and in some cases, they generate toxic gases that are detrimental to the human beings. In this regard, alternative absorber materials such as $\text{Cu}_2\text{ZnSnS}_4$, Sb_2S_3 , SnS, Cu_2SnS_3 , AgSbS_2 and SnSb_2S_4 have been investigated due to the availability of the constituent elements and low toxicity (Daniel, Henry, Mohanraj, & Sivakumar, 2016; Escorcia-García, Becerra, Nair, & Nair, 2014; Garcia-Angelmo, Nair, & Nair, 2014; Lee, Choi, Kim, Jeong, & Park, 2016; Marquez Prieto et al., 2016; Rabeh, Khedmi, & Kanzari, 2015). These materials have excellent optoelectronic properties which make them suitable as absorbers in photovoltaic applications.

Justificación

The techniques of chemical bath deposition and thermal evaporation used to prepare the Cu,Se doped SnS thin films are relatively of low cost; also, the constituent elements of SnS thin films are not toxic and abundant on the earth crust. Besides, there are no reports of SnS thin films doped with Cu and Se.

Problema

SnS is a material with good optoelectronic properties so it can be used as absorber in photovoltaic structures.

However, the main problem with SnS is its low electrical conductivity, which decreases the short circuit current density and so the efficiency of photovoltaic structures. Copper and selenium are elements that are commonly used as doping elements for increasing the conductivity of semiconductors. However, selenium is mostly deposited by a selenization process in which toxic selenium vapor is generated and this vapor is detrimental for the human health.

Hipótesis

It is possible to prepare Cu,Se doped SnS by heating layered precursor structures consisting of chemically deposited SnS and thermally evaporated Cu after dipping in sodium selenosulfate solution for various durations, and tune the optoelectronic properties of the samples by controlling the Se content.

Objetivos

Objetivo General

Prepare and characterize Cu,Se doped SnS thin films by heating layered precursor structures consisting of chemically deposited SnS and thermally evaporated Cu after dipping in sodium selenosulfate solution for various durations, and study the effect selenium deposition time on the optoelectronic properties of SnS thin films.

Objetivos específicos

- Prepare Cu,Se doped SnS thin films by heating layered precursor structures consisting of chemically deposited SnS and thermally evaporated Cu after dipping in sodium selenosulfate solution for various durations.
- Determine the structural characteristics of the samples by XRD.

- Measure the composition of the samples by XPS.
- Determine the morphology of the samples by AFM.
- Measure the %T and %R of the samples by UV-Vis-IR spectrophotometry and calculate the absorption coefficient and band gap.
- Measure the electrical characteristics of the samples with an electrical array and calculate the conductivity.

Marco Teórico

SnS is a promising candidate for photovoltaic applications due to its good opto-electronic properties. SnS belongs to the family of the IV-VI compounds and crystalizes in orthorhombic or cubic structures when deposited via chemical bath deposition, depending on the bath conditions (García-Angelmo et al., 2014). It has a high absorption coefficient ($>10^4 \text{ cm}^{-1}$) and a direct bandgap in the range of 1.1 to 1.7 eV, depending on the crystal structure (García-Angelmo et al., 2014). Due to the high resistivity of the SnS thin films, some dopants such as Ag, Cu, In and Sb have been added to SnS thin films to improve their electrical properties (Kumar, Manohari, Dhanapandian, & Mahalingam, 2014). In this paper, we report the preparation of Cu,Se doped SnS thin films by heating multilayers of Glass/SnS/Cu/Se and study the effect of the selenium content on the electrical and optical properties of the material. The thin films formed under different conditions were characterized using X-ray diffractometer (XRD), Atomic Force Microscope (AFM), X-ray Photoelectron Spectroscopy (XPS), UV-Vis-IR spectrophotometer and photocurrent set up.

Metodología de Investigación

Preparation of Cu,Se SnS thin films.

a) Deposition of SnS thin films

SnS thin films were deposited on clean glass substrates. The substrates were cleaned with neutral detergent, rinse with deionized water and dried with hot air. For the preparation of SnS thin films, 1 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ was dissolved in 5 ml of acetone, and to this solution 12 ml of triethanolamine (3.7M) was added, followed by 65 ml of deionized water, 8 ml of tioacetamide (1M), and 10 ml of NH_3 (4M) (García-Angelmo et al., 2014). Cleaned glass substrates were placed vertically on a 100 ml beaker and the temperature was maintained at 40 °C for 23 h. Uniform SnS thin films of ~ 600 nm were obtained. The thickness was measure using an Ambios XP-200 Stylus profilometer.

b) Deposition of Cu thin films

On the top of Glass/SnS thin films, copper was deposited by thermal evaporation. For this, copper wire with a purity of 99.999% was evaporated onto Glass/SnS thin films using a high vacuum thermal evaporation system (INTERCOVAMEX-TE12P). Thickness of copper layer was measured using a quartz crystal thickness monitor incorporated in the deposition system. The copper thickness deposited was 30 nm.

c) Selenization

The samples of Glass/SnS/Cu were selenized using a solution method at room temperature conditions. Selenium bath was prepared by dissolving 2.2 ml of acetic acid (25% volume) in 37.8 ml of deionized water at room temperature. Then, 7 ml of 0.1 M Na_2SeSO_3 was dissolved in 33 ml of deionized water and finally both solutions were mixed in a 100 ml beaker (González et al., 2014).

Glass/SnS/Cu multilayers were placed vertically in the solution for different durations of 30 min, 1 and 2 h.

d) Heating

The selenized multilayers, Glass/SnS/Cu/Se were heated at 350 °C for 1 h, in low vacuum at 10^{-3} torr (TMVacuum products model No V/IG-803-14).

e) Characterization

X-ray diffraction (XRD) patterns of the thin films were recorded on a Panalytical Empyrean diffractometer using Cu $K_{\alpha 1}$ radiation ($\lambda = 1.54059 \text{ \AA}$). The scan range (2θ) was $10 - 90^\circ$. Elemental analysis was done using a thermo scientific XPS (K-alpha). Morphological studies were done using an AFM (NT-MDT). The optical transmittance (T) and specular reflectance (R) of the films were recorded using a Jasco V-770 spectrophotometer in the 300 – 2500 nm wavelength range. Electrical measurements were carried out using Keithley 6487 Picoammeter/Voltage source interfaced with a computer. For the DC conductivity measurements, the contacts used were two planar electrodes of 3 mm in length and 3 mm in separation using carbon paint. The light source used was a tungsten halogen lamp and the intensity was 870 W/m^2 .

Tipo de Investigación

Scientific research

Resultados

Figures 1(a) and (b) show the XRD patterns of as deposited and heat treated SnS thin films, respectively. In the figure, we can observe major peaks at 2θ angles of 21.93° , 26.08° , 30.69° and 31.65° , corresponding to the planes (110), (120), (101) and (111), respectively; these peaks match the standard of SnS (pdf#39-0354).

The grain size of these thin films was calculated using the Sherrer's equation (Lakhe & Chaure, 2014):

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

Where λ is the X-ray wavelength, β is the line broadening at half the maximum intensity and θ is the Bragg angle. The calculated grain size were 11 and 16 nm for the as-deposited and heat treated SnS thin films, respectively. The increase in size is due to the heat treatment.

Figure 1(c), (d) and (e) show the XRD patterns of heat treated Cu,Se doped SnS thin films with 30 min, 1 h and 2 h of selenium, respectively. From the figure, we can observe intense peaks at 2θ : 22° , 26.13° , 30.46° and 31.48° corresponding to the planes (110), (120), (101) and (111), respectively; these peaks match the standard of SnS (pdf#39-0354). When incorporating Cu and Se to the SnS thin films no new peaks were observed, indicating that the incorporation of Cu and Se neither change the structure of SnS nor resulted in the formation of new phases. The grain size for these samples was $\sim 17 \text{ nm}$.

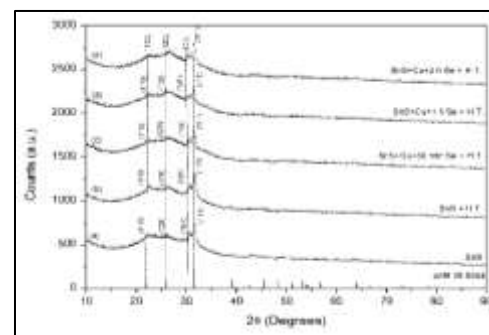


Figure 1 XRD patterns for multilayers of (a) as-deposited SnS thin films, (b) heat-treated SnS thin films, (c) Cu + Se (30 min) + SnS + H.T. thin films, (d) Cu + Se (1 h) + SnS + H.T. thin films and (e) Cu + Se (2 h) + SnS + H.T. thin films.

In figure 2(a), (b), (c), (d) and (e) show the XPS survey for as-deposited SnS, heat treated SnS, Cu-Se(30min) doped SnS, Cu-Se(1h) and Cu-Se(2h) doped SnS samples, respectively. In figure 2(a) and (b), the binding energy peaks of Sn 3s, 3p, 3d, 4s, 4d, and S 2s, 2p were identified, confirming the presence of these elements on the surface of the sample, along with C 1s and O 1s which can be attributed to the exposure of the samples to the atmosphere. In figure 2(c), (d) and (e), in addition to Sn, S, C and O peaks, we also observe the presence of Cu 2p, 3p and Se 3s, 3p, 3d.

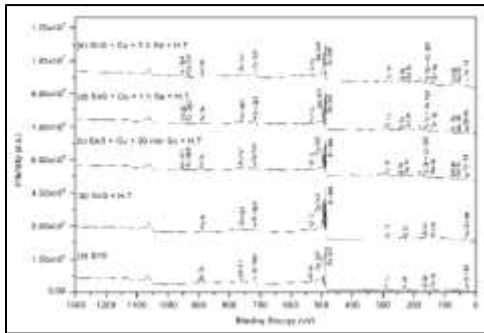
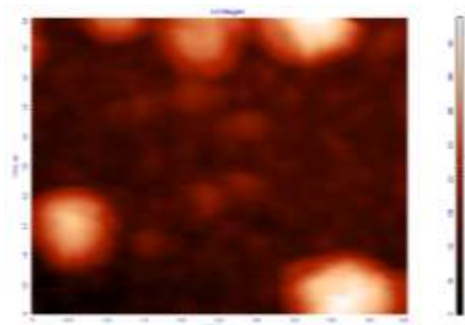


Figure 2 XPS survey spectrum of multilayers of (a) as-deposited SnS thin films, (b) heat-treated SnS thin films, (c) Cu + Se (30 min) + SnS + H.T. thin films, (d) Cu + Se (1 h) + SnS + H.T. thin films and (e) Cu + Se (2 h) + SnS + H.T. thin films.

The chemical composition the samples was measured by XPS. As-deposited SnS and heat treated SnS samples showed nearly the same composition with SnS ~ 60 at% and S ~ 40 at%. For Cu,Se doped SnS thin films, the S at% remained constant as 40%, however Sn at% reduced to ~ 40% as Cu and Se were incorporated, suggesting substitution of Sn atoms by Cu atoms as both have similar ionic radii (~70 pm). Also, the selenium content increased from 16.30 to 19.23 at% as the deposition time was increased from 30 min to 2 h.

Morphology of heat treated SnS and Cu,Se(30min) doped SnS, are depicted in figure 3(a) and (b), respectively. From the figure, we can observe compact structures with spherical interconnected grains and grain boundaries well defined, also large grains were observed that consisted of small grains; in the case of 3(b) flakes were also observed. No pin holes were observed in any sample.

a)



b)

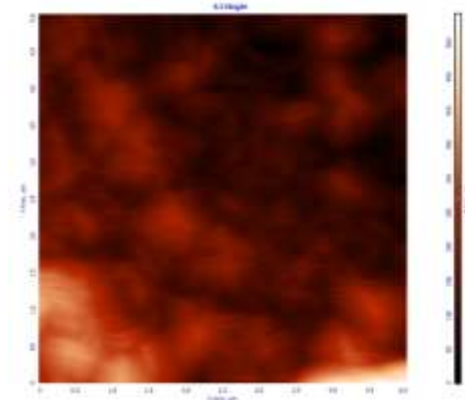


Figure 3 Atomic force micrographs of multilayers of (a) heat-treated SnS thin films (5mm), (b) Cu + Se (30 min) + SnS + H.T. thin films (5mm).

Figure 4 (a), (b), (c), (d) and (e) show the optical transmission (%T) and reflection (%R) spectra of as-deposited SnS, heat treated SnS, Cu,Se(30 min) doped SnS, Cu,Se(1 h) doped SnS and Cu,Se(2 h) doped SnS, respectively, recorded over a wavelength range of 250 - 2500 nm.

Using the transmission (%T) and reflection (%R) values from the spectra, absorption coefficient (α) at each wavelength was calculated using the following relation (González et al., 2014):

$$\alpha = 1/d [(1 - R)^2/T] \quad (2)$$

Where, d is the thin film thickness and the value was ~ 600 nm for un-doped samples and ~ 700 nm for the doped ones. In figure 4(f), we can observe that all the samples show an indirect transition with an absorption coefficient $\alpha \sim 10^5 \text{ cm}^{-1}$ in the visible range. From the spectra, the optical band gap of the thin films was evaluated using the formula (González et al., 2014):

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (3)$$

where E_g is the optical band gap and “n” can take the values of 2, 1/2, 2/3 for allowed direct, allowed indirect and forbidden direct transitions, respectively, α is the absorption coefficient at frequency ν and A is a constant. Figure 4 (g) shows the Tauc plots for all the samples. From the figure, we observe that all samples show indirect allowed transitions, as-deposited SnS shows a band gap of ~ 1.25 eV, when a heat treatment is applied to the sample the band gap decreases to 1.1 eV which can be attributed to the increase in grain size; when Cu and Se are added to the sample we observe a band gap of ~ 0.9 eV.

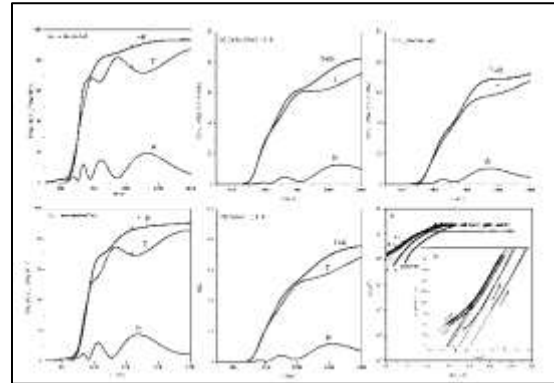


Figure 4 Optical characteristics: transmittance (%T), reflectance (%R) and transmittance + reflectance (%T + %R) for (a) as-deposited SnS thin films, (b) heat-treated SnS thin films, (c) Cu + Se (30 min) + SnS + H.T. thin films, (d) Cu + Se (1 h) + SnS + H.T. thin films and (e) Cu + Se (2 h) + SnS + H.T. thin films; (f) absorption coefficient (g) Tauc plots.

The type of conductivity was determined using the hot probe method. All samples show p-type conductivity. P-type conductivity for Cu,Se doped SnS thin films may be to the presence of defects of selenium interstitials as reported by K. Bindu et al. (González et al., 2013).

Figure 5 shows the photocurrent response curve for all samples. To measure the photo-generated current, a bias voltage of 10 V was applied and the current through the sample was measured for a period 20 s under dark (I_0), 20 s under illumination (I) and 20 s after switching off the illumination. We observe that as-deposited SnS sample showed a high resistivity in the order of $\sim 10^{-7} (\Omega \text{ cm})^{-1}$, when a heat treatment was applied to the sample an increase in conductivity was observed $\sim 10^{-4} (\Omega \text{ cm})^{-1}$ which can be attributed to the increase in grain size. In the case of samples of Cu,Se doped SnS, we observed conductivities in the range of $10^{-3} - 10^{-2} (\Omega \text{ cm})^{-1}$, also the conductivity increased as the selenium content in the sample increased confirming the suggestion that the type of defects present in the sample are selenium interstitials.

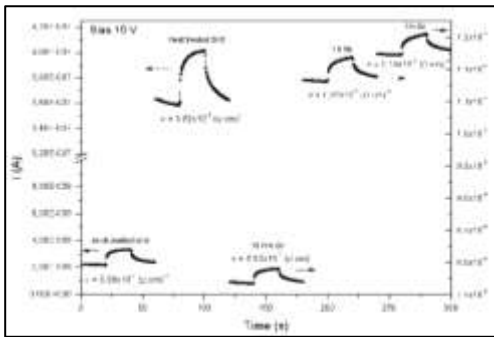


Figure 5 Photocurrent response

Conclusiones

In this work, we prepared Cu,Se doped SnS thin films by heating multilayers of Glass/SnS/Cu/Se at 350 °C for 1 h in vacuum. Different techniques were used to determine the structure, morphology, optical and electrical properties of these thin films. XRD showed the formation of SnS thin films for all samples. AFM showed compact structures and no pin holes were observed. All samples showed indirect allowed transitions, when Cu and Se were added to the samples the band gap was reduced to 0.9 eV. All samples showed p-type conductivity and increased as the selenium content in the samples increased. The optical and electrical properties of the Cu,Se doped SnS thin films make them suitable for photovoltaic applications.

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