Characterization of Cu_3BiS_3 thin films annealing layers of Bi_2S_3-CuS chemically deposited

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Recibido 30 octubre 2022, Aceptado 30 noviembre 2022

Abstract

Cu_3BiS_3 thin films with values of thickness 170 nm were obtained; these films were characterized using X-ray diffraction, Electron Microscopy Scanning, UV-Vis spectrophotometry, and photoconductivity. We obtained values of bang gap energy 1.65 eV and electrical conductivity approximately 2.58 $(\Omega\text{-cm})^{-1}$. A second layer of Cu_3BiS_3 was deposited over the first one, thickness increased to 450 nm and band gap energy was 1 eV and electrical conductivity approximately 1 $(\Omega\text{-cm})^{-1}$.

Keywords: Thin film, Cu_3BiS_3, Chemical Bath Deposition, Photovoltaics.

1. Introducción

An alternative to avoid the use of toxic or expensive compound in solar cells are ternary copper sulphides based on Cu-Bi-S as Cu_3BiS_3, these materials exhibit promising properties as absorbent materials for thin films solar cells. The search for earth-abundant non-toxic materials for large scale deployment of photovoltaics is becoming increasingly important. Current technologies using rare elements such as indium and gallium are unlikely to be able to satisfy the rapidly growing demand for thin film solar cells [1]. The potential application of the sulfosalt Cu_3BiS_3 as a p-type absorber film in photovoltaics was first considered by Nair et al. [2]. This compound, which occurs naturally as the mineral Wittichenite, crystallizes in an orthorhombic unit cell (a=7.723 Å, b=10.395 Å, c=6.715 Å) [3]. An optical bandgap of 1.4 eV was achieved for the film deposited at 400 °C [4]. Some authors used CBD technique [2, 6] to deposit the film but some others have preferred other routes to grow thin films, some of these are co-evaporation [5], electrodeposition [1] spray pyrolysis [6], physical vapor deposition [7], among others. The chemical bath deposition (CBD) is probably the simplest method available for this purpose, all that is needed is a container for containing the solution (an aqueous solution composed of a few, generally common, chemicals) and the substrate on which deposition is required [8].In this paper, we report the formation of a ternary compound Cu_3BiS_3 by annealing for 30 and 90 min at 350 °C a coating obtained by depositing CuS on Bi_2S_3 thin films, both by the chemical deposition technique. Subsequently a second Cu_3BiS_3 layer was deposited over the first one in order to increase thickness.

2. Experimental details

2.1 Deposition of bismuth sulphide (Bi_2S_3) thin films

The deposition bath for the Bi_2S_3 film was prepared by dissolving bismuth (III) nitrate ($Bi(NO_3)_3{\cdot}5H_2O$, 99% J. T. Baker) in sodium tartrate 1M ($C_4H_4Na_2O_6{\cdot}2H_2O$ 99.9% J. T. Baker) in a baker and mixing with 1 ml of ammonia buffer pH 10, thioacetamide 1M (CH_3CSNH_2, 99.8%, Fisher Chemical) and making the volume up to 50 ml by adding de-ionized water, the reagents were continuously stirred. The glass substrates (Corning, 25mm×75mm) were cleaned in a commercial detergent

solution, rinsed in de-ionized water, and dried, then placed vertically in the solution at 35 °C for 7 h without stirring. The thickness obtained for films was 95 nm.

2.2 Deposition of copper sulphide (CuS) thin films

The procedure given in [9] was followed to deposit copper sulfide thin films by using 2.5ml of 0.5M solution of copper (II) chloride ($CuCl_2 \cdot 2H_2O$, 99%, Fisher Chemicals) mixed with 4.5ml of 1M solution of sodium thiosulfate ($Na_2S_2O_3$, 99.7%, Fermont), 5 ml of 0.5M dimethylthiourea ($C_3H_8N_2S$, 99%, Aldrich) and making the volume up to 50 ml by adding de-ionized water, the reagents were continuously stirred. Bismuth sulfide thin films were used as substrates, and for the deposition the substrates were placed vertically in the solution at 70 °C for 2 h without stirring. After the deposition, the slides were rinsed well with de-ionized water

Two-layer films Bi_2S_3–CuS were deposited on both sides of the substrates. Thin film deposited on the side of the substrate facing the beaker wall was retained for the optical and electrical characterization. The coating on the other side was wiped off with dilute hydrochloric acid (HCl). The thickness obtained for CuS films deposited for 2 h was 85 nm.In this work, we report the formation of Cu_3BiS_3 thin films by CBD on glass substrates applying thermal treatment at 350 °C in vacuum oven for 30 and 90 min at $5.8x10^{-3}$ Torr on chemical deposited layers of Bi_2S_3 and CuS to obtain the crystalline phase of Cu_3BiS_3. Two-layer films were annealed at 350 °C in vacuum oven for 30 and 90 min at $5.8x10^{-3}$ Torr to obtain the crystalline phase of Cu_3BiS_3.

2.3 Characterization

The x-ray patterns are recorded on a Rigaku D-Max 2200 diffractometer using CuKαradiation (λ=0.1541 nm) in the grazing incidence mode at Ω = 0.5 º. The thickness was measured with a profilometer KLA-Tenco Alpha step D-100. The Optical transmittance spectra (air as reference) and reflectance spectra (clean substrate as reference) are measured using a Shimadzu-UV-3101PC spectrophotometer in the wavelength range 2500-250 nm. For electrical characterization of the thin films, pairs of silver-paint electrodes of 5 mm in length at 5 mm separation, were applied on the surface and allowed to dry. Photocurrent response of the films was obtained using a tungsten–halogen lamp and a Keithley 6487 multimeter. For these measurements were applied 5 V. Topography and morphology of the deposited films was analyzed using a Hitachi FESEM S 5500 scanning electron microscope at electron beam energy of 3 and 5 keV.

3. Results

3.1 *X-Ray Diffraction*

Fig. 1 shows the X-ray diffraction (XRD) patterns of the Cu_3BiS_3 thin films of 170 nm, recorded after the films were annealed in vacuum at 350 ◦C and $5x10^{-3}$ Torr for (a) 30 min and b) 90 min. The XRD pattern shown in Fig. 1(a) match well with that of the standard pattern of the orthorhombic phase Cu_3BiS_3 (AMCSD0009490) The main diffraction peaks of this compound are: (020), (111), (200), (210), (211), (031), (131), (122) peaks, but also one additional peak due to an excess of sulfur (026) was identified. Fig. 1(b) shows the XRD pattern corresponding to Cu_3BiS_3 peaks mentioned above without the excess of sulfur peak. This event was due to an increase in the time of heat treatment. With this diffractogram and using the Scherrer equation on the diffraction plane (131) it was possible to determine the average crystallite size, finding a value of 20.2 nm.

After the Cu_3BiS_3 pure phase was confirmed, second two-layer films Bi2S3–CuS were deposited and annealing over the first one, in order to increase thickness, obtaining a value of 450 nm.

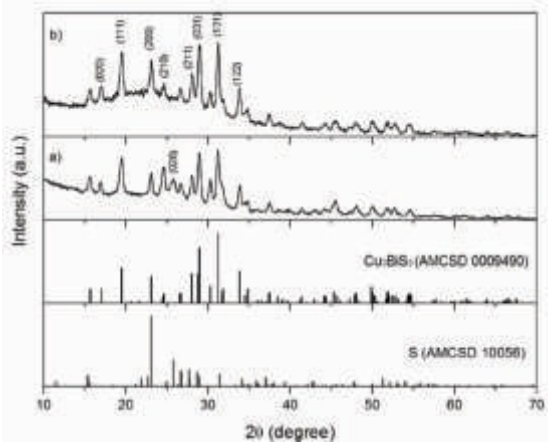

Fig 1. XRD patterns for Cu_3BiS_3 films: (a) after annealing in vacuum for 30 min at 350 °C and $5x10^{-3}$ Torr, and (b) after annealing in vacuum for 90 min at 350 °C and $5x10^{-3}$ Torr.

Fig. 2 shows the X-ray diffraction (XRD) patterns of the Cu_3BiS_3 thin films of 450 nm and presents the same main diffraction peaks of this compound, matching well with that of the standard pattern of the orthorhombic phase Cu_3BiS_3.

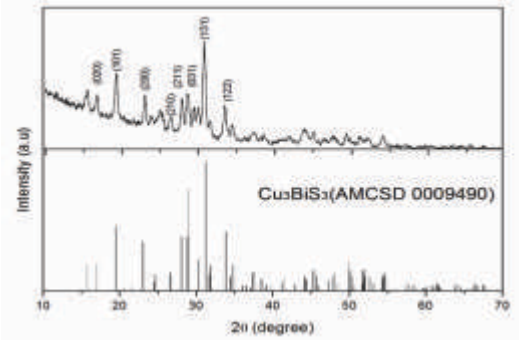

Fig 2.XRD patterns for Cu_3BiS_3 (450 nm) film after annealing in vacuum for 90 min at 350 °C and $5x10^{-3}$ Torr.

3.2 Morphological analysis

SEM analysis of the film shows a homogeneous surface of Cu_3BiS_3 obtained after annealing and grain size in the order of nanometers with the formation of some agglomerates, because using CBD is difficult to control the growth of the film (Fig. 3). The morphology of Cu3BiS3 films obtained heating at 350 ºC and $5x10^{-3}$ Torr for 90 min can be observed in Fig. 3(a) 170 nm and (b) 450 nm. In Fig. 3(a) it cannot be observed a defined shape but a rocky surface with void areas. Inthe other hand, the Fig. 3(b) shows that with larger film thickness (450 nm) surface appears with more uniform formation, like flowers, but we can see some dispersed clusters.

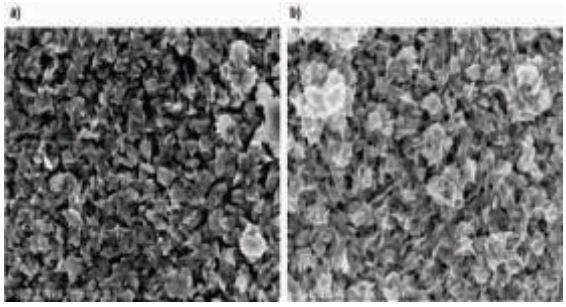

Figure 3. Scanning electron micrographs for Cu_3BiS_3 films obtained heating at 350 ºC and $5x10^{-3}$ Torr for 90 min (a) 170 nm and (b) 450 nm.

3.3. Optical characterization

Fig. 4 shows the optical transmittance and reflectance spectra for the 170 and 450 nm Cu_3BiS_3 films. As we can see, the signal of the transmittance spectra for the film with thickness 170 nm starts around 50% in the near-IR region, and this value decrease strongly when enters to the visible region, from 20% down to value of 0% when reach the UV region. In the other hand, the signal of the transmittance spectra for the film with thickness 450 nm starts around 15% in the near-IR region and remains stable up to a wavelength of 1375 nm, where the %T starts to decrease, reaching a value of 0% around 625 nm. With both spectra we can assume the films have promising optical properties to be used as an absorber material in a solar cell because of the low percent of transmittance and reflectance found.

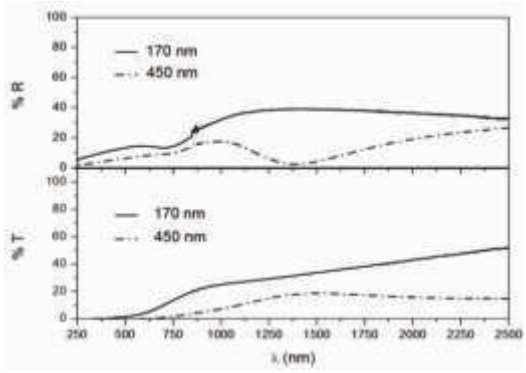

Figure 4. Transmittance and Reflectance spectra for the Cu_3BiS_3 films after annealing in vacuum for 90 min at 350 °C and $5x10^{-3}$ Torr.

The band gap was calculated using the relationship ec. 1.

$$(\alpha h\nu)^n = A(h\upsilon - E_g) \quad (1)$$

Where A is a constant as a function of the transition probability and Eg is the optical band gap. The Eg values can be obtained from the best linear approximation of (αhν)2versus hlplot, and its extrapolation to (αhν)2 = 0 as seen in figure 5. The Eg value obtained for the 170nm thickness Cu_3BiS_3 film after annealing in vacuum for 90 min at 350 ◦C and $5x10^{-3}$ Torr was 1.6 eV this Eg value is slightly higher to the value reported for this material [5]. The 450 nm thickness Cu_3BiS_3 film shows an Eg value of 1 eV, which is comparable to what others authors have reported [6].

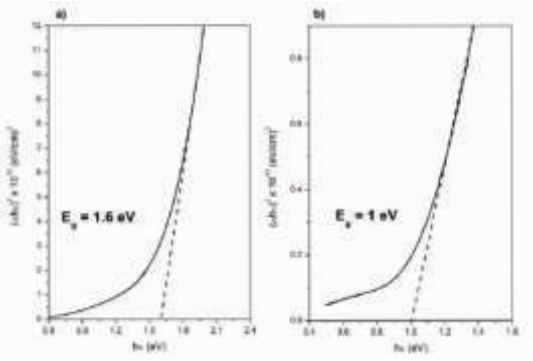

Figure 5. Plot of $(vhv)^2$ versus hv for the Cu_3BiS_3 films after annealing in vacuum for 90 min at 350 ◦C and $5x10^{-3}$ Torr, a)170nm - Eg = 1.6 eV, b) 450nm - Eg = 1 eV.

3.4. Electrical characterization

The electrical conductivity value obtained for the 170 nm thickness Cu_3BiS_3 films, after annealing in vacuum for 90 min at 350 ◦C and $5x10^{-3}$ Torr was: 2.58 (Ωcm)-1, and for the 450 thickness Cu_3BiS_3 films, the electrical conductivity value was 1.01 (Ωcm)-1. In both cases, useful conductivity values of semiconductors were obtained, and both have potential application in solar cells. In the present case, hot-probe testwas perform heating the positive probe of a voltmeter while the cold probe is connected to the negative terminal, the material yields a negative voltage, indicated p-type conductivity in all the Cu_3BiS**3** films after they are annealed [11].

4. Conclusions

Cu_3BiS_3 thin films can be prepared by annealing chemically deposited Bi_2S_3–CuS thin films at 350 ◦C vacuum for 30 and 90 min at 350 ◦C and $5x10^{-3}$ Torr, but with 30 min an excess of sulfur occurs, that´s why it is necessary increase the time of annealing. The thickness of the films was 170 and 450nm for the one and two layers respectively. The SEM analysis revealed that these films have a homogeneous surface and grain sizes in the order of nanometers. The conductivity value for the films was 2.58 and 1.01 (Ωcm)-1. The low values of transmittance and reflectance spectra in addition to the optical band gap of 1.65 and 1 eV obtained for the Cu_3BiS_3 films suggests the use of this film in photovoltaic structures as a absorber layer.

5. References

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