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Laser power density effect on the properties of Sb_2S_3 thin films prepared by pulsed laser assisted chemical bath deposition

Efecto de la densidad de energía en las propiedades de películas delgadas de Sb_2S_3 preparadas por baño químico asistido con láser pulsado

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Abstract

Antimony Sulfide (Sb_2S_3) thin films were prepared using the laser assisted chemical bath deposition technique. The precursors used in the chemical bath were antimony chloride and sodium thiosulfate, the deposit was made at room temperature on glass substrate, while it was irradiated with a wavelength of 532 nm of the pulsed Nd:YAG laser. In this work, we studied the effects of energy density (1.97×10^7 and 7.07×10^6 W/cm^2) and the irradiation time (30, 45 and 60 min) during the deposition process on the structure and the optical and electrical properties of the antimony sulfide films. The structure, composition, and optical and electrical properties were analyzed by X-Ray Diffraction (XRD), Raman Spectroscopy and X-Ray Emitted Photoelectron Spectroscopy (XPS), UV-Vis spectroscopy and photoconductivity. The results showed that the laser assisted chemical deposition technique is an effective synthesis technique for obtaining thin films of antimony sulfide for optoelectronic applications or in solar cells.

Thin Films, Laser, Power density

Resumen

Películas delgadas de sulfuro de antimonio (Sb_2S_3) fueron preparadas utilizando la técnica de deposición por baño químico asistido con láser. Los precursores utilizados en el baño químico fueron cloruro de antimonio y tiosulfato de sodio, el depósito se realizó a temperatura ambiente sobre sustratos de vidrio mientras se irradiaba con la longitud de onda de 532nm de un láser pulsado Nd:YAG. En este trabajo se estudió el efecto de la densidad de energía (1.97×10^7 y 7.07×10^6 W/cm^2) y el tiempo de irradiación (30, 45 y 60 minutos) durante el proceso de depósito, en la estructura, propiedades ópticas y eléctricas de las películas de sulfuro de antimonio. Se analizó la estructura, composición, propiedades ópticas y eléctricas mediante Difracción de Rayos X (DRX), Espectroscopía Raman y Espectroscopia de Fotoelectrones Emitidos por Rayos X (XPS), espectroscopia UV-Vis y fotoconductividad. Los resultados mostraron que la técnica de depósito químico asistido con láser es una técnica de síntesis efectiva para obtener películas delgadas de sulfuro de antimonio para aplicaciones optoelectrónicas o en celdas solares.

Películas Delgadas, Láser, Densidad de energía

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Introduction

Global warming, coupled with the growing global energy demand are problems that concern us all. Global warming occurs due to greenhouse gases generated from the burning of fossil fuels to produce electrical energy. Due to this, it is necessary to look for alternative sources for the generation of energy, such as the photovoltaic solar source. Photovoltaic solar technology based on thin films uses semiconductor materials with thicknesses of several nanometers up to several microns (Ismail, Abeduljabbar, & Fatehi, 2019). In thin films of metal chalcogenides, we find Antimony Sulfide (Sb_2S_3) as absorbing material, due to its high absorption coefficient and a bandgap interval between 1.7-2.5 eV. Sb_2S_3 thin films have attracted great interest due to their potential applications in various optoelectronic devices. Although an important aspect of the Sb_2S_3 films obtained by chemical bath is the absence of crystallinity, it is necessary to subject them to post-deposit treatments or *in situ*, to improve the crystalline properties of the material and the subsequent performance of the device (Messina, Nair, & Nair, 2007; Shaji et al., 2010; Virt et al., 2017; Virt et al., 2013).

Methodology

The methodology used for the preparation of thin films was the deposition of Sb_2S_3 by means of a pulsed laser assisted chemical bath deposition (PLACBD). This procedure consists in irradiating with a pulsed laser a solution of chemical precursors at a constant temperature, which upon finding a surface nucleation occur and they grow in two dimensions, subsequently a heat treatment is necessary to obtain a thin film with the expected phase. The first step for the deposition of thin films is the cleaning of the substrates.

The substrates used were Fisher Scientific, with dimensions of 72x25x1.1 nm, which were previously washed with chromic solution, rinsed with distilled water and finally dried with hot air. After the precursor solution was prepared, 0.650 g of $SbCl_3$ (antimony trichloride, 99% Fermont brand) were weighed and dissolved in 2.5 ml of $CH_3(CO)CH_3$ (acetone, 99.5% Fermont brand) using a beaker of 100 ml, then 25 ml of a solution of 1 M $Na_2S_2O_3.5H_2$ (99.5% sodium thiosulfate, Fermont brand) was added, followed by 72.5 ml of distilled water (González et al., 2013).

Finally, the clean glass substrates were placed horizontally in a glass container and the chemical precursor solution was added. The vessel was placed in a temperature controlled bath at 40 °C and the solution was irradiated with a 532 nm wavelength of a pulsed Nd: YAG Solar Systems laser (10ns, 10 Hz) using a concave lens with the objective of expanding the light beam over a greater part of the surface of the substrates.

The lens was placed at two distances (5 and 10 cm) on the surface of the solution resulting in two energy densities, 1.97x107 and 7.07x106 W/cm^2, to irradiate the solution at different times (30, 45 and 60 minutes.) After irradiation, the film deposited at the bottom of the substrate was subjected to heat treatment at 350° in vacuum for one hour, because the deposited film was amorphous. The thin films were characterized to study their structure and optoelectronic properties.

Results

X-ray diffraction

The crystalline structures for thin films of Sb2S3 prepared by chemical bath deposition (CBD) and pulsed laser assisted chemical bath deposition (PLACBD) were subjected to heat treatment at 350 °C for one hour in vacuum. For the analysis, an Empyrean PANalytican diffractometer was used, with CuKα radiation of wavelength 1.5406 Å operated at 45 kV and 40 mA, in a mode of gracing incidence at an angle of incidence of 1 °.

The scan range (2θ) was 10 to 60 ° at a scan speed of 0.005 ° / s. Figure 1 (a, b) shows the diffraction patterns for thin films of Sb_2S_3 with PLACBD deposited for 30 and 60 minutes under energy densities 1.97X107 and 7.07X106 W/cm^2. The patterns corresponding to the CBD are included in the comparison.

The peaks identified correspond to the stibin phase of Sb_2S_3 with orthorhombic structure (PDF # 42-1393), the most intense peak is located along the plane (130), while the peaks corresponding to the planes can also be identified (110) , (020), (120), (220), (320), (211), (221), (301), (240), (231), (340), (411), (250), (530), (531) and (360) [7,11-13], this orientation can be seen in Figure.-1 (b). However, in Figure (b) there is a preferential orientation towards the plane (211), that does not exist in Figure 1 (a).

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The DRX analysis showed that the thin films annealed under the different irradiation conditions were polycrystalline; the changes may be attributable to the deposition technique, the heat treatment of the films and their thickness.

Raman spectroscopy

Raman spectroscopy measurements were carried out at the excitation wavelength of 532 nm and 3 mW laser energy using a Raman DXRTM Thermo Scientific Microscope. Figure 2 (a) shows the Raman spectrum for Sb_2S_3 films prepared during 30 minutes of pulsed laser irradiation, obtained by CBD, Figure 2 (b) shows that of 45 minutes and Figure 2 (c) that of 60 minutes, respectively.

In the Raman spectrum, Sb_2S_3 films prepared by a pulsed laser assisted chemical bath deposition have higher intensity peaks compared to those obtained by chemical bath without irradiation. There were peaks with small variations in intensity, at the positions of 126, 155, 189, 236, 282 and 307 cm^{-1}, for all samples. It has been reported that the presence of the peaks in wave numbers 280 and 236 cm^{-1} is due to the preferential orientation along the crystalline plane (130) (Shaji et al., 2017). These bands have been reported for thin films of Sb_2S_3 (Chen et al., 2009; Han et al., 2010; Liu, Eddie Chua, Sum, & Gan, 2014). Raman's active vibration modes are identified as $10A_g$, 5B1g, $10B_{2g}$ and $5B_{3g}$. Peaks 155, 189 and 282 cm^{-1} of Figure 2 (a, b and c) correspond to A_g modes and peaks 126, 236 and 307 cm^{-1} are attributed to vibration modes B_{1g}.

X-ray Emitted Photoelectron Spectroscopy

The elemental composition and the chemical state of the antimony sulfide thin films were determined by means of the X-ray photoelectron spectra using a Thermo Scientific K-alpha XPS system that uses a monochromatized X-ray energy radiation of Al Kα 1486.6 eV. Figure 3 (a, b) shows the analysis of the chemical states of the 30, 45 and 60 minute samples where the pulsed laser assisted chemical bath deposition technique was used with energy densities of 1.97x107 and 7.07x106 W/cm^2, respectively. The spectra were obtained after surface cleaning by pickling with argon ions. The binding energy peaks were adjusted to the adventitious carbon corresponding to C1s at 284.6 eV. All peaks observed in the spectra were identified as Sb and S in the Sb_2S_3 samples.

Figure 3 (a) shows the spectra of Sb3d with a double in the link energies of ~ 530.3 and 539.7 eV for $Sb3d_{5/2}$ and $Sb3d_{3/2}$ separated by 9.4 eV, which are reported link energies for Sb^{3+} (Bierman et al., 2016; Huerta-Flores, García-Gómez, de la Parra, & Sánchez, 2015; Krishnan, Shaji, & Ernesto Ornelas, 2015; Liu et al., 2014). The spectra corresponding to S2p are presented in Figure 3 (b), which were deconvolved in individual states for $S2p_{3/2}$ and $S2p_{1/2}$ with bond energy values of 161.40 and 162. 6 with a difference of link energy (ΔE) of 1.2 eV. These binding energies are characteristic of sulfur (S^{2-}) (Ornelas-Acosta et al., 2015; Shaji et al., 2019; Vinayakumar et al., 2018; Vinayakumar et al., 2017). For the deconvolution, the peaks were adjusted using the Gaussian-Lorentz function and care was also taken to maintain the intensity ratio of $S2p_{3/2}$ to $S2p_{1/2}$ as 2:1 and the same FWHM value. The XPS results confirmed the elemental composition and chemical states of the thin antimony sulfide films in all conditions.

Optical Properties

The optical transmittance at normal incidence, T (%), and the mirror reflectance spectrum, R (%), of the samples were measured using a Shimadzu UV-1800 model spectrophotometer. Measurements were made in the UV-vis-NIR region in the wavelength range of 200 to 1200 nm. The transmittance (%T) and reflectance (%R) spectra for Sb_2S_3 thin films deposited by chemical bath and by pulsed laser-assisted chemical bath are presented in Figure 4. Figure 4 (a) shows the comparison between the transmittance and reflectance spectra of the Sb_2S_3 films prepared with irradiation for 30 minutes, in Figure 4 (b) those obtained at 45 minutes and in Figure 4 (c) those of 60 minutes.

Figure 4 (a) shows the highest percentage of reflectance in the wavelength range of 800 to 600 nm for the spectrum of the Sb_2S_3 film prepared without irradiation compared to Sb_2S_3 films prepared with irradiation at densities of 1.97x107 and 7.07x106 W/cm^2 energy. Films prepared without irradiation at 45 and 60 minutes have a higher percentage of reflectance in the wavelength range of 700 to 1000 nm compared to those obtained at 45 and 60 minutes with laser irradiation at different energy densities. According to Table 1, thin films of Sb_2S_3 prepared without irradiation have a greater thickness than those prepared with pulsed laser and their thickness increases with increasing irradiation time.

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The greatest reflectance in the wavelength range of 600 to 800 nm, for films obtained with laser irradiation, was for 45 minutes with an energy density of 1.97x107 W/cm^2, the thickness of which was 152.7 nm. The difference in reflectance is due to the difference in the thicknesses of the films prepared under the different conditions and the maximum reflectance moves to longer wavelengths as the thickness of the film increases (Han et al., 2010).

The oscillatory behavior of the reflectance is explained by the interference of the light reflected from the upper and lower surface of the film. In the region between 600 nm to 800 nm, the Sb_2S_3 films prepared with laser irradiation for 45 and 60 minutes show greater reflectance than those prepared without laser irradiation. The absorption coefficient (α) for the absorption wavelength region was calculated using the equation:

$$\alpha = \frac{1}{d} ln \left[\frac{(1-R)^2}{T}\right] \quad (1)$$

Where d is the thickness of the film. The term (1-R)^2 considers transmission through the upper and lower surfaces of the film, while the natural logarithm factor explains how the intensity decreases due to absorption according to Beer's law.

Figure 5 (a) shows the absorption coefficients of Sb_2S_3 films prepared with and without irradiation for 30 minutes, in Figure 5 (b) those obtained at 45 minutes and in Figure 5 (c) those of 60 minutes using two energy densities, 1.97x107 and 7.07x106 W/cm^2. All graphs show high absorption coefficients (greater than 105 cm^{-1}) in the energy range of 2 to 3 eV. Based on the absorption coefficient, the energy gap values were estimated using the ratio:

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (2)$$

Where E_g is the energy gap and n = 2, 1/2 and 2/3, are the values for the direct, indirect and direct bandgap transition semiconductors, respectively, α is the frequency *h* absorption coefficient and A is a constant. The graphs of $(\alpha h\nu)^2$ versus hν (Tauc graph) for Sb_2S_3 films prepared with and without irradiation are shown in Figure 6. The energy gap values for the films obtained by irradiation for 30 minutes, Figure 6 (a), were between 2.6 to 2.7 eV.

The energy gap for Sb_2S_3 films prepared at 45 minutes and 60 minutes of irradiation were in the range of 2.5 to 2.7 eV, Figure (b) and (c). The energy gaps had no significant change for the thin films of Sb_2S_3 obtained by pulsed laser assisted chemical bath deposition, this due to the lower thickness for said films.

Photoconductivity

To analyze the effect of pulsed laser irradiation on the electrical properties of Sb_2S_3 films, conductivity was measured both in the dark and under lighting conditions. The samples were exposed to light using a tungsten halogen lamp (intensity of 240W/m^2) to measure photoconductivity maintaining a constant voltage.

For this experiment, a voltage of 100 V was applied through ohmic contacts (2 flat silver paint electrodes 3 mm long and 3 mm apart) using a Keithley 6487 current/voltage meter. Measurements of conductivity were made for periods of 20 seconds, starting with the conductivity in the dark, then under light and finally in the dark.

All samples showed photocurrent in values of the order of 10-10 and in the dark the photocurrent declined to its initial value, as can be seen in Figure 7.

Figure 7 (a) shows the photocurrent graphs for the Sb_2S_3 films prepared by chemical bath with irradiation for 30 minutes and their comparison against that obtained without irradiation, in which there is a greater photocurrent in the prepared film with pulsed laser irradiation using the energy density of 7.07x106 W/cm^2. The same effect was observed for the films produced by laser irradiation for 45 and 60 minutes, the ones with the highest photocurrent were those obtained at lower energy density (7.07x106 W/cm^2). The conductivity in the dark and the photoconductivity of the Sb_2S_3 films produced were evaluated using their respective thicknesses and the data in the graphs of Figure 7, all conductivity values are shown in Table 1.

Making a comparison of the results of structure, composition and of the optical and electrical properties on the Sb_2S_3 thin films, it is observed that the thin films prepared at the lowest energy density are those that show greater energy gaps, as well as higher conductivity.

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Conclusions

In this work, the preparation and characterization of thin films using the laser-assisted chemical bath technique demonstrated that it is possible to obtain thin films with crystalline phase, this was established by X-ray and Raman Diffraction.

The energy gaps of the thin films of Sb_2S_3 prepared by laser-assisted chemical bath had no significant change, because they showed smaller thicknesses than those obtained without laser irradiation. However, for the Sb_2S_3 thin films prepared under laser irradiation, at the lowest energy density and for all irradiation times, the conductivity was higher. The present work showed that it is possible to obtain thin films of antimony sulfide with potential for application in photovoltaic cells.

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