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Optoelectronical properties of indium sulfide thin films prepared by spray pyrolysis for photovoltaic applications

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Abstract

Indium sulfide (In_2S_3) thin films have been prepared by the spray pyrolysis (SP) technique using indium acetate and *N-N* dimethyl thiourea as precursor compounds. Samples prepared at different temperatures and atomic ratio of In to S in the starting solution, $(In/S)_{sol}$, have been characterized using several techniques. X-ray diffraction studies have shown that the preparation temperature (T_p) affects the crystallinity of the deposited materials as well as the optoelectronic properties. For $(In/S)_{sol}$=1/8, the optical band gap (E_g) increases from 2.2 up to 2.67 eV when T_p increases from 250 up to 450 °C. For $(In/S)_{sol}$=1 and T_p=450 °C, the deposited material shows *n*-type electrical conductivity with a dark value of 1 $(\Omega cm)^{-1}$, and E_g=2.04 eV. The In_2S_3 thin films prepared under these conditions have a big potential use as a window material for photovoltaic heterojunction devices.
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Keywords: Indium sulfide; Spray pyrolysis; Solar cell

1. Introduction

It is well known that the actual technology for solar cells based on a single crystal Si has reached a mature state. However, in some cases, the involved costs for getting higher efficiencies are too high to use the devices for terrestrial applications. Thus, it is commonly accepted that a high-efficient thin film solar cell, prepared with a simple technology and in large-scale mass-production, could be an alternative to reduce the involved costs in the fabrication process. These ideas support the fact that thin film research is an essential matter in photovoltaic development.

There are a number of techniques that can be used to prepare thin film materials [1,2]. Among of them, spray pyrolysis (SP) is a technique that meets the requirements looking for technologies involved in the manufacturing process for solar cells devices. Many materials have been deposited by this technique, including insulators and semiconductors [3].

Some of the metal chalcogenide materials have optoelectronic properties that suggest its use in photovoltaic structures [4]. A great number of research works have been done on these kinds of materials, especially those that can be prepared by "soft" techniques like SP [2] and chemical bath deposition [5]. Among them, the compounds based on the binary system In–S can be cited. They have received a lot of attention for their potential in optoelectronic device applications, especially in solar cells, which is the case of In_2S_3. With optimal physical properties, the semiconductor material In_2S_3 can meet the requirements to be used as a window material or buffer layer for photovoltaic structures [6].

Indium sulfide (In_2S_3) is a crystalline compound that exists in four allotropic forms, depending on temperature and pressure: ϵ, α, β, and γ [7]. The beta phase (β-In_2S_3), with a tetragonal structure, has shown to be stable up to 693 K. The In_2S_3 thin films have been prepared by several techniques (see for instance the description presented in

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short by L. Bhira et al. [8] and the recent description done by T.T. John et al. [9]). Among them, SP has been chosen by several authors due to its simplicity and versatility to prepare semiconductor materials. It has been found that In_2S_3 thin films prepared by the SP technique show optoelectronic properties whose values depend on the deposition parameters. By controlling the deposition parameters, In_2S_3 thin films could be produced with optimized optoelectronic properties.

Most of the research work on In_2S_3 prepared by SP has been carried out by using $InCl_3$ and thiourea as starting materials. However, Cl from the In precursor could unintentionally dope the material being deposited, thus affecting its electrical properties. For this reason, we have chosen indium acetate as the source compound to grow In_2S_3 thin films by the SP technique. This work deals with the deposition and characterization of In_2S_3 thin films prepared from indium acetate and *N-N* dimethyl thiourea as precursor compounds using different preparation temperatures (T_p) and atomic ratio of In to S in the starting solution, $(In/S)_{sol}$.

2. Experimental details

Indium acetate [In $(CH_3CO_2)_2$] and *N-N* dimethyl thiourea ($CH_3NHCSNHCH_3$) were used as precursor materials to grow In−S-based compounds. A mixture of ethyl alcohol and osmosis inverse-treated water at a 3:1 ratio was chosen as the solvent to dilute the precursor compounds. After a careful screening, it was found that the maximum allowed molar concentrations for both starting materials were 0.025 and 0.5 for indium acetate and *N-N* dimethyl thiourea, respectively, if they are to be dissolved in the same solvent. With these values, the $(In/S)_{sol}$ was selected and varied using the molar concentrations of indium acetate to *N-N* dimethyl thiourea ratio. Regardless of the $(In/S)_{sol}$ selected, acetic acid in a 1/10 ratio was added to the starting solution in order to avoid the formation of precipitate compounds, mainly indium hydroxide. Borosilicate microscope glass slides from Corning, with dimensions of 1.25 cm×2.5 cm, were used as substrates. The substrates were cleaned using standard procedures.

The spray pyrolysis setup is described in Ref. [10]. Air at a pressure of 4 Pa was used as carrier gas. The gas and solution flow rate were kept constant at 10 l/min and 5 ml/min, respectively, in all the cases. The substrate-to-nozzle distance was 30 cm.

The substrates were heated using a tin bath. The temperature was measured by having a thermocouple in contact with the bottom face of the substrate and regulated. The temperature of the bath, called the preparation temperature, T_p, was varied from 250 to 450 °C in steps of 50 °C.

In order to determine the dependence of the deposition rate for each $(In/S)_{sol}$ selected from T_p, film depositions up to 10 min were made. Knowing the thin film deposition rate, a thickness of ≈0.1 μm was selected for characterization purposes and to understand the role of $(In/S)_{sol}$ and T_p.

The thickness of the deposited thin films was measured with an Alpha Step model 100 profilometer from Tencor Instruments. The structural properties were determined by X-ray diffraction (XRD) measurements using a Siemens D-500 diffractometer with Cu Kα1 radiation (λ=1.5406 Å). The average dimension of the crystallites was determined by the well-known Scherrer method. The surface morphology was studied by scanning electron microscopy (SEM) using a Cambrigde–Leica Stereoscan 440 SEM equipment. The film composition was determined by energy dispersive spectroscopy (EDS) using an Oxford system detector attached to the scanning electron microscope.

The optical transmittance at normal incidence, $T(\lambda)$, and specular reflectance, $R(\lambda)$, of the deposited thin films were measured with a double-beam spectrophotometer Shimadzu model 3101PC in the UV-VIS-NIR region. From these data, the absorption coefficient (α) was calculated, and from its dependence on the photon energy ($h\nu$), the optical band gap (E_g) was determined.

For the electrical measurements, four indium strips (each one 1.25-cm long and 0.1-cm wide, with a separation of 0.1 cm between them) were deposited by thermal evaporation. Electrical contacts were made to these strips to measure the current–voltage (*IV*) characteristics at room temperature. The ohmicity between the evaporated metal contacts and the deposited material was tested in the range of ±1 V at room temperature. In all cases, the In–In_2S_3 contact was found to be of the Ohmic nature. The electrical conductivity in the dark, σ_D, was measured using the well-known Van der Pauw technique [11]. The electrical conductivity of the samples under light, σ_L, was measured by the DC two-point probe method, using a 70 mW/cm^2 white light tungsten–halogen lamp. The electrical conductivity type was determined using the "hot point probe" technique [11].

3. Results and discussion

In order to know the effect of T_p on the physical properties of the deposited material, a solution containing 0.00625M of indium acetate and 0.05M of *N-N* dimethyl thiourea, resulting in $(In/S)_{sol}$=1/8, was selected. The deposited thin films were found to be uniform for all T_p investigated. Under these conditions, the growth rate, crystal structure, optical characteristics, and σ_D were studied as a function of T_p.

The results from EDS analysis carried out on the deposited material are shown in Table 1. According to these results, the composition of the as-deposited thin films corresponds to those of the compound In_2S_3.

Fig. 1 shows the XRD patterns for typical thin films with similar thicknesses (≈0.1 μm) deposited under the selected

Table 1
Concentration of In and S in In–S-based thin films as a function of T_p

T_p (°C)	In content (at.%)	S content (at.%)
<400	39.22	60.78
≥400	40.82	59.18

conditions. It can be seen that, for T_p<400 °C, no diffraction peaks can be identified on these patterns. It is possible that the material is growing either amorphous or with nanometric grains. For T_p≥400 °C, the diffraction pattern matches those of the standard pattern for In_2S_3 (β-In_2S_3: JCPDS file No. 73-1366) which has a tetragonal structure. Since the diffraction peaks are due to the reflections from the (103), (206), (309), and (4 0 12) planes, which are parallel planes, the deposited material is highly oriented along them. The differences between this behavior and those reported by other authors [8,9,12] could be ascribed to the starting materials and its thermodynamic properties.

The mean value of the crystallite sizes for films prepared at 400 and 450 °C, as calculated by the Scherrer technique, are 13.7 and 19.6 nm, respectively, showing a trend to increase as the preparation temperature increases from 400 to 450 °C.

The behavior of $T(\lambda)$ and $R(\lambda)$ for those samples which have shown XRD diffraction peaks are presented in Fig. 2. The films exhibit a good transparency in the visible and infrared regions (60–85%). For a weakly absorbing slab of transmission T, reflection R, and thickness d, the absorption coefficient, $\alpha(\lambda)$, can be calculated using the well-known relationship [13]

$$T = \frac{(1-R)^2}{\exp(\alpha d) - R^2\exp(-\alpha d)}. \quad (1)$$

The typical behavior of α with respect to the photon energy ($h\nu$), at the fundamental absorption edge is shown in Fig. 3(a). As it can be seen, α increases slightly as $h\nu$

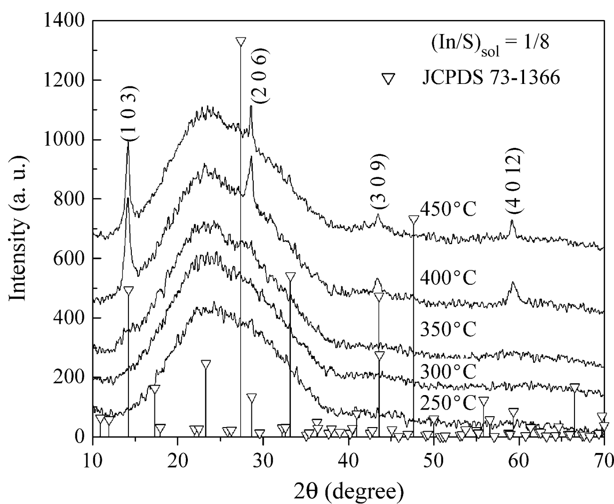

Fig. 1. Typical XRD patterns for samples deposited at different preparation temperatures and $(In/S)_{sol}$=1/8.

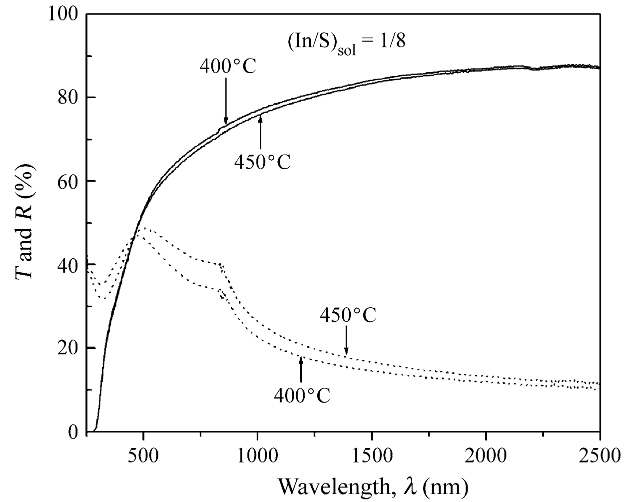

Fig. 2. Optical transmittance [T(%) solid lines] and specular reflectance [R(%) dotted lines] for In_2S_3 thin films prepared at 400 and 450 °C, respectively.

increases, which is a typical behavior of a semiconductor with optical indirect transitions [13,14]. For indirect transitions, α is given by [14]

$$\alpha h\nu = A\left(h\nu - E_g \pm E_p\right)^r, \quad (2)$$

where A is a constant, E_g is the optical band gap, and E_p is the energy of the absorbed (+) or emitted phonons. In Eq. (2), r=2 holds for allowed and r=3 for forbidden transitions. Thus, from a plot of $(\alpha h\nu)^{1/2}$ against $h\nu$, the optical band gap value E_g can be obtained for indirect allowed transitions. From the best fit of the $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plot and its extrapolation to $(\alpha h\nu)^{1/2}$=0, the E_g value was calculated for all the samples under analysis. For samples prepared at T_p<400 °C, the E_g remains almost constant with a value of 2.2 eV. However, for samples prepared at 400 °C,

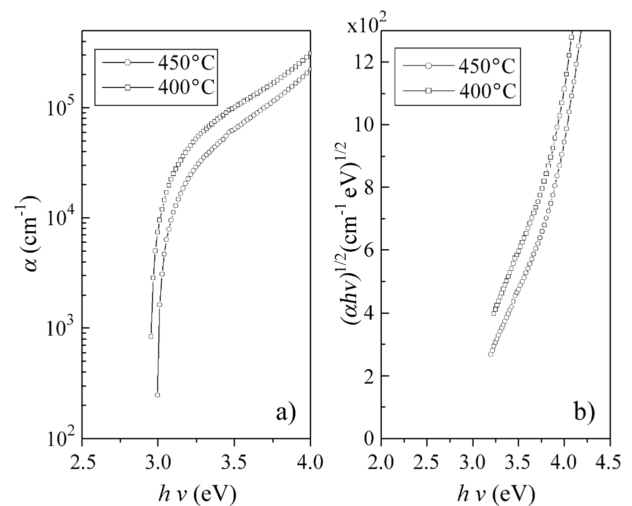

Fig. 3. Optical characteristics of In_2S_3 thin films prepared at 400 and 450 °C, respectively. (left) Behavior of α vs. hν and (right) best fit of $(\alpha h\nu)^{1/2}$ vs. hν for typical samples.

E_g=2.54 eV, while for samples prepared at 450 °C, E_g=2.67 eV. These values are in close agreement with those reported by W. Kim and C.D. Kim [12] and by C.D. Kim et al. [15], and also with those reported by T.T John et al. [9], although they calculated the band gap for their materials using the model for direct optical transitions.

From the hot point probe tests, it could not be deduced by any type (*n* or *p*) for the electrical conductivity of the films. To get more insight on the electrical properties of the samples, we carried out Van der Pauw measurements. For samples prepared at T_p<400 °C, σ_D was difficult to measure [low values, in the order of 1×10^{-7} $(\Omega cm)^{-1}$]. For T_p=400 °C and 450°, it was found that σ_D is 5.1×10^{-6} $(\Omega cm)^{-1}$ and 4.1×10^{-5} $(\Omega cm)^{-1}$, respectively, thus showing a trend to increase as the preparation temperature increases.

From the electrical and the EDS results, we can assume that our films are intrinsic in nature. The trend observed for σ_D could be explained by the structural properties of the films. Using XRD, it was found that films prepared at T_p<400 °C are either amorphous or nanocrystalline, whereas those prepared at $T_p \geq 400$ °C become polycrystalline with well-defined XRD patterns. The crystallinity is increased when the preparation temperature increases. Generally, the electron transport properties depend on the structural nature of an amorphous or polycrystalline material [16]. Then, it is expected that σ_D for samples grown at T_p<400 °C is very low but slightly higher for $T_p \geq 400$ °C.

The photoresponse, defined as the ratio σ_L/σ_D, was found to be of two orders in magnitude for all the deposited thin films. These values are of the same order than those reported elsewhere [9].

In order to improve the electrical conductivity for the In_2S_3 thin films, the $(In/S)_{sol}$ was changed in the starting solution by adding more In. Thus, a new spraying solution was prepared, using 0.025M of indium acetate and 0.025M of *N-N* dimethyl thiourea, resulting in an $(In/S)_{sol}$=1. Samples were deposited onto glass substrates at T_p=450 °C, keeping all other parameters unchanged.

All samples have good optical appearance. EDS analysis had revealed that these films have 65.6 at.% of In and 34.4 at.% of S, confirming our hypothesis as the deposited material has more In than S. The In excess could be incorporated in the film in the grain boundaries or at interstitial sites. If In atoms were at interstitial sites, they could produce a distortion in the crystal structure that can be identified from the XRD patterns. Fig. 4 shows an XRD pattern of a typical sample. From this figure, it can be seen that the deposited materials are polycrystalline in nature. The observed peaks match with those of the standard pattern for the β-In_2S_3 (JCPDS file No. 73-1366). There is no noticeable shift in the position of the diffraction peaks, even after close inspection. Then, the excess of In is not located at interstitial sites but at grain boundaries. Thus, the thin films grew with the same crystal structure as those obtained before for samples prepared at 400 and 450 °C with an atomic ratio $(In/S)_{sol}$=1/8. The mean value of the crystallite sizes is in the order of 18 nm, which is of the same order than the values obtained for T_p=450 °C but slightly lower compared with those reported by T.T. John et al. [9].

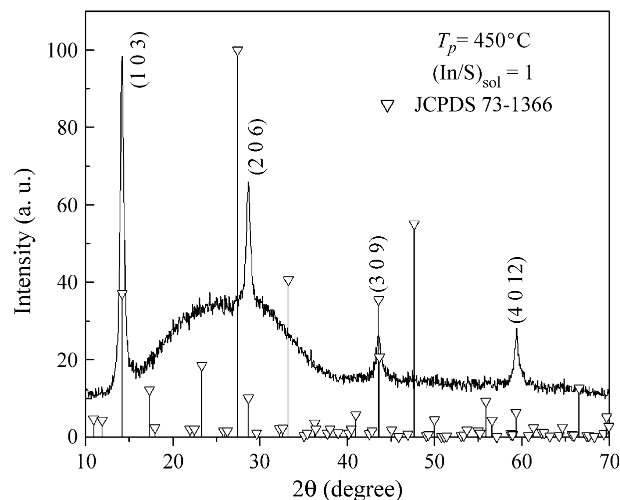

Fig. 4. Typical XRD pattern for the In_2S_3 thin films using $(In/S)_{sol}$=1.

From optical measurements, α(λ) was obtained, and the allowed indirect optical band gap was calculated to be 2.04 eV. This value is lower than those reported elsewhere [9,12,15,17] and could be ascribed to the excess of indium.

From the hot point probe tests, an *n*-type conductivity for these films can be deduced. For the In-rich In_2S_3 samples, σ_D=1.05 $(\Omega\ cm)^{-1}$ at room temperature. The conductivity type and its high value could be due to the excess of In that has been incorporated in the film. It is necessary to carry out more studies in order to identify the role of indium excess.

The electrical and optical properties obtained (conductivity type, σ_D and E_g) could be reproduced over several runs. These results suggest us that our In_2S_3 (In rich) thin films are good candidates to be used as an alternative window material for solar cells based on $CuInS_2$.

4. Conclusions

We reported on the deposition of β-In_2S_3 by the spray pyrolysis technique using indium acetate and *N-N* dimethyl thiourea as precursor compounds. It has been demonstrated that $(In/S)_{sol}$ and T_p are the dominant parameters in the growth process. For $(In/S)_{sol}$=1/8 and T_p ranging from 250 up to 450 °C, EDS studies showed that the deposited materials are stoichiometric In_2S_3. For T_p<400 °C, XRD studies revealed that the material may be grown as an amorphous or nanocrystalline compound with an indirect optical band gap of 2.2 eV. For $T_p \geq 400$ °C, the deposited material is well crystallized, with a preferred orientation along the [103] direction perpendicular to the substrate's surface. From the XRD patterns, it was found that our films are β-In_2S_3, in good agreement with our EDS results. E_g increases as T_p increases, its maximum value (E_g=2.67 eV) was found for T_p=450 °C.

For $(In/S)_{sol}$=1 and T_p=450 °C, the deposited materials are β-In_2S_3. The films are well crystallized with a preferred orientation along the [103] direction normal to the substrate's surface. They show an n-type electrical conductivity with a value of 1 $(\Omega cm)^{-1}$ in the dark and E_g=2.04 eV. The high value in σ_D and the low value in E_g are ascribed to an excess of In in the film. Since these values are optimal for using the material in a photovoltaic structure like a window material, this work opens the opportunity to use (In rich) In_2S_3 in $CuInS_2$-based solar cells.

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References

[1] L.I. Maissel, R. Glang, Handbook of Thin Film Technology, McGraw-Hill, New York, NY, 1970.
[2] J.L. Vossen, W. Kern, Thin Films Processes, Academic Press, New York, NY, 1978.
[3] S. Oktik, Prog. Cryst. Growth Charact. 17 (1988) 171.
[4] O. Madelung, Data in Science and Technology: Semiconductors other than Group IV elements and III–V Compounds, Springer-Verlag, Berlin-Heidelberg, 1992.
[5] P.K. Nair, M.T.S. Nair, V.M. Garcia, O.L. Arenas, Y. Peña, A. Castillo, I.T. Ayala, O. Gomez-Daza, A. Sanchez-Juarez, J. Campos, H. Hu, R. Suarez, M.E. Rincon, Sol. Energy Mater. Sol. Cells 52 (1998) 313.
[6] N. Barreau, J.C. Bernède, S. Marsillac, C. Amory, W.N. Shafarman, Thin Solid Films 431–432 (2003) 326.
[7] N. Bouguila, H. Bouzouita, E. Lacaze, A. Belhadj Amara, H. Bouchriha, A. Dhouib, J. Phys., III 7 (1997) 1647, (In French).
[8] L. Bhira, H. Essaidi, S. Belgacem, G. Couturier, J. Salardenne, N. Barreaux, J. Bernède, Phys. Status Solidi, A Appl. Res. 81 (2000) 427.
[9] T.T. John, S. Bini, Y. Kashiwaba, T. Abe, Y. Yasuhiro, C. Sudha Kartha, K.P. Vijayakumar, Semicond. Sci. Technol. 18 (2003) 491.
[10] A. Sánchez Juárez, MSc thesis, Facultad de Ciencias-UNAM, México, 1995.
[11] W.R. Runyan, Semiconductor Measurements and Instrumentation: Texas Instruments-Electronics Series, McGraw-Hill, New York, NY, 1975, p. 145.
[12] W. Kim, C. Kim, J. Appl. Phys. 60–7 (1986) 2631.
[13] T.S. Moss, Optical Properties of Semiconductors, Butterworths, London, 1959.
[14] K.L. Chopra, S.R. Das, Thin Films Solar Cells, Plenum Press, New York, NY, 1983.
[15] C.D. Kim, H. Lim, H.L. Park, H.Y. Park, J.E. Kim, H.G. Kim, Y.G. Kim, W.T. Kim, Thin Solid Films 224 (1993) 69.
[16] Lawrence L. Kazmerski, Polycrystalline and Amorphous Thin Films and Devices, Materials Science and Technology Series, Academic Press, New York, NY, 1980.
[17] S. Choe, T. Bang, N. Kim, H. Kim, C. Lee, M. Jin, S. Oh, W. Kim, Semicond. Sci. Technol. 16 (2001) 98.