IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Effects of precursor concentration on the optical and electrical properties of Sn_XS_Y thin films prepared by plasma-enhanced chemical vapour deposition

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 Semicond. Sci. Technol. 17 931

(http://iopscience.iop.org/0268-1242/17/9/305)

The Table of Contents and more related content is available

Download details:
IP Address: 132.248.12.226
The article was downloaded on 06/04/2010 at 21:03

Please note that terms and conditions apply.

Semicond. Sci. Technol. **17** (2002) 931–937 PII: S0268-1242(02)32822-0

Effects of precursor concentration on the optical and electrical properties of Sn_XS_Y thin films prepared by plasma-enhanced chemical vapour deposition

A Sanchez-Juarez[1] and A Ortíz[2]

[1] Department of Solar Energy Materials, Energy Research Center, Universidad Nacional Autonoma de Mexic, PO Box 34, Temixco, Morelos, 62580 Mexico
[2] Materials Research Institute-UNAM, PO Box 70-360, Coyoacan, DF 04510, Mexico

Received 15 January 2002, in final form 13 June 2002
Published 22 July 2002
Online at stacks.iop.org/SST/17/931

Abstract
We have carried out the electrical and optical characterization of thin films of compounds based on Sn–S bonds (SnS_2, Sn_2S_3), prepared by plasma-enhanced chemical vapour deposition (PECVD), as a function of the relative concentration of the precursor vapours, $SnCl_4$ and H_2S, keeping all other deposition parameters constant. In all studied cases, the deposited films were formed by polycrystalline materials. The optical bandgap values of deposited materials were calculated from optical transmittance and reflectance measurements. The SnS_2 compound produced under certain deposition conditions has a forbidden bandgap around 2.2 eV. This compound shows n-type electrical conductivity, whose dark value at room temperature is 2×10^{-2} $(\Omega\ \mathrm{cm})^{-1}$. Also, it shows the typical semiconductor dependence of its electrical conductivity on the temperature with an activation energy of about 0.15 eV. However, thin films of a mixture of SnS_2 and Sn_2S_3 compounds were deposited with higher values of the relative concentration of source vapours than those used to obtain the SnS_2 compound. The optical bandgap shows a decreasing trend as the relative concentration increases. A similar trend is observed for dark electrical conductivity. These results create the opportunity to use Sn_XS_Y compounds in thin films for building heterojunction solar cells prepared completely by PECVD.

1. Introduction

Due to their electrical and optical properties the binary compounds based on the Sn–S system have a high potential use in optoelectronical devices [1–5]. Three compounds of this system are interesting from a technological point of view: tin sulfide (SnS), tin disulfide (SnS_2), and the compound Sn_2S_3. Single crystals and polycrystalline thin films of SnS have shown p-type electrical conductivity whose dark value can be increased by doping with Ag, Al, N and Cl [6, 7]. This material has shown indirect optical transitions with an optical bandgap of about 1.3 eV [6, 8], which lies in the optimum range in which absorber materials can be used in solar cell applications [9]. Single crystals and polycrystalline thin films of SnS_2 have shown n-type electrical conductivity [10], and optical bandgaps in the range of 2.12–2.44 eV [11–13] meaning that the SnS_2 compound could be a good choice 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 behaviour whose optoelectronic properties are dependent on its crystalline structure and stoichiometry. Therefore, these compounds could be used to build photovoltaic p–n or p–i–n structures with a conversion efficiency of about 25% [9]. These structures would be low cost devices because the materials involved are inexpensive, non-strategic, and abundant in nature.

Thin films of SnS, SnS_2 and Sn_2S_3 compounds have been prepared by different techniques [1–8, 10–13]. Among these, plasma-enhanced chemical vapour deposition (PECVD) is a process that meets the requirements of controllable, simple and inexpensive large-area thin-film deposition to produce low cost materials and devices. In our previous work [14] we found that the relative concentration of the precursor materials determines the relative chemical composition, the crystallinity and the preferential growth of the deposited Sn_XS_Y thin films. In the present work we have studied the electrical and optical properties of Sn_XS_Y thin films prepared by PECVD as a function of the concentration ratio of the source materials.

2. Experimental details

Sn_XS_Y thin films were prepared by the decomposition of H_2S and $SnCl_4$ vapour mixtures, whose respective flow rates are designed as Q_{H_2S} for H_2S and Q_{SnCl_4} for $SnCl_4$, in a capacitively coupled 13.56 MHz radio frequency glow discharge chamber with a radially symmetric flow pattern. Hydrogen was used as a diluent gas and for removing radicals related with chlorine generated by the $SnCl_4$ decomposition. Details of the chamber and microstructural features of deposited films have been reported elsewhere [14].

2.1. Thin film preparation

The gas flow rates of the precursor vapours Q_{SnCl_4} and Q_{H_2S} and that of diluent gas Q_{H_2} (for H_2 gas) were controlled by the use of electronic mass flow controllers. The flow rates of the precursor vapours were chosen to meet a maximum flow rate of five standard cubic centimetres per minute (sccm) for the $SnCl_4$ and H_2S mixture to minimize corrosion problems at valves and fittings. The relative concentration of the precursor vapours, g, defined by the relation

$$g = \frac{Q_{SnCl_4}}{Q_{SnCl_4} + Q_{H_2S}}, \qquad (1)$$

was varied from 0.0 to 1.0. H_2 was added at a flow rate of $Q_{H_2} = 20$ sccm as a diluent gas and to avoid chlorine incorporation to the Sn_XS_Y network. The total gas flow rate $Q_{SnCl_4} + Q_{H_2S} + Q_{H_2}$ was kept constant in all cases at 25 sccm. The deposition pressure was kept constant at 50 mTorr, measured by an absolute pressure transducer; it was controlled automatically with a throttle valve. The plasma power density was maintained at 25 mW cm^{-2}. The values of these two parameters, plasma power density and deposition pressure, were chosen from a set of values that define a 'low pressure' regime in our plasma system [14]. The electrode temperature, on which the substrates were disposed, was controlled by means of a temperature controller at a fixed value of 150 °C through a K-type thermocouple. The materials have been deposited on to two kinds of substrates: Pyrex glass slices, chemically and ultrasonically cleaned, and 200 Ω cm n-type (100) single-crystal silicon wafers (x-Si), both with an area of 1.5×2.5 cm^2.

2.2. Film characterization

The thickness of the deposited films on glass was measured by means of an Alpha Step 100 profilometer.

The optical transmittance spectra at normal incidence and specular reflectance spectra at 5° incidence were obtained using a Shimadzu UV-VIS-NIR PC-100 double-beam spectrophotometer in the wavelength range of 290– 2500 nm. All optical measurements were carried out on samples deposited on Pyrex glass slices having air as reference for transmittance and a standard aluminium mirror for reflectance. The samples deposited on c-Si were used in ellipsometric measurements to determine the refractive index at $\lambda = 630$ nm.

The electrical properties were measured in samples deposited on the Pyrex glass. Four tin, aluminium and indium strips, each 1.5 cm long and with 0.1 cm separation, were deposited on the samples by thermal evaporation. Electrical contacts were made to these strips to measure the current–voltage (I–V) characteristics at room temperature. The variation of the electrical conductivity as a function of temperature during the characterization was measured in the range of 120–450 K. The type of electrical conductivity was determined using the 'hot point probe' [15].

3. Results and discussion

In our previous work, we established the deposition conditions where only the SnS_2 compound was produced and other conditions where mixtures of SnS_2 and Sn_2S_3 compounds were deposited. In that work, the microstructural characteristics were correlated with variations in the relative concentration of vapour source. In the present work, we limit our results and discussion to the optical and electrical characteristics of thin films prepared under the same condition as those that we have previously reported. In order to avoid thickness effects on the interpretation of the optical and electrical properties of deposited films, Sn_XS_Y thin films were deposited onto glass substrates with a thickness of around 150 nm, in all reported cases.

Figure 1 shows the optical transmittance (T) and specular reflectance (R) spectra for samples prepared with different g values. We observe a change in the absorption edge towards higher wavelengths as g increases. This shift is associated with the different materials that are deposited when g is varied. Following the analysis given by Moss [16], the transmission T through a weakly absorbing slab of reflectivity R, thickness d, and absorption coefficient α in air is given by

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

where $R = (n - 1)^2/(n + 1)^2$ and n is the refractive index. From equation (2), α was calculated by using the values of R and T shown in figure 1. Figure 2 shows the variation of absorption coefficient with photon energy for the fundamental absorption edge for SnS_2, Sn_2S_3, and mixtures of Sn_2S_3 and Sn_2S compounds. Concerning the plot of absorption coefficient versus photon energy ($h\nu$), the following points have been found. (a) For deposited thin films related to the SnS_2 compound, α increases slightly as $h\nu$ increases, which is a typical behaviour of an indirect bandgap semiconductor [17]. This result is in agreement with results reported elsewhere [13, 18, 19]. (b) For thin films formed by the Sn_2S_3 compound, the plot of α versus $h\nu$ corresponds to that of a direct bandgap

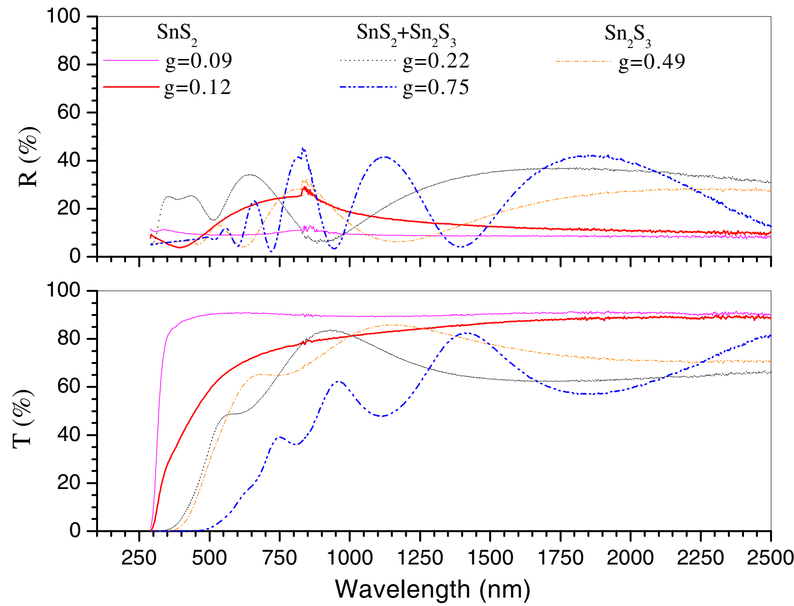

Figure 1. Optical transmittance T (%) and specular reflectance R (%) spectra of $Sn_X S_Y$ thin films deposited using different values of g.

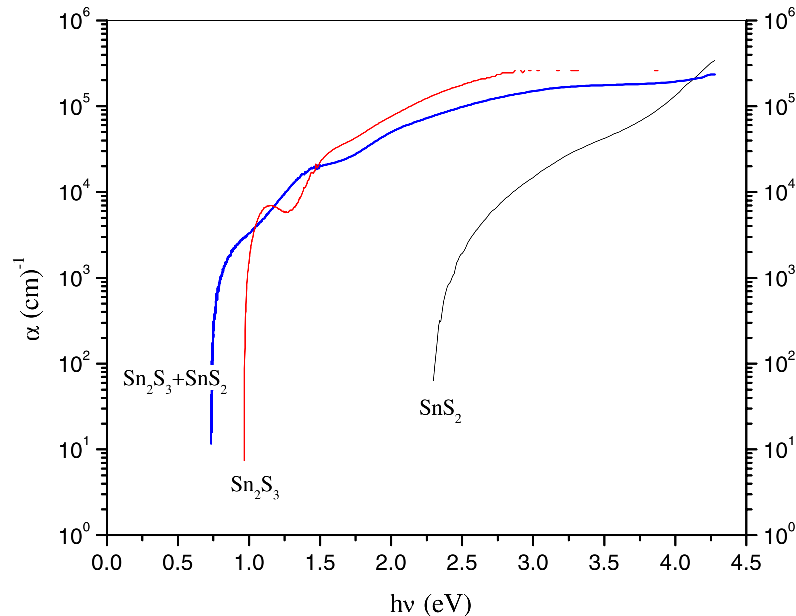

Figure 2. Absorption coefficient versus photon energy for SnS_2, Sn_2S_3, and mixtures of SnS_2 and Sn_2S_3 compounds.

material. This behaviour is in agreement with that observed by Alpen *et al* [20] for single-crystal materials and that of Lopez *et al* [21] for thin-film polycrystalline materials.

The optical bandgap has been determined based on the theory of Bardeen *et al* [22]. Thus, for indirect transitions, α is given by

$$\alpha = \frac{A(h\nu - E_g \pm E_p)^r}{h\nu}, \quad (3)$$

where A is a constant, E_g is the optical bandgap, and E_p is the energy of the absorbed (+) or emitted (−) phonons. If $r = 2$ the transition is allowed and if $r = 3$ the transition is forbidden. On the other hand, for direct transitions, α is given by

$$\alpha = \frac{A(h\nu - E_g)^r}{h\nu}, \quad (4)$$

where $r = 1/2$ for allowed transitions and $r = 3/2$ for forbidden transitions.

By plotting graphs of $(\alpha h\nu)^{1/r}$ against $h\nu$ for the various values of r given above, it has been possible to determine which of these transitions dominates, and hence to determine the value of E_g. Figure 3 shows the best fit of $(\alpha h\nu)^{1/r}$ against $h\nu$ for the transitions studied. It has been confirmed that the SnS_2 material, obtained with $g = 0.6$ and $g < 0.2$, has indirect transitions, while the Sn_2S_3 material obtained with $g = 0.49$ has direct transitions, both of the allowed kind. For materials prepared with other values of g, it was not possible to define a unique transition. In these cases, the bandgap was obtained using the best fit of the $(\alpha h\nu)^{1/r}$ versus $h\nu$ curve. Thus, for samples prepared in the range of $0.2 < g < 0.4$, the bandgap

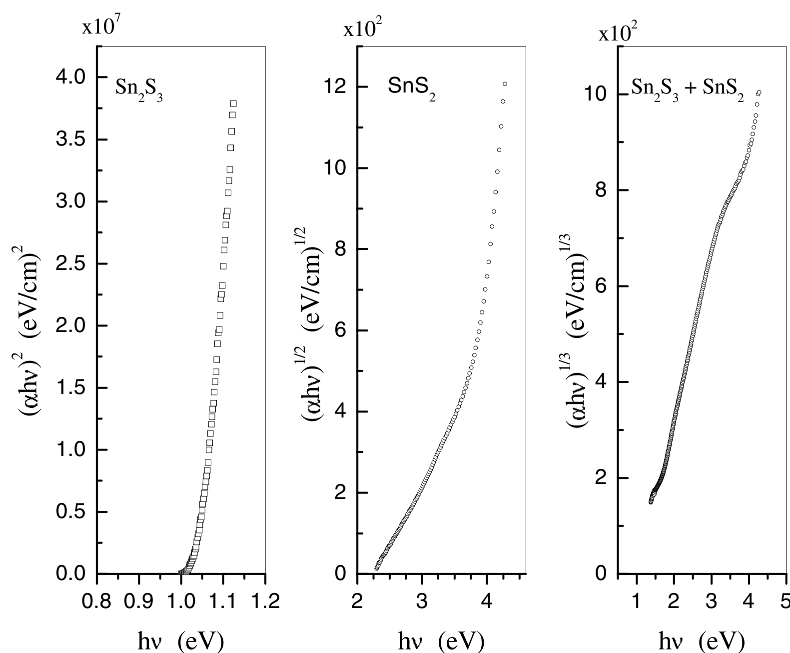

Figure 3. Best fits of $(\alpha h\nu)^{1/r}$ versus photon energy for some of the deposited materials.

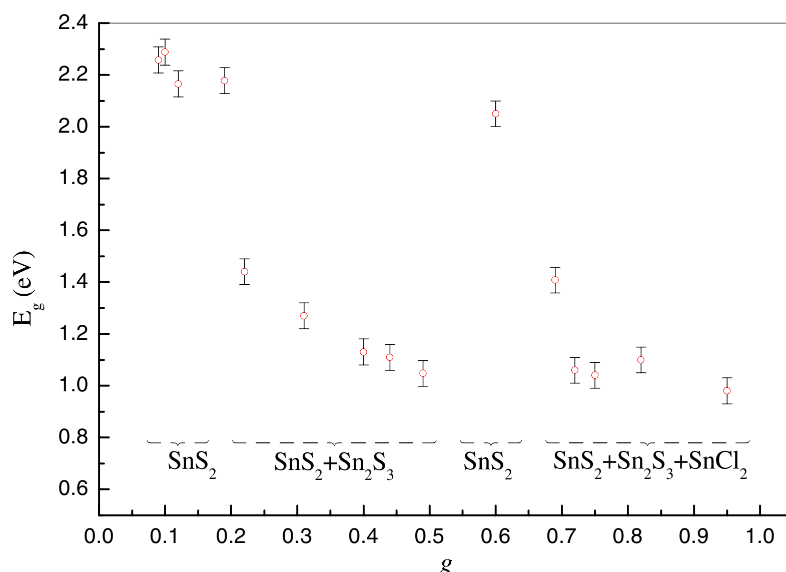

Figure 4. Variation on the optical bandgap for samples prepared with different values of g. Each point represents the mean value of E_g for at least six samples prepared under the same conditions. The composition of the film is indicated.

was calculated using equation (3) with $r = 3$ (phonon-assisted forbidden indirect transitions), while for other values of g the bandgap was calculated using equation (3) with $r = 2$ (allowed indirect transitions).

Figure 4 shows the behaviour of the bandgap against g. No monotonic behaviour is observed in the band gap for the g values studied here. E_g has a decreasing trend as the $SnCl_4$ concentration increases in the gas mixture. This decreasing trend is due to the fact that two or three compounds (SnS_2, Sn_2S_3 and $SnCl_2$) are simultaneously deposited when g increases, as reported previously [14]. This behaviour can be explained by taking into account the following [14]. In cases where the deposited material is of the SnS_2 compound, the calculated bandgap is almost constant with a mean value of 2.22 eV, which is typical for the SnS_2 compound, as reported [8, 12, 13, 18, 23, 24]. The phonon involved in the indirect transition has an estimated mean energy value of 0.08 eV. This value is larger that that reported previously by Arora *et al* [25] for SnS_2 single-crystal material. The difference might be associated with the polycrystalline nature of the deposited films and the strong anisotropy of the optical properties, which have been reported elsewhere [10, 11, 13, 18, 23]. For deposited thin films formed by the mixture of two compounds, SnS_2 and Sn_2S_3, the bandgap has a decreasing trend, from 1.45 eV for $g = 0.21$ down to 1.05 eV for $g = 0.49$. At the later relative composition, the deposited material corresponds

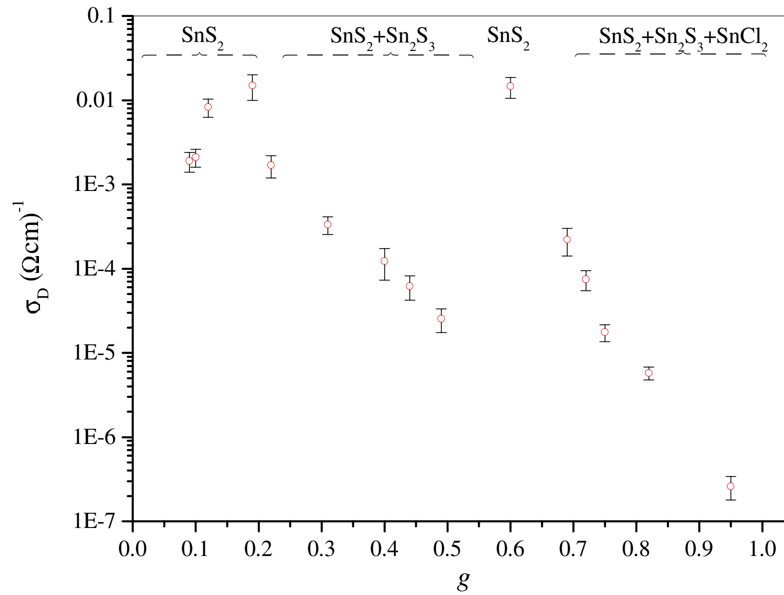

Figure 5. Variation in the mean value of dark electrical conductivity of the different samples as a function of g.

to the Sn_2S_3 compound. The determined bandgap value for this compound is in agreement with the values reported by Engelken *et al* [8] ($E_g = 1.1$ eV), Alpen *et al* [20] ($E_g = 0.95$ eV) and Lopez *et al* [21] ($E_g = 1.16$ eV). The decreasing trend observed in the bandgap can be explained as follows. It has been demonstrated [14] that, as g increases, the deposited material transforms from SnS_2 to SnS_2–Sn_2S_3 and to the Sn_2S_3 compound, changing the bandgap from 2.22 eV to 1.05 eV. Then, as the quantity of Sn_2S_3 compound increases in the deposited thin film, the optical behaviour is dominated by the material with the lower bandgap. This is clear because, if two thin films with different bandgaps are in contact and light goes through the structure, the absorption process will be dominated by the material with the lower bandgap. There is a critical point, for $g = 0.6$, at which the deposited material corresponds to the SnS_2 compound (see [14] for a full explanation of this behaviour). The determined bandgap is 2.05 eV, which is in the same range for values reported elsewhere [8, 12, 13, 18, 23, 24]. For higher values of g, the determined bandgap shows a decreasing trend because, again, there is the formation of different compounds: SnS_2, Sn_2S_3 and $SnCl_2$. An explanation of this behaviour is possible with the consideration mentioned above.

A thermoelectric study (hot point probe) [15] was carried out for all the prepared samples in order to identify the type of electrical conductivity of the deposited material. It was found that all the thin films prepared in this work show n-type electrical conductivity. Since the deposited materials are of SnS_2, SnS_2–Sn_2S_3 and Sn_2S_3 compounds, this result is in agreement with n-type electrical conductivity reported for these compounds (see, for instance, [12, 13, 18, 21, 26]). The I–V characteristics of the Sn_XS_Y thin films were measured at room temperature in the range of -1 to 1 V to determine the ohmic behaviour between the evaporated metal contacts and the deposited material. For all the considered samples, it was found that the indium contacts have ohmic behaviour, while the aluminium and tin contacts have quasi-ohmic behaviour. These results are in agreement with the Schottky theory of a metal–semiconductor contact. This theory predicts ohmic behaviour in the contact if the work function of the metal is lower than that of the n-type semiconductor. Since the work function values of indium, aluminium and tin are 4.12 eV, 4.28 eV and 4.42 eV, respectively [27], and the estimated electron affinity of the SnS_2 compound is 4.2 eV [28], the electrical transport across the metal–semiconductor contact must have ohmic behaviour for indium. Further work will be carried out in order to study the electrical behaviour between the deposited material and the aluminium and tin contacts. Due to an applied bias of 10 V, there was no observed significant difference in the dark conductivity of the films against temperature for different metal contacts. Also, because indium contacts are soft compared with aluminium contacts, the latter contacts were used to analyse the dark electrical characteristics for all the deposited materials with a thickness of 0.15 μm.

The dark electrical conductivity (σ_D) measurements were carried out in the temperature range of 120–500 K using the dc two point probe method and the well-known van der Pauw technique [15] with a square electrical contact geometry (1.0 cm size). In all the studied samples it was found that σ_D increases as temperature increases, suggesting a semiconducting behaviour of the Sn_XS_Y thin films. The dark electrical conductivity of the films at room temperature is depicted in figure 5. It is seen that the thin films of SnS_2 have a mean value of σ_D of 8.2×10^{-3} (Ω cm)$^{-1}$ with maximum values around 1.3×10^{-2} (Ω cm)$^{-1}$. It has been shown that single crystals of SnS_2 may have electrical conductivity in the range of 10^{-12} up to 10^{-2} (Ω cm)$^{-1}$ depending on the preparation technique, with lower values for stoichiometric materials and higher values for non-stoichiometric or doped materials [12, 29, 30].

The maximum value can be explained as follows. For $g < 0.1$, the deposited material has Sn vacancies without Cl incorporation, as reported. These vacancies produce some incomplete bonds in the SnS_2 network, which might introduce

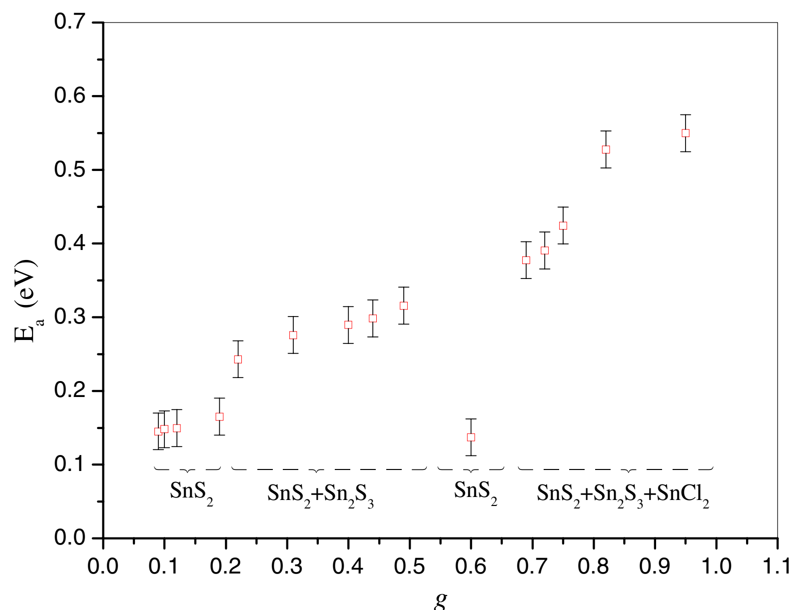

Figure 6. Variation in the mean value of the activation energy of the Sn_XS_Y thin films as a function of g.

donor states at the bandgap [12]. For $0.1 < g < 0.2$ and $g = 0.6$, Sn vacancies and Cl incorporation are present. Chlorine atoms can replace sulfur sites with -1 valence, also producing donor states, which lie close to the conduction band edge [12]. The donor levels generated are ionized at room temperature, thereby increasing the value of σ_D. Thus, as Cl incorporation increases, donor levels increase [12] and therefore σ_D increases. The σ_D values found for the thin films of SnS_2 are one order of magnitude lower than those of single crystals of SnS_2 prepared by chemical vapour transport [12]. Even though in both studies the Cl incorporation is of the same order, the polycrystalline nature of the SnS_2 thin films is responsible for the reduction in σ_D compared with that in single crystals of SnS_2.

At $g = 0.49$, Sn_2S_3 is deposited. The thin films of this compound have a low value of σ_D, of the order of 2×10^{-5} $(\Omega\ \mathrm{cm})^{-1}$, which is typical for this stoichiometry [20]. Similar values have been found for thin films prepared by chemical precipitation [8], thermal synthesis [20] and spray pyrolysis [21].

Since some of deposited films are formed by a mixture of compounds, their electrical conductivity must be a certain combination of the conductivity due to each compound. If it is assumed that the deposited materials build a series resistance combination, then the equivalent resistance will be the sum of each resistance. Since the resistance is proportional to the resistivity, and resistivity is the reciprocal of conductivity, the total conductivity of a thin film formed by several compounds will be dominated by the material with lowest conductivity. Using this argument, it is possible to explain why the value of σ_D has the behaviour shown in figure 5. As g increases from 0.2 to 0.49, the conductivity decreases from the value for SnS_2 up to the value of Sn_2S_3, since more material of Sn_2S_3 is formed on the SnS_2 basis [14]. Thus, the conductivity is mainly dominated by the conductivity of the Sn_2S_3 compound. For g values higher than 0.6, Sn_2S_3 and SnS_2 are deposited along with the $SnCl_2$, compound, which is more resistive than Sn_2S_3. From this, the reason is understood for the pronounced reduction in σ_D as g increases in that interval.

The activation energy of the material of the films was determined by using the equation

$$\rho = \rho_0 \exp(E_A/kT) \qquad (5)$$

where ρ is the electrical resistivity ($\rho = 1/\sigma$), T is the absolute temperature, ρ_0 is a constant, E_A is the activation, and k is the Boltzmann constant. The variation of E_A with g is shown in figure 6. The observed behaviour is a reversal of that shown by the electrical conductivity. As g increases, E_A increases. This behaviour is due to the participation of one, two or three different materials in the electrical properties, as explained above. The SnS_2 compound has an activation energy mean value of 0.15 eV with a minimum value of 0.14 eV for the compound prepared using $g = 0.6$. This value is lower than values reported by Said and Lee [10] and George and Kumari [11] for undoped SnS_2 single crystals. This discrepancy can be associated with Cl incorporation into the thin films reported here. However, compared with those reported by Kourtakis *et al* [12] for Cl doped single crystals, the presented values are higher. The reason could be associated to the different degrees of doping and the polycrystalline nature of the films studied here. Films formed by the stoichiometric Sn_2S_3 compound have an activation energy of 0.32 eV. This value is lower than values reported by Alpen *et al* [20] and Lopez *et al* [21], probably due to the Cl incorporation.

The optical and electrical properties of the SnS_2 compound reported here suggest that this material can be used as a window material in heterojunction solar cells. Since a change in the deposition conditions in the PECVD technique can produce a thin film of SnS_2, Sn_2S_3 (present work) or SnS (Ortíz *et al* [4]), with optical and electrical properties that are optimal to build heterojunction solar cells, the present work opens up the opportunity to use these materials to produce complete solar cells by the PECVD technique based on Sn–S.

4. Conclusions

In this paper, we have presented an analysis of the effects of precursor concentrations on the optical and electrical properties of $Sn_X S_Y$ thin films prepared by PECVD. The films were grown using deposition parameters, which remained in the 'low pressure' regime of the system. All the deposited materials were semiconductors of polycrystalline nature. It was found that, for a deposited material with a chemical composition corresponding to the SnS_2 compound, the energy bandgap has a value around 2.22 eV showing indirect optical transitions. The electrical characteristics have shown n-type electrical conductivity with a maximum dark value of 1.3×10^{-2} $(\Omega\ cm)^{-1}$, and an activation energy of 0.14 eV. The deposited material corresponding to Sn_2S_3 composition has shown an optical bandgap of 1.05 eV with forbidden direct transitions. Its electrical characteristics have shown n-type electrical conductivity with a dark value of 2.5×10^{-5} $(\Omega\ cm)^{-1}$, and an activation energy of 0.32 eV. Since these values are among the optimum for solar cells applications, this work opens up the opportunity to use the PECVD technique for building a complete solar cell structure based on Sn–S compounds.

Acknowledgments

We wish to thank Ms Leticia Baños (IIM-UNAM) for XRD analysis, Ms Ana Ma Ramirez Romero for library assistance, and Mr Jose Guzman (IIM-UNAM) for SEM and EDS analyses. One of the authors (AS-J) is thankful to the PADEP-UNAM programme for the financial support given through the project no 5338 in the initial stage of the work. CONACyT, Mexico, has supported this work under the contract 3723-PA.

References

[1] Valiukonics G, Guseinova D A, Krivaite G and Sileica A 1990 *Phys. Status Solidi* b **135** 299

[2] Nair M T S and Nair P K 1991 *J. Phys. D: Appl. Phys.* **24** 83

[3] Koteswara Reddy N and Ramakrishna Reddy K T 1997 *Proc. IEEE 26th Photovoltaic Specialist Conference* (New York: IIE) p 515

[4] Ortíz A, Alonso J C, Garcia M and Toriz J 1996 *Semicond. Sci. Technol.* **11** 243

[5] López S and Ortíz A 1994 *Semicond. Sci. Technol.* **9** 1

[6] Albers W, Hass C, Vink H J and Wasscher J D 1996 *J. Appl. Phys. Suppl.* **32** 2220

[7] Parenteau M and Carbone C 1990 *Phys. Rev.* B **41** 5227

[8] Engelken R D, McCloud H E, Lee C, Slayton M and Ghoreishi H 1987 *J. Electrochem. Soc.* **134** 2696

[9] Lofersky J J 1956 *J. Appl. Phys.* **27** 77

[10] Said G and Lee P A 1973 *Phys. Status Solidi* a **15** 99

[11] George J and Valsala Kumari C K 1983 *J. Cryst. Growth* **63** 233

[12] Kourtakis K, DiCarlo J, Kershaw R, Dwight K and Wold A 1988 *J. Solid State Chem.* **76** 186

[13] Domingo G, Itoga R S and Kannewurf C R 1966 *Phys. Rev.* **143** 536

[14] Sanchez-Juarez A and Ortíz A 2000 *J. Electrochem. Soc.* **147** 3708

[15] Runyan W R 1975 *Semiconductor Measurements and Instrumentation* (Texas Instruments Electronics Series) (New York: McGraw-Hill) p 145

[16] Moss T S 1959 *Optical Properties of Semiconductors* (London: Butterworths)

[17] Chopra K L, Kainthala R C, Pandya D K and Thakoor A P 1982 *Physics of Thin Films* (New York: Academic)

[18] Lee P A, Said G, Davis R and Lim T H 1969 *J. Phys. Chem. Solids* **30** 2719

[19] George J, Valsala Kumari CK and Joseph K S 1983 *J. Appl. Phys.* **54** 5347

[20] Alpen UV, Fenner J and Gmelin E 1975 *Mater. Res. Bull.* **10** 175

[21] López S, Granados S and Ortíz A 1996 *Semicond. Sci. Technol.* **11** 433

[22] Bardeen J, Blatt F J and Hall L H 1956 *Proc. Photoconductivity Conf. (Atlantic City)* (New York: Wiley) p 146

[23] Shibata T, Kambe N, Muranushi Y, Miura T and Kishi T 1990 *J. Phys. D: Appl. Phys.* **23** 719

[24] George J and Joseph K S 1982 *J. Phys. D: Appl. Phys.* **15** 1109

[25] Arora S K, Patel D H and Agarwal M K 1994 *J. Mater. Sci.* **29** 3979

[26] Sankapal B R, Mane R S and Lokhande C D 2000 *Mater. Res. Bull.* **35** 2027

[27] Michaelson H B 1977 *J. Appl. Phys.* **48** 4729

[28] Williams R H, Murray R B, Govant D W, Thomas J M and Evans E L 1973 *J. Phys. C: Solid State Phys.* **6** 3631

[29] Whitehouse C R and Balchin A A 1979 *J. Cryst. Growth* **47** 203

[30] Paloz B 1983 *Phys. Status Solidi* a **80** 11