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Optical Properties of Wide Band Gap Indium Sulphide Thin Films Obtained by Physical Vapor Deposition

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Thin films of indium sulphide containing oxygen have been synthesized following a dry physical process. The constituents are deposited by thermal evaporation on glass substrates and then annealed under argon flow. Polycrystalline β-In$_2$S$_3$ containing oxygen thin films are obtained as soon as the temperature of annealing is between 623 and 723 K. In this paper, these β-In$_2$S$_3$ thin films have optically been studied. The optical band gap is direct. Its value is not dependent on the temperature of annealing. It is about 2.8 eV, which is higher than that of β-In$_2$S$_3$ single crystal. This high value is related to the presence of oxygen in the films. The extinction coefficient k and the refractive index n of the films have also been found independent of the annealing temperature. These optical properties make the films studied good candidates to be substituted to CdS in Cu(In,Ga)Se$_2$ based solar cells.

Cet article est consacré à l'étude des propriétés optiques de couches minces de sulfure d'indium (In$_2$S$_3$) réalisées par évaporation thermique sous vide suivie d'un recuit sous flux d'argon. L'influence de la température de traitement thermique sur le coefficient d'extinction et sur l'indice de réfraction des couches a été étudiée. La largeur de la bande interdite des couches traitées à 623, 673 ou 723 K est de 2,8 eV, mettant en jeu une transition de nature directe. Une bande interdite aussi large, celle du monocristal étant de 2,0 eV, a déjà été trouvée par des auteurs à partir de couches obtenues par des processus chimiques et est liée à la présence d'oxygène. Ces propriétés font de ces films d'excellents candidats à la substitution du CdS comme couche tampon dans les cellules solaires à base de Cu(In,Ga)Se$_2$.

1. Introduction

Thin film solar cells based on Cu(In, Ga)Se$_2$, CuInSe$_2$ and CuInS$_2$ absorber layers have shown promising solar energy conversion efficiency [1–3]. They are actually the best candidates for large-scale production due to the low material consumption and preparation techniques appropriate for large areas. The highest conversion efficiencies of Cu(In, Ga)Se$_2$ based solar cells have been achieved with a chemical bath deposited (CBD) CdS buffer layer prior to rf sputtered ZnO : Al [4]. However, from the environmental safety point of view, the establishment of a process to fabricate cadmium-free buffer layers and the minimization and eventual elimination of Cd-containing waste water discharged from the CBD process are desirable. Moreover, in order to improve the light transmission in the blue region, it is desirable to substitute a material with a wider band gap than that of CdS.

Several CBD deposited Cd-free materials have already been used as buffer layers. Conversion efficiencies higher than 10% have been achieved with Zn(S, O, OH), ZnSe [5] or Sn(S, O)$_2$ [2] as buffer layers and higher than 15% with In$_x$(OH, S)$_y$ [6]. Nevertheless, the large scale development of such buffer layers containing solar cells is limited by the break in the production chain because of their CBD deposition process. The absorber and the transparent conducting oxide (TCO) being deposited following a dry vacuum physical process could be interesting if the buffer layer could be deposited under the same conditions.

The optical properties of indium sulfide (In$_2$S$_3$) thin films depend on their synthesis process and on their composition. It can be found in literature that its band gap varies from 2.0 eV [7] to 2.4 eV [8]. Band gap values of 2.75 and 3.25 eV have been found by Lokhande et al. [9] from In$_2$S$_3$ thin films deposited by CBD process and by Yousfi et al. [10] from In$_2$S$_3$ thin films deposited by atomic layer deposition, respectively. These large band gaps make these films good candidates to substitute CdS as buffer layer in thin film solar cells.

The thin films studied in this paper are oxygen containing β-In$_2$S$_3$ deposited on soda lime glass substrates. They were synthesized by annealing under constant argon flow of structures composed of thin layers of indium and sulfur sequentially deposited by thermal evaporation. We have already shown that these films have a wider optical band gap than pure β-In$_2$S$_3$ [11, 12]. In this paper the optical properties of these thin films are accurately studied, the annealing temperature being used as parameter.

2. Experimental Details

2.1 Thin film preparation and physico-chemical properties

The thin film preparation process and their physico-chemical properties were described earlier [11, 13] and will be briefly recalled here.

The synthesis of the films can be divided in two steps: the deposition of the constituents (indium and sulphur), sequentially evaporated in a vacuum chamber, and the post-annealing of these structures under a constant argon flow.

The evaporations were done in a vacuum of 10^{-4} Pa. The indium and sulphur layers were sequentially deposited on soda lime glass substrates by thermal evaporation using a tungsten crucible for indium and a "laboratory made" Pyrex crucible for sulphur. The layer thickness and evaporation rates were measured in-situ by an hf quartz monitor. The evaporation rates were 0.3 nm s^{-1} for indium and 1–2 nm s^{-1} for sulfur. During the deposition, the substrates were at room temperature. Electronic microprobe analysis has shown that the structures, before heat treatment, only contain indium and sulphur in the atomic ratio S/In > 1.5 [13].

The structure were then annealed under a constant argon flow of 0.6 dm^3/min.

Before annealing, the films are amorphous. X-ray diffraction peaks of β-In$_2$S$_3$ quadratic structure appear on the diagrams as soon as the annealing temperature is 623 K and more. Therefore, in this paper only the optical properties of the films annealed at 623 K or more are studied.

Electronic microprobe analysis has shown that after annealing at 623 and 673 K, the thin films contain about 5 at% of oxygen substituted to sulfur forming In–O bonds. Those heated at 723 K contain about 10 at% of oxygen in their bulk [13]. The oxygen

is introduced during the annealing and proceeds from the argon which is not pure but
Nertal argon.

The thickness of the films studied has been determined observing their cross section
by scanning electronic microscopy (SEM) and it was 250 nm.

2.2 Optical measurements

In order to determine the absorption coefficient α of the films versus the incident en-
ergy, transmission $T(\lambda)$ and reflectivity $R(\lambda)$ measurements were carried out at room
temperature. The transmission measurements were performed between 300 and
2000 nm using unpolarized light in normal incidence by means of a Shumadsu UV 3100
F double-beam spectrophotometer equipped with an integrating sphere LISR 3200.
Barium sulphate and air were taken as references for the reflection and transmission
measurements, respectively.

3. Experimental Results

Figure 1 shows the transmission spectra obtained when the structure evaporated is an-
nealed at 623, 673 and 723 K. One can see that the three curves have similar shape,
their transmission threshold is about 450 nm and for larger wavelengths, the films trans-
mit about 70% of the incident photons in spite of their 250 nm thickness. Figure 2
shows the results of reflectivity measurements. The values obtained as a function of
wavelength never exceed 30% of the incident light. Both transmission and reflectivity
spectra show large interference fringes when the wavelength is larger than 450 nm.

The absorption coefficients of the films have been calculated using the following rela-
tion valid for the mean absorption edge:

$$\alpha = -\frac{1}{t} \ln \left\{ \frac{T}{(1-R)^2} \right\}, \tag{1}$$

where α is the absorption coefficient, t is the thickness of the film, T and R are the
transmission and reflectivity, respectively.

The obtained results have been plotted as a function of the energy of the incident
photons for the three different temperatures of annealing (not shown). These spectra
show same variations in all cases in-
dicating no significant effect of tem-
perature on the absorption of
layers.

In order to determine the value
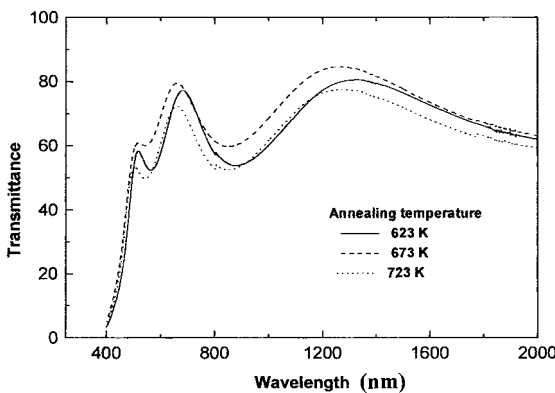of the optical band gap as well as

Fig. 1. Transmittance traces obtained
from the different films versus the wave-
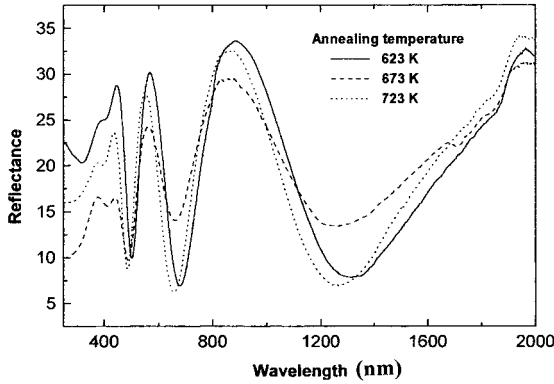length of incident light

Fig. 2. Reflectance traces obtained from the different films versus the wavelength of incident light

the nature of the transition occurring, we develop a method which was already used by Bhattacharyya et al. [14]. In general, the absorption coefficient is written as a function of the incident photon energy $h\nu$ so that [15]

$$\alpha = \frac{A}{h\nu}\{h\nu - E_g\}^m, \qquad (2)$$

where A is a constant, m is a value depending on the nature of the transition and E_g is the corresponding band gap. For a material having one kind of transition, the value of m is 1/2, 2, 3/2 or 3 for allowed direct, allowed indirect, forbidden direct or forbidden indirect transition, respectively. The nature of the transition can therefore be determined finding the value of m. Nevertheless, the value of E_g must first be found.

From Eq. (2), the following equations can be deduced:

$$\ln \alpha = \ln A - \ln(h\nu) + m \ln(h\nu - E_g) \qquad (3)$$

and

$$\frac{d(\ln \alpha)}{d(h\nu)} = -\frac{1}{h\nu} + \frac{m}{h\nu - E_g} \qquad (4)$$

Equation (4) suggests that the plot of $\ln \alpha$ versus $h\nu$ will indicate a divergence at $h\nu = E_g$, from which the value of E_g can be determined. Once E_g is found, the value of m can easily be obtained from the slope of the straight line plot of $\ln(\alpha h\nu)$ as a function of $\ln(h\nu - E_g)$.

This paper only details the calculations performed from the results of a 673 K annealed film. The results concerning the films annealed at 623, 673, and 723 K are summarized in Table 1.

Table 1
Summary of the values determined from the calculations of all films

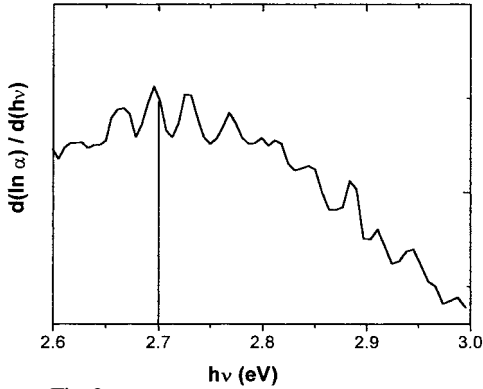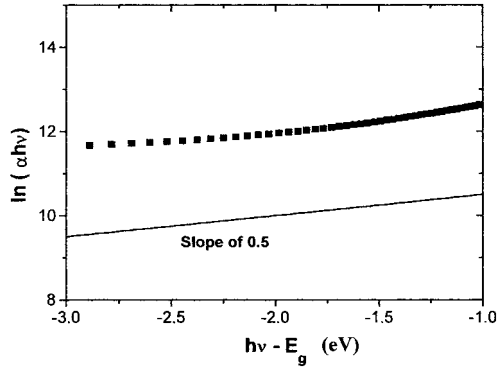| temperature of annealing	E_g determined from the maximum of $f(h\nu) = \dfrac{d(\ln \alpha)}{d(h\nu)}$	nature of the transition	E_g determined from the curve $(\alpha h\nu)^2 = f(h\nu)$
(K)	(eV)		(eV)
623	2.7 ± 0.1	allowed direct	2.80 ± 0.05
673	2.7 ± 0.1	allowed direct	2.80 ± 0.05
723	2.7 ± 0.1	allowed direct	2.80 ± 0.05

Fig. 3

Fig. 4

Fig. 3. Plot of the function $\dfrac{d(\ln \alpha)}{d(h\nu)} = f(h\nu)$; case of the film annealed at 673 K

Fig. 4. Plot of $\ln (\alpha h\nu)$ versus $\ln (h\nu - E_g)$, where E_g is 2.7 eV, case of the film annealed at 673 K

The plot of $\ln \alpha$ versus $h\nu$ does not exhibit clear divergence and cannot be used in this form to determine the value of E_g. Therefore, in order to visualize an increase in the slope of the curve, the plot of its differentiated form has been shown. The curve representing the function $\dfrac{d(\ln \alpha)}{d(h\nu)} = f(h\nu)$ has a maximum for the value of $h\nu$ about 2.7 eV (Fig. 3). This approximate value of E_g allows the determination of the nature of the transition occurring during the absorption in the material. The drawing of $\ln (\alpha h\nu)$ as a function of $\ln (h\nu - E_g)$, where E_g is 2.7 eV, is shown in Fig. 4. In this figure, a straight line, the slope of which is 0.5, is also represented. One can see that the two curves have approximately the same slope. It can therefore be concluded that $m = 0.5$ and the transition occurring has a direct allowed nature. It can also be concluded that relation (2) can be written as

$$\alpha = \frac{A}{h\nu} (h\nu - E_g)^{\frac{1}{2}} \tag{2'}$$

The value of E_g (2.7 eV) determined above is not accurate enough. A more precise value can be obtained extrapolating the linear part of the spectrum $(\alpha h\nu)^2 = f(h\nu)$ to zero. Figure 5 represents the result obtained from the film annealed at 673 K, the value of E_g found is about 2.80 eV. The same value has been found from films annealed at 623 or 723 K (see Table 1).
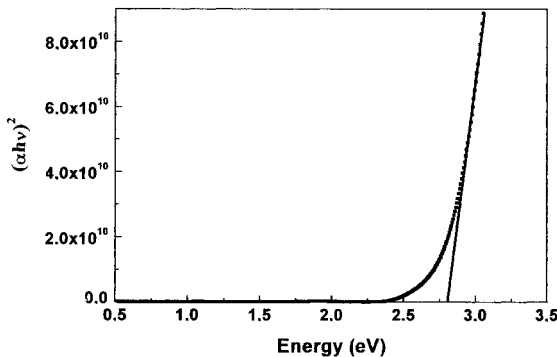
On the other hand, using data of the optical transmission and reflec-

Fig. 5. Plot of $(\alpha h\nu)^2$ versus $h\nu$, case of the film annealed at 673 K
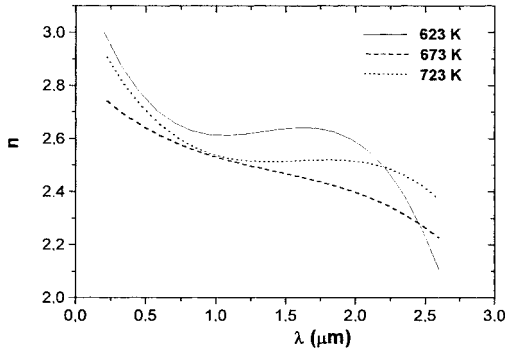
Fig. 6. Evolution of the refractive index n versus the wavelength of incident photon obtained for different films

tivity spectra, the refractive index $n(\lambda)$ and the extinction coefficient $k(\lambda)$ were calculated in the visible and infrared region by the Mueller method for nonlinear equations [16]. The obtained plots of n and k, Figs. 6 and 7, respectively, show slight differences as function of the annealing temperature with mean variations situated in the range (2.1–2.8) and (0.01–0.3) for n and k, respectively.

4. Discussion

The curves of transmission obtained from the samples annealed at 623, 673 and 723 K have the same transmission threshold and life-like interference fringes (Fig. 1). These similarities have also been found in the curves of reflectivity (Fig. 2). It is well known that the amplitude of the interference fringes is a measure of the film quality; the larger the amplitude is, the better is the film. This is because if the surface film is highly reflecting and if there is not much absorption in the bulk of the film, there will be large interference fringes. This phenomenon, due to multiple reflections, is characteristic of relatively homogeneous layers.

The optical properties of β-In$_2$S$_3$ single crystal are well known. Its optical coefficient shows a fundamental absorption edge at about 2 eV and at higher energies a second but faint critical point is observed at about 2.45 eV [17, 18]. As far as thin films are concerned, their optical properties depend on the synthesis process and the chemical composition. As referred in the literature, if the films obtained by reactive evaporation of indium in an atmosphere of sulfur [7] or by sulphurization of indium layers [19] have an optical band gap which value is approximately that of the single crystal (2 eV), those synthesized by atomic layer epitaxy [20] or by spray pyrolysis [8] have a larger optical band gap of about 2.3–2.4 eV.
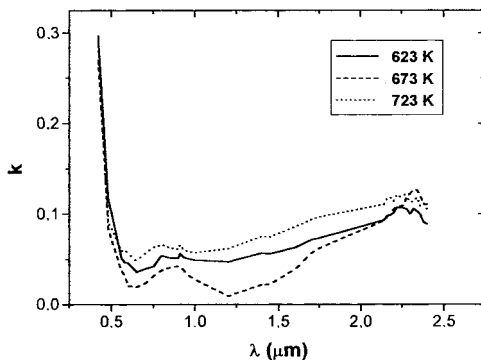

Fig. 7. Evolution of the extinction coefficient k versus the wavelengths of incident photons obtained for different films

It can be concluded from the present study that the optical properties of the films do not depend significantly on the annealing temperature T_a, when 623 K < T_a < 723 K. It has been checked that, at least, about 5 at% of oxygen is present in the films [11, 13]. Therefore, it means that there is a threshold value of the concentration of oxygen which induces the broadening effect of the optical band gap. For higher concentration, no significant modification is visible, the extra oxygen behavior only corresponds to a contamination of the samples but does not influence the gap value.

The values of the refractive index n and of the extinction coefficient k calculated in the visible and infrared regions are of the same order as that found by Kamoun et al. [21] from films obtained by airless spray. The increase of the annealing temperature from 623 to 723 K does not induce a variation of n and k values, which confirms the small importance of this parameter on the optical properties of the films studied in this paper.

All the results obtained show that the nature and the value of the optical band gap and the values of n and k do not significantly depend on the temperature of annealing as soon as it is between 623 and 723 K. In this temperature range, the films are crystallized in the β-In$_2$S$_3$ structure [13]. The small influence of the annealing temperature, in the range defined above, on the optical properties of the thin films is very interesting for multilayer applications. The films can be obtained on sublayers at quite low temperature (623 K) and their optical properties would not be altered by a higher synthesis temperature of the covering film.

The width of the optical band gap of the films studied in this paper is about 2.80 eV. Such wide gap β-In$_2$S$_3$ thin films have ever been obtained by Lokhande et al. [9], Yoshida et al. [22] or Kitaiev et al. [23] using a chemical bath deposition process. These authors have deduced from this band gap value that In$_x$OH$_y$S$_z$ films are good candidates for Cd-free buffer layers. Effectively, they transmit more than 70% of the visible light, their gap is slightly higher than that of CdS what is interesting for the transmission in the blue region. Moreover, the transition occurring has a direct nature. All these properties are very promising, moreover, it should be noted that in the present work, films with similar properties have been obtained by a simple dry physical process. Therefore, in the present case, the whole cell depositing process can be achieved by PVD, which is very interesting for industrial production and environmental difficulties related to the liquid waste resulting from the CBD process. With our PVD technique, such liquid waste could be avoided.

5. Conclusion

We have studied in this paper the optical properties of In$_2$S$_3$ thin films synthesized by a dry physical vapor deposition process precisely described elsewhere [11, 13]. The high homogeneity and the excellent surface state of the films have been confirmed by the presence of interference fringes on transmission and reflectivity spectra. The values of refraction index and extinction coefficient calculated as a function of the wavelength of incident photons are close to those found in the literature. Moreover, they do not significantly depend on the temperature of annealing when it is between 623 and 723 K. This very small influence of the annealing temperature on the optical properties has also be found as far as the optical band gap was concerned. The transition occurring has always been found as an allowed direct one and its width is equal to 2.80 eV what-

ever the temperature of annealing was. This value of 2.80 eV is higher than that obtained from single crystals (2.0 eV). Nevertheless, such wide band gap value is often found by several authors from thin films of In_2S_3 synthesized by different processes [9, 10, 21, 22]. The optical properties of cadmium-free thin films obtained following a dry physical process studied in this paper make them good candidates to substitute CdS as buffer layer in Cu(In, Ga)Se$_2$ based solar cells.

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