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Absorption Coefficient and Energy Gap of Vacuum Free CSVT Deposited $CuInSe_2$ Thin Films

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Abstract: In order to determine the suitable source temperatures to deposit $CuInSe_2$ thin films for solar cells, absorption coefficient α and energy gap E_g of this compound were evaluated. The films were grown by vacuum free CSVT technique for 3 h. The source temperatures of deposition ranged from 400 to 600°C. Absorption coefficient and energy gap were determined from transmittance (T) and reflectance (R) of obtained films. Transmittance (T) and reflectance (R) were characterized using a spectrophotometer with wavelength λ range 1-2.5 μm. Curves (α) and $(h\nu\alpha)^2$ versus photon energy ($h\nu$) were analysed. At source temperatures of 450-500°C, the value of α was found to be about 10^4 cm^{-1}. At source temperature higher than 500°C, α dropped to lower values of 10^4 cm^{-1}. $CuInSe_2$ thin films were found to have a direct allowed transition and the best E_g value was estimated between 0.94-0.96 eV at source temperatures of 450-500°C. A decrease in E_g value was observed when the source temperature became higher than 500°C. In view of these results, the source temperature range of 450-500°C was found to be more appropriate to grow $CuInSe_2$ films for solar cells. Indeed, α and E_g values can be increased by introducing Gallium into ternary $CuInSe_2$ for a better alignment with the solar spectrum, e.g., a $CuIn_{1-x}Ga_xSe_2$ heterojunction device.

Key words: Vacuum free CSVT, $CuInSe_2$, thin films, source temperatures, absorption coefficient, energy gap

INTRODUCTION

Copper indium diselenide ($CuInSe_2$ or CIS) is one of the most promising materials studied for solar cell applications due to its direct band gap of about 1.02 eV at room temperature and its high absorption coefficient in the range of 10^4-10^5 cm^{-1}.

$CuInSe_2$-based thin films solar cells exhibit high conversion efficiencies (Ramanathan *et al*., 2003; Contreras *et al*., 1999; Rau and Schock, 1999; Tuttle *et al*., 1995). Its high absorption coefficient allows the reduction of required thickness of absorber layer down to about 0.5-1.5 μm.

$CuInSe_2$ thin films have been deposited by various processing techniques, like solution growth technique (Chavhan and Sharma, 2006), RF sputtering (Müller *et al*., 2006), chemical spray pyrolysis (Terasako *et al*., 2006), multi-source co-evaporation (Chityuttakan *et al*., 2006), UV laser ablation (Tverjanovich *et al*., 2006), metal-organic decomposition (Nakamura and Ando, 2005), electrodeposition (ED) technique (Huang *et al*., 2004), Close-Spaced Vapour Transport (CSVT) under vacuum (Massé *et al*., 2004; Moukadir *et al*., 2004; Kannan *et al*., 2004; El Hadj Moussa *et al*., 2002), electron beam and flash evaporation (Castaòeda and Rueda, 2000).

However, the characteristics of the films obtained depend strongly on the growth process and conditions.

The present study reports absorption coefficient and energy gap of $CuInSe_2$ thin films deposited by vacuum free CSVT technique at different source temperature. Absorption coefficient and energy gap were evaluated versus the source temperature in the range of 400 to 600°C. Then, optimal source temperature to deposit $CuInSe_2$ films for solar cells was determined.

MATERIALS AND METHODS

Figure 1 shows the vacuum free CSVT device for the preparation of $CuInSe_2$ thin films as already used (Konan *et al*., 2007, 2006). It consists of an open quartz tube reactor set horizontally without vacuum, which has a length of 40 cm and an interior diameter of 3.5 cm. The entrance of the quartz tube is composed of two openings for argon flow which can be closed by valves V1 and V2.

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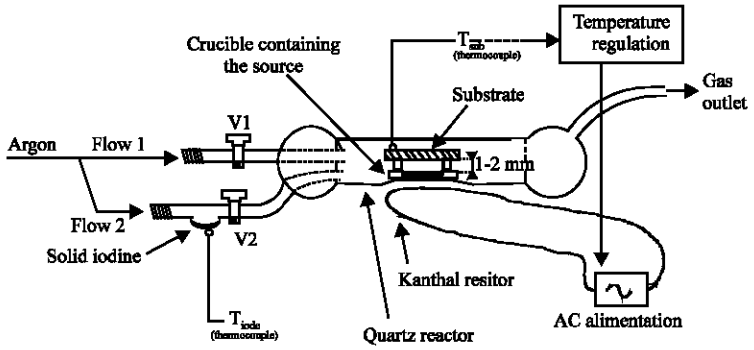

Fig. 1: Schematic diagram of the CSVT device

The argon pressure through V1 and V2 were identical and adjusted between 1.5 and 2 bar to allow the transport of iodine vapour into the reactor. The end of the quartz tube is composed of a gas outlet which was kept opened during films deposition process. The source is a powder of $CuInSe_2$ placed in a graphite crucible and hand pressed. This powder with the ratio (Cu/In) = 0.99 was obtained from bulk $CuInSe_2$ synthesized from elements of high purity (6N) of Cu, In and Se. The substrates used are flat pyrex glass of 1 mm thick. The substrates were successively well cleaned in alcohol, de-ionised water and acetone baths and then well dried. The substrates were placed above the source and separated from it by an 2 mm thick glass spacer. A U-form Kanthal resistor placed just under the crucible is used to heat both the source and the substrate. The source temperature indicated by a regulator varied between 400 and 600°C. The substrate temperature directly measured using a chromel-alumel thermocouples, is colder than the source of about 100-180°C. Solid iodine used as a transporting agent was heated to the remaining temperature of 30°C. At the early stage of the heating up of the system, valve V1 was opened and V2 closed. The first argon-flow was bypassed the iodine source and removed the air from the reactor. Therefore, no iodine vapour was present in the reactor. After the source temperature was stabilized, valve V1 was closed and V2 opened so that the second argon-flow transported iodine vapour into the reactor. After the deposition time of about three hours, the two valves were closed during cooling period. Therefore, no more iodine vapour was transported into the reactor.

$CuInSe_2$ thin films were deposited at source temperatures of 400, 450, 500, 550 and 600°C. The films thicknesses were measured by a surface profilometer (DEKTAK 3). A spectrophotometer (Brucker IFS 66v) was used to characterize transmittance (T) and reflectance (R) of films with wavelength (λ) range 1-2.5 μm.

RESULTS

The samples of films obtained at source temperatures of 400, 450, 500, 550 and 600°C were, respectively noted S1, S2, S3, S4 and S5, as shown in Table 1.

Evaluation of absorption coefficient α: The absorption coefficient α was calculated with the following formula (Huang *et al*., 2004; Djessas *et al*., 2000):

$$\alpha = \left(\frac{1}{d}\right)\ln\left[\frac{(1-R)^2}{2T} + \left[\frac{(1-R)^4}{2T^2} + R^2\right]^{\frac{1}{2}}\right] \quad (1)$$

Where:

d = The film thickness.
T = The films transmittance
R = Reflectance data, respectively.

Transmittance (T) and reflectance (R) depend on wavelength λ. Transmittance (T) and reflectance (R) spectra of thin films are shown respectively in Fig. 2 and 3. Wavelengths were converted into incident photon energy using the relationship below:

$$h\nu = \frac{1.24}{\lambda} \quad (2)$$

where, $h\nu$ is expressed in eV and λ in μm.

The Eq. 1 gives then curves α as a function of $h\nu$ (Fig. 4).

Each curve exhibits a linear portion that contains an inflexion point. The fundamental value of α was noted α_o. The values of α_o were the intercept points between the α axis and a horizontal straight-line starting from the inflexion point. Thus, α_o was evaluated for each sample.

Table 1: Samples obtained at different source temperatures

Samples	Source temp. (°C)	Substrate temp. (°C)	Average thickness (μm)
S1	400	228	0.495
S2	450	274	0.835
S3	500	318	1.255
S4	550	371	0.899
S5	600	422	0.845

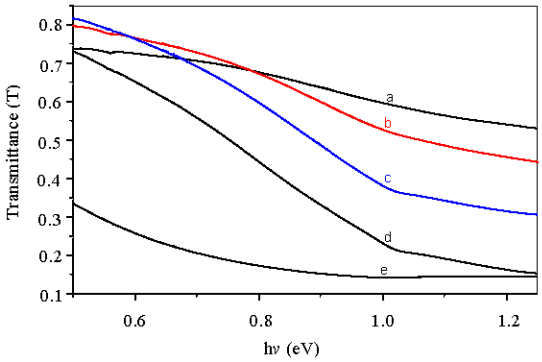

Fig. 2: Transmittance (T) spectra of $CuInSe_2$ films. (a) T_{source} = 400°C; (b) T_{source} = 450°C; (c) T_{source} = 500°C; (d) T_{source} = 550°C and (e) T_{source} = 600°C

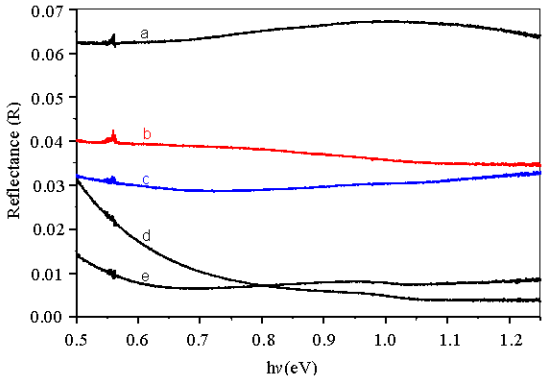

Fig. 3: Reflectance (R) spectra of $CuInSe_2$ films. (a) T_{source} = 400°C; (b) T_{source} = 450°C; (c) T_{source} = 500°C; (d) T_{source} = 550°C and (e) T_{source} = 600°C

Table 2 gives values of α_0 of the films deposited at different source temperatures. The results showed that at source temperatures of 400-500°C, the values of α_0 were found to be in the range of 10^4-2.3 10^4 cm^{-1}. This range values is in a good agreement with the absorption coefficient values reported by other researchers such as Massé *et al.* (1997) and Zouaoui *et al.* (1999). At source temperatures above of 500°C, α_0 became lower than 10^4 cm^{-1} at 550°C. At source temperature of 600°C, the corresponding curve (curve e) in Fig. 4 has not an inflexion point. α_0 could not be so clearly evaluated.

Table 2: Absorption coefficient α and energy gaps E_g estimated from Fig. 4 and 5

Samples	Thickness (μm)	α_0 (10^4 cm^{-1})	E_{g0} (eV)
S1	0.495	2.3	0.90
S2	0.835	1.0	0.94
S3	1.255	1.0	0.96
S4	0.899	0.5	0.83
S5	0.845	-	0.57

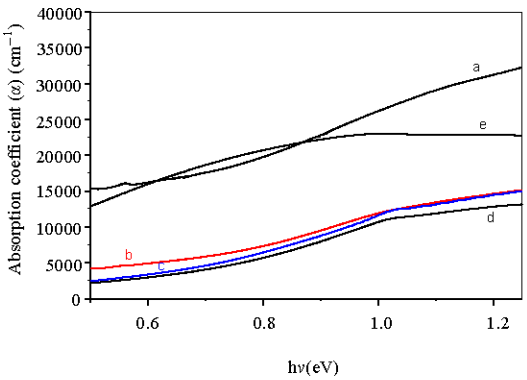

Fig. 4: Absorption coefficient α as a function of photon energy hν for samples. (a) Sample S1; (b) Sample S2; (c) Sample S3; (d) Sample S4 and (e): Sample S5

Evaluation of energy band-gap E_g: The energy gaps E_g and the absorption coefficient α are correlated according to the following equation (Kannan *et al.*, 2004; Tverjanovich *et al.*, 2006):

$$\alpha = \left(\frac{k}{h\nu}\right)\left(h\nu - E_g\right)^{\beta} \quad (3)$$

Where:
k = A constant.
h = The Plank's constant.
hν = The incident photon energy.

As the electronic transition between the valence and conduction bands can be direct or indirect, the exponent β is a number which characterizes the transition process: β = 1/2 for direct allowed transitions, β = 3/2 for direct forbidden transitions, β = 2 for indirect allowed transitions and β = 3 for indirect forbidden transitions. As $CuInSe_2$ is a direct band-gap, the corresponding E_g is obtained with β = 1/2 (Chavhan *et al.*, 2006; Muller *et al.*, 2006; Huang *et al.*, 2004; Djessas *et al.*, 2000; Massé *et al.*, 1997). Therefore the formula used is:

$$\alpha = \left(\frac{k}{h\nu}\right)\left(h\nu - E_g\right)^{\frac{1}{2}} \quad (4)$$

or

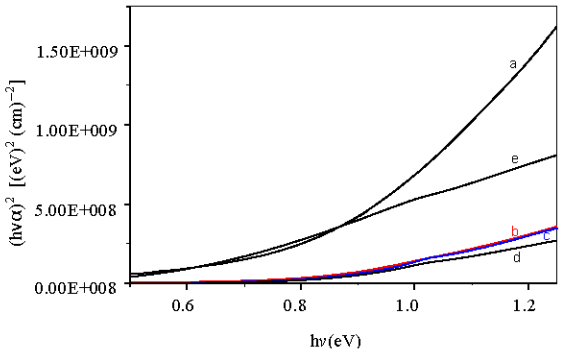

Fig. 5: Plot of $(h\nu\alpha)^2$ versus photon energy hν for samples. (a) Sample S1; (b) Sample S2; (c) Sample S3; (d) Sample S4 and (e) Sample S5

$$(h\nu\alpha)^2 = K(h\nu - E_g) \quad (5)$$

where, K is a constant equal to k^2.

The formula (5) gives curves $(h\nu\alpha)^2$ as a function of hν (Fig. 5).

All the curves of Fig. 5 exhibit a nonlinear and linear portion, which is characteristic of direct allowed transitions. Such transitions have been reported by Chavhan *et al.* (2006), Muller *et al.* (2006), Huang *et al.* (2004), Djessas *et al.* (2000) and Massé *et al.* (1997). According to Muller (2006), the nonlinear portion corresponded to a residual absorption which could be attributed to factors: which are absorption involving impurity states, interference due to multiple reflections that take place at the surface and backside of the films. The straight line portion characterizes the fundamental absorption.

The fundamental value of E_g was noted E_{go}. The energy gaps E_{go} of the samples was evaluated from the intercept of the linear portion of each curve (Fig. 5) with the hν axis. Table 2 gives values of E_{go} of the films deposited at different source temperatures. At source temperatures of 400°C, E_{go} value of 0.90 eV was lower than the expected value. At source temperatures of 450-500°C, E_{go} values were in the order of 0.94-0.96 eV. This range values agree well with results early reported by Muller *et al.* (2006), Chavhan *et al.* (2006), Huang *et al.* (2004), Djessas *et al.* (2000) and Massé *et al.* (1997) from Eq. 4. These E_{go} values corroborated with the α_o values in the same range of source temperatures 450-500°C.

When the source temperatures became higher than 500°C, E_{go} values dropped to 0.83 and 0.57 eV, respectively at 550 and 600°C.

The α_o and E_{go} values obtained versus source temperatures of $CuInSe_2$ thin films deposition were in good agreement with the results of structural and morphological analysis reported in the same range of source temperatures (Konan *et al.*, 2007). In both case of study, the optimal source temperature to deposit suitable $CuInSe_2$ thin films for solar cells was about 500°C. At this source temperature, thin films obtained can be used as $CuInSe_2$-based solar cells. Indeed the corresponding α_o and E_{go} values, respectively 10^4 cm^{-1} and 0.96 eV can be increased by introducing Gallium into ternary $CuInSe_2$ for a better alignment with the solar spectrum, e.g., a $CuIn_{1-x}Ga_xSe_2$ heterojunction device (Ramanathan *et al.*, 2003; Contreras *et al.*, 1999; Rau *et al.*, 1999; Tuttle *et al.*, 1995).

CONCLUSIONS

$CuInSe_2$ thin films were deposited by vacuum free CSVT technique at different source temperatures. Absorption coefficient and energy gap of the obtained thin films were determined versus source temperatures through measurements of transmittance (T) and reflectance (R) of films. For films deposited at source temperatures of 450 and 500°C, the value of absorption coefficient was about 10^4 cm^{-1}. Above 500°C, it lowered down to 10^4 cm^{-1} at 550°C and could not be clearly evaluated at 600°C.

$CuInSe_2$ thin films were found to have a direct allowed transitions and the best energy gap value was estimated in the order of 0.94-0.96 eV at source temperatures of 450-500°C. At source temperature higher than 500°C, a decrease in energy gap value was observed. These results, compared to structural and morphological analysis previously reported in the same range of source temperatures, confirmed that the source temperature of 450-500°C was required to deposit $CuInSe_2$ films for solar cells.

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