Investigation of the optical properties of $CuInSe_2$ and $CuInS_2$ thin films for photovoltaic application

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Abstract— **In this study, the deposition of $CuInSe_2$ and $CuInS_2$ thin films on ITO substrates by the electroplating technique was investigated. After optimizing the electrodeposition operating parameters, the films morphology was examined by optical microscopy. All optical parameters such as band gap energy, refractive index, extinction coefficient and dielectric constant were extracted using visible UV spectroscopy.**

Key words: $CuInSe_2$, $CuInS_2$, Thin films, Spectroscopy, Gap, Refractive index, Dielectric constant.

I. INTRODUCTION

One of the most promising solutions for the future energy of mankind is photovoltaic. Photovoltaic energy comes from the conversion of sunlight into electricity. This conversion takes place within semiconductor materials, which have the property of releasing their charge carriers under the influence of external excitation.

Thin film solar cells based on a compound of the elements Copper, Indium, Gallium, and Selenium, that is, CIGS semiconductors, are considered as highly promising light-to-electricity converters thanks to their direct bandgaps which can be efficiently matched to the solar spectrum.

The choice of CIS thin films as an absorbent material is due to their band gap which can hold values between 1.018 and 1.701 eV [1] and a high absorption coefficient in visible light and near infrared of about 10^5 cm^{-1} for 1.5 eV which shows the high absorption of the sun rays. Interesting yield up to (20.3%) by comparing with other absorbers also long-lasting stability and high durability [2].

For the production of thin films, several techniques can be used, such as spray [3] [4], sputtering [5], thermal evaporation [6], sol-gel assisted with spin and dip coating, CBD, laser ablation. There are several processes for making the absorbent layers, electroplating is one among them but remains the least expensive technique compared to other expensive technologies. One of the most important conditions for successful electroplating in a single step is to optimize the composition of the deposited films in a reliable and reproducible manner, the composition of the electrolytic bath for the CIS preparation.

In the present study, we have tested two different precursors, H_2SeO_3 and $SC(NH_2)_2$, to understand the effect on the optical properties of each of them and select the best one.

II. EXPERIMENTAL

The electroplating technique involves preparing CIS ($CuInSe_2$ and $CuInS_2$) from two electrolytic baths containing the Cu-In--Se elements often in the form ($CuCl_2$, $InCl_3$, H_2SeO_3) and he Cu-In--S elements often in the form ($CuCl_2$, $InCl_3$, $SC(NH_2)_2$) The cations discharge into the electrolysis on the cathode surface. When they are numerous, the layer can then be formed and the crystal develops in specified directions.

The equilibrium potential (deposition) of each element makes the electrodeposition of the elements very difficult.

In our case the deposition potentials of the Cu, In, and Se or S elements are different, in order to deposit them at the same time the individual potentials must be brought closer together, using 0.1 M of the sodium citrate which was chosen to be a complexing agent in deionized (DI) water

For the $CuInSe_2$ the electrochemical deposition reaction of the elements is given by Eq. 1 [8].

$$Cu^{2+} + In^{3+} + 2H_2SeO_3 + 13e^- + 8H^+ \rightarrow CuInSe_2 + 6H_2O \qquad (1)$$

Conductive indium tin oxide (ITO) coated glass substrates of $1.5 \times 1\ cm^2$ dimension were used as substrates. They were ultrasonically cleaned with ethanol and deionized water during 10 min.

All deposition parameters were fixed. Only the precursor compositions were varied, using two different precursors based on Se and on S. The CIS films were electrodeposited on the cleaned ITO-glass substrates.

The electrodeposition technique was carried out potentiostatically using an Autolab potentiostat/galvanostat connected to a three-electrode cell. The used working electrode was ITO-coated glass substrate, the reference electrode was an Ag/AgCl (3 M NaCl) and a platinum plate was used as a counter electrode (Figure 1).

The composition of the deposition bath consisted of 3 mM of $InCl_2$, 3 mM of $CuCl_2.2H_2O$, 6 mM of $HSeO_2$ and 0.1 M of the sodium citrate which was chosen to be a complexing agent in deionized (DI) water. The pH of the solution has been adjusted to 1.5 by adding HCl. The cathodic potential and deposition time have been fixed at −750 mV and 60 min, respectively.

Afterwards, the samples were rinsed under DI water and dried in 60 °C oven for 5 min. Due to improvement crystallinity of the deposited films and their amorphous nature, all as-deposited films have been annealed in tubular annealing at 350 °C during 5 min. To minimize the exhausting of the selenium and sulfur from samples, it was necessary to stabilize the temperature for 10 min before to put the samples. [9]

Various characterization techniques, such as optical microscopy, were used for showing the phase formation. UV-Visible for extracting optical parameters to know gap energy, refractive index, extinction coefficient, dielectric constant.

Figure 1. Three-electrode electrochemical cell (RE-reference electrode, WE-working electrode (coated sample), AE-auxiliary electrode) [10]

III. RESULTS AND DISCUSSION

A. *Morphology properties*

Optical Microscopy:

Optical Microscopy (OM) is able of producing to produce high resolution images of the sample surface using the principle of electron-matter interactions. OM analysis of the surface of the layers shows that the surface of our sample exhibits well defined morphology. For the present case, the homogeneity of the thin films produced by electrodeposition is well shown, and the surface of $CuInS_2$ (Figure 2) is clearly more homogeneous than $CuInSe_2$ (Figure 3).

Figure 2. Optical microscopy image of $CuInS_2$.

Figure 3. Optical microscopy image of $CuInSe_2$

B. Optical properties:

- Absorbance, transmittance and gap energy

Fig. 4 and Fig. 5 show the transmittance and absorbance spectra of CIS thin films prepared with two different precursors $SC(NH_2)_2$ and H_2SeO_3 were recorded in the wavelength range (500 nm - 1000 nm). It is found that all the films have a high absorbance and low transmittance. But there is a small difference in results in terms of percentage (%) of the absorbance and transmittance of the films. The highest value of transmittance is seen for selenium (12%). The film deposited with sulfur has the lower transparency of 9% at 800 nm than films prepared with selenium. Using sulfur, the films deposited show a high absorbance in visible region with a maximum value of about 3.

Figure 4. Optical transmittance spectra of the CIS thin films obtained by electrodeposition

Figure 5. Optical absorbance of the CIS thin films obtained by electrodeposition

The optical band gap energy of films was calculated from the linear diagram of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for direct band gap semiconductors,

$$(\alpha h\upsilon)^2 = B\,(h\upsilon - E_g) \quad (2)$$

where α is absorption coefficient, h is Planck constant, B is a constant, E_g is the band gap energy and t is the thickness of the thin films.

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \quad (3)$$

Figure 6. band gap energy of the CIS thin films obtained by electrodeposition.

Fig. 6 indicates the variation of $(\alpha h\upsilon)^2$ according photon energy ($h\upsilon$) of the CIS thin films deposited with different precursors. The calculated values of band gap energy are 1.46 eV for $CuInS_2$, 1.52 eV for $CuInSe_2$ and are in good agreement with reported values [1]. For the films deposited by sulfur, a strong absorbance and band gap energy of the order of 1.46 eV make the films prepared by this precursor a good choice for solar cells application [10].

- Optical constants

Fig. 7, Fig. 8, Fig. 9 and Fig. 10 show the optical constants, namely refractive index (n), extinction coefficient (k), real part (ε_r) and imaginary part (ε_i) of dielectric constant for $CuInSe_2$ and $CuInS_2$, which were calculated using Eqs. (4) (5) (6) and (7) and whose values are tabulated in table 1 [11],

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (4)$$

$$K = \frac{\alpha\lambda}{4\Pi} \quad (5)$$

(6)

(7)

where n is the refractive index, k is the extinction coefficient, λ is the wavelength, α is the absorption coefficient and R is the reflectance of the films.[12]

Figure 7. Refractive index of the CIS thin films obtained by electrodeposition.

Figure 8. Extinction coefficient of the CIS thin films obtained by electrodeposition.

Figure 9. Imaginary part of dielectric constant of the CIS thin films obtained by electrodeposition

Figure 10. Real part of dielectric constant of the CIS thin films obtained by electrodeposition

The value of refractive index for the films prepared using sulfur as precursor is attributed to the thickness of the films. The high extinction coefficient value is observed for this precursor due to the high absorption into this film compared by other precursor selenium. [13][[14].

The high extinction coefficient values are attributed to the absorbance. The both real and imaginary part of dielectric constant decrease with the wavelength and the maximum values are observed on the sample using sulfur precursor (see Table 1).

TABLE1. OPTICAL CONSTANTS FOR CIS THIN FILMS DEPOSITED WITH DIFFERENT PRECURSORS.

Precursor	n	k	ε_r	ε_i
selenium	3.21	0.045	9.11	0.25
sulfur	3.5	0.055	10.15	0.30

IV. CONCLUSIONS

CIS thin films were prepared using different precursors and deposited by electrodeposition technique for obtained a high films quality with a low cost. For the two precursor, the optical microscopy show the homogeneity of (CIS).

The strong absorbance and low transmittance are observed for the films prepared by the sulfur precursor with bang gap energy about 1.46 eV. The optical constants such us refractive index (n), extinction coefficient (k), real part (ε_r) and imaginary part (ε_i) of dielectric constant were extracted by absorbance/transmittance data.

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