

FABRICATION AND CHARACTERIZATION OF CuInSe_2 THIN FILM SOLAR CELLS WITH FLUORINE DOPED ZnO AS NEW BUFFER LAYER

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Copper indium diselenide CuInSe_2 (CISe) thin films are very important semiconductor material for solar cell applications. In this study, CuInSe_2 (CIS), and Fluorine doped ZnO (ZnO:F) thin films were electrodeposited from aqueous solutions consisting of CuCl_2 , InCl_3 , and SeO_2 with Na-citrate as complexing agents onto Fluorine doped tin oxide (FTO) substrates for CuInSe_2 , and $\text{ZnCl}_2, \text{NH}_4\text{F}$ were used as sources of ZnO and fluorine doping respectively. The microstructures, morphologies, and optical properties of the CuInSe_2 With new buffer layer fluorine doped ZnO (FZO) were characterized. X-ray diffraction analysis showed that all the films CuInSe_2 are tetragonal chalcopyrite with favored orientation along (112) direction and Cu:In:Se crystals are nearly 1:1:2 atomic ratio. The surface morphology of all layers were void free, compact and fairly uniform. The near stoichiometries CuInSe_2 film (annealing at 350°C), has the optical band gap of 1.05 eV. Such a band gap is highly beneficial for the solar cell application.

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1. Introduction

Harry Hahn et al. were the first synthesized the ternary chalcopyrite CuInSe_2 (CIS) in 1953 [1], and has been studied extensively by several groups since 1983 when Bhattacharya published the first paper on a one-step electrodeposition of CuInSe_2 (CISe) thin films [2]. CISe are promising materials for thin film solar cell absorber layers because they have a high absorption coefficient (10^4 cm^{-1}), strong anti-radiative capacity, good thermal stability and comparatively low cost, non-vacuum techniques, and suitable direct band gap (1.04 eV) for solar spectrum [3,4,5,6,7], high conversion efficiency greater than 21% [8]. The band structure it can be made both n- and p- type conducting over wide range of resistivity, make the material a strong candidate for photovoltaic devices [9]. The CIS crystals have been grown by various methods, such as co-evaporation, RF sputtering, molecular beam epitaxia, spray pyrolysis, pulsed laser deposition, and electro-deposition. While the later and spring, (so-called low-cost, non vacuum deposition techniques) have been applied to preparation of CuInSe_2 (CISe) thin films.

The research performed in this paper is focused on the preparation of CuInSe_2 powder materials suitable for solar cell applications on a Fluorine doped tin oxide (FTO) substrates. Fluorine-doped tin dioxide films were prepared with a spray ultrasonic technique using SnCl_2 and NH_4F as sources of SnO_2 and fluorine dopant [6], of minimum resistance sheet (R_{sh}) of $21 \Omega/\text{cm}^2$ [10], with tin chlorides as the precursors [11], chemical vapor deposition (CVD) [12,13], sputtering [14].

Fluorine doped tin oxide (FTO) is used in place of ITO because it is relatively stable under atmospheric conditions, better transparent to visible light. Has an excellent thermal stability, a good conductivity, directly coated on glass surface, consist tetragonal structure unit cell (space

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group P42/mmm) [15,16], has a higher reflectance in infrared zone and is cheaper as compared to ITO glass.

One of the materials candidates for the replacement of the CdS, is the Fluorine doped ZnO (ZnO:F), abundant material with a higher band gap. Fluorine was expected to occupy the oxygen site in ZnO and hence promote the film conductivity and built a good pn junction. CuInSe₂ (CIS), and Fluorine doped ZnO (ZnO:F) thin film were electrodeposited from a solution of CuCl₂, InCl₃, and SeO₂ onto Fluorine doped tin oxide (FTO) substrates for CuInSe₂, and ZnCl₂, NH₄F were used as sources of ZnO and fluorine doping respectively to replace the toxic CdS layer for non-toxic heterojunction solar cells.

2. Experimental

Deposition solutions were prepared by dissolving 10mM of CuCl₂, 10mM of InCl₃, and 20 mM of SeO₂ in deionized water. Na-citrate was added as added complexing agent at 0.1M in order to shift the reduction potentials of Cu and In closer together and/or to improve the film quality, and pH of deposition solution adjusted to 2 by an appropriate amount of HCl to maintain electrical resistance on the deposition surface due to enhanced ion mobility in solution or inhibition of secondary phase formation [18]. In the second step, a homogeneous solution is prepared by dissolving zinc chloride (ZnCl₂) with a concentration of 0.05 mol/l in a volume of 200 ml (150 ml of distilled water + 50 ml of ethanol). Finally, a homogeneous solution is prepared by dissolving ZnCl₂ and ammonium fluoride (NH₄F) in the same solvent volume and keeping the same mass and concentration of ZnCl₂ used in the case of ZnO without doping.

Firstly the CuInSe₂ compound was synthesised. Electrodeposition of CISe thin films was carried out using a three electrode potentiostatic system with a saturated calomel electrode (Ag/AgCl) as reference electrode and a platinum sheet as counter electrode. Fluorine-doped tin dioxide (FTO)-coated glass substrates were used as working electrode of size 1×2.0 cm². using an potentiostat model Voltlab 40 at room temperature (25 °C) connected to a computer (Figure 1). At room temperature, CISe film deposition was proceeded for 15 min. The films were deposited at various growth potentials ranging from -0.5 to -0.9 V with respect to Ag/AgCl at -0.8V n-type buffer layer (n-fluorine doped ZnO) created by electrodeposition method too.

The potentiostat measures and controls the potential of the working electrode with respect to the reference electrode. The layers were annealed 350°C for 30 min to improve homogeneity and crystalline nature.

The deposition of selenium and copper will precede the deposition of indium because that the electrode potentials for selenium and copper are more positive than that of indium.

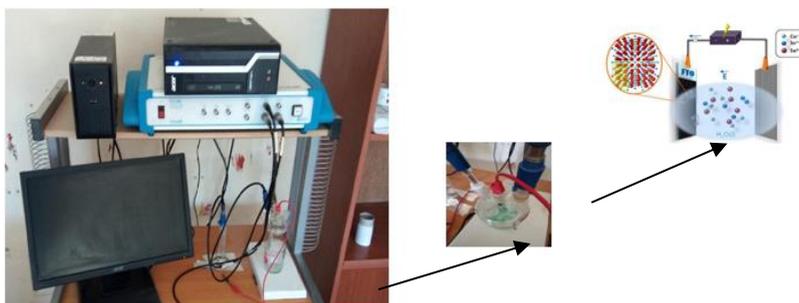


Fig. 1. The experimental process.

Structural properties of the CuInSe₂ thin films are carried out using a Rigaku Ultima-IV Diffractometer system with CuK α anode of wavelength 0.154 nm. Where as the scanning range of (2 θ) was between 10° and 90° at a speed of 0.02 °/s.

Film morphology was studied with a scanning electron microscope (SEM), and film composition was analyzed with an EDS attached to the SEM at the Laboratory of Physics of Thin Films and Applications, Biskra University, Algeria.

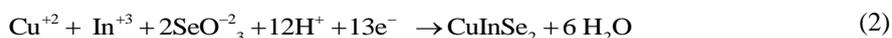
The spectra were registered using an UV/Vis spectrophotometer (Model T90) in the wavelength range 190-1100nm at room temperature at the Laboratory of chemicals Enset of Skikda.

And according to the relation (1) we can be calculated the thickness of CIS thin films:

$$d = \frac{IMt}{Fn\rho A} \quad (1)$$

where I is the current (mA), M is the molar mass (336.3 g/mol for CuInSe₂), t is the deposition time (sec), n is the number of electrons, F is Faraday constant, and ρ the density of the material (5.7 g/cm³ for CuInSe₂), and A the area of deposition.

The number of transferred electrons is equal to 13 for CuInSe₂; following the Deposit reactions listed below:



Thickness measured for the samples deposited at potential (-0.5 to -0.9 V) was (1150 to 2000 nm).

The CIS is a direct gap semiconductor, so the absorption coefficient (α) in the region of strong absorption obeying to the equation [19]:

$$(\alpha h \nu)^2 = A(h \nu - E_g) \quad (3)$$

where α is the absorption coefficient, h is the Planck constant, ν is the radiation frequency, E_g is the band gap energy and A is a constant which depends on the nature of the radiation.

The extrapolation of the straight line to $(\alpha h \nu)^2 = 0$ axis gives the value of the direct optical energy band gap E_g .

For high performance CISE solar cells, we process heat treatment to increase grain size and crystallize thin film CISE.

3. Results and discussion

3.1. Structural properties

The crystal structure of as-prepared CISE thin films was investigated by XRD patterns, as shown in Fig.2.

There are clear peaks in the DRX showing that the CIS is polycrystalline in nature. A characteristic peaks was identified, such as 112, 204, and 312, corresponding to the chalcopyrite tetragonal phase of the CuInSe₂. for the film deposited at -0.5 V. -0.6, -0.7 and -0.9 V, secondary binary phases Cu_xSe and In_xSe were observed, while stoichiometric film along with high intensity CIS peaks were observed for the layer deposited at -0.8 V. for film deposited at -0.8 V no secondary phases were observed. The (FTO) peaks are marked as a triangle.

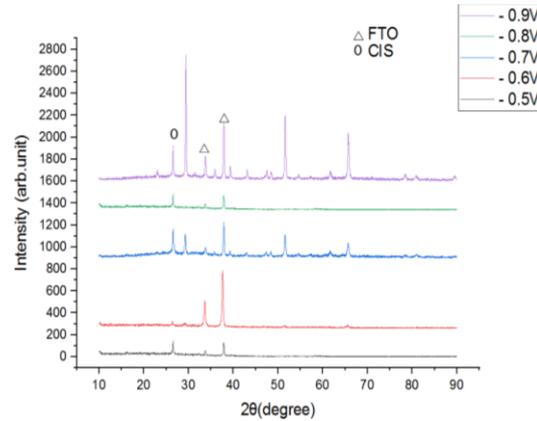


Fig. 2. XRD patterns for as grown CIS thin films deposited at -0.5 V (a), -0.6 V (b), -0.7 V (c), -0.8 V (d) and -0.9 V (e), After heat treatment (350°C for 30 min under air).

From Fig. 3 the characteristic peaks from tetragonal CuInSe_2 is present in a sample and no other phases of CIS compounds are seen, which indicates that the stoichiometry during electrodeposition and the annealing temperature range are within acceptable values to form CuInSe_2 . Also that the reduced oxygen vacancies in ZnO resulted in an improved p-n junction between FZO and CIS and better device performance.

The crystallographic plane (112) is the prominent diffraction plane, indicating that the single crystal growth has occurred along the (112) direction [21-22]. The lattice parameter was calculated to be 5.77 and 11.74 Å which is directly related to the anion position displacement in chalcopyrites was found to be near to 1 (The tetragonal deformation parameter $\eta = c/2a$) [23, 24] confirming CuInSe_2 phase.

The size of the crystallites D in the grains can be estimated by the Debye-Scherrer formula [20]:

$$D = 0.9 \lambda / B \cos \theta \quad (4)$$

where λ is the X-ray wavelength of 1.5418 Å, θ is the Bragg diffraction angle, and B is FWHM. D size was about 92.81 nm at 350°C and has high intensity of (112) peak.

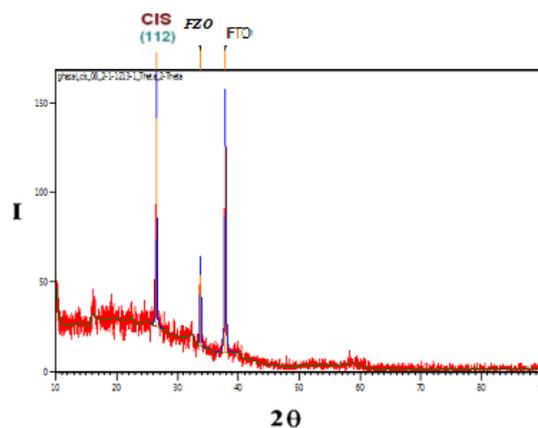


Fig. 3. XRD patterns for as grown CIS/FZO thin films deposited at -0.8V after heat treatment (350°C for 30 min under air).

3.2. Morphological properties

The SEM images of annealed CIS layers grown at -0.5 to -0.9 V are shown in Fig. 4. All layers were void free, compact and fairly uniform. The CuInSe_2 film is very compact, and a nanograin-like morphology was observed Fig. a and b. as seen from Fig. c, d and e, the films

shows particles of bigger size with a more remarkable cauliflower appearance. A part of these films were selenized in tubular furnace at 350°C for 30 min.

It is clear that of all selenized layers layers has changed, and this is what we clearly see in SEM images. The large globular clusters of size 2 micron are formed by agglomeration of small particles. at potential -0.8V CIS layer was nearly stoichiometric 25:25:50 for Cu:In:Se.

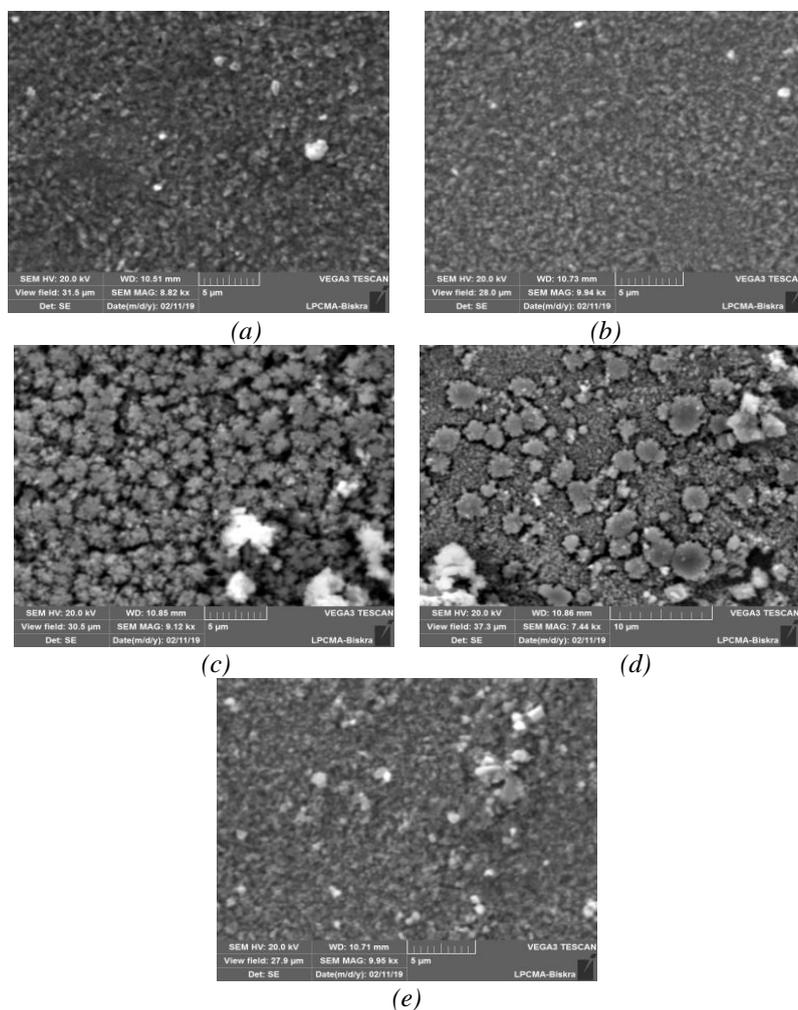


Fig.4. SEM images of CIS thin films annealed at -0.5 V (a), -0.6 V (b), -0.7 V(c) -0.8 V(d) and -0.9 V (e).

The SEM image of CIS layer grown at -0.8 V is shown in Fig.5. A layer is void free, compact, fairly and cauliflower shape.

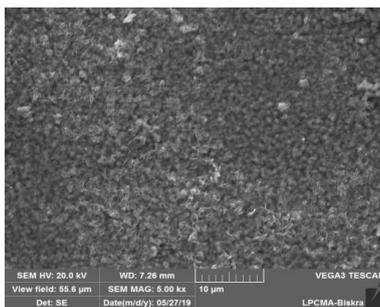


Fig. 5. SEM image of CIS/FZO thin film annealed at -0.8 V.

4. Optical properties

The absorption spectra of CuInSe₂ thin films deposited on FTO substrate are recorded in the range of 300 nm to 900nm on a UV-Vis spectrophotometer.

The absorption spectra and band gap is shown in the Fig.6. The nature of obtained data confirms that a CuInSe₂ thin film shows a direct allowed type of transition with a band gap 1.05 eV. Such a band gap is highly beneficial for the solar cell application.

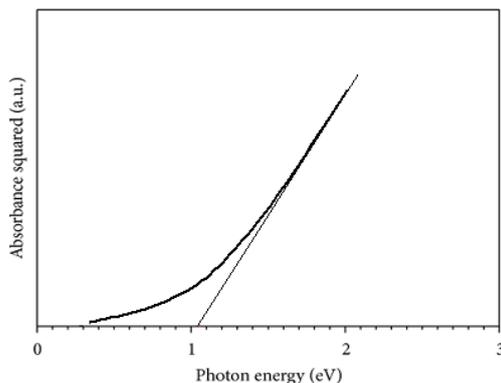


Fig. 6. Plot of $(\alpha h\nu)^2$ versus $(h\nu)$ of CIS deposited film at -0.8V annealed at 350°C for 30 min.

4. Conclusions

The ternary CuInSe₂ chalcopyrite thin film was deposited by electrochemical deposition (ED). The effect of deposition potential and substrate was studied. The good stoichiometry composition and high crystalline nature of the electrodeposited CuInSe₂ films were confirmed by EDS, XRD and UV-Vis, respectively.

-0.8 V is suitable potential for the deposition of CIS films onto FTO substrates. All CIS films deposited were polycrystalline with tetragonal chalcopyrite structure. Also the analysis of the absorbance spectrum recorded employing UV-Vis spectroscopy showed the thin film possesses direct optical bandgap.

The analysis of these results shows that the addition of zinc oxide doped with fluorine as a buffer layer is a prominent candidate to be an alternative buffer layer to so-called toxic cadmium sulphide (CdS) in CIS based solar cells. The near stoichiometric CuInSe₂ film (annealing at 350°C), the optical band gap was estimated to be 1.05 eV.

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