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Effect of Sb Doping on $CuAlSe_2$ Thin Films and Their Behavior on the Preparation of $CuAlSe_2$/Si Heterojunction Solar Cells

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Abstract: $CuAlSe_2$ (CAS) thin films polycrystalline structure deposited by thermal evaporation at RT with thickness (500±20) nm then doped with antimony (Sb) with ratios (X = 0.0, 0.01, 0.03 and 0.05) to study the (structural, optical and electrical) properties. The crystal structure of alloy and thin film carried out tests X-Ray Diffraction (XRD), it found (Tetragonal) and has a polycrystalline orientation prevalent (112). It was also from (EDX-Energy Dispersive of X-rays) to make sure the weight ratios of alloy match them with the prepared ratios. From AFM images can calculated roughness and average diameter. The optical properties measurements showed that the thin films (CAS) have high absorbance in the visible region wavelengths of (400-700 nm). The energy gap was the allowed direct transition, the energy gap decreased with doped. The hall effect results showed that all thin films have (p-type). By use thermal evaporation technology in vacuum, a solar cell where manufactured from heterojunction (p-$CuAlSe_2$/n-Si) which achieved by the deposition of the composite alloy thin films (CIS) with deferent ratios on a single crystal silicon substrate with direction (111) of the (n-type). The illumination (current-voltage) characteristics showed that the solar cell with thin films (t = 500 nm and X = 0.05) has highest efficiency (η = 5.89%).

Key words: $CuAlSe_2$/n-Si, efficiency, heterojuncion, solar cell, calculated, wavelength

INTRODUCTION

The photovoltaic investigation has moved beyond the usage of single crystalline materials like as group IV and III-V compounds to extra complex compounds of the group I-III-VI_2. The ternary ABC_2 chalcopyrites (A = Ag, Cu; B = Ga, In and Al; C = Se, S and Te) form a big group of semiconductor materials with various electrical and structural properties. These ternary chalcopyrites materials are attractive for photovoltaic application of thin film (Hussien and Khudayer, 2016). The I-VI_2 compound semiconductors such as $CuAlSe_2$ are considered for possible applicant in solar cells. This compounds is chalcopyrite (tetragonal) structure, the $CuAlSe_2$ is having large energy gap 2.67 eV at RTS, Chichibu *et al*. (1991) have been reported the resistivitys, carrier concentrations, optical absorption and photolumine scence's of undoped and Cd, Zn-doped $CuAlSe_2$. The thin films showed p-type conductivity even when doped with Cd or Zn (Chichibu *et al*., 1991). Thin films of $CuAlSe_2$ have been manufactured by of Cu and Al thin layers consecutively deposited by vacuum evaporation method. It is exposed that $CuAlSe_2$ films are found with some Cu_2-rise and Se phases current at the surface. The gap of the films is 2.7 eV as expected (Marsillac *et al*., 1997). $CuAlSe_2$ have been grown by epitaxial layers on the GaAs substrate by of molecular beam epitaxy to preparation of hetero structures and quantum structures. The double hetero structures, $CuAlSe_2/CuGaSe_2/CuAlSe_2$ with several well coating thicknesses (lz) have been ready. The PL measure displayed that the Cu(AlxGa1-x)Se_2 alloy is formed at the $CuAlSe_2/CuGaSe_2$ interface (Shirakata *et al*., 2000).

The energy range between 1.4 and 5.2 eV for chalcopyrite semiconductor $CuAlSe_2$ at room temperature, it determined the complex dielectric tensor components for $CuAlSe_2$ by spectroscopic ellipsometry (Alonso *et al*., 2000). The thin films $CuAlSe_2$ compound was prepare with low cost onto commercial microscope glass substrates by chemical bath deposition method at difference of deposition temperature. The deposition temperature above RT (300 K) effected on the optical properties of the films were investigated by Jenway Software 6405 UV-Vis spectrophotometer, depending on the deposition temperature the optical band gap energy ranges from 2.00-2.14 eV (Ezike and Okoli, 2012).

Thin films $CuIn_{1-x}Al_xSe_2$ (CIASe) were prepared by a simple sol-gel route shadowed by vacuum annealing.

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High oriented (002) aluminum doped (2%) ZnO, thin films with thickness 100 nm were co-sputtered based solar cells for $CuIn_1$-$xAlxSe_2$/AZnO. Ideality factor varied from 1.3186-2.095 and barrier height 0.63-0.51 eV in the dark and under solar illumination 1.38 AM 1.5, respectively (Murali and Krupanidhi, 2014).

Due expensive nature of silicon solar cells with indirect energy band gap, low-cost fabricated chalcogenide thin films are in focus. Copper Aluminium diselenide ($CuAlSe_2$) compound thin films are prepared by Chemical Bath Deposition (CBD) technique. The optical properties of deposited films were studied using UV-Vis spectrophotometer energy band gaps (2.3-3.0 eV) of the deposited films as pH values decrease (Ezike, 2017).

MATERIALS AND METHODS

This research include the preparation of the ternary composite alloy $CuAlSe_2$ (CAS) of elements Copper (Cu) Aluminum (Al) and Selenium (Se_2) percentages by weight (1:1:2), respectively by mixing these three elements and put them in a quartz tube under a pressure of (10^{-4} mbar), the tube placed diagonally in an electric oven at temperature (1700 K) for (7 h). By use thermal evaporation technology in vacuum, thin films (CAS) of the prepared alloy with thickness (500±20) nm at RT and then doped with Sb with ratios (X = 0.0, 0.01, 0.03 and 0.05) where deposited on glass substrates to study its structural, optical and electrical properties. Also, they deposited on a silicon substrates to use them in solar cell manufacturing, the deposition rate was (2±0.1 nm/sec).

In order to study the crystal structure of alloy and thin films using tests X-Ray Diffraction (XRD)-6000 Shimadzu-Japan with (λ = 1.5418 Å). Scherrer's formula used to calculate the average Crystallite size (C_S) of $CuAlSe_2$ thin film:

$$C_s = \frac{0.94\lambda}{B\cos\theta_B} \quad (1)$$

where, the full-width at half-maximum of the main peak is β and the reflection angle is θ (Cullity, 1978). It was also conducting tests (EDX-Energy Dispersive of X-rays) in order to make sure the weight ratios and the atomic components of the alloy and match them with the prepared ratios.

We used (AFM technology) to study the nature of the surface topography, determine both surface roughness and grain size.

The optical properties measurements for thin films (CAS) on glass substrates were found using UV/Visible 1800 spectrophotometer from 400-1100 nm. The energy gap E_g (eV) calculated from Eq. 2 (Lekse *et al*., 2007):

$$\propto h\upsilon = C\left(h\upsilon - E_g\right)^n \quad (2)$$

Where:

C = The constant reliant on on the properties of the band
n = The constant may take value of (2, 3, 1/2, 3/2) dependent on the type of the optical transition

A is absorbance and absorption coefficient α with thickness t were determined by Eq. 3 (Yamada *et al*., 2006):

$$\propto = 2.303\ A/t \quad (3)$$

The Hall effect results showed (n or p) type of CAS thin films have been managed by Van der Pauw (Ecopia-HMS-3000), it is determine majority carrier concentrations for CAS and mobility in thin films.

By use thermal evaporation technology in vacuum, a solar cell where manufactured from (p-$CuAlSe_2$/n-Si) which achieved by the deposition of the Composite Alloy thin films (CAS) on a single crystal silicon substrate with direction (111) of the (n-type).

The measurements of I-III-VI_2 for standardized illumination (100 mW/cm^2) and dark determined by using Eq. 4 (Cullity, 1978):

$$I = I_S\left(\exp\left(\frac{qV}{\beta K_B T}\right) - 1\right) - I_L \quad (4)$$

The photovoltaic efficiency η and Fill Factor FF is given by Mohanty (2012):

$$\eta = \frac{P_m}{P_{in}} \times 100\% = \frac{I_m V_m}{P_{in}} \times 100\% \quad (5)$$

$$F.F = \frac{J_m V_m}{J_{sc} V_{oc}} \quad (6)$$

RESULTS AND DISCUSSION

To examine the weight ratios and the atomic components of the alloy. It was use the EDX-Energy Dispersive of X-rays of the elements (Cu, Al, Se). The results are shown in Fig. 1 and Table 1.

Figure 2 shows the XRD pattern of (CAS) powder of alloy which clear that the $CuAlSe_2$ was polycrystalline (tetragonal phase) structure as it compared with the standard values in ICDD 00-044-1269 card. The spectrum is considered to exhibit sharp peaks at (101, 112, 103, 200, 220, 204, 312, 116, 400, 332 and 316) corresponding to 2θ values equal to 17.83, 27.86, 28.99, 31.9, 45.84, 46.3, 54.3, 55.32, 66.67, 73.76 and 74.5, respectively. The X-ray

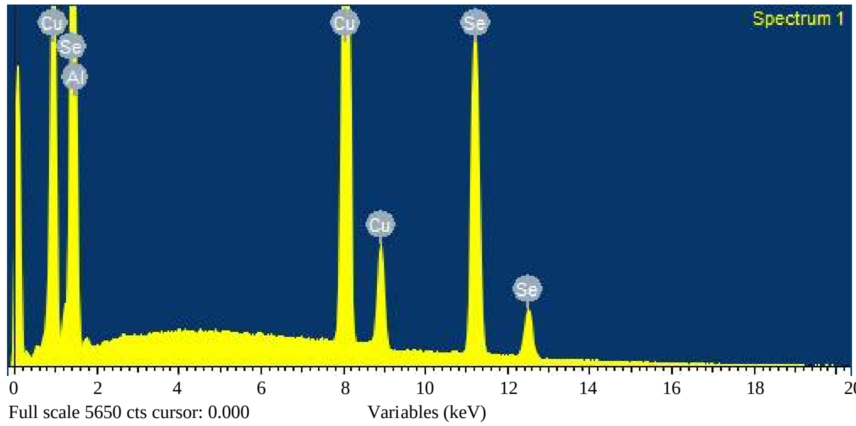

Fig. 1: EDS patterns for $CuAlSe_2$ alloy

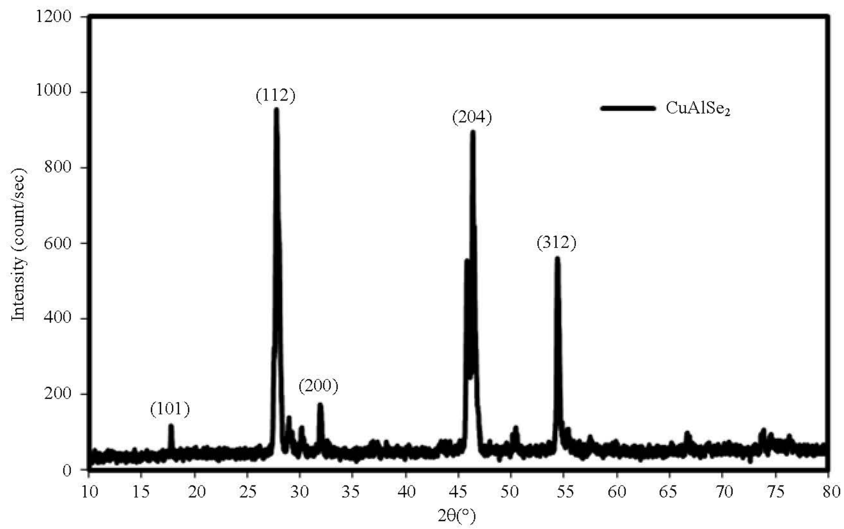

Fig. 2: X-ray diffraction pattern of $CuAlSe_2$ alloy

Table 1: The composition of $CuAlSe_2$ alloy determined by (EDS)

Variables	Calculated (wt.%)	Test (wt.%)
Cu	25.57	25.52
Al	10.85	10.83
Se	63.56	63.49

Table 2: Structural parameters of $CuAlSe_2$ alloy

2θ (ASTM) (°)	2θ (observed) (°)	d_{hkl} (ASTM) (Å)	d_{hkl} (observed) (Å)	hkl
17.759	17.83	4.990	4.9600	(101)
27.733	27.86	3.210	3.1990	(112)
29.09	28.99	3.060	3.070	(103)
31.90	31.90	2.800	2.799	(200)
45.73	45.84	1.980	1.970	(220)
46.23	46.30	1.960	1.950	(204)
54.33	54.30	1.687	1.685	(312)
55.22	55.32	1.660	1.670	(116)
66.70	66.67	1.400	1.400	(400)
73.67	73.76	1.280	1.200	(332)
74.40	74.50	1.270	1.270	(316)

diffraction parameters inter planar spacing (d) and Miller indices for $CuAlSe_2$ alloy are listed in Table 2, they prefer orientation at (112) planes.

Figure 3 shows the XRD patterns of $CuAlSe_2$ thin film at RT doped with Sb ratios (X = 0.0, 0.01, 0.03 and 0.05), thickness 500 nm it can see from Fig. 3 and Table 3 that the CAS thin films have the polycrystalline type tetragonal structure have two sharp peaks referred to directions (112) and (204) with prefer orientation is (112). From the FWHM values for the (112) peak we can estimate the crystallite size by using Scherrers equation and is observed the crystallite size decreased when ratios of Sb increase as displays in Table 3-5. Note from Table 3 that there is a significant shift in the position of the peaks of the prepared films after the doping process. This is due to

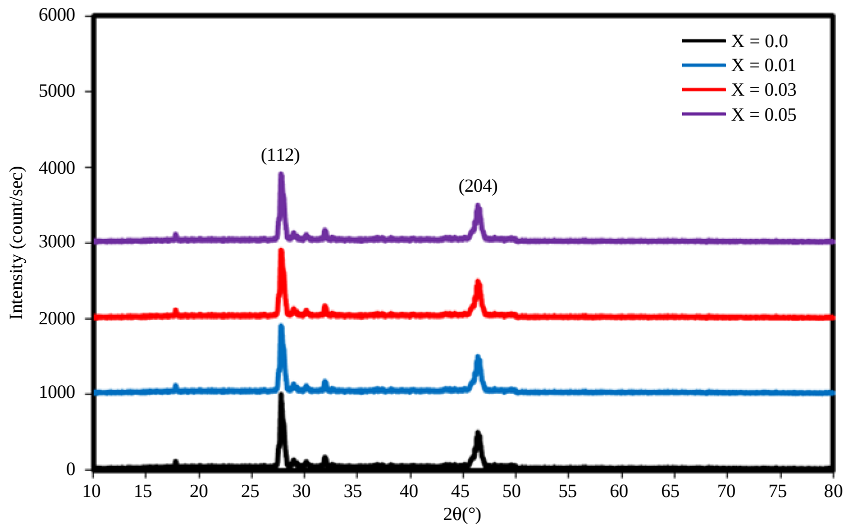

Fig. 3: XRD patterns for thin films $CuAlSe_2$ with (X = 0.0, 0.01, 0.03 and 0.05)

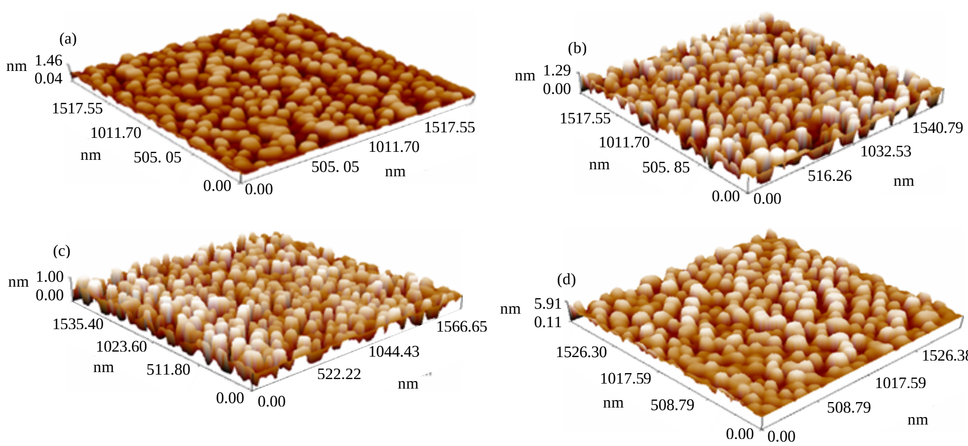

Fig. 4: 3D Atomic Force Microscopy (AFM) of thin films $CuAlSe_2$ with (X = 0.0, 0.01, 0.03 and 0.05)

Table 3: Experimental XRD data for thin films $CuAlSe_2$ with (X = 0.0, 0.01, 0.03 and 0.05)

Thin film sample	2θ (°)	d_{hkl} (Exp.) (Å)	β (°)	C_S (nm)
$CuAlSe_2$(Pure)	27.900	3.190	0.45680	18.720
$CuAlSe_2$:Sb(0.01)	27.860	3.198	0.45880	18.630
$CuAlSe_2$:Sb(0.03)	27.801	3.205	0.46680	18.310
$CuAlSe_2$:Sb(0.05)	27.780	3.208	0.49280	17.344

Table 4: The average grain size and roughness for thin films $CuAlSe_2$ with (X = 0.0, 0.01, 0.03 and 0.05)

Thin film sample	Grain size (nm)	Roughness average (nm)	rms (nm)
$CuAlSe_2$(Pure)	102.00	0.233	0.272
$CuAlSe_2$:Sb(0.01)	89.13	0.308	0.359
$CuAlSe_2$:Sb(0.03)	84.03	0.521	0.603
$CuAlSe_2$:Sb(0.05)	70.00	0.956	1.130

the simple stress arising from entering the doped atoms and spreading it in the host material and occupying sites in the $CuAlSe_2$ crystal lattice (Klug and Alexander, 1974). The intensities of the peaks decreases by increasing the

Table 5: Direct optical band gap and absorption coefficient of thin films $CuAlSe_2$ with (X = 0.0, 0.01, 0.03 and 0.05) (λ = 500 nm)

Thickness (500 nm)	E_g^{opt} (eV)	$\alpha\times10^4$ cm^{-1}
$CuAlSe_2$(Pure)	2.6	5.3
$CuAlSe_2$:Sb(0.01)	2.4	6
$CuAlSe_2$:Sb(0.03)	1.8	12.2
$CuAlSe_2$:Sb(0.05)	1.62	14

Sb ratios this gives the probability that the crystallization of the films material decreases by increasing the doping ratios and sometimes crystalline defects are centers for recrystallization (Warren, 1990).

Figure 4 shows the 3-Dimensional (3D) of $CuAlSe_2$ thin films with different doped ratios X = 0.0, 0.01, 0.03 and 0.05 of Sb. The value of roughness and the grain sizes are studied. It has been saw that a surface roughness were equal to (0.233, 0.308, 0.521 and 0.956) for different ratios X = 0.0, 0.01, 0.03 and 0.05 of Sb,

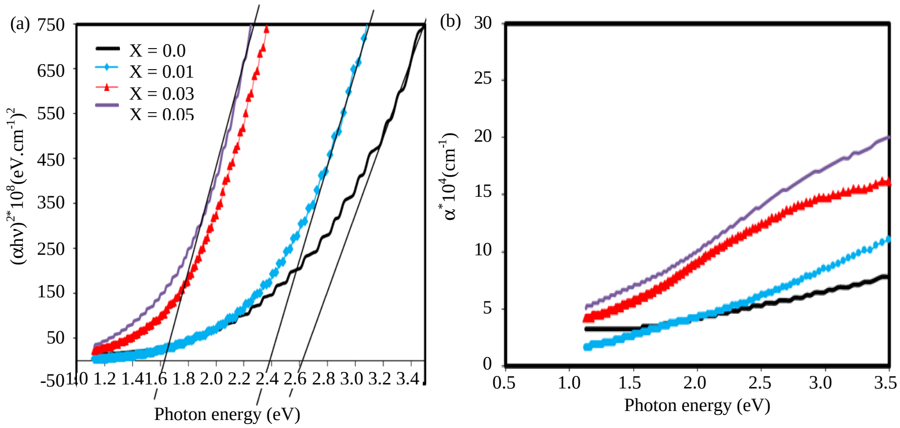

Fig. 5: a) $(\alpha h\nu)^2$ verse with photon energy and b) Absorption coefficient verse with photon energy of thin films $CuAlSe_2$ at (X = 0.0, 0.01, 0.03 and 0.05)

Table 6: Hall parameters for $CuAlSe_2$ thin films with (X=0.0, 0.01, 0.03 and 0.05)

Thickness (500 nm)	ρ (Ω.cm)	μ_H (cm^2/VS)	N_{A*10}^{18} (cm^{-3})	$R_{(H)}$ ($cm^3.C^{-1}$)
$CuAlSe_2$ (pure)	0.090	63.13131	1.1	5.681818
$CuAlSe_2$:Sb(0.01)	0.047	41.55585	3.2	1.953125
$CuAlSe_2$:Sb(0.03)	0.043	30.92528	4.7	1.329787
$CuAlSe_2$:Sb(0.05)	0.040	25.61475	6.1	1.024590

Table 7: The parameters of solar cell for $CuAlSe_2$/Si heterojunction with (X = 0.0, 0.01, 0.03 and 0.05)

Thickness (500 nm)	V_{oc} (V)	J_{sc} (mA/cm^2)	V_{max} (V)	J_{max} (mA/cm^2)	FF	η (%)
$CuAlSe_2$ (pure)	0.25	20	0.15	14	0.420000	2.10
$CuAlSe_2$:Sb(0.01)	0.32	24	0.20	17	0.442708	3.40
$CuAlSe_2$:Sb(0.03)	0.34	27	0.30	18	0.588235	5.40
$CuAlSe_2$:Sb(0.05)	0.35	29	0.31	19	0.580296	5.89

respectively. The grain size has been find (102, 89.13, 84.03 and 70) for X = 0.0, 0.01, 0.03 and 0.05 of Sb, respectively. So, the average diameter of thin film CAS with doping ratios X = 0.05 (Fig. 4d) is smaller than the CAS thin film (Fig. 4a-c).

To determine the effect of doping ratios (X = 0.0, 0.01, 0.03 and 0.05) of the optical measurements of thin films $CuAlSe_2$. The absorption coefficient is a important for calculating the material's ability to light absorption, considered a function of the falling photon energy (hv) and the Energy gap (E_g) (Neamen, 2003). Figure 5 shows that the absorption coefficient (α) values that calculated using Eq. 3, high value ofá above (10^4) cm^{-1}. The α values in general increases (from 5.3-14)×$10^4 cm^{-1}$ as doping ratios (X = 0.0, 0.01, 0.03 and 0.05) increases. That is mean an increase in absorbance of used CAS films. While the values of band gap decreases from 2.6-1.62) eV through increase doping ratios (X = 0.0, 0.01, 0.03 and 0.05). The decrease in the values of band gap (Eg^{opt}) may be attributed to the vagaries of the quality of $CuAlSe_2$ with increase doping in Sb that is agreement with (Marsillac *et al*., 1997; Ezike and Okoli, 2012; Hussien, 2017).

The Hall coefficient R_H was calculated to determine the type of majority carriers and mobility of the pure (CAS) and Sb doped thin films. The obtained results showed that all pure and doped films were positive type (p-type) where the values of the Hall coefficient were positive as in Table 6. This indicates that the carriers are hols while our results agree with the study (Al-Maiyaly *et al*., 2014).

We can show from Table 6 the increase in the ratio of Sb (x) in the (CAS) films leads to a decrease in the value of the Hole coefficient (R_H) due to an increase in the carrier concentration (N_A) will leads to an increase in the current passing through the films with the voltages and the decrease in the value of mobility (μH) due to the increased probability of collisions between the carriers. The highest percentage of the charge carriers was the ratio of the addition (x = 0.05).

Figure 6 display the (1-5) characteristics of manufactured $CuAlSe_2$/Si heterojunction with different doped ratios (X = 0.0, 0.01, 0.03 and 0.05) with illumination and dark conditions that calculated using Eq. 4. All results found from this investigation displayed in Table 7, we observe that the values of J_{sc} current

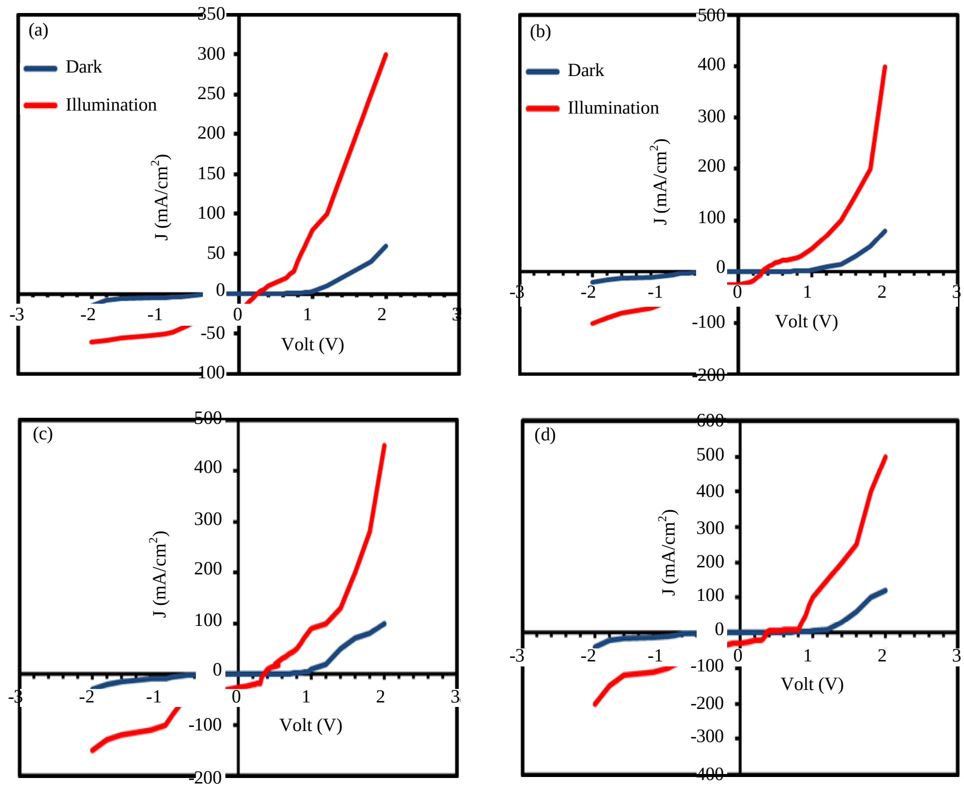

Fig. 6: I-5 Characteristic for $CuAlSe_2$/Si solar cell under illumination and dark with (X = 0.0, 0.01, 0.03 and 0.05): a) $CuAlSe_2$; b) X = 0.01; c) X = 0.03 and d) X = 0.05

density began to increase with the increase of the ratio (X). That is due to the result of increasing the energy gap value as mentioned in the study of optical properties. However, there is an increase the value of open circuit voltages (V_{OC}) that will increase in concentration of carriers. This has led to increased efficiency with an increase in the added ratios (X = 0.0, 0.01, 0.03 and 0.05) with the incident photo power (100 mw/cm^2) and this belong to as it have already increase the charge carriers roughness and the absorption coefficient.

CONCLUSION

The $CuAlSe_2$ alloy was successfully preparation and then deposited as thin films by thermal evaporation method with different of Sb ratios. XRD for alloy and thin films showed that polycrystalline and have the tetragonal structure and the (112) direction was prefer orientation. Optical properties show that films could be useful in photovoltaic solar cell applications. The influence of doping ratios is investigated. The band gap energy decreases as the X increased. Allowed direct optical energy band gap for all preparation thin films, high absorption in the visible region. The efficiency increases with Sb ratios, the maximum values of fill factor and efficiency were 0.580 and 5.89 when X = 0.05.

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