

## Influence of copper on zinc oxide films and solar cell performance

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Copper doped Zinc oxide and (n-ZnO / p-Si and n-ZnO: Cu / p-Si) thin films through thickness (400±20) nm were deposited by thermal evaporation technique onto two substrates. The influence of different Cu percentages (1%, 3% and 5%) on ZnO thin film besides hetero junction (ZnO / Si) characteristics were investigated, with X-ray diffractions examination supports ZnO films were poly crystal then hexagonal structural per crystallite size increase from (22.34 to 28.09) nm with increasing Cu ratio. The optical properties display exceptional optically absorptive for 5% Cu dopant with reduced for optically gaps since 3.1 toward 2.7 eV. Hall Effect measurements presented with all films prepared pure and doped have n-types conductive, with a maximum carriers concentrate of  $3.9 \times 10^{16}$  (cm<sup>-3</sup>) besides lower resistivity of 59.6 (Ω.cm) for films doped with 5% (Cu). The current- voltage (I-V) characteristics of heterojunction below illumination by incident power density (100 mW/cm<sup>2</sup>) showed that heterojunction (n-ZnO: 5%Cu / p-Si) has maximum efficiency ( $\eta = 3.074$  %).

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### 1. Introduction

Great attention in semiconductor metal oxide ZnO that has superior wide gaps of 3.34 eV, highest infrared reflectivity then good visible-spectrum transparency, high electron mobility with higher photo-generated electrons [1-3], similarly highest technological applicator, lowest costs, resources available, non-toxicity besides highest thermally/chemically stable, making it suitable for optoelectronic and photovoltaic devices [4]. Besides, applications including ZnO sufficient group with lights emitted devices, gases instruments, piezo electrical transduce then ultrasonic oscillator [5,6]. There employs were by reason of its original nonlinear optically property, exciton emissions on room temperatures plus quantum's effected [7]. Zinc oxide was n-types II-VI semiconductor compounds through larger exciton banded energy. Hall mobility at ZnO single crystals was that orders of (200 cm<sup>2</sup>v<sup>-1</sup>s<sup>-1</sup>) with room temperature [8]. Furthermore, informal for device dopant as a result of lowest epitaxy growths temperature, lately, numerous investigators have remunerated marvelous consideration for dopant a varied range of element (Fe, Ni, Ag, Cu, Al, Ga etc.) [9]. additional main contest confronted via researchers was the non-available for efficiently p-type dopant of ZnO, where that measured the energetic build block of slightly quantum well-based optoelectronics expedient [10,11]. With that dopant procedure, optically and catalytically property could be adjusted thru dopant [12], besides ZnO bandgaps produces intra gap electronics state private the semiconductors [13]. Around transitions metal had be utilized for improve that property for ZnO [14-17], copper was an inexpensive selection. Since that ionic size of Cu<sup>2+</sup> was closely toward Zn<sup>2+</sup>, Cu<sup>2+</sup> ions canister substitute Zn<sup>2+</sup> ion near modified the absorption spectrums [18]. The aim of this work was fabricated (n-ZnO/p-Si) hetero junction via utilize vacuums evaporate system besides studied the impact Cu dopant ratio for films plus heterojunction characteristics.

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## 2. Experimental

Zinc oxide pure, Cu doped ZnO with (1, 3, 5) % ratios and n-ZnO: Cu/ p-Si hetero junction films have been prepared for glasses then SI substrate thru thermally evaporate process used Edward coating unit model (E 306) in vacuum ( $3 \times 10^{-6}$ ) torr. First step of prepared these films were deposited pure metal Zinc on glass and Si substrates with thickness ( $400 \pm 50$ ) nm at room temperature by thermal evaporation, where Si substrates used single crystal (111) and p-type, by put Zn powder in molybdenum boat, the distance from the substrate to boat was about 18 cm. Then to get Zinc oxide (ZnO) thin films, thermal oxidation procedures with exist air flow at (673K) temperature for one hour were using, another step were doped these films with Cu of 1, 3 and 5% ratios.

The crystal structure properties for pure besides dopant ZnO per dissimilar ratio of Cu thin films was detected by X-ray diffraction XRD method using (SHIMADZU Japan XRD 600) X-ray deflect meter with  $\text{CuK}\alpha$  radiate where ( $\lambda = 1.5418 \text{ \AA}$ ), 40Kv, 20 mA currents and record  $2\theta$  values from  $20^\circ$  to  $80^\circ$ .

In order to calculated the inter planar spacing (d) of miller index (hkl) be using the Bragg's law [19]

$$2d\sin\theta = n\lambda \quad (1)$$

Scherer's Formula were utilized for calculated the crystalline size (C.S) for all films [20,21]

$$C.S = \frac{0.94\lambda}{\beta \cos\theta} \quad (2)$$

where  $\lambda$ : XRD wave length,  $\beta$ : FWHM of the peaks, and  $\theta$ : Bragg's angle.

The dislocations density ( $\delta$ ) was estimated by using equations [22]

$$\delta = \frac{1}{(C.S)^2} \quad (3)$$

Optical property was determined by UV/VIS spectrophotometer, recorded the absorbance A and transmittance T spectrum within the range of (400 – 1000) nm, Tauc's equation applied to calculated the energy gap [23,24]

$$(\alpha h\nu) = D (h\nu - E_g)^n \quad (4)$$

where  $h\nu$ : the incident photon energy, D: is constant, n: is a number which depending on the transition type and  $\alpha$ : the absorption coefficient which estimate from equation: [25, 26]

$$\alpha = \frac{2.303A}{t} \quad (6)$$

where t: film thickens.

The electrical properties of these films have been investigation by Hall measurement utilized Van der Pauw Ecopia-HMS -3000, Hall mobility ( $\mu_H$ ) and Carrier concentrations ( $n_H$ ) were calculated from Hall voltage and resistivity [27]. The opto-electrical properties of n-ZnO /p-Si and n-ZnO: Cu /p-Si hetrojunction were determined by studied I-V Current voltage characteristic applied Shockley equation [28]. Also the efficient solar cells is considered [29].

### 3. Results and discussions

#### 3.1. Structural property

The structural characterization of synthesized Nano crystalline thin films of pure ZnO besides doping by diverse ratio of Cu using thermal evaporation were recorded by X-ray diffraction in the range of  $2\theta$  between  $20^\circ$  to  $80^\circ$ . Figure 1 signifies XRD patterns for these films with diffraction sharp peaks appear at  $2\theta = 31.68^\circ, 34.2^\circ, 36.18^\circ, 47.6^\circ, 56.52^\circ, 62.88^\circ, 66.4^\circ$  and  $67.96^\circ$  corresponded to (100), (002), (101), (102), (110), (103), (200) and (112) which means all films prepared have polycrystalline structure. These films have a hexagonal structure with preferential direction at (002), and no distinguishing peaks of Copper element are observed where the diffraction peaks closely correspond to the standards XRD data (JCPDS card No. 36-1451); the results are in good contract with [30]. This may be due to Cu ions are completely occupied privileged the substitutional location for ZnO structures. Notice from figure (1) and Table (1) that there is a shift in the position of the peaks after doping besides peaks convert sharpest as a result of films crystallinities improved after doped. FWHM values for (002) peak were used to calculated crystallite size (C.S) and dislocations density ( $\delta$ ) which are offered in Table 1. Note from fig.2 and table (1), the crystallite size (C.S) value increase while decrease the dislocation density values with increasing doping ratio due to enhanced crystal structure of these films. These remarks are good agreed with ref [30,31].

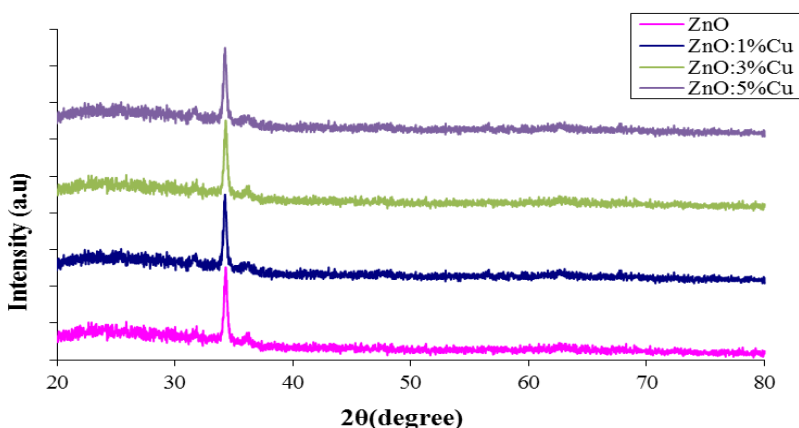


Fig. 1. XRD pattern of ZnO thin film pure and Cu doped as a function of Cu ratio.

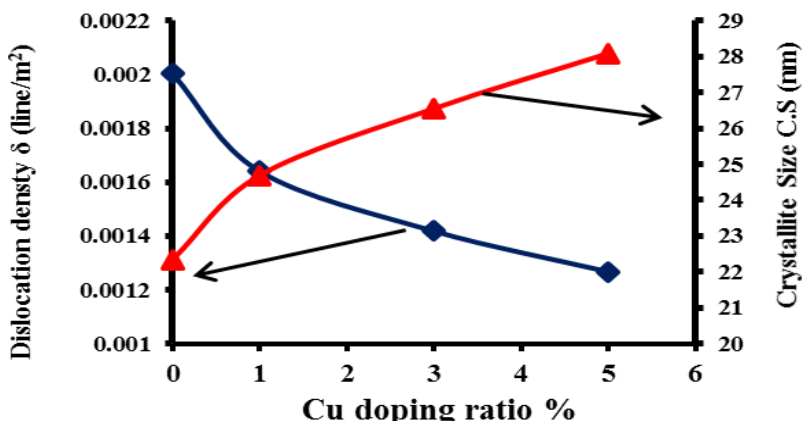


Fig. 2. (C.S) and ( $\delta$ ) for pure and Cu doping ZnO as a function of doping ratio.

Table 1. Structures parameter of ZnO thin film pure and Cu doped as a function of Cu ratio.

Sample	2 $\theta$ (Deg.)	FWHM(Deg.)	C.S (nm)	$\delta \times 10^{16}$ (lines/m <sup>2</sup> )
ZnO	34.339	0.3844	22.34159	2.00342
ZnO:1%Cu	34.3044	0.3477	24.6899	1.640443
ZnO:3%Cu	34.3151	0.3233	26.55563	1.418034
ZnO:5%Cu	34.2597	0.3057	28.09325	1.267057

### 3.2. Optical measurement

Fig. 3 shows optical absorbance and transmittance spectra in the wavelengths amongst 400 nm to 1200 nm of un doped ZnO and Cu dopant film through diverse percentages of Cu. It is clear from this figure that the absorbance values amplified after doping thru cumulative Cu ratio, this may be due to the impurities level doing as good absorption site in the UV-Visible region leads to decrease transmittance values after doping. The increased absorbance from (40% to 80%) while the transmittance value decreased observed for all samples with increase concentration of Cu (0, 1, 3 and 5) % correlation with increase crystallite size values of these films. Absorption coefficient of films prepared was displayed in Fig. 4, it is clear that all films had highest values ( $\alpha > 10^4 \text{ cm}^{-1}$ ) which means possible occur allowed direct transition and the value of absorption coefficients increase after doping for the same explanations we mention before. Also, this figure show decrease optical energy gap values from (3.1 to 2.7) eV with increase Cu concentration (0, 1, 3 and 5) % as in Table 2, due to increase in tensile stress which reason a red shifts on band gaps values of films doped, this result is comparable per studied [30,31]. The optically energy gaps were calculated from Tauc equation as in figure (5) which display the relation between  $(\alpha h\nu)^2$  verses  $h\nu$  for pure ZnO and Cu doped. These results for doped films with Cu produce them good material for solar-cells application.

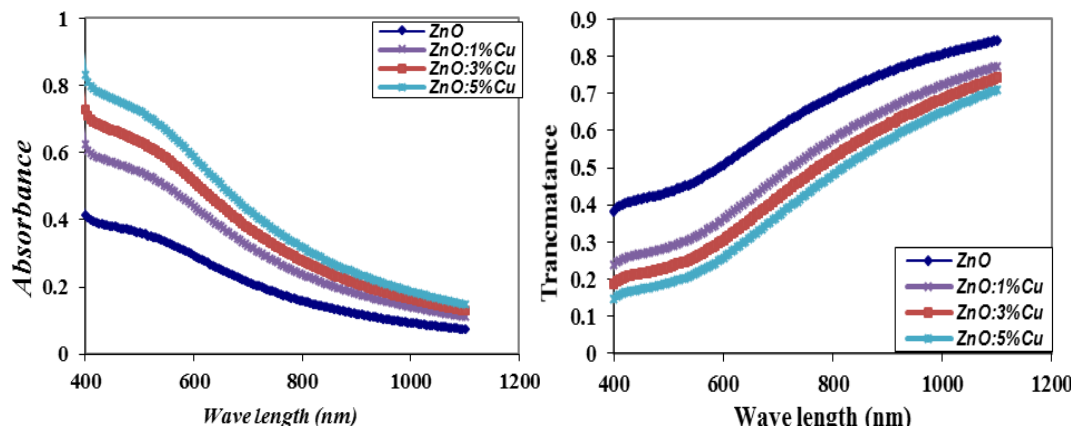


Fig. 3. Optical absorbance and transmittance versus wave length of un doped thin film ZnO and Cu doped with different ratios of Cu.

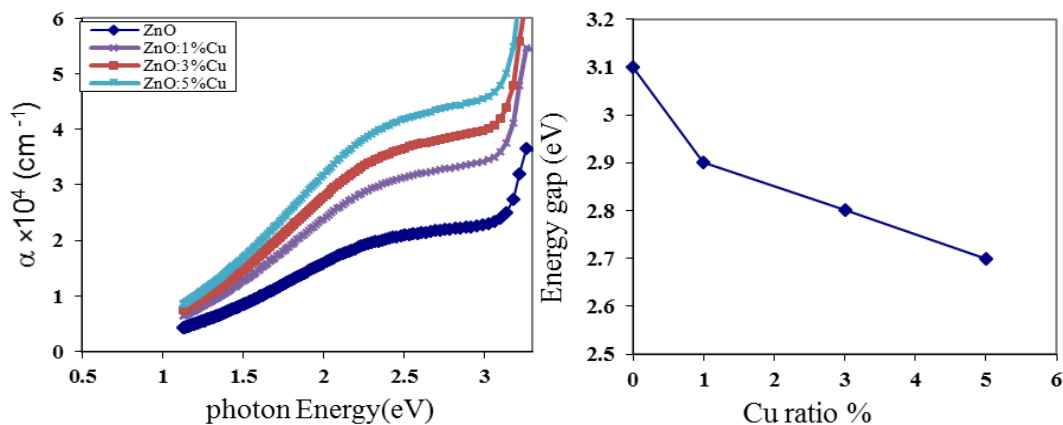


Fig. 4. Absorption coefficients and optical energy gap for pure ZnO thin film and Cu doped as a function of Cu ratio.

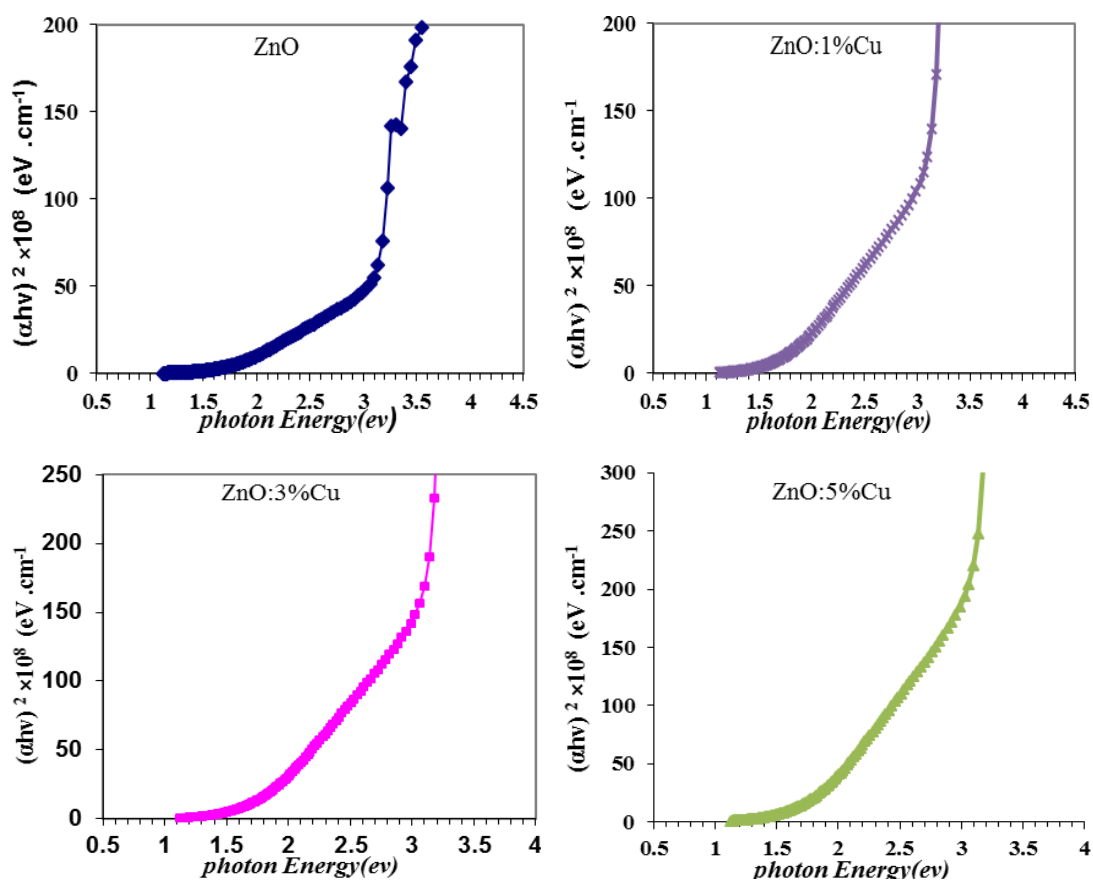


Fig. 5. Variation  $(\alpha h\nu)^2$  versus  $(h\nu)$  of ZnO thin film pure and Cu doped as a function of Cu ratio.

Table 2. Directly optically gaps then absorptive coefficient of pure ZnO plus dopant Cu

Sample	$E_{g}^{opt}$ (eV)	$\alpha \times 10^4 \text{ cm}^{-1}$
ZnO	3.1	2.083
ZnO:1%Cu	2.9	3.124
ZnO:3%Cu	2.8	3.645
ZnO:5%Cu	2.7	4.166

### 3.3. Electrical properties

Hall Effect was used for regulate that types of major carriers, Hall coefficient  $R_H$ , carriers concentrate ( $n_H$ ), mobility ( $\mu_H$ ) and resistivity ( $\rho$ ), and carrier of the pure (ZnO) then Cu doping thin film. The consequences revealed completely film pure besides dopant have negative signs of Hall coefficients which confirmed that all films prepared were (n-type) conductivity also all electrical parameters for these films was influent thru doping percentages for Cu, totally factor value was presents at Table (3).

This table and Fig ( 6 ) showed the enhancement in the electrical characteristic of ZnO films after doping with Cu by increased carrier concentration values as a result decrease Hall coefficient ( $R_H$ ) values while decreased resistivity and mobility values, due to an increase in the voltages and current passing through ZnO films, maybe increased possibility of collisions among carriers lead to reduction mobility ( $\mu_H$ ) values, this behavior might be credited to replacement of Cu with Zn, as well as on doping film, the crystallite size amplified thru Cu ratio as we mention before, which reduced scattering carries at grain boundary and increase conductivity, this result is in agreement with references [8, 30,31 ]

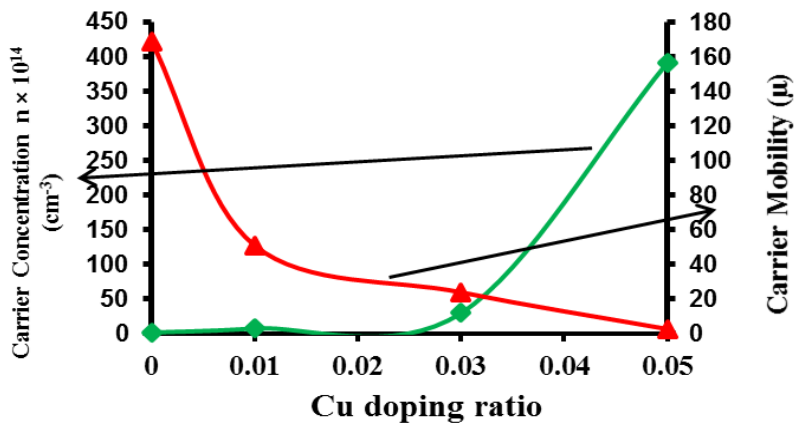


Fig. 6. The carrier concentration, and mobility for pure ZnO thin film and Cu doped as a function of Cu ratio.

Table 3. Hall effect parameter for ZnO thin films with Cu dopant ratios.

Sample	Carriers concentrate	Mobility	Resistivity	$R_H$
ZnO	$1.63 \times 10^{14}$	168.72	227	$-3.83 \times 10^4$
ZnO:1%Cu	$7.6 \times 10^{14}$	50.931	161	$-8.2 \times 10^3$
ZnO:3%Cu	$2.97 \times 10^{15}$	23.89	87.9	$-2.1 \times 10^3$
ZnO:5%Cu	$3.9 \times 10^{16}$	2.68	59.6	$-1.6 \times 10^2$

### 3.4. I-V characteristic

Figure ( 7 ) illustrations currents voltage curve for n-ZnO/p-Si and n- ZnO:Cu/p-Si heterojunction thru dissimilar dopant proportion for Cu below darks and illumination conditions. This figure displays the dark forward currents was created by means of the movements of major carrier while the reverse current are very weak. It is clear from this figures and table (4) the values ( $V_{oc}$ ,  $J_{sc}$ ,  $V_m$ ,  $I_m$ , F.F) and the efficiency of solar cell growth as the doping percentage for Cu increase since(0, 1,3 , 5)%, the high value of efficiency for the sample doped with ratio 5% which equal to 3.074%. When Cu concentration increases in films, the surface area increases because increase the quantity of Cu absorbed molecules which cause increase faster electron transport by sunlight with decreasing the electron-hole pair recombination which leads to improve the solar cell efficiency.

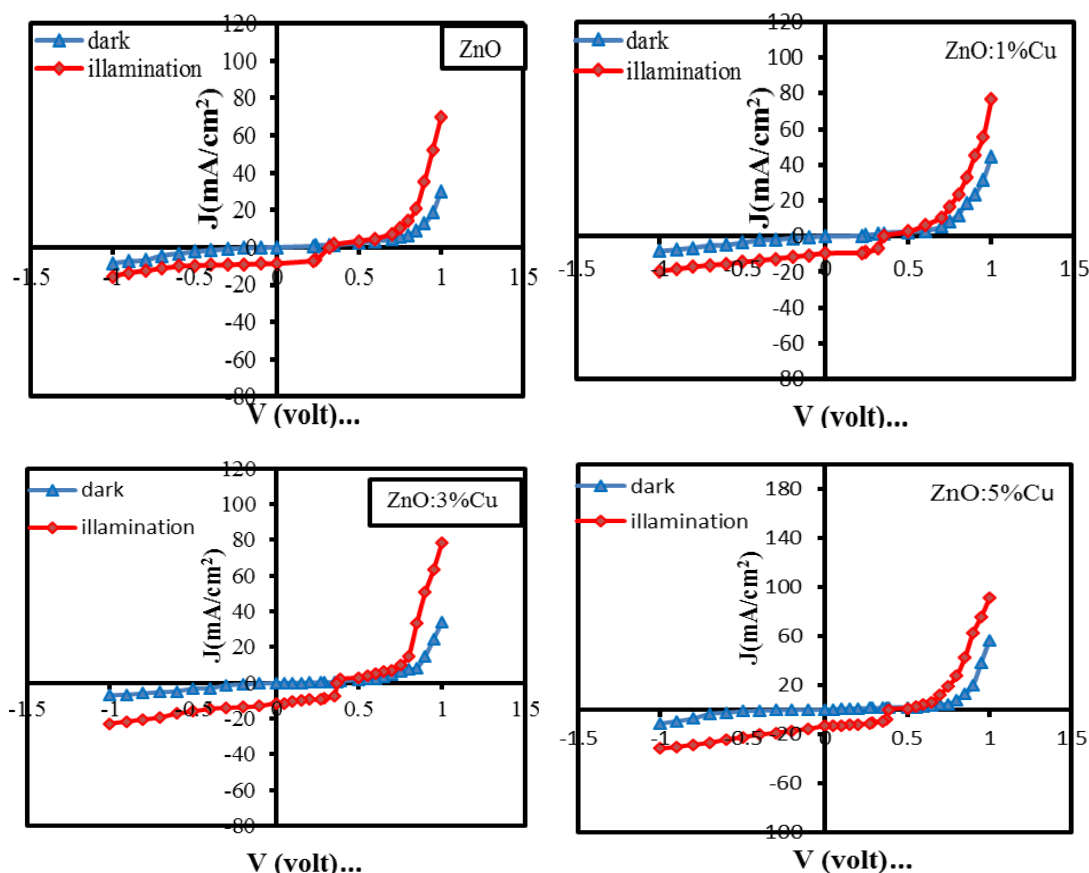


Fig. 7. J-V characteristic for pure ZnO and n-ZnO:Cu /p-Si heterojunction thin films.

Table 4. Solar cell factors for pure ZnO and n-ZnO:Cu /p-Si heterojunction thin films.

Sample	Voc (mV)	Jsc (mA/cm <sup>2</sup> )	Vmax (mV)	Jmax (mA/cm <sup>2</sup> )	F.F	$\eta$ %
ZnO	0.32	8.72	0.22	7.23	0.570026	1.5906
ZnO:1%Cu	0.35	9.54	0.24	8.89	0.638994	2.1336
ZnO:3%Cu	0.37	11.35	0.27	9.2	0.591499	2.484
ZnO:5%Cu	0.39	13.25	0.29	10.6	0.594872	3.074

#### 4. Conclusion

Un doped ZnO and Cu-doped films were synthesized by thermally evaporate method, the influence of Cu concentration on structurally, optically, besides electrically properties of ZnO thin film and on heterojunction (n- ZnO:Cu/p-Si) was examined. XRD analysis demonstration poly crystal natures with hexagonal structure of the prepared thin film, where the crystallite size of these films upsurges from (22.34 to 28.09) nm with the doping ratio. The thin films doped demonstration narrow at optical band gap per increase in the absorption. Hall Effect results show an increase carrier concentration and conductivity with Cu doping ratio as well as all films exhibit n-type conductivity. I-V characteristic under 100 mW/cm<sup>2</sup> illumination for heterojunction (n-ZnO:Cu/p-Si) were effect by Cu ratios, film doped with 5% Cu has maxim values efficiency (3.074%) and fill factor 0.594 because this sample has better crystallite size, good absorptive coefficient, lower resistivity thru higher carrier concentration value.



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