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Effect of Potential on Electrodeposited Cu_2O Thin Film onto Copper Substrate at Low Duration

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Abstract- This work is devoted to the electrodeposition of Cu_2O on copper-substrate (Cu) by linear-sweep-voltammetry (LSV) method at short time of deposition (10 min) and a bath temperature of 50 °C. The influence of potential value ({E_1} = {-100; -200 mV}; {E_2 = -200; -300 mV}, {E_3 = -300; -400 mV}, {E_4= -400; -500 mV}, {E_5 = -500; -600 mV} and {E_6 = -600; -700 mV}) on structural, optical, and morphological properties of the electrodeposited Cu_2O thin-films on Cu-substrate were investigated. The synthesized Cu_2O thin films were analyzed by several techniques such as Raman-spectroscopy, X-ray-diffraction, UV-vis measurements and FEG-Scanning-Electron-Microscopy (FE-SEM-EDS). The X-ray-Diffraction has revealed that the electrodeposited thin-films correspond well to the cubic structure ($Pn\bar{3}m$) and has revealed the good crystallinity for those deposited in the potential range -400 to 500 mV. Raman measurement confirm the cubic crystal structure ($Pn\bar{3}m$) of the synthesized samples, all the thin-films have a high light absorption capacity in the visible spectrum and the estimated value of the optical gap are close to 1.9 eV.

Keywords- Cu_2O; Thin films; Electrodeposition; Linear voltammetry; Optical properties

1. INTRODUCTION

The considerable technological development in recent years in fields such as electronics, optoelectronics, environmental and photovoltaics, has contributed to the emergence of new avenues of research aimed at developing low-cost materials with good properties [1-3]. It is in this context that semiconductor oxides such as copper oxide Cu_2O, have emerged as a promising semiconductor material, due to its electrical and optical properties, in particular its p-type conductivity and narrow direct band gap (2.0-2.6 eV) allowing the absorption of visible light, can be used in a cost-effective way in many fields [4]. Some of these notable applications include the utilization of Cu_2O material in photoelectrochemical cell [5], photocatalytic [6], photo-detector [7], thermo-electric [8], photodiode devices [9], and electro-chromic material [10]. Also, Cu_2O was presented as an anodic material with interesting properties for Na-ion battery systems [11]. The exploration of the copper (I) oxide as a light absorber material was really the purpose of this work.

Low-cost manufacturing of absorber thin-film has emerged as the primary concern of the optoelectronics industry; the copper (I) oxide thin film can be produced by various chemical and physical technics like, chemical vapor deposition technique [12], spray [13], SILAR [14], chemical bath deposition (CBD) [15], spin coating [16], thermal evaporation [17], vacuum diffusion [18], and electrodeposition [19].

The electrodeposition technique is a simple and inexpensive method and an effective technic for the deposition of ternary, binary and quaternary materials such as Cu_2SnS_3, Cu_2MSnS_4, and Cu_2O [20,21]. The electro-deposition technique permits the control of the structural, electrical, and optical properties by adjusting a number of factors such as bath composition, thickness of the film, time of electrodeposition, concentration, pH, temperature of bath and potential of electrodeposition.

In spite of the multitude of studies concerning the electrodeposition of Cu_2O on different substrates, only one was carried out on copper and all the studies made on Cu_2O report a synthesis for a duration higher than 40 min.

The aim of the present work is to adapt the electrochemical process on copper substrate, by determining the conditions for the electrodeposition of Cu_2O on Cu-substrate, and especially, the study of the effect of the potential on structural, morphological and optical properties of the synthesized Cu_2O thin-films, and that by the use of several technic like X-ray diffraction (X.R.D), energy dispersive spectroscopy (E.D.S), raman spectroscopy and U.V-Visible-N.I.R spectrophotometry.

2. MATERIALS AND METHODS

The copper (I) oxide (Cu_2O) thin–films have been electrodeposited on Cu-substrates by the linear sweep voltammetry (LSV) technic. Prior to Cu_2O thin–films electrodeposition, an

equimolar solution of citric-acid (0.05 M) and Cu^{2+} have been prepared by dissolving the $CuSO_4$ (Sigma -Aldrich, 99%) and $C_6H_8O_7$ (Sigma-Aldrich, 99.8%) in 25 mL of bidistilled water, the pH of the solution has been set to value of 10.7, using sodium hydroxide, and the temperature was fixed at T=50 °C in order to obtain the p-type Cu_2O layer on the Cu metal substrate. The citric acid was used as a complexing agent, to avoid increasing the precipitation of Cu in the basic media.

The Cu-substrates were watched for fifteen minutes successively in nitric acid, ethanol, acetone, bidistilled water and finally dried in air prior to be used for electrodeposition. The copper (I) oxide (Cu_2O) thin–films have been deposited by linear-sweep-voltammetry (LSV) technique by using the three mounting electrodes wired to the galvanostat-potentiostat PGZ100. The potential was ranged from -0.1V to -0.7V/SCE and the scan rate was set at 0.3 mV/s.

Lastly, the synthesized films were removed from the solution, rinsed with distilled water, and air-dried at room temperature, and the resulting samples have been characterized by an X-ray diffractometer (XPERT-3) with Cu-Kα1source. $\lambda = 1.5406$ Å. The determination of the optical properties was obtained by the use of JASCO-V-670 spectrophotometer. For the morphological image and elemental composition of the deposited thin films, they were obtained by scanning electron microscopy (SEM) and energy–dispersive X-ray spectrometry (EDS). The Raman spectroscopy measurement was conducted using a Thermo-scientific DXR2 system in the range of 100 to 700 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. Structural characterization

Figure 1 shows the X-Ray diffraction spectra, of all synthesized thin films under various potential ranges (E_1 = -100; -200 mV, E_2 = -200; -300 mV, E_3 = -300; -400 mV, E_4= -400; -500 mV, E_5 = -500; -600 mV and E_6 = -600; -700 mV). The peak located at 2θ = 36.43° correspond to the (hkl) = (111) plane of copper (I) oxide (Cu_2O) in cubic crystal structure (($Pn\bar{3}m$), that is in accordance with previous other reported results [22] and with the standard Data card (01-078-2076). The (111) peaks get more marked for the produced Cu_2O samples at E_3 = -300; -400 mV and E4= -400; -500 mV. In addition, and all the electrodeposited Cu_2O thin–films reveal a preferential orientation along the (1.1.1) reticular plan, that is due to the impact of Cu-substrate [22]. The XRD show that the E_1 = -100; -200 mV and E_6 = -600; -700 mV did not lead to the synthesis of the copper (I) oxide (Cu_2O) thin-film, therefore in the following subsection, we will only introduce the Cu_2O samples that were successfully synthesized at E_3 = -300; -400 mV, E_4= -400; -500 mV, and E_5 = -500; -600 mV.

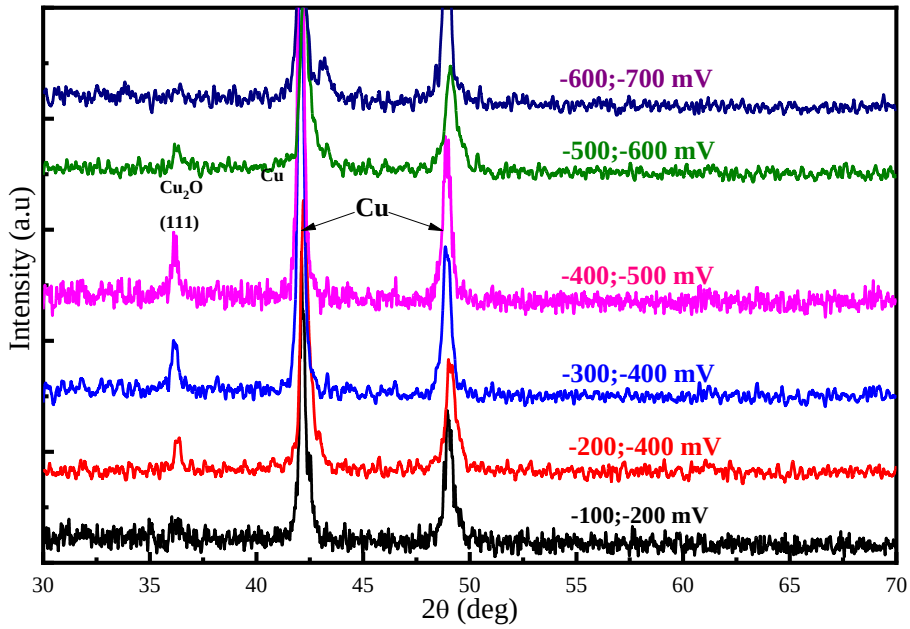

Figure 1. X.R.D patterns of Cu_2O thin–films electrodeposited at various potential ranges (-100;-200 mV), (-200;-300 mV), (-300;-400 mV), (-400;-500 mV), (-500;-600 V) and (-600;-700 mV)

The lattice-parameter have been determined from the equation (6) and founded value is a = 4.2693 Å, that are in accordance with the following standard pdf data (N.o. 01-079-2076) (a=c=b=_4.2612 Å) [22].

$$\frac{1}{d^2}=\frac{h^2}{a^2}+\frac{h^2}{b^2}+\frac{h^2}{c^2} \tag{1}$$

The grain size of the thin–film was determined from the unique (111) intense peak, using Deby-Scherer's Equation (2) [23,24]:

$$D=\frac{k\times\lambda}{\beta\times\cos(\theta)} \tag{2}$$

where λ is the Cu-Kα1wavelength of 1.5.4.06 Å; θ is the Bragg's angle, k is a constant equal to 0.9.4 and β is the angular line width at half maximum intensity (F--WH--M) of the diffraction peaks (in radians). To have more information on the measure of defects in the thin-films, the dislocation density (δ) was calculated from the equation (3) [23,24].

$$\delta=\frac{1}{D^2} \tag{3}$$

The strain (ε) was determined using the formula (4) [23,24].

$$\varepsilon=\frac{\beta\times\cos(\theta)}{4} \tag{4}$$

The changes in the structural parameters are presented in Table 1 and demonstrate that the crystallite size increase when the potential increase. In the opposite, the microstrain and dislocation density decreases with the increase of potential.

Table 1. Structural parameters obtained from (111) plane for the synthesized Cu_2O thin films

Potential of deposition (mV)	Miller indices	Observation diffraction angle (°)	FWHM (β) (°)	Crystallite size (D) (nm)	Dislocation density (δ) $\left(x10^{-3}nm^{-2}\right)$	Microstrain (ε) $\left(x10^{-3}\right)$
-200;-300	1 1 1	36.26	0.631	2.72	135	132
-300;-400		36.20	0.614	2.79	128	129
-400;-500		36.14	0.625	2.74	133	131

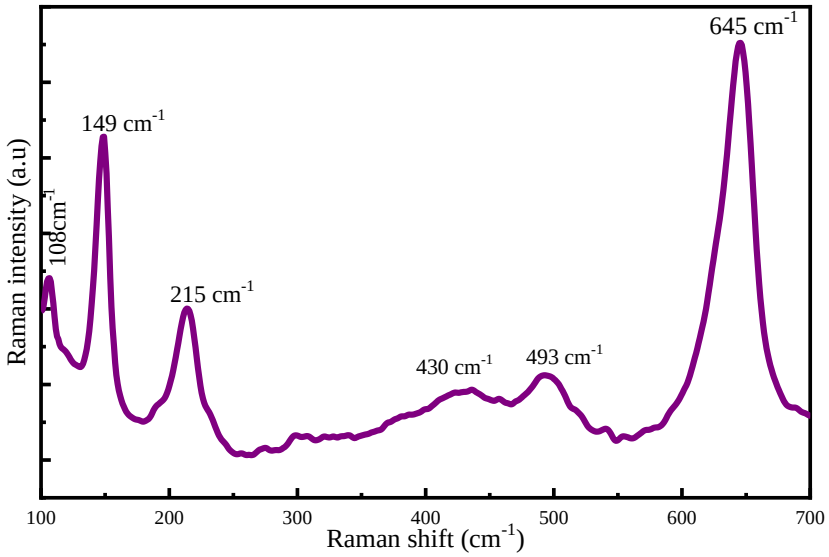

Figure 2. Raman spectra of electrodeposited Cu_2O at pH=10.7 and applied potentials (-400mV; -500mV)

3.2. Raman spectroscopy analysis

The Raman analysis was used with a laser excitation wavelength of 633 nm. The copper (I) oxide Cu_2O have a cubic crystal structure with space group of $Pn\bar{3}m$ and 6 atoms per unit cell of Cu_2O, therefore there are 18 vibration mode [22]:

$$\Gamma = Eu \oplus A2u \oplus 3T1u \oplus T2g \oplus T2u \quad (5)$$

where A, E, and T symmetry are one-, two-, and three-fold degenerated, respectively. According to the literature two active modes E_u and T_{1u} were observed and the two others mode A_{2u} and T_{2g} are absence. Figure 2 displays the raman spectra of copper (I) oxide Cu_2O films within 100 – 700 cm^{-1}. The peaks located at about 109 cm^{-1} (E_u), 149 cm^{-1} (T_{1u}), 215 cm^{-1} ($2E_u$),

298 cm^{-1}, 430 cm^{-1} ($2E_u$), 493 cm^{-1} ($2E_u$), and 645 cm^{-1} (T_{1u}) are characteristic of the Cu_2O (cubic) materials, that is in good agreement with other reported work [25].

3.3. Morphological properties

Figure 3 (a-c) show the FE-SEM image of Cu_2O layers deposited at pH = 10,7 and different applied potential ({-200 mV; -300mV}, {-300mV;- 400mV} and {-400mV;-500mV}). The synthesized Cu_2O thin films display a uniform surface coverage with good crystalline quality, which confirms the previous analysis and shows numerous well-distributed pyramid-like nanostructures that are characteristic of Cu_2O (Figure 3). The sample prepared at E_2={-200mV; -300mV} shows that the nano-grains were none uniformly distributed on the smooth surface, and we observe the presence of some void. When the potential increase to E_3={-300mV; -400mV} the image shows the apparition of the pyramid with variable sise and inhomogeneous nanostructure. Finally, for E_4={-400mV; -500mV}, the nanostructure becomes apparent with uniform distribution of pyramid as is shown in Figure 3(c).

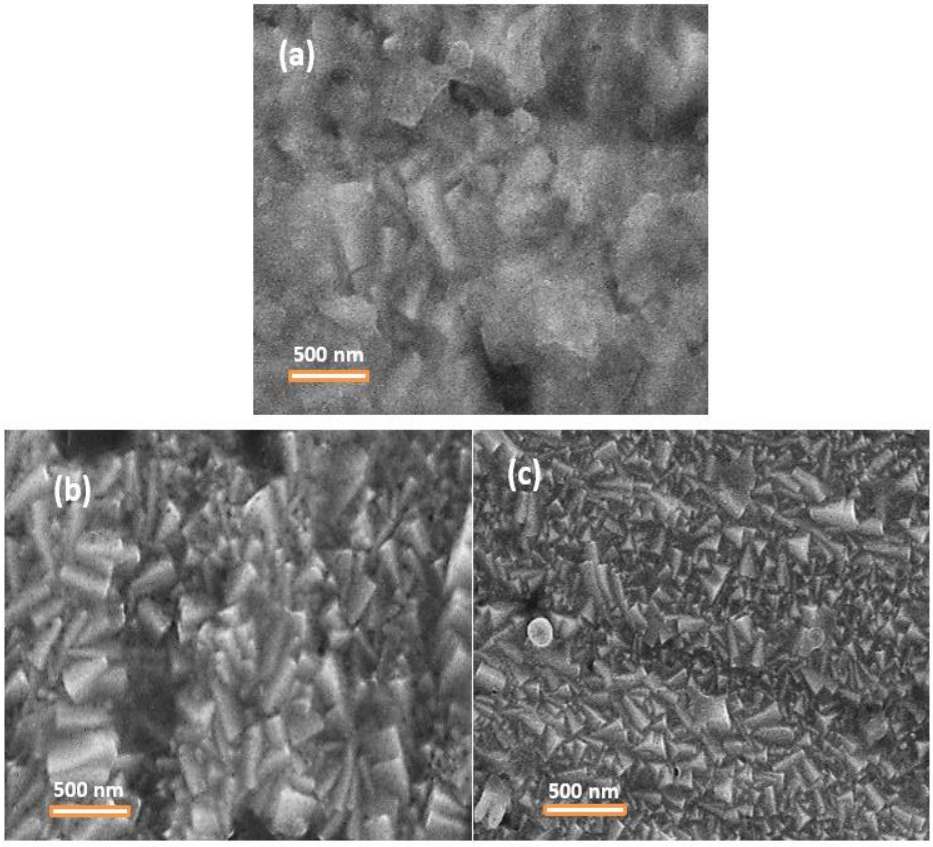

Figure 3. SEM image of Cu_2O thin films electrodeposited at various Potential rang (a) E_2={-200mV; -300mV} (b) E_3={-300mV; -400mV}and (c) E_2={-400mV; -500mV}

Furthermore, the EDS analyses (Figure 4 a-c) affirm the presence of copper and oxygen atoms that constitute our thin–film. However, the quotient Cu/O for the Cu_2O thin film deposited at E_2, E_3 and E4 are equal to 2.4 (70.65 at. % Cu and 31.12 at. %O), 1.5 (60.2 at. %Cu and 40.19 at. %O) and 1.92 (65.61 at. %Cu and 34.39 at. %O) respectively. The deposited thin film at E4 has the value closest to the ideal value of 2 for pure Cu_2O, which is in agreement with the previous XRD and SEM results.

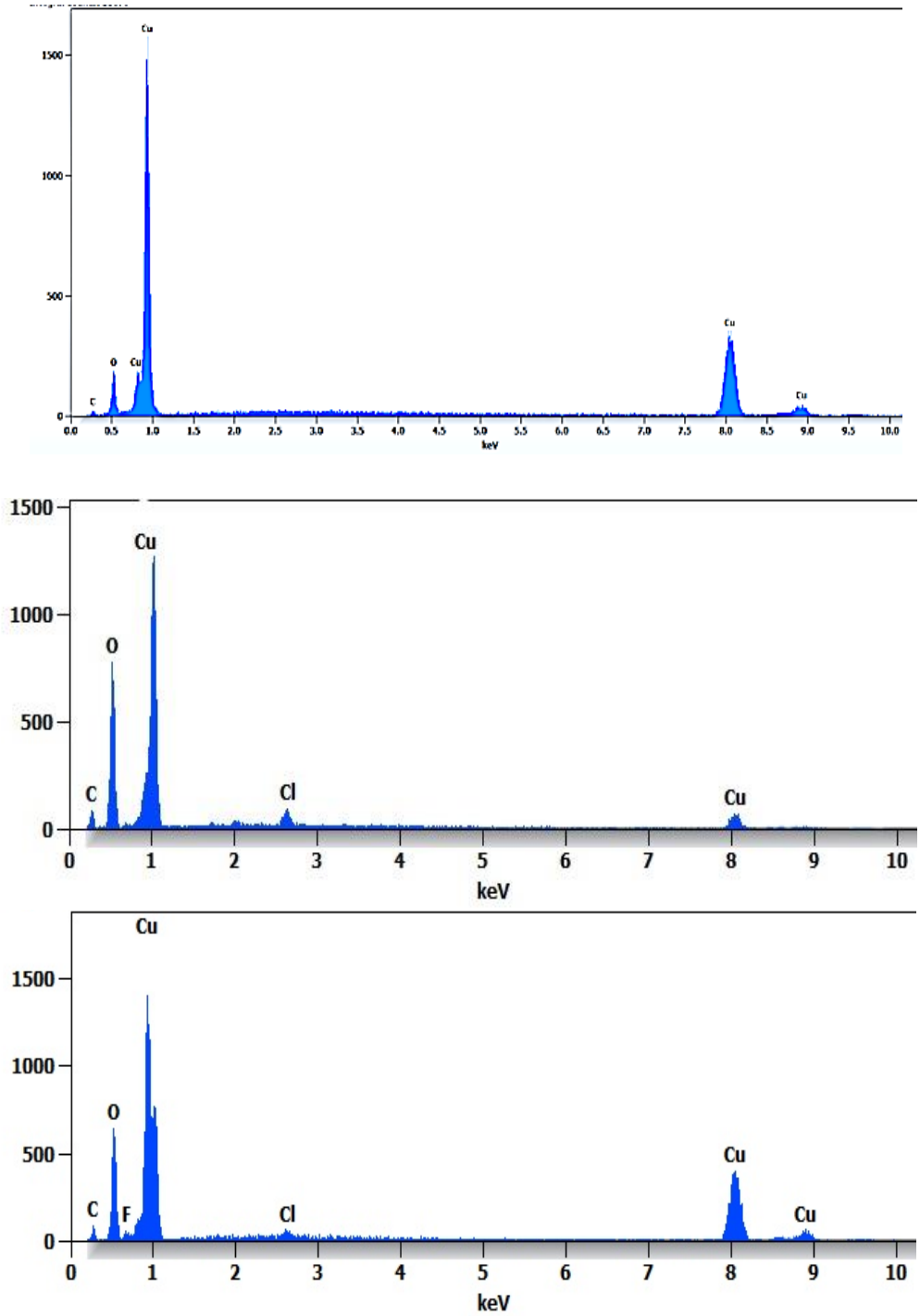

Figure 4. EDS spectrum of Cu_2O thin films electrodeposited at different Potential (a) E_2={-200mV; -300mV} (b) E_3={-300mV; -400mV}and (c) E_4={-400mV; -500mV}.

3.4. Optical Properties

The optical properties of the deposited copper (I) oxide (Cu_2O) films onto Cu-substrates have been calculated from transmittance measurement in the wavelength ranging from 400 to 650nm and are showing in Figure 5. All the synthesized thin-films display a good absorption in the solar spectrum region of 400-500 nm., with the appearance of sharp optical absorption transitions at 457 nm. This absorption is due to the transition between the conduction band and the valence band in the Cu_2O materials [26,27]. Figure 5 shows that the sample deposited at E_4={-400mV; -500mV} has the greatest light absorption in the wavelength range below 500 nm.

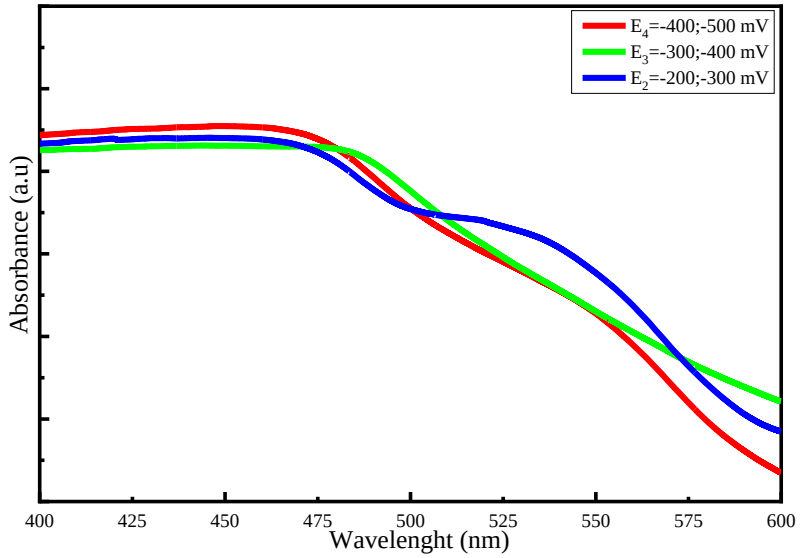

Figure 5. Absorbance-spectra of Cu_2O thin-films electrodeposited on Cu-substrates at different potential

The bandgap values were calculated from the T.auc's formula (Eq.6) [28], and were determined by extrapolating the linear part of the curve $(\alpha.h\nu)^2$ vs energy $h.\nu$ (Figure 6).

$$(\alpha \times h \times \nu) = A(h\nu - E_g) \quad (6)$$

Where A is a constant characteristic of the semiconductor, $h\nu$ is the photon energy and α the absorption coefficient.

The values of the band-gap E_g of Cu_2O thin films electrodeposited at E_2={-200mV; -300mV}, E_3={-300mV; -400mV} and E_4={-400mV; -500mV} are found to be 1.84 eV, 1.84 and 1.91 eV respectively, that are similar to the other report and then are well suited for the use in thin film based solar-cell [29]. The utilization of a Cu-substrate has permitted the decreasing of optical gap value (1.8 eV) in comparison to other report (Figure 6). The variation of deposition potential has not affected the optical gaps values (E_g) of the synthesized thin films.

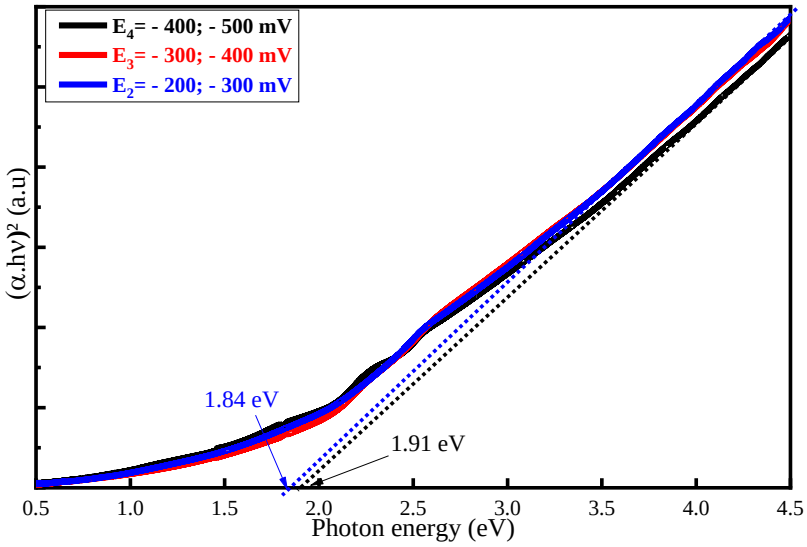

Figure 6. The $(\alpha.hv)^2$ versus hv plot for Cu_2O thin-films at different Potential (a E_2={-200mV; -300mV} (b) E_3={-300mV; -400mV}and (c) E_2={-400mV; -500mV}

4. Conclusions

The Cu_2O layers were successfully electrodeposited by the linear-sweep-voltammetry (LSV) technique at short duration on the Cu-substrate by the variation of the electrodepsition potential range. From the results, XRD, EDS, Raman and morphological characterizations were showed the successful synthesis of Cu_2O (cubic), that have (111) planes as preferential orientation. Micrograph image reveal the presence of small pyramid nano-structure characteristic of cubic Cu_2O, dense, homogeneous, and adherent layers. The band gap value is near 1.9 eV value and are slightly affected by the potential variation. The synthesis of Cu_2O at low duration makes the electrodepostion by the linear sweep voltammetry technique an economical and low-cost method.

Conflict of Interest

All Authors declare that there is no any conflict of interest in this study.

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