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Electrochemical, microstructural, compositional and optical characterization of copper oxide and copper sulfide thin films

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Abstract
In this work, we have focused the effect of substrate on electrochemically grown copper oxide and copper sulfide thin films. The prepared films have been subjected to X-ray diffraction, scanning electron microscopy, Energy dispersive X-ray analysis, UV–Visible spectroscopic techniques for the determination crystalline nature, morphology, composition and optical properties. X-ray diffraction results indicated the deposited films exhibited cubic structure with most reflection along (110), (220) planes for copper oxide and copper sulfide. Scanning electron microscopy along with energy dispersive analysis by X-rays showed that films with uniform morphology and nearly stoichiometry have been obtained for film obtained on SnO_2 substrate. Optical absorption and transmittance measurements showed that the deposited films exhibited band gap value of 2.28 and 2.45 eV for copper oxide and copper sulfide.

1 Introduction

For the past few years, there has been growing interest in metal oxides and metallic alloys for its wide range of applications in opto electronic devices and solar cells [1–10]. Among the former ones, cuprous oxide (Cu_2O) is a p-type semiconductor attracted many researchers due to the reason that it has direct band gap semiconductor with an energy gap value in the range between 2.0 and 2.35 eV [7]. Copper sulfide with stoichiometric phases Cu_2S and CuS attracted many researchers due to its applications in solar absorber coatings, photo thermal conversion and solar energy conversion devices. Cuprous sulphide (Cu_2S) is a p-type semiconductor with a ideal band gap value in the range between 1.2 and 2.5 eV which make them interesting as absorber material in solar cells due to its low cost with non toxic nature [9, 10]. Selman et al. have prepared Cu_2O thin films on glass and Si substrates by frequency magnetic reactive sputtering method and investigated its structural, morphological and optical

properties, respectively [2]. Dolai et al. [3] have prepared Cu_2O thin films by d.c reactive sputtering technique and investigated its properties using X-ray diffraction, scanning electron microscopy, X-ray photoelectron spectroscopy and Raman spectroscopic techniques, respectively. Cu_2O thin films prepared by microwave-activated reactive sputtering technique and its properties were analyzed using X-ray diffraction, X-ray photoelectron spectroscopy, UV–Visible and Raman spectroscopic techniques and reported by Alajlani et al. [4]. Liu et al. have prepared Cu_2O thin films by pulsed laser deposition method and determined its properties by X-ray diffraction, Transmittance and Hall effect measurement techniques, respectively [5]. Cu_2O thin films prepared using thermal oxidation of copper layer and its absorption coefficient, band gap and photoluminescence properties were determined by Karapetyan et al. [6]. Badillo-Ávila were determined structural, morphological, and optical properties of Cu_2O thin films annealed at different temperatures in the range between 300 and 550 °C. They have reported that the prepared films possess band gap value in the range between 1.20 and 2.35 eV [7]. Ozaslan et al. prepared Cu_2O thin films using SILAR method and investigated its properties by XRD, XANES and UV–Visible spectroscopic techniques, respectively [8].Cu_2S thin films prepared on glass substrates by chemical bath deposition technique and its UV–Visible and current voltage characteristics are reported by Patil et al. [9]. Sabah have reported the effect of annealing on structural,

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morphological and electrical properties of Cu_2S thin films deposited on different substrates [10]. When compared to the techniques mentioned electrochemical deposition has been evidenced as a powerful ability to control the crystallization of Cu_2O, Cu_2S and it presents a simple, economical, cost effective, less time consuming as well as the stoichiometry of the deposited films should be easily controlled by adjusting the deposition parameters as well as composition of the electrolytic bath etc., [11–13].

In the present investigation, Cu_2O and Cu_2S thin films are prepared on stainless steel (SS), aluminium (Al) and tin oxide (SnO_2) substrates using an electrodeposition technique. Electrochemical behaviour of the films has been analyzed using cyclic voltammetry. Structural, morphological properties of the prepared films are characterized using X-ray diffraction and scanning electron microscopy. Energy dispersive X-ray analysis has been carried out to determine composition of the deposited films. Optical absorption and transmittance measurements are determined using an UV–Visible spectroscopic analysis to find out the parameters such as band gap, refractive index, extinction coefficient of the deposited films. The effect of substrate on structural, morphological, compositional and optical properties of the deposited films are investigated.

2 Experimental details

The chemicals used in the present work were of AR grade reagents. Thin films of Cu_2O and Cu_2S were prepared by electrochemical reduction process of 0.02 M $CuSO_4$, 0.1 M tartaric acid and 0.1 M $CuSO_4$, 0.005 M $Na_2S_2O_3$ for Cu_2O and Cu_2S with three electrode cell configuration consists of SS, Al, SnO_2 substrates, platinum electrode and saturated calomel electrode (SCE) as working, counter and reference electrode, respectively. Initially, the pH value of the electrolytic bath was found to be 4.5 ± 0.1. The pH value of the electrolytic bath was adjusted to 9.0 ± 0.1 and 2.5 ± 0.1 by the addition of flexible amount of KOH and H_2SO_4 for the deposition of Cu_2O and Cu_2S. The substrates were cleaned ultrasonically in a bath of isopropanol, acetone followed by distilled water for 15 min. The SCE was kept into the solution by luggin capillary arrangement whose tip was closed as possible to the working electrode. The deposition potential was found to be in the range between 0 and -400 mV versus SCE, 0 and -550 mV versus SCE for Cu_2O and Cu_2S. The deposition time was found to be in the range between 0 and 60 min. The temperature of the electrolytic bath was found to be in the range between 50 and 80 °C for all depositions.

Growth mechanism of the deposited films was analyzed by an in-situ characterization cyclic voltammerty employing Potentiostat/Galvanostat (SP 50 Bio Logic, France) with SS, Al, and SnO_2 substrates. Thickness of the deposited films

was estimated by Stylus profilometry (Mitutoyo SJ 301, Japan). Structural properties was determined from X-ray diffraction data which is obtained from X-ray diffractometer (XPERT PRO PANalytical, Netherland) with CuKα radiation ($\lambda = 0.15418$ nm). Film composition with surface morphology was analyzed using an Energy dispersive X-ray analysis set up attached with scanning electron microscope (JEOL JSM 840). An optical absorbance and transmittance was analyzed using UV–Visible-NIR (Schimadzu, Japan) spectrometer to find out the associated optical properties of the deposited films.
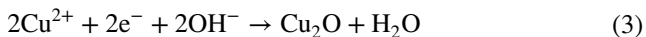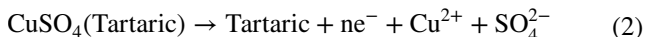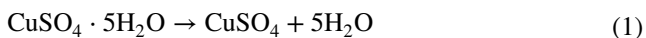
3 Results and discussion

3.1 Cyclic voltammetry

Growth of thin films using electrochemical deposition is based on the formation of solid phase from an electrolytic bath involves nucleation and growth processes. The process of heterogeneous reaction takes place thus leads to produce films with certain thickness value due to the combination of particles on the surface of the substrate. Cyclic voltammetric curves recorded for Cu_2O thin films prepared on SS and SnO_2 substrates which is obtained from an alkaline bath consists of 0.02 M $CuSO_4$ with 0.1 M tartaric acid is shown in Fig. 1. It is noted that the appearance of oxidation peak at $+300$ mV versus SCE indicated the reduction of metallic Cu^{2+} ion to metal Cu. The pH value was increased to 9.5 ± 0.1 by the addition of an adjustable amount of KOH to the electrolytic bath. The observation of reduction peak shifted towards negative region and the appearance of cathodic reduction peak at -350 mV versus SCE, results
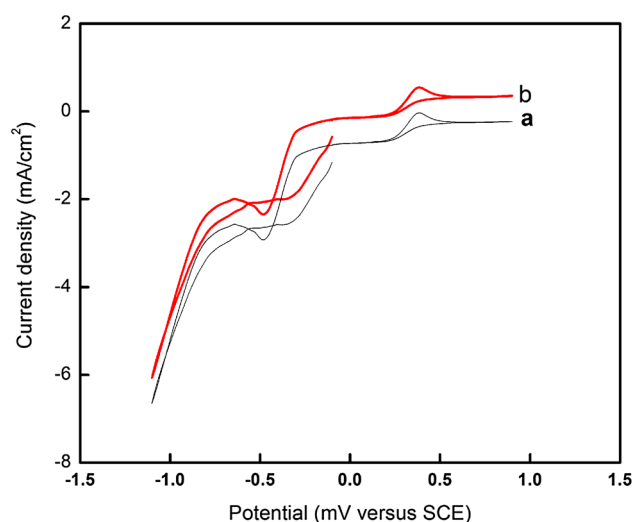
Fig. 1 Cyclic volammetric curve of Cu_2O film obtained on (a) SS and (b) SnO_2 substrate from an alkaline bath of $CuSO_4$ with tartaric acid

the formation of Cu_2O on the substrate according to Eq's from (1) to (3) mentioned below.

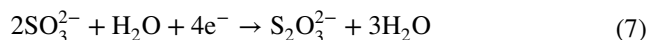$$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 + 5H_2O \tag{1}$$

$$CuSO_4(Tartaric) \rightarrow Tartaric + ne^- + Cu^{2+} + SO_4^{2-} \tag{2}$$

$$2Cu^{2+} + 2e^- + 2OH^- \rightarrow Cu_2O + H_2O \tag{3}$$

Initially, $CuSO_4 \cdot 5H_2O$ decomposed into $CuSO_4$ according to Eq. (1). Thereafter, decomposed $CuSO_4$ reacts with tartaric acid in the electrolytic bath leads to produce the complex of $CuSO_4$ (Tartaric). The concentration of OH^- ion in the electrolytic bath adjusted the pH value to 9.5 ± 0.1, show the way of formation of Cu_2O due to the redox reaction of Cu^{2+} with OH. The appearance of anodic peak at $+330$ mV versus SCE may be due to the oxidation of Cu_2O from $Cu(OH)_2$ and CuO. As a result, the pH value of the electrolytic bath determines the formation of metal oxides by the technique of electrodeposition. It is observed from Fig. 2, that the appearance of cathodic reduction peak at -350 mV versus SCE indicated the reaction of Cu metal with O thus leads to produce CuO films on the substrate of SS and SnO_2. It is evident from Figure that the formation of Cu takes place in the potential range between $+300$ and -550 mV versus SCE.

The mechanism of formation of Cu_2S thin films on Al and SnO_2 substrate is described by the following Eq's (4)–(9). The formation of Cu_2S is more complex process, since they involved several thermodynamic problems such as poor adhesion of film to the substrate due to the process of hydrogen evolution whereas electrolytic bath with more acidic nature produces peel off film from the substrate. In this process, the deposition of less noble constituent of the alloy
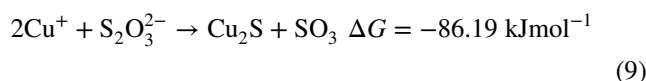
takes place first, in which its reduction potential is quite closer to the standard reduction potential of $S_2O_3^{2-}$ according to Eq. (7). The formation of Cu_2S thin films takes place according to Eq's from (5) to (10).

$$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-} \tag{4}$$
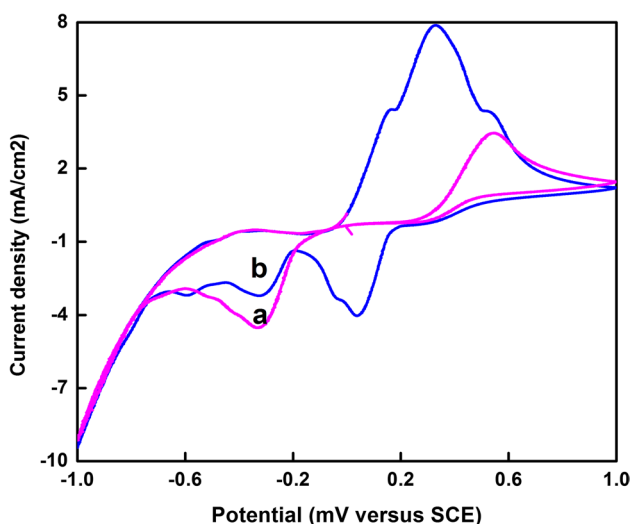
$$Cu^{2+} + 2e^- \rightarrow Cu \tag{5}$$

$$E_{Cu} = E_{Cu}^0 + \left[\frac{RT}{2F}\right] \ln \left[\frac{a_{Cu}^{2+}}{a_{Cu}}\right] \tag{6}$$

$$2SO_3^{2-} + H_2O + 4e^- \rightarrow S_2O_3^{2-} + 3H_2O \tag{7}$$

$$E_S^0 = E_{Cu}^0 + \left[\frac{RT}{4F}\right] \ln \left[\frac{a_{S_2O_3}^{2-}}{a_s}\right] + \left[\frac{RT}{2F}\right] \ln \left(a_H^+\right)^4 \tag{8}$$

$$2Cu^+ + S_2O_3^{2-} \rightarrow Cu_2S + SO_3 \quad \Delta G = -86.19 \text{ kJmol}^{-1} \tag{9}$$

where E_{Cu} and E_S are the potential of the working electrode in a given solution, E_{Cu}^0, E_S^0 are the standard electrode potential for Cu and S with respect to SCE, R is an universal gas constant, T is absolute temperature of the electrolytic bath, N is the number of electrons required for the reduction and F is Faraday constant. The deposition of Cu occurs at potentials more positive than their standard reduction potential by gaining free energy in the compound formation. The formation of Cu_2S thin film takes place with negative free energy $\Delta G = -86.19$ kJmol^{-1}. Cyclic voltammogram of Cu_2S thin films on Al and SnO_2 substrates those are obtained from an electrolytic bath consisting of 0.05 M $CuSO_4$ and 0.05 M $Na_2S_2O_3$. The voltammetric curves recorded with in the potential range between $+1000$ and -1000 mV versus SCE with a scan rate of 20 mV/s is shown in Fig. 2. The observation of oxidation peak at $+540$ mV versus SCE which may be due to the oxidation of Cu^{2+} to metal Cu according to Eq. (5) It is also observed that the reduction peak I at -325 mV versus SCE which may be due to the formation of Cu_2S on the substrate. It is noted that the reduction peak at -40 mV versus SCE which may be due to the process of reduction of solvent in the electrolytic bath. The observation of slight shift in reduction potential which may be due to the usage of different substrates for deposition.

3.2 Stylus profilometry

Thickness of the deposited films has been controlled by adjusting the deposition parameters such as potential, time of deposition, plating current, bath temperature and pH value of the electrolytic bath [11]. The temperature of the electrolytic bath is found to be in the range between 50 and 80 °C


Fig. 2 Cyclic volammetric curve of Cu_2S film obtained on (a) Al and (b) SnO_2 substrate from an acidic bath of $CuSO_4$ with $Na_2S_2O_3$

for even deposition of film on the substrate of SS, Al and SnO$_2$. Variation of films thicknes with deposition time for Cu$_2$O thin films obtained on SS and SnO$_2$ substrate is shown in Fig. 3. It is noted that film thickness increases linearly with deposition time and attained its maximum value at a deposition time of 40 min. If the deposition time is increased above 40 min, the rate of deposition is found to decrease thus results decrease in value of film thickness which is indicated in Fig. 3. Similar behaviour is exhibited for Cu$_2$S thin films obtained on Al and SnO$_2$ substrates which is shown in Fig. 4. The higher value of film thickness is obtained at a time of deposition of 40 min for both Cu$_2$O, Cu$_2$S, respectively.

3.3 Structural analysis

Structural properties of Cu$_2$O and Cu$_2$S thin films have been determined using X-ray diffractometer with the diffraction angle in the range between 20 and 80. XRD pattern showed that the prepared films possess polycrystalline nature with cubic structure for Cu$_2$O and Cu$_2$S. XRD pattern obtained for Cu$_2$O thin films prepared on SS and SnO$_2$ substrate is shown in Fig. 5. The value of lattice spacing "d" is calculated from the observed 2θ values and compared with standard JCPDS ICDD file for cubic Cu$_2$O [14]. The diffraction peaks of Cu$_2$O are found at 2θ values of angles 37.03, 43.02, 52.39, 62.22, 66,45 corresponding to the lattice planes (111), (200), (211), (220), (221) respectively. It is observed from Fig. 5a,b that the height of the peak observed at 2θ value 37.13, 52.39 is found to be higher than all other peaks in the diffractogram indicated that the crystallites are preferentially oriented along (111) and (211) plane for films obtained on SnO$_2$ and SS substrates. XRD pattern recorded for Cu$_2$S thin films on Al and SnO$_2$ substrate is shown in Fig. 6. The value
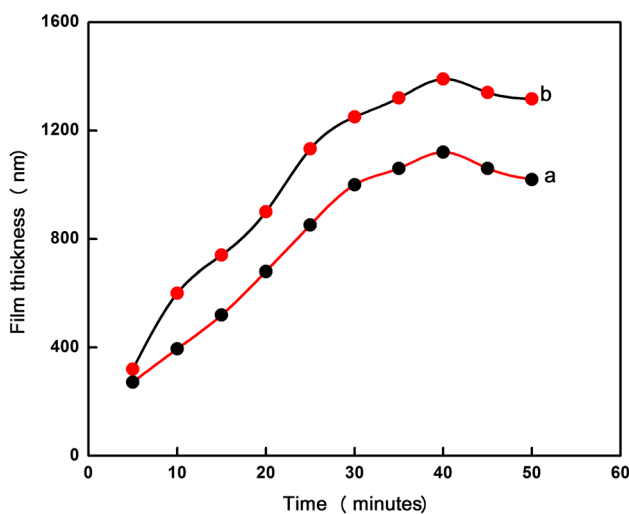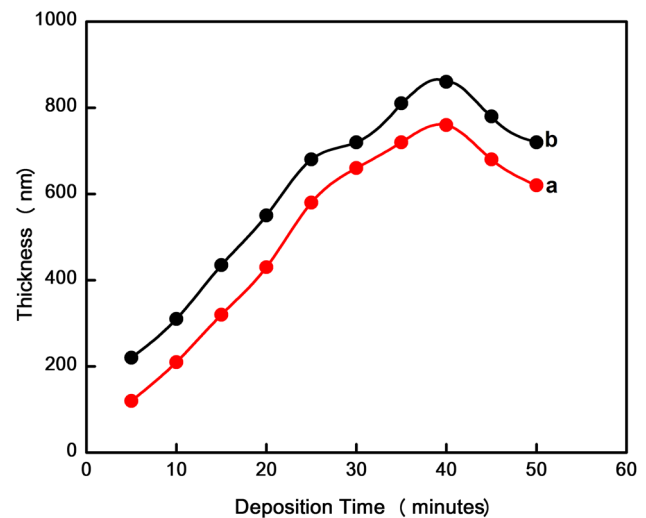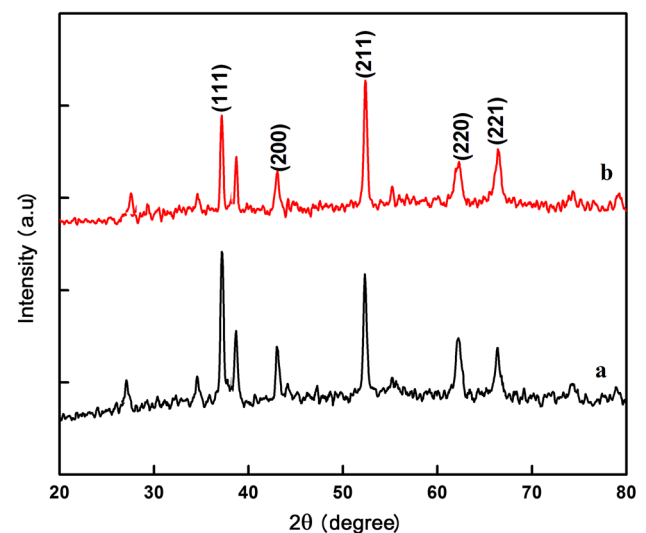

Fig. 4 Variation of film thickness with deposition time for Cu$_2$S thin films thin films prepared on: (*a*) Al (*b*) SnO$_2$ substrates

of interplanar spacing "d" is calculated from the observed 2θ values and compared with standard JCPDS ICDD file for cubic Cu$_2$S [15]. The height of (111) plane is found to be higher than all other peaks in the diffraction pattern indicated that the crystallites have most prominent reflection along (111) plane. The observation of considerable increase in peak height of preferential plane (111) represents the usage of different substrates for deposition. Crystallite size is defined as the sizes of the crystallites formed along the surface of the substrate [11, 12]. Debye Scherrer formula is used to calculate the value of crystallite size from the FWHM data which is obtained from XRD pattern [13].

Fig. 3 Variation of film thickness with deposition time for Cu$_2$O thin films prepared on: (*a*) SS (*b*) SnO$_2$ substrates
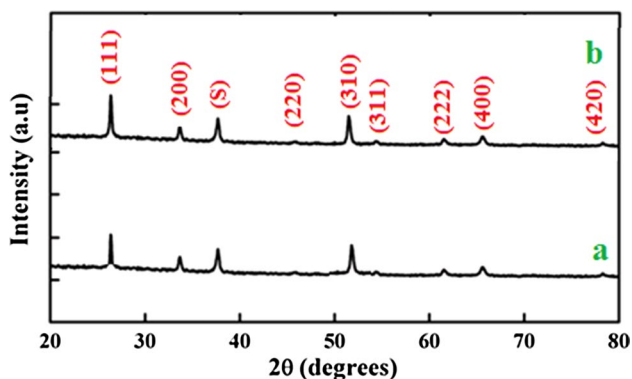

Fig. 5 XRD pattern of Cu$_2$O thin films prepared on: (*a*) SS (*b*) SnO$_2$ substrates

Fig. 6 XRD pattern of Cu_2S thin films prepared on: (*a*) Al (*b*) SnO_2 substrates

Fig. 7 SEM image of Cu_2O thin films obtained on SnO_2 substrate

Strain is defined as the restoring force which can be acts on the surface of the substrate to restrict the formation of crystallites on its surface [12, 13]. Dislocation density is defined as the number of dislocation lines per unit volume of the crystal [12, 13]. The estimated value of crystallite size and dislocation density for Cu_2O and Cu_2S thin films on different substrates are given in Table 1.

3.4 Surface morphology and composition

Surface morphology of Cu_2O thin films on SnO_2 substrate is shown in Fig. 7. It is observed that the surface is covered with small uniform spherical shaped grains. It is observed that the sizes of the grains are found to be in the range between 0.7 and 0.9 μm. SEM image of Cu_2S thin films obtained on SnO_2 substrate is shown in Fig. 8. It is noted that the substrate covered with unshaped crystal grains as shown in Fig. 8. The observation of slight change in surface morphology which may be due to usage of different substrate for deposition. The sizes of the grains are found to be in the range between 500 and 700 nm. This value of atomic percentage in EDX results indicated, the that the results is consistent with X-ray diffraction analysis of the sample with phase corresponds to Cu_2O and Cu_2S. There is slight shift in value of atomic percentage is noted for films prepared on different substrates (Table 1).

3.5 Optical absorption analysis

Optical absorption analysis have been carried out by absorption and transmittance measurements for Cu_2O and Cu_2S thin films prepared on SnO_2 substrates using Schimadzu UV–Visible-NIR spectrophotometer within the wavelength range between 300 and 1100 nm. The value of absorption coefficient for the deposited films which has been calculated using Eq. (10) [13]

$$\alpha = \frac{1}{t} \ln \left[\frac{A}{T} \right] \tag{10}$$

where α is the absorption coefficient in cm^{-1}, t is thickness of the deposited film in nm, A and T are the percentage of absorbance and transmittance of the deposited films. The nature of transition present in the deposited film is calculated using Eq. (11) [12, 13].

$$\alpha h\nu = A \left(h\nu - E_g \right)^n \tag{11}$$

where (hν) is photon energy in eV, E_g is an band gap energy in eV, A is an energy dependent constant and n is an integer. The percentage of transmittance for Cu_2O and Cu_2S thin films obtained on SnO_2 in shown in Figs. 9 and 10. A plot of (hν) versus $(\alpha h\nu)^2$ for Cu_2O and Cu_2S films prepared on SnO_2 substrate is indicated inset of Figs. 9, 10. It is observed that linear portion of the plot is extrapolated to X (energy)-axis gives band gap value of the deposited films. The band

Table 1 The estimated value of film thickness, crystallite size, dislocation density and band gap for Cu_2O, Cu_2S thin films prepared on different substrates

| Film	Substrate	Thickness (nm)	Crystallite size (nm)	Dislocation density $(\delta) \times 10^{14}$ lines/metre^2	Atomic percentage			Bandgap (eV)
					Cu	O	S	
Cu_2O	SS	1200	42.33	5.5	69.14	30.86		–
	SnO_2	900	46.44	4.6	67.32	32.28		2.28
Cu_2S	Al	760	42.85	5.44	72.78	–	27.22	–
	SnO_2	860	52.39	3.50	70.90	–	29.10	2.45
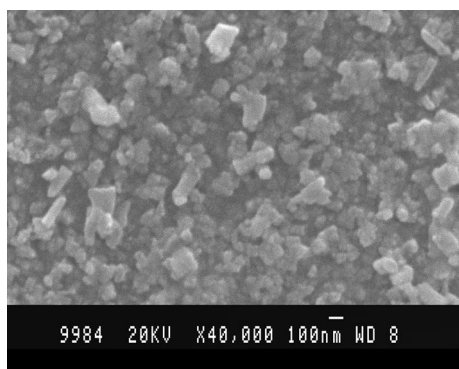
Fig. 8 SEM image of Cu_2S thin films obtained on SnO_2 substrate
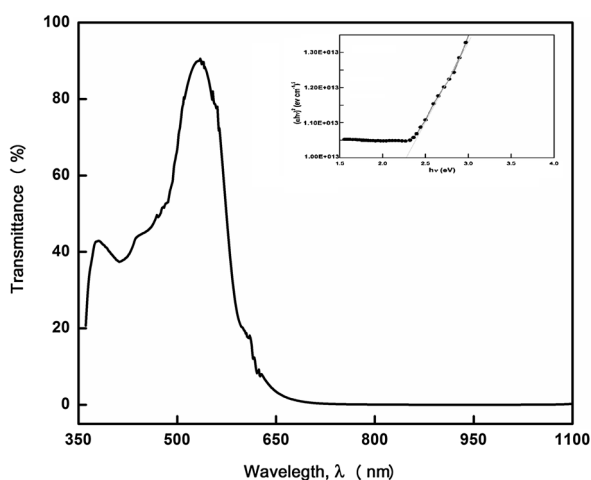
Fig. 9 Plot of $(h\nu)$ versus $(\alpha h\nu)^2$ for Cu_2O thin films prepared on SnO_2 substrate
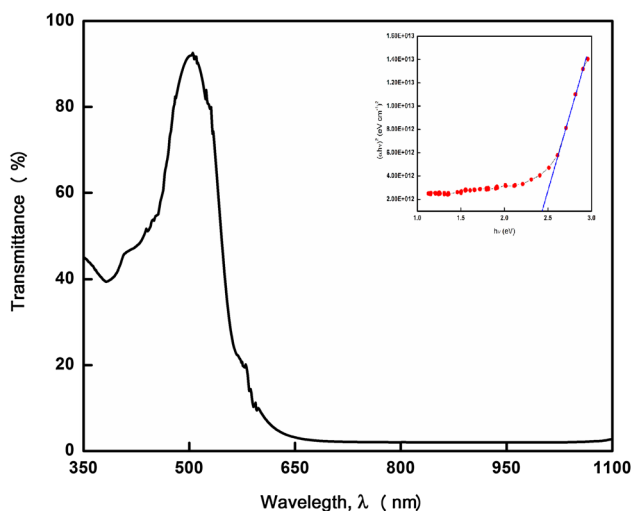
Fig. 10 Plot of $(h\nu)$ versus $(\alpha h\nu)^2$ for Cu_2S thin films prepared on SnO_2 substrate

gap value is found to be 2.28 and 2.45 eV for the deposited films of Cu_2O and Cu_2S.

4 Conclusions

Cu_2O and Cu_2S thin films were successfully prepared on SS, Al and SnO_2 substrates by potentiostatic electrodeposition technique. Structural investigation showed that the deposited layer exhibited cubic structure with preferential orientation along (111) and (200) plane. The observation of lower value of strain and dislocation density indicated that the films deposited on SnO_2 substrate exhibited better microstructural properties. Surface morphology showed that the surface covered with uniform spherical shaped grains for films obtained on SnO_2 The value of band gap was found to be 2.28 and 2.45 eV for Cu_2O and Cu_2S. Hence, we have concluded that the films prepared on SnO_2 substrate is found to exhibit well oriented microstructural, compositional and optical properties.

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