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RESEARCH

Annealing temperature effect on the properties of untreated and treated copper films with oxygen plasma

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Abstract In this work, the copper films were deposited on quartz substrates by DC magnetron sputtering method and then, the prepared films were annealed in air atmosphere at different annealing temperatures. Before annealing, some of the copper films, treated by oxygen plasma, for comparison of the results. The structural and morphological properties of the films have been investigated using X-ray diffraction (XRD), atomic force microscopy, and four point probe techniques. XRD results exhibited that the cuprous oxide phase changes to cupric oxide by enhancing of annealing temperatures. Also, oxygen plasma treatment can cause the better crystallinity for the prepared copper oxide films. The results confirm that oxygen plasma treatment, affected the crystal size, grain size, average roughness, sheet resistivity and strain of the films. The optical characteristics of the oxygen plasma treated films, such as refractive index, extinction coefficient and absorption coefficient were calculated by straight forward method proposed by Swanepoel using transmittance measurements. Moreover it was found that annealing temperature augmentation lead to decrease the optical band gap energy calculated using Tauc's relation from 2.45 to 1.80 eV.

Keywords Copper oxide · Oxygen plasma · Annealing temperature · Optical properties

Introduction

Copper oxide is a P-type semiconductor with a band gap in the visible or near infrared regions, non toxic nature and good electrical and optical properties [1–12]. There are two crystalline forms of copper oxides, cuprous oxide or cuprite (cubic Cu_2O) and cupric oxide or tenorite (monoclinic CuO). Copper oxides have many applications in diverse fields such as, solar cells [2] and photovoltaic materials [3], electrochromic devices [4], catalytic application and high-T_c superconductors [5].

Variety methods such as, electro deposition [6], sol–gel [7], molecular beam epitaxy [8], ultrasonic spray pyrolysis technique [9], DC reactive sputtering [10], thermal oxidation [11] and ion beam sputtering [12] have been used for the production of copper oxide films on various substrates. However, the focus of the present study is to investigate and compare the structural and morphological properties of thermal annealed Cu films treated and untreated with oxygen plasma. Also, for optical device applications, it is very important to study optical characteristics of copper oxide films over a wide range of wavelengths. So, the optical characteristics, including the refractive index, absorption coefficient and optical band gap of oxygen plasma treated films were determined from transmittance spectra using Swanepoel's method [13].

The structure of the paper is as follows. Following the introduction in "Introduction" we present the experimental details for the preparation, annealing and characterization of the prepared films in "Materials and methods". "Result and discussion" devoted to our results and discussions and we conclude the paper in "Conclusion".

Materials and methods

The cuprous oxide films were prepared on quartz substrates by thermal oxidation of untreated and treated copper (Cu) films with oxygen plasma. In the first step, Cu thin films

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Table 1 The Cu films preparation conditions

Target	Cu
Substrate	Quartz
Target-substrate distance (cm)	6
Base pressure (Torr)	8×10^{-5}
Deposition pressure (Torr)	6×10^{-2}
Voltage (V)	200
Current (mA)	75
Deposition time (min)	2

were deposited on quartz substrates using DC planar magnetron sputtering system with Cu target (purity of 99.999 %) under the same conditions that were shown in Table 1. Before deposition, the substrates were ultrasonically cleaned in acetone and ethanol for 15 min prior to loading into the deposition chamber. Thermal oxidation of Cu film was carried out in a quartz tube furnace at air atmosphere. For oxygen plasma treatment, some of the copper films were placed in plasma chamber of cylindrical magnetron sputtering system and exposed to the oxygen plasma at fixed conditions (without Ar gas) for 15 min at the pressure of 5×10^{-2} Torr. The detail of the system can be found in ref [14]. Finally, all the prepared films were annealed in air atmosphere at different temperatures ranging from 250 to 550 °C for 240 min in electrical furnace.

For study of annealing temperature effect on structural and morphological properties of Cu films and comparison of results, the prepared films were analyzed by different methods such as X-ray diffraction (XRD; Philips PW1800), atomic force microscopy (AFM; Park Scientific Instruments Auto Probe CP) in a contact mode, Spectrophotometry (UV Ikon 922) and four-point probes.

Results and discussion

XRD analysis

XRD patterns of the prepared films were shown in Fig. 1a, b. It should be noted that the wide and broad peak at 22.1° is related to quartz substrate. Figure 1a shows comparative patterns of XRD analysis for the untreated Cu films before and after annealing at different temperatures. An unannealed Cu film shows the diffraction peak of the (111) plane of cubic Cu phase (JCPDS Card no. 85-1326). This is expected, since the Cu has an fcc structure and the (111) facet has the lowest surface energy. The Cu films oxidized to the Cu_2O and CuO after annealing at 250 °C. By increasing the annealing temperature from 350 to 550 °C, a single phase of CuO can be obtained. In addition, it can be observe that the intensity of the CuO peaks increases with an increase of annealing temperature up to 450 °C and, at higher temperature of 550 °C is reduced. These results are in good agreement with those reported by [15].

The XRD patterns of the Cu films treated by oxygen plasma and annealed at different temperatures are observed in Fig. 1b. The films formed without annealing, exhibited a broad peak corresponding to Cu_2O phase with (111) direction (JCPDS Card no. 77-0199). When the film was annealed at 250 °C the (111) orientation of Cu_2O peak amplified. The broadness of the peak in the as-deposited and the annealed film at 250 °C is due to small size of grains formed in these films as it can be observed in the AFM images of these films.

The film annealed at temperature of 450 °C, was observed to be polycrystalline and characterized by three diffracted peaks, these diffracted peaks correspond to CuO of indices hkl ($\bar{1}11$), (111) and (202) (JCPDS Card no. 80-1917) that the intensity of CuO peaks is slightly higher than the films prepared without oxygen plasma interaction.

The average crystalline size and microstrain of the films have been obtained from the following Scherrer relations:

$$D = 0.9\lambda/\beta\cos\theta \text{ and } \varepsilon = \beta/4\tan\theta \qquad (1)$$

Where, β is the full-width at half maximum (FWHM) of the diffraction peaks in radians, λ is the wavelength of X-ray (1.5406 nm for Cukα) and θ is the Bragg's angle. The comparison of structural parameters (FWHM, miller indices, average crystalline size and microstrain) of untreated and oxygen plasma treated Cu films are shown in Table 2. According to results of Table 2, we can observe that annealing temperature augmentation lead to increase of average crystal size and decrease of microstrain. The increase in crystallite size is related to decrease in strain. Also, the increase in average crystal size after annealing might be due to decrease in grain boundaries and the amount of defect in the films. It was observed that the plasma treated films have slightly larger crystal size and smaller microstrain as compared to the untreated films. This may be due to the formation of cuprous oxide phase in the oxygen plasma treated films before annealing.

Surface morphology

The surface morphology and roughness of films were studied by atomic force microscopy (AFM). Figure 2a–d shows three dimensional AFM images of untreated and treated films with oxygen plasma that were annealed at temperature of 250 and 450 °C, for comparison of the results. Also, the root mean square (RMS) roughness and the average roughness values obtained from AFM measurements are shown in Table 3. It can be seen from the Fig. 2a, b that the pyramidal types of grains were grown

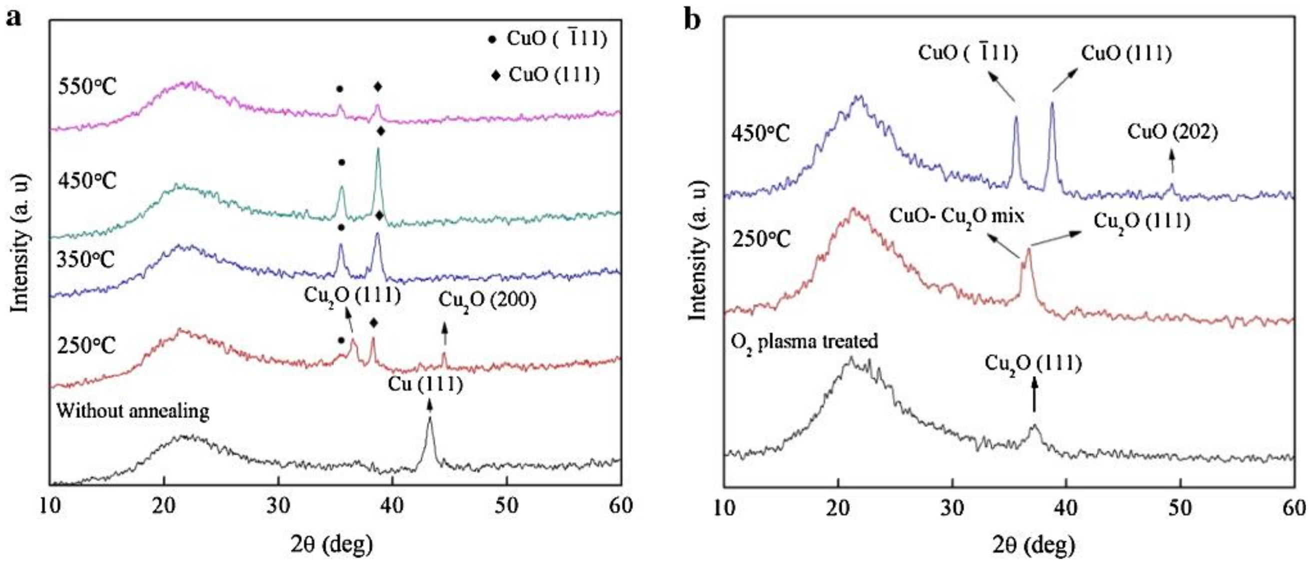

Fig. 1 **a** XRD patterns of untreated Cu films with oxygen plasma and annealed at various temperatures. **b** XRD patterns of the Cu films treated by oxygen plasma and annealed at different temperatures

Table 2 Comparison of copper oxide films structural parameters (FWHM, Miller indices, Average crystalline size and Micro strain)

Conditions	Sample number and annealing temperature	Diffraction angle 2θ (deg.)	Phase composition	Miller indices (hkl)	FWHM (Rad)	Average crystalline size (nm)	Micro strain
Oxygen plasma treatment	(Sample 1) without annealing	37.26	Cu_2O	(111)	1.67×10^{-2}	8.75	3.95×10^{-3}
	(Sample 2) 250 °C	36.76	Cu_2O	(111)	1.20×10^{-2}	12.17	2.84×10^{-3}
	(Sample 3) 450 °C	35.64	CuO	($\bar{1}$11)	8.37×10^{-3}	17.39	1.99×10^{-3}
	(Sample 3) 450 °C	38.76	CuO	(111)	6.97×10^{-3}	21.05	1.64×10^{-3}
Without oxygen plasma treatment	(Sample 4) without annealing	43.25	Cu	(111)	1.30×10^{-2}	11.46	3.02×10^{-3}
	(Sample 5) 250 °C	36.56	Cu_2O	(111)	1.30×10^{-2}	11.23	3.05×10^{-3}
	(Sample 6) 450 °C	35.56	CuO	($\bar{1}$11)	1.01×10^{-2}	14.41	2.04×10^{-3}
	(Sample 6) 450 °C	38.76	CuO	(111)	7.50×10^{-3}	19.59	1.76×10^{-3}

perpendicular to the substrate surface for the films formed without oxygen plasma. The surface roughness of films increased by enhancing of annealing temperature may be due to the phase change and the formation of larger grains due to the diffusion effect. In addition, it can observe that the films treated by oxygen plasma are rougher than the untreated films. The increase of roughness in this case can be attributed to the interaction of reactive particles from plasma with the surface and surface oxidation that can be seen in XRD results (Fig. 1b).

Electrical properties

The sheet resistance of films was measured using a four point probe, several measurements were taken from each sample and average is reported with a deviation of <10 % in Table 3. The results showed that by increasing of annealing temperature the sheet resistivity of films decreased may be due to the phase transition from Cu_2O to CuO and increase of films crystallinity that have been shown in XRD results. Also, the sheet resistivity of oxygen plasma treated films is larger than the untreated films.

Optical characteristics

For optical investigation, the films treated with oxygen plasma were chosen. Because interference fringes due to the high quality and good structure properties of these films can be observed in optical transmittance spectra and we can employ the Swanepoel's method to determine the optical constant such as refractive index (*n*) and extinction

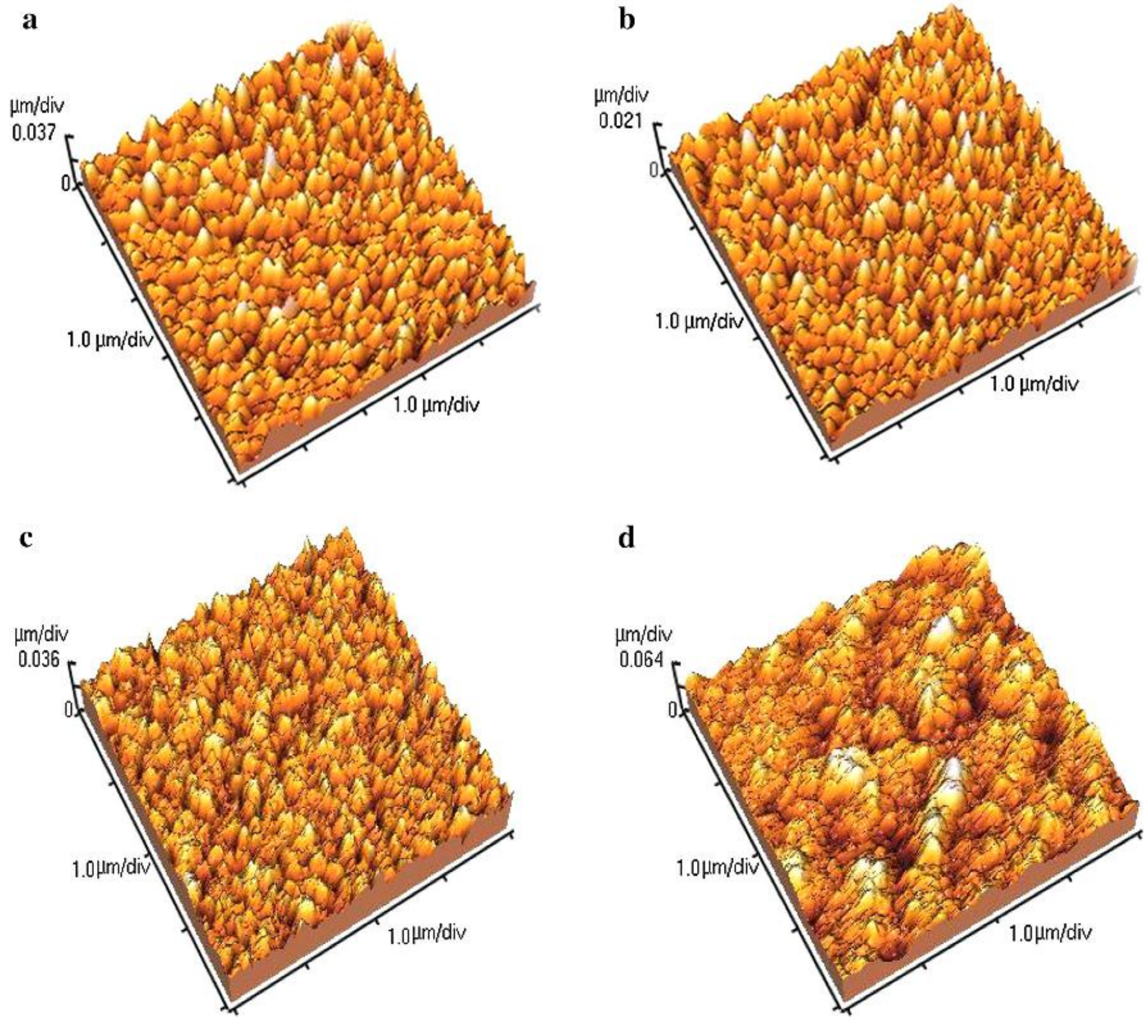

Fig. 2 3D AFM images of untreated copper films with oxygen plasma and annealed at: **a** 250 °C, **b** 450 °C and oxygen plasma treated films and annealed at: **c** 250 °C, **d** 450 °C

Table 3 The roughness and sheet resistivity of untreated and treated cu films with oxygen plasma and annealed at 250 and 450 °C

Sample	Annealing temperature (°C)	RMS roughness (nm)	Average roughness (nm)	Sheet resistivity (Ω/□)
Untreated films with oxygen plasma	250	5.36	4.25	8.96×10^3
	450	10.65	8.49	4.83×10^2
Treated films with oxygen plasma	250	7.36	5.64	2.50×10^4
	450	13.72	10.64	1.67×10^3

coefficient (k). The normal incidence optical transmittance spectra of the films and quartz substrate in the wavelength range of 400–1,500 nm are shown in Fig. 3.

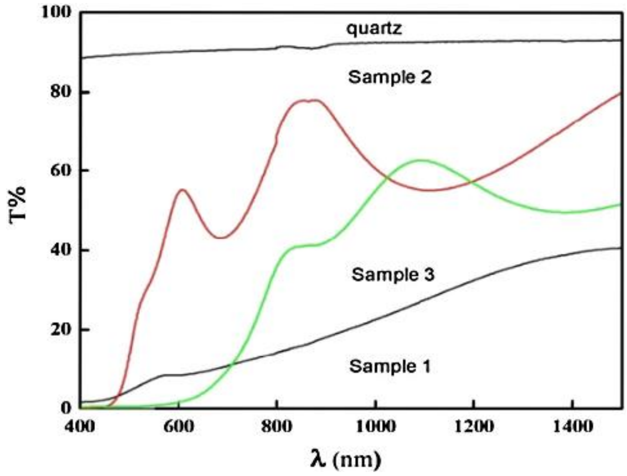

Fig. 3 Transmittance spectra of treated copper films with oxygen plasma, and annealed at different temperatures

We can observe that the curve of the unannealed Cu_2O film is smooth, whereas the curves corresponding to annealed films exhibit interference fringes. The annealed Cu_2O films are transparent in the visible region and exhibit sharp absorption edges that can be attributed to the good crystallinity and low defect concentration in the film. Whereas an unannealed film doesn't shows sharp absorption edge due to the low crystallinity level and high defect density near the band edge. Also by annealing, the film's transparency is increased and the optical properties of films improved due to the increase of crystallinity and decrease the defect density at the edge of energy band gap. The transmittance of the annealed film at 450 °C is lower than the annealed film's at 250 °C. These results are due to the transformation of Cu_2O to CuO as it was evidenced by the XRD results.

The annealed films refractive index computed using the Swanepoel's method, are shown in Fig. 4. The refractive index was modeled by the two-term Cauchy dispersion relations [16]. The Cauchy dispersion relations for two annealed samples 2 and 3 are:

$$n_{\text{sample2}} = 2.30 + \frac{2.19 \times 10^5}{\lambda^2},\ n_{\text{sample3}} = 2.15 + \frac{8.6 \times 10^4}{\lambda^2}. \tag{2}$$

Figure 4 shows the dispersion curves of the calculated refractive index, n, along with the experimental values. It is

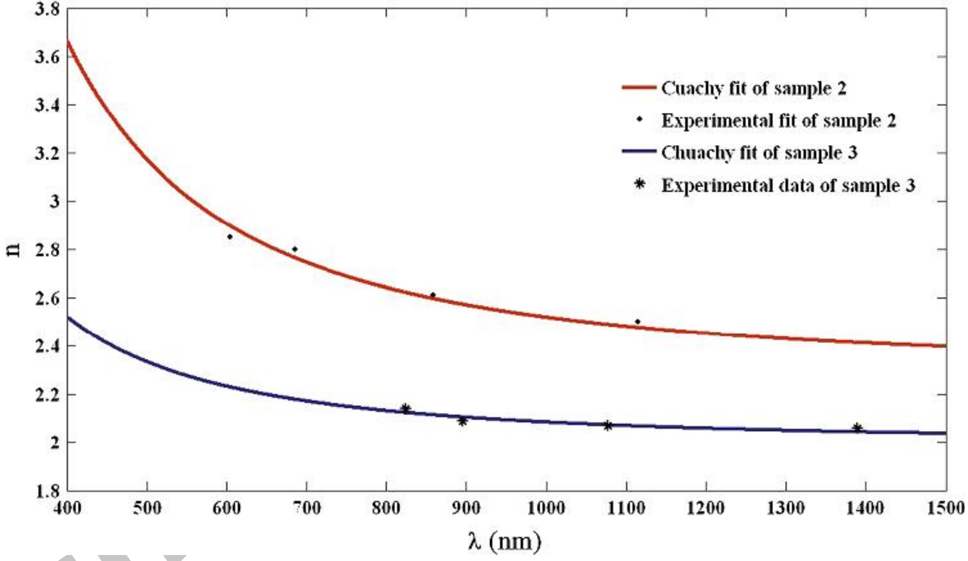

Fig. 4 Variation in refractive index (n) versus wavelength (λ) for samples 2 and 3

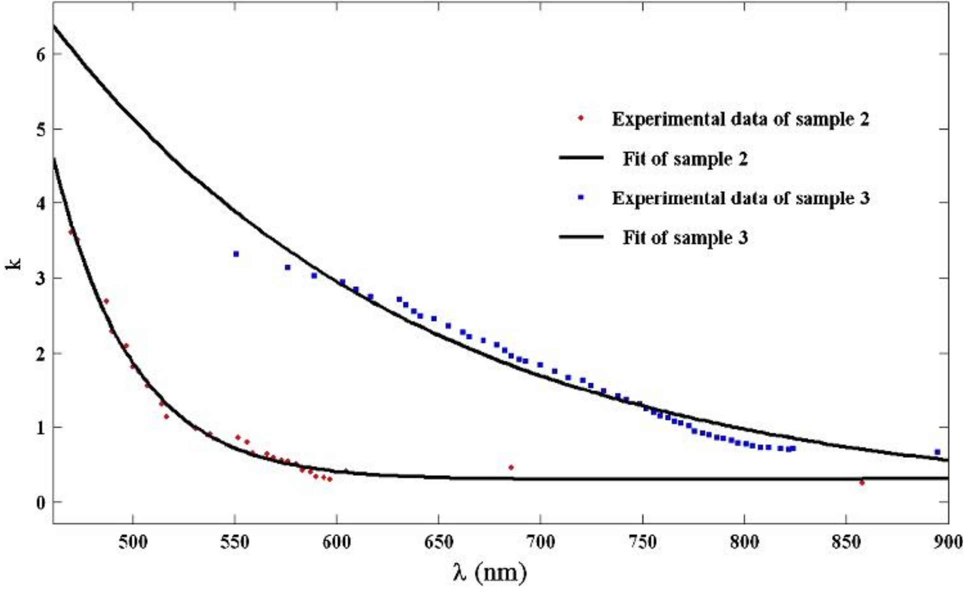

Fig. 5 Dependence of extinction coefficient (k) on wavelength (λ) for samples 2 and 3

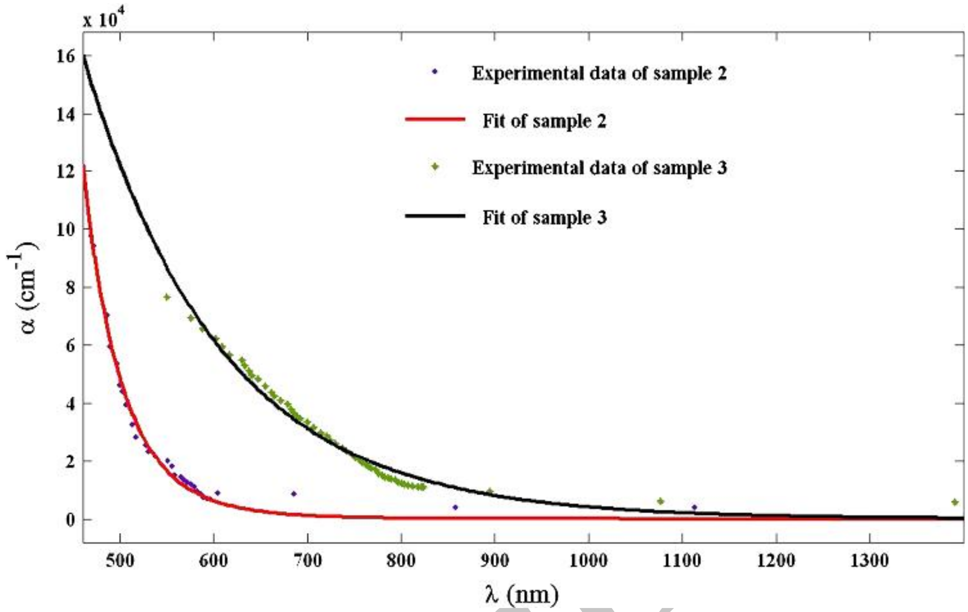

Fig. 6 Dependence of absorption coefficient (α) on wavelength (λ) for samples 2 and 3

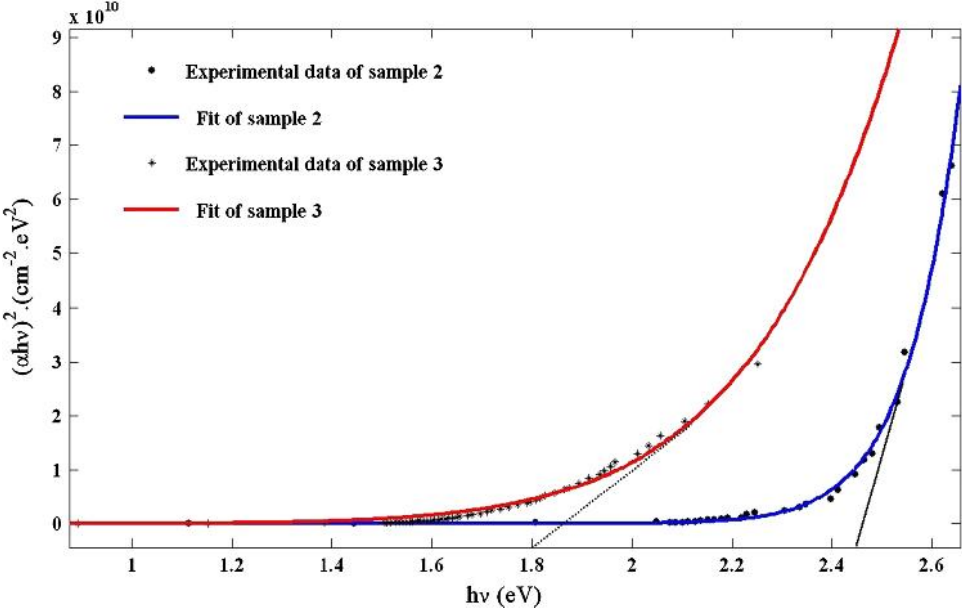

Fig. 7 Plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for annealed Cu_2O films

clear that both the experimental and calculated values of refractive index using the Cauchy dispersion are extensions to each other. Also, it is observed that the refractive index, *n*, decreased with increasing wavelength and tends to be constant at longer wavelength. The values of the refractive index in this study decreased from 2.91 to 2.39 and 2.23 to 2.04 for samples 2 and 3 respectively, with increase of wavelength from 600 to 1,500 nm. The n values of the copper oxide films calculated in the present study are in good agreement with those reported by [1, 17, 18] for crystalline films. Moreover, *n* of sample 3 (that was annealed at 450 °C) is lower than of sample 2 over the entire measured wavelength range. This reduction of refractive index can be attributed to phase transition from Cu_2O to the CuO.

The extinction coefficient, *k*, is determined by $k = \frac{\alpha\lambda}{4\pi}$, and the wavelength dependence of *k*, is shown in Fig. 5. It is clearly observed that the extinction coefficient decreases with increasing wavelength. The wavelength dependence of the absorption coefficient for the annealed films is given in Fig. 6. It can be seen that the annealed films show a very weak absorption coefficient at the range of 800–1,500 nm but for the photon energies in the visible region and near-IR spectral range, the films have relatively high absorption coefficient of 10^4 cm^{-1}. Such a high absorption coefficient implies that these films are very suitable for solar energy applications. Using the derived absorption coefficient α, the optical band gap of the films was estimated by extrapolating the linear portion of the plot of $(\alpha h\nu)^2$ versus $(h\nu)$ to $(\alpha h\nu) = 0$ according to Tauc's relation [19]. Figure 7 shows the plot of $(\alpha h\nu)^2$ versus $(h\nu)$ for two annealed samples.

The plots indicate a direct optical band gap for both annealed films which is a desired property for photovoltaic application. We can observed that the value of optical band gap of the annealed film at 250 °C is 2.45 eV but for 450 °C annealed film, when the diffraction peaks of CuO are detected in the X-ray pattern, the optical band gap decreases close to 1.80 eV. The values of optical band gap estimated in this study are in good agreement with the values reported by [20–23] for copper oxide films.

Conclusions

Influence of annealing temperature on structural and morphological properties of untreated and treated Cu films with oxygen plasma were investigated. The results show that the films prepared with oxygen plasma treatment have a larger crystal size, average roughness, sheet resistivity and smaller strain comparison to the untreated films. Also, all the films crystallinity is improved by annealing temperature up to 450 °C. Optical characteristics of the films treated by oxygen plasma were studied by Swanepoel's method. The refractive index decreased when the annealing temperature enhanced from 250 to 450 °C and the direct allowed band gap values were changed from 2.45 to 1.80 eV, due to the conversion of Cu_2O to CuO phase.

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