Effect of Annealing Temperatures on the Color Properties of Copper Oxide Films Prepared by the Sol-Gel Technique

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Sol-gel spin coating was employed to produce thin films on the glass substrate, which were subsequently heated to 300,400, 500, and 600 degrees for annealing. The effect of annealing temps on some physical features of the prepared films, such as XRD, AFM, FESEM, and UV-visible spectrophotometer, was studied. X-ray diffraction patterns showed the coexistence of two phases, Cu2O and CuO. According to the AFM findings, the root mean square (RMS) for thin films has been found to increase from 50.72nm at 300°C annealing temp to 122.0nm at 600°C and surface roughness and grain size rate increase with increasing annealing temp. Experimental findings indicated that the transmittance of films increases with increasing annealing temp. The viewable region's transmittance was 88% at 500°C. In this work, the color coordinates of copper oxide were determined. Three critical color attributes were measured utilizing CIE1931 technology to monitor color values: brightness, color purity, and dominant wavelength. The findings illustrated that the color purity and the dominant wavelength decrease with increasing annealing temp, and these values ranged between (0.7-0.51) and (563-556), respectively, when the temp increased from 300°C to 500°C, in contrast to the brightness values, which increased with increasing annealing temps.

Keywords: Thin films; Copper oxide; Atomic fprce microscopy; CIE1931
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1. Introduction

Copper oxide, as a metal oxide, is a semiconductor widely utilized in photovoltaic devices, including the absorption layer, electron transport layer, transparent electrodes, and photo anode [1]. Copper oxide exhibits p-type conductivity and has a monoclinic crystal structure [2]. Copper oxide has three various phase structures: the monoclinic tenorite (CuO) phase, in which the band gap value ranges from 1.3 to 2.1 eV, and sometimes it has a larger band gap of about 3 eV [3,4]. Moreover, the cuprite phase (Cu_2O) has A cubic structure and a band gap between 2.0 and 2.6 eV in addition to the parameclonide phase (Cu_3O_4) [5]. The development of thin film technology began to increase when the world urgently needed to manufacture integrated circuits. The most crucial feature of thin films is their low cost and small size compared to matter in its volumetric state [6]. Numerous deposition techniques involving spray pyrolysis, vacuum evaporation, chemical vapor deposition (CVD), and molecular beam epitaxy have been utilized to prepared Copper oxide thin films [7]. Among the techniques for preparing thin films is the spin coating technique due to its low cost and the possibility of obtaining a homogeneous film with a large area. In addition to controlling the features of the thin film depending on the concentration and type of material and the annealing temp [8]. Sol-gel technique is ideal for preparing thin films of one thickness on solid, flat substrates [9,10]. In general, the principle of sol-gel synthesis is based on chemical colloidal materials, representing solid raw materials that dissolve in specific solvents and transform into homogeneous solutions under controlled conditions, for example temp and pressure. The dispersed phase is then converted into a gel under the same controlled conditions [11]. In general, the gelation process includes the transformation of the system from the liquid state (sol) to the gel state (gel) [12].

In this research, color was studied in order to control the color and its intensity, because thin films are used in many applications that may need to remove the color or control it according to what is required. It was found that the best color removal was at a temperature of 500°C.

2. Experimental detail

Thin films of copper oxide were prepared at various annealing temperatures. A 0.2 g of copper acetate was dissolved in 50 ml isopropanol alcohol. The mixture was stirred on a magnetic mixer for 20 minutes. The temperature of the solution was gradually raised until it reached 60°C and maintained at this temp. A 1 mL diethanolamine was added drop by drop to the solution with continuous stirring until the solution was homogeneous and became a clear, dark blue color. The solution was removed from the magnetic mixer and kept in an airtight glass bottle for one day. After one day, the solution was filtered with filter paper and deposited on the glass bases. The glass bases were cleaned with water and detergent and then washed with distilled water. The glass bases were placed in acetone and ethanol for ten minutes. The bases were dried in an oven at 250°C for ten minutes. The glass base was placed in the middle of the rotary coating device, and the solution was dropped onto the base in drops. The device was rotated at a speed of 3000 rpm for 30 minutes, and then the deposited film was dried at a temperature of 250°C. The process was repeated ten times. Finally, it was annealed at temperatures ranging in 300-600°C. The morphological and optical features have been investigated utilizing x-ray diffraction (XRD) patterns, atomic force microscopy (AFM), field-emission scanning electron microscopy (FE-SEM), and UV-visible spectrophotometry in the spectral range of 300-1100 nm.

3. Results and Discussion

Figure (1) illustrates the XRD patterns of CuO and Cu_2O thin films prepared by sol gel spin coating method at different annealing temperatures. The results of XRD examination of copper oxide films prepared using the gel solution technique and at temperatures of 300, 400, 500, and 600°C showed that they have a polycrystalline structure. They confirm the coexistence of two phases: the cubic copper oxide phase (Cu_2O) at a temperature of 300 °C and it turns into a monocrystalline copper oxide phase, inclination (CuO) when temperatures increase. They are detected by JCPDS standard card number 00-005-0667 and 00-045-0937, respectively.

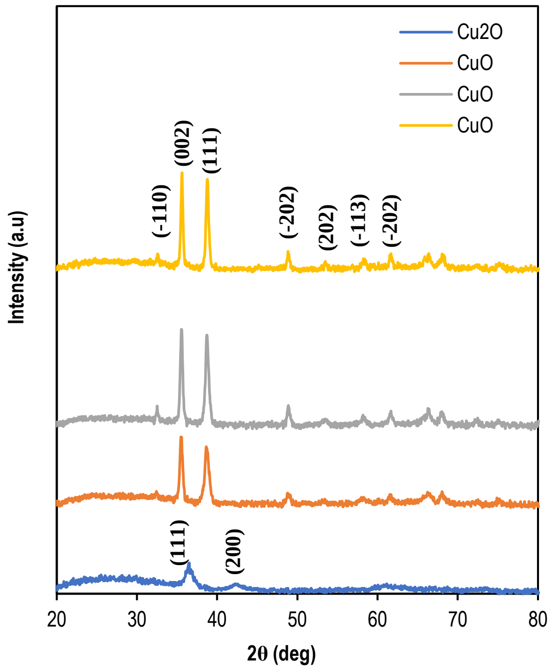


Fig. (1) XRD patterns of CuO and Cu_2O thin films prepared by sol gel spin coating method at different annealing temperatures

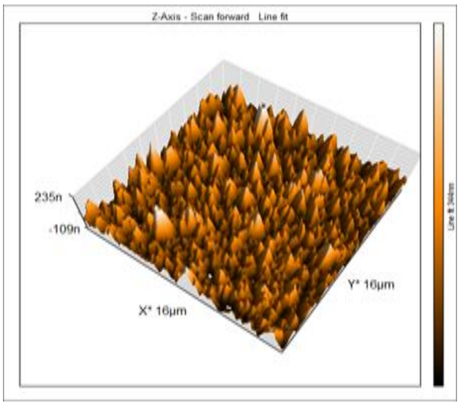
As for the Cu_2O phase, peaks 36.436° and 42.151° appeared at levels (111) and (200), and these results are consistent with the results of researchers [13]. As the annealing temperature increases, the CuO phase begins to appear with peaks at 32.47°, 35.48°, 38.60°, 48.70°, 53.29°, 58.34°, 61.52°, 66.35°, 68.07°, 72.49°, and 75.14° for levels (-110), (002), (111), (-202), (020), (202), (-113), (-311), (-220), (311), and (004), respectively, and with the prevailing trend of growth (002), these results are consistent with the results of researchers [14-16].

Atomic force microscopy (AFM) was utilized to study the topography of the surfaces of deposited films and the extent of the effect of annealing on them. Figure (2) illustrates AFM images. From table (1) and Fig. (3), it was found that the root-mean-square (R.M.S.) roughness, the surface roughness, and the grain size increase with increasing annealing temperature; it has been detected that all surfaces of the films are regular and homogeneously distributed in the form of a horizontal matrix with low peaks facing upward, separated by nanoscale spaces and that the films possess a large number of crystals that are aligned and connected regularly on the, without interstitial cracks or voids, and holes in the structures.

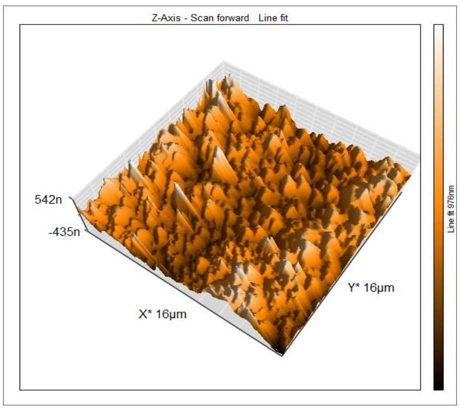
The topography of the surfaces of the prepared Cu_2O films and annealed at temperatures of 300, 400, 500, 600°C was studied utilizing the FE-SEM, which depicts the surfaces with high resolution and magnification. Figure (4) illustrates the FE-SEM images of the prepared copper oxide films with magnification of 50kX and 100kX.

Table (1) Results of the AFM examination

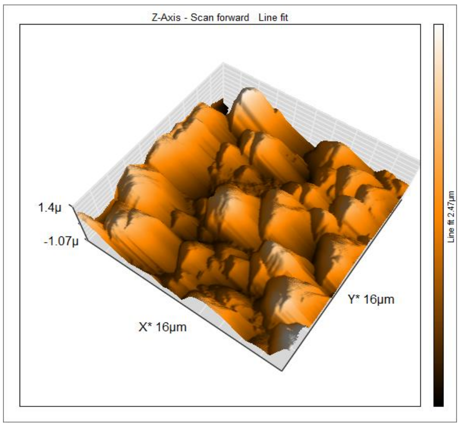
A-T (°C)	R.M.S. S_q (nm)	Surface Roughness S_a (nm)	Average Grain Size (nm)
300	50.72	39.26	142.8
400	91.21	68.68	146.4
500	417.8	343.2	197.4
600	122.0	99.82	100.6



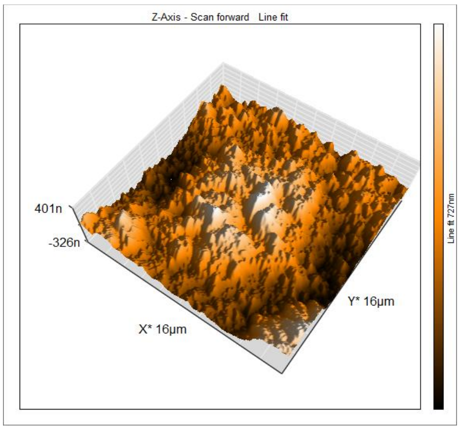
300°C



400°C



500°C



600°C

Fig. (2) 3D AFM images at various annealing temperatures for the prepared Cu_2O and CuO thin films

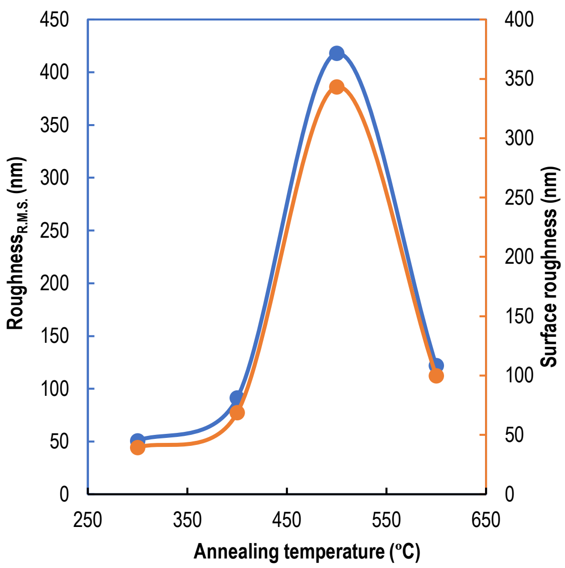


Fig. (3) Variation of the RMS roughness and surface roughness with annealing temperature

It is noted from the figure that the surface composition of the films consists of cauliflower-like shapes, with an apparent increase in the particle size composition with increasing temp due to increased granular growth. It was observed through energy-dispersive x-ray spectroscopy (EDS) examination that the copper oxide films consist of copper and oxygen concentrations only, and there are no concentrations of other elements, indicating the purity of the copper oxide films deposited on the substrate. Table (2) illustrates the percentages of oxygen and copper, and figure (5) illustrates images of EDS analysis.

Table (2) Approximate percentages of elements present in the thin films prepared at various annealing temperatures

T (°C)	Element	Atomic %	Weight %
300	O	49.28	19.65
	Cu	50.72	80.35
400	O	4.43	1.15
	Cu	95.57	98.85
500	O	37.28	13.02
	Cu	62.72	86.98
600	O	43.93	16.48
	Cu	56.07	83.52

The transmission spectra as a function of wavelength for films made of CuO and Cu_2O that were prepared and annealed for one hour at annealing temperatures of 300, 400, 500, and 600°C are displayed in Fig. (6). It has been observed that as the wavelength and annealing temperature rise, the transmittance also rises. The transmittance of the film annealed at 600°C is an exception to this rule, as its transmittance drops. The cause is that the glass utilized in the deposition process distorted due to the high annealing temperature, which reduced the glass's transmittance. The coordinates and color values can be found in the CIE 1931 system from the transmittance measurements.

After obtaining the transmittance spectrum curve for copper oxide utilizing a UV-visible spectrophotometer, some mathematical conversions can be made on the transmittance or absorbance values, which will yield a table of T_λ values for light with equal gradations of wavelengths for the range 380-770nm. The transmitting light's tristimulus values (XT, YT, ZT) and color coordinates (x, y, z) can be computed by applying successive steps to the transmittance values T_λ, which were ascertained by CIE [17,18].

$$X_T = k \sum P_\lambda \; T_\lambda \; X_\lambda \quad (1)$$

$$Y_T = k \sum P_\lambda \; T_\lambda \; Y_\lambda \quad (2)$$

$$Z_T = k \sum P_\lambda \; T_\lambda \; Z_\lambda \quad (3)$$

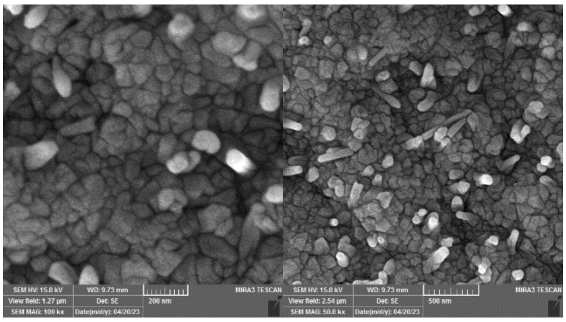
$$k = \frac{100}{\sum P_\lambda \; Y_\lambda} \quad (4)$$

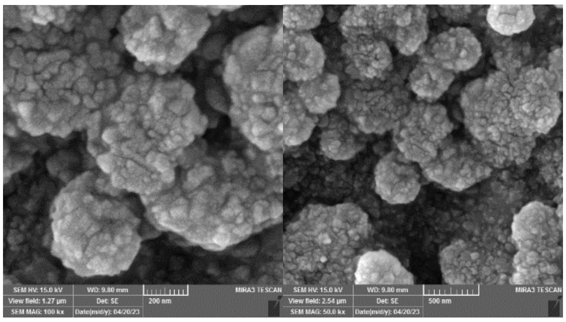
P_λ represents the power distribution curve of the employed light source, and (X_λ ،Y_λ،Z_λ) represents the distribution coefficient values of the light source. The color coordinate magnitudes for the CIE system are determined utilizing the specimen's Tristimulus values of X_T, Y_T, and Z_T.

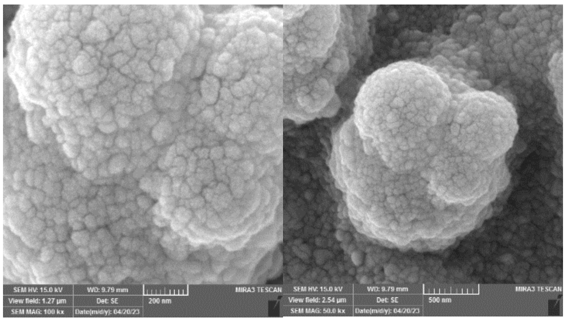
$$x = \frac{X}{X+Y+Z} \quad (5)$$

$$y = \frac{Y}{X+Y+Z} \quad (6)$$

$$z = \frac{Z}{X+Y+Z} \quad (7)$$


300°C


400°C


500°C

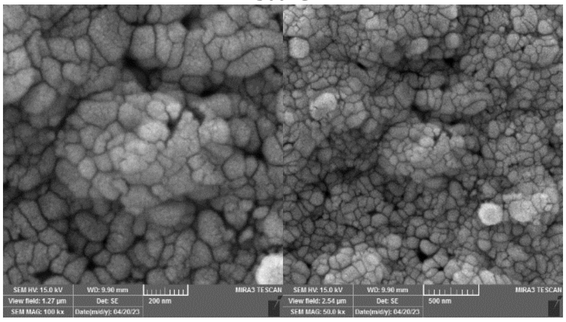
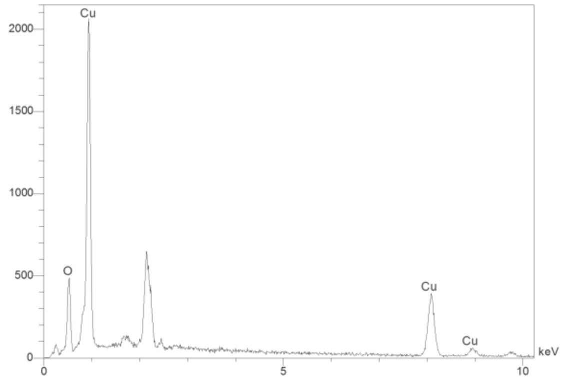

600°C

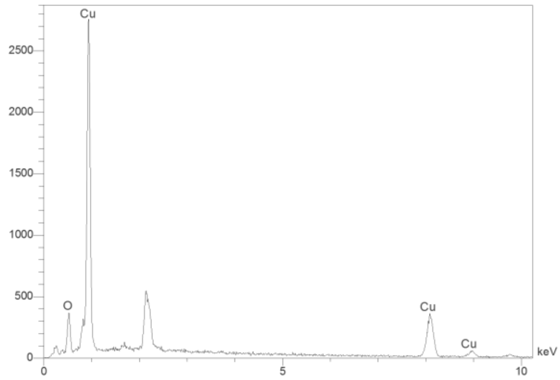
Fig. (4) FE-SEM images for the prepared Cu_2O and CuO thin films at various annealing temperatures

Tables (3) illustrate the color coordinate value (x, y, and z) of the CIE color system, which is utilized to find three other critical color value: dominant wavelength, color purity, and brightness.

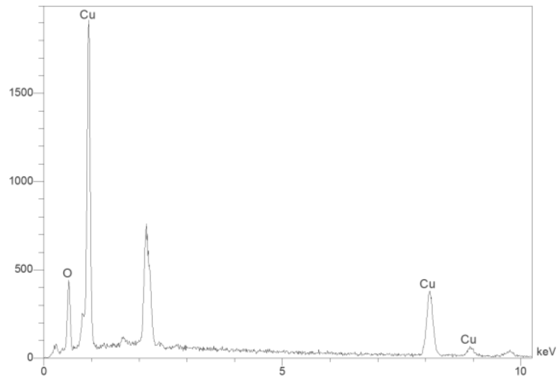
The color purity change at various annealing temps is depicted in Fig. (7). A sample with a lower color purity values implies that it contains less color; hence, a sample with a purity of 0% indicates that all color has been removed. Figure (8) illustrates the brightness of thin films. A perfect white diffuser is represented by a thin film when its brightness value reaches 100%.



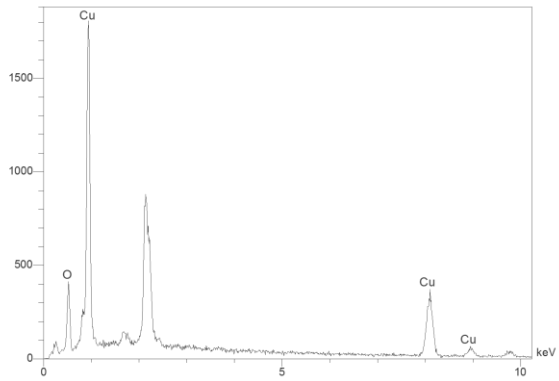
300°C



400°C



500°C



600°C

Fig. (5) EDS analysis results for the prepared Cu_2O and CuO thin films at various annealing temperatures

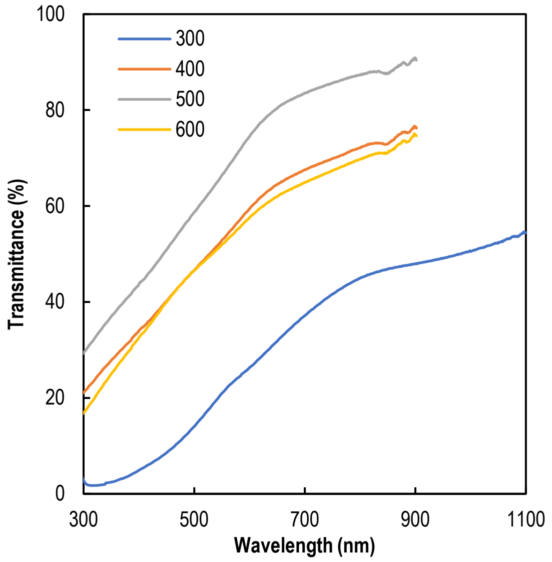


Fig. (6) Transmittance as a function of wavelength for the Cu_2O and CuO thin films prepared at various annealing temperatures

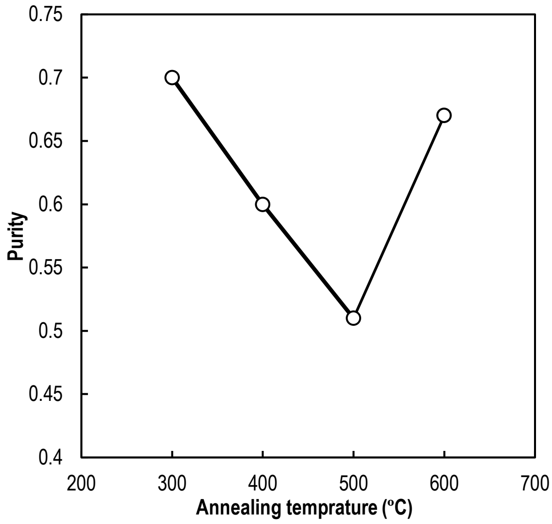


Fig. (7) The color purity of Cu_2O and CuO thin films prepared at various annealing temperatures

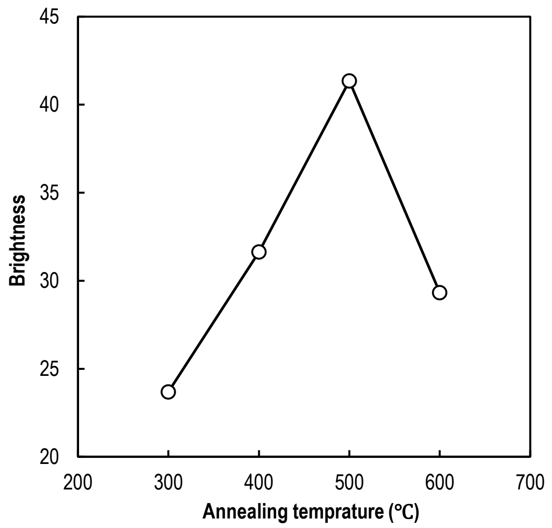


Fig. (8) The brightness of Cu_2O and CuO thin films prepared at various annealing temperatures

4. Conclusions

Thin films of copper oxide have been prepared on glass substrates utilizing the sol-gel spin coating technique, and the impact of annealing temp on the morphological, optical features, and color coordinates was studied. The coexistence of Cu_2O and CuO phases was confirmed. The results confirmed that the grain size and surface roughness increased with increasing annealing temperature. The highest transmittance of 88% has been gained at the annealing temperature of 500°C in the visible region. The best color removal was at temperature of 500°C.

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Table (3) Results of the coordinates and color value copper oxide prepared at various annealing temperatures

T (°C)	Color coordinates CIE			Dominant wavelength (nm)	Brightness	Purity
	x	Y	Z			
300	0.5495	0.3363	8.04	563	23.69	0.7
400	0.5197	0.3261	14.95	562	31.63	0.6
500	0.5052	0.3239	21.80	556	41.35	0.51
600	0.5488	0.3310	10.63	569	29.32	0.67