



Formation of Cupric Oxide Films on Quartz Substrates by Annealing the Copper Films

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Abstract

In the present work, cupric oxide (CuO) films were obtained through thermal annealing of the copper (Cu) films deposited on quartz substrates by DC magnetron sputtering method. The annealing was performed in air atmosphere for different times ranging from 60-240 min at temperature of 400 °C. The influence of annealing times on structural and morphological properties of the films was investigated by different analyses. The XRD results showed that the as-deposited film was Cu, while those annealed at different times were composed of CuO. By increasing annealing times up to 180 min, the intensity of CuO diffraction peaks increased and further enhancement of annealing times led to decrease of the crystallinity. Also, the AFM images of the films conformed the dependence of surface morphology to annealing times.

Keywords: CuO, DC magnetron sputtering, Annealing, Structural and Morphological properties.

Introduction

Copper oxide has two main crystalline form such as cuprous oxide (Cu₂O) and cupric oxide (CuO) that both of them are p-type semiconductors materials. The crystal structure of Cu₂O and CuO are cubic and monoclinic respectively. These oxides have been widely used in solar cells, electrochromic devices, gas sensors and superconducting

devices [1-3]. For preparation of copper oxide films several techniques have been developed such as sol-gel, spin coating, reactive magnetron sputtering, ion beam sputtering, ultrasonic spray pyrolysis and chemical deposition [1-11], but in the present work the CuO films were obtained successfully through the air annealing of Cu films deposited on quartz substrates by means of DC magnetron

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sputtering method. The objective of this work is to prepare and characterize high quality cupric oxide films by this low cost technique and studying the influence of annealing times on structural and morphological properties of the prepared films.

Following the introduction, in this article we presented the experimental details for the preparation, annealing and characterization of the prepared films. Finally, the results were discussed and conclusion was drawn based on the experimental findings.

Experimental

Materials and methods

In the first step, the Cu thin films were deposited on quartz substrates by using DC magnetron sputtering system at the same conditions. The argon (Ar) (99.995% pure) gas was used as the sputtering gas and the copper (99.99% pure) with 10 cm diameter was employed as a target. The distance between the target and substrate

was about 6cm. The deposition chamber was evacuated down to a base pressure of 2×10^{-5} mbar using combination of diffusion and rotary pumps and after introducing the Ar gas into the deposition chamber the pressure was maintained at 8×10^{-2} mbar.

For all the films, the deposition times were kept 3 min and during the deposition, the substrates were not intentionally heated. In the second step, the as-deposited Cu films were post-annealed in air atmosphere at temperature of 400 °C for different annealing times ranging from 60-240 min in an electrical furnace (Table 1). Finally, all the films were characterized by the X-ray diffraction (XRD) (Philips, PW 3710, Cu K α radiation $\lambda=0.15406$ nm) for analyzing the crystallographic structure and orientation of the films. The surface morphology and microstructure of films were analyzed by atomic force microscopy (AFM) (Auto probe cp, Park scientific instrument).

Table 1. The annealing conditions of copper films deposited on quartz substrates.

Sample's name	Time of Annealing (min)	Annealing Temperature (°C)
Sample Q0	-	-
Sample Q1	60	400
Sample Q2	120	400
Sample Q3	180	400
Sample Q4	240	400

Results and discussion

The XRD patterns of as-deposited and annealed films at different annealing times

ranging from 60-240 min in temperature of 400 °C are shown in Figure 1. It should be noted that the wide and broad signals at 22.3°

originated from quartz substrate. Also we observed that the as-deposited films showed the (111) diffraction peak corresponding to the cubic Cu phase (JCPDS Card no.85-1326).

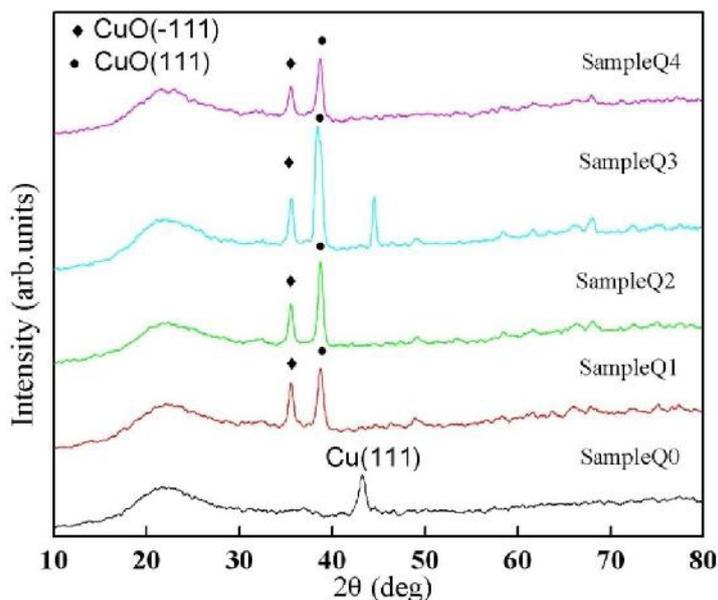


Figure 1. XRD patterns of as-deposited and annealed Cu films at different annealing times.

After annealing the Cu films in temperature of 400 °C for different annealing times, the diffraction peaks of (-111) and (111) corresponding to the CuO phase (JCPDS Card no.80-1917) were obtained that exhibit the conversion of Cu to CuO. Since the two peaks were sharp, it was evident that the deposited films are polycrystalline. When the annealing times increased from 60-180 min, the intensity of CuO diffraction peaks increased. It suggested that the films were well crystallized. The dominant XRD peak, corresponded to (111) plane of CuO. For annealing time of 180 min another peak at $2\theta = 44.6^\circ$ belonged to Cu_2O (200). By annealing the films for

240 min (sample Q4), the intensity of CuO diffraction peaks decreased. Similar results were obtained earlier by Figueriedo et al [9]. The similarities and differences of the results can be summarized as follow: In both of works, the copper oxide films were obtained by post-annealing of Cu thin films in air environment. In our case the annealing times effect on the properties of copper oxide films was studied while those authors investigated the different properties of the copper oxide films as a annealing temperature. Those authors showed that the cubic Cu phase changes into single cubic Cu_2O phase for the annealing between 200 - 300 °C whereas the

films annealed between 350 - 450 °C shows a single monoclinic CuO. In our work, the CuO phase was observed in annealing temperature of 400 °C for all the annealing times.

The average crystalline size and microstrain of the prepared films have been obtained from the following Scherrer relations [12]:

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

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 $\text{CuK}\alpha$) and θ is the Bragg's angle. The structural parameters of CuO films can be observed in table 2. According to results of table 2, we can observe that all the cupric oxide films are nano crystalline and the average crystalline size increases from 9.3-14.9 nm with annealing time. Also, the annealing time augmentation leads to increase of average crystal size and decrease of microstrain. The increase in crystallite size is related to decrease in strain.

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

Sample	Phase composition	Miller indices (hkl)	Diffraction Angle 2 (deg.)	Average Crystalline size (nm)	Micro strain
Sample Q1	CuO	(111)	35.57	13.6	8.29×10^{-3}
		$(\bar{1}\bar{1}\bar{1})$	38.75	12.2	8.56×10^{-3}
Sample Q2	CuO	(111)	35.55	14.9	7.62×10^{-3}
		$(\bar{1}\bar{1}\bar{1})$	38.75	13.6	7.69×10^{-3}
Sample Q3	CuO	(111)	35.58	14.4	7.88×10^{-3}
		$(\bar{1}\bar{1}\bar{1})$	38.46	9.3	11.25×10^{-3}
Sample Q4	CuO	(111)	35.57	13.2	8.56×10^{-3}
		$(\bar{1}\bar{1}\bar{1})$	38.72	12.9	8.94×10^{-3}

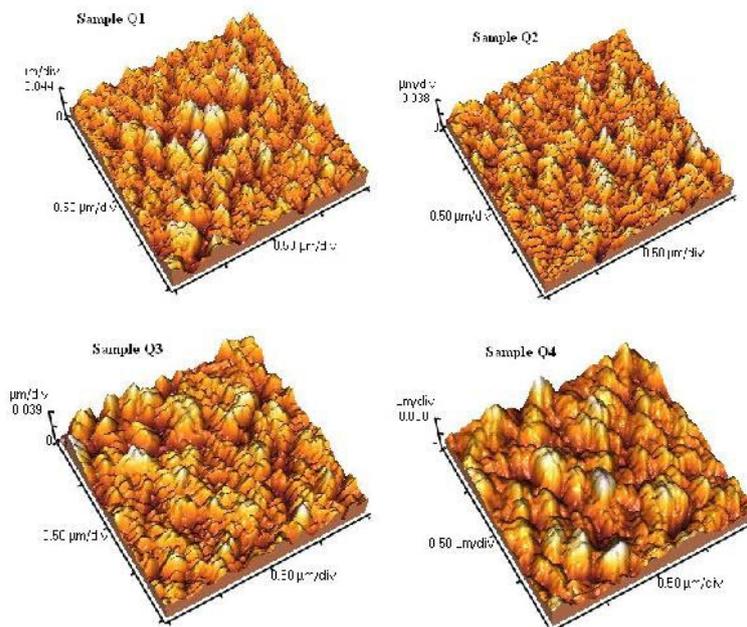


Figure 2. 3D AFM images of the cupric oxide films annealed at different annealing times: Q1; 60min Q2; 120min, Q3; 180, and Q4; 240min.

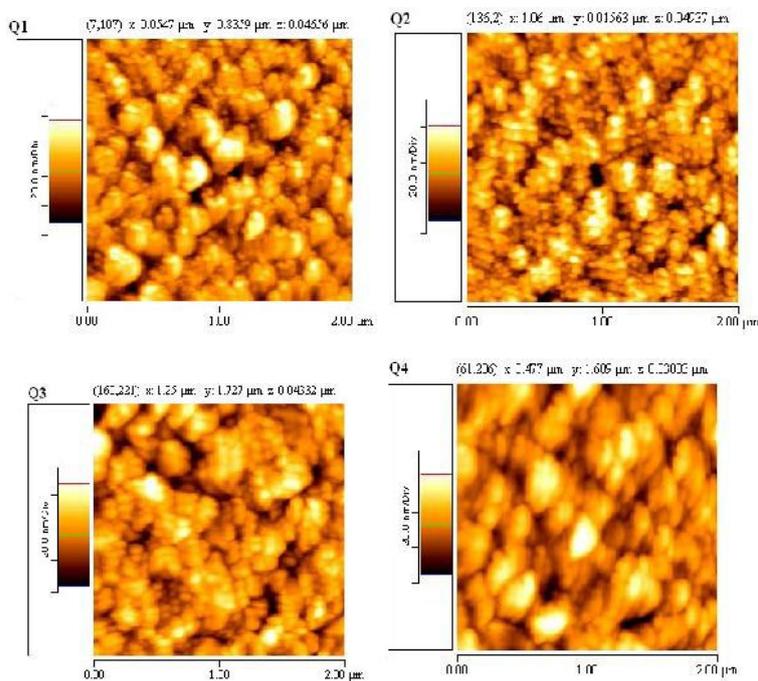


Figure 3. 2D AFM images of the cupric oxide films annealed at different annealing times: Q1; 60min Q2; 120min, Q3; 180, and Q4; 240min.

Surface morphology of the prepared films is examined with an atomic force microscopy in contact mode. Scans $2 \times 2 \mu\text{m}^2$ were recorded for all samples. Figures 2 and 3 exhibit the AFM images of copper oxide films formed at different annealing times. The RMS surface roughness of as-deposited Cu films was 3.81 nm, which is increased to 11.62 nm after annealing for 60 min due to the conversion of Cu to CuO. By increasing the annealing times to 120 min the RMS roughness decreased to 8.59 nm because of increasing the diffusion of particles. With increasing the annealing times to 180 min the RMS roughness again increased to 10.48 nm for sample Q3. Sample Q4 shows

the RMS roughness of 9.71 nm. The change in surface roughness of the annealed films is due to the grain growth in the films.

On the other hand the average grain size measured by two dimensional AFM images was varied between 46 nm and 83 nm that are much larger than that calculated by XRD. This is due to the fact that AFM measurements results from agglomeration of the particles whereas XRD gives an average crystallite size. The plot of film surface roughness versus annealing time is obtained in Figure 4. It is observed that the root mean square (RMS) roughness and average roughness have similar trends.

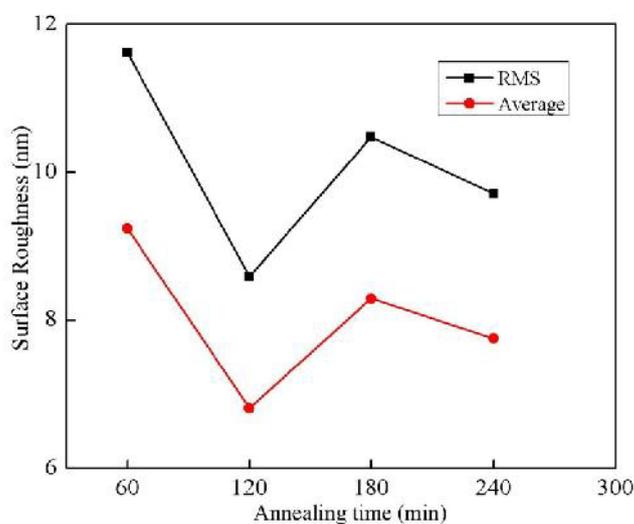


Figure 4. The surface roughness of CuO films versus annealing time.

Conclusion

The nanocrystalline CuO thin films were prepared by post-annealing of copper thin films deposited on quartz substrates using DC magnetron sputtering. The annealing

time was varied between 60-240 min and the influence of annealing times on nanostructural and morphological properties of the films was investigated by different analysis. The XRD results confirmed that the cubic Cu phase of

as-deposited films changes into CuO phase by annealing. Also, the films crystallinity is improved by annealing times enhancement up to 180 min. The AFM results showed that the films exhibited different morphology and grain sizes in the range of 46nm and 83 nm depending on annealing time. Minimum surface roughness and microstrain were observed for the film annealed for 120 min.

Acknowledgments

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