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Annealing temperature effect on nanostructure and phase transition of copper oxide thin films

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ABSTRACT

This paper addresses the annealing temperature effect on nanostructure and phase transition of copper oxide thin films, deposited by PVD method on glass substrate (at 110 nm thickness) and post annealed at different temperatures (200-400°C) with a flow of 1 cm^3s^{-1} Oxygen. The X-ray diffraction (XRD) was employed for crystallographic and phase analyses, while atomic force microscopy (AFM) was used for morphology investigation. The results showed (CuO_2) cuprite phase for samples annealed at 200 and 250°C and (CuO) tenorite phase for samples annealed at 350 and 400°C, while sample annealed at 300°C had a complex phases (CuO_2 and CuO). The size of the grains increased, but roughness increased and then decreased by increasing of annealing temperature. Furthermore, calculated activation energy from grain diameter (at arrhenius plot) was 0.54 eV.

Keywords: *Thin film; Copper Oxide; Annealing temperature; Nanostructure and phase transition.*

INTRODUCTION

Copper oxide can exist in two crystalline phase's viz. cuprous oxide or cuprite (Cu_2O) and cupric oxide or tenorite (CuO). Both these materials are semiconductors with specific applications in solar cells [1], magnetic devices [2] and catalysis [3], and they have radiation properties similar to those of an ideal black body [2]. Cu_2O is a p-type semiconductor of cubic structure with a direct band gap of 2.1-2.6 eV [4]. Its outstanding excitonic properties including a large exciton binding energy (~ 140 MeV) have been the target of much fundamental research during the past decades [5]. Cu_2O layers on semiconductor and insulator substrates have interesting properties for alternative photovoltaic devices and photoelectrodes in high-efficiency photoelectrochemical cells [6] and different techniques have been explored to fabricate Cu_2O layers with device quality electronic properties [7].

CuO is also a p-type semiconductor having monoclinic structure and an indirect band gap of 1.9-2.1 eV[4]. However, CuO is also reported to possess n-type conductivity. This material is widely used in applications such as gas sensors [1], magnetic storage media [8], solar energy transformation [9], varistors and catalysis [10], too.

Many researchers have reported on obtaining copper oxide thin films, using different methods such as Chemical vapour deposition and post annealing [1], e-beam evaporation and post annealing [11 and 12], pulsed magnetron sputtering [13], sol-gel-like dip technique and post annealing [14], glancing-angle deposition and post annealing [15] and so on. Among the modern methods of thin film preparation, we have selected physical vapor deposition (resistive evaporation) and post annealing for flexibility and simplification in this study, and have investigated the influence of annealing temperature on nanostructure, phase transition and the morphology of copper oxide thin films.

EXPERIMENTAL

Copper films were deposited on glass substrates (20 × 20 × 1 mm cut from microscope slide) by resistive evaporation from tungsten boats at room temperature. The purity of copper was 99.98%. An Edwards (Edwards E19 A3) coating plant was used. Evaporation was performed at one step, and 10 Cu films were produced at 110 nm thickness. Film thickness and deposition rate were measured using a quartz crystal deposition rate controller (Sigma Instruments, SQM- 160, USA) positioned close to the substrate. Deposition angle and deposition rate were 14° and 2 Å/s, while base pressure was 1.5×10^{-6} mbar. Post-annealing of the Cu/glass films were performed at five different temperatures of 200, 250, 300, 350 and 400 °C in oxygen environment with a flow rate of 1.0 $cm^3\ s^{-1}$ for 30 min. Prior to deposition, all glass substrates were ultrasonically cleaned in heated acetone then ethanol. The surface roughness of the substrates was measured by a Talysurf profilometer. The rms substrate roughness R_q was 0.3 nm. The nanostructure of these films were obtained using a Philips XRD X'pert MPD Diffractometer (Cu K_α radiation) with a step size of 0.02 and count time of 1 s per step, while the surface physical morphology and roughness was obtained by means of AFM (Park Scientific) analysis.

RESULTS AND DISCUSSION

X-ray Diffraction

The XRD patterns for the unheated and annealed samples are shown in Figure 1. X-ray diffraction pattern of as deposited sample shows one pick that can be attributed to Cu(111) crystallographic orientation (with reference to JCPDS Card No: 04-0836, 2θ= 43.297°, system: cubic and space group: 225). At 200°C annealed sample X-ray pattern, another pick is observed that can be related to Cu_2O (111) crystallographic orientation (with reference to JCPDS Card No: 05-0667, 2θ= 36.419 °, system: cubic and space group: 224). By increasing of annealing temperature to 250 °C, the intensity of Cu_2O(111) pick was increased and Cu_2O or cuprous oxide phase was amplified. But by annealing at 300 °C the intensity of this pick (Cu_2O(111)) decreased, while two other picks were detected that can be attributed to crystallographic orientations CuO($\bar{1}$11) and CuO(111) (with reference to JCPDS Cards No: 45-0937, 2θ= 35.496 °,and 48-1548, 2θ= 38.709 °, system: monoclinic and space group: 15). A similar kind of mixed Cu_2O–CuO phase for the films produced by e-beam and post annealed at 300 °C is reported earlier [12].

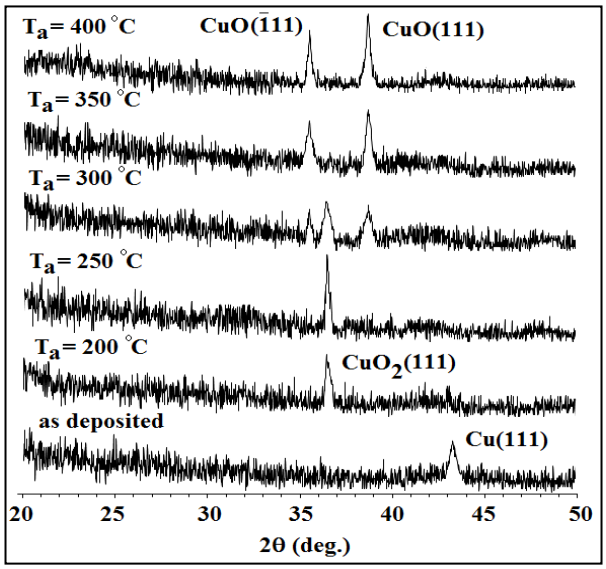

Fig. 1. XRD patterns of as deposited and all annealed samples.

In X-ray diffraction pattern of 350 °C annealed sample, it was observed that the $Cu_2O(111)$ pick was omitted and the intensity of $CuO(\bar{1}11)$ and CuO(111) picks were increased, while increasing of annealing temperature to 400 °C caused increasing of the intensity of these picks.

On the other hand, these results show formation of Cu_2O or cuprous oxide phase for cu thin films annealed at 200 and 250 °C, CuO or cupric oxide phase for cu thin films annealed at 350 and 400 °C and mixed CuO_2 & CuO phases for samples annealed at 300 °C.

Atomic force microscopy

2D AFM pictures for selected samples, unheated and annealed at 200, 300 and 400 ˚C samples are shown in Figure 2a-d, while grain size calculated from 2D AFM images, using JMicrovision Code for all samples are given in column 6 of Table 1 and Figure 2. The results show the increasing of annealing temperature caused the increasing of the size of the grains. This behavior can be explained as follows:

The mobility and the migration increase by increasing of annealing temperature resulting in the large grains. The rms and average roughness of films obtained AFM analysis (Figure 3 and columns 7& 8 of Table 1) show a rough Surface for as deposited film, while the roughness was increased by increasing of annealing temperature to 200°C. At 250°C annealing temperature roughness reaches the maximum of value. But roughness was decreased by increasing of annealing temperature, so that it reaches minimum of value at 400°C.

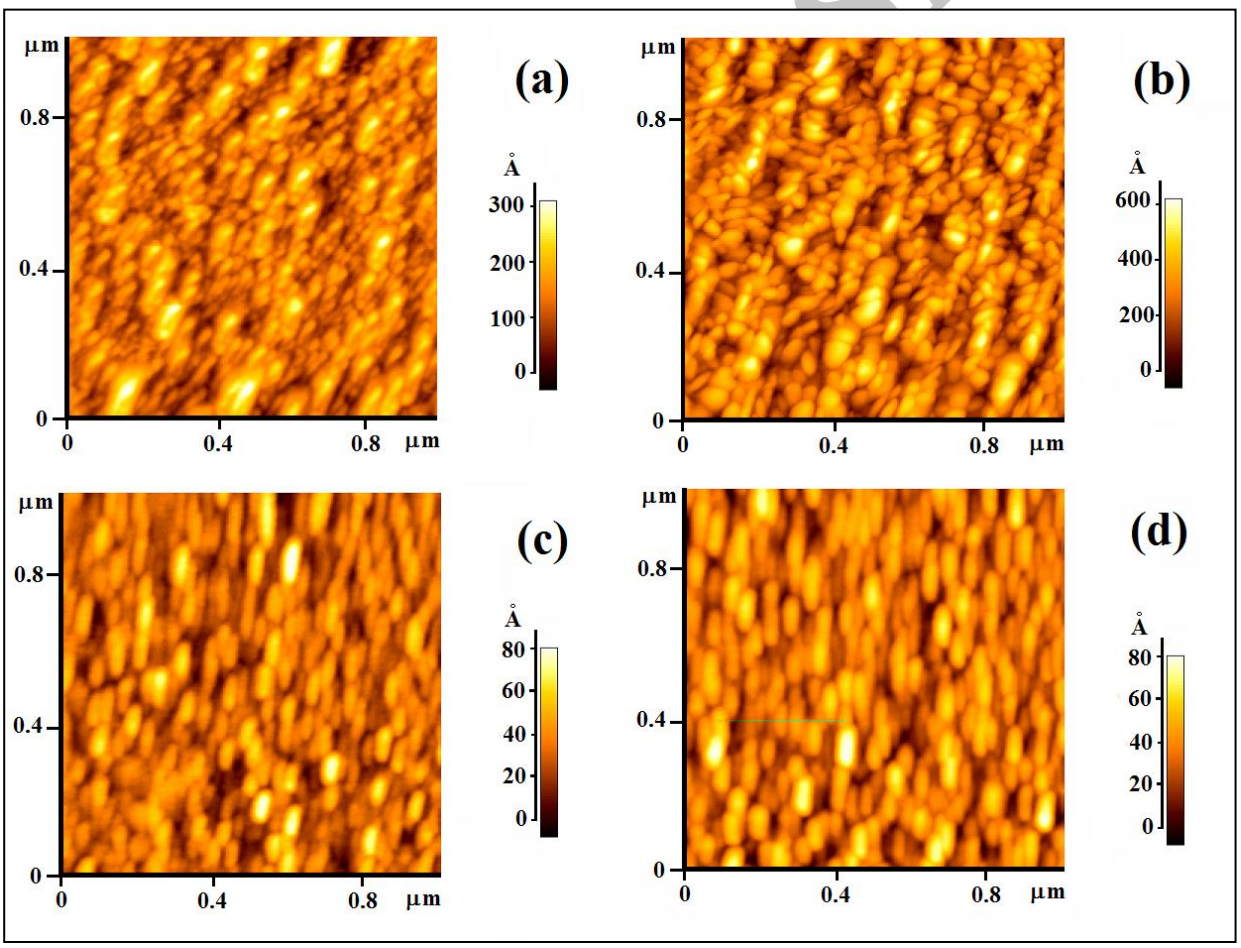

Fig. 2. 2D AFM pictures of selected samples, a) unheated, b) annealed at 200˚C, c) annealed at 300˚C and d) annealed at 400˚C.

Table 1. Results of XRD and AFM analyses.

Information of Samples		XRD analysis			AFM analysis		
No.	T_a (°C)	Phase	(hkl)	pick position (2θ)	Grain diameter (nm)	R_{ms} (Å)	R_{ave} (Å)
I	As deposited	Cu	(111)	43.29	14	81.4	69.2
II	200	CuO_2	(111)	36.47	18.5	93.0	73.7
III	250	CuO_2	(111)	36.49	27.1	98.0	82.1
IV	300	CuO_2/CuO	(-111)/(111)/ (111)	35.55/36.49/38.73	33.4	40.8	32.2
V	350	CuO	(-111)/(111)	35.57/38.73	41.7	16.4	11.3
VI	400	CuO	(-111)/(111)	35.57/38.71	43.1	11.4	9.3

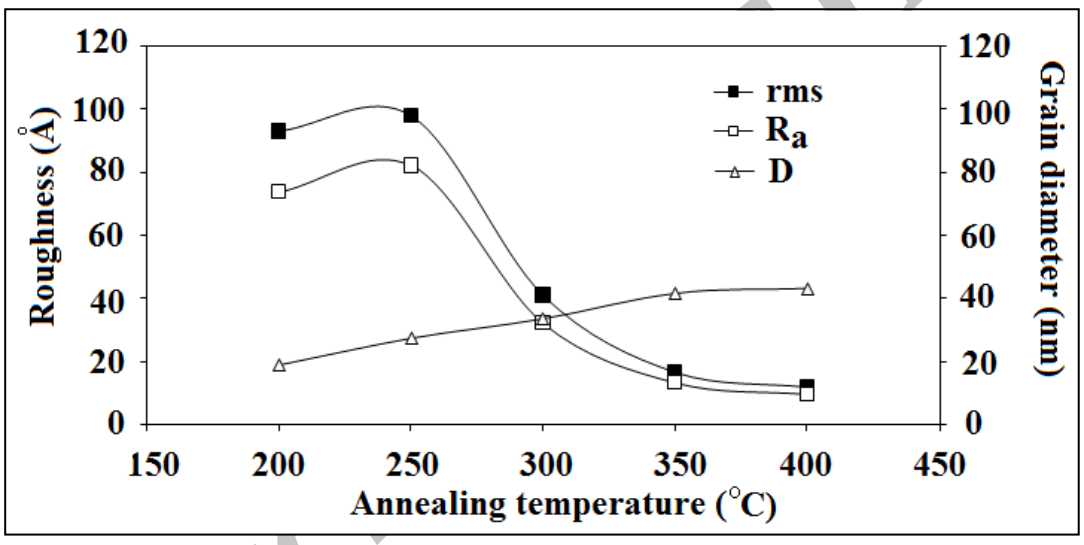

Fig. 3. Variation of roughness and grain diameter calculated from 2D AFM for annealed samples as function of annealing temperature.

3D AFM pictures of selected samples (unheated and annealed at 200, 300 and 400 °C samples) are shown in Figure 4(a-d). In this image and Figure 2, a binary feature (formed of small and large grains) was observed at surfaces of unheated and annealed samples at 200 and 250 °C, while the size of the grains is approximately the same and the grains are distributed uniformly at annealed samples at high temperature (300, 350 and 400 °C) that can be attributed to the increases of surface energy at high temperatures. In addition, this result can be explained low roughness of samples annealed at high temperatures.

Figure 5 shows the variation of grains diameter of samples in the form of Arrhenius plot. Linear fits were performed in order to determine the apparent activation energy E_a.Using of the following equation:

$$D = \exp\left(-\frac{E_a}{K_B T}\right)$$

If grains diameter is plotted as 1000/T, tangent of fitted line equals to activation energy. The calculated activation energy is E_a=0.54 (eV).

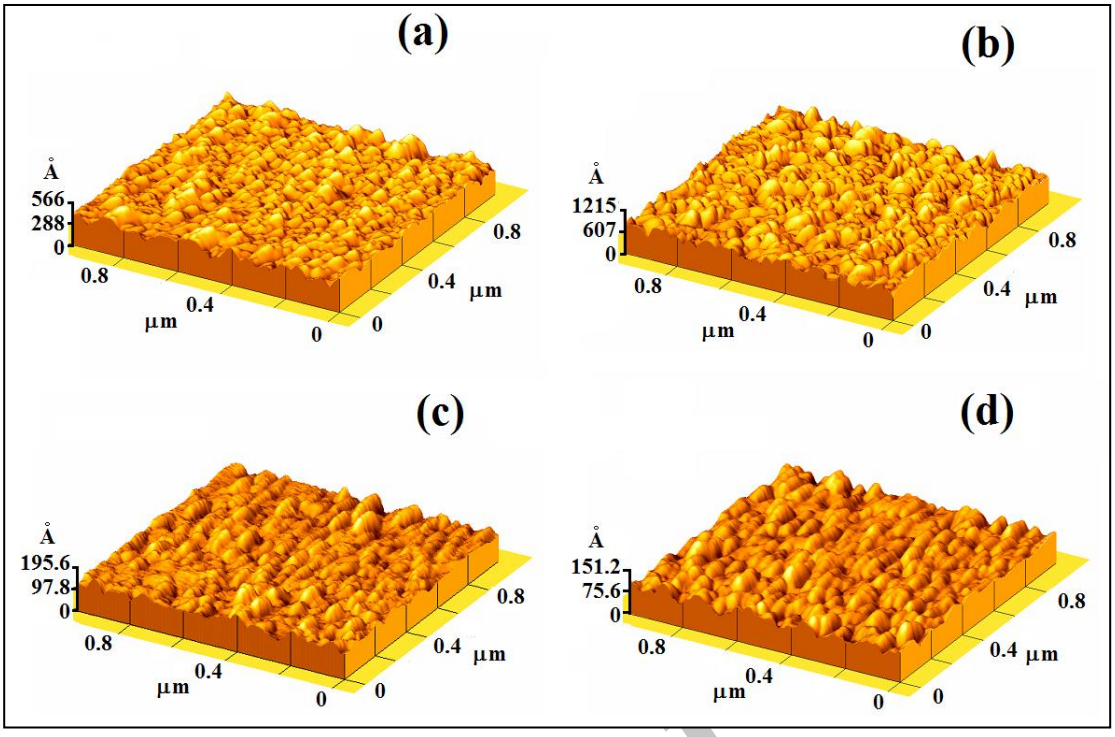

Fig. 4. 3D AFM pictures of selected samples, a) unheated, b) annealed at 200˚C, c) annealed at 300˚C and d) annealed at 400˚C.

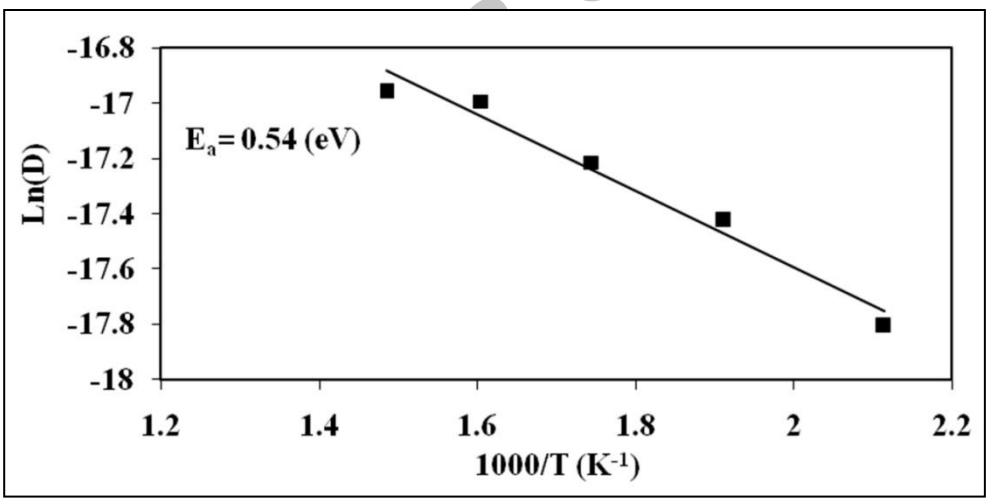

Fig. 5. Arrhenius plot of grain sizes for all samples.

CONCLUSION

Copper thin films at 110 nm thickness were produced by resistive evaporation on glass substrate and post annealed at different temperature (200, 250, 300, 350 and 400 °C) in oxygen environment with a flow rate of 1.0 $cm^3 s^{-1}$ for 60 min. The crystallographic orientation and phase transition were studied using X-ray diffraction (XRD), while morphology, roughness and grain size were investigated by atomic force microscopy (AFM). The XRD results showed, CuO_2 phase with cubic structure for annealed samples at 200 and 250 °C, while the samples annealed at 350 and 400 °C have CuO phase with monoclinic structure. The sample annealed at 300 °C had a mixed CuO_2/CuO

phase, too. The results obtained of AFM showed the increasing of annealing temperature caused the increasing of the size of the grains. The surface roughness increases by the increasing of annealing temperature and then decreases by the increasing of annealing temperature of 250 to 400 °C. Activation energy calculated in the form of Arrhenius plot is E_a=0.54 (eV).

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