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Effect of deposition oxygen pressure on the properties of cuprous oxide thin films

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Abstract. This study presents the effect of the oxygen pressure during deposition on the properties of cuprous oxide (Cu_2O) thin films. The Cu_2O is a p-type semiconductor material with a cubic crystallinity structure that has potential applications in solar cells, photo catalysis, gas sensing, superconductor, hydrogen production and thermoelectric generators. Different thicknesses of Cu_2O films and different surface parameters are obtained if the oxygen pressure is modified during the depositions process. The samples were characterized by atomic force microscopy technique (AFM) and the results clearly demonstrate that Cu_2O thin films properties are improved if the oxygen pressure during deposition decreases. The thickness of films and the surface parameters were measured using the AFM non-contact mode. The thickness and the surfaces roughness increase if the oxygen pressure during deposition decreases. This effect is based on obtaining higher particle sizes at low pressures. The modulus of elasticity and the hardness dependence on the deposition oxygen pressure is monitored by nanoindentation using a diamond Berkovich tip. The materials mechanical properties increase significantly if the oxygen pressure during deposition decreases, respectively. The results are useful to micro and nano- systems designers to fabricate reliable structures based on Cu_2O thin films.

1. Introduction

In this study, copper (Cu) metal was used to deposit cuprous oxide (Cu_2O) thin films for thermoelectrical applications. Cu_2O thin films were studied as low-cost power generation because they are nontoxic materials and their deposition process is harmless [1-3]. Cu_2O is typical of the oldest p-type semiconducting material and it is capable of absorbing thermal energy and transform in electricity useful in thermoelectrical generators. The raw materials for making Cu_2O thin films are readily available and the oldest semiconducting materials known to solid-state physicists and using them to fabricate thermoelectrical cells will be low-cost.

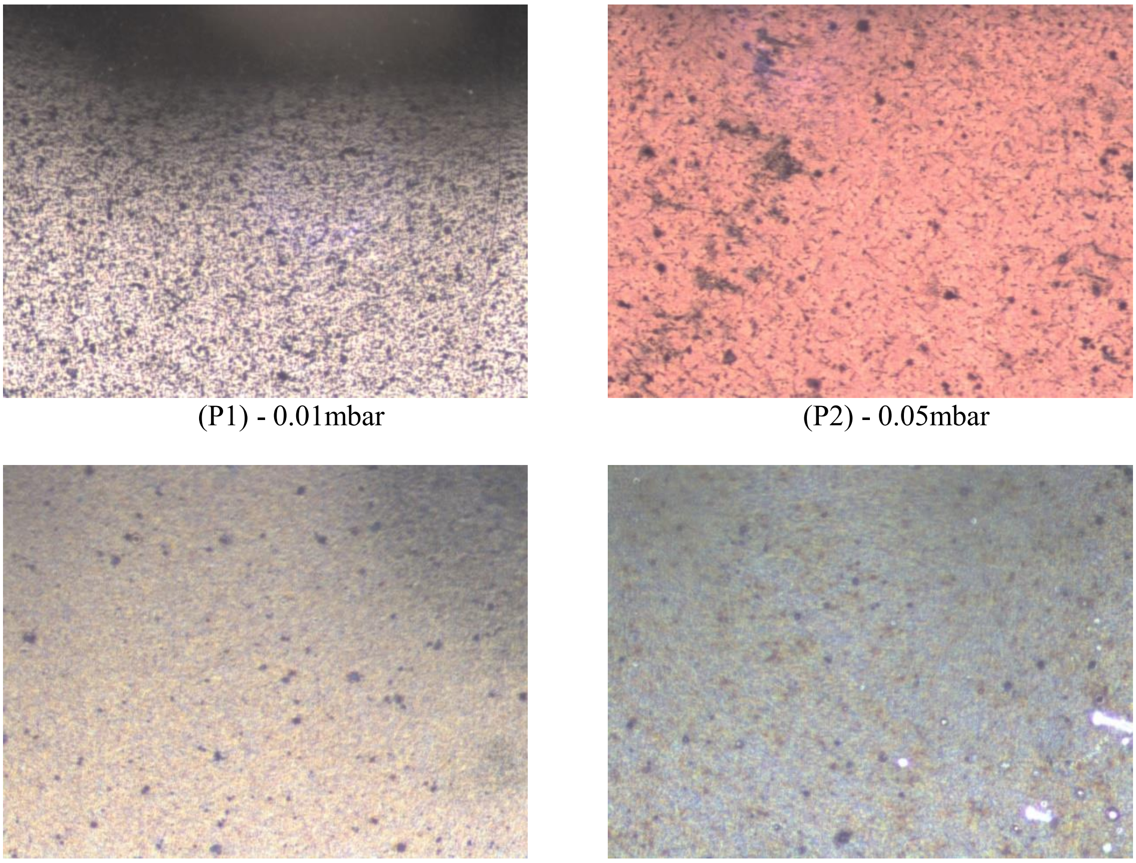
The temperature and oxygen flow rate during deposition are the main parameters with influence on the crystalline phase of copper oxide thin films with effect on the material properties [1]. The microstructural and nanomechanical properties of Cu_2O thin films also are modified if the growth temperature is changed during deposition process. The hardness of Cu_2O decreases with increasing the growth temperature [2]. The other important parameter with influence on the properties of Cu_2O thin films is the deposition time [4]. One way to control the thicknesses of thin films is by changing the oxygen pressure during deposition as presented in this paper. The O_2 flow ratio affects the phase of deposited copper oxide thin films and also their surface morphologies [1].

The Cu–O system has two stable oxides as cupric oxide (CuO) and cuprous oxide (Cu_2O). Each of them has different crystal structures and properties. However cuprous oxide has much better crystallinity, bigger grains and direct band gap structure and has being frequently studied as absorber for low cost solar cell [5-8].

First, this paper presents the deposition process of investigated Cu_2O thin films on MgO/Si substrate and the optical images of samples. Secondly, the experimental characterization methodology is described and the obtained results of films thickness, surfaces characteristics and the materials mechanical properties. The nanoindentation technique was used to determine the dependence of mechanical properties of Cu_2O thin films (hardness and modulus of elasticity) on the deposition oxygen pressure. The results and their interpretations are included at the end of paper as well as the conclusions.

2. Samples description

The electrodeposition of Cu_2O on MgO/Si substrate was carried out at different oxygen pressure namely 0.01mbar, 0.05mbar, 0.1mbar and 0.2mbar. The Cu_2O on MgO/Si thin films were deposited by Pulsed Laser Deposition (PLD) technique. The PLD system is equipped with a laser excimer (KrF, λ=248nm, pulse duration of 20ns). The target to substrate distance is set to 55mm. The Cu_2O films were deposited on an MgO buffer layer on Si (100). The MgO buffer layer was deposited from an MgO target in two-step deposition procedure. Laser fluency was set to 2.3J/cm^2 with a frequency of 1Hz. The first step was carried out in vacuum (10^{-6} mbar), using 180 pulses and the substrate temperature was set to 550 °C. In the second step oxygen was introduced into the deposition chamber, at a pressure of 0.1mbar, and deposition was made with 1800 pulses at a substrate temperature of 650 °C. On top of this layer Cu_2O was deposited at a temperature of 700 °C, and various oxygen pressures in the deposition chamber. The laser parameters used for the deposition were: 2.3J/ cm^2 fluency, frequency of 2Hz, and the deposition time were set for 1 hour. The oxygen depositions pressures were 0.01 mbar; 0.05 mbar; 0.1 mbar and 0.2 mbar. The optical images of obtained Cu_2O thin films are presented in figure 1.



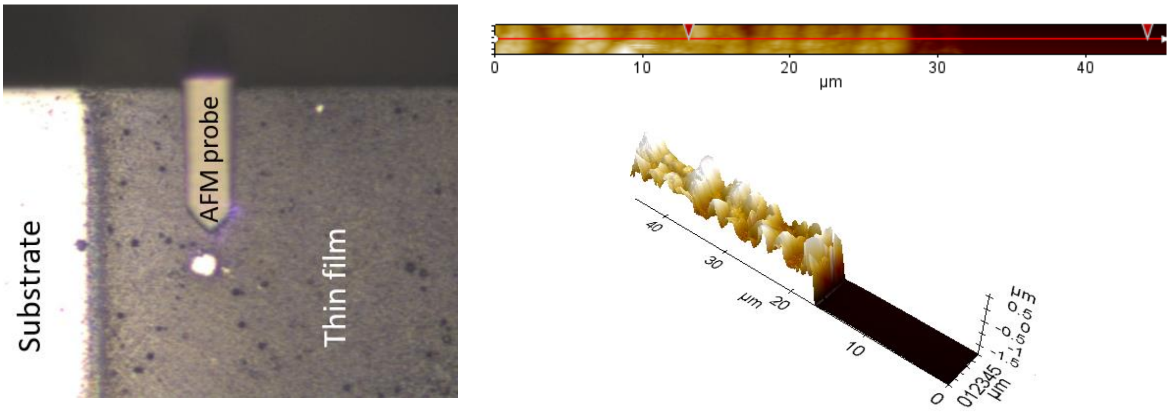
(P1) - 0.01mbar (P2) - 0.05mbar

(P3) - 0.1mbar (P4) - 0.2mbar

Figure 1. Optical images of deposited Cu_2O thin films.

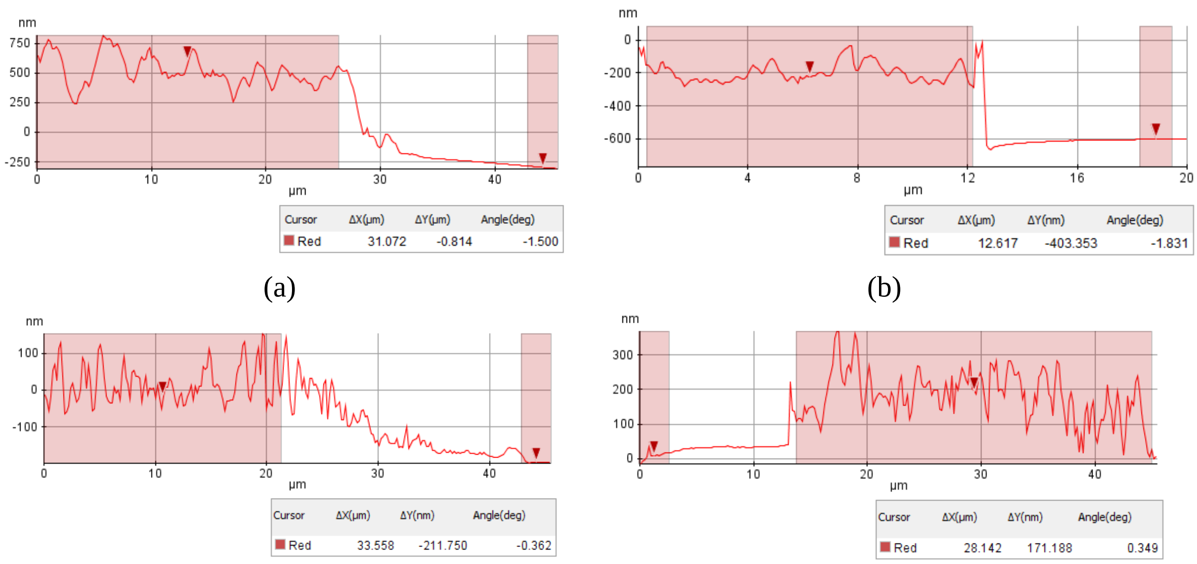
3. Experimental procedure

The scope of experimental tests is to determine the effect of deposition O_2 pressure on properties of investigated Cu_2O thin films. The tests are performed using an atomic force microscope XE70 with a nanoindentation module. The testing temperature in cleanroom was kept constant at 20°C and the relative humidity was 40%RH. The tapping mode of AFM was used to scan the Cu_2O thin films. After scanning the variation of the roughness parameters as a function of the deposition pressure were determined as well as the films thickness. In order to estimate the film's thickness the AFM tip is positioned at the edge of the deposited thin films. The scanning area includes the investigated thin film and the substrate (figure 2a). The selected scanning area is 5µm × 45µm (figure 2b). The cross-section of the scanning area provides information about the film thickness ΔY(nm), as the difference between the substrate and the bottom surface of films (difference between cursors from figure 3). The measurements were performed in different location of the edges of thin films and the results confirm the film uniformity during the deposition process.



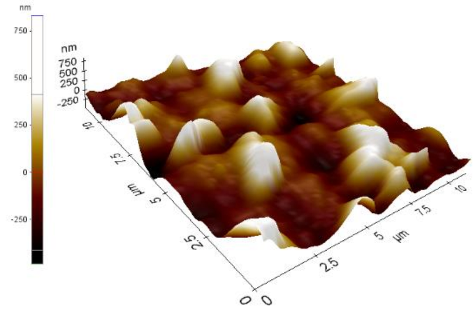
(a) (b)

Figure 2. Thickness measurement of Cu_2O thin films: (a) scanning of the border area between the substrate and the deposited film; (b) the selected scanning area (5µm × 45µm) and 3D image.



(a) (b) (c) (d)

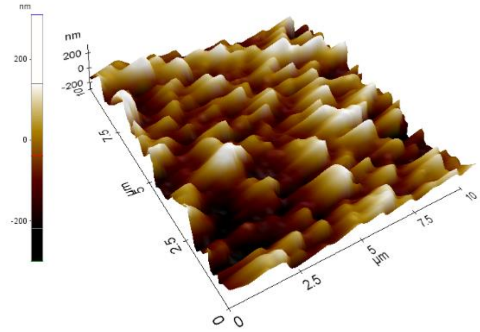
Figure 3. Thickness measurements of Cu_2O/MgO/Si for different oxygen pressure during deposition process: (a) 0.01mbar, (b) 0.05mbar, (c) 0.1mbar, (d) 0.2mbar.



Statistics

Region	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Red	-485.221	831.042	172.910	0.000	1316.263	211.402	161.420	1269.857	-1.176	4.386

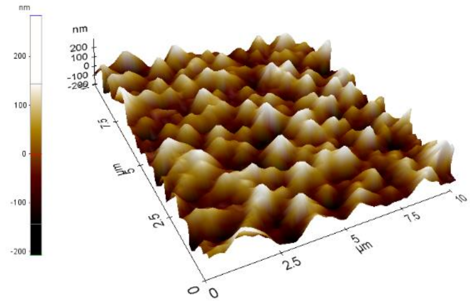
(a)



Statistics

Region	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Red	-299.290	310.037	5.373	-39.495	609.328	91.430	73.603	557.340	-0.214	2.934

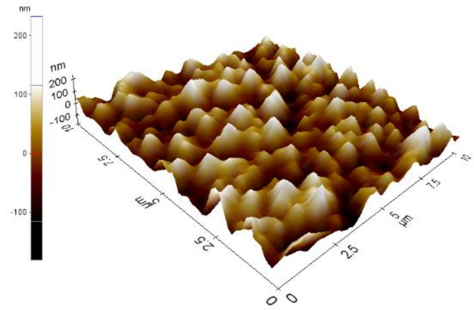
(b)



Statistics

Region	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Red	-207.324	283.617	38.146	0.000	490.941	73.338	59.650	426.271	-0.310	2.801

(c)



Statistics

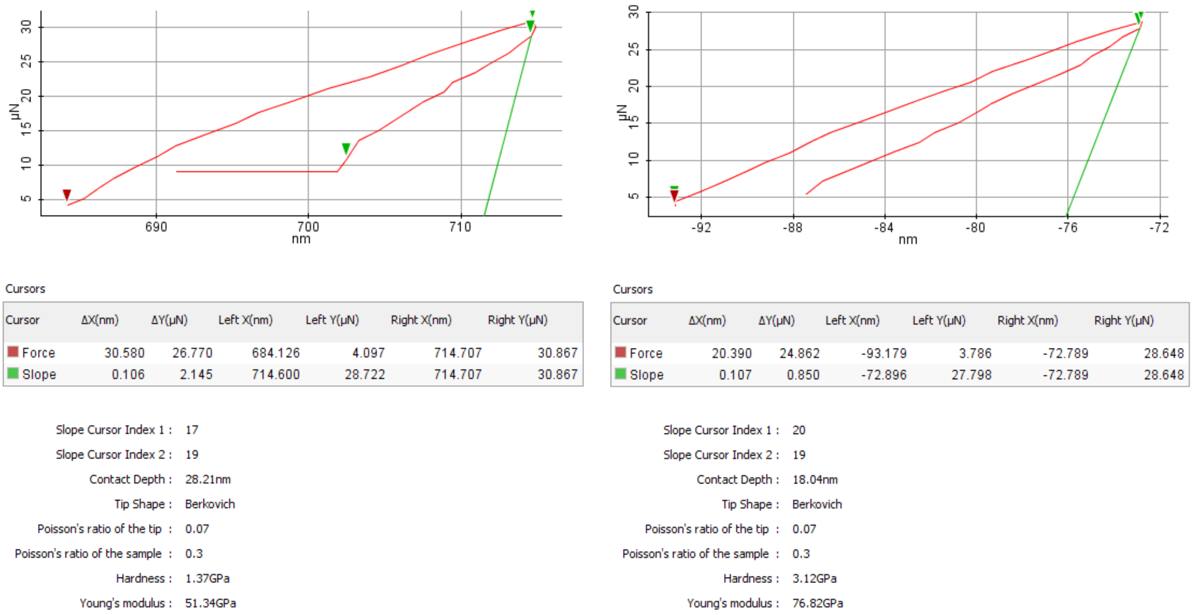
Region	Min(nm)	Max(nm)	Mid(nm)	Mean(nm)	Rpv(nm)	Rq(nm)	Ra(nm)	Rz(nm)	Rsk	Rku
Red	-180.785	232.549	25.882	0.000	413.334	59.022	47.576	360.149	-0.357	2.978

(d)

Figure 4. Roughness parameters of investigated thin films deposited at different O_2 pressure: (a) 0.01mbar, (b) 0.05mbar, (c) 0.1mbar, (d) 0.2mbar.

After selection of the scanning surfaces the thickness values of thin films are indicated by the XEI interpretation software. The difference between cursors from figure 3 gives information about the Cu_2O thickness. As the O_2 pressure increases during the deposition process, keeping constants the other deposition parameters, the thickness of thin films decreases, respectively. Using the same tapping mode of the AFM the surfaces parameters of investigated thin films deposited at different O_2 pressure were measured. The 3D images of Cu_2O thin films and the roughness parameters are presented in figure 4.

For instance, the precise determination of modulus of elasticity for samples represents a crucial point for calculating shear stress. To approach the modulus of elasticity the load-displacement curves obtained by nanoindentation have been interpreted using the Oliver & Pharr contact model. The Poisson's ratios of the films in the interpretations on the experiment data are taken as 0.3, since literature has shown that the Poisson's ratio has a minor effect on the indentation results. Using the nanoindentation module of AFM and a Berkovich diamond tip TD23838 with a stiffness of 272N/m, the measurements of hardness and modulus of elasticity were performed for investigated thin films deposited at different oxygen pressure. The set point was 5μN and the loading force 40μN. Figure 5 presents the results of the indentation depth, hardness and modulus of elasticity under applied force in the case of the Cu_2O deposited at 0.2mbar (figure 5a) and in the case of Cu_2O obtained at 0.01mbar (figure 5b).



(a) (b)

Figure 5. Nanoindentation of the Cu_2O thin films deposited at different O_2 pressure: (a) 0.2mbar and (b) 0.01mbar.

The indentation was performed in 4 different points for each sample and the average results were considered. Conforming to figure 5, it can be observed that the hardness and modulus of elasticity increase if the oxygen pressure decreases during the deposition process.

4. Results and discussions

By modifying the oxygen pressure during the deposition process, keeping constant the other parameters, the characteristics of Cu_2O thin films can be changed. The experimental tests developed in this paper were directed toward:

- Determination of the effect of the deposition O_2 pressure on the thickness of Cu_2O thin films,
- Investigation of the deposition O_2 pressure on the surface parameters,
- Measurement of the Cu_2O thin films properties (hardness and modulus of elasticity).

The tests were done using the AFM technique. The tapping mode was applied to scan the thin films in order to measure the thickness and the roughness parameters. After, the nanoindentation mode of AFM was used to determine the materials mechanical properties. Table 1 presents the experimental results obtained for the investigated thin films. It can be observed that, as the oxygen pressure decreases toward vacuum, the thickness of thin films increases as well as the R_a roughness. Moreover, we can affirm that the modulus of elasticity and hardness are improved if the oxygen pressure decreases during the deposition process.

Table 1. Experimental results of Cu_2O thin films as a function of the deposition oxygen pressure.

Deposition pressure [mbar]	Investigated parameters*			
	h [nm]	R_a [nm]	E [GPa]	H [GPa]
0.2	171.1	47.57	51	1.47
0.1	211.7	59.65	59.6	1.84
0.05	403.3	73.60	64.3	2.45
0.01	814	161.42	76	3.59

* h - thickness, R_a - average roughness, E - modulus of elasticity, H - hardness.

5. Conclusions

The effect of oxygen pressure during deposition on the material properties and surface characteristics of Cu_2O thin films was investigated and presented in this paper. This material can be implemented in thermoelectrical application. The scope of research work was to identify the influence of the deposition parameter on the characteristics of thin films in order to obtain reliable systems. After deposition process the samples were experimentally investigated using the atomic force microscopy technique.

The modification of oxygen pressure during deposition process change the properties of Cu_2O thin films. Moreover, as the deposition pressure decreases, the thickness and the roughness increase. This effect is based on obtaining higher particle sizes at low pressures. The hardness and modulus of elasticity increase as the deposition pressure decreases, respectively.

Acknowledgments

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