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CuO FILMS OBTAINED BY OXIDATION OF Cu LAYERS DEPOSITED BY THE PVD PROCESS - MAGNETRON SPUTTERING

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ABSTRACT

The experimental research carried out and described in this paper aimed to obtain thin films from copper oxides and their characterization from the structural point of view and the optical and electrical properties. To obtain the copper films, a PVD spray deposition system was used, consisting of a vacuum chamber with a capacity of 2 liters, a planar magnetron with ferrite magnets (ϕ40x22x9) neodymium (ϕ15x8), a vacuum pump with sliding blades, a variable source of direct current of voltage 100 - 600 volts. The atmosphere used for plasma maintenance during deposition was argon rarefied in a pressure range between $3 \cdot 10^{-2}$ - $8 \cdot 10^{-3}$ mbar. The deposits were made on glass plates. The films thus obtained were subsequently subjected to oxidation at temperatures of 200, 300 and 450 °C. It was found that the transparency of the films increases with the oxidation temperature from $1.464 * 10^{-4}$ for 200 ºC to 0.5 for 450 ºC and the surface electrical resistance also increases from 0.984 Ω for 200 ºC to 3882857,1428 Ω for 450 ºC. With increasing spray power, transparency and surface strength decrease.

KEYWORDS: CuO thin films, d.c. magnetron, electrical and optical properties

1. Introduction

Cupric oxide (CuO) is one of the most studied p-type oxide semiconductors. CuO is a semiconductor with direct transition, with the forbidden band energy in the range of 1.2-1.5 eV, with a monoclinic crystalline structure and characterized by excellent physical and chemical properties. Fig. 1 shows that in the elementary cell of CuO, a copper atom is coordinated by four oxygen atoms in a square plane configuration [1, 2].

The elementary cell contains four CuO units and is indicated by the parallelepiped. The oxygen atoms are light gray and the copper atoms are dark gray. The network parameters of the elementary cell are: a = 4.6837 (5), b = 3.4226 (5), c = 5.1288 (6), α = 90°, β = 99.54 (1) °, γ = 90° [1].

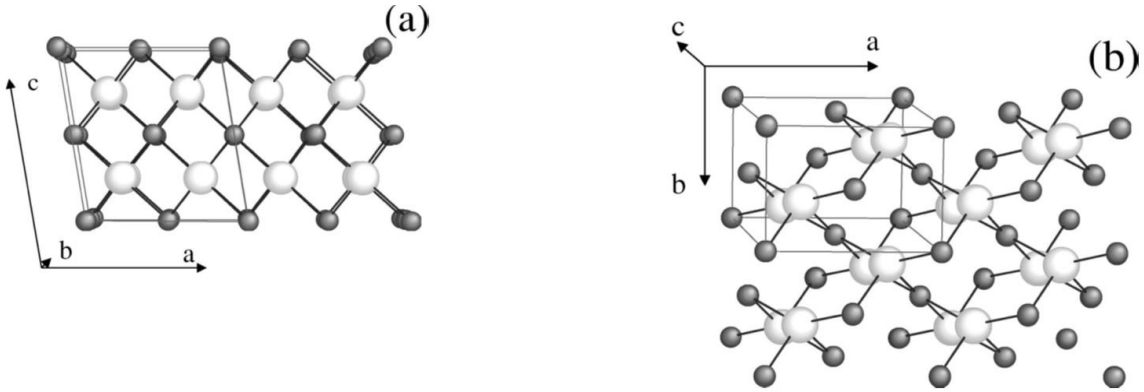

Fig. 1. *The crystalline structure of CuO* [1]

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The CuO nanostructured materials, especially the 1D - CuO nanowires, have enjoyed special attention, being already applied in the field of field effect transistors, photovoltaic cells, field emission Nano devices, as well as in the field of gas sensors [7].

Documentary studies have shown that different nanostructured CuO morphologies can be obtained such as: nanowires, nanowands, nanoplates, nanocureas, nanowhiskers [7].

Cu forms two types of thermodynamically stable oxides CuO and Cu_2O.

Cu_2O (copper oxide) has a cubic crystalline structure and has a forbidden band energy of 2-2.2 eV. It is a p-type semiconductor, which has a variable optical behavior due to stoichiometric deviations arising from the methods and parameters of obtaining.

Cu_2O films have a high transparency, a slightly yellowish appearance and usually absorb at wavelengths below 600 nm, while CuO (cupric oxide) absorbs strongly along the visible spectrum and is black in appearance [2].

CuO films can be obtained by different methods, such as: electrodeposition, sol-gel method, hydrothermal method, pyrolysis with sprayers, chemical vapor deposition, physical vapor deposition (thermal evaporation, sputtering), thermal oxidation.

Physical vapor deposition by magnetron sputtering is used in applications aimed at obtaining layers with multifunctional properties: hard, wear-resistant, with a low coefficient of friction, with high corrosion resistance and with specific optical and electrical properties [2-6].

The method of thermal oxidation is simple, non-polluting, has a low cost and is quite little used. It involves the deposition of a thin layer of Cu by the magnetron-assisted PVD process and its oxidation in an oven at different temperatures.

The research undertaken in this paper aimed to obtain thin copper films using magnetron sputtering process followed by thermal oxidation at different temperatures and their characterization in terms of morphology, electrical and optical properties.

2. Experimental conditions

To obtain the Cu films, a copper plate of 99.9% purity, circular with a diameter of 46.5 mm and a thickness of 1 mm was used as a target.

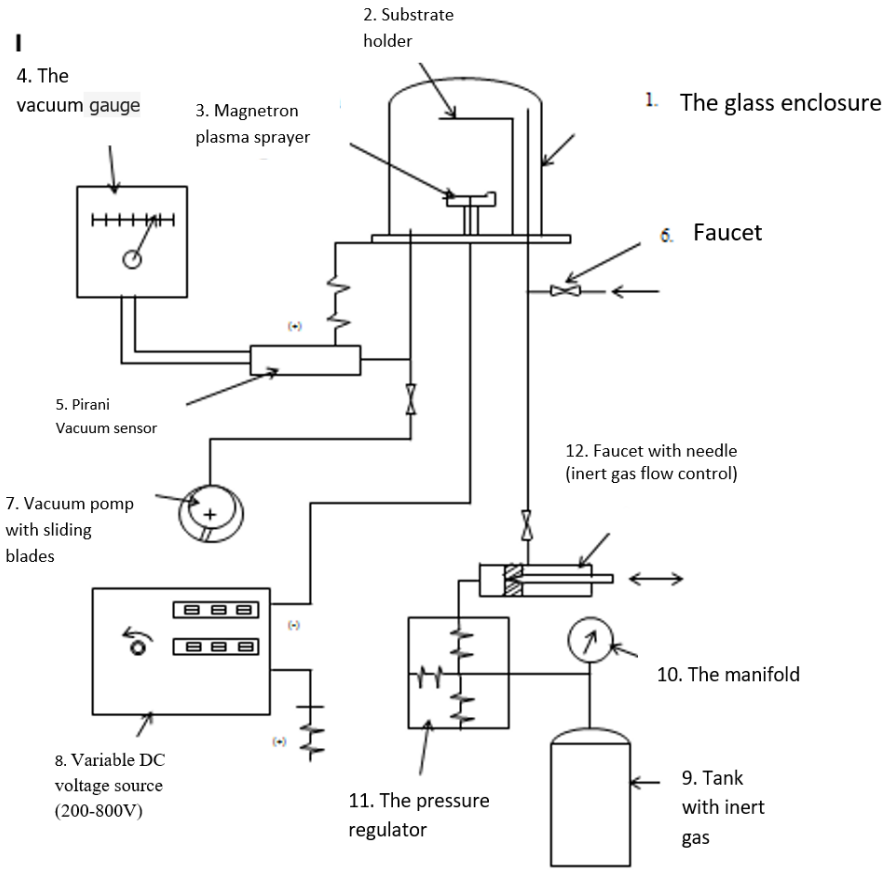

Fig. 2. *Diagram of the PVD magnetron sputtering system*

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We used a PVD spray deposition system, consisting of a vacuum chamber with a capacity of 2 liters, a planar magnetron with ferrite magnets (ϕ 40x22x9) neodymium (ϕ 15x8), a vacuum pump with sliding blades, a variable DC voltage source 100 - 600 volts. The scheme of the installation is shown in Fig. 2.

The deposits were made on glass plates, measuring 76x25x1 mm, which were subjected to an ultrasonic cleaning with acetone and ethanol, and finally they were rinsed with distilled water and then dried.

The installation allows the variation of the magnetron deposition substrate distance between 25 and 90 mm, and the substrate temperature can be monitored with a chromel - alumel thermocouple.

The atmosphere used for plasma maintenance during deposition was argon rarefied in a pressure range between $3 \cdot 10^{-2}$ - $8 \cdot 10^{-3}$ mbar.

A series of regimes shown in Table 1 were used to obtain the films.

Oxidation of the copper films was performed by heating them to 200 °C, 300 °C to 450 °C for 1/2 h.

Before and after oxidation, each sample was subjected to transparency and electrical resistance measurements.

The microscopic analysis of the obtained films was performed using a Neophot 2 optical microscope with computerized data acquisition.

The transparency of the films was determined using an electronic device that uses a light source and a photoreceptor. The light after passing through the deposited film is measured with the help of a photoreceptor and an amplifier and the result is displayed with an analog device.

Table 1. *Regimes for obtaining the copper films*

Sample code	Voltage [V]	Current [mA]	Pressure [mbar]	Substrate temperature [ºC]	Target distance - substrate [mm]	Deposition time [min]
1	485	100	$4x10^{-2}$	70	60	15
2	470	110	$5x10^{-3}$	68	60	10
3	470	100	$5x10^{-3}$	74	85	10
4	470	100	$5x10^{-3}$	60	85	10
5	470	100	$5x10^{-3}$	65	85	10

The electrical properties (resistivity) of the films were determined using the method of the four collinear points (probes), using a laboratory installation. As a principle it consists in injecting the current through two external points and measuring the voltage in two internal points.

In the case of thin layers, the resistivity is calculated with the relation:

$$\rho = \frac{\pi \cdot t}{\ln 2}\left(\frac{U}{I}\right)$$

where: t - layer thickness, U - measured voltage, I - applied current;

$\rho = \frac{\pi \cdot t}{\ln 2}\left(\frac{U}{I}\right)$ - represents the surface resistance of the film.

3. Results and discussions

Following the microscopic analysis, it was observed that the copper films obtained are glossy, have no cracks, are homogeneous and adherent, have a reddish colour and have a low roughness as it can be seen in Fig. 3.

The results of the transparency and electrical resistance measurements are presented in Table 2.

Corresponding to the temperature at which the oxidation took place, the structure of the samples was formed as follows [2-4, 8, 9]:

- for samples 1, 2, 3, oxidized at a temperature of 450 ºC, it is made of CuO;
- for sample 4 with the oxidation temperature of 200 ºC from Cu_2O + Cu, so there is a partial oxidation highlighted by a color different from that obtained at a temperature of 450 ºC;

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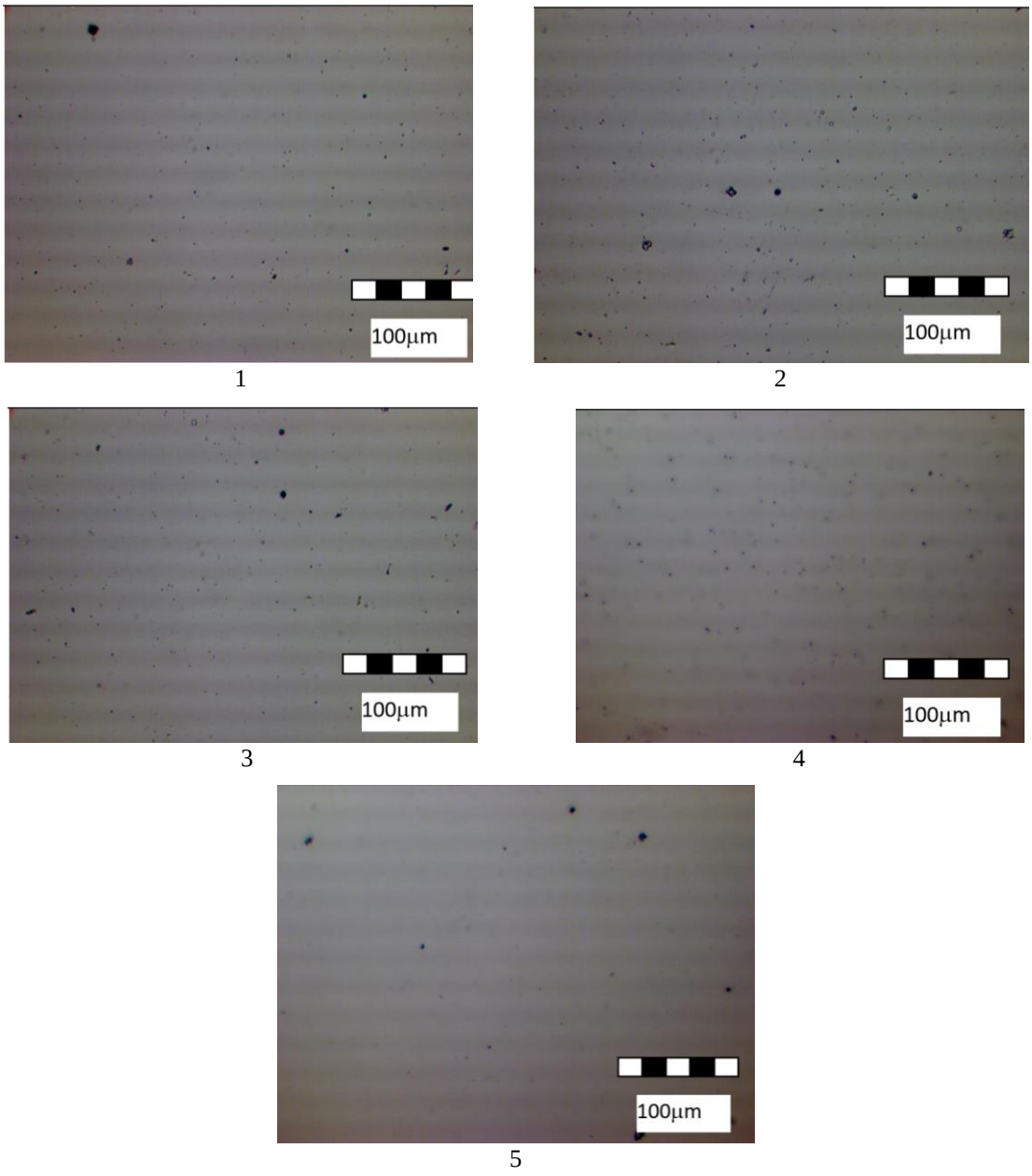
➢ for sample 5 where the oxidation temperature was 300 ºC the structure contains Cu_2O + CuO

Figure 4 shows the appearance of copper films for samples 1, 2, 3, oxidized at 450 °C, 1/2 h, as well as for samples 4, 5, oxidized at 200 °C, respectively 300 °C for 1/2 h.



1 2 3 4 5

Fig. 3. *Micrographs of the deposited Cu films*

Analyzing Table 2 it is observable that in all films subjected to oxidation the transparency and surface resistance increase, more accentuated at a temperature of 450 ºC, and at temperatures lower than this value the increases are much smaller. This is due to the partial oxidation of the deposited copper films as well as the formation of different structures which consist of CuO in sample 3, Cu_2O+Cu in sample 4 and Cu_2O+CuO in sample 5 characterized by other properties.

The dependence of the conductive behavior of temperature CuO films leads to potential applications in the chemical industry and gas sensors.

It was found that with increasing spray power, due to improved mobility of pulverized atoms and increased energy of adsorbed atoms, there is an intensification of nucleation and growth processes

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which increases the crystallinity of the film and changes its characteristics, respectively decreasing transparency and strength (samples 2,3).

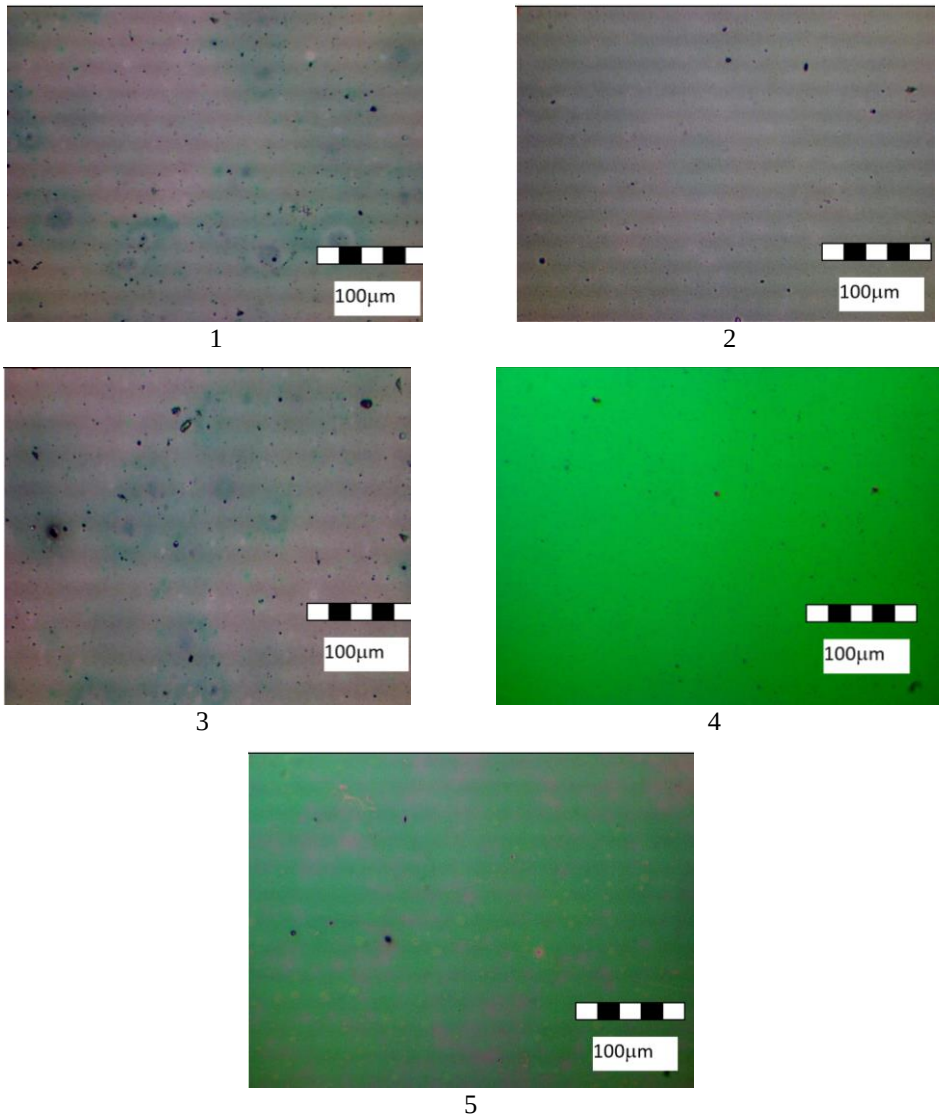
To study the kinetics of the transformation of metallic Cu into oxide, sample 5 was oxidized at 300 °C in several stages (1/2 h per stage), with a total time of 2 h. The results are shown in Tables 3 and 4.

Analysing Tables 3 and 4 it is obvious that in the case of oxidation at low temperatures a longer oxidation time is required to obtain the required electrical and transparency characteristics.

This may be due to changes in the structure and morphology of the oxidized films.

Table 2. *Determination of transparency and electrical properties of Cu films subject to oxidation*

Sample code	Initial transparency	Final transparency	Initial resistance [Ω]	Resistance after oxidation [Ω]
1	$3.906*10^{-3}$	0.437	0.7	483200
2	$2.929*10^{-4}$	0.25	0.697	198996.43
3	$3.662*10^{-4}$	0.5	0.454	3882857.1428
4	-	$1.464*10^{-4}$	0.7	0.984
5	-	0.0132	0.503	1.647



1 2 3 4 5

Fig. 4. *Micrographs of Cu films deposited and oxidized at different temperatures*

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Table 3. *Kinetics of Cu into oxide transformation*

Sample 5	Oxidation stages at 300 ºC				
	Initial status	I	II	III	IV
Transparency [%]	-	0.0132	1	2	2
Time [h]	0	1/2 h	1 h	1and 1/2 h	2 h

Table 4. *Kinetics of Cu into oxide transformation*

Sample 5	Oxidation stages at 300 ºC				
	Initial status	I	II	III	IV
Surface resistance [Ω]	0.503	1.647	51.46	1101041.7	2613461.5
Time [h]	0	1/2h	1h	1and 1/2h	2h

4. Conclusions

Following the experimental research, the following conclusions can be highlighted:

- The method of spraying copper in magnetron regime has a series of advantages such as: high deposition speed, obtaining films with high purity and homogeneity, high adhesion, high precision in controlling the thickness and size of grains;
- Due to the high electrical and thermal conductivity and a relatively high melting temperature, the copper deposits are intended for the realization of high-performance integrated circuits;
- The structures and properties of the obtained films depend on the sputtering power (voltage, current intensity), duration, target distance - substrate, substrate temperature;
- Following the microscopic analysis, it was observed that the obtained films showed no cracks, are homogeneous and adherent with a mirror surface;
- with the increase of the sputtering power (increase of the current and voltage) there is an increase of the film thickness;
- with the increase of the deposition time there is an increase of the film thickness and of the grain size (which can lead to the increase of the roughness); grain size is important in the case of semiconductors because it influences the size of the forbidden band and the physical properties;
- the deposition speed decreases with the increase of the distance from the target, thus determining both the decrease of the film thickness and the increase of its transparency;
- the transparency of the obtained films increased at all samples subjected to oxidation, this varying between 1,464 * 10^{-4} for oxidation at the temperature of 200 ºC and 0.5 for the oxidation temperature of 450 ºC; this is due to the change in the structure of the film following oxidation;
- the surface resistance increases after oxidation, the more accentuated the higher the oxidation temperature; it varies between 0.984 Ω for the oxidation temperature of 200 ºC and 3882857,1428 Ω for oxidation at the temperature of 450 ºC;

The modification of the conductive behavior with temperature of the obtained films is recommended in applications in the chemical industry and gas sensors.

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