



CRYSTALLOGRAPHY OF COOPER OXIDE COATINGS DEPOSITED ON Si SUBSTRATE BY REACTIVE MAGNETRON SPUTTERING

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ABSTRACT

Copper oxide (CuO) is used in the photovoltaic (PV) industry and modern biomedicine. These coatings are applied to increase the wear and corrosion resistance, and to improve the biocompatibility of the materials.

In this work, copper oxide coatings were deposited on silicon substrates by reactive magnetron sputtering. During the process, the substrate temperature was in the range from 100 °C to 400 °C and the deposition time was 60 minutes.

The crystallographic structure of the obtained samples was characterized by X-ray diffraction. The experiments were performed in a symmetrical Bragg-Brentano geometry using Cu K α radiation. The patterns were registered in the range from 30° to 80° at 2 θ scale.

The crystallographic structure of the deposited CuO coatings is discussed with respect to the applied technological conditions. The results obtained in the present study are expected to add knowledge about the processes occurring during reactive magnetron sputtering under different technological conditions, as well as their influence on structure formation in CuO films.

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INTRODUCTION

Metal oxide coatings are multifunctional materials due to their many potential applications in optoelectronics, photovoltaic devices, as well as in biomedicine [1,2,3]. Their properties are expressed in good chemical stability, high resistance to wear and corrosion, and others [4]. The purpose of metal oxide coatings is to improve the performance properties of materials [5, 6]. Reactive magnetron sputtering (RMS) is a universal method to deposit such metal oxide coatings like TiO₂ [7], HfO [8], ZnO [9], VO_x [10], Fe₂O₃ [11], CuO [12] etc.

Copper oxide has two stable states – CuO (cupric oxide or tenorite) and Cu₂O (cuprite), which are characterized by monoclinic and cubic structures, respectively. Copper oxide is used as gas sensors, battery electrodes, solar cells and antibacterial materials [13, 14, 15].

The researchers of [4] have successfully synthesized a new nanocomposite CuO-TiO₂ using an oxalate method for use as nanofillers for epoxy coatings to protect the steel surface against corrosion and bacterial growth. The results obtained exhibited an increased resistant to corrosion and improved antibacterial properties of the initial material after the addition of CuO/TiO₂ nanocomposite.

The authors of [16] have deposited TiO₂, Cu₂O and TiO₂/Cu₂O thin-film heterojunctions by direct-current magnetron sputtering on the different substrates (n-type Si (100) and glass slides with indium tin oxide (ITO)) for application in photovoltaic devices. The influence of the technological parameters on the structural, optical and

surface properties of the obtained coatings was investigated. The results in this study showed that increased distance between the source and substrate led to a decrease in the thickness, surface roughness and porous structures of thin films. Similarly, the researchers of [17] studied the influence of oxygen flow rates and substrate temperatures during the deposition of TiO₂/CuO heterojunctions. It was found that the increase in the substrate temperature is accompanied by greater mobility of atoms, which led to group agglomeration of the crystallites and an increase in crystallite size.

In another study [12], optical properties of sputter deposited nanocrystalline CuO thin films were investigated. The results show that increasing the oxygen flow rate from 2.5 sccm to 5.5 sccm led to a decrease in the thickness (from 3.25 μ m to 1.5 μ m) and surface roughness (from 32 nm to 20 nm) of CuO coatings. On the other hand, the thickness of the deposited CuO coatings does not affect the optical band gap, which ranges from 1.42 eV to 1.54 eV.

The main aim of our study is to show the possibility of successfully obtaining oxide coatings based on copper using reactive magnetron sputtering method. Also to investigate the influence of the substrate temperatures on the phase composition and crystallographic structure of the CuO coatings.

MATERIALS AND METHODS

The experiments were conducted on substrates of Si (100). Copper oxide (CuO) coatings were deposited on Si

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substrates using reactive magnetron sputtering (RMS). The diameter of the sputtered target was 100 mm as the purity of Cu was 99.8%. Before the deposition of CuO films, the substrates were etched by Ar ions for 10 minutes to remove surface contaminations. The process took place in an Ar-O₂ atmosphere at a working pressure of 5x10⁻⁴ mbar and the deposition time for CuO coatings is 60 minutes. During the process, the temperature of the substrate was in the range of 100 to 400 °C.

The phase composition and crystallographic structure of the samples were analyzed by X-ray diffraction (XRD, Empyrean system, Malvern Panalytical), where Cu K α radiation was used. The measurements were carried out within the range of 30–70° at a 2 θ (theta) scale.

RESULTS AND DISCUSSIONS

X-ray diffraction measurements of phase composition were carried out in Bragg-Brentano (symmetrical) mode. The XRD patterns of the samples are presented in fig. 1. The phase identification was performed by means of the ICDD (International Center for Diffraction Data) Database file PDF (Powder Diffraction File) #05-0661 for the CuO crystal phase. The obtained results show the presence of a monoclinic crystal structure with space group C2/c (15).

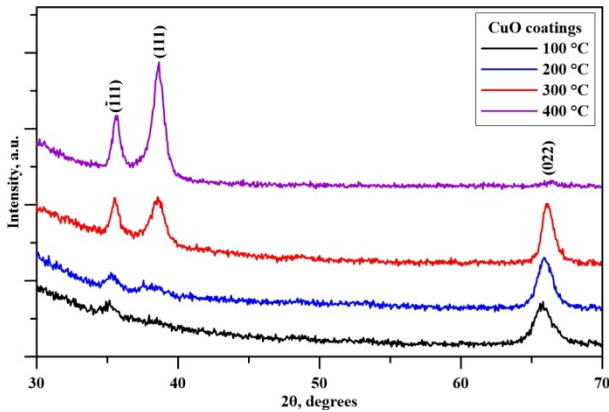


Fig.1. XRD patterns of the CuO coatings deposited at different temperatures on Si substrates

The preferred crystallographic orientation was characterized by the pole density, which measures the relative degree of preferred orientation of a specific (hkl) plane. In the present study, as in Ref. [15], this coefficient is calculated according to the equation (1):

$$T_c(hkl) = \frac{I(hkl)}{I_0(hkl)} \left(\frac{1}{n} \sum_{i=1}^n \frac{I(h_i k_i l_i)}{I_0(h_i k_i l_i)} \right)^{-1} \quad (1)$$

where I_0 is the standard intensity of the considered peak taken from a powder diffraction file (PDF) card, n is the number of the considered diffraction maxima, and I is the measured intensity of ($h_i k_i l_i$) plane. The crystallite size (D) is calculated using Scherer's equation described in detail in ref. [15].

It was found that at a substrate temperature of 100 °C, the preferred orientation is (022) with contribution of about 89%. The subsequent increase in the substrate temperature to 300 °C leads to a decrease in the contribution of (022) to below 80%. A change in the orientation of the crystallites in the sample with the highest substrate temperature (400 °C) was observed. In this case, the preferred orientation is (111), where its contribution is about 56%. The change in the texture coefficient of the copper oxide coatings could be

explained by the change in the temperature of the substrates.

Table 1 Shares of micro-volumes belonging to different texture components (T_c), full width at half-maximum (FWHM) of ($\bar{1}11$) diffraction peak and crystallite size (D)

Samples	T_c , %			FWHM, degrees	D, nm
	$T_{c\bar{1}11}$	T_{c111}	T_{c022}		
100 °C	10.95	-	89.05	1.0	8.30
200 °C	8.57	7.33	84.10	0.9	9.24
300 °C	9.93	10.40	79.67	0.7	11.95
400 °C	43.75	56.25	-	0.6	13.86

The deposition of copper oxide coatings at lower temperatures is accompanied by low diffusion mobility of the copper and oxide atoms arriving on the substrate, which leads to lower nucleation kinetics and growth of crystallites [18]. It is obvious that the profiles of the diffraction peaks of copper oxide coatings deposited at lower temperatures are non-smooth and similar to those obtained by studying materials with a porous microstructure. As the substrate temperature increases, the diffraction peaks acquire a smoother shape and become narrower.

The lattice imperfections can be characterized by the broadening of the diffraction maximum, as it is a function of the crystallographic imperfections [19]. In our study, the crystallographic perfection was evaluated by FWHM of ($\bar{1}11$) diffraction peak, where the results are given in fig. 2 and Table 1. It was found out that the increase in substrate temperature is accompanied by a decrease in FWHM. Therefore, the concentration of the crystallographic imperfections decreases with an increase in substrate temperatures.

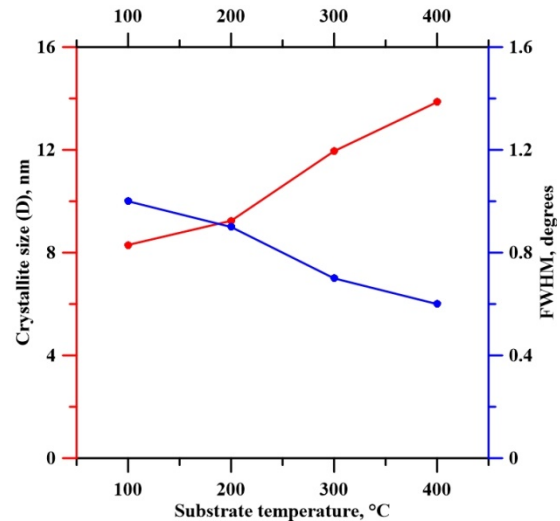


Fig.2. Full width at half-maximum (FWHM) and crystallite size (D) for CuO coatings deposited on Si substrates at different temperatures

The crystallite sizes were calculated from ($\bar{1}11$) diffraction peak and the results are present in fig. 2 and Table 1. Their values are equal to ~ 8.3 nm and 13.9 nm, at a substrate temperatures from 100 °C to 400 °C, respectively. It's obvious that the crystallite size increases with an increase in the substrate temperature. The obtained results confirm once again the fact that the deposition process at higher temperatures is accompanied by lower cooling rates, which in turn leads to greater mobility of atoms, and agglomeration of the crystallites, and an increase in their size. [17, 20]

CONCLUSIONS

This study demonstrates the possibility of the successful deposition of CuO coatings on silicon substrates by reactive magnetron sputtering. The influence of the substrates temperature during the deposition process of the phase composition of the oxides coatings is investigated. It was found out that the increase in the substrate temperature has a significant effect on the texture coefficient and crystallite size of the copper oxide films.

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