IOP Conf. Series: Materials Science and Engineering **387** (2018) 012030 doi:10.1088/1757-899X/387/1/012030

Study of nanoscale metal oxide coatings produced by magnetron sputtering of copper followed by heat treatment

I N Kashkul, L D Bakhchova, K G Elanskaia and D N Redka

Saint-Petersburg State Electrotechnical University "LETI", 197376, St. Petersburg, Russia

E-mail: rd89@bk.ru, k.elans@yandex.ru

Abstract. The composition and microstructure of nanoscale metal oxide coatings deposited by magnetron RF sputtering copper on the quartz glass with followed heat treatment were investigated. The dependence of the film thickness and the content of oxides CuO and Cu_2O in it depending on the temperature and time of heat treatment conditions were obtained. Studies have shown that, depending on the mode of receipt of copper oxide films may be multiphasic and include various oxide phases, predominantly, CuO and Cu_2O with different bandgap and p-type conductivity.

1. Introduction

Copper oxides are widely used in solid state electronics and optoelectronics [1]. One important advantage of using the copper oxide lies in non-toxicity and widely availability [2]. Various methods for the obtaining of copper oxide, such as thermal oxidation, a reactive high-frequency magnetron sputtering, hydrothermal synthesis, electrodeposition, thermal evaporation, and others are known [3]. It is also known that copper oxide has two phases with different stoichiometry, Cu_2O and CuO [3]. Interest in the study of copper oxide films of different stoichiometries connected with the possibility of their use in solar cells [4, 5]. Application of this type of photovoltaic constrained insufficient knowledge of the physical processes at the interface of oxide structures with developed surface morphology.

Theoretical efficiency conversion of solar energy into electrical energy for copper oxide is 9–12 %, but still the experimental oxide thin film heterostructures CuO_x/ZnO, obtained by different research groups [4–8], have low efficiency. In addition to the n-ZnO/p-CuO heterojunctions, the heterostructures of copper oxide with PZT are also of interest for photovoltaic applications [9] due to the ferroelectric photovoltaic effect and significant electric fields at the interface of the PZT and different semiconductors [9–13]. Thus, copper oxide can be considered as a promising photosensitive layer in combination with ZnO or PZT. The main method of increasing the efficiency of solar cells based on copper oxide is to improve the quality of the oxide layers, which requires a detailed examination and developing of processes for obtaining oxide layers.

This is a continuation study for the works [3] about development and investigation of thin-film layers of copper oxides for photovoltaic applications. As a convenient method of depositing layers, we use magnetron sputtering.

IOP Conf. Series: Materials Science and Engineering **387** (2018) 012030 doi:10.1088/1757-899X/387/1/012030

2. Methods of obtaining and studying samples

On a purified quartz and glass substrates have deposited at room temperature copper thin film, 100 nm thick by magnetron sputtering on installation Plasmalab System 100 (at a pressure of 5 mbar and a charge power of 100 mW). Substrates were cut mechanically into rectangular samples of size 10x20 mm. Then, the samples were placed in electric furnace PT-1,2-70 and have suffered thermal oxidation in air at temperatures ranging from 220 to 500 °C and the time (*t*) from 5 to 60 minutes.

Evaluation of the film thickness were performed at the facility AlphaStep D-120. The values of film thickness by temperature and annealing time of copper film are shown in table 1. As seen from the profilometry data, metal film 100 nm thick is fully oxidized at 500 °C for 30 minutes.

Table 1. The values of film thickness after oxidation in air.

Temperature, °C	Thickness, nm						Phase composition
	t= 0 min	*t*= 5 min	*t*= 10 min	*t*= 20 min	*t*= 30 min	*t*= 60 min	($t \geq 30$ min)
250	100	110	115	128	140	165	Cu_2O
300	100	135	145	160	175	185	Cu_2O + CuO
350	100	140	155	170	180	190	Cu_2O + CuO
500	100	190	200	210	215	215	CuO

The prepared samples were investigated by Raman spectroscopy, X-ray analysis and atomic force microscopy. Optical and electrical properties have been studied.

Survey of the phase composition of the films by Raman spectroscopy performed with the setup LamRam HR800 using green laser with wavelength 532 nm, 2 mW beam power, accumulation time 30 seconds and the number of scans 10. The surface morphology was studying by the atomic force microscope "Integra Thermo" with a resolution of 10 nm in the horizontal plane, and the vertical better than 1 nm. The optical properties of the films were studied by Varian Cary® 50 UV-Vis Spectrophotometer. Measurements of the changing electrophysical parameters were carried out on the installation ECOPIA HMS-5000.

3. Results and discussion

Studying the phase composition of the films formed by oxidation at various temperatures of nanoscale copper layers on the air, carried out independently in two ways – by Raman spectroscopy and X-ray analysis (figure 1). Analyzing of Raman spectra identified lines Cu_2O (98 cm^{-1}, 145 cm^{-1}, 217 cm^{-1}) and CuO (296 cm^{-1}, 342 cm^{-1}, 627 cm^{-1}). Results showed that structure of the copper oxide film varies depending on the temperature and time of annealing in air. Therefore, Cu_2O phase formed by isochronous annealing for 30 minutes at temperatures of 220–250 °C. With further increasing the temperature to 350 °C is obtained the film as a mixture phases Cu_2O and CuO, but at a temperature above 500 °C formed a single phase CuO.

X-ray analysis allowed to draw similar conclusions about the change in the phase composition of the copper oxide films with increasing annealing temperature. In a manner, by varying the annealing temperature in the range of 220 – 500°C we are able to manage phase composition and to obtain copper oxide as single-phase CuO or Cu_2O and multiphasic Cu_2O + CuO films.

Morphology of obtained surface layers were examined by atomic force microscopy (AFM) in tapping mode on a Nano-lab NTEGRA-Therma. Analysis of the data showed particles ranging in size from 100 to 300 nm are evenly distributed on the sample surface. The surface of obtained layers rough, while the scope of heights at the characteristic surface topography length of 10 microns. For samples subjected to thermo processing at higher temperatures, this scope is larger. Investigation results of copper oxide films surface morphology can be concluded that the oxidation process leads to increase surface roughness.

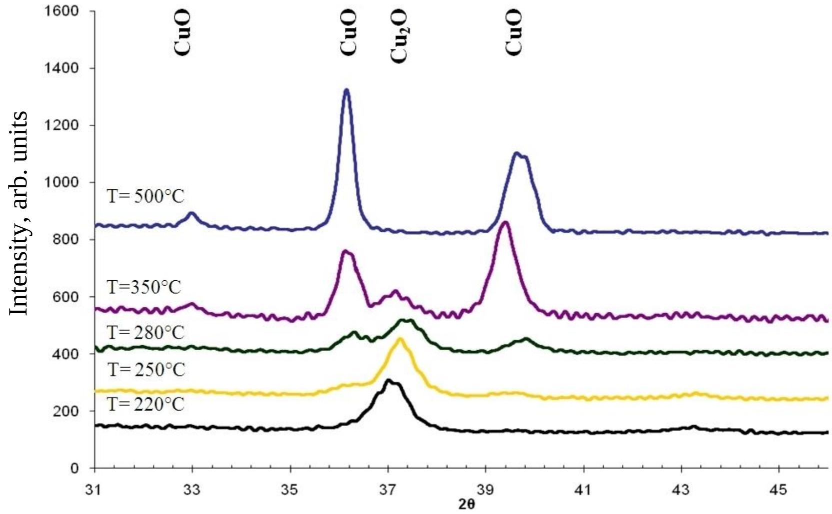

Figure 1. X-ray diffraction patterns copper oxide film obtained by oxidizing in air at various temperatures for 30 min.

According to the theory, in the process of annealing molecular oxygen at atmospheric pressure depending on the processing temperature may oxidize copper fully, partially or in two stages:

$$Cu + 0{,}5O_2 \leftrightarrow CuO;\ 2Cu + 0{,}5O_2 \leftrightarrow Cu_2O;\ Cu_2O + 0{,}5O_2 \leftrightarrow 2CuO.$$

Due to the polycrystalline structure of copper, according to [9], the rate of oxidation of copper with the bulk diffusion of deposits in the lattice and grain boundary diffusion can be expressed as

$$\frac{\mathrm{d}\left(x^2\right)}{\mathrm{d}t} = 2D_\upsilon V\Delta c + \frac{4D_\mathrm{b}V\Delta c\delta}{d_t} = K_\upsilon + K_\mathrm{b} f,$$

wherein x – thickness of the oxide layer at time t; D_υ – bulk diffusion coefficient; V – molar volume of the oxide; Δc – gradient of the concentration of point defects across the oxide layer; D_b – the grain boundary diffusion coefficient; δ – the width of the grain boundary; d_t – the average grain size at time t; K_υ – component of parabolic constant oxidation associated with the bulk diffusion in the crystal lattice; K_b – component associated with the grain boundary diffusion; $f=2\delta/d_t$ - the proportion of all diffusion regions disposed along the grain boundaries.

Analysis of experimental data have shown that the data in table 1 are well described by semiempirical equation:

$$h(t) = h_m \int_0^{Dt/h_0^2} e^{-k^2} dk,$$

where h_m and h_0 – maximal and the initial film thickness of the copper oxide, t - time, D - the effective diffusion coefficient.

Study optical properties of the films obtained at temperatures of 220–250 °C showed that samples have high transmittance (50%). Whereas the films obtained at temperatures of 350–500 °C have a high absorption coefficient in the visible spectrum and substantially transparent in the infrared spectrum (figure 2). By transmission and absorption spectra were calculated band gap of 1.2 and 2.28 eV for CuO and Cu_2O respectively. Based on the differences in transmission for samples more promising for use in photovoltaics is Cu_2O. Investigation of electrophysical parameters showed that the samples have p-type conductivity and high surface resistance.

IOP Conf. Series: Materials Science and Engineering **387** (2018) 012030 doi:10.1088/1757-899X/387/1/012030

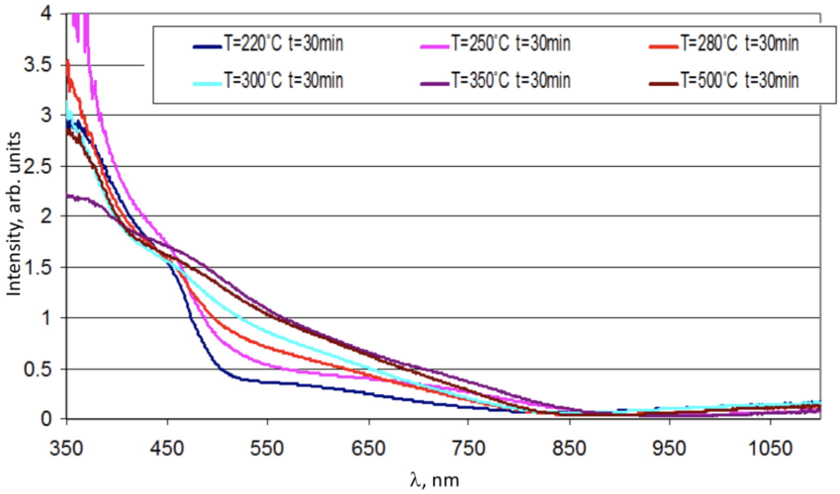

Figure 2. Absorption spectra of samples obtained at annealing for t=30 minutes at different temperatures.

4. Conclusions

As a result of experimental studies were obtained dependences of the oxide film thickness and the percentage content of CuO and Cu_2O oxides upon the annealing temperature-time conditions. Thus, at isochronous annealing for 30 minutes at temperatures of 220–250 °C formed Cu_2O, by further increasing the temperature to 350 °C obtained mixture phase Cu_2O and CuO and at a temperature above 500 °C formed a single phase CuO.

Acknowledgment

This work was supported by the grant of The Ministry of Education and Science (Minobrnauka) of the Russian Federation (project Goszadanie № 3.3990.2017/4.6).

References

[1] Jia W, Reitz E, Shimpi P, Rodriguez E G, Gao P X and Lei Y 2009 *Materials Research Bulletin* **8** 1681–6
[2] Oral A Y, Mensur E, Aslan M H and Basaran E 2004 *Materials Chemistry and Physics* **1** 140–4
[3] Adilov Sh R, Afanasiev V P, Kashkul I N, Kumekov S E, Mukhin N V and Terukov E I 2017 *Glass Phys. Chem.* **3** 272–5
[4] Adilov Sh R, Kumekov M E, Kumekov S E and Terukov E I 2013 *Semiconductors* **5** 655–6
[5] Omayio E O, Karimi P M, Njoroge W K and Mugwanga F K 2013 *Int. J. Thin Film Sci. Tec.* **1** 25–8
[6] Redka D N, Mukhin N V and Zakharov I G 2016 *Technical Physics* **61** 1744–6
[7] Afanasjev V P, Konoplev G A, Chigirev D A, Mukhin N V, Terukov E I and Terukova E E 2016 *Proc. of SPIE* **9896** 98980V
[8] Afanasjev V P, Mukhin N V, Redka D N, Rudenko M V, Terukov E I, Oseev A and Hirsch S 2017 *Ferroelectrics* **508** 124–9
[9] Cao D, Wang C, Zheng F, Dong W, Fang L and Shen M 2012 *Nano Letters* **6** 2803–9
[10] Afanasjev V P, Chigirev D A, Mukhin N V and Petrov A A 2016 *Ferroelectrics* **1** 170–6
[11] Agafonova D S, Kozyrev A B, Mukhin N V, Red'ka D N, Elanskaya K G, Rudenko M V, Oseev A, Hirsch S. 2018 *Glass Phys. Chem.* **1** 15–20
[12] Mukhin N V 2016 *Glass Phys. Chem.* **1** 64–6
[13] Afanas'ev V P, Vorotilov K A and Mukhin N V 2016 *Glass Phys. Chem.* **3** 295–301