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INVESTIGATION OF THE INFLUENCE OF ANODIZING MODES OF COPPER OXIDE FILMS ON THEIR MORPHOLOGY

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This work presents experimental data on the surface morphology of Cu_2O films obtained by single-stage electrochemical anodization. The process was carried out at a constant applied potential of 50V and at a temperature of 13°C (90 seconds) in an electrolyte based on phosphoric acid. During the experimental work, the optimal synthesis parameters were determined. The morphology of copper porous films was studied using atomic force microscopy Ntegra Therma. The effect of the main anodizing parameters on the morphology of the nanoporous Cu_2O film was investigated. According to the results of experimental work, it was found that, depending on the parameters of the anodizing process, it is possible to vary the pore diameter of copper oxide from several tens of nanometers to hundreds of microns, while it is also possible to change the film thickness.

Keywords: nanoporous, copper oxide, electrochemical anodizing, phosphoric acid, atomic force microscopy.

Introduction

Recently, one of the most rapidly developing scientific areas is the production of new nanostructured materials. Such materials include nanomaterials based on copper oxide. Copper oxide is a narrow bandgap semiconductor material with a high absorption coefficient in the visible region. Low cost, environmental friendliness, richness of resources makes copper oxide promising for use in sensors [1], hydrogen production [2], energy conversion [3, 4], supercapacitors [5], semiconductor catalysis [6, 7], and biosensors [8, 9], etc.

In connection with the method of synthesis of nanostructured copper oxide, the direction of research for optical and electronic devices increases significantly [10]. Numerous methods have been used to synthesize Cu_2O nanostructures [11-13]. However, the above methods have their drawbacks such as expensive equipment, expensive reagents, harsh reaction conditions, uncontrolled structures, and complicated experimental setup.

Among the methods, the most effective is the anodizing process. Anodizing is a scalable, versatile, economical (technological equipment cost is low) method for obtaining oxide coatings for metals. In addition, by changing the main parameters of the anodizing process, such as electrolyte composition, etching voltage, and anodizing duration, it is possible to control the morphology and size of the copper oxide nanostructure [14, 15]. Recently, nanostructures of copper oxides have been synthesized based on the anodizing process [14-16]. For example, in [17], copper oxide nanostructures were synthesized by anodizing copper deposited on glass from tin oxide doped with fluorine, and the thickness of the deposited copper was 500 nm. In [18], nanostructured Cu_2O thin films with different morphologies were fabricated by anodizing in an ethylene glycol electrolyte containing 0.15M potassium hydroxide, 0.1M ammonium fluoride with 3 wt. % deionized water. In this study, a mechanism for the formation of a thin Cu_2O film was proposed and the effect of anodizing voltage and electrolyte temperature on morphology was investigated.

Using the anodizing process, Cu_2O nanostructures with different morphologies can be easily synthesized, which can help expand the scope of this material.

1. Experimental part

During the experimental work, a copper plate (99.61%) with a thickness of 40 μm was used as the starting material. The process of one-stage anodizing was carried out at a constant applied potential of 50V in an electrolyte of 0.4M H_3PO_4 at a temperature of T=13°C for 35-90 seconds. Before starting the anodizing process, the copper plate was preliminarily annealed in a muffle furnace at a temperature of T= 400°C for 60 minutes. The surface morphology of the nanoporous copper oxide was studied by Ntegra Therma (NT-MDT)

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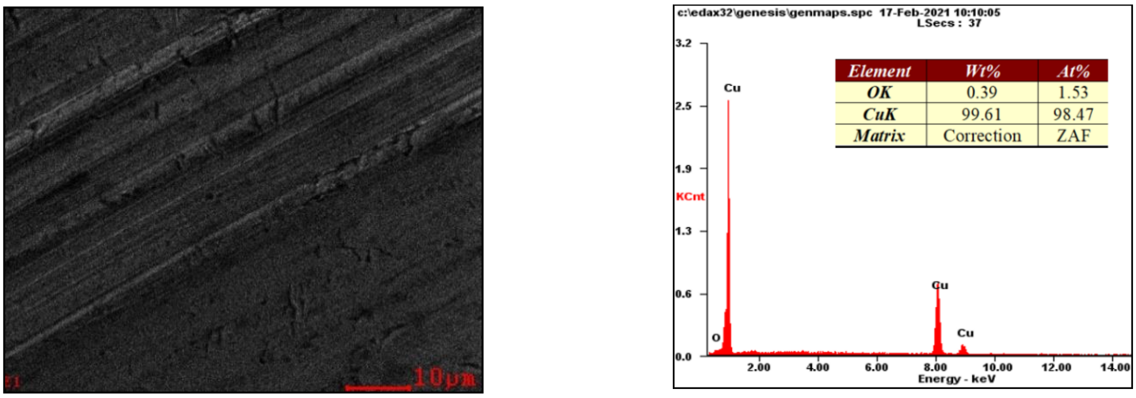
atomic force microscopy and scanning electron microscopy (Quanta 200i 3D FEI). To study porous copper films, we used a semicontact AFM and an NSG30 type cantilever. Elemental analysis was carried out on the basis of energy dispersive X-ray analysis (EDAX).

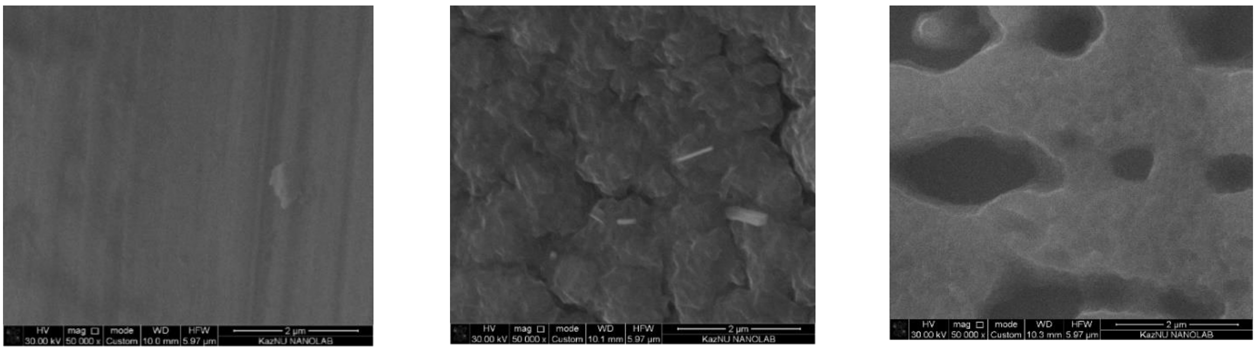
2. Results and discussion

The process of formation of a porous structure and the degree of ordering primarily depend on the chemical purity of the initial copper. To study the influence of the chemical purity of the initial copper on the structure of the obtained films, elemental analysis was carried out on a scanning electron microscope (fig. 1). Elemental analysis was carried out on the basis of energy dispersive X-ray spectroscopy. As the results of the analysis showed, the composition of the original copper plate contains oxygen impurities. Figures 2 (a, b, c) show the SEM image of copper before heat treatment, after thermal annealing at 400°C in the air, and after the anodizing process. As can be seen from figure 2 c, there will be much fewer areas with orders pores on the surface of copper films. Therefore, before carrying out studies on the production of copper oxide films, it is necessary to select a starting material with a high chemical purity.



a) b)

Fig. 1. Results of elemental analysis of a copper plate: a – SEM micrograph, b – EDX spectrum and table for the weight percent and atomic percent



a) b) c)

Fig. 2. SEM image of copper: a-pure; b-after the annealing process; c-after anodizing process

The main parameters affecting the structure of the synthesized Cu_2O are the temperature and time of the anodizing process, the composition of the electrolyte, and the applied voltage. Depending on the choice of electrolyte composition, primarily on the type of acid, it is possible to form pores with different pore sizes. As already noted, in the present work, porous copper oxide was obtained at a temperature of 13°C. Stabilization of the electrolyte temperature during the anodizing process is necessary in order to avoid local heating in the layer of electrolyte contact with the surface of the original copper. At sufficiently low temperatures, the electrolyte can freeze and the anodizing process slows down, which, accordingly, leads to a slowdown in the formation of the pores themselves. Consideration must be given to the importance of temperature stabilization during the anodizing process. Voltage is another key parameter of the anodizing process that determines the porosity and the morphology of the nanostructured copper film. Anodizing at a voltage of 50 V, a nanoporous film is formed on the Cu wafer. At voltages above 50 V, a highly oriented porous film is formed [18]. In general, it should be noted that the porosity of the nanostructured film increases with an increase in the anodizing voltage. Figure 3 shows AFM images of porous copper after anodization, , where the pore size and their structural features can be estimated.

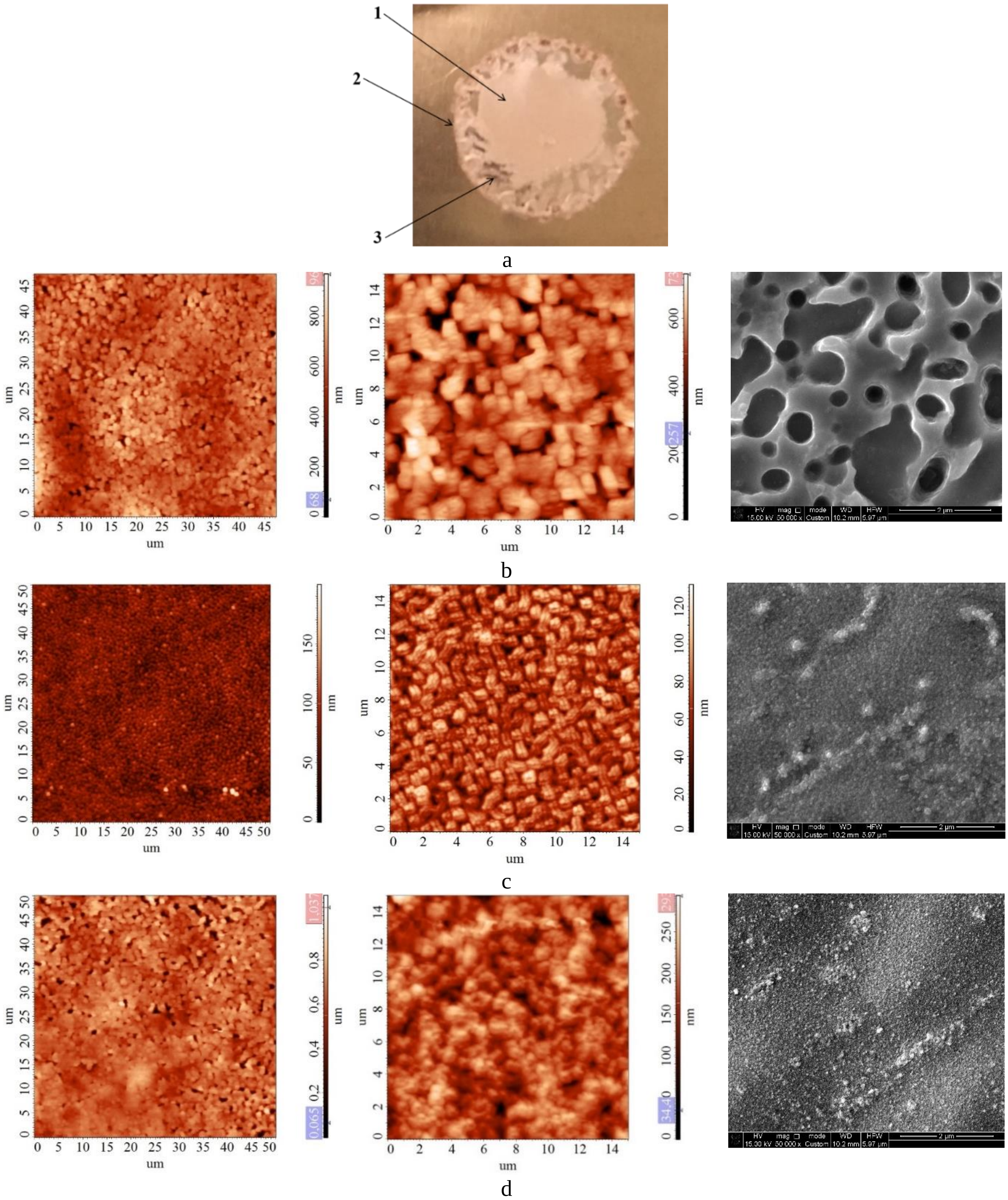


Fig. 3. AFM and SEM images of copper films after anodizing:
a-copper plate; b- matte area (a1); c - dark area (a2); d- oval area (edge, a3)

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Figure 3a shows the sample itself, as can be seen from the figure, the anodizing process is unstable over the entire surface of the plate and, accordingly, have a different morphology (fig. 3 b, c, d). This may be due to different chemical bonds on the surface and in the volume of copper. In addition, experimental data show that the formation of a porous structure and the degree of ordering are affected by the chemical purity of copper. As a result of the study, it was found that porous structures begin to form on the copper surface and with different pore diameters, depending on the anodizing parameter. The pore diameters ranged from several tens of nm to hundreds of microns. Such porous structures are formed under the following anodizing process conditions: U = 50-100V, T = 13-16°C, t = 35 s, 60 s, 90 s.

Conclusion

Based on the results of the study, the following conclusions can be drawn:

1. Nanostructured copper oxide films were synthesized using single-stage electrochemical anodization in 0.4M H_3PO_4 electrolyte at a temperature of T=13°C at a voltage of 50 V.

2. Technological conditions for the synthesis of Cu_2O samples have been worked out. It was found that, depending on the parameters of the anodizing process, it is possible to control the thickness and vary the pore diameter from several tens of nm to hundreds of microns. The average thickness of the synthesized nanoporous films is 1 μm.

3. The surface morphology of the obtained samples was studied by atomic force microscopy and scanning electron microscopy. As the results of the study showed, the degree of pore ordering depends not only on the process parameters, but also on the chemical purity of the initial copper.

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