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Nanostructure Changes of Magnetron Copper Films with a Glass Ceramic Substrate

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The present paper deals with the results of comprehensive research of heated in the air magnetron copper films by atomic-force and scanning electron microscopy, Raman scattering, IR-Fourier and X-Ray phase analysis, and spectral ellipsometry. According to the results of nano techniques, the relationship between amplitude and phase-frequency components of ellipsometric measurements and phase structure transformations has been established. The structural transition in the vicinity of 573 K, has been found.

Keywords: Nanostructure, Magnetron method, Ceramic Substrate.

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1. INTRODUCTION

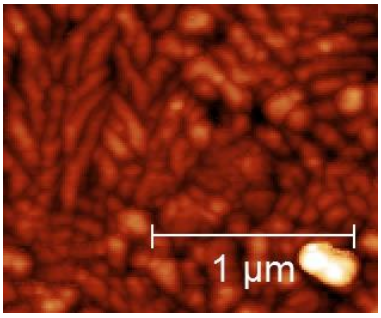
In electronic and electrotechnical items, pure copper is presented as a basic metal, at whose surface the oxides are easily formed at the interaction with the environment: tenorite – CuO and cuprite – Cu_2O [1-3]. In copper films of nanometers thickness produced by nanoparticles (with deposition, for example, by thermal and magnetron techniques and molecular beam epitaxy) these features acquire new properties. In particular, under heating other oxides can be produced, such as Cu_2O_3 and Cu_3O_4, which has become the goal of the present investigations with the advanced nano techniques.

2. INVESTIGATION RESULTS

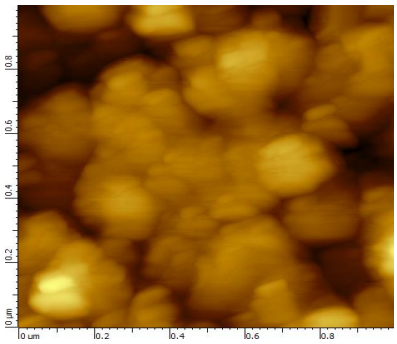
In a magnetron copper film the structural changes at stabilized heating were investigated with the help of AFM (Fig. 1a, b). The temperature was increased with a step of 10 degrees at the thermo table to 423 K. In doing so, the size of copper nanoparticles virtually did not vary up to 593 K. At higher temperature, the process of cluster formation was observed. (Fig. 1b). The cluster size reached 350 nm. However, these were produced from individual nanoparticles size of the same tens of nm.

SEM images given are in Fig. 2a and b. The coatings were produced by nanoparticles of spherical and cylindrical shape, which is characteristic both for adhesive from chromium and the copper layer. The size of those structures was for chromium 165 and 519 nm, and for copper a bit less – 66 and 188 nm. It should be noted that the magnetron coatings were, as a rule, formed by nanoparticles of a cylindrical shape with a round cross-section, which were located perpendicular to the substrate [4]. Structural inhomogeneities found on the coating surface at room temperature indeed were of a cylindrical shape, as is seen from Fig. 2a and b.

Changes in surface morphology due to heating to 673 and 1073 K are most distinctly shown by Fig. 2c, d. It is worthy of note that the temperature for each sample was increased from room to set temperature with with a step of 100 K. The structure at 673 K was notably of a non-organized character and had fragments of



a



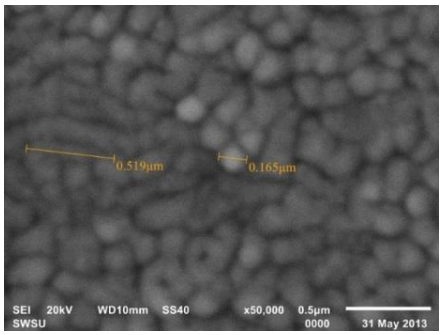
b

Fig. 1 – Atomic-force images of structure of magnetron coatings on glass ceramics from copper at a temperature: 293 K – a and 593 K – b

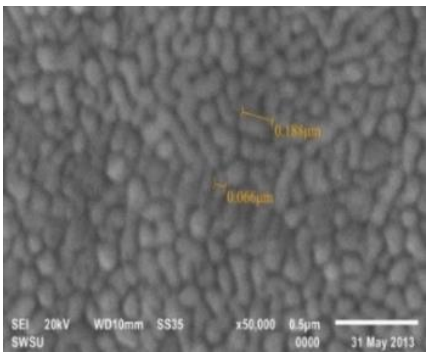
melted nanoparticles of most easily melted copper oxide Cu_2O_3 [5]. The size of components that formed that structure varied from 100 to 350 nm.

With all SEM- and AFM-images of the surface of magnetron copper coatings at various heating temperatures granulometric analysis was performed (Fig. 3). It is seen that the range of 573-673 K the size of copper nanoparticles forming the film increase sharply from 100 to 350 nm.

The observed chemical structure in a copper film is illustrated by diffraction patterns of XRD at room temperature and also near the temperature of cluster



a



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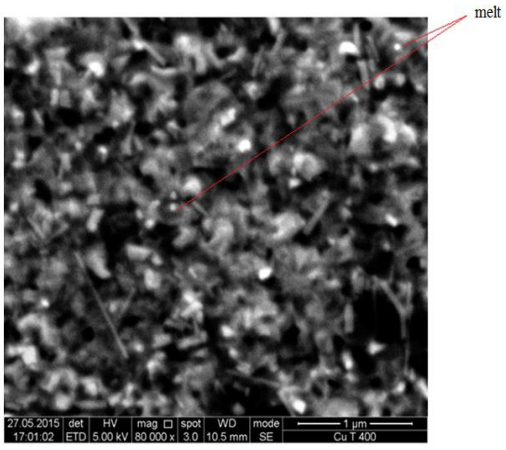
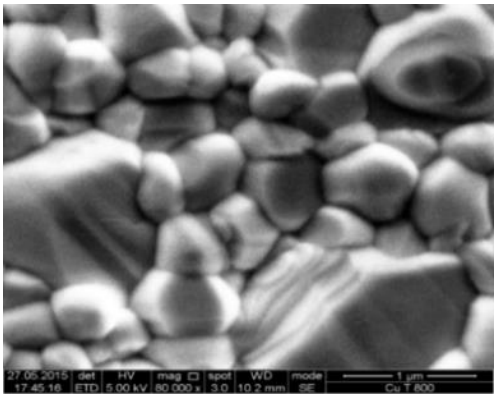


c



d

Fig. 2 – SEM-images of the magnetron film surfaces at TR Cu (a), and also Cu at 673 (b) and 1073 K (c)

formation, namely, 573 K when the structure is not changed, the XRD spectrum has changed dramatically at 1073 K. When the temperature of the coating reached 673 K copper was fully oxidized, according to XRD. In air, copper oxides Cu_2O_3 and Cu_2O were the first to appear beginning at T_R to 573 K. At further heating [5], a complex of oxides Cu_2O_3 + CuO began to form. However, the contribution of Cu_2O_3 is apparently small. Near 873 K the oxidation rate begins to considerably depend on temperature. Both oxide CuO originates and further oxidation of Cu_2O to CuO occurs at nearing to 773 K (Fig. 4).

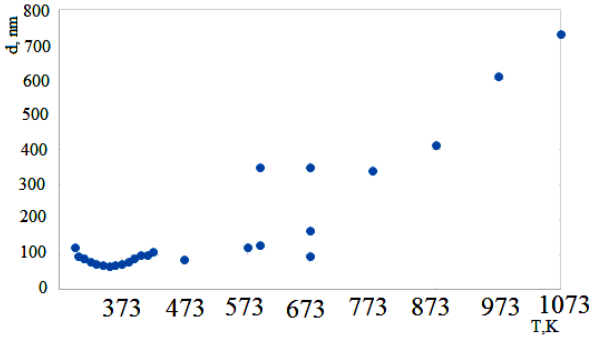


Fig. 3 – Data of granulometric analysis of nanoparticle size changes in a heated copper film

As is seen from (Fig. 4), reflection for Cu_2O appears at 673 K, and at 773 K practically vanishes. There is a transformation of Cu_2O into CuO. As a result, with heating the intensity of line CuO is slightly increased in the whole range studied to 1073 K. Nonetheless, in the range under consideration cuprite Cu_2O plays the dominant role. The line corresponding to Cu_4O_3 appears at 473 K (Fig. 4), and starting with 573 K it sharply decreases, which is not in agreement with phase diagram [5].

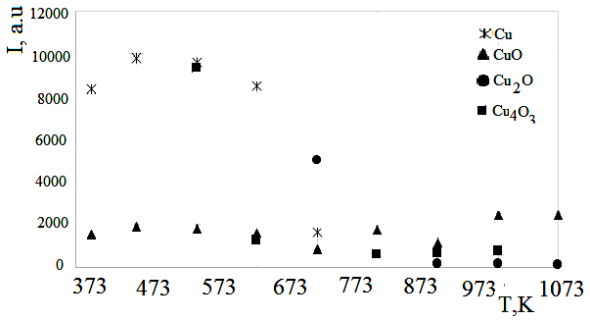


Fig. 4 – Temperature dependence of intensity of the most important X-ray lines for copper magnetron films

RS spectra are represented by lines of major copper oxides and were compared with data [6] on studying pure oxides. Analysis of changes in the intensity of most characteristic lines of copper oxides (Cu_2O – 151, CuO – 319, Cu_4O_3 – 541 cm^{-1}) in RS spectrum occurring with heating is represented in Fig. 5. As the film heated, the intensity enhancement of line 151 cm^{-1} corresponding to Cu_2O supports the dominant role of oxidation [5]. with phase diagram within this temperature range.

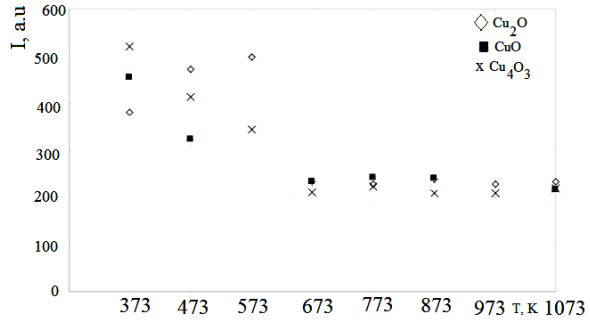


Fig. 5 – Variation with temperature of intensity of individual lines in RS spectrum for copper films

IR-spectra of magnetron films were investigated at temperature variation from 298 to 1073 K with a step of 100 K in near and middle regions according to the optical scheme of IR-radiation absorption on glass ceramic substrate-copper film in accordance with, for example [7], for nanopowders of those oxides two types of copper atoms vibration with different oxygen environment such as Cu(I) – O in Cu_2O – 623 cm^{-1}, and also Cu(II) – O in CuO – 480, 534 and 588 cm^{-1} have been found. The vibration of the second type (Cu (II) – O) appears only with heating to 473 K. Spectral ellipsometry method analysis, $\rho = R_p/R_s = \mathrm{tg}\psi\exp(i\Delta)$. We studied ellipsometric spectral characteristics for copper magnetron film as a function of temperature that varied with a step of 100 K. Variation in polarized characteristics $\Delta(\lambda)$ and $\psi(\lambda)$ at T_R and 573 K are shown in Fig. 6a, b. If in air even at T_R the film was oxidized to produce Cu_2O, then in the spectral range 530-605 nm the amplitude component $\psi(\lambda)$ reached 0.21°, and a change of phase component $\Delta(\lambda) \sim 0.15°$ (Fig. 6a). At 573 K, the spectrum on the ellipsometric dependence (Fig. 6b) broadens by almost 2 times, which is explained both by an increase in the formation rate for Cu_2O at the film surface and its structural rearrangement. The broadening is due to the particle clusterization near this temperature [8]. The phase component $\Delta(\lambda)$ becomes positive only beginning with 673 K. Before that temperature, the change in sine occurred at T_R with a variation of phase component approximately from 0.3 to – 0.6, and at $T = 573$ K – from 0.6 to – 0.3. Beginning with $T = 673$ K, $\Delta(\lambda)$ starts linearly increases from 0.3 to 0.7 at $T = 1073$ K. Thus, qualitative analysis of spectral dependencies $\Delta(\lambda)$ and $\psi(\lambda)$, as well as the above results, support the possibility for the first order phase transition in the rearrangement of the structure of magnetron films from copper.

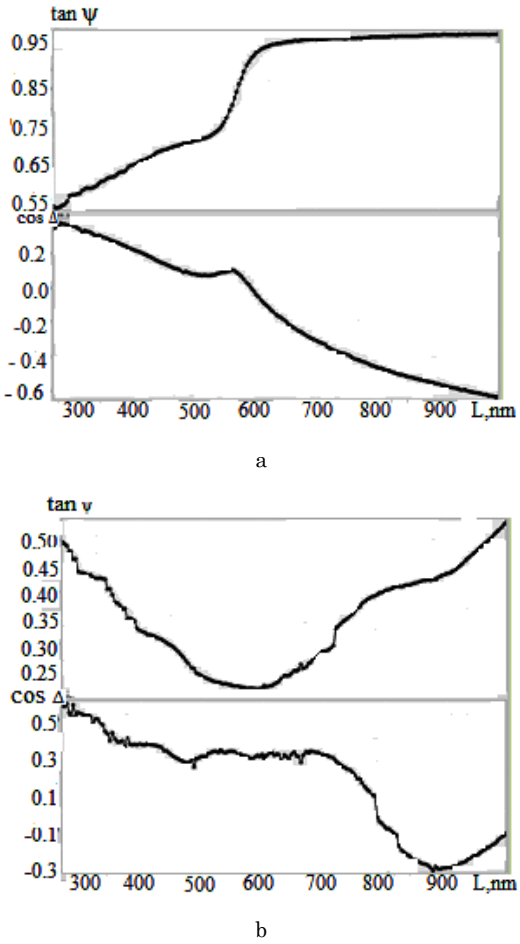


Fig. 6 – Spectral ellipsometric dependencies for magnetron copper film: a – without heating, b – at heating to 573 K

3. CONCLUSION

Comprehensive research of morphological and chemical structural changes of the magnetron copper film has been done. In this case the origination of the structural first order phase transition within the temperature range 473-673 K, the following processes occur successively: 1– clusterization to the size of 350 nm from nanoparticles the size less than 100 nm; 2– melting of low-melting oxides, and 3 – crystallization at nuclei both from nanoparticles and clusters and melts, which determines the scatter in crystallite size from 200 to 1000 nm.

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