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Degradation of Structure of Magnetron Ni and Cr Nanofilms at their Heating on Air

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The present results of comprehensive researches of degradation processes for magnetron metal nanofilms of Ni and Cr when heated on air (373-1273 K) conducted by nanotechnology instruments. Temperatures of structural and phase transformations, interrelation of amplitude and phase-frequency components of ellipsometry measurements with "ferromagnetic-antiferromagnetic" for NiO phase transition are established

Keywords: Magnetron, Ferromagnetic-antiferromagnetic, Nanofilms, Ellipsometry.

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1. INTRODUCTION

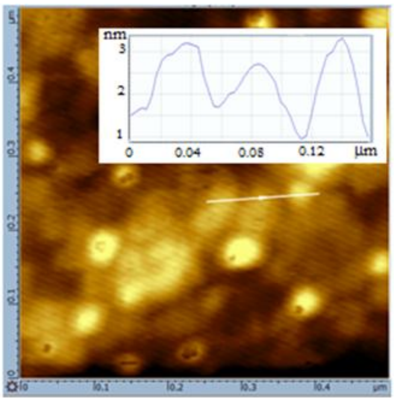
Cr and Ni are widely use in the production of high-resistive conductors with a reduced width of transitions on multilayered microelectronic printed- circuit boards. Substrates boards are metallized with chromium, which increases adhesion, and gold contacts are coated with nickel, which improves service life and prevents from copper migration [1]. After heating of a chromium film to 773 K, the crystalline randomly oriented structures of Cr_2O_3 [2] are found, and heating from 973 to 1273 K leads to coagulation processes [3]. The surface of nickel oxide NiO is formed after heating of a nickel film over 423 K [4].

2. INVESTIGATION RESULTS

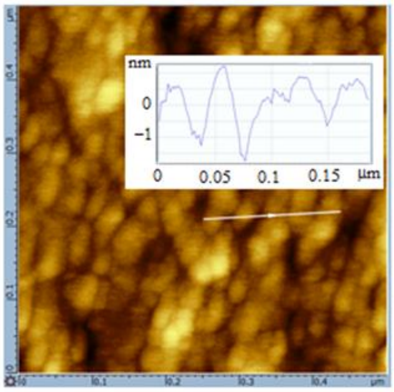
Structural changes of magnetron films from Cr and Ni when heated on air, according to atomic force microscopy (AFM), had a features of distinct number are shown in Fig. 1. The sizes of chromium nanoparticles are practically did not change when heated to 673 K, had spherical shape with a minimum size of 30 nm (Fig. 1, a and b). At the temperature increased, the forming of nanoparticles size of the film were becoming larger and the formation of clusters up to 125 nm at $T = 1073$ K was noted (Fig. 1, b). Beginning with 1173 K, the structure of Cr films, according to AFM, became clearly disordered in character.

The nanoparticles size of nickel, according to AFM, at room temperature were ~ 30 nm. When heated in the range of 373-673 K, the clusterization to the sizes ~ 100 nm with an oval form was observed (Fig. 1, c). Further when heated up to 1273 K the form of particles became acute angled, crystals with sizes up to 1 μm were formed in (Fig. 1, d).

In the range of 773-1073 K, the temperature dependence of the nanoparticle sizes $d(T)$ of Cr became nonlinear in character; the sizes of nanoparticles increased from 30 to 125 nm. As distinct from the presented in Fig. 1 topographical images, the changes on it of the lateral amplitude



a



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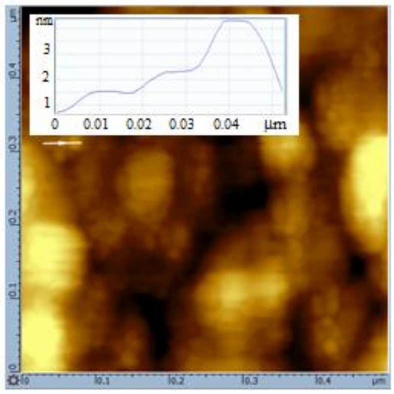

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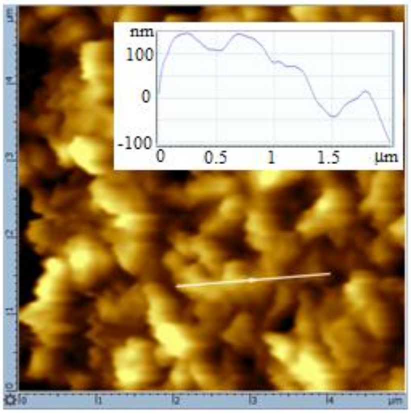


d

Fig. 1 – Atomic–force images of the structure of magnetron nanofilms on polycrystalline glass from Cr (a, b) and Ni (c, d) at a temperature: a – 373 K; b – 673 K; c – 378 K; d – 873 K

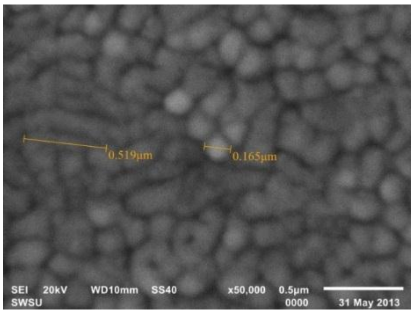
and a phase established borders between separate structural elements more distinctly. So, at $T = 1073$ K the sizes of separate nanoparticles increased up to more than 100 nm and also their form changed from typical at lower temperatures – oval to angulated, but with a clear boundary.

AFM-images of a magnetron coating from Ni show single-phase surface and sphere-like shape of the constituent nanoparticles which a minimum size of 30 nm. Beginning with 373 K, in the same contrast AFM-images demonstrate the emergence of two phases. However, the form of the particles forming the surface structure remained spherical. At 773 K, step-like structures began to arise and angularity of the shape of separate nanoparticles (Fig. 1, d) manifested itself, whose development increased up to the largest studied temperature 1273 K. In the temperature range of 973-1273 K $d(T)$ became nonlinear in character. The arising restructuring was followed by growth of the sizes and change of the form, the formation of crystallites. At 973 K the melting of particles began.

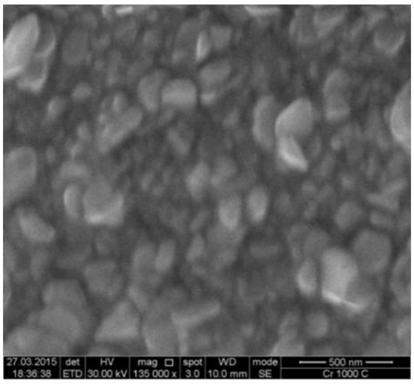
Changes of the sizes and surface structure of magnetron films from Cr and Ni are investigated also on scanning electron microscopy SEM-images given in Fig. 2. According to SEM-images, the chromium film at all temperatures lower than 1173 K is regular in structure and is formed by particles whose sizes vary from 50 to 200 nm. Different changes of structure were observed in nickel films when heated. So, when heated up to 673 K, the structure did not undergo changes and the sizes of particles were within 100 nm (Fig. 2, c). Beginning with 673 to 873 K, the sizes of acute-angled crystallites were observed to become larger by several times (Fig. 2, d); however, at further heating their form became blurred.

The changes of spectral ellipsometry (SE) characteristics of the surface of magnetron nanofilms of Cr and Ni arising when heated in the muffle furnace in the air atmosphere are analyzed. The initial one to one correspondence between the coefficient of reflection [5]:

$$\rho = R_p/R_s = \mathrm{tg}\psi\exp(i\Delta) \qquad (1)$$



a



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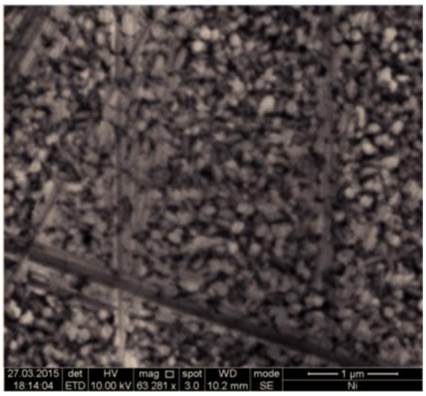

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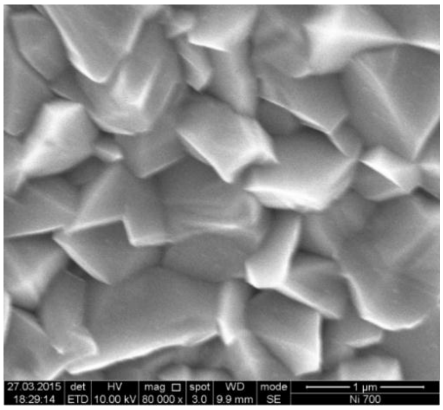

d

Fig. 2 – SEM-images of the surface of magnetron films Cr (a, b) and Ni (c, d) a – 298 K; b – 1273 K; c – 298 K; d – 973 K

for all ellipsometry angles ($\cos\Delta(\lambda)$ and $\mathrm{tg}\psi(\lambda)$) and reflection coefficients (R_p and R_s) with orthogonal polarization was determined by this fact.

Both for Cr and Ni changes in polarizing characteristics $\Delta(\lambda)$ and tg $\psi(\lambda)$ are found. For example, for Cr the changes in tg $\psi(\lambda)$ were recorded beginning with 473 K at a wavelength of 450 nm, which were remained constant up to 973 K when the jump of $\Delta(\lambda)$ occurred, which disappeared with consecutive heating.

By using the dispersive dependence of phase $\varphi(\lambda) = \mathrm{arctg}\ (\mathrm{Im}\rho(\lambda)/\mathrm{Re}\rho(\lambda))$, the wavelength and temperature ranges were determined. So, for Cr only one exceptional point at $\lambda = 450$ nm in a temperature range 473-973 K was found. Phase changes for Ni were of more difficult character. In the range from T_R to 573 K switching of $\varphi(\lambda)$ occurred at $\lambda = 320$ nm, which, probably, corresponded to a plasmon resonance. At 673 K in the range $\lambda = 280$-600 nm, $\varphi(\lambda)$ was positive, and then at 773 K overturned and the point of switching was shifted into the long- wave area.

In the dependence of an amplitude component $|\rho(\lambda)| = ((\mathrm{Re})^2 + (\mathrm{Im}\rho)^2)^{1/2}$ just at $\lambda = 450$ nm a jump was observed when Cr film was heated up to 970 K. At temperatures higher than 1073 K, $|\rho(\lambda)|$ for λ from 270 to 600 nm monotonously decreased, and then it increased, which was indicative of the structure of the film surface intact. In Ni films, to 573 K $|\rho(\lambda)|$ remained constant in all spectral range. At 673 K $|\rho(\lambda)|$ monotonously increased to 600 nm, and then it decreased. At further temperature, increase $|\rho(\lambda)|$ remained invariable, but decreased in value, which indicated the dispersion growth owing to disordering of the film surface.

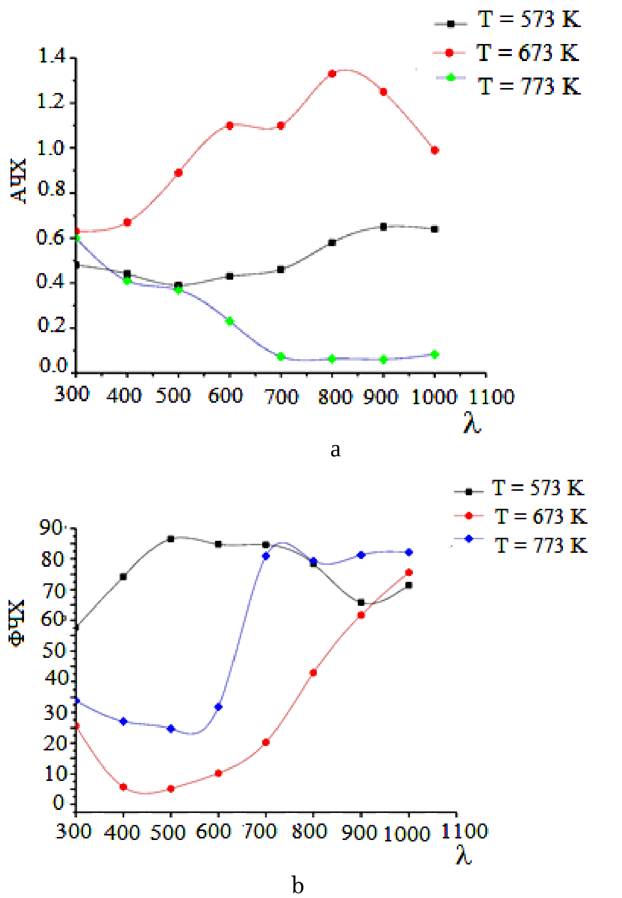

Fig. 3 – Temperature changes in spectral ellipsometry characteristics in a Ni film: a – AFC; b – PFC

Double growth of AFC for SE at the Curie temperature in the visible range was observed, up to 800 nm, to the border of the near IR-area. At the same time, PFC at the same lengths was close to zero, whereas at 573 K $\varphi(\lambda)$ changed in an antiphase, and after T_K (at 773 K) its change became in-phase. Thus, according to SE, the second-order ferromagnet-to-anti-ferromagnet phase transition in magnetron nanofilms of Ni at their heating to the Neel temperature T_H (520 K) was recorded.

Structural research of morphology of the studied surfaces at the same heating temperatures was supported with evidence of changes in their chemical structure. All reorganizations of phase structure arising at all stages at all studied heating temperatures are shown in Fig. 4. It is possible to stress that already prior to the beginning of heating $NiO_2 - 2\theta = 46°$ traces are found:

$$Ni + O_2 \rightarrow NiO_2 \qquad (2)$$

At the same temperature, in X-ray spectrum a number of lines appeared corresponding to a glass ceramic substrate, for example: TiO_2 $2\theta = 44$, 54, 63, 74°; $MgAl_2\ O_5$ $2\theta = 49°$. The analysis results of the temperature changes of intensity of the most significant lines both for Ni and its oxides are presented in Fig. 4. An increase in the intensity of the reflexes corresponding to Ni and its oxides when heated is found. After heating of the coating to 573 K, according to X-ray phase analysis, Ni began to be oxidized [4]:

$$Ni + 1/2O_2 \rightarrow 2NiO \qquad (3)$$

This reaction is corroborated by the changes that were noted in [6, 7]

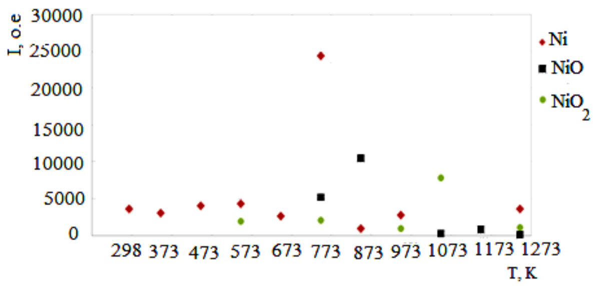

Fig. 4 – Temperature dependence of the intensity of the most significant X-ray reflexes for a magnetron Ni nanofilm

The changes in the intensity of the most characteristic lines in Raman scattering spectrum arising at heating are presented in Fig. 5, which confirms the possible oxidizing reactions (2) and (3).

3. CONCLUSION

The magnetron nanofilms of Ni and Cr widely used in electronics have been investigated. The morphological and chemical structural changes of their surfaces arising at their heating on air (up to 1273 K) were obtained by methods of probe and raster microscopy, Raman light scattering, the X-ray phase analysis and the spectral ellipsometry. The temperature

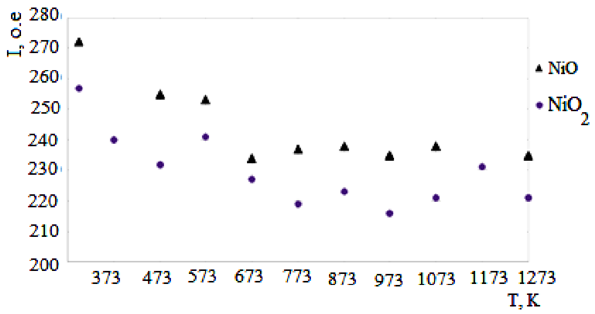

Fig. 5 – Temperature dependence of the intensity of separate lines in the Raman spectrum for nickel magnetron films

of the first-order structural phase transition as a partial melt of some oxides is determined, and according to phase- and amplitude-frequency ellipsometry components at a temperature which coincided with the Curie temperature for Ni, the second-order ferromagnet to antiferromagnet phase transition in a nickel nanofilm is confirmed.

REFERENCES

1. Wei-Xi Zhou, Yan Shen, Er-Tao Hu, *Opt. Express* **20** No 27, 28953 (2012).
2. T. Ivanova, K. Gesheva, A. Cziraki, *J. Phys.: Conference Series* **113**, 012030 (2008).
3. U.V. Naidich, I.I. Gab, B.D. Kostyuk, *Reports of the National Academy of Sciences of Ukraine* No 5, 97 (2007).
4. A. Ionescu, S. Holmes, C.H.W. Barnes, *J. Vac. Sci. Technol. B* **32** No 5, 051808 (2014).
5. H.Y. Joo, H.J. Kim, S.J. Kim, *Thin Solid Films* **368**, 67 (2000).
6. P.R. Dahoo., T. Hamon, B. Negulescu, *Appl. Phys. A* **79**, 1439 (2004).
7. I. Dhanya, B. Sasi, *J. Coat.* **2013**, ID981515 (2013).