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FUNCTIONAL MULTICOMPONENT METAL OXIDES IN THE ANODIC ALUMINA MATRIXES

The use of porous anodic alumina (PAA) matrixes for the nanostructuring of thin films based on the multicomponent metal oxide compounds containing atoms of the various metals makes it possible to reduce the grain sizes of such films and to form microstructures with a controlled aspect ratio of active surface area to volume [1], as well as to improve their functional properties [2]. The most suitable and effective methods for the formation of metal oxide films with a controlled composition and properties on nanoporous matrixes are chemical methods, among which we can distinguish the method of the electrophoretic layer-by-layer deposition and the method of dropping from the solution [3]. The electrophysical and chemosensitive characteristics of the composite films thus formed are related to their structural ordering, which is determined by the presence of the regularity of the arrangement of elementary crystallites, and the use of PAA matrixes makes it possible to form a specified array of nanoclusters with controlled sizes and surface distributions [4]. This paper presents the results of the multicomponent oxides formation of Sn, Fe, and Mo in anodic alumina matrixes and studies of composite films.

Electrophoretic deposition $Sn_xMo_yO_z$ systems in PAA matrixes

The nanoporous PAA were formed by anodizing of the sputtering-deposited onto silicon substrates aluminium films (99.99%, 1.2 μm thick) in 0.4 mol/dm^3 malonic acid electrolyte with current density of 6 mA/cm^2 at anodic potential of 85 V. To improve pore regularity and enlarge the surface of the uppermost pore layer in the films, a multi-step anodizing process was applied here, following generally the procedure described in Ref. [5]. The first anodizing step was performed in the above electrolyte, followed by selective dissolution of the porous alumina formed. This is due to the specific swelling and widening of the distances between the concaves during the compact oxide formation, which confines effectively the surface available for pore nucleation and, ultimately, makes the pores grow straight and vertical just from the film surface. The second anodizing step was done to the concaved aluminium surfaces pre-textured by anodic oxidation at anodic potential of 90 V, to cover the concaved aluminium surface with a

layer of compact alumina of 1 μm thickness. To increase the surface-to-volume ratio, the films were subjected to pore modification in mixture of phosphoric and chromic acids at 323K during 5 minutes. The pore diameters were ~ 120 nm. Matrix $Sn_xMo_yO_z$systems were formed by ion layering interleaved films of molybdenum and tin hydroxides. The films $Sn(OH)_2$ were prepared by electrophoretic deposition on PAA from an aqueous solution of 0.01M $K_2[Sn(OH)_4]$ at pH = 8. To make the transition of Sn^{+2} to Sn^{+4} the resulting films were annealed at T = 1023K. Further, the molybdate ions were deposited on the resulting film from 0.01 M solution of $(NH_4)_2MoO_3$. Generated, thereby a film of the insoluble tin polymolybdates were annealed at T = 1023K for forming the $Sn_xMo_yO_z$ compound. Such sequences of operations for the formation of $Sn_xMo_yO_z$ layers were repeated 10 - 30 times for a complete filling of the alumina templates pores.

The surface morphology and cross-sections of the PAA with metal oxides films were examined in a Hitachi S-806 scanning electron microscope (SEM) operated at 15 kV of accelerated voltage. Fig. 1 shows SEM images of the surface morphology (a) and cross-section (b) of AAM with $Sn_xMo_yO_z$ films.

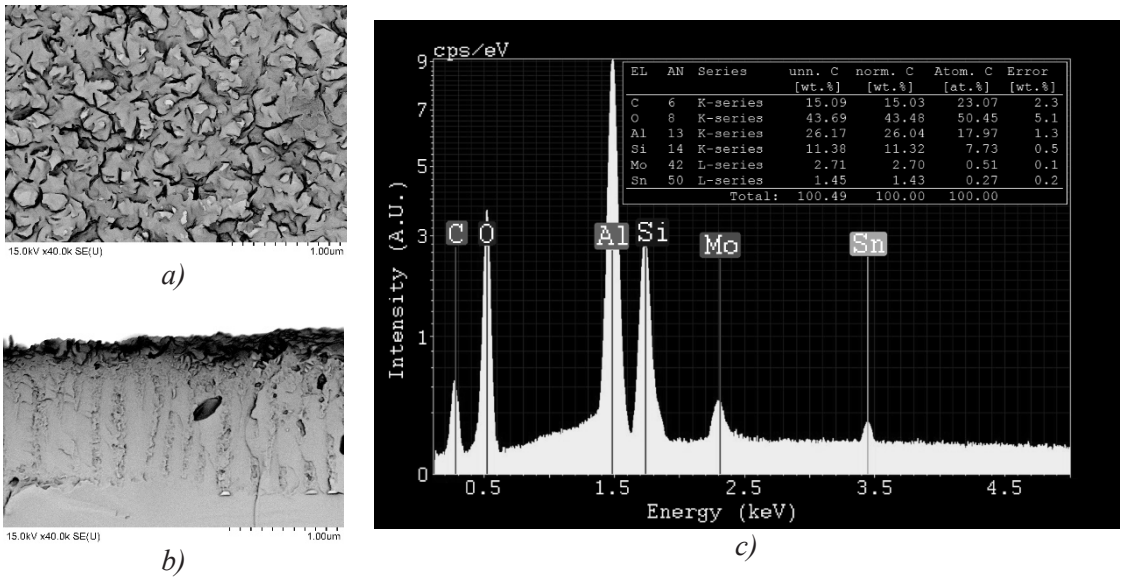

Figure 1 – SEM microphotographs of the surface morphology (a) and cross-section (b) of PAA with $Sn_xMo_yO_z$films and the energy dispersive X-ray spectrum of $Sn_xMo_yO_z$ layers deposited onto the PAA (c).

The electron probe X-ray microanalysis of $Sn_xMo_yO_z$ layers deposited onto the PAA demonstrated the presence of the following elements: Al (1.432 keV), O (0.56 keV), Si (1.77 keV), Mo (2.31 keV), and Sn (3.44 keV), and their quantitative ratio in the composition of the films (Fig. 1, c).

Formation of nanocomposites based on carbon nanotubes and $Fe_xMo_yO_z$

To apply carbon nanotubes (CNT) to the surface of PAA matrixes such as in the two previous cases, we used a slurry containing 1% CNT in propylene carbonate (*Cnano Technology Limited*), which, after the deposition (1 ml/cm^2), was dried at 470K for 0.5 hour. The semiconductor layer of the molybdenum and iron oxides were precipitated from aqueous solution of 1% $(NH_4)_6Mo_7O_{24}\,4H_2O$ and 1% $FeSO_4\,7H_2O$ on top of CNT layer (0.3 ml/cm^2). The samples were then annealed in argonat 1023K for 0.5 hour. The morphology of the patterns before and after annealing was presented in the Fig. 2.

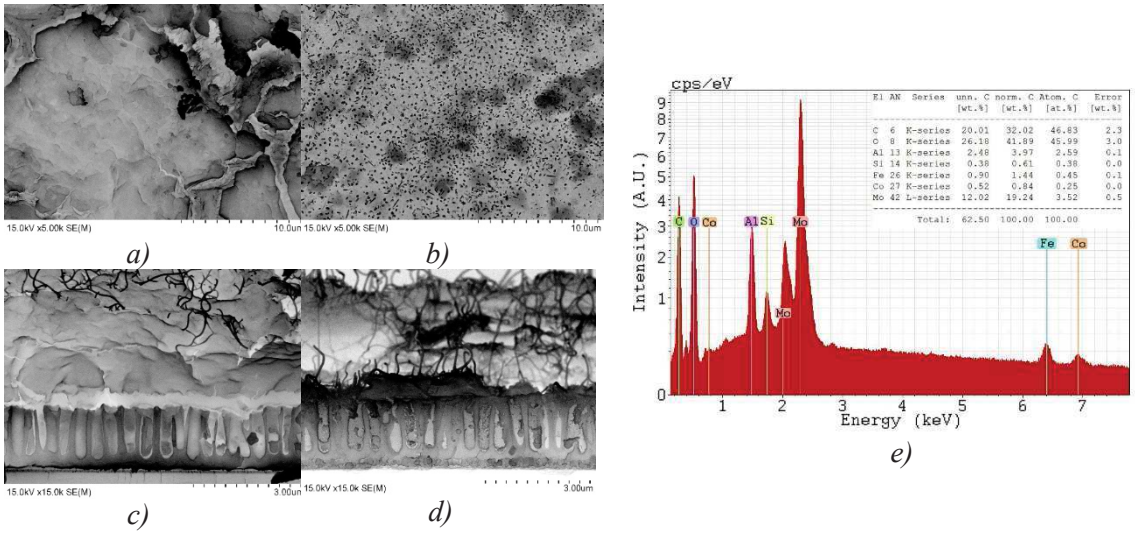

Figure 2 – SEM images of surfaces (a,b) and the cross-sections (c,d) of PAA matrixes with CNT/$Fe_xMo_yO_z$before (a,c) and after (b,d) annealing T = 1123K, t = 0.5 h, and the results of the electron-probe X-ray microanalysis (e)

The electron microscopic studies have shown that after drying the resulting coating is a homogeneous system in which the CNT penetrate the metal oxide film and exit to the surface(Fig. 2. a, c). The results of the electron-probe X-ray microanalysis showed the presence of molybdenum, oxygen and iron, which indicates the metal-oxide character of the formed semiconductor oxide film (Fig. 2, e). After annealing (Fig. 2, b, d), the film is compacted on the surface and in the pores, CNT are exposed above the film and increase the working surface of the functional layer, its electrical conductivity. Also after annealing, the porous structure of anodic alumina matrix filled with CNT and the semiconductor metal oxide layer is clearly manifested, in which predominant molybdenum oxides (19.24%) are doped with iron (1.44%).

So, the variation of the qualitative and quantitative composition of the solutions, the heat treatment regimes, the configuration and micro-

geometry of the anodic alumina matrixes allows for a directed change in the phase composition of synthesized metal oxide structures. The developed technique based on the using of ordered PAA matrixes allows the functional films forming of different complex composition compounds with reproducible structure and properties. The formed multicomponent films can be used as the chemosensitive layers of promising gas sensors and sensory microsystems, the magnetoresistive films of magnetically operated devices for electronic engineering, as well as the photosensitive layers of optoelectronic devices.

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