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# Formation of multicomponent matrix metal oxide films in anodic alumina matrixes by chemical deposition

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**Abstract.** The metal oxide films of  $\text{Sn}_x\text{Zn}_y\text{O}_z$  and  $\text{Sn}_x\text{Mo}_y\text{O}_z$  systems deposited onto anodic alumina matrixes by chemical and ion layering from an aqueous solutions were characterized by scanning electron microscopy, Raman spectroscopy, electron probe X-ray microanalysis and IR spectroscopy. The obtained matrix films had reproducible composition and structure and possessed certain morphological characteristics and properties.

## 1. Introduction

The semiconductor metal oxide films such as  $\text{SnO}_2$ ,  $\text{ZnO}$ ,  $\text{WO}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{MoO}_3$ , and others due to their high chemosensitive properties are among the most promising materials for gas sensors [1-2]. The structuring of metal oxides by applying of high ordered dielectric anodic alumina matrixes (AAM) allows to form the systems possessing a large active surface area and a heightened sensitivity to various gases [3]. The formation of mixed metal oxide films with various morphology and an aspect ratio of the surface area of formed structures to their thickness can improve the selectivity of these materials [4]. Therefore, the structuring of the metal oxides in combination with the selection of the composition allows to create a matrix system possessing certain morphological characteristics and properties.

This paper presents the results of matrix-forming of metal oxide film by chemical sedimentation of transition metals into the porous anodic alumina as well as investigations of their morphology and microstructure.

## 2. Experimental

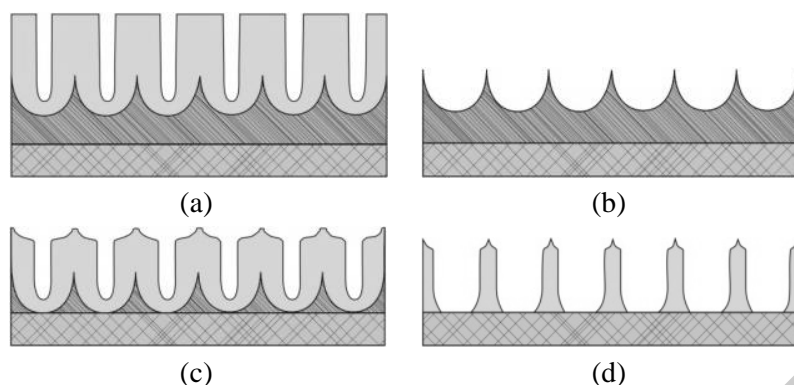
### 2.1. Formation of nanoporous anodic alumina matrixes

The initial specimens were pure (99.99%) aluminum films, 1.2  $\mu\text{m}$  thick, sputtering-deposited onto silicon substrates. Nanoporous AAM were formed by anodizing of the aluminum films in 0.4  $\text{mol/dm}^3$  malonic acid electrolyte with current density of 6  $\text{mA/cm}^2$  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 developed and applied here, following generally the procedure described in Ref. [3]. 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 aluminum surfaces pre-textured by anodic oxidation at anodic potential of 90 V, to cover the concaved aluminum surface with a layer of compact alumina of 1  $\mu\text{m}$  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  $\sim 120$  nm.

The schematic diagram showing the main steps for forming of AAM is presented on Figure 1.



**Figure 1.** Schematic diagram showing the main steps for forming of anodic alumina matrixes: first stage of anodizing the Al layer (a), selective removal of the anodic alumina (b), second anodizing step (c), pore widening treatment of anodic alumina (d).

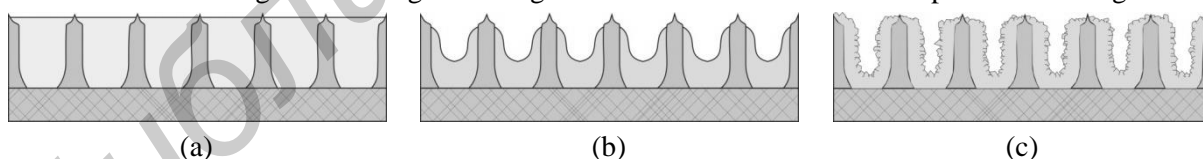
## 2.2. Formation of metal oxides matrix systems

Matrix  $\text{Sn}_x\text{Zn}_y\text{O}_z$  systems were formed by chemical deposition metal oxide films from aquatic solutions on the AAM [5]. At the first step, the samples were subjected to chemical precipitation  $\text{Sn}(\text{OH})_2$  in 1%  $\text{SnSO}_4$  solution with subsequent annealing to form  $\text{SnO}_2$  films. At the second step, the  $\text{Zn}(\text{OH})_2$  layers were prepared by the chemical precipitation method using aqueous solution of 0,01 M  $\text{ZnSO}_4$  and high-temperature annealing of formed structures at  $T = 750^\circ\text{C}$  for 30 minutes to form  $\text{Sn}_x\text{Zn}_y\text{O}_z$  system.

Matrix  $\text{Sn}_x\text{Mo}_y\text{O}_z$  systems were formed by ion layering interleaved films of molybdenum and tin hydroxides [6]. The films  $\text{Sn}(\text{OH})_2$  were prepared by electrophoretic deposition on AAM from an aqueous solution of 0.01 M  $\text{K}_2[\text{Sn}(\text{OH})_4]$  at  $\text{pH} = 8$ . To make the transition of  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$  the resulting films were annealed at  $T = 750^\circ\text{C}$ . Further, the molybdate ions were deposited on the resulting film from 0.01 M solution of  $(\text{NH}_4)_2\text{MoO}_3$ . Generated, thereby a film of the insoluble tin polymolybdates were annealed at  $T = 750^\circ\text{C}$  for forming the  $\text{Sn}_x\text{Mo}_y\text{O}_z$  compound.

Such sequences of operations for the formation of  $\text{Sn}_x\text{Zn}_y\text{O}_z$  and  $\text{Sn}_x\text{Mo}_y\text{O}_z$  layers were repeated from 10 to 30 times for a complete filling of the alumina templates pores.

The schematic diagram showing the filling of AAM of metal oxide films is presented on Figure 2.

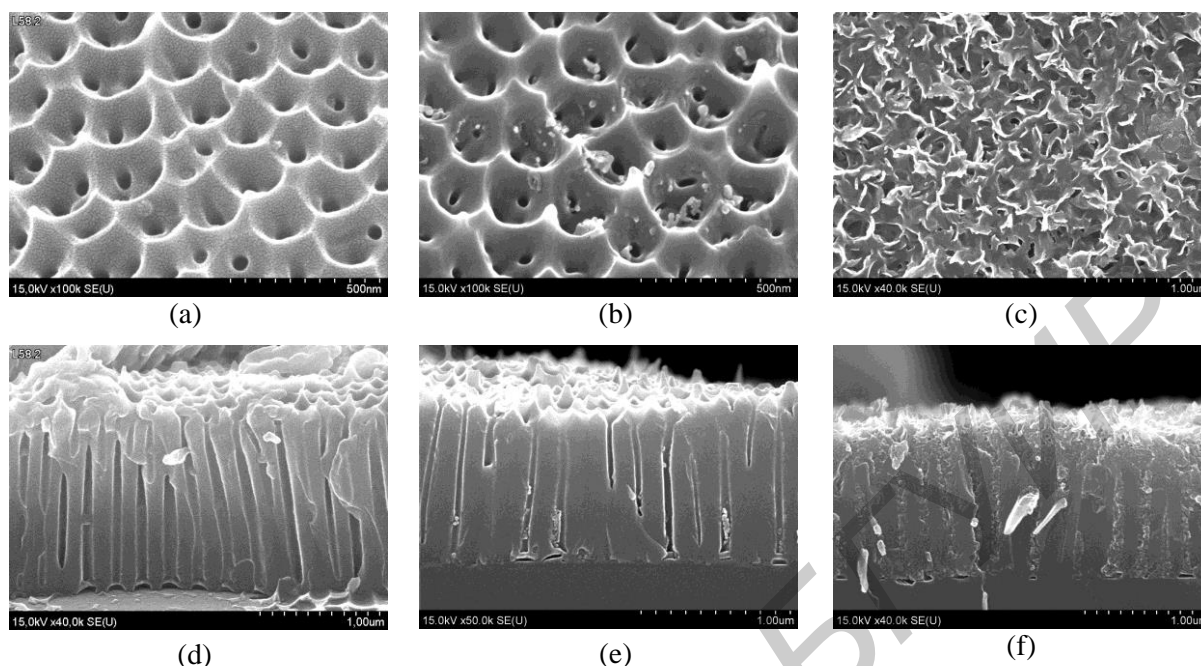


**Figure 2.** Schematic diagram showing the filling of AAM of metal oxide films: deposition metal hydroxides into the matrixes from aqueous solutions (a), low-temperature drying of filled matrixes (b) high-temperature annealing of formed structures (c).

## 3. Results and discussion

### 3.1. Investigation of morphology and structure of formed systems

The surface morphology and cross-sections of the AAM with metal oxides films were examined in a Hitachi S-806 scanning electron microscope (SEM) operated at 15 kV of accelerated voltage. Figure 3 shows SEM images of the surface morphology (a-c) and cross-section (d-f) of the initial AAM (a,d) AAM with  $\text{Sn}_x\text{Zn}_y\text{O}_z$  (b,e) and AAM with  $\text{Sn}_x\text{Mo}_y\text{O}_z$  (c,f) films.

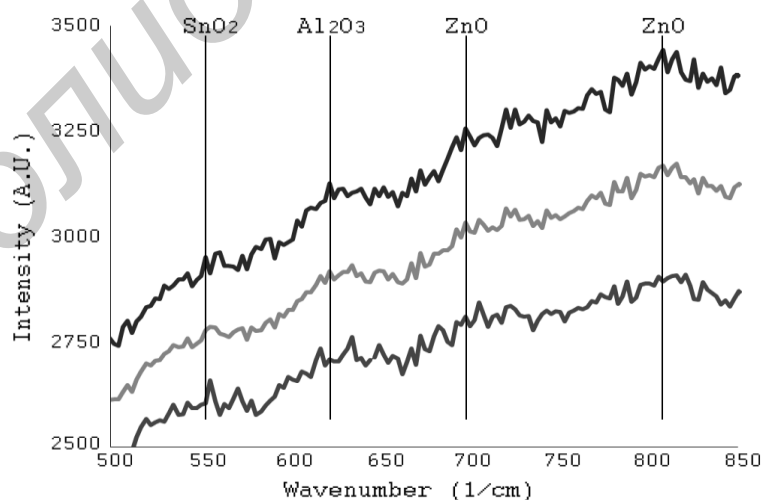


**Figure 3.** SEM microphotographs of the surface morphology (a-c) and cross-section (d-f) of the initial AAM (a,d), AAM with  $\text{Sn}_x\text{Zn}_y\text{O}_z$  (b,e) and AAM with  $\text{Sn}_x\text{Mo}_y\text{O}_z$  (c,f) films.

As we can see from these pictures, in the matrices filled by the method of chemical deposition,  $\text{Sn}_x\text{Zn}_y\text{O}_z$  grains of various sizes are formed, wherein the pores of the anodic oxide are filled non-uniformly. The most uniform filling of matrixes is observed during the formation of structures by ion layering.

### 3.2. Study of composition of mixed metal oxides

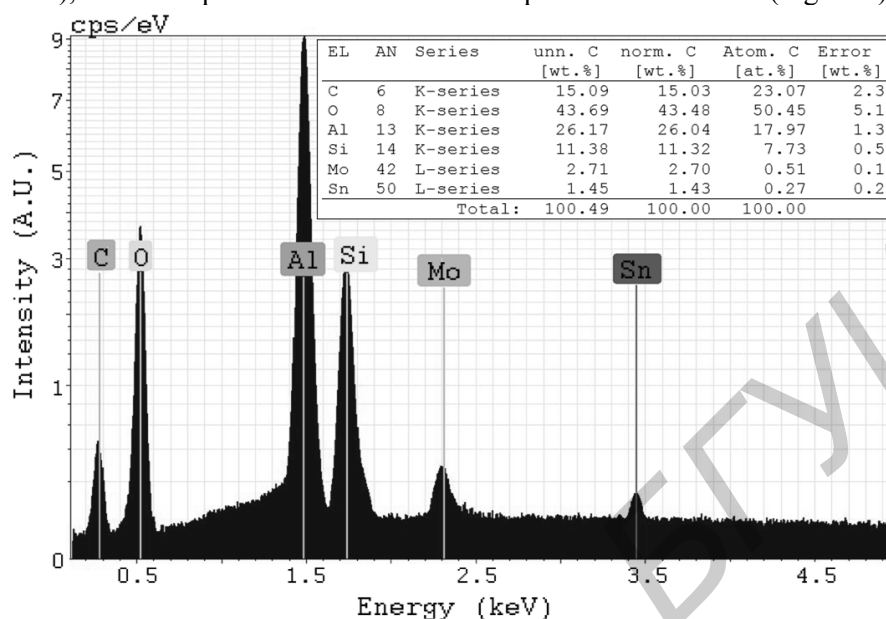
The composition of the AAM with  $\text{Sn}_x\text{Zn}_y\text{O}_z$  and  $\text{Sn}_x\text{Mo}_y\text{O}_z$  films were clarified by Raman spectroscopy (Figure 4) and the electron probe X-ray microanalysis (Figure 5).



**Figure 4.** The Raman spectra of AAM/ $\text{Sn}_x\text{Zn}_y\text{O}_z$  structures.

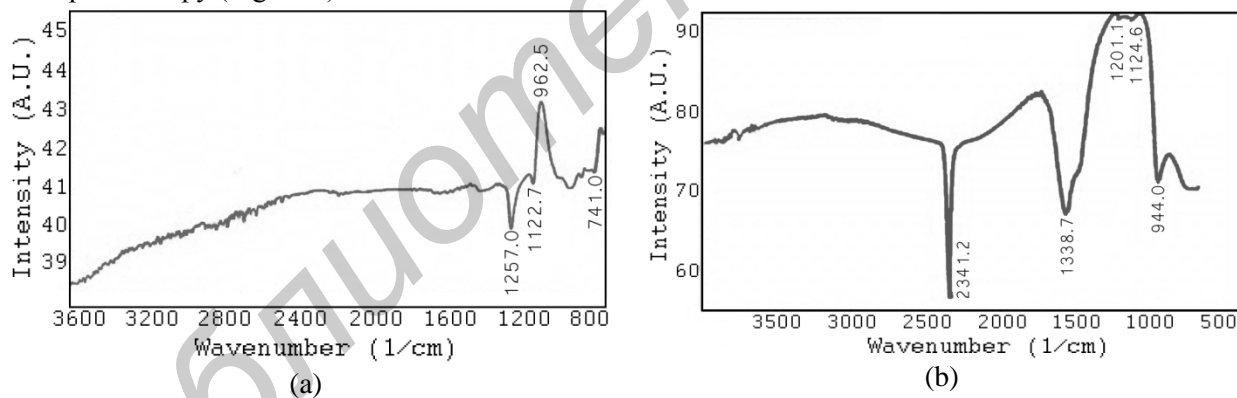
The Raman spectra of AAM/ $\text{Sn}_x\text{Zn}_y\text{O}_z$  structures show the presence of crystalline phases with  $\text{SnO}_2$  ( $550\text{ cm}^{-1}$ ),  $\text{Al}_2\text{O}_3$  ( $625\text{ cm}^{-1}$ ), and  $\text{ZnO}$  ( $705\text{ cm}^{-1}$ ,  $820\text{ cm}^{-1}$ ), which corresponded to the composition of metal oxide films deposited on the AAM.

The electron probe X-ray microanalysis of  $\text{Sn}_x\text{Mo}_y\text{O}_z$  layers deposited onto the AAM 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 (Figure 5).



**Figure 5.** The energy dispersive X-ray spectrum of  $\text{Sn}_x\text{Mo}_y\text{O}_z$  layers deposited onto the AAM.

The identification of chemical bonds present in the formed  $\text{Sn}_x\text{Mo}_y\text{O}_z$  layers was carried out using IR spectroscopy (Figure 6).



**Figure 6.** The Infrared spectra of initial AAM (a) and  $\text{Sn}_x\text{Mo}_y\text{O}_z$  films (b).

The initial surface of the AAM is characterized by peaks which corresponding to the bonds of hydrated alumina [7]. The surface of  $\text{Sn}_x\text{Mo}_y\text{O}_z$  layers, as we can see from IR spectra, contains molecular water ( $3300\text{ cm}^{-1}$ ) and hydroxyl forms ( $1440\text{ cm}^{-1}$ ), which bonds Sn-OH and Mo-OH forms with surface metal ions. The bands at  $960$ ,  $876$ , and  $710\text{ cm}^{-1}$  correspond to the Mo-O groups in Mo=O and Mo-O-Mo, the band at  $540\text{ cm}^{-1}$  correspond to the Sn-O-Sn bonds [8]. The absence of  $1640\text{ cm}^{-1}$  band is associated with dehydration of the layers during their thermal annealing. The presence of  $1260\text{ cm}^{-1}$  peak is typical to formation of polycordination bonds in nanostructured films of complex composition [9].

#### 4. Conclusion

So, the variation of the qualitative and quantitative composition of the solutions, the heat treatment regimes, the configuration and microgeometry 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 AAM allows the functional films forming of different complex composition compounds with reproducible structure and properties. The formed multicomponent films can be used as chemosensitive layers of promising gas sensors and sensory microsystems.

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