## Synthesis of matrix nanostructures from oxides and sulfides of transition metals

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**Abstract**

An original technology for the formation of spatially ordered planar $TiO_2/Bi_2O_3$ and $TiO_2$/CdS nanosystems is proposed, which based on the electrochemical anodization of titanium through anodic alumina mask and ionic cyclic layering of composite films based on $Bi_2O_3$ and chemical deposition of CdS on nanostructured $TiO_2$ surface. Comprehensive studies of multicomponent composites with three-dimensional architecture specified for practical use have been carried out, and prospects for the creation of effective photovoltaic and sensoric devices on their basis have been determined.

**Keywords**: ionic cyclic layering, nanostructures, metal oxide nanocomposite, photovoltaics.

### Introduction

In modern photovoltaic, sensor and thermoelectric devices, multicomponent metal oxides and sulfides of transition metal metal oxides are widely used [1], while the use of combined oxide and sulfide layers can significantly increase their functional properties [2]. Previously, the methods of deposition of Sn, Mo, W, Bi oxides using the processes of local chemical and ionic coprecipitation of the corresponding components on the prepared nanoporous templates were studied and developed [3]. This article describes an original technology for the formation of multicomponent composites based on oxides and sulfides, using electrochemical anodizing of titanium through an anodic alumina mask and successive ionic layer adsorption and reaction (SILAR method) of composite films based on $Bi_2O_3$ and CdS on the island surface of $TiO_2$. The SILAR method is based on cycle treatment of substrates in ion-containing solutions such as metal chlorides, nitrates, and acetates. As a result of reaction between adsorbed metal cations and anions, a nanolayer of hard-to-dissolve compound is formed on the substrate surface [4]. Combination of the SILAR method with the nanostructured matrices allows to create the systems which properties depend on their morphology and composition. So, investigations of the metaloxide and sufide films formation on the film of $TiO_2$ nanoislands by the SILAR method are especially interesting nowadays.

### Experimental

To create a template with $TiO_2$ island nanostructures, a two-layer Ti/Al thin-film system (Ti – 200 nm, Al – 1 μm), deposited on a silicon substrate, was used. Anodizing of two-layer Ti/Al composition was carried out in 0.4 M $H_3PO_4$ in a combined mode: first, the layer of porous anodic alumina (PAA) was formed at a constant current density of 6 A/cm2; when the anodizing front reached the titanium sublayer, the voltage was stabilized at 120 V. During this period, the formation of the PAA matrix was completed, and through its pores, local oxidation of the titanium sublayer and the formation of $TiO_2$ nanoislands, accompanied by a sharp drop in the current, began. The anodizing process was stopped after the anodic current decreased to 60 μA/cm$^2$. Then, the formed PAA was etched away in a 50% orthophosphoric acid solution at 50°C. As a result, a structure remained on the silicon wafer, which was the titanium layer with the nanostructured film of $TiO_2$ nanoislands.

The process of layer-by-layer deposition of bismuth oxide on island nanostructures of titanium oxide, as in the case of ionic deposition on PAA matrices [5], included surface preparation, consisting in boiling the initial workpiece in distilled water for 30 minutes at a temperature of 100°C. An aqueous solution of 0.1 M $Bi(NO_3)\times 5H_2O$ was used as a cationic solution. Heated distilled water was used as an anionic solution. Composite multioxide films were obtained by ionic layer-by-layer cyclic deposition by sequential processing of the initial samples in cationic and anionic solutions for 30 s. at temperature of 30°C. One deposition cycle included treatment in cationic and anionic solutions with intermediate washings in distilled water for 5 s. to remove ions weakly bound to the surface. The total of 150 cycles were carried out.

The CdS compound was obtained by preparing two intermediate solutions and mixing them. First, the 2 g of ammonia was added to 1 g of $CdSO_4$ and gradually mixed until a homogeneous mass was obtained. Then, the 1 g of thiourea was dissolved in the 10 ml of distilled water. The resulting compositions were mixed in 1:2 ratio. The resulting mass was placed in a water bath and intensively stirred at temperature of 30°C for 5-10 minutes until complete dissolution and obtaining the homogeneous solution. Then the resulting solution was applied to heated substrate with the nanostructured $TiO_2$ film with 2 ml dispenser and centrifuged at 1000 rpm for 30 s. The resulting film was dried in a SNOL 3.2/1100 muffle furnace under air at 70°C for 30 min. and 150°C for 60 min.

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. Investigations of formed structures elemental compositions were performed by the electron-probe X-ray spectral microanalysis (EDX) using add-on "Bruker" for scanning electron microscope.

**Results and discussion**

Figure 1 shows SEM images of the formed nanocomposites $TiO_2/Bi_2O_3$. The deposition of $Bi_2O_3$ films occurred uniformly over the entire surface of the $TiO_2$ island matrix, filling the space between the oxidized titanium regions. The bismuth oxide film with thickness of about 400 nm is an accumulation of grains in the form of plates. The grain length was about 250 nm, and the width was up to 40 nm.

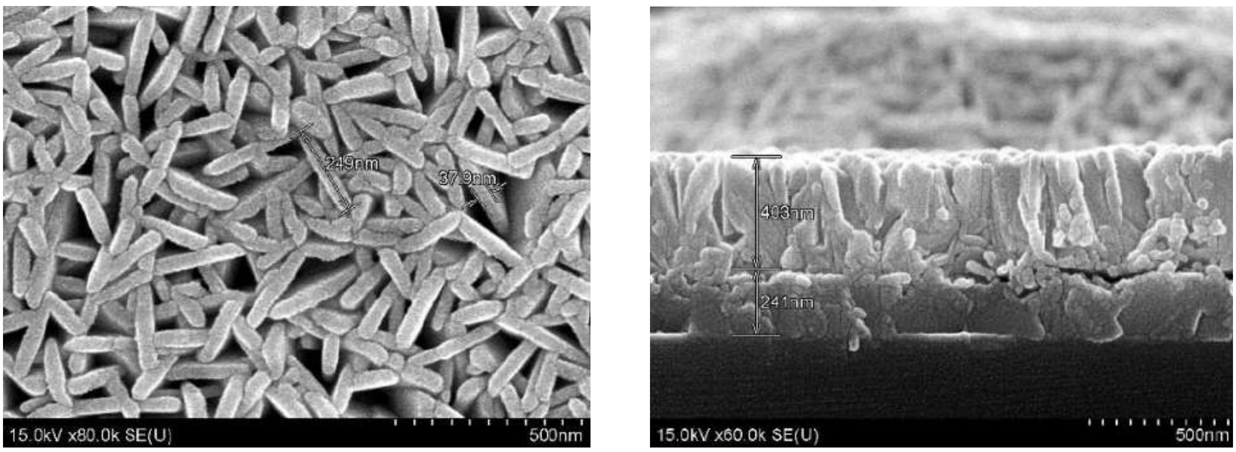


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Figure 1. SEM images of the surface (a) and cleavage (b) of $TiO_2$ matrix with deposited $Bi_2O_3$ film

The results of EDX studies of formed structures are shown in Figure 2. The EDX spectrum contains all elements of the studied system with a predominance of Bi. The atomic ratio of Bi, Ti, and O, taking into account all the elements that make up the films, was 31.46% Bi: 3.78% Ti: 51.05% O.

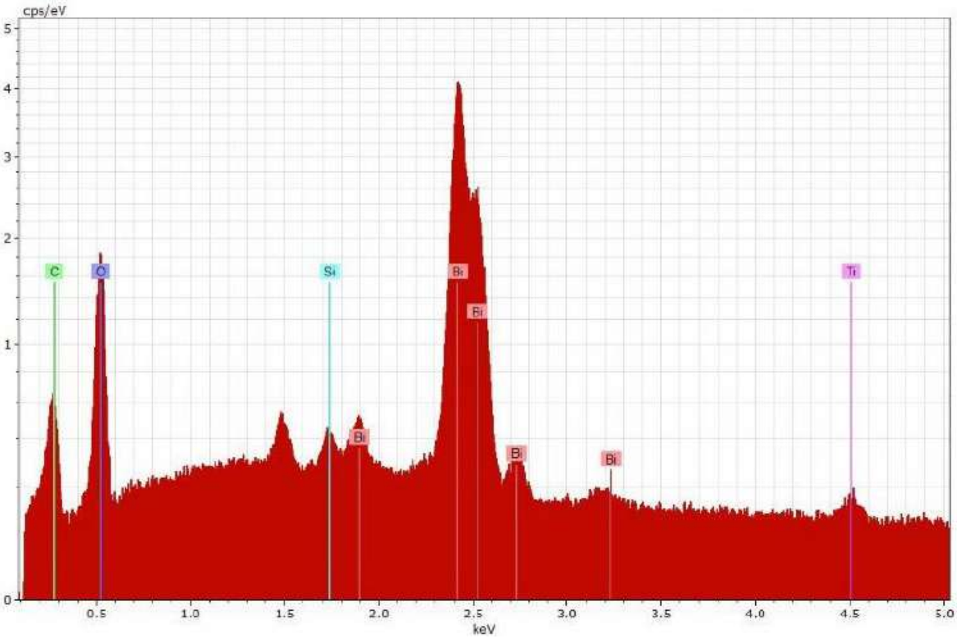


Figure 2. The electron-probe X-ray spectral microanalysis of $TiO_2$ island matrix with deposited $Bi_2O_3$ film formed after 150 SILAR cycles

Sulfide compounds of CdS were also deposited on the nanostructured surface of titanium oxide. Figure 3 shows micrographs of the formed $TiO_2$/CdS composites. The CdS film is granular formation with the grain size of about 20 nm, the thickness of the film is about 3 μm, and the total thickness of titanium and its oxide is about 265 nm. The formed CdS films are characterised by high level of agglomeration and small grain size [6].

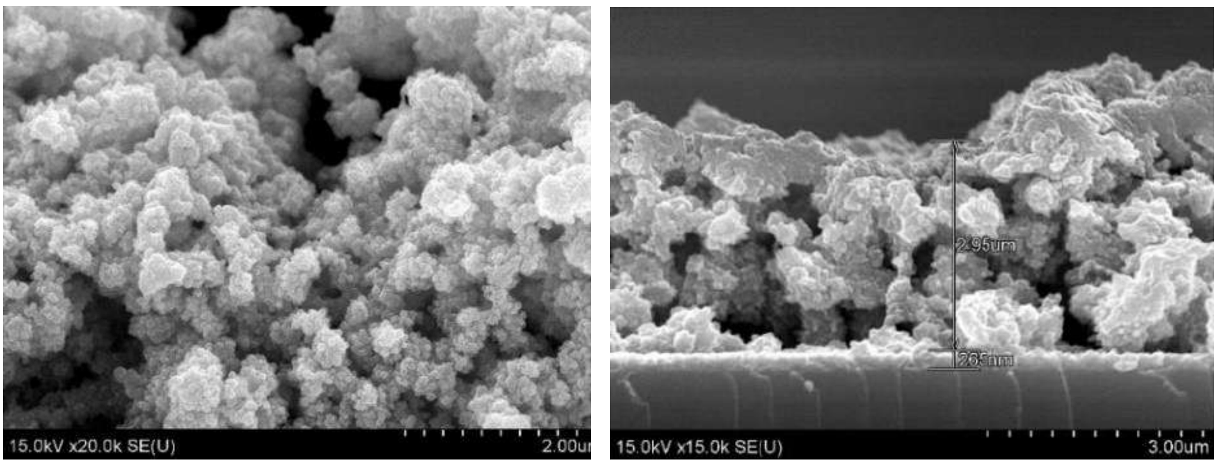


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Figure 3. SEM images of the surface (a) and cross-section (b) of $TiO_2$ matrix with deposited CdS film

Figure 4 shows the results of EDX studies of a nanostructured $TiO_2$ film with a CdS film deposited on it. The formed structure is dominated by cadmium and sulfur, which confirms the formation of the CdS compound; in addition to cadmium sulfide and titanium oxide, the film contains nitrogen and carbon atoms. Probably, these are the reaction products when two initial solutions are combined. As a result, CO, $(NH_4)$ $2SO_4$, $4NH_3$ were formed.

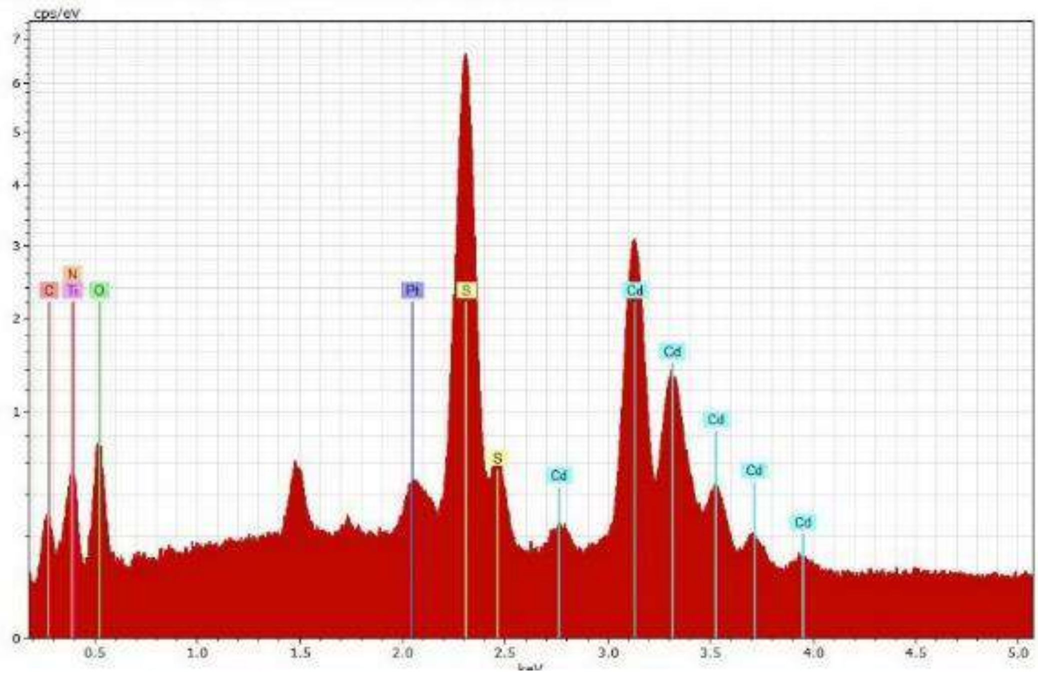


Figure 4. The electron-probe X-ray spectral microanalysis of $TiO_2$ island matrix with deposited CdS film

**Conclusion**

The composite $TiO_2/Bi_2O_3$ and $TiO_2$/CdS layers were formed by SILAR method of Bi–O-containing films and chemical deposition of CdS on the island $TiO_2$ films. The $Bi_2O_3$ film with thickness of about 400 nm was an accumulation of grains in the form of plates. The grain length was about 250 nm, and the width was up to 40 nm. According to elemental analysis, an atomic ratio of elements was 31.46% Bi: 3.78% Ti: 51.05% O. The CdS film was granular formation with the grain size of about 20 nm, the thickness of the film was about 3 μm, and the total thickness of titanium and its oxide was about 265 nm. The electrochemical and chemical methods allows to form nanostructured multicomponent oxides consisted of two or three metal components. The formed multicomponent films have great potential to applicate in high-sensitivity gas sensors, photovoltaic and thermoelectric devices.

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