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ELECTROCHEMICAL DEPOSITION OF THE Sb AND Sb-Bi NANOCRYSTALLINE FILMS

SUMMARY. In this paper, we attempt to investigate the deposition of the Sb and Sb-Bi nanocrystalline films from the chloride, citrate, and tartrate electrolytes. The alkaline tartrate electrolyte ($0.25 mol/dm^3$ $KNaC_4H4O_6$, 0.2 mol/dm^3 KOH, 0.01 mol/dm^3 $SbCl_3$, and 0.01 mol/dm^3 bismuth tartrate) with PA-1 as an additive is found to be the most suitable electrolyte for high-quality glossy films. It is possible to use the alkaline citrate electrolyte. It is demonstrated that low electric current densities (not more than 0.4 A/dm^2) should be used to obtain glossy films. It is important to meet the quality requirements while preparing the base surface where the metal or alloy film is deposited. It is impossible to obtain nanoparticles and nanocrystalline structures on the poorly polished surface. It is evident that if the microcrystal size is smaller than the short light wave length, the microroughness of the surface is invisible, and the deposit has a full gloss. The investigation of the Sb and Sb-Bi samples with the atomic-force microscope confirms that the nanocrystalline film structure is formed. The films of perfect quality are formed at any ratio of the antimony (III) and bismuth (III) concentrations in the solution. The Sb-Bi electrodeposit coatings can be used for further study of their electrical and mechanical properties.

KEY WORDS. Nanocrystalline films, nanostructures, electrochemical deposition, thermoelectric, semiconductor.

In recent two decades, since 1990s, the considerable attention has been paid to producing thin film devices by the deposition of semiconductor materials [1-6].

The innovative technologies based on nanostructured thick films are also significant [7-9]. For example, such nanostructured thermoelectric materials provide a sufficient increase in the ZT thermoelectric index to 2.4 which is caused by the high thermoelectric power, high electrical conductivity, and low thermal conductivity [3].

The nanostructured thin films of antimony and antimony-bismuth are of a particular practical interest.

The Bi-Sb system is characterized by the unrestricted solubility of the components in each other in solid and liquid states [10].

The thermoelectric properties of the antimony-bismuth solid solutions in the range of 0-9 at. % Sb depending on their composition and temperature are studied in [11]. It is established that with the increase in the antimony content, the nature of the dependencies of the electrical conductivity and Seebeck coefficient on temperature regularly changes. The increase in thermoelectric effectiveness for the nano-sized

antimony-bismuth alloy structures is demonstrated. As a rule, the ZT thermoelectric index for the Sb-Bi bulk materials containing 12% of antimony is equal to 0.88 [12]. The parameters of the infrared (IR) thermoelectric detectors based on antimony, bismuth, and the Sb-Bi alloys are calculated and optimized [13]. The comparative analysis of the fiber- or film-based detectors is carried out. The analysis results proves the high quality and prospects of the structures studied [13].

The antimony and antimony-bismuth thin films demonstrate optical properties, which are the functions of the film thickness. Such films are used in modern optical technologies.

Various techniques are used for the film deposition. The existing techniques for producing nanoparticles and nanostructures are time-consuming and costly. In this context, the electrochemical technologies for producing films of different thickness are noted for their low cost and simplicity. The electrochemical deposition provides the opportunity to control the nanostructure synthesis process; and not only the nanostructured films but single nanoparticles on various substrates playing the leading part in the nanoparticle stabilization can be obtained [6], [14-15]. The phenomenon of nanoparticle self-organization is studied under the strict control of the electrochemical conditions [15].

The purpose of this work is to apply the electrochemical methods to the deposition of the antimony and the antimony-bismuth alloys in the acid and alkaline solutions for producing the nanocrystalline films. The direct and stripping (reverse) voltammetry, potentiostatic, and galvanostatic methods are used (producing the Sb and Sb-Bi films).

The experiment. The antimony alloys are deposited from the chloride, citrate, and tartrate solutions. The pH value for the solutions is experimentally adjusted in every particular case. To obtain the nanocrystalline deposits, the electric current density or electrodeposition potential should be controlled. The metal ion concentration in the solution is of crucial importance. It is significant to meet the quality requirements while preparing the base surface where the metal or alloy film is deposited. It is impossible to obtain nanoparticles and nanocrystalline structures on the poorly polished surface. First of all, the electrochemical behavior of metals is studied, and then the conditions of metal co-deposition and the metal atom interaction on the electrode are investigated. As a result, the conditions of film deposition on the substrate are stated.

From all this scope of the research, we will focus on the discussion of the results obtained on the antimony and bismuth deposition from the acid chloride and alkaline tartrate solutions. The Sb-Bi system is a model one, the study of its behavior in the chloride solutions enables general regularities of the deposit formation on the electrode to be determined. The high-quality deposits as glossy films are produced from the alkaline tartrate solutions. But this does not imply that it is impossible to obtain nanocrystalline films from the citrate solutions.

The antimony and Sb-Bi films were electrodeposited from the aqueous solutions containing 0.25 mol/dm^3 of KNaC$_4$H$_4$O$_6$, 0.2 mol/dm^3 of KOH, 0.01 mol/dm^3 of SbCl$_3$, and 0.01 mol/dm^3 of bismuth tartrate. The atomic-force microscopy method was used

to study the structure of the antimony and antimony-bismuth films electrodeposited on the copper substrate. The *INTEGRA-AURA* scanning probe microscope in the semi-contact mode was used in the investigation. When measuring, the topography and contrast images were recorded. When scanning, the areas 150×150 nm in size for the films 1 μm thick were studied.

To carry out the voltammetric study, the measuring unit consisting of the *PI-50-1* pulse potentiostat equipped with the *PR-8* programmer, the *Grafit-2* electronic recorder, and the three-electrode cell was used.

The glassy-carbon electrode of 0.2 cm in diameter was used as a working one. All the potentials are given in reference to the silver-chloride electrode (EVL-1M4). The platinum plate, 1 x 2 cm, was used as an auxiliary electrode. The working electrode was given the mechanical and electromechanical treatment until the constant potential was set.

The pulse I-t curves in the cathode mode were also studied on the glassy-carbon electrode.

Results and discussion. In the chloride solutions, Sb(III) and Bi(III) form the $SbCl_n^{3-n}$ and $BiCl_n^{3-n}$ complexes, where n=1÷6: Since the high-concentration solutions (2 mol/dm³ of HCl) are used, the complexes with n=4÷6 are predominant. The stability constant values for the Sb (III) and Bi (III) complexes are given in Table 1 [15].

Even at low pH values, it should be kept in mind that the SbO^+ and BiO^+ particles are formed while reacting:

$Sb^{3+} + H_2O \rightarrow SbO^+ + 2H^+$ (1)

$Bi^{3+} + H_2O \rightarrow BiO+ + 2H^+$, (2)
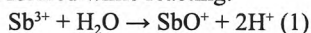
though these ion concentrations are low.

Table 1

The stability constant values for the Sb(III) and Bi(III) complexes in the chloride solution

M	K_1	K_2	K_3	K_4	K_5	K_6
Sb	$1.8 \cdot 10^2$	$3.1 \cdot 10^3$	$1.5 \cdot 10^4$	$5.3 \cdot 10^4$	$5.2 \cdot 10^4$	$1.3 \cdot 10^4$
Bi	$2.3 \cdot 10^2$	$3.1 \cdot 10^3$	$2.2 \cdot 10^4$	$1.2 \cdot 10^4$	$5.2 \cdot 10^6$	$3.6 \cdot 10^6$

The electrode potential depends on the concentration of the $SbCl_n^{3-n}$ and $BiCl_n^{3-n}$ (n=4÷6) complexes. Based on the data published in [15], the standard potentials of $BiCl_4^-$/Bi and $SbCl_4^-$/Sb are equal to +0.16 B and +0.17 B (NHE), respectively. The antimony and bismuth deposition potentials are expected to be rather low (small negative values).

Since the reduction potentials of the antimony and bismuth ions coincide, in the metal co-deposition, only one maximum (Fig. 1) is recorded on the cathode branch of the cyclic current-potential curve at the potential of Em = -0.3 V. The dissolution of the antimony-bismuth deposition formed resultes in recording one anodic peak of the cyclic curve. Such a cyclic curve is peculiar to the systems, whose components form a solid solution.
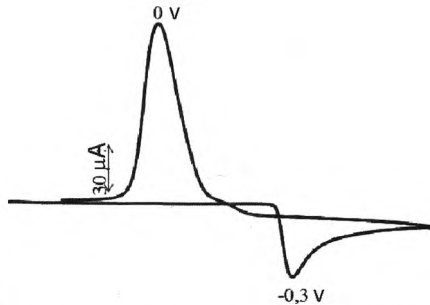
Fig.1. The cyclic current-potential curve of the Sb-Bi dissolution-deposition in the chloride solution 2M HCl, $C_{Sb(III)}=C_{Bi(III)}=10^{-3}$ mol/dm^3, W=0.05 V/s
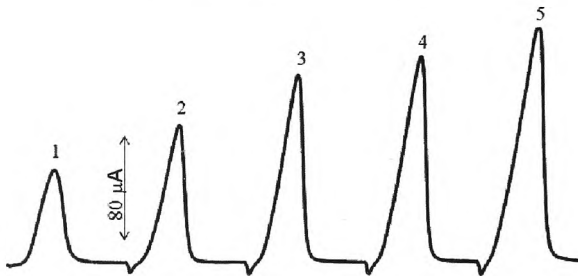

Fig.2. The inverse current-potential curves of the antimony deposition dissolution in the chloride solution, at the various bismuth concentrations ($C_{Bi(III)} \cdot 10^{-3}$ mol./dm^3): 1) 0; 2) 0.16; 3) 0.33; 4) 1.65; 5) 2; $C_{Sb(III)} = 10^{-3}$ mol/dm^3

The study of the current-potential curves of the Sb-Bi deposition dissolution at various concentrations of Bi (III) in the solution demonstrates that, when the bismuth ion concentration increases, the rise in a peak is observed in the solution, and the electric quantity rises (Fig. 2). Each peak is equivalent to the amount of the Sb-Bi deposition on the electrode. Such a type of the dependence indicates the solid solution formation with the antimony and bismuth co-deposition.

As the results of our study demonstrate, alkaline tartrate solutions are the most appropriate electrolytes to produce high-quality glossy nanocrystalline coats.

The study of the effect of potential on the antimony electrodeposition (Fig. 3, curve 1) demonstrates that antimony starts depositing at E=-1.25 V, the maximum deposition coincides with the E=-1.45 V potential, the optimal potentials are in the range from -1.4 to -1.5 V.

The dependence of the peak height on the electrolysis potential is a well-distinct curve with a maximum, both branches are flat. The flat ascending branch indicated some problems with nucleating on the electrode surface.
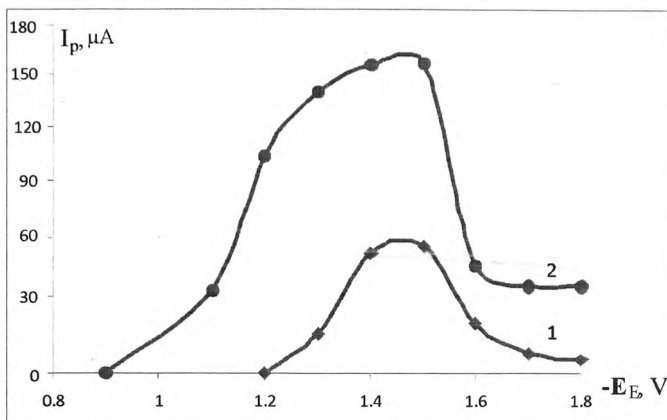
Fig. 3. The dependence of the current of the antimony dissolution-deposition (1) and the antimony and bismuth co-dissolution-co-deposition (2) in the alkali tartrate solution on the electrolysis potential; $C_{Sb(III)}=10^{-3}$mol/dm^3, $C_{Bi(III)}=10^{-3}$mol/dm^3

Under the conditions of the antimony and bismuth co-deposition, the reduction process starts at E=-1.0 V (Fig. 3, curve 2). The maximum is in the potential range of -1.4÷-1.5 V. The ascending branch is flatter than the one of curve 1. (Fig. 3).

The bismuth ions in the solution prevent nucleating. This is demonstrated by the shape of the potentiostatic I-t curve of the antimony and bismuth co-reduction (Fig. 4). At minor potential shifts from the initial value, the curves quickly take the normal shape specific to the deposition of metals with a fine-crystalline structure. In this case, the deposition potential variation provides the conditions for a nanocrystalline structure to be formed.
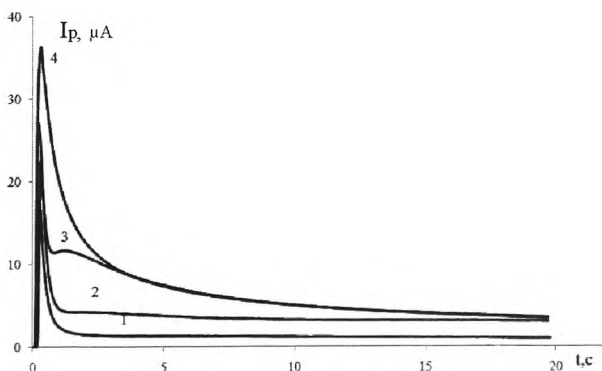

Fig. 4. The potentiostatic curves of the antimony and bismuth reduction in the alkali tartrate solution at various values of the potential (E, V): 1) -1.1; 2) -1.2; 3) -1.3; 4) -1.4; $C_{Sb(III)}=10^{-3}$ mol/dm^3, $C_{Bi(III)}=10^{-3}$ mol/dm^3

To study the metal interaction in the fine-dispersed antimony-bismuth system, the current-potential curves of antimony dissolution at various bismuth ion concentrations in the tartrate solution are recorded. A peak of the Sb-Bi dissolution is registered on the inverse current-potential curves. When the bismuth concentration increases in the solution, the peak potential shifts from $E_p=-0.52$ V to $E_p=-0.46$ V, and the bismuth ion concentration changes from 0 to $2 \cdot 10^{-3}$ M.

Based on the data obtained, the dependency of the dissolution currents on the bismuth concentration is plotted (Fig. 5). The graph demonstrates that the dependency is curvilinear (it slants, which indicates the formation of the non-perfect Sb-Bi solution). This curve is approximated by the third-degree polynomial with the accuracy of $R^2=0.9994$.
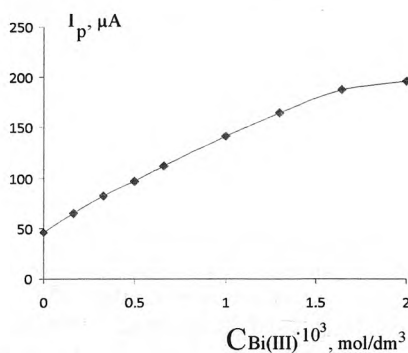

Fig.5. The dependence of the dissolution current for the antimony-bismuth deposition on the bismuth concentration in the alkali tartrate solution $C_{Sb(III)}= 10^{-3}$ mol/dm^3

Then the film surfaces of bismuth and antimony electrochemically deposited on the copper substrate at DC were studied. The topography of the film surfaces is formed by the substrate roughness, the growth cluster agglomeration, the cluster size, and cluster shape. Fig. 6 demonstrates the results of the study of the Sb and Sb-Bi film surfaces.

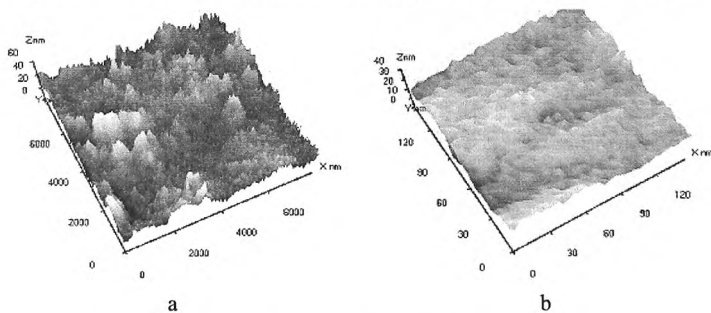a   b

Fig.6. The topography of the antimony deposition surface
(a) and antimony-bismuth (b) on the copper substrate, in 3D

On the surface of the antimony deposition (Fig. 6a), there are two types of non-homogeneity: the needle-shaped formations (growth patterns) and fine-grained structure of the film itself. The height of the needle-shaped formations is in the range of 20 to 60 nm. The Sb-Bi film is characterized by fine-grained structure (Fig. 6b), the grain size is in the range from 10 to 12 nm.

Conclusion

1. The optimal potential (-1.4 V) for the antimony and bismuth thin film co-deposition from the alkaline tartrate and citrate solutions was determined by the stripping voltammetry.

2. The potentiostatic curves of the antimony and antimony-bismuth alloy reduction in the alkali tartrate and citrate solutions were studied. The conditions of producing the films of the fine-crystalline structure were determined (the potential electrolysis is 1.4 V, the current density is not more than 4 mA/cm^2).

3. The stripping voltammetry demonstrated that when antimony and bismuth co-deposited, the solid solutions were formed with any component ratio.

4. The investigation with the atomic-force microscope of the Sb и Sb-Bi samples confirmed the formation of the nanocrystalline film structure. The glossy films were obtained. The produced Sb-Bi electrodeposited films can be used for further studying their electric, thermoelectric, and mechanical properties.

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