Bulgarian Chemical Communications, Volume 40, Number 3 (pp. 254–260) 2008

Investigations of the surface morphology of electrodeposited Ag-In coatings by means of optical, scanning-electron and atomic-force microscopy

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Received November 1, 2007; Revised February 1, 2008

Comparative investigations of the surface morphology of electrodeposited silver-indium alloys with chaotic distribution of the different phases, as well as with spatio-temporal structures onto their surface were performed by means of optical, scanning–electron and atomic–force microscopy.

The morphology of the different phases forming the heterogeneous chaotic structures is quite different and they are well distinguishable both in the SEM and AFM measurements. The coatings with periodical spatio-temporal structures are multilayered with very small thickness of the separate sublayers and in the SEM images the areas of the different phases (dark and light areas) are well visible only using low electron beam voltages. The AFM investigations show in some areas ordered structures, probably connected with the natural convection during the electrodeposition.

Key words: Atomic-force microscopy, electrodeposition, phase composition, scanning-electron microscopy, silver-indium alloy.

INTRODUCTION

The first "crystallization" spirals on the surface of an electrodeposited alloy coating were observed by E. Raub and A. Schall [1]. They obtained dark silver-indium coatings which "…color is non-uniform and spotted. The electrodeposition of the indium-richer gray phase leads to the formation of wounded spirals and other figures onto the indium-poor basic material..." [1]. A microscope image was published in this article without any scale and without any description of the conditions for deposition of the observed structures. Almost 50 years later the formation of similar structures, due to self-organization phenomena, has been observed and widely investigated by I. Krastev and co-workers during electrodeposition of silver alloys such as Ag–Sb [2–4], Ag–Bi [5] and Ag–Sn [6].

Self-organization is a process of evolution where the development of new, complex structures takes place in the system itself. Systems consisting of components of different nature follow one and the same principles of the self-organization processes, forming electrical oscillations, structures in liquids, chemical waves, lasers, animal population, etc. For this reason, the investigations of these pheno-mena are considered an important part of the fundamental science [7–10].

As a result of numerous investigations in the recent years a procedure for obtaining of clear and stable indium electrolytes was proposed [11, 12]. From the electrolytes obtained by addition of a silver salt to the indium cyanide solutions was possible to deposit compact, heterogeneous coatings with an indium contents of up to 60% [13, 14]. The phase composition of the alloy coatings was determined in dependence on the electrolysis conditions [14] and it was established that with the increase in the current density the contents of indium in the coatings increases also, which leads to the formation of not only the α-phase (solid solution of indium in silver), but also of the indium-richer Ag_3In, In_4Ag_9 and $AgIn_2$ phases [14, 15]. By means of anodic linear sweep voltammetric technique (ALSV) it was shown that each silver-indium phase is dissolved in a typical potential range in the especially chosen electrolyte [16].

The above mentioned phases are stable in the indium concentration range as follows [17]:

α-phase – solid solution of indium in silver, containing up to 20.4% In at room temperature;

γ-phase – hexagonal phase (Ag_3In) with a range of homogeneity between 29% and 29.7% In at room temperature;

ε-phase – cubic phase, which corresponds to In_4Ag_9 (Ag_2In). The range of its homogeneity is between 32.8% and 36.82% In. This phase is hetero-

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geneous with the γ-phase up to 32.8% as well as with the φ-phase;

φ-phase -– body-centred tetragonal phase, which exists together with the ε-phase from 36.8% up to 67% In, as well as with pure indium in the case of more than 67% indium in the alloy. The phase corresponds to the $AgIn_2$ compound.

Practically silver is not soluble in indium.

During previous investigations on the electrodeposition of silver-indium alloys the conditions of reproducible formation and observation of spatio-temporal structures as waves, spirals and targets onto the electrode surface have been established [14]. The determination of the phase composition of alloy coatings with spatio-temporal structures by means of X-ray diffraction analysis [14, 15] as well by using anodic linear sweep voltammetry have shown that the spatio-temporal structures are formed by silver and the Ag_3In phase [15, 18].

The spiral structures are stable during a long time of storage at room temperature and do not change for months. The heterogeneity of the surfaces is optically well visible. However, the differences in the surface morphology of the dark and light areas of the periodic spatio-temporal structures are not substantial [14].

The atomic-force microscopy (AFM) is characterized by enhanced resolution ability, which in contrast to the scanning electron microscopy (SEM), could reach atomic dimensions, so that comparative SEM and AFM investigations of the optically well distinguishable dark and light areas of the spatio-temporal structures seem to be useful for determination of their morphological differences.

The aim of this study was to perform comparative investigations of the surface morphology of electrodeposited silver-indium alloy coatings through optical, scanning-electron and atomic-force microscopy.

EXPERIMENTAL

The composition of the electrolyte for deposition of the alloy coatings is shown in Table 1.

Table 1. Electrolyte composition.

Electrolyte composition	Concentration	
	$g \cdot dm^{-3}$	$mol \cdot dm^{-3}$
In as $InCl_3$ (Alfa Aesar)	22.4	0.2
Ag as $KAg(CN)_2$ (Degussa)	8	0.08
D(+)-Glucose (Fluka)	20	0.1
KCN (Merck)	65	1

The electrolytes were prepared using chemicals of *pro analisi* purity and distilled water by the following procedure: The necessary quantities of D(+)-Glucose were added to the water solution of indium chloride. The electrolyte was pre-electrolyzed for a short time during a cyclic voltammetric measurement, and after that, the total amount of KCN, according to the molar proportion of KCN to indium of 5:1, was added in one step to the electrolyte under stirring. After dissolution, the silver salt was added.

The alloy coatings with thickness between 5–7 μm were deposited onto copper cathodes with an area of 2×1 cm. The preliminary preparation of the copper cathodes includes a standard procedure of electrochemical degreasing followed by pickling in a 20% solution of sulphuric acid. In order to avoid the contact deposition of silver, the cathode was immersed into the electrolyte under current. Two platinum counter electrodes (about 4 cm^2 each) were used.

The In percentage in the coatings depending on the electrodeposition conditions was determined by X-ray fluorescence analysis (Fischerscope X-RAY HDAL). The element composition on the coating surface was measured by EDAX.

The X-ray patterns were measured in the 2θ range between 20–140° with Cu-Kα irradiation. The surface morphology was studied by SEM and optical microscopy.

The topography of the samples was investigated with atomic-force microscopy, (microscope NTEGRA) using the semicontact method.

The morphological investigations have been performed onto the whole surface of the electrodes, but the presented results of the AFM investigations were obtained from the area situated about 3–5 mm below the upper end of the electrode which was also observed by a CCD camera. As far as possible, the same area was observed by SEM.

RESULTS AND DISCUSSION

Figure 1 shows the optical microscope image of an alloy coating deposited at 0.8 $A \cdot dm^{-2}$. The coating is matt, heterogeneous with the characteristic of silver dull-white colour in the light zones and with grey colour in the dark ones.

Reflexes of the phases In_4Ag_9 and $AgIn_2$ could be found in the X-ray pattern (Fig. 2) in addition to the reflexes of the silver phase (α-phase). This is in conformity with our previous X-ray investigations of coatings, deposited at the same current densities [14, 15].

The coating presented in Fig. 1 was observed by scanning-electron microscopy (Fig. 3a). Three different types of surface morphology have been observed. Figure 3b presents the marked area from

Fig. 3a with the three different and typical for the coating motphological characteristics. The results of EDAX analysis in the different areas are shown with arrows.

On the basis of the XRD pattern of the coating shown in Fig. 1 and the EDAX analysis it could be supposed that with the increase in the indium contents in the coatings they become fine-grained. The topography of the same areas investigated by AFM is presented in Figs. 4b, 5b and 6b and seems to be in a good correlation with the SEM images 4a, 5a and 6a.

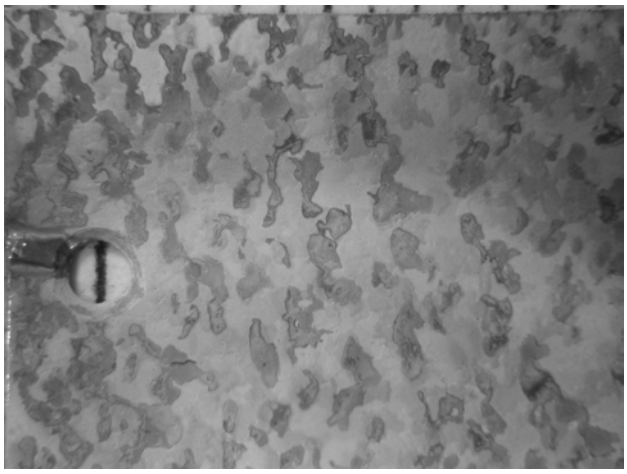


Fig. 1. Optical microscope image of a Ag-In coating; c.d. = 0.8 A·dm^{-2}; $C_{D+\text{-Glucose}}$ = 0.1 mol·dm^{-3}; C_{KCN} = 1 mol·dm^{-3}; C_{Ag} = 0.08 mol·dm^{-3} (as $KAg(CN)_2$); C_{In} = 0.2 mol·dm^{-3} (as $InCl_3$); deposition time – 18 min.

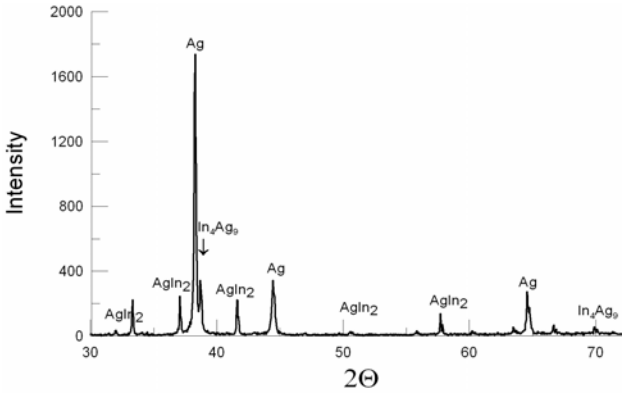
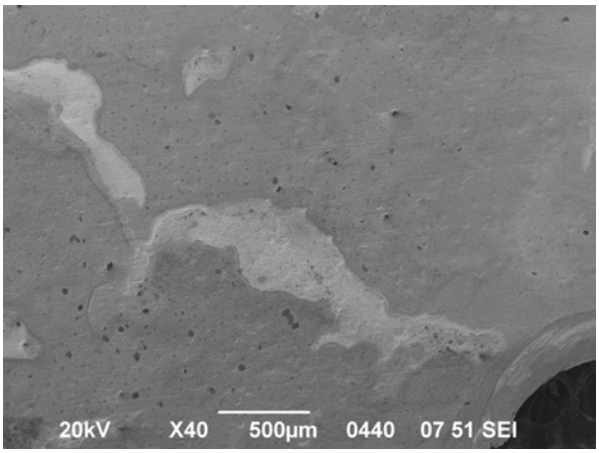
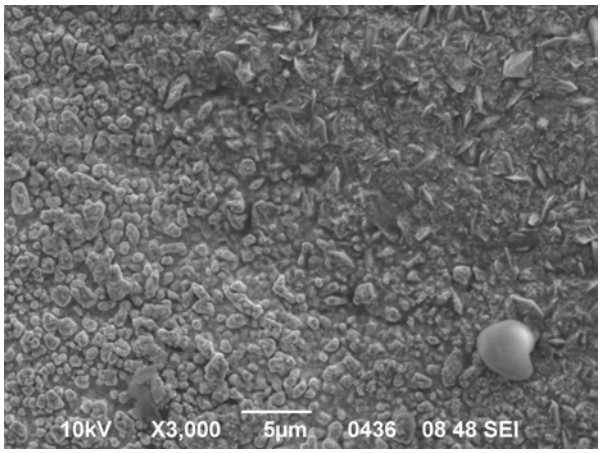


Fig. 2. XRD pattern of the coating of Figure 1.

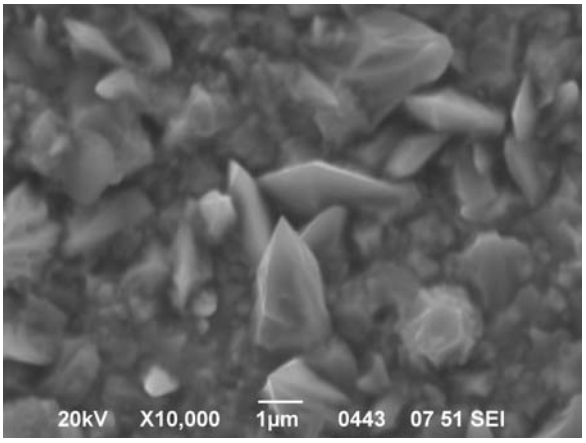


a

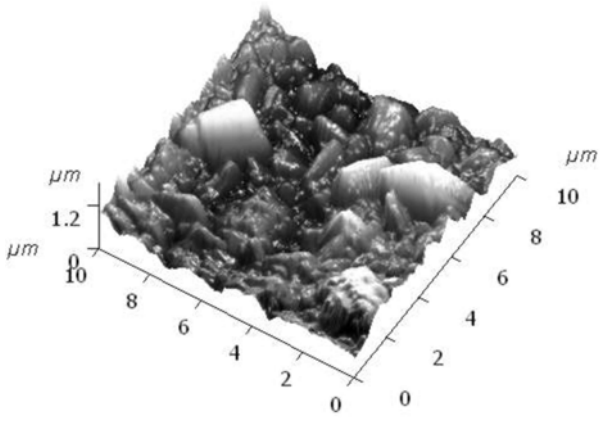


b

Fig. 3. a. SEM image of the coating of Figure 1; b. SEM image of the marked area of Figure 3a.

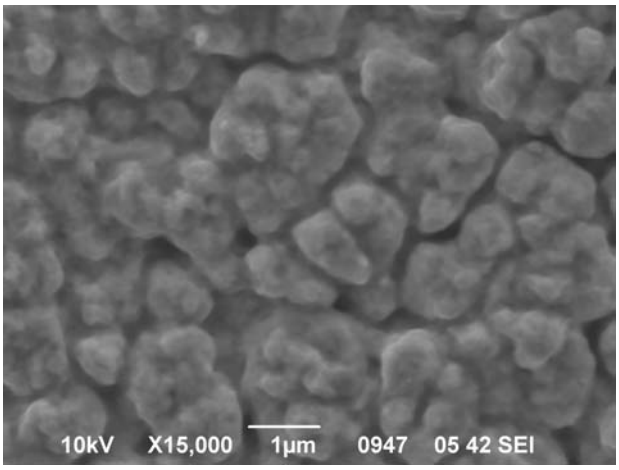


a

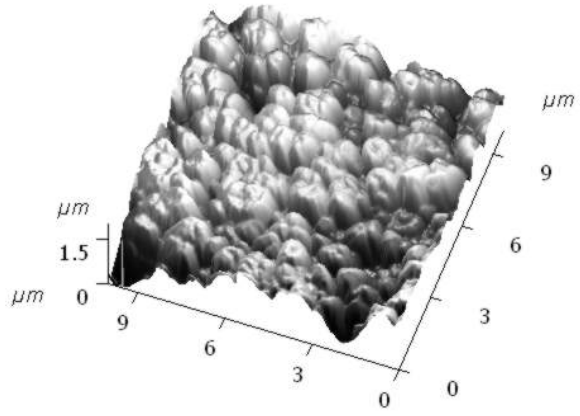


b

Fig. 4. a. Optical image of the area from Figure 3b with 100% Ag; b. AFM image of the surface presented in Figure 4a.

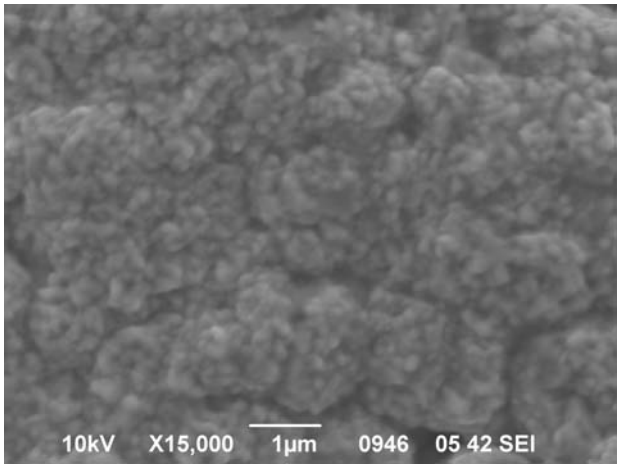


a



b

Fig. 5. a. Optical image of the area from Figure 3b with 34% Ag; b. AFM image of the surface presented in Figure 5a.



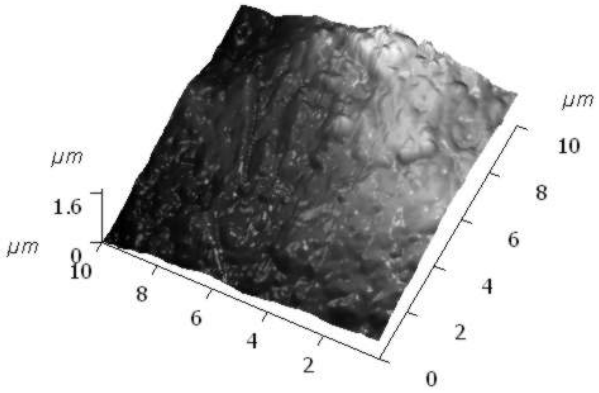


Fig. 6. a. Optical image of the area from Figure 3b with 43% Ag; b. AFM image of the surface presented in Figure 6a.

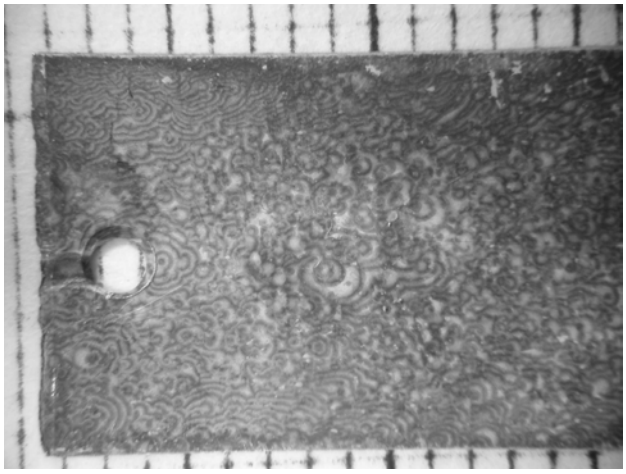


Fig. 7. Optical microscope image of an Ag-In coating; c.d. = 0.4 A·dm^{-2}; $C_{D+\text{-Glucose}}$ = 0.1 mol·dm^{-3}; C_{KCN} = 0.75 mol·dm^{-3}; C_{Ag} = 0.04 mol·dm^{-3} (as $KAg(CN)_2$); C_{In} = 0.15 mol·dm^{-3} (as $InCl_3$); deposition time – 35min.

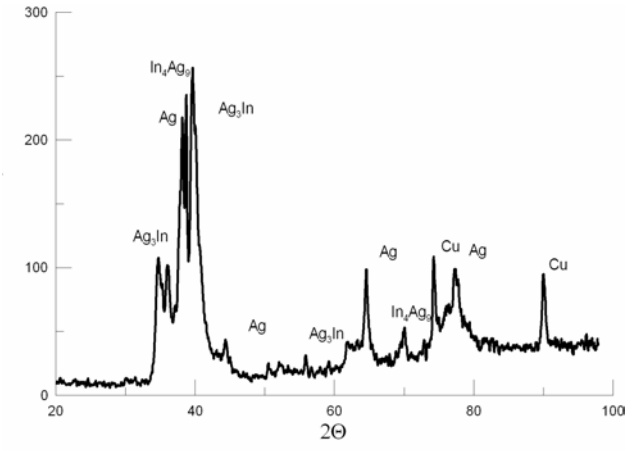


Fig. 8. XRD pattern of the coating shown in Figure 7.

In many cases, a wide variety of spatio-temporal structures has been observed on the electrode surface [1, 13–15, 18]. An attempt was made to answer the question wether there are differences in the morphology of the optically well distinguishable (dark and light) areas (Fig. 7) by means of SEM and AFM techniques. As mentioned above, the periodical spatio-temporal structures consist most probably of the phases Ag and Ag_3In [15, 18]. Figure 8 shows the XRD pattern of the coating, presented in Fig. 7.

The XRD pattern of the coating of Figure 7 shows the presence of the phases Ag, Ag_3In and In_4Ag_9, as well as the reflexes of the copper substrate. The data are also in conformity with previous investigations [14, 15, 18], where it was established that the spatio-temporal structures consist of the silver phase and Ag_3In phase. According to previous investigations [16], In_4Ag_9 (ε) phase was not registered in freshly deposited coatings, immediately investigated in the X-ray camera. Our experience shows that the ε-phase In_4Ag_9 appears about 1 h after the deposition of the alloy coating. Taking into account that the spatio-temporal structures appear on the electrode surface in the electrolytic cell and after that long time remain unchanged, it can be concluded that this phase transformation is not connected with the spatio-temporal structure formation, but is a very interesting object for future investigations.

Figure 9 shows SEM images, obtained from the different surface areas of the coating of Fig. 7. The composition in the dark and light areas is very similar and they have also similar surface morphology. In a previous study it has been concluded that the wave fronts move with sufficiently high speed forming a layered coating, so that the thickness of the formed during deposition dark and light sublayers is substantially smaller than the penetration depth of the electron beam during EDAX analysis. As a result the beam penetrates through several light and dark sublayers and the estimated average content of indium in both zones on the surface is almost the same. That is the reason for the observation both of dark and light zones with high quality only at low electron beam voltages, in our case – 2.5 keV (Figs. 9a-b). At higher voltages the different areas of the spatio-temporal structures are not well discernable.

Very interesting stairs-like topographical images are observed during the AFM investigations of the coating, presented in Fig. 7 (Figure 10).

Both images, presented in Figs. 10a and 10b, are obtained by scanning with cantilever onto the surface in axes X and Y as well as in Z and X. The observed morphology is in a good correlation with the morphology observed during SEM investigations (see Fig. 9c) and is most probably a result of the influence of the natural convection appearing in the viscinity of the vertically placed electrode during electrolysis.

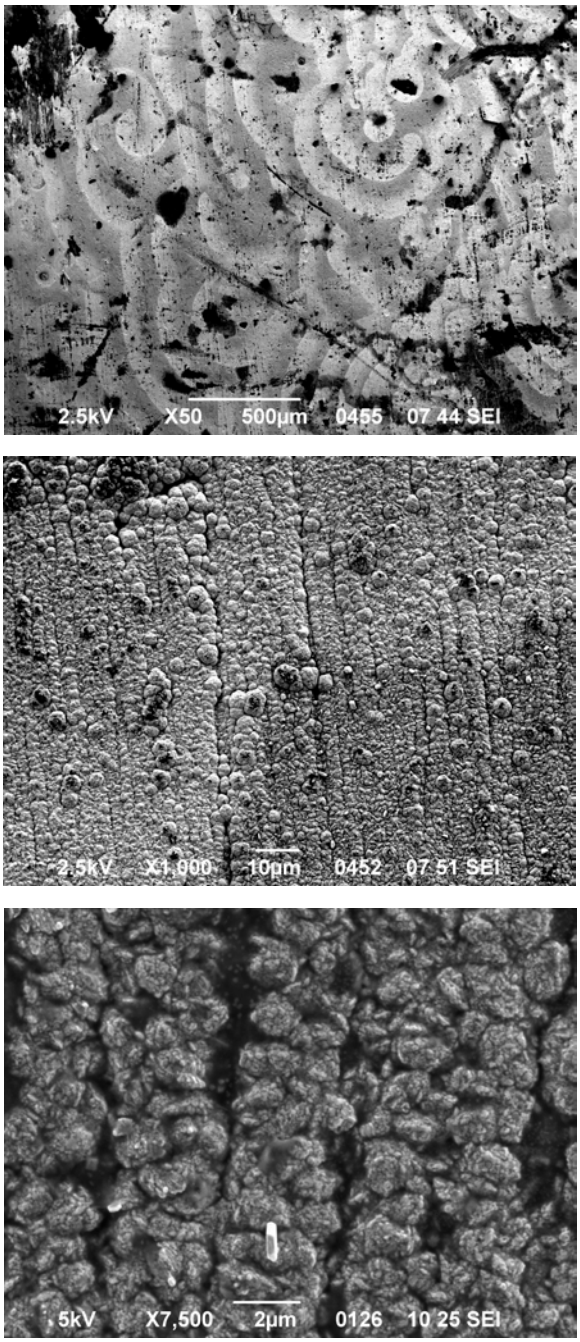


Fig. 9. a-c. SEM images of the surface areas in Fig. 7 at different magnifications.

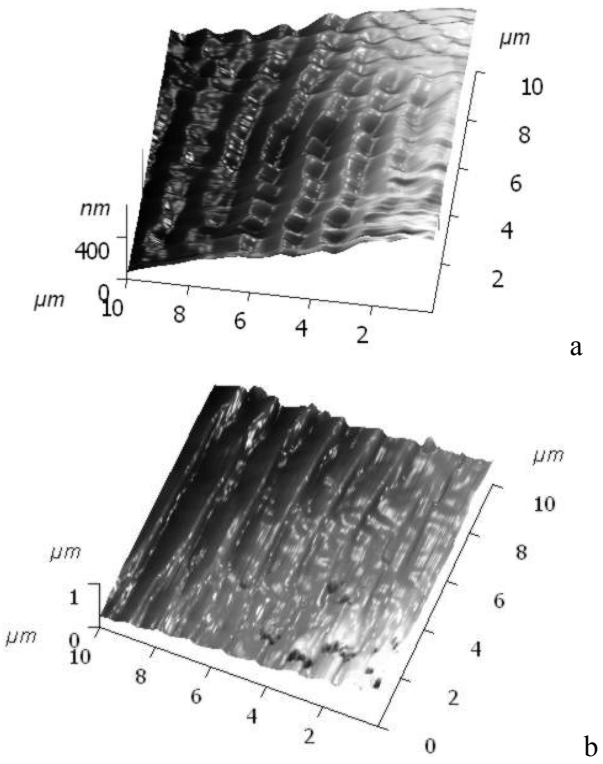


Fig. 10. AFM images 10×10 μm of the surface presented in Figure 7 (see also Figure 9c).

CONCLUSIONS

The surface morphology of the different indium-rich areas of the heterogeneous chaotic structures is very different and a correlation between the SEM and FEM results is observed.

The coatings with periodical spatio-temporal structures on their surface are multilayered with a very small sublayer thickness and the different dark and light zones on the electrode surface are well distinguishable only at low acceleration voltages of the electron beam. The AFM investigations show in similar areas some ordering, most probably connected with convection effects during electrodeposition, rather than with the separate zones of the periodical structures.

***Acknowledgments**: The authors gratefully acknowledge the NANOPHEN (FP6 Project INCO – CT – 2005 – 016696) and NATO Reintegration grant RIG 981967 awarded to Ts. Dobrovolska.*

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ИЗСЛЕДВАНИЯ НА ПОВЪРХНОСТНАТА МОРФОЛОГИЯ НА ЕЛЕКТРОЛИТНО ОТЛОЖЕНИ Ag-In ПОКРИТИЯ ЧРЕЗ ОПТИЧНА, СКАНИРАЩА ЕЛЕКТРОННА И АТОМНО-СИЛОВА МИКРОСКОПИЯ

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Постъпила на 1 ноември 2007 г.; Преработена на 1 февруари 2008 г.

(Резюме)

Проведени са сравнителни изследвания на повърхностната морфология на електролитно отложени сребърно – индиеви покрития с хаотично и пространствено-подредено разпределение на различните фази, чрез оптична, сканираща електронна (SEM) и атомно-силова (AFM) микроскопия.

Морфологията на фазите при хаотично разпределение е добре различима както при SEM, така и AFM изследвания. Оптично добре различимите зони в пространствено-временните структури на електроотложените сребърно-индиеви сплавни покрития са с много малка дебелина и при SEM изследванията са добре видими само при ниско ускоряващо напрежение.