Investigations of Structural, Mechanical and Optical Properties of Silver Electrodeposits

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The electrodeposits of silver on velour copper underlayers from dicyanoargentate-thiocyanate solutions were obtained. The surface relief, morphology and hardness of silver deposits were studied and their dependences on deposition conditions were examined. The gloss and specular reflectance spectra in the infrared region were measured and modelled. The morphology of thin silver coatings with the thickness of about 1 μm, exhibiting good velour effect, was found to be consistent with the underlayer one. With increasing silver layer thickness, the specific morphology with smaller dimensions of surface crystallites forms and velour effect disappears. The correlation between the optical properties and dimensions of surface irregularities of silver coatings as well as velour effect was observed.
Keywords: silver electrodeposits, velour coatings, hardness, optical properties, gloss, specular reflection.

INTRODUCTION

In the electronics, automobile production and other fields of industry there is a great demand not only for protective bright but also for matte decorative metallic (nickel, chrome, bronze) coatings which are reffered to as velour ones. The velour coatings are harder, more plastic and have higher corrosion resistance [1 – 3] as compared to the convenient ones. The decorative appearance of velour coatings is related to the changing in their colours when observed at different angles. This effect is caused by diffraction of light from surface irregularities [4, 5].

The most simple and cheap way for producing the velour metal (Ni, Cr) coatings is their epitaxial growth on a velour copper underlayers [3 – 7]. The intensity of velour effect of such coatings is known to depend on the morphology of the underlayer and composition of electrolyte as well as on the coating thickness and dimensions of crystallites [3, 5]. Although the silver deposits from dicyanoargentate-thiocyanate solution on velour copper underlayer were produced [6] however their physical-mechanical and optical properties including velour effect are weakly studied to date. Therefore, the purpose of this work is to examine the dependences of structural, mechanical and optical properties of silver electrodeposits on technological conditions and deposits thickness and to gain further insight into the velour effect.

SAMPLES AND EXPERIMENT

Silver electroplates were deposed on velour copper [2 – 7] underlayers from dicyanoargentate-thiocyanate solutions containing (g/l): $KAg(CN)_2$ – 55, KSCN – 250, K_2CO_3 – 20, $Sb\{K(SbO)C_4H_4O_6 \cdot 1/2H_2O\}$ – 1.5, $KNaC_4H_4O_6 \cdot 4\,H_2O$ – 50, Na ricinoliate – 1. The electrolytes without Sb and Na additives were also used.

Polarization of silver separation was studied using a silver disk of an area of 2 cm^2. Anode was a silver plate of an area of 6 cm^2. Reference electrode was saturated AgCl - 1 M which from the solution under study was separated by indifferent solution bridge. A potential of electrode was maintained by potentiostat P-5848 (Russia). The current and the potential were recorded by x-y recorder H-307/1. The values of potentials were recalculated to the hydrogen scale. The experiments were carried out at the temperature of 20 ±1 ºC.

The thicknesses of electrodeposits studied were evaluated from the measured values of the cathode current density and deposition time as well as by using special micrometers [8]. The relief of coating surface was studied by profilograph-profilometer 252 (Russia). The surface structure was examined by a scanning electron microscope (SEM) PEM-100. From the data of structural studies the dimensions of surface crystallites were established. The hardness of coatings was measured by Wicker's method.

The specular reflectance spectra of silver coatings in the region of 2.5 – 25 μm were measured by a double beam spectrometer "Specord M-82" (Germany) at the angle of the incidence of light $\theta = 22^o$ at room temperature. From the comparison of experimental specular reflectance spectra with the calculated ones using the previously developed model for a random rough surface with a saw-tooth profile of irregularities [5] the dimensions of coutings surface crystallites were evaluated. The specular gloss at an angle of 45º and diffuse reflection coefficient at an angle of 0º with respect to the black glass in the visible spectral range of 0.4 – 0.8 μm were measured by the glossmeter-reflectometer 45/0/45 [9] constructed at the Semiconductor Physics Institute.

RESULTS AND DISCUSSION

Polarization curves

To estimate optimum conditions for deposition of silver coatings, the cathode polarization curves were studied both in simple electrolyte (Fig. 1, curve 1) and in the one with additives of Sb (Fig. 1, curve 2). As it can be seen from Fig. 1, the dependence of cathode potential E

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on current density i_k is not linear but rather complicated function especially by employing simple electrolyte (Fig. 1, curve 1). In this case the polarization curve consists of 6 regions each of them being related to different processes taking place at the cathode during the silver deposition. Horizontal regions 3 and 5 correspond to the first and second limiting currents at which the silver coatings of different quality and surface morphology are formed. The first limiting current may be related to the ineffective diffusion and reduction of silver complexes on electrode surface passivated by chemosorbed cyanides [10]. It should be noted that the evolution of hydrogen from our electrolyte as in the case of simple cyanide solutions [11] occurs at the cathode potential equal to about –1 V, i. e. at the beginning of the second limiting current. It was observed that high quality silver coatings exhibiting velour effect may be obtained in the 1 and 2 regions of polarization curve where $i_k < 3$ mA/cm^2, i. e. before the first limiting current and evolution of hydrogen. The $i_k = 3$ mA/cm^2 corresponds to the first limiting current when the specific structure of silver coatings consisting of small crystallites begins to form itself. In the region of second limiting current ($i_k \approx 20$ mA/cm^2) the structure of silver deposits changes essentially. Dark coatings of poor quality are characteristic of this region.

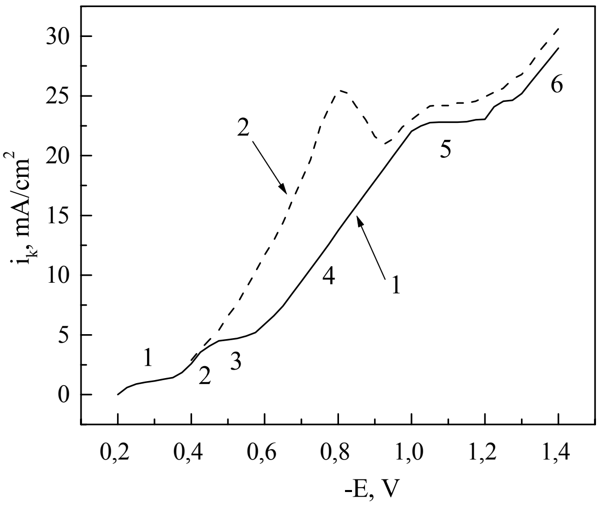

Fig. 1. The dependence of silver cathode potential E on the cathode current density i_k in various electrolytes (g/l): 1 – $KAg(CN)_2$ – 55, KSCN – 250, K_2CO_3 – 20; 2 – (the same as for 1) + $KNaC_4H_4O_6 \cdot 4H_2O$ – 50, Sb{$K(SbO)C_4H_4O_6 \cdot 1/2H_2O$} – 1.5, Na ricinoliate – 1

It is important to note that the first limiting current disappears (Fig. 1, curve 2) when the salts of metals doping silver (in our case Sb) or brighteners are introduced into electrolyte. In such a case the metals deposited on the cathode surface inhibit the absorption of cyanides. As a result, the region 2 of polarization curve becomes more extended and good quality silver coatings may be obtained in the larger interval of cathodic current densities.

Hardness

In order to get information on the dependence of the properties of silver electrodeposits on technological conditions, the dependence of coatings hardness on the composition of electrolyte, type of underlayer as well as

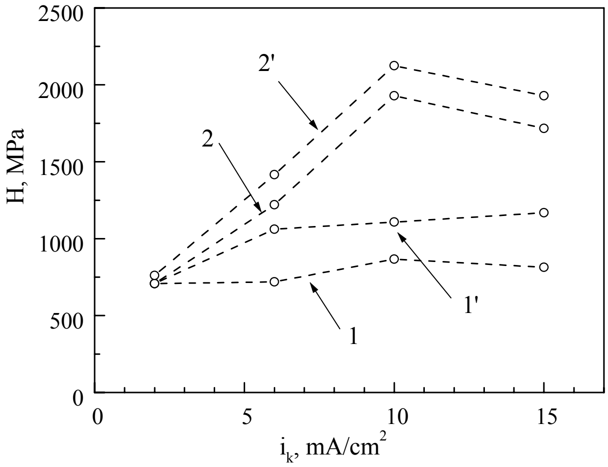

Fig. 2. The dependence of silver electrodeposits hardness (H, MPa) on the cathode current density i_k in various electrolytes (g/l): 1, 1′ – $KAg(CN)_2$ – 55, KSCN – 250, $KNaC_4H_4O_6 \cdot 4\ H_2O$ – 50; 2, 2′ – (the same as for 1, 1’) + Sb{$K(SbO)C_4H_4O_6 \cdot ½\ H_2O$} – 1.5, Na ricinoliate – 1. 1, 2 – Cu plate underlayer, 1′, 2′ – velour Cu underlayer of thickness of 15 μm. The thickness of silver deposits studied is 15 μm

cathode current density (Fig. 2) was studied. As may be seen from Fig. 2, in the region of small i_k (~ 2 mA/cm^2) the hardness of silver deposits almost does not depend on type of underlayer and composition of solution. However, with increasing in current density the influence of these factors remarkably enhances. It is evident that silver coatings deposited on velour copper (curves 1′ and 2′) are harder (up to ~40 %) than that’s deposited on a brass (curves 1 and 2). Moreover, the influence of underlayer is more effective in the case of simple electrolyte (curves 1 and 1′). Besides that, as is seen from Fig. 2, the hardness of silver deposits remarkably increases when additives of Sb are introduced into the electrolyte (curves 2 and 2′). In this case the hardness of silver coatings deposited on velour copper reach even ~2100 MPa, when $i_k \approx 10$ mA/cm^2 (curve 2′). Previously was also observed [12, 13] that increasing in current density and employing of additives result in the enhancement in coatings hardness while the rise in electrolyte temperature has an opposite effect. Moreover, it was found [14] that the hardness of coatings having the [111] and [110] orientations of crystallites is larger than that’s with the [100] orientation. In our case, the increase in hardness in the region of higher current densities may be related to the penetration of Sb additives into the coatings. This may cause the changes in the coating morphology as well as in the orientation and dimensions of the crystallites. This assumption is thought to be checked in the future experiments.

Morphology

Now we will consider the thickness dependence of morphology of silver coatings deposited from the electrolyte with Sb additives.

The profilograms presented in Fig. 3 show that the profile of the surface irregularities of silver deposits of the thickness of 0.5 μm (Fig. 3 b) is close to that of velour Cu underlayer (Fig. 3 a). At the same time it is evident that

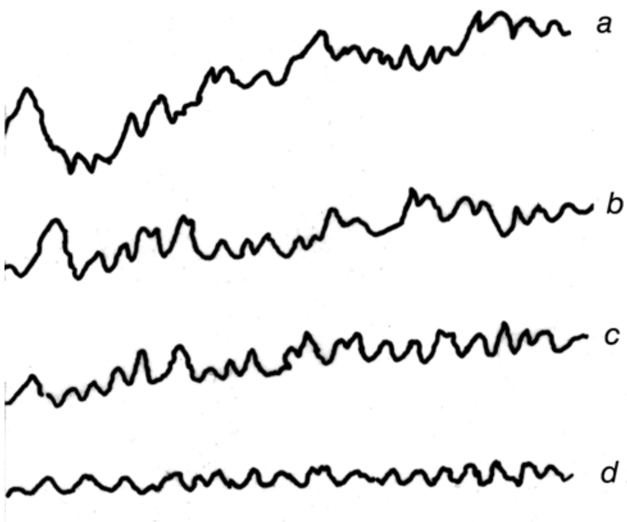

Fig. 3. Profilograms of silver deposits on velour copper: a – velour Cu underlayer of the thickness of 15 μm, b – a + 0.5 μm Ag, c – a + 1 μm Ag, d – a + 5 μm Ag; i_k = 1 A/dm^2. 1.5 mm in vertical direction correspond to 0.2 μm while in horizontal – 5 μm

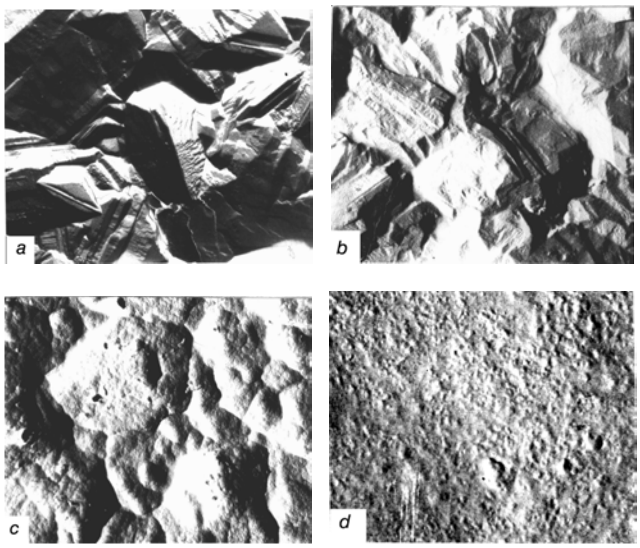

Fig. 4. Micrographs of silver electrodeposits on velour Cu underlayer obtained by SEM: a – velour Cu underlayer, b – a + 1 μm Ag, c – a + 5 μm Ag, d – a + 20 μm Ag; i_k = 1 A/dm^2. Magnification: a, b, c – ×6000, d – ×12000

with increasing silver layer thickness up to 1 – 5 μm the surface relief changes remarkably and the dimensions of the surface crystallites diminish (Fig. 3 c, d). This reveals that the formation of specific morphology of silver deposits begins. It should be noted that because of relatively large diameter of the profilograph's needle the presented profilograms only approximately reflect the size and shape of surface crystallites of coatings studied.

More exactly the surface morphology of silver deposits appears in micrographs (Fig. 4) obtained by SEM. As was observed previously [15], the surface of velour copper consists of relatively large and identical pyramidal-type crystallites – mainly laminar twins with clearly expressed steps (Fig. 4 a). The most of crystallites have the [111] and [110] orientations. The heights of crystallites are evaluated to be ~ 1.9 – 2.1 μm while the widths - ~ 3 – 4 μm. The data of SEM show that silver deposits with the thicknesses of 0.5 – 1 μm (Fig. 4 b) repeat rather well the morphology of velour copper underlayer. Although the edges and surfaces of crystallites are slightly rounded however their dimensions almost do not change. When the thickness of silver deposits reaches 5 μm (Fig. 4 c) the crystallites become still more round and their heights decrease up to ~ 1 – 1.5 μm. As it can be seen from Fig. 4 d, with further increasing the thickness of silver coatings up to 20 μm, the specific morphology appears and the dimensions of the surface crystallites reach only ~ 0.2 – 0.4 μm.

It is important to note that the varying in silver coating thickness and their morphology is accompanied by the changes in their colour and velour effect: the matte gray colour and good velour effect are characteristic of thin coatings with the thickness of about 1 μm, while the thick coatings exhibit lightly white colour and no velour effect.

Specular reflectance spectra

Fig. 5 shows the specular reflectance spectra of silver coatings deposited on velour copper underlayers from the electrolyte with Sb additives. As it is seen, with increasing the wavelength of the incident radiation λ from 2.5 to 25 μm the specular reflectance coefficient R_s of velour copper underlayer grows from ~ 2 – 3 % to ~ 84 %. The deposition of silver coatings on velour copper and increasing in their thicknesses lead to some growth of R_s at short wavelengths. Moreover, the reflection curves become less steep and at longer wavelengths they approach to the value of $R_s \approx 0.7$ which is less than R_s for the velour copper in this region.

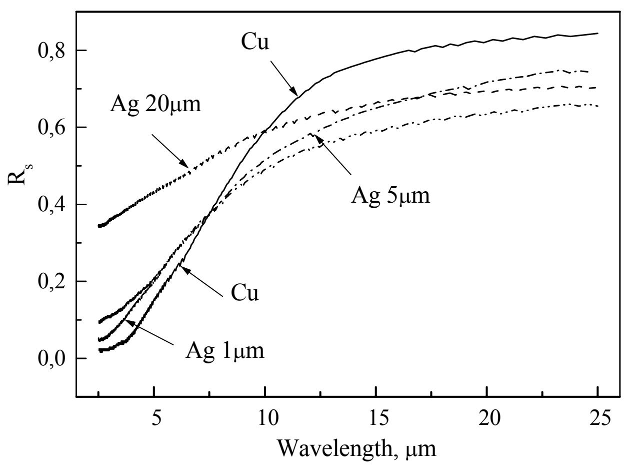

Fig. 5. Specular reflectance spectra of velour copper underlayer and silver electrodeposits of various thicknesses

The observed increase in specular reflection coefficient with the wavelength of radiation may be explained by transition from diffuse to specular reflection [5, 16]. Such a transition is known [5, 16] to take place when the dimensions of irregularities of rough surface reflecting radiation become comparable with the wavelength of this radiation. To get quantitative information on the dimensions of the surface irregularities of the coatings studied, the modelling of the specular reflectance spectra has been performed according to previously developed model [5]. The surface of electrodeposits was approximated by a hypothetical random rough surface with a saw-tooth profile of irregularities. The irregularities were characterized by mean width of tooth, d, by its height, h, and by the angle φ = const defining the slope of irregularities. It should be noted that within our model the values of R_s and its spectral dependence are caused by characteristic structural parameter $d\tan\varphi = 2h$ and by the angle of the incidence of radiation θ as well as by the deviation of dimensions of surface irregularities from periodicity, $\delta d/d$. From the comparison of measured specular reflectance spectra of velour copper coating (Fig. 5) with the calculated ones it was found that the reasonable agreement between spectra exists for $d\tan\varphi = 2h \leq 4$ μm and $\delta d/d = 0.2$. Thus, the spectroscopic values of heights of surface crystallites of velour copper $h \leq 2$ μm correspond to that's ($h \approx 1.9 - 2.1$ μm) established by SEM.

The comparison of the experimental reflectance spectra of silver coatings deposited on velour copper underlayer with the calculated ones is shown in Fig. 6. It should be noted that in accordance with the experimental data, the calculated spectra were normalized to $R_s = 0.7$. The deviation of R_s from unity in the long wavelength region may be associated with the inclusion of additives of Sb into the coatings during the electroplating process. As is seen from Fig. 6, the silver deposits with the thicknesses of 1 and 5 μm may have characteristic parameters 2 μm $\leq d\tan\varphi = 2h \leq 3$ μm when $\delta d/d = 1$. Thus, in this case the optical data also correspond to the ones of SEM which for silver layer with the thickness of 5 μm provide $h = 1 - 1.5$ μm. As to the silver deposit with the thickness of 20 μm (Fig. 6), which reflection coefficient slowly changes with the wavelength, one may say that the dimensions of surface irregularities should be probably less than 1 μm.

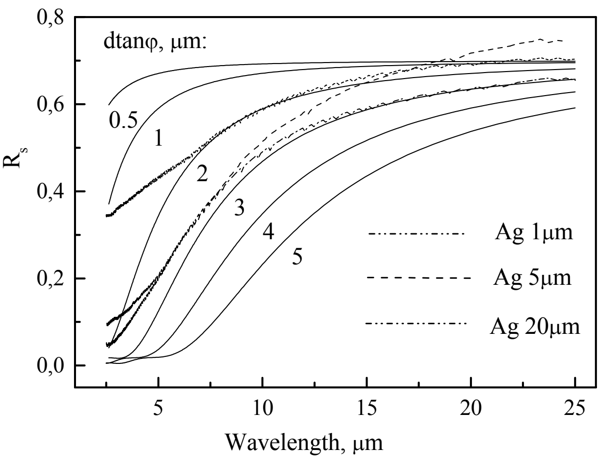

Fig. 6. Comparison of experimental (broken curves) and model led (solid curves) specular reflectance spectra of silver electrodeposits on velour copper

Thus, although our hypothetical surface does not reveal all peculiarities of real surfaces of silver deposits studied especially the thick ones with the small round crystallites however the analysis of spectroscopic data confirms the trend estimated by SEM that the dimensions of surface crystallites decrease with increasing coating thickness. Moreover, at the same time one may expect that the deviation from the periodicity in the surface microstructure should enhance.

Gloss and diffuse reflectance

The values of specular gloss R_s at angle of 45° and diffuse reflection coefficient R_d at angle of 0° of silver deposits on velour copper are presented in Table 1. It should be noted that specular gloss represents the specular reflection coefficient R_s measured at the angle of the incidence of light $\theta = 45°$ with respect to black glass [9] in the visible spectral range for $\lambda = 0.4 - 0.8$ μm. The diffuse reflection coefficient R_d is measured by the same way at 0° [9]. It is seen that after the deposition of silver on velour copper underlayer its gloss increases and fast grows with increasing silver layer thickness. At the same time, the diffuse reflection for thin silver coatings of thickness of 0.5 – 1 μm does not differ appreciably from the one of velour copper underlayer, while with increasing silver thickness it decreases. Remarkable that the smallest difference between the specular and diffuse reflections are found to have thin silver deposits (of the thickness of 0.5 – 1 μm) showing good velour effect.

Table 1. The values of specular reflection coefficient R_s (gloss) at 45° and diffuse reflection coefficient R_d at 0° of silver deposits on velour copper measured with respect to black glass. The i_k = 1.0 A/dm^2 for Cu underlayer and 0.3 A/dm^2 for silver deposits

Coating	Thickness, μm	R_s (gloss) at 45°, %	R_d at 0°, %
Cu	12.0	59.0	35.9
Cu+Ag	0.5	80.0	36.0
Cu+Ag	1.0	110.7	37.2
Cu+Ag	5.0	378.0	13.0
Cu+Ag	20.0	653.0	6.5

The observed dependences of specular and diffuse reflections of silver deposits on their thickness may be accounted for by the changes of morphology and dimensions of surface crystallites with the thickness. The data of SEM and specular reflectance study in the infrared region reveal that with increasing deposit thickness the dimensions of surface crystallites decrease. Therefore, in the fixed spectral range of 0.4 – 0.8 μm where the measurements were carried out the ratio h/λ characterizing the surface roughness [5, 16] should also decrease with the thickness of deposits. Consequently, the surfaces of thicker deposits should become more smooth reflecting more light specularly in a single direction which should lead to the decrease in intensity of light diffusely scattered in various directions [5, 16]. This was observed experimentally as the rise in the difference between the specular and diffuse reflection with increasing the thickness of silver deposits. From this point of view it is natural that better velour effect exhibit coatings with smaller difference between specular and diffuse reflection because the velour effect arises not from specularly reflected light but from the one diffracted at various angles from the surface irregularities. Besides that, it should be noted that the orientation of surface crystallites may also influence the gloss and velour appearance. As it was mentioned above, the silver deposits with the thickness of 0.5 – 1 μm repeat the morphology and preferential [111] as well as [110] orientations of crystallites. One may assume that with increasing coating thickness when the specific morphology forms the most of crystallites may be reoriented towards the [100] direction. This assumption may be confirmed by the fact that in metallurgic silver even 54 % of crystallites exhibit the [100] orientation [17]. Moreover, it is known [11] that the coatings with the [100] orientation of crystallites have higher gloss than that's with the [111] one. Thus, the increasing of specular gloss in thicker silver deposits may be partly related to the changing in orientation of surface crystallites.

CONCLUSIONS

1. The good quality velour silver electrodeposits on the velour copper underlayer may be obtained from simple cyanide electrolyte at cathode current density $i_k < 3$ mA/cm^2 (before the first limiting current), and from the electrolyte with the additives of Sb – at $i_k \leq 10$ mA/cm^2.
2. The largest values of hardness (up to 2100 MPa) are characteristic of silver coatings deposited on velour copper underlayer from the electrolyte with the additives of Sb at $i_k \approx 10$ mA/cm^2.
3. Thin (~ 1 μm) silver deposits on velour copper repeat the morphology and dimensions of surface crystallites of underlayer and show good velour effect. Thick (20 μm) silver deposits are found to have specific morphology and no velour effect.
4. The peculiarities of specular reflectance spectra of silver electrodeposits in the infrared region correlate with the dimensions of surface crystallites.
5. The silver deposits exhibiting intensive velour effect are found to have smallest difference between the specular and diffuse reflection coefficients.

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