Determination of the mutual influence of additives for a sulfate copper electrolyte on adsorption by the ellipsometry method

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Abstract

The mutual influence of different functional organic additives in sulfate electrolyte of copper plating during co-adsorption on the surface of copper cathode was investigated by ellipsometric method. The tendency to adsorption on copper increases in the series: bis-(sodium sulfopropyl) disulfide (SPS) < 4,4′-dibenzene disulfonic acid disulfide disodium salt (Avangard) < bis(2-amino-phenyl)disulfide (APhDS). This can be explained by the transition from an aliphatic to an aromatic structure, as well as the presence of two amino groups, which may contribute to the increased stability of the chemisorption complexes. The adsorption-desorption behavior of polyethylene glycol studied as an inhibitor is practically independent of the molecular weight, but PEG-8000 with high molecular weight promotes more pronounced adsorption in the blends. Among the levelers, Janus green is more adsorption efficient towards copper compared to aminobenzothiazole due to the presence of several aromatic and heterocyclic rings as well as nitrogen-containing functional groups in its structure. As a result, the highest adsorption capacity is shown by mixtures containing APhDS and Janus green, for which the maximum change in the ellipsometric phase angle is observed if PEG-8000 is additionally present.

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Introduction

Electrochemical deposition of copper is widely used to obtain various functional coatings. The process of local copper plating is used in the microelectronics industry in the production of printed circuit boards. In order to ensure high productivity and quality of products during metallization of blind holes in silicon wafer using the modern through silicon vias (TSV) technology, high requirements are imposed on the uniformity and roughness of the copper coating surface, as well as filling of topological windows with high aspect ratio, which causes special attention to the selection of the optimal electrolyte composition.

Copper coatings electrochemically deposited from sulfate electrolytes without the use of organic additives have a coarse-grained structure with an average crystallite size of 3–4 microns. Such coatings are non-uniform in thickness, which is mainly due to non-uniformity of the primary current distribution over the cathode surface. The ability of the electrolyte to improve the primary current distribution over the surface of the part or, in other words, the ability of the electrolyte to form coatings uniform in thickness on complexly profiled products is called the throwing power (TP) [1–3]. The TP is expressed as a percentage and shows how much the actual distribution differs from the primary distribution.

A sulfate electrolyte containing Cu^{2+} ions added as $CuSO_4 \cdot 5H_2O$ is the simplest electrolyte that is stable in storage and in operation and allows one to obtain fine-grained and elastic coatings. However, its disadvantages include the relatively low productivity and low TP, which significantly complicates the deposition of a uniform coating on printed circuit boards with complex geometry. To improve the properties of sulfate electrolytes, various additives are utilized. They are classified in the literature and in practice as “Inhibitors”, “Levelers” and “Brighteners” [4–7].

Inhibitors decrease the rate of copper precipitation. Long chain polymers such as polyethylene glycol (PEG) are commonly used as such additives. Additives of this type act in combination with chloride ions. It is assumed [8–10] that the suppression of copper deposition is due to the formation of an adsorbed surface layer in the presence of Cl^-. The molecular weight of PEG is at least 1000 g/mol. Cu^+ or Cu^{2+} ions coordinate with the oxygen atoms of PEG and are adsorbed on copper simultaneously with Cl^- ions, which improves the adsorption of the Inhibitor on the electrode surface. It is argued [11] that a surface complex of univalent Cu^+ with PEG is formed during the electrodeposition process: each Cu^+ ion has three coordination bonds with two oxygen atoms and one Cl^- ion to form a PEG–Cu–Cl complex, where the Cl^- ion is adsorbed on the cathode surface.

Brighteners are additives after the introduction of which a “depolarizing” effect is observed, *i.e.* an increase in the rate of copper plating. Therefore, they also called accelerators, and sometimes they are called anti-inhibitors. Most researchers note that, along with the accelerating effect on the copper reduction process described above, additives of the Brighteners type also affect the microdistribution in accordance with the adsorption-diffusion theory of leveling, providing the gloss of the coating [12]. Additives of this type belong to sulfur-containing compounds, such as compounds with a disulfide bond R–S–S–R and/or a thiol bond R–S–H.

Levelers are organic additives that prevent unwanted copper growth at the top of printed circuit board (PCB) holes (so-called “dog bone” or “mushrooming” effect). Adsorption od levelers locally suppresses the copper electrodeposition process, allowing the coating to equalize in thickness in the middle of the hole and on the PCB surface [13–15]. The conclusion has been made that currently the majority of the known levelers are nitrogen-containing dyes (phthalocyanine, azine, triarylmethane) such as 2-diethylamino-3,6-dimethyl-9-phenylphenazonium-7-azo-4′-dimethylaniline chloride, alcian blue, diazine black, *etc*., or heterocyclic aromatic compounds such as 2-amino-4-methylbenzothiazole, 2-mercaptopyridine, and Janus Green B (JG) [16–19].

Thus, the uniformity of electroplating can be regulated by introducing special additives into the copper electrolyte. Their adsorption on the cathode leads to redistribution of active deposition centers and to a decrease in grain size. Thus, to solve the actual problem of microelectronics involving the creation of printed circuit boards with a high-aspect ratio of functional holes, it is important to establish the optimal ratio of both the basic components of the sulfate electrolyte and the organic additives included in its composition.

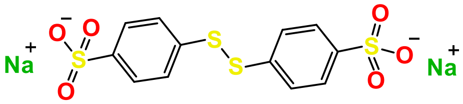
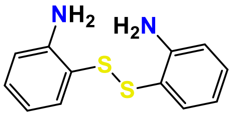
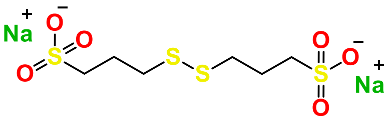
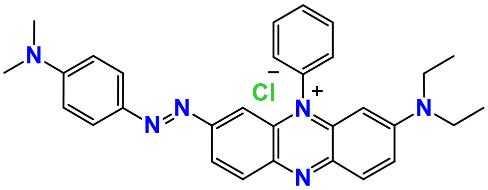
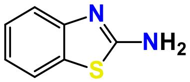
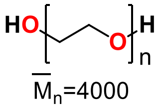
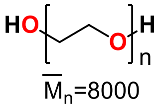
Earlier [20] we investigated by the ellipsometric method the co-action of chloride ions and organic additives used in the electrodeposition of copper: the "Brighteners" Avangard and APhDS (bis(2-aminophenyl)disulfide) and the "Inhibitor" PEG-115. The following solution was proposed for the application of the ellipsometry method: 0.5 M H_2SO_4 + 0.10 g/L $CuSO_4$. Below we call this the background solution. We have shown that Avangard enhances the adsorption of NaCl and PEG-115 upon sequential addition (Avangard, then NaCl, then PEG-115). The (NaCl+PEG-115) mixture is almost not adsorbed on the electrode. Comparing the effect of Avangard and APhDS on the adsorption of the (NaCl+PEG-115) mixture, a more stimulating effect of APhDS addition on adsorption was observed. We obtained the adsorption isotherm of APhDS on the surface of copper electrode from the background solution at $E = 0$ V. Adsorption is not limited to monolayer formation, and the thickness of APhDS film increases with increasing concentration.

The aim of the present work is an ellipsometric study of adsorption of organic additives PEG-8000 (Inhibitor), JG and ABT (Levelers) and SPS (Brightener) on a copper electrode from a sulfate solution from both individual solutions and from three-component mixtures, including in comparison with the formulations containing Avangard, PEG-115, ABT and APhDS studied earlier in [20].

Experimental

Adsorption of organic additives from a copper–sulfate solution on copper electrode was investigated using the ellipsometric method. The Teflon electrochemical cell had a window for the entrance of the incident beam and a window for the exit of the reflected beam. A laser with a wavelength of $\lambda = 640$ nm served as the light source. The electrode made of M1 copper (Cu – 99.9%, GOST 859-2014) was pressed into the Teflon holder and arranged vertically relative to the bottom of the cell. The surface area of the electrode was 0.33 cm^2. Before the experiment the electrode was ground on fine-grained sandpaper P2000–P2500, polished on felt impregnated with an aqueous suspension of aluminum oxide, and degreased with acetone. A platinum plate parallel to the surface of the working copper electrode served as an auxiliary electrode. The reference electrode was a silver chloride electrode located in a separate vessel and connected to the working solution by a Luggin capillary. In the article, potentials (E) are given relative to the standard hydrogen electrode. In the background solution at $E = 0$ V the surface of the copper electrode is stable, *i.e.* it is possible to determine the ellipsometric angles Δ_0 and Ψ_0 related to the original surface. The accuracy of determining the ellipsometric phase angle Δ is ±0.05°. As the film grows, the angle Δ decreases, so the difference $\delta\Delta = \Delta - \Delta_0 < 0$. The variation in δΔ will be a criterion for the additive efficiency. If $\delta\Delta \sim 0$, no adsorption occurs, while if $\delta\Delta < 0$, the additives (individually or from a mixture) adsorb on the surface of the copper electrode. In the curves below, the initial Δ_0 values depend on the surface preparation of the copper electrode and can range from 98° to 105°. In the plots below, the value of Δ_0 is located on the Y axis. From this point the kinetics of the angle change Δ starts.

Table 1. Name and structural formulas of additives.

Designation	Name	Structural formula
Avangard	4,4′-Dibenzene disulfonic acid disulfide disodium salt	
APhDS	Bis-(2-aminophenyl)disulfide	
SPS	Bis-(sodium sulfopropyl) disulfide	
JG	Janus Green B	
ABT	2-Aminobenzo[*d*]thiazole	
PEG-115	Polyethylene glycol-115	
PEG-8000	Polyethylene glycol-8000	

Avangard was synthesized according to the methodology previously described in [21]. APhDS was synthesized according to the methodology [22], while the other additives were purchased from commercial suppliers (Acros Organics, Alinda Chemical Ltd.) and used without additional purification.

Brighteners – Avangard and SPS

Figure 1 shows a comparison of brightening additives: Avangard and SPS. Avangard (curve 1) adsorbs on the electrode; in 60 min, δΔ ~ −1°. SPS (curve 2) is not adsorbed, δΔ~0 in the entire range of concentrations. SPS is inferior in adsorption to Avangard, while Avangard is inferior to the APhDS studied earlier, see the corresponding isotherm [20]. Avangard and APhDS are aromatic compounds, unlike the SPS additive, which contains only an aliphatic backbone. It is known [23] that compounds having aromatic or heterocyclic mos in their structure have greater capability for adsorption on metal surfaces. More pronounced adsorption of APhDS additive is obviously related to its complexing properties [24] due to the presence of two amino groups, which further promotes chemisorption.

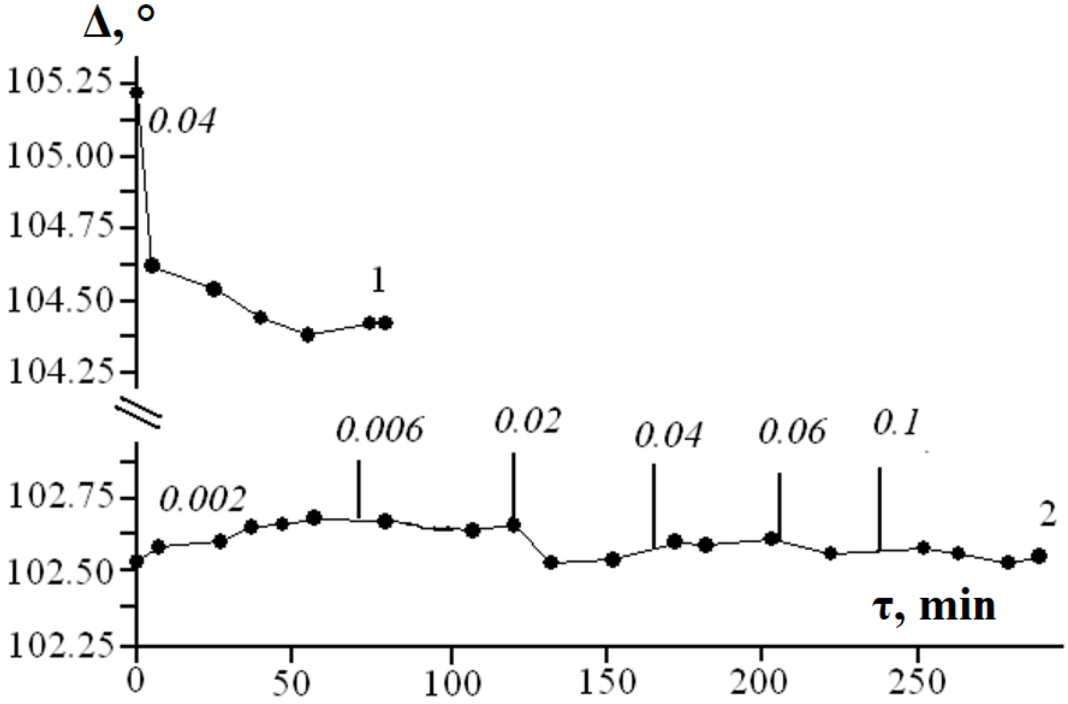


Figure 1. Kinetics of angle Δ variation on the copper electrode surface in the background solution ($E = 0$ V) upon addition of: Avangard (1) and SPS (2). The corresponding concentrations (g/L) are indicated in italics.

Inhibitors – PEG-115 and PEG-8000

Figure 2 shows a comparison of PEG-115 and PEG-8000 inhibitor additives. Both of these additives are not adsorbed on the electrode. For PEG-115 the changes Δ are smoother, while for PEG-8000 the changes are jumps due to adsorption and desorption processes, resulting in δΔ ~ 0 for both PEG-115 and PEG-8000.

PEG is a non-ionogenic surfactant. The presence of an unshared electron pair on the oxygen atoms causes the tendency of PEG molecules to form complexes with transition metal ions, but this weakly contributes to the adsorption on the cathode surface, which is mainly determined by van der Waals forces [25, 26].

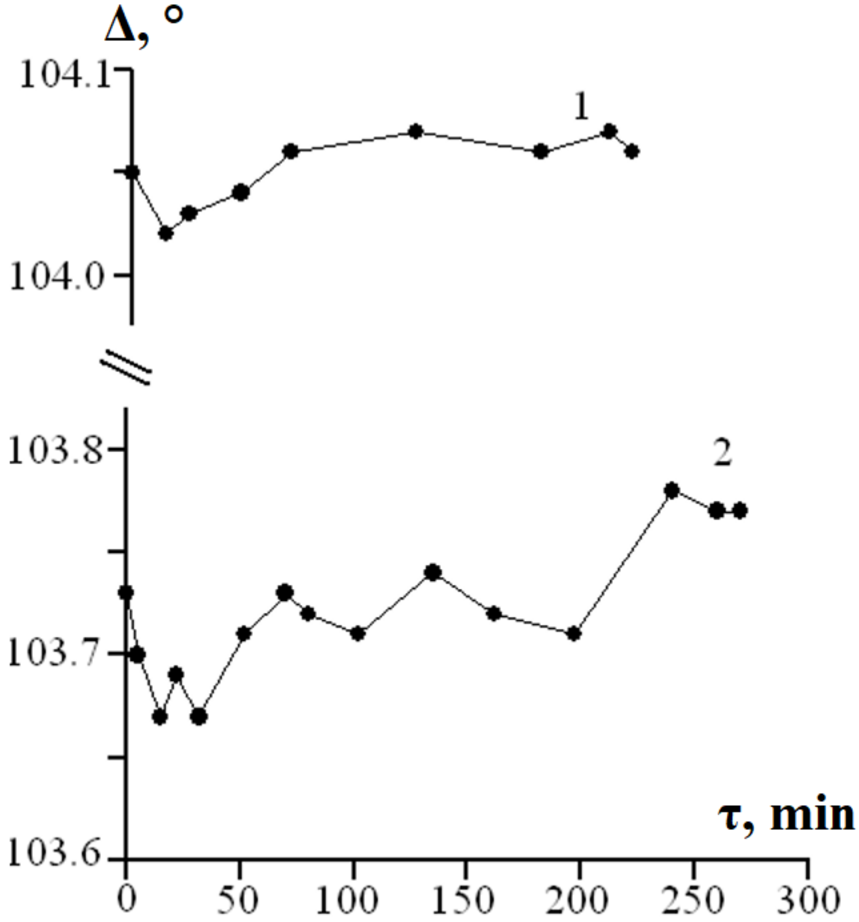


Figure 2. Kinetics of angle Δ variation on the copper electrode surface in the background solution ($E = 0$ V) upon addition of PEG-115 (1) and PEG-8000 (2). The concentration in the solution is 0.5 g/L.

Levelers – ABT and JG

Figure 3 shows a comparison of the ABT and JG additives. For ABT, $\delta\Delta > 0$, so there is no adsorption. Solutions with JG are colored blue. Solutions with high concentrations ($C > 0.002$ g/L) absorb light, which makes ellipsometric studies impossible. Reliable results were obtained only for $C = 0.002$ g/L. Despite the jump-like changes of the angle, a tendency to its decrease is observed. The total variation of $\delta\Delta$ is ~−2.20. It can be said that JG is more effective in adsorption on Cu compared to ABT. JG can be classified as a heterocyclic compound of phenazine class (Table 1). It contains two aromatic and one diazine heterocyclic rings, as well as additional nitrogen-containing functional groups, which are connected to the substituted aniline moiety *via* an azo group. In [27], based on quantum-chemical calculations, it was found that the electron-donating ability of JG is higher than that of the structural analog Safranin T. In addition, quantum chemical analysis showed that the aminoazobenzene moiety of JG is a likely reaction site for the adsorption of JG on the copper surface. Thus, the presence of two substituted amino groups, an azo group, and a quaternary ammonium cation in JG probably favors the formation of complexes with metals as well as adsorption on the cathode surface. In turn, ABT is a bicyclic compound with only one unsubstituted amino group. The observed weak adsorption properties of ABT on copper surface from acid sulfate solution can be explained by the fact that the amino group bound to the benzothiazole moiety has low basicity and is weakly protonated.

Each of the formulations investigated below includes a "Brightener" (Avangard, SPS, APhDS), an "Inhibitor" (PEG-115, PEG-8000), and a "Leveler" (ABT, JG).

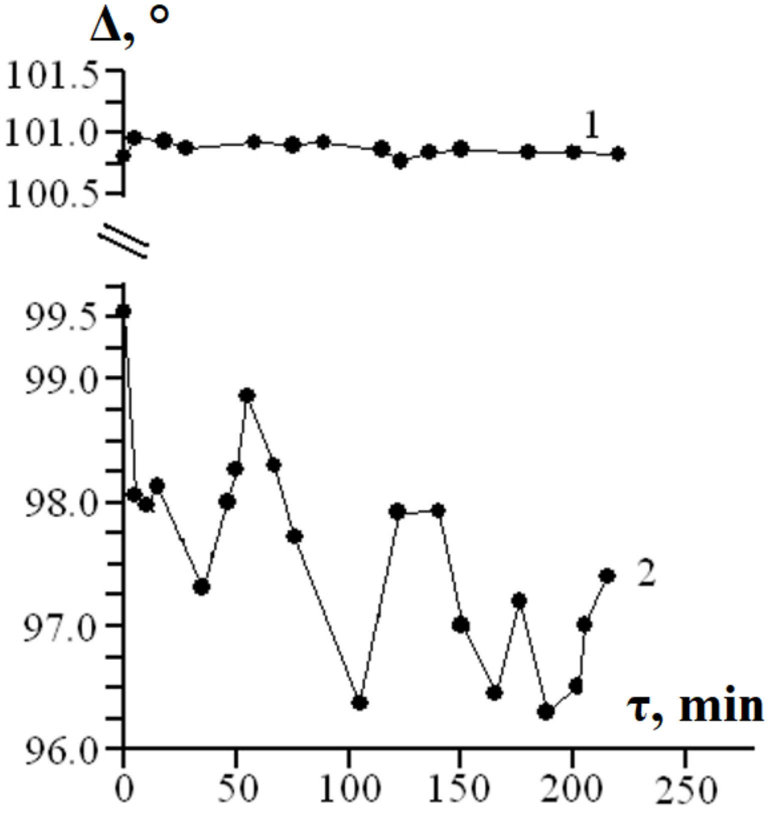


Figure 3. Kinetics of angle Δ variation on the copper electrode surface in the background solution at $E = 0$ V upon addition of: ABT (1) and JG (2). The concentration of JG in solution is 0.002 g/L and that of ABT is 0.01 g/L.

Blends: APhDS+PEG-115+ABT and APhDS+PEG-8000+ABT

Figure 4 shows a comparison of the kinetics of the angle Δ change for the mixtures (APhDS+PEG-115+ABT) and (APhDS+PEG-8000+ABT). The components of both mixtures adsorbed on the electrode, with almost the same δΔ and without features. For the mixture with PEG-115 the changes in the angle Δ are equal to (–1.3°), while for the mixture with PEG-8000 $\delta\Delta = -1.1°$. This can be explained by the presence of the APhDS additive in these mixtures, for which a more pronounced adsorption on the copper surface under the conditions studied above has been confirmed.

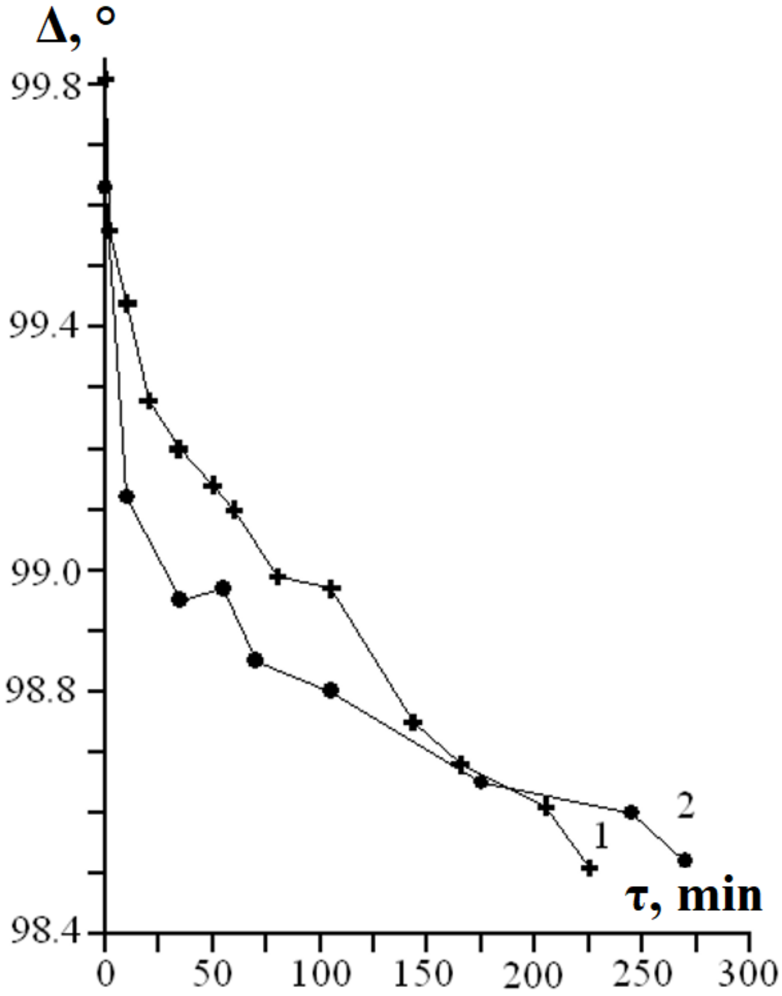


Figure 4. Kinetics of angle Δ variation on the copper electrode surface in the background solution ($E = 0$ V) upon addition of the mixtures: APhDS+PEG-115+ABT (1) and APhDS+PEG-8000+ABT (2). Concentrations in the solution of APhDS – 0.01 g/L, ABT – 0.01 g/L, PEG-115 and PEG-8000 – 0.44 g/L.

Blends: Avangard+PEG-115+JG and Avangard+PEG-8000+JG

Figure 5 shows a comparison of the kinetics of the angle Δ change for the mixtures (Avangard+PEG-115+JG) and (Avangard+PEG-8000+JG). The mixture with PEG-115 is practically not adsorbed on the electrode, while for the mixture with PEG-8000 the value δΔ is ~−0.6°, which confirms more pronounced adsorption of polyethylene glycol with higher molecular weight.

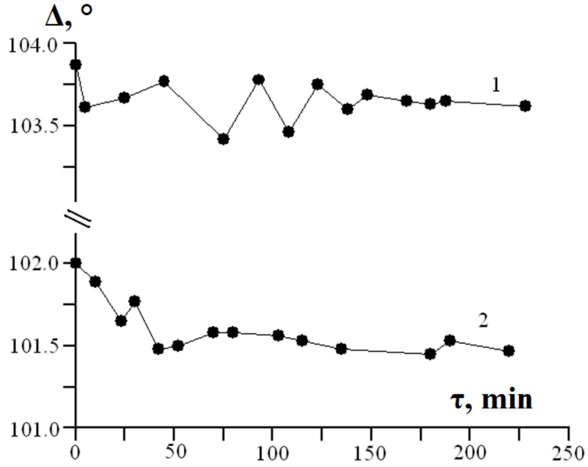


Figure 5. Kinetics of angle Δ variation on the copper electrode surface in the background solution ($E = 0$ V) upon addition of the mixtures: Avangard+PEG-115+JG (1) and Avangard+PEG-8000+JG (2). Concentrations in the solution Avangard – 0.04 g/L, JG – 0.002 g/L, PEG-115 and PEG-8000 – 0.5 g/L.

Blends: SPS+PEG-115+ABT and SPS+PEG-8000+ABT

Figure 6 shows a comparison of the kinetics of the angle Δ change for the mixtures: SPS+PEG-115+ABT (1) and SPS+PEG-8000+ABT (2). For the mixture with PEG-115, δΔ ~ 0, while for PEG-8000 the value of δΔ is ~ 0.1°, which may also be due to the presence of a higher molecular weight representative of PEG in the mixture. Small values of the δΔ agree with the data for individual additives, according to which SPS and ABT in the studied conditions are not characterized by a pronounced adsorption ability.

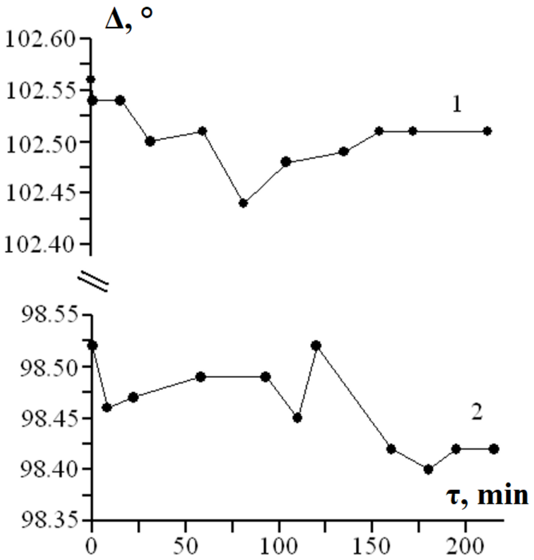


Figure 6. Kinetics of angle Δ variation on the copper electrode surface in the background solution ($E = 0$ V) at the addition of the mixtures: SPS+PEG-115+ABT (1) and SPS+PEG-8000+ABT (2). Concentrations in the solution were 0.03 g/L for SPS, 0.01 g/L for ABT, 0.47 g/L for PEG-115 and PEG-8000.

Blends: SPS+PEG-115+JG and SPS+PEG-8000+JG

Figure 7 shows a comparison of the kinetics of the angle Δ change for the mixtures: SPS+PEG-115+JG (1) and SPS+PEG-8000+JG (2). For the mixture with PEG-115, δΔ ~ −0.1°, while for the mixture with PEG-8000, δΔ ~ −0.2°. Compared to the previous blend, the effect is not much higher, but still higher, which can be explained by the introduction of JG additive, which, as shown above, adsorbs on copper better than ABT.

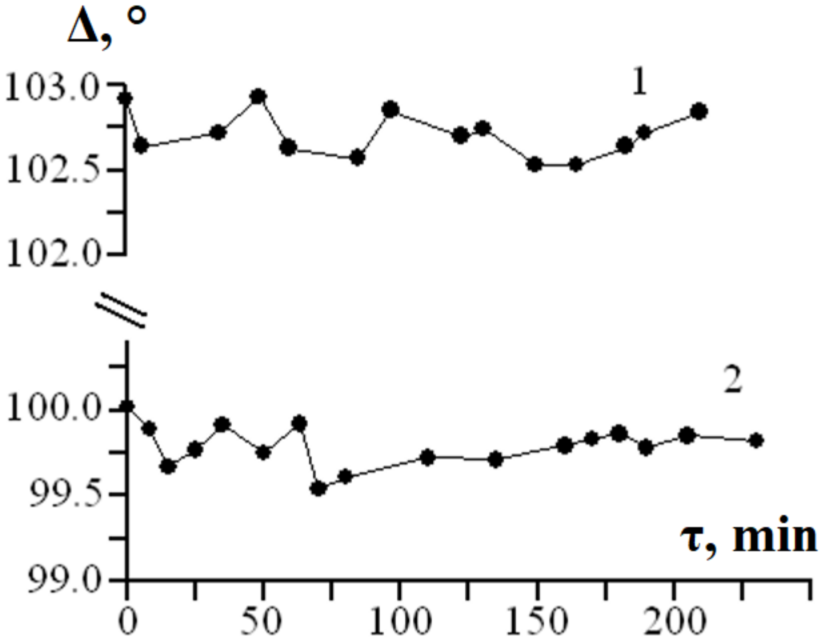


Figure 7. Kinetics of angle Δ variation on the copper electrode surface in the background solution ($E = 0$ V) upon addition of the mixtures: SPS+PEG-115+JG (1) and SPS+PEG-8000+JG (2). Concentrations in the solution of SPS – 0.036 g/L, JG – 0.002 g/L, PEG-115 and PEG-8000 – 0.5 g/L.

Blends: APhDS+PEG-115+JG and APhDS+PEG-8000+JG

Figure 8 shows a comparison of the kinetics of the angle Δ change for the mixtures: APhDS+PEG-115+JG and APhDS+PEG-8000+JG. In the case of both mixtures, a pronounced adsorption effect is observed: in the case of the mixture with low molecular weight PEG-115, the parameter δΔ is ~ −1°, while for the mixture with PEG-8000 the value is δΔ ~ −1.4°. This can be explained by the simultaneous presence in these mixtures well adsorbed additives APhDS and JG, and when introducing high molecular weight polyethylene glycol PEG-8000 the effect is expectedly enhanced.

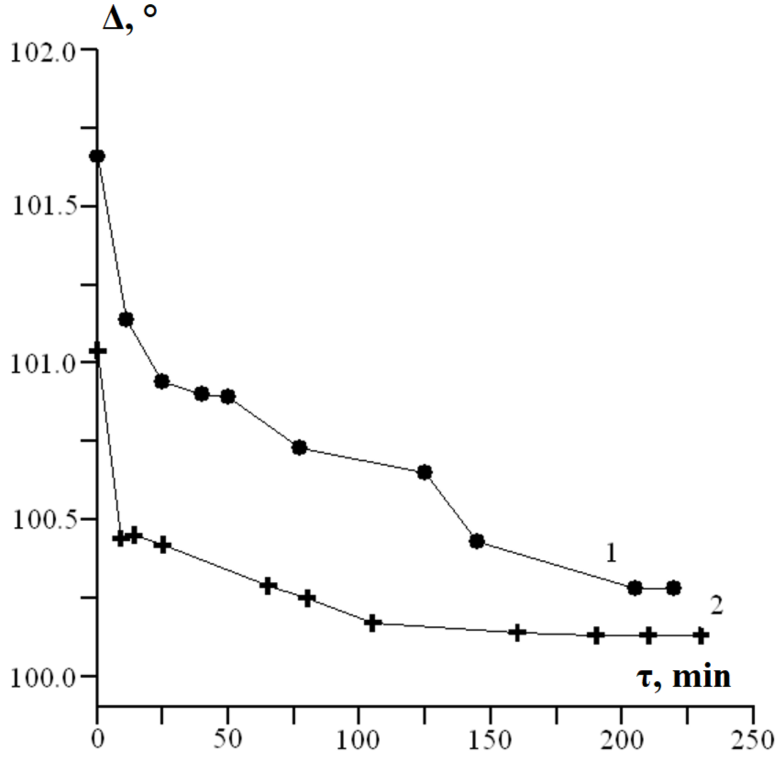


Figure 8. Kinetics of angle Δ variation on the copper electrode surface in the background solution ($E = 0$ V) upon addition of the mixtures: APhDS+PEG-8000+JG (1) and APhDS+PEG-115+JG (2). Concentrations in the solution of APhDS – 0.01 g/L, JG – 0.002 g/L, PEG-115 and PEG-8000 – 0.47 g/L.

Conclusion

The mutual influence of various functional organic additives in sulfate electrolyte of copper plating during joint adsorption on the surface of copper cathode has been investigated by ellipsometric method. Comparison of the ellipsometric phase angle change in solutions with individual brightener additives shows that the propensity to adsorb on copper will increase in the series: bis-(sodium sulfopropyl) disulfide (SPS) < 4,4′-dibenzene disulfonic acid disulfide disodium salt (Avangard) < bis(2-amino-phenyl)disulfide (APhDS). This can be explained by the transition from aliphatic to aromatic backbone, as well as the leading of two amino groups with the additive composition, which may contribute to the increased stability of the chemisorption complexes. For the inhibitor, as which polyethylene glycol was studied, adsorption-desorption behavior is independent of molecular weight, while high-molecular PEG-8000 contributes to more pronounced adsorption in mixtures. Among the levelers, Janus Green B has higher adsorption efficiency with respect to copper compared to aminobenzothiazole, which can be explained by the presence of several aromatic and heterocyclic rings in its structure at once, as well as nitrogen-containing functional groups. As a result, mixtures containing APhDS and JG exhibit the greatest adsorption capacity for which, in the presence of PEG-8000 the maximum change in the ellipsometric phase shift angle is observed.

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