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Kinetics of cathodic deposition of copper from an acid sulfate solution in the presence of organic disulfides

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Abstract

Objectives: In this work, we established the kinetic patterns and evaluated the main parameters of heterogeneous nucleation and growth of a new phase during the electrocrystallization of copper during cathode deposition from an acid sulfate solution in the presence of organic disulfides (disodium salts of 3,3′-dithiodipropanedisulfonic acid, 4,4′-dithiodibenzene disulfonic acid and 3,3’-dithiodi(4-aminobenzene)sulfonic acids). The additives under study contain a disulfide group (-S-S-), which is characteristic of accelerators of the copper cathode deposition process in the implementation of electrochemical void-free filling of through holes (through silicon vias) of silicon wafers used in microelectronics in the manufacture of microcircuits.

Experimental: Electrodeposition of copper coatings was carried out from aqueous sulfate solutions of copper plating in galvanostatic mode. Using scanning electron microscopy, it was found that in the presence of all the studied organic disulfides, copper crystallites with clearer edges are formed in the acid sulfate electrolyte of copper plating than in solutions without additives. The presence of aromatic groups in the structure of the accelerator molecule increases the size of the crystallites of the galvanic copper deposit, and the additional introduction of terminal amino groups into the disulfide structure, on the contrary, leads to a decrease in the size of the crystallites. The latter can be explained by the bifunctional nature of 3,3′-dithiodi(4-aminobenzene)sulfonic acid, capable of exhibiting both an accelerating and leveling effect due to the presence of a disulfide group and an amino group in the structure, respectively. The kinetics of cathodic deposition of copper coatings was studied using transient electrochemical methods of voltammetry, chronopotentiometry, and chronoammetry. In the presence of the studied additives, the overvoltage of copper electrodeposition decreases, while the kinetics of the process does not change: the charge transfer stage proceeds irreversibly, the activation of nucleation sites is progressive, and the growth of a new phase is controlled by the diffusion of copper ions from the solution to the cathode surface.

Conclusions: The functionalization of aliphatic disulfide by the introduction of aromatic and amino groups does not lead to significant changes in the parameters of heterogeneous nucleation and the growth of a new phase during cathodic deposition of copper from an acid sulfate solution. However, the rate of electrocrystallization increases with the transition from aliphatic disulfide (disodium salt of 3,3′-dithiodipropanedisulfonic acid) to disodium salt of 3,3’-dithiodi(4-aminobenzene)sulfonic acid, which contains both aromatic groups and amino groups in its structure.

Keywords: Copper, Cathodic deposition, Organic disulfides, Kinetics, Voltammetry, Chronopotentiometry, Phase formation

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1. Introduction

The process of copper cathodic deposition forms the basis of TSV (through silicon vias) technology used in microelectronics to form electrical contacts (interposers) between different levels of semiconductor devices [1–3]. The technology is based on creating interconnections in the holes of a silicon wafer by filling them with metal, which must be superconformal. This means that when creating interposers, it is necessary to exclude the formation of voids in the forming galvanic deposits [4, 5]. This process cannot be implemented in simple copper deposition electrolytes containing only two main components: copper sulfate and sulfuric acid. The fact is that such electrolytes have a low scattering capacity, which negatively affects the deposition quality in micro-sized holes with a high aspect ratio "depth/height". In this regard, special functional additives are introduced into the electrolyte, among which accelerators play a special role [6–10].

Accelerator molecules are adsorbed mainly in the depth of the micro-holes, which provides a superconformal "bottom-up" filling mode. This is facilitated by the relatively small size and sufficiently high diffusion mobility of accelerator molecules. In addition, their composition and structure play an important role. The most common are organic disulfides containing a disulfide (-S-S-) bond, for example, bis-(3-sulfopropyl)-disulfide (SPS) [11, 12]. According to modern concepts, during the first stage of the mechanism of the accelerating action, SPS molecules decompose to form monomers – 3-mercaptopropanesulfonic acid (MPS). This stage occurs either in the volume of the solution [13, 14] or on the surface of the cathode [15]. Next, MPS forms a thiolate complex with a Cu^{+} ion, which is formed during the first stage of the cathodic reduction of Cu^{2+} ions [16]. The subsequent reduction of the Cu^{+}-MPS thiolate complex to copper proceeds faster than the process of purely electrochemical conversion of Cu^{2+} in the absence of organic disulfide in the electrolyte. In this case, the rate of copper electrodeposition correlates with the concentration of the thiolate complex [17]. The accelerating effect is manifested in the presence of chloride ions [18, 19], which promote chemisorption of Cu^{+} ions and increase their concentration on the cathode surface, thereby reducing the capacity of the double electric layer and polarization, which ultimately creates favorable conditions for nucleation and growth of a new copper phase. In addition, an accelerator can contribute to a change in the contribution of these stages to the deposition kinetics, which, in turn, leads to morphological changes due to the formation of crystallites of a different size [19].

Along with accelerators, an important component of TSV electrolytes are levelers, which are most often used as nitrogen-containing aromatic compounds, including heterocyclic ones [20, 21]. Their functional N-containing groups, including amino groups, contribute to the adsorption of leveler molecules on the copper surface [22]. As a result, the adsorption of a leveler is most pronounced, first of all, in areas with high cathodic current density, which prevents the unwanted deposition of copper in the upper part of TSV holes, but has almost no effect on electrodeposition in areas with low current density (i.e. in the depth of the TSV holes).

The simultaneous action of an accelerator and a leveler ensures superconformal filling of TSV structures with copper. At the same time, both the selection of the most appropriate deposition regime in the presence of both additives and the selection of their optimal concentrations is a difficult task [23, 24]. Therefore, an urgent problem of TSV technology is the search for a single bifunctional additive that would combine the properties of an accelerator and a leveler. Obviously, the use of such a universal additive will simplify the process of optimizing the copper plating regime and reduce the cost of an electrolyte. In addition, it will help to increase its environmental friendliness by reducing the total number of organic components. One of the approaches to finding such a universal additive is to evaluate the possibility and conditions of using already known commercial organic

additives as the only additional component of a copper electrolyte providing superconformal filling [25–27]. In addition, it seems promising to modify the accelerator molecule by introducing functional groups that are characteristic of leveler molecules. It was found [28] that the introduction of nitrogen into the MPS molecule promotes the manifestation of compounds such as 3-S-thiuronium propanesulfonate and 3-(benzothiazolyl-2-mercapto)-propyl sulfonate, along with accelerating, also leveling action. In [29], the possibility of implementing superconformal deposition using a single additive 3-(1-pyridinio)-1-propanesulfonate was shown, the dual effect of which (leveling in the upper part and accelerating in the lower part of the TSV hole) is explained within the framework of model concepts of the dual nature of the molecule due to the presence of a nitrogen-containing heterocycle and a sulfonic acid groups.

When functionalizing an accelerator molecule, the general requirements for it must be met: the presence of a terminal sulfonate group, $-SO_3$, is mandatory, since it accelerates copper deposition, while additives containing terminal groups, -COOH, -OH, and $-CH_3$, do not affect the rate of the process [21]. In addition, the introduction of additional groups into the accelerator molecule should not lead to changes in the kinetics and parameters of electrocrystallization [19]. Thus, along with an assessment of the overall effect of functionalized accelerator molecules on the rate and polarization of the electrochemical copper plating process, it is advisable to study the kinetics of nucleation and growth of a new phase in their presence. Indeed, based on the results of a potentiostatic study of this process, it is possible to evaluate the effect of various additives on the main parameters of phase formation: the density of nucleation sites, rate constant, and the mechanism of their activation [30, 31]. It should be borne in mind that the process of copper cathodic deposition can be complicated by the adsorption of solution components on the electrode surface, as well as by the side reaction of hydrogen evolution [32], since the pH of the copper deposition solution is quite low. The data obtained on the kinetics of copper coating formation, as well as on the patterns and parameters of electrocrystallization, will make it possible to draw a reasonable conclusion and can be used as the basis for further research on the possibility of using universal additives combining the properties of an accelerator and an leveler to purposefully regulate the filling process of TSV structures by varying the structure of accelerator molecules.

In this work we study the role of the functionalization of the bis-(3-sulfopropyl) disulfide molecule, used as an accelerator in TSV technology, by introducing electron-donating aromatic groups and amino groups into the structure of its molecule, in the electrocrystallization kinetics of copper electrodeposition.

The purpose of the work is to establish kinetic patterns and evaluate the main parameters of heterogeneous nucleation and growth of a new phase during electrocrystallization of copper during cathodic deposition from an acid sulfate solution in the presence of organic disulfides of various structures and compositions.

Work objectives:

1. To identify the role of the structure of organic disulfides in the non-stationary electrochemical deposition of copper from a sulfate solution.

2. To determine the effect of the structure of organic disulfides on the morphology of electrodeposited copper coatings.

3. To establish the parameters of heterogeneous nucleation during electrodeposition of copper in the presence of the studied organic disulfides and to evaluate the effect of the introduction of aromatic groups, as well as terminal amino groups into their structure, on the kinetics of copper electrocrystallization.

2. Experimental

Electrodeposition of copper coatings was carried out from aqueous solutions of the following composition: (1) – 156 g/L $CuSO_4 \cdot 5H_2O$ + 10 g/L H_2SO_4 + 50 mg/L Cl^- (pH 1.3); (2) – 12.5 g/L $CuSO_4 \cdot 5H_2O$ + 0.8 g/L H_2SO_4 + 50 mg/L Cl^- (pH 2.1) at room temperature (~20 °C) in a three-electrode electrochemical cell with undivided cathode and anode spaces, without mixing, under conditions of natural aeration. Solution (1) was used for galvanostatic deposition and morphology analysis of the obtained coatings, solution (2) was used for

non-stationary electrochemical measurements and study of copper electrocrystallization kinetics. The thickness of the coatings, determined by the gravimetric method, averages 5.571±0.003 microns.

A copper electrode reinforced in polymerized epoxy resin was used as a working electrode in non-stationary studies. To determine the coating morphology and the current efficiency, deposition was performed on a copper plate. Before electrochemical studies, the working electrode was cleaned on sandpaper with a grain size of P2500, polished on vacuum rubber with Al_2O_3 powder with a grain size of F800, washed with distilled water, cleaned using an ultrasonic bath, then the surface was degreased with isopropyl alcohol, rinsed again with distilled water and dried with filter paper. The preparation of the copper plate surface for electrochemical deposition included degreasing with isopropyl alcohol, rinsing with distilled water, etching in HNO_3 for 7 seconds, repeated rinsing with distilled water and drying with filter paper. The auxiliary electrode was a platinum plate, and a silver chloride electrode (SCE) was used as a reference electrode, connected to the working solution by an electrolytic bridge filled with a saturated solution of potassium nitrate.

The kinetics of cathodic deposition of copper coatings was studied using transient electrochemical methods of voltammetry, chronopotentiometry, and chronoammetry. The measurements were carried out using a computerized P-40X potentiostat/galvanostat. The potentials are given relative to a standard hydrogen electrode. The current density i is calculated per unit of the visible (geometric) area of the electrode, which is 0.045 cm^2. Chronopotentiograms of copper deposition were recorded at a current density of $i = -1.5$ A/dm^2 for 1000 s. Cathodic potentiodynamic curves were recorded by changing the electrode potential over time t from an open-circuit value to $E = -1000$ mV with a scan rate $\upsilon = dE/dt$. The kinetics of electrocrystallization was studied by chronoamperometry method, recording current I,t-transients at different deposition potentials E_{dep} (−200 mV, −300 mV) in the region of the voltammetric maximum. The current efficiency was determined by gravimetric method. The morphology of the coatings was studied by scanning electron microscopy on a JSM-6380LV JEOL installation.

The following organic disulfides were used as additives in concentration of 0.14 mmol/L: disodium salt of 3,3′-dithiodipropanedisulfonic acid (SPS), disodium salt of 4,4′-dithiodibenzenedisulfonic acid (DTBS), and disodium salt of 3,3′-dithiodi(4-aminobenzenesulfonic acid)-acids (AFDS) (Fig. 1). The DTBS molecule contains aromatic groups, and amino groups are additionally introduced into the AFDS molecule.

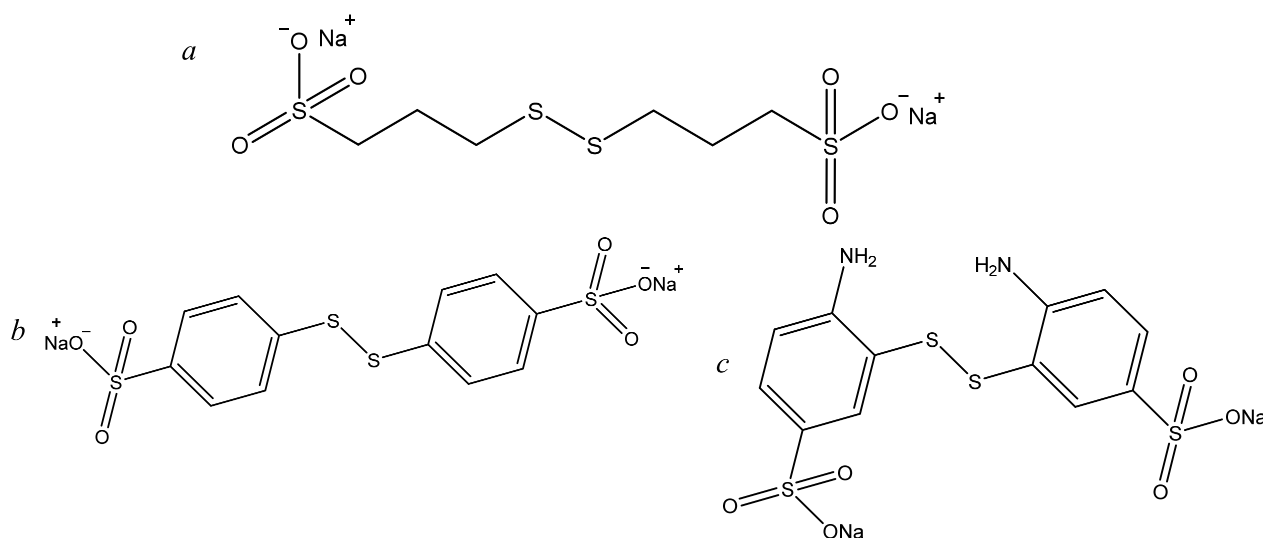

Fig. 1. Molecular structure of the studied organic disulfides: (a) – SPS, (b) – DTBS, (c) – AFDS

3. Results and discussion

The cathodic chronopotentiograms (Fig. 2) obtained in the studied electrolytes show a shift of the electrode potential in the negative direction relative to the open-circuit value (325±4 mV vs. standard hydrogen electrode). It can be seen that during galvanostatic deposition of copper, the introduction of all the studied organic disulfides – both aliphatic SPS and aromatic DTBS and AFDS – such a potential shift is expressed to a lesser extent compared with a solution containing no additives. This indicates a decrease in the electrode polarization of the deposition process, i.e. an acceleration of the cathodic reduction of copper from the sulfate electrolyte in the presence of SPS, DTBS, or AFDS. When aromatic groups are introduced into the structure of the disulfide molecule, the deposition potential shifts by about 15 mV in the positive direction relative to the solution containing the aliphatic chain (SPS). The presence of terminal amino groups in the disulfide structure (AFDS), in turn, leads to an even greater refinement of the deposition potential (~35 mV). Indeed, the greatest potential shift in the positive direction relative to the solution without additives is observed with the addition of AFDS, the smallest with the addition of SPS.

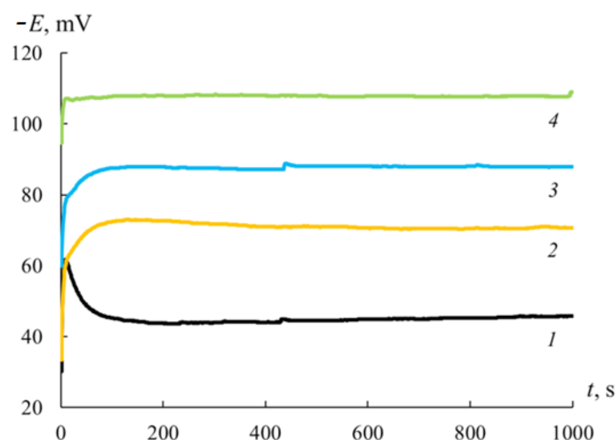

Fig. 2. Chronopotentiograms of copper deposition from solution (1) at i = -1.5 A/dm^2 in the absence of additives (*1*) and in the presence SPS (*2*), DTBS (*3*) and AFDS (*4*)

SEM images of the surface of copper coatings obtained from solutions of various compositions are shown in Fig. 3. The surface of the coating obtained from an electrolyte without additives is characterized by a coarse-grained structure with partial blurring of the grain boundaries. The effect of organic disulfides is manifested in the formation of crystallites with clearer edges. The introduction of the DTBS additive does not significantly affect the size of the crystallites, the use of the SPS additive leads to a decrease, and the AFDS leads to a significant decrease in the size of the crystallites. Thus, the introduction of an aromatic group accelerator (DTBS) into the structure of the molecule increases the size of the crystallites compared to a solution containing an aliphatic chain (SPS). On the contrary, additional functionalization of aromatic disulfide by introducing terminal amino groups (AFDS) into its structure leads to significant grinding of crystallites. This may be due to the fact that the presence of nitrogen in the AFDS molecule contributes to the manifestation, along with the accelerating, also the leveling effect of the additive, which is consistent with [28, 29].

A comparative analysis of the cathodic polarization curves (Fig. 4) shows that the shape of the voltammograms does not change when the studied additives are introduced into the sulfate

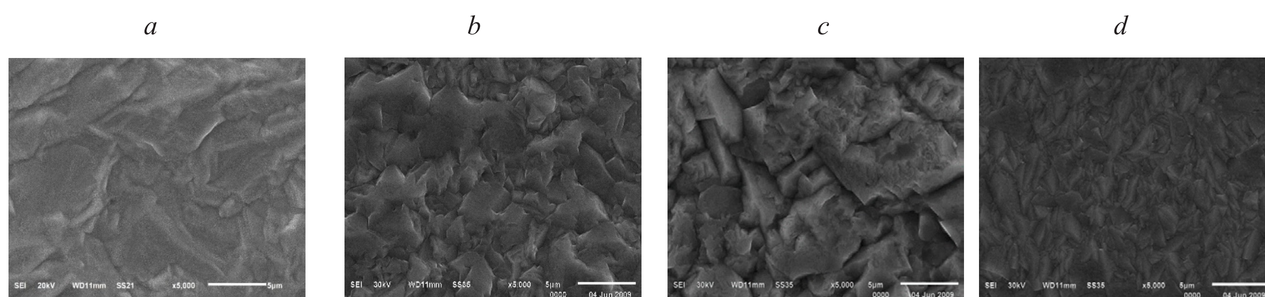

Fig. 3. SEM images obtained with magnification x5000 of the surface of copper coatings galvanostatically deposited (current density i = –1.5 A/dm^2, deposition time 1000 s) from solution (1) without additives (*a*) and in the presence of organic additives SPS (*b*), DTBS (*c*) and AFDS (*d*)

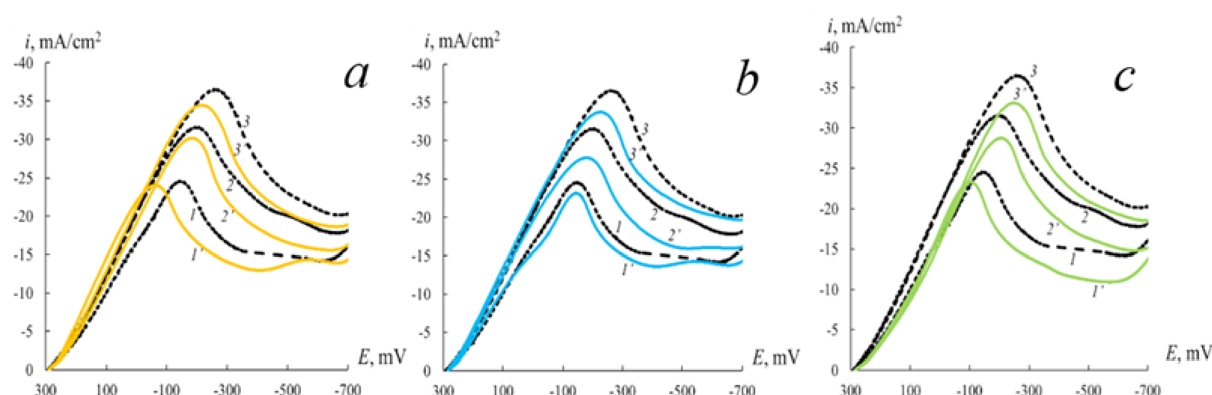

Fig. 4. Cathodic voltammograms obtained in solution (2) at υ = 100 (1,1′), 200 (2,2′), 300 (3,3′) mV/s in the absence of additives (1,2,3) and with the introduction of organic additives (1′,2′,3′): SPS (*a*), DTBS (*b*) and AFDS (*c*)

solution of copper plating. At the same time, the current density of the voltammetric maximum i_{max} decreases with the introduction of the studied disulfides compared with the solution without additives. The peak potential E_{max} shifts slightly to the positive region, with the exception of the solution containing the AFDS additive. The greatest shift to the positive area is observed when using an SPS additive based on an aliphatic structure. In addition, unlike DTBS and AFDS, in the case of SPS, acceleration of the process is observed at $E > E_{max}$ (Fig. 4). The totality of these data confirms the purely accelerating effect of SPS. The presence of aromatic groups (DTBS) in the structure of the molecule leads to a slight decrease in the current density of the voltammetric maximum i_{max} and a shift in the potential of the maximum E_{max} to a negative region compared with a solution containing an aliphatic chain (SPS). The additional introduction of terminal amino groups into the disulfide structure (AFDS) leads to a more noticeable shift of the maximum potential E_{max} to the negative region.

Thus, based on the observed changes in the voltammetric response, it is difficult to unambiguously judge the accelerating or inhibitory effect of the additives under study on the copper deposition process. This can be explained by the fact that the ratio of the contributions of the accelerating and leveling effects of the functionalized additives DTBS and AFDS changes in a complex way during recording the polarization curve under potentiodynamic conditions, and at $E < E_{max}$, the non-stationary mass transfer stage has the greatest effect on the kinetics of the process, which is apparently weakly sensitive to the presence of organic additives in solution. The diffusion limitations of the process are confirmed by the linear dependence of the maximum current density i_{max} vs. root of the potential scan rate $\upsilon^{1/2}$ (Fig. 5a). The i_{max} – $\upsilon^{1/2}$ curves for all additives are close and do not extrapolate to the origin, probably due to a parallel side process (for example, hydrogen evolution). Indeed, the current efficiency according to gravimetric measurements is 85±4 %. At the same time, a significant shift of the maximum potential to the negative side with an increase in the scan rate indicates the irreversibility of the charge transfer stage (Fig. 5b).

The role of organic disulfides in the kinetics of electrocrystallization was established by determining the parameters of nucleation and growth of a new phase during copper deposition. The kinetics of the process is usually determined under the assumption of instantaneous or continuous activation of nucleation sites [33] within the framework of the 3D nucleation model proposed by Scharifker and Hills [34]. However, a preliminary comparison of the experimental chronoamperograms with the theoretical equations of the Scharifker-Hills model showed their significant discrepancy, which made it impossible to establish the nucleation kinetics, much less to quantify the characteristics of the copper electrocrystallization. The most likely causes of the revealed deviation are the significant contribution of the hydrogen evolution reaction, as well as the presence of substances capable of adsorption in the solution. In this regard, for

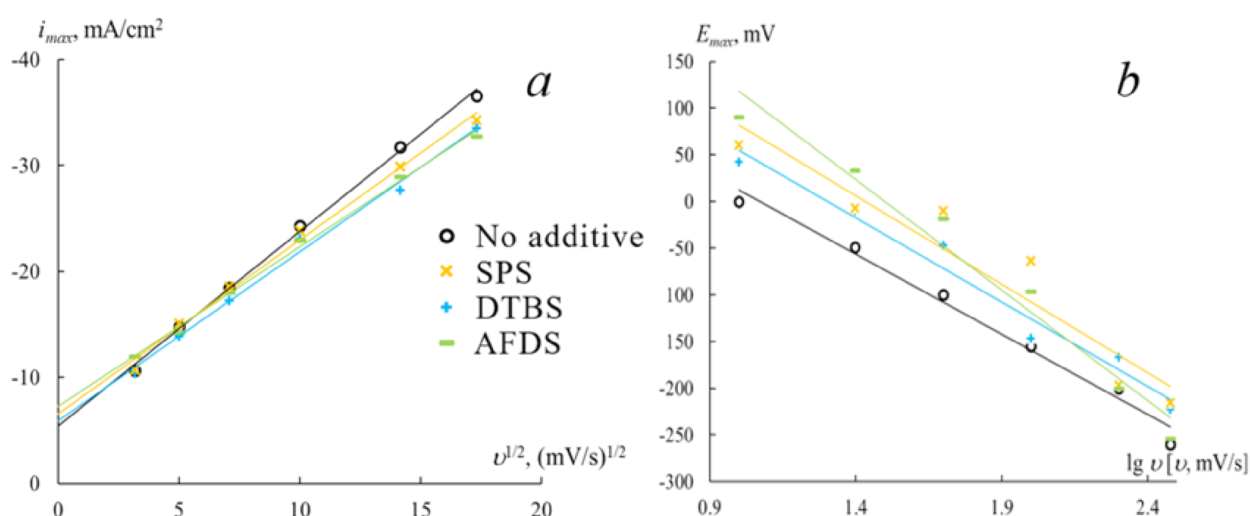

Fig. 5. (*a*) – Current density of the voltammetric maximum vs. root of the potential scan rate, (*b*) – potential of the voltammetric maximum vs. decimal logarithm of the potential scan rate obtained in solution (2) without additives and with the introduction of organic additives SPS, DTBS and AFDS

further analysis, we used an extended model of nucleation and growth of a new phase [32], which takes into account that diffusion-controlled electrodeposition of metal occurs together with hydrogen reduction and adsorption of solution components. The extended model makes it possible to describe the potentiostatic transient current $i(t)$ obtained during electrodeposition as the sum of three components:

$$i(t) = i_{Cu}(t) + i_{H}(t) + i_{ads}(t).(1)$$

Here, the current density i_H determines the rate of the proton reduction reaction [32] and can be described by the ratio:

$$i_H(t) = P_1 S(t), \quad (2)$$

in which the coefficient $P_1 = z_H F k_H$ includes the charge $z_H F$ responsible for the reduction of 1 mole of protons ($z_H = 1$, $F = 96485$ C/mole), k_H is the rate constant of the proton reduction reaction. The fraction of the surface occupied by electrodeposited copper

$$S(t) = (2c_0 M/\pi\rho)^{1/2}\theta(t) \quad (3)$$

it includes c_0 – the initial volume concentration of copper ions (0.05 M), M – the molar mass of copper (63.5 g/mole), r – the density of the copper deposit (8.96 g/cm³), as well as the function

$$q(t) = \{1-\exp\{-P_2[t-(1-\exp(P_3 t))/P_3]\}\}. \quad (4)$$

Here, the parameters $P_2 = N_0\pi kD$ and $P_3 = A$ include the density of active nucleation sites on the electrode surface (N_0), the diffusion coefficient of copper ions (D), the nucleation rate (A), and the constant $k = (8\pi c_0/\rho)^{1/2}$.

The current density i_{Cu}, which determines the rate of the diffusion-controlled copper reduction process, is determined as follows [32]:

$$i_{Cu}(t) = P_4 t^{-1/2}\theta(t), \quad (5)$$

where $P_4 = 2FD^{1/2}c_0/\pi^{1/2}$.

Finally, the third term i_{ads} is due to the adsorption process described in [32] as an exponential decrease in current:

$$i_{ads}(t) = K_1\exp(-K_2 t). \quad (6)$$

Thus, the total current density will be described by the following expression:

$$i(t) = \{P_1^* + P_4 t^{-1/2}\}\times \times\left\{1-\exp\left\{-P_2\left[t-\frac{1-\exp(P_3 t)}{P_3}\right]\right\}\right\} + K_1\exp(-K_2 t), \quad (7)$$

where $P_1^* = P_1(2c_0 M/\pi\rho)^{1/2}$.

To identify the effect of organic disulfides on the stage of heterogeneous nucleation during cathodic deposition of copper, kinetic parameters of the electrocrystallization process were obtained by approximating equation (7) and experimental chronoamperograms recorded at potentials in the vicinity of the voltammetric peak: –200 and –300 mV. Experimental chronoamperograms have the shape of a curve with a maximum (Fig. 6),

which is typical for nucleation processes: a sharp increase in current during the initial period of the electrodeposition process is followed by a decrease in current and its tending to a constant value. Their comparison with the current transients found in accordance with the extended model of the 3D nucleation process shows that the use of generalized equation (7) made it possible to obtain a complete coincidence of experimental and theoretical chronoamperograms. In addition, *i*,*t*-curves were calculated for three parallel processes (electrocrystallization, hydrogen evolution, and adsorption). As expected, the rate of adsorption is higher in solutions containing additives than in their absence. The current caused by the hydrogen evolution reaction increases and reaches a constant value, which does not significantly depend on the presence of additives.

The nucleation current is characterized by the formation of a maximum in the initial period

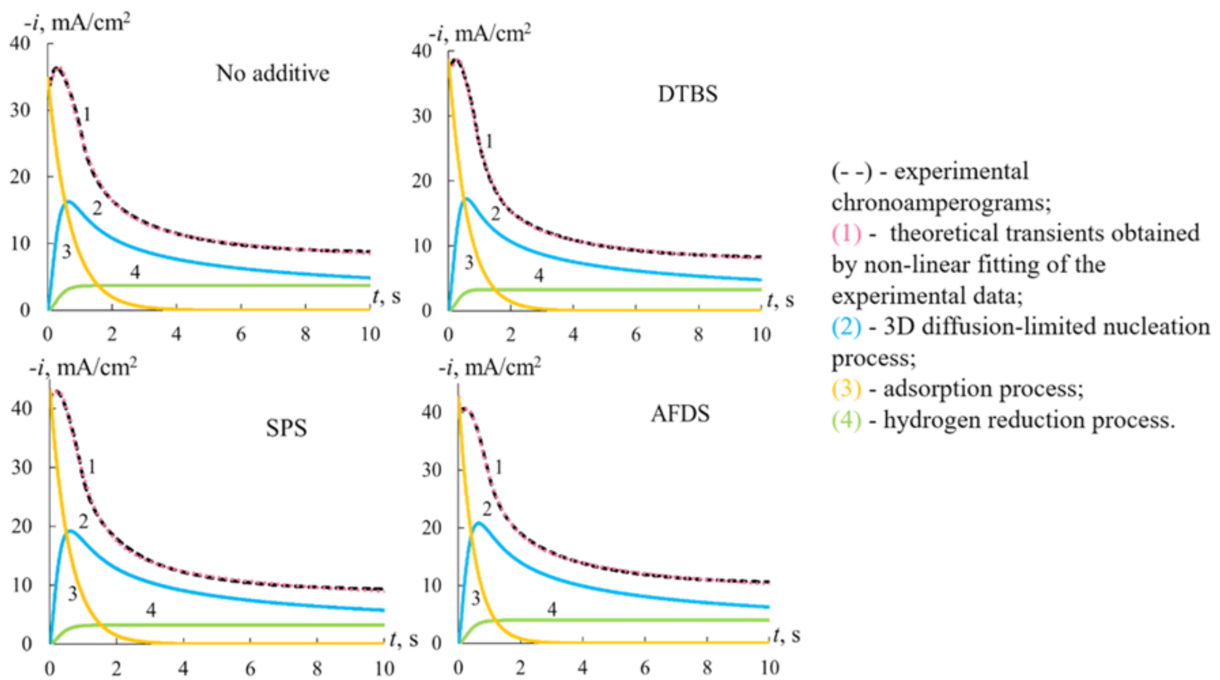

Fig. 6. Experimental and theoretically calculated chronoamperograms obtained by electrodeposition of copper at a potential of -300 mV

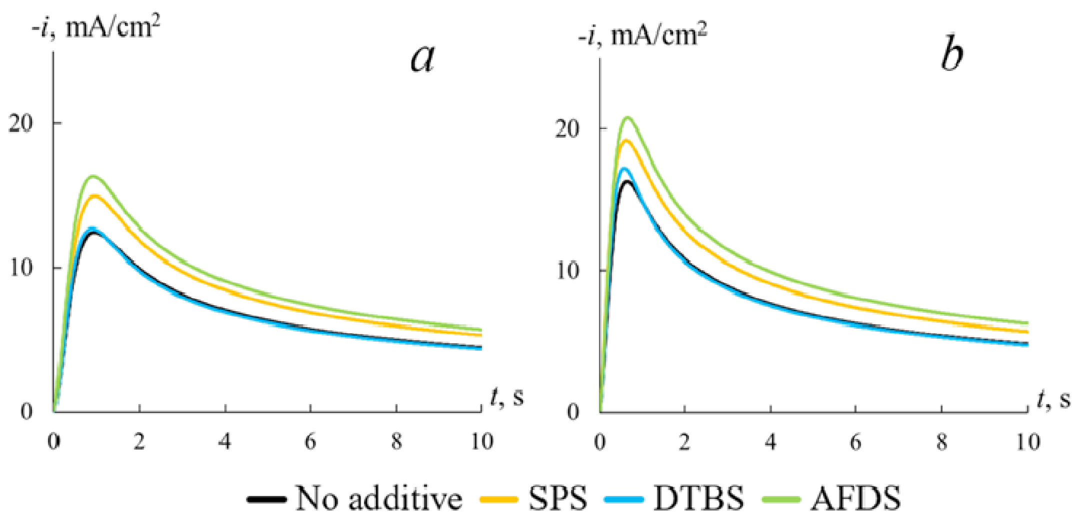

Fig. 7. Partial curves of copper electrocrystallization at a cathode potential of -200 mV (*a*) and -300 mV (*b*)

of the process, the height of which depends on the deposition potential and the presence of additives in the electrolyte (Fig. 7). With an increase in the cathodic potential, the rate of electrocrystallization increases, as with the introduction of all the studied organic disulfides into the solution. At the same time, DTBS gives a minimal accelerating effect (4–5 %), while SPS and AFDS increase the nucleation current by 17–22 % and 24–34 %, respectively.

Using the extended electrocrystallization model, it was also possible to determine the values of kinetic parameters of electrodeposition at the stage of nucleation and growth of a new phase, including in the presence of organic disulfides (Fig. 8). The analysis shows that the transition from aliphatic (SPS) to functionalized (DTBS, AFDS) organic disulfides is unsystematic and to a small extent affects both the density of nucleation sites and the rate constant of activation of potential nucleation sites, which on average are N_0 = (1.3±0.3)·10^{-5} cm^{-2} and A = (2.8±0.6) cm^{-1}, respectively. It is known that, depending on the value of parameter A, the activation process can be classified as instantaneous if $At \gg 1$, otherwise as continuous [34]. The estimation of At value by the time the maximum is reached on the nucleation curve ($t \approx 1$ s) leads, both in the case of a solution without additives and with additives, to the value of $At \approx 3$, which allows us to consider the activation of nucleation sites as continuous.

Thus, despite the introduction of aromatic groups and/or amino groups into the structure of DTBS and AFDS disulfides, the kinetics and parameters of electrocrystallization do not change significantly, which is a prerequisite [19] when choosing a universal organic additive that exhibits accelerating and leveling effects depending on the current distribution inside the TSV structure. At the same time, the results of non-stationary electrochemical studies and scanning electron microscopy allow us to consider the addition of AFDS, characterized by the presence of both aromatic groups and amino groups in its structure, the most promising as a bifunctional additive in relation to cathodic deposition of copper, since for this compound the most pronounced effect of accelerating the rate of electrocrystallization is observed (Fig. 7), on the one hand, and a noticeable morphological smoothing of the surface, on the other hand (Fig. 3), while maintaining the kinetics and parameters of copper electrocrystallization.

4. Conclusion

The introduction of organic disulfides (disodium salts of 3,3′-dithiodipropanedisulfonic acid, 4,4′-dithiodibenzene disulfonic acid and

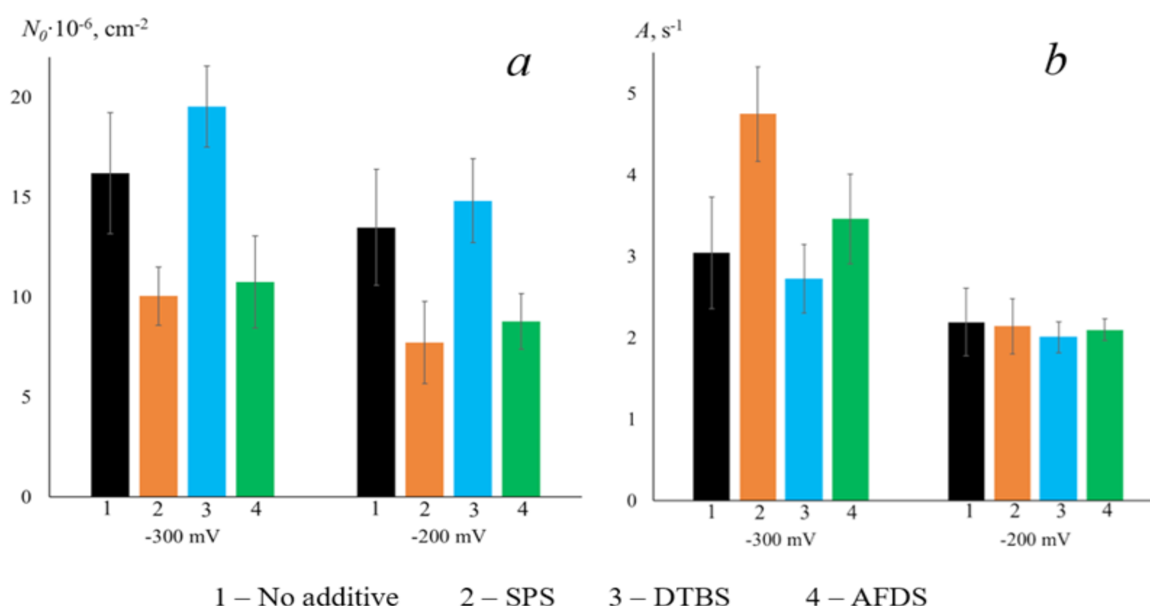

Fig. 8. Kinetic parameters of nucleation: *a* – nucleation active site densities (N_0), *b* – activation rate constant of potential nucleation active site (A)

3,3′-dithiodi(4-aminobenzenesulfonic acid) into an acidic sulfate solution leads to a decrease in the cathodic polarization of the copper reduction process during galvanostatic deposition, which confirms the accelerating effect of these additives. The functionalization of the aliphatic disulfide (SPS) molecule by including aromatic groups in the structure enhances the deposition potential by about 15 mV, while the additional introduction of amino groups into the disulfide structure leads to an even greater (about 35 mV) shift in the deposition potential to the positive side.

Scanning electron microscopy revealed that in the presence of the studied additives of organic disulfides, crystallites with more pronounced faces form on the surface of the copper coating. Moreover, if the introduction of a 4,4′-dithiodibenzene disulfonic acid salt does not significantly affect the size of the crystallites, then the use of 3,3′-dithiodi(4-aminobenzenesulfonicacid leads to their significant reduction. According to literature data, this effect can be explained by the presence of amino groups responsible for the leveling effect in the molecule of the AFDS accelerator. The dual nature of functionalized additives in relation to the copper deposition process is indirectly confirmed by the results of potentiodynamic measurements, the analysis of the critical parameters of which allowed us to establish that the charge transfer stage during copper deposition is irreversible, and the process is complicated by the non-stationary diffusion of ions of the deposited metal to the cathode surface.

The role of organic disulfides in the kinetics of electrocrystallization has been established taking into account the double-layer and adsorption processes which occur during the initial deposition period, as well as the side reaction of hydrogen evolution, the contribution of which is confirmed by the value of the current efficiency of 85±4 %. It was found that the rate of electrocrystallization increases with the introduction of all the studied organic disulfides into the solution (DTBS by 4–5 %, SPS by 17–22 %, and AFDS by 24–34 %), which confirms their accelerating effect. However, the kinetics of 3D nucleation during copper deposition in the presence of the studied additives remains unchanged and corresponds to the mechanism of continuous activation of nucleation sites. During the functionalization of organic disulfide molecules, their density and the rate constant of activation vary slightly and unsystematically, averaging $(1.3\pm0.3)\cdot10^{-5}$ cm^{-2} and 2.8 ± 0.6 cm^{-1}, respectively.

Contribution of the authors

Ilina E. A. – conducting electrochemical research, writing a text. Kozaderov O. A. – scientific guidance, research concept, methodology development, text editing, final conclusions. Sotskaya N. V. – conducting research, editing text. Golovinsky A. D. – conducting electrochemical research. Kolbeshkina E. D. – conducting electrochemical research. Polikarchuk V. P. – conducting organic synthesis.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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