

Article

Electrocrystallization and Morphology of Copper Coatings in the Presence of Organic Additives

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Abstract: Copper coatings with refined grains and smooth surface morphology were electrodeposited from electrolytes comprising a novel accelerator, the disodium salt of 4,4-dithiobenzene disulfonic acid (DBDA), with sodium chloride and polyethylene glycol (PEG) as inhibitors and 2-aminobenzothiazole (ABT) as a leveler. It was found that the morphology of the coatings strongly depends on the presence and type of additives. In the presence of only DBDA and NaCl, large crystallites are formed, whereas the addition of PEG and ABT significantly decreases their size, and the most fine-grained, smooth, and defect-free copper coating is formed with the combined use of all additives. To establish the correlation between the observed morphology and the kinetics of the additive-assisted copper electrocrystallization in the proposed electrolytes, the nucleation mechanism and its parameters were determined by transient electrochemical characterization. The extended nucleation model, which takes into account not only the copper deposition but also the electric double-layer charging and hydrogen reduction process, was used to establish the electrocrystallization kinetics in the presence of the additives. The results of such kinetic analyses can help to explain the morphological effect. By using the chronopotentiometry method, it was found that the addition of the disodium salt of 4,4-dithiobenzene disulfonic acid with chloride ions gives a catalytic effect, while the sequential introduction of polyethylene glycol and 2-aminobenzothiazole provides an increasing inhibitory effect. Voltamperometry and chronoamperometry tests showed that the process is controlled by the diffusion of ions to the growing three-dimensional cluster of a new phase. The introduction of additives into the electrolyte slows down the copper electroplating process at comparatively negative potentials and increases the probability of transition from instantaneous to progressive nucleation. Moreover, the rate of the process and the density of nucleation active sites increase (up to 2–3 times) with the addition of DBDA but decrease significantly (up to 5–8 times) in the presence of PEG and ABT, which additionally confirms their catalytic and inhibitory effects, respectively, and explains the significant smoothing effect on the morphology of the Cu-coatings.

Keywords: copper; electrocrystallization; nucleation kinetics; morphology; acidic sulfate electrolyte; organic additives



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1. Introduction

The electrochemical deposition of metals is widely used to obtain functional coatings. Copper is of particular preference because of its high conductivity, solderability, and plasticity. The electrodeposition of copper is of great interest for the semiconductor industry [1] in the manufacture of printed circuit boards (PCBs) and interconnects in microelectronic devices [2]. At the same time, high requirements for the morphological properties of copper coatings cause careful selection of the electrolyte composition. The deposits obtained from solutions containing only copper (II) sulfate and sulfuric acid have a coarse-grained

structure due to low cathodic polarization, and the moderate throwing power of such electrolytes does not provide sufficient uniformity of copper deposition. This is of particular importance when filling the through-silicon vias (TSVs) with a high aspect ratio [3], and in particular, a superfilling process [4–6] should be implemented because it is significantly important to realize an effective deposition mechanism in microvia metallization for PCBs so as to interconnect those electronic components [7]. Therefore, various organic additives are introduced into the copper plating electrolyte [8–19], which, depending on the specific function performed during deposition, are divided into inhibitors, accelerators, and levelers.

Inhibitors are high-molecular compounds, for example, polyethylene glycol (PEG) [4,11,18,20,21]. Acting together with chloride ions, PEG forms a blocking layer on the copper surface, thereby increasing the overpotential of the deposition process [21] and decreasing its rate. Adsorption of chloride ions at the electrode surface in the copper electrodeposition potential range [22] provides strong binding sites for PEG adsorption [23].

In TSV technology, due to their large size and slow diffusion, the inhibitor molecules practically cannot reach the bottom of the micro-hole, the relatively fast filling of which is provided primarily by accelerators. These include sulfur-containing organic compounds with disulfide (R-S-S-R) and/or thiol (R-S-H) bonds, e.g., bis-(3-sulfopropyl) disulfide (SPS) [1] and 3-mercapto-1-propanesulfonate (MPS) [24]. The acceleration of copper electrodeposition is provided [25] because of the depolarization effect arising as a result of chemical Cu^{2+} reduction with the formation of a Cu(I) thiolate complex with subsequent regeneration of SPS, instead of a purely electrochemical Cu^{2+} to Cu^+ transformation in the absence of an organic disulfide in the electrolyte. It was found [26] that the mercapto head group and the sulfonate end group play a decisive role in acceleration in the presence of Cl^- ions. Its interaction with the sulfonate functional groups is of high importance for the implementation of superfilling deposition, since in the presence of chloride ions, accelerator molecules are able to be adsorbed [27] at the bottom of the micro-hole, which leads to depolarization and an increase in the rate of copper electroplating.

Levelers are used to obtain smooth coatings since they locally decrease the copper electrodeposition rate on the surface protrusions and promote its growth in hollows, as a result of which the surface roughness of the copper deposit decreases. Nitrogen-containing heterocyclic and high-molecular compounds are among the most common levelers [28–32].

The morphology and film properties of copper deposits highly depend on the types and concentrations of additives [33], but their collective effect on the electroplating process is also important. Along with the abovementioned joint action of chloride ions with inhibitor or accelerator molecules, it is necessary to note possible synergistic [6,31,32,34–36] and antagonistic [37] effects of additives of various types. The synergism of the additives enables a bright, dense, and smooth copper coating to be achieved. Therefore, compositions of organic additives are used, the simultaneous presence of which in the electrolyte solution should provide the highest quality coating [5,38].

This paper considers in more detail one of the most important factors determining the choice of additive-assisted electrolyte composition, namely their influence on the kinetics and mechanism of the electrochemical deposition of copper at the limiting stages of charge transfer and electrocrystallization [6,29,34,39,40]. It is well known that the quality of electrodeposited copper depends on the rate of the early stage of electroplating and especially that of nucleation [41]. The organic additives with different heteroatoms and functional groups differ in their effect on copper electrodeposition in acidic sulfate media [42] because of different actions on the nucleation stage. A possible explanation for the additives' effect is that the number of nucleation sites for copper deposition varies in the presence of organic surfactants due to their strong, potential-dependent adsorption both on the electrode surface and on the growing clusters of the new phase [43]. There are data in the literature concerning the nucleation mechanism during copper electrodeposition; however, understanding of the different additives' impact on copper nucleation and the characteristics of the process are not yet established quite completely. At the same time,

it is this detailed knowledge about the copper nucleation mechanism that is very much required by the technological process. The available data, being obtained in a rather narrow cathodic potential window (usually near the voltammetric reduction peak position), do not meet such requirements. In this work, the nucleation kinetics of copper electrodeposition are examined in a wider overpotential interval, combining voltammetry and potential step methods to obtain results that are important for industrial copper plating carried out at rather high overpotentials [43]. Thus, it is crucial to investigate the effects of additives on the copper nucleation kinetics in detail to form the basis for the optimization of the electrolyte composition and technological modes of the electrodeposition of copper coatings.

The purpose of the present experimental study is to investigate the effect of additives of different types (the disodium salt of 4,4-dithiobenzene disulfonic acid, chloride ion, polyethylene glycol, and 2-aminobenzothiazole) and their compositions on the morphology of Cu-coatings and the nucleation kinetics of copper electroplating from a model acidified sulfate electrolyte. In this paper, for the first time, an electrolyte containing a novel prospective organic disulfide—the disodium salt of 4,4-dithiobenzene disulfonic acid—is considered, which differs from the traditionally used ones (e.g., SPS) by the presence of aromatic rings rather than a linear hydrocarbon chain, which can contribute to more efficient adsorption of this electrolyte component.

2. Materials and Methods

The baths used for Cu-coating electrodeposition were electrolytes made of 220 g/L of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 50 g/L of H_2SO_4 for galvanostatic tests, and a diluted solution with the same ratio of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ / H_2SO_4 containing 12.5 g/L of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 2.8 g/L of H_2SO_4 for voltammetry and chronoamperometry tests. The solutions were not stirred to avoid a possible non-controlled influence of convection on the process kinetics and to be sure that the conditions of use of the theoretical nucleation model are met in the system. The disodium salt of 4,4-dithiobenzene disulfonic acid (0.06 g/L), sodium chloride (0.05 g/L), polyethylene glycol (0.5 g/L), and 2-aminobenzothiazole (0.5 g/L) were used as additives to the bath. The molecular structures of the additives are shown in Figure 1. The codes of the used solutions are shown in Table 1.

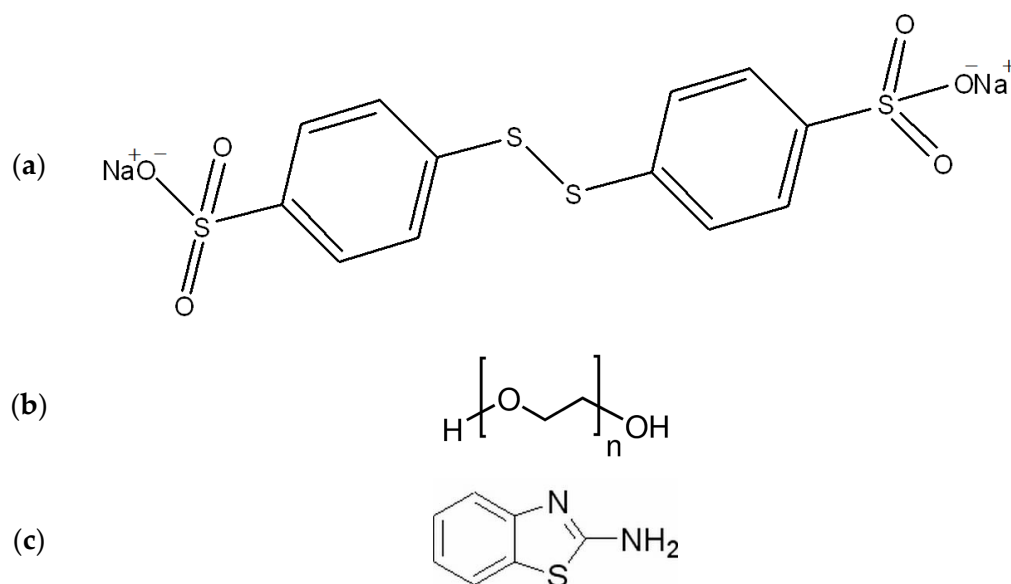


Figure 1. Molecular structures of (a) DBDA, (b) PEG, and (c) ABT.

Table 1. The solution codes used in the paper.

Additives and Their Concentrations	Electrolyte Code
No additive	0
DBDA (0.06 g/L)	I
DBDA (0.06 g/L) + NaCl (0.05 g/L)	II
DBDA (0.06 g/L) + NaCl (0.05 g/L) + PEG (0.5 g/L)	III
DBDA (0.06 g/L) + NaCl (0.05 g/L) + PEG (0.5 g/L) + ABT (0.5 g/L)	IV

The role of additive concentration has not been studied in this work. When choosing this parameter for this or that additive, we took into account that the concentration range of the accelerator, inhibitor, and leveler varies quite widely when studying their effect on the process of copper electrodeposition: from 0.001–1 mg/L [6,25,28,38,44–49] to 1–5 g/L [19,29,50–52]. In this study, concentrations close to the average values for the particular type of additive were used.

The coatings were deposited on M1 copper plates (for surface characterization), and electrodes made of M1 copper samples were armored in epoxy resin (for kinetic characterization). Preparation of the copper plate surface for electrochemical deposition and morphological characterization included degreasing the surface with ethanol, washing with distilled water, etching in concentrated HNO_3 for 7 s, and then washing with distilled water. Preparation of the surface of the copper electrode for electrochemical studies included grinding on abrasive paper, polishing on chamois with an aqueous suspension of MgO , repeated washing with distilled water, degreasing the surface with ethanol, and then washing with distilled water.

The electrochemical behavior of the additives was characterized by chronopotentiometry, linear sweep voltammetry, and chronoamperometry measurements at room temperature in a water bath. All the electrochemical experiments were performed using an IPC-Pro L potentiostat with a three-electrode system in an electrolytic cell with undivided cathode and anode spaces, without mixing, under conditions of natural aeration. The auxiliary electrode was made of platinum. The potentials E in the study are presented relative to the silver/silver chloride reference electrode, which was located in a separate vessel with 3 M KCl and connected to the cell by an electrolytic bridge filled with a saturated solution of potassium nitrate. The reference electrode potential with respect to a standard hydrogen electrode was $E_{\text{ref}} = 213$ mV. Cathodic potentiodynamic curves were recorded on a copper electrode, changing the electrode potential E in time t from an open-circuit value to -800 mV at different scan rates $v = dE/dt$. To determine the kinetics of nucleation, current I - t transients were recorded at different deposition potentials E_{dep} . Current density i was calculated by normalizing the current strength I per unit geometric (visible) area of the electrode. Galvanostatic deposition was carried out at $i = 1.5$ A/dm² for 1000 s.

The surface morphology of the obtained copper coatings was investigated using a JSM6510LV JEOL scanning electron microscope. The elemental composition of the coatings was studied by X-ray microanalysis using an INCA Energy 250 electron microscope attachment. X-ray diffraction analysis of the Cu-coatings was carried out at room temperature using a DRON-4.07 diffractometer with $\text{CuK}\alpha$ radiation (Figure 2). According to the data of elemental and phase analysis in all samples of the obtained copper coatings, the Cu content is 100%.

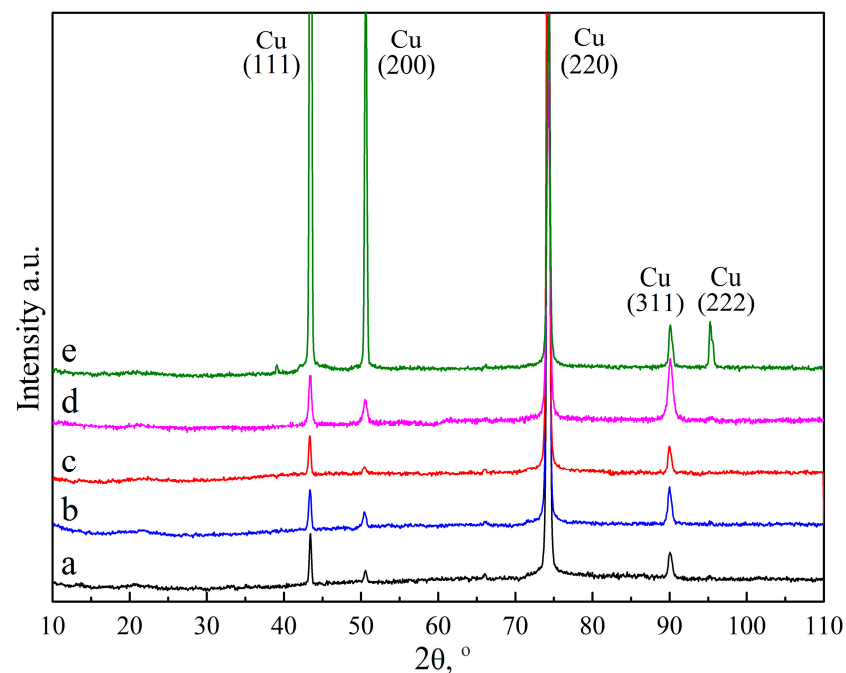


Figure 2. XRD patterns of the copper coatings, deposited at $i = 1.5 \text{ A/dm}^2$ (deposition duration is 1000 s), from the solutions of type 0 (a), I (b), II (c), III (d), and IV (e) based on the composition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (220 g/L) and H_2SO_4 (50 g/L).

The method for theoretical analysis of the kinetics of copper electrodeposition was chosen based on the following. The kinetics of the process are usually determined in the framework of instantaneous or progressive nucleation [53] within the 3D nucleation theory proposed by Scharifker and Hills (SH theory) [54]. The experimental chronoamperograms obtained in this work were found to be deviated (especially in the initial period of potentiostatic electrocrystallization) from the transient curves theoretically calculated within SH theory. The possible reasons could be a prominent impact of the hydrogen evolution reaction on the observed current density, and the presence of substances capable of being adsorbed. That is why we used the extended nucleation model [55], taking into account that 3D diffusion-limited metal electrodeposition occurs along the hydrogen reduction and adsorption processes. This model describes the potentiostatic $i(t)$ transients obtained during the electrodeposition process as a sum of three different contributions:

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

The current density i_{H} is associated with the proton reduction reaction, and it is given by [55]:

$$i_{\text{H}}(t) = P_1 S(t) \quad (2)$$

with $P_1 = z_{\text{H}} F k_{\text{H}}$, where $z_{\text{H}} F$ is the molar charge transferred during the proton reduction process, $z_{\text{H}} = 1$, F is the Faraday constant (96,485 C/mol), and k_{H} is the rate constant of the proton reduction reaction. $S(t)$ is the fractional surface area of electrodeposited copper:

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

where c_0 is the concentration of copper ions in the bulk solution (0.05 M), M is the molar mass of copper (63.5 g/mol), ρ is the density of the copper deposit (8.96 g/cm³), and

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

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

The current density i_{Cu} associated with the contribution due to the diffusion-limited copper reduction process is given by [55]:

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

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

A third contribution i_{ads} due to an adsorption process is described in [55] as an exponential current decay:

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

with $K_1 = E/R_s$, $K_2 = 1/R_s C$, where E is an applied potential, R_s is the solution's resistance, and C is the electric double-layer (EDL) capacitance.

The total current density is the sum of all contributions and is hence given by:

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

where $P_1^* = P_1(2c_0M/\pi\rho)^{1/2}$.

The theoretical current–time transients were generated by non-linear fitting of Equation (7) to the experimental data. During the iterative fitting process, the parameters P_1^* , P_2 , P_3 , P_4 , K_1 , and K_2 were allowed to vary freely.

3. Results and Discussion

Chronopotentiometry of the galvanostatic deposition of copper coatings from the studied electrolytes with the sequential introduction of DBDA, NaCl, PEG, and ABT additives showed that the addition of DBDA leads to a shift in the deposition potential of copper towards more negative values compared with a solution that does not contain DBDA (Figure 3). This indicates its inhibitory effect on Cu-electroplating.

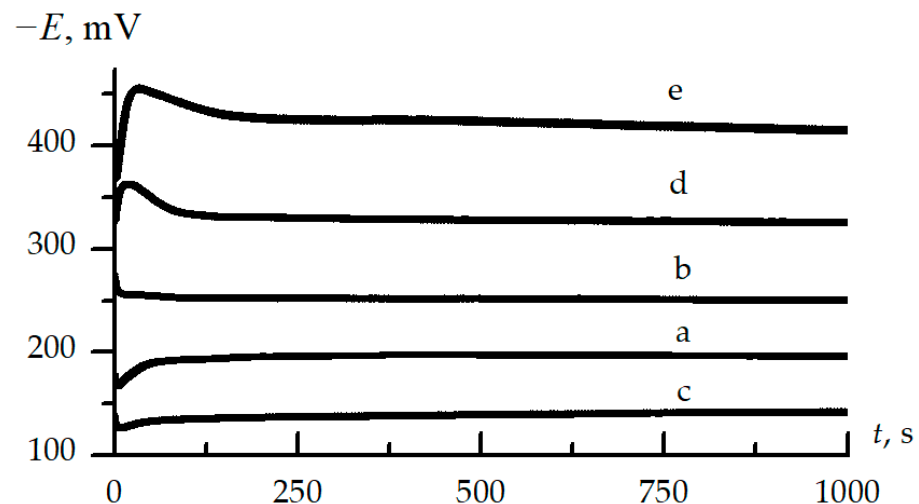


Figure 3. Chronopotentiograms of copper deposition from the solutions of type 0 (a), I (b), II (c), III (d), and IV (e) based on the composition of 220 g/L of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 50 g/L of H_2SO_4 at $i = 1.5 \text{ A/dm}^2$ with sequential introduction of additives.

The introduction of sodium chloride into a solution with DBDA, on the contrary, contributes to the ennobling of the deposition potential of copper. Hence, in a composition with sodium chloride, DBDA exhibits catalytic action, which is consistent with the data [27] on the effective adsorption of organic disulfide molecules in the presence of Cl^- ions. Further introduction of polyethylene glycol into the solution leads to a significant potential shift (by about 200 mV) in the negative direction. Such a shift indicates the strong inhibitory

action of PEG, which should significantly affect the quality of the coating. Finally, the introduction of the ABT additive further shifts the electrode potential (by about 100 mV) in the negative direction, which confirms the inhibitory effect of this organic compound too. It can be assumed that when copper is deposited on a planar surface, PEG and ABT additives will have the maximum smoothing effect. In turn, the catalytic action of DBDA should contribute to the deposition of copper in micro-holes, where the concentration of inhibitory additives should be negligible due to diffusion restrictions.

Surface micrographs of the copper coatings obtained from solutions of different compositions are shown in Figure 4. Their thickness estimated gravimetrically was $5.571 \pm 0.003 \mu\text{m}$. It can be seen that in the absence of additives, the size of the metal grains of the coatings obtained is $\sim 3\text{--}4$ microns (Figure 4a). The introduction of DBDA into the electrolyte leads to the enlargement of metal grains with an average size of ~ 5 microns or more (Figure 4b). This confirms that this organic disulfide having aromatic rings in its structure, as expected, has the role of an accelerator in copper electrodeposition, and behaves like the well-known SPS [3,4,35,37,38,51], which has a linear hydrocarbon chain in its molecule.

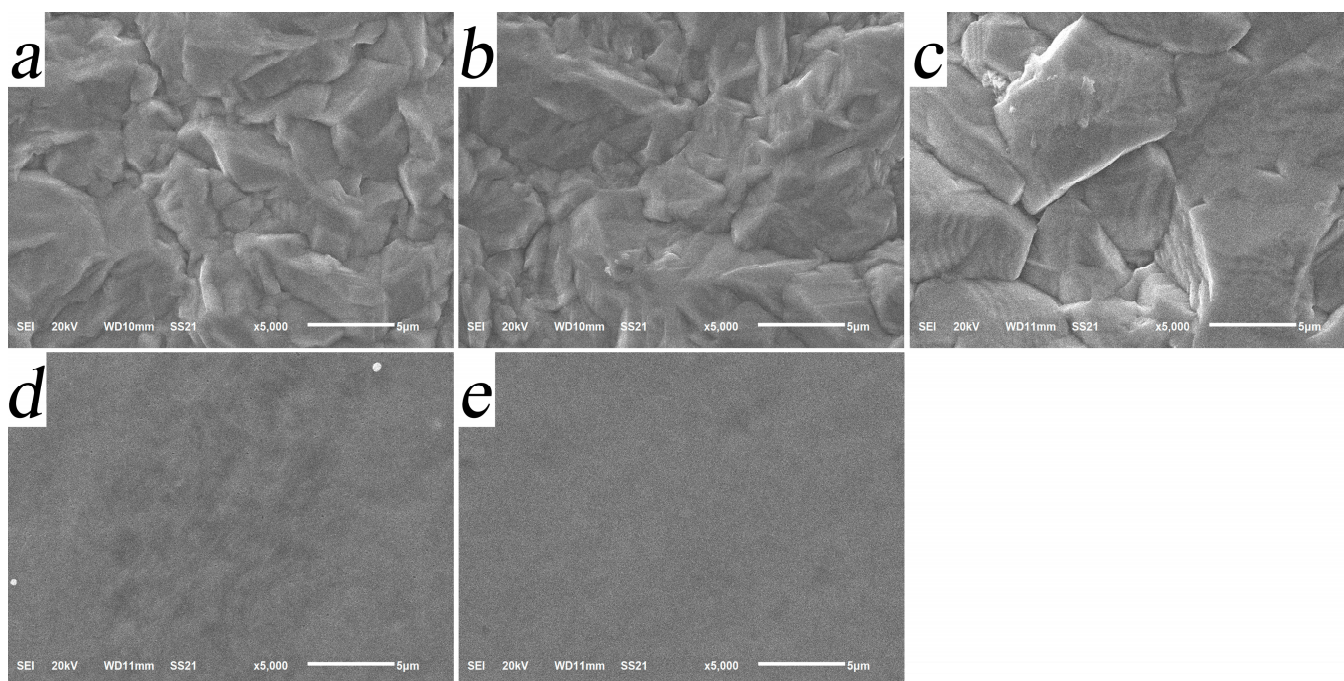


Figure 4. Micrographs of the copper coating surface ($\times 5000$), deposited at $i = 1.5 \text{ A/dm}^2$ (the deposition duration is 1000 s), from the solutions of type 0 (a), I (b), II (c), III (d), and IV (e) based on the composition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (220 g/L) and H_2SO_4 (50 g/L).

After the addition of NaCl, a significant increase in the size of the crystallites is observed on average up to ~ 10 microns (Figure 4c). Herewith, the crystallites start to combine into larger agglomerates with partial blurring of the grain boundaries. This effect is consistent with the data obtained earlier on the synergistic effect of organic disulfides and chloride ions [4,35,38,51].

The addition of the PEG organic additive into the electrolyte already containing the DBDA and NaCl additives (solution III), on the contrary, leads to a significant smoothing of the copper coating surface, although small pores are still observed (Figure 4d). Finally, after the introduction of the ABT additive (solution IV), the surface morphology of the sample almost does not change, but there are no defects in the copper coating, and the surface is the smoothest (Figure 4e). These observations correlate with the data on the smoothing and leveling effects of PEG and ABT [4,11,18,20,21] and confirm that this effect remains in the presence of the DBDA additive as an accelerator.

To identify the role of the studied additives in the kinetics of copper electrodeposition, cathodic polarization curves were obtained at different potential scan rates for the electrolytes with and without additives (Figure 5). The addition of DBDA with sodium chloride has almost no effect on the polarization curves. At the same time, the sequential introduction of the PEG and ABT additives leads to a noticeable shift in the maximum potential in the negative direction, an increase in the overpotential, and a decrease in the current density of the voltammogram maximum (Figure 5). This behavior additionally confirms the inhibitory effect of the polyethylene glycol and 2-aminobenzothiazole additives on the electrodeposition of copper from acidic sulfate solutions.

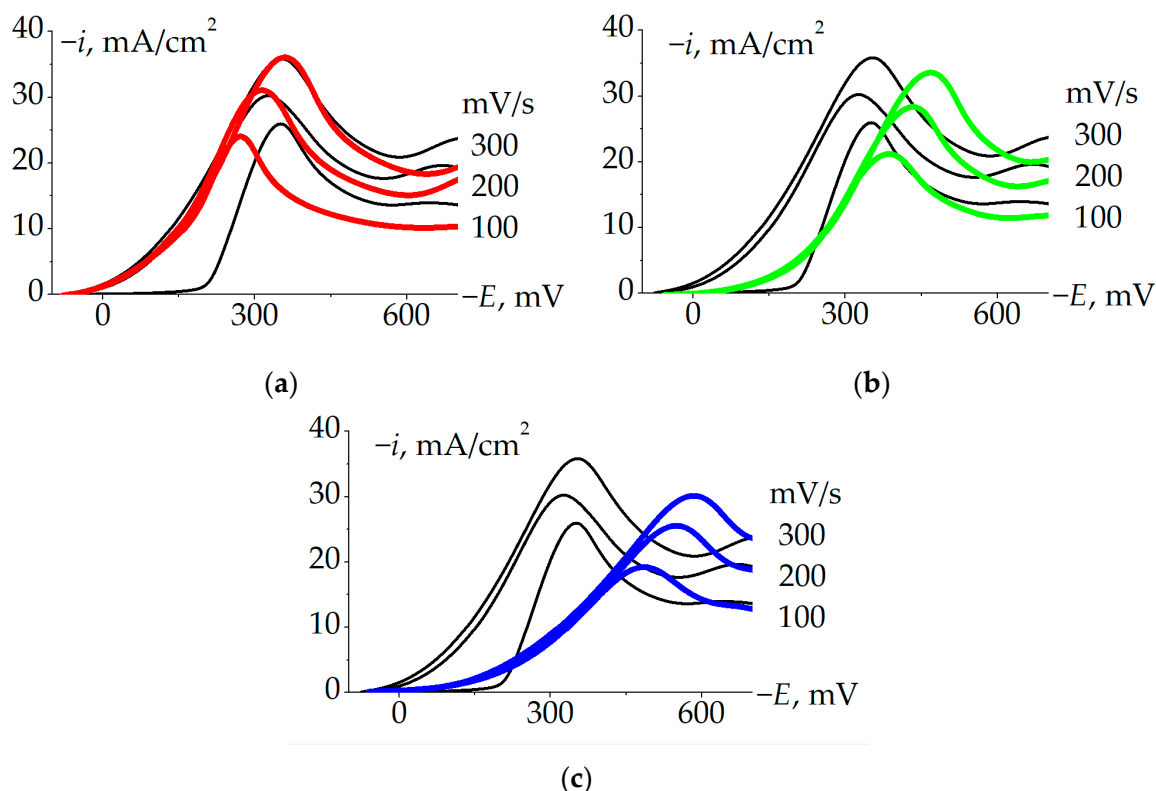


Figure 5. Cathodic voltammograms obtained in the solutions of type 0 (black lines), II (a, red lines), III (b, green lines), and IV (c, blue lines) based on the composition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (12.5 g/L) + H_2SO_4 (2.8 g/L).

The linearity of the maximum current density vs. potential scan rate dependence in the Randles–Ševčík coordinates indicates the diffusion limitations of the electrodeposition process in all of the studied solutions (Figure 6a). These dependencies are not extrapolated to the origin, and the possible reason can be a side reaction of the hydrogen reduction. At the same time, in contrast to the base electrolyte containing only copper (II) sulfate and sulfuric acid, a significant shift in the voltammetric peak's potential is observed in solutions with additives when increasing the scan rate (Figure 6b). This indicates the strong irreversibility of the charge transfer stage and is consistent with the data [56].

To identify the effect of the studied additives on the stage of heterogeneous nucleation during the cathodic deposition of copper, current transients were recorded at potentials in the vicinity of voltammetric peaks in solutions of various compositions. Chronoamperograms have the shape of a curve with a maximum, which is characteristic of nucleation processes: a sharp increase in current during the initial period of the electrodeposition process is replaced by a decrease in current, which obeys the Cottrell equation and does not depend on the cathodic potential (Figure 7). This confirms the diffusion control of the potentiostatic electrodeposition of copper, regardless of the presence and nature of the additives introduced.

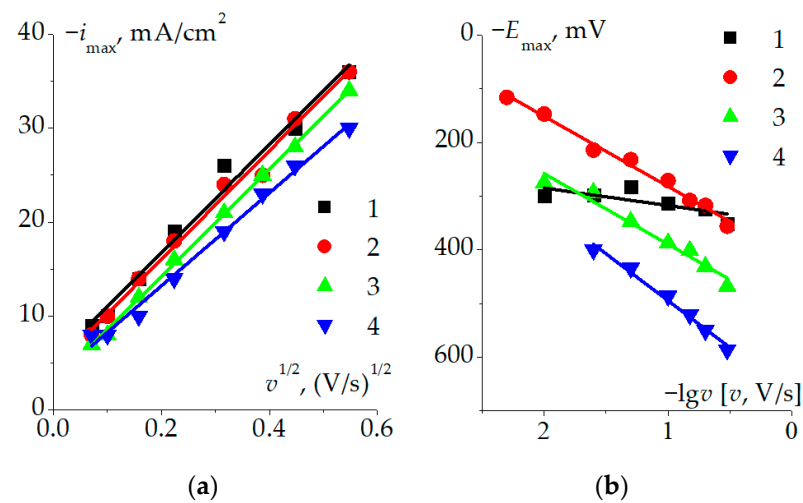


Figure 6. (a) Maximum current density vs. root of the potential scan rate and (b) potential of the voltammetric maximum vs. decimal logarithm of the potential scan rate dependencies in solutions of type 0 (1), II (2), III (3), and IV (4) based on the composition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (12.5 g/L) + H_2SO_4 (2.8 g/L).

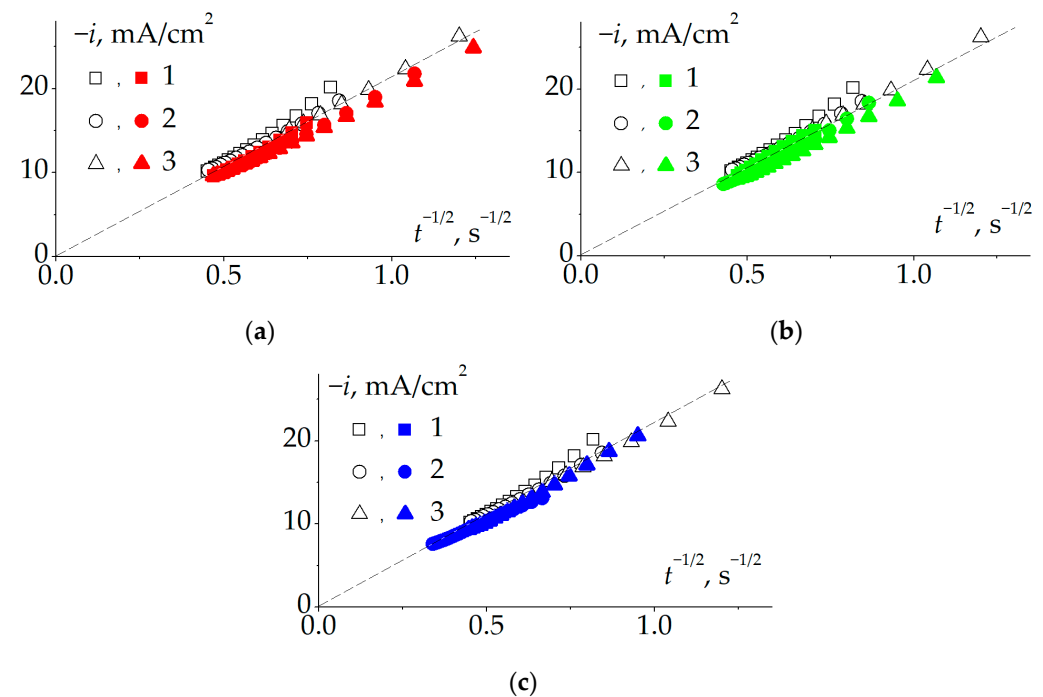


Figure 7. Cottrell chronoamperograms obtained at $E = -300$ mV (1), -400 mV (2), and -500 mV (3) in solutions of type 0 (empty symbols), II (a), III (b), and IV (c) based on the composition $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (12.5 g/L) + H_2SO_4 (2.8 g/L). Dashed lines show the linearity of the experimental curves and their extrapolation to the origin.

Figure 8 shows a comparison of the experimental transients obtained at $E = -400$ mV during the electrodeposition of copper (empty circles) and the current–time transients generated by the non-linear fitting of Equation (7) (red lines) according to the extended nucleation model of the process. It can be seen that the use of this equation has provided an accurate description of the experimental chronoamperograms. The values of diffusion and kinetic parameters D , N_0 , and A , calculated using the fitting parameters P_2 , P_3 , and P_4 , are presented in Tables 2–4, respectively.

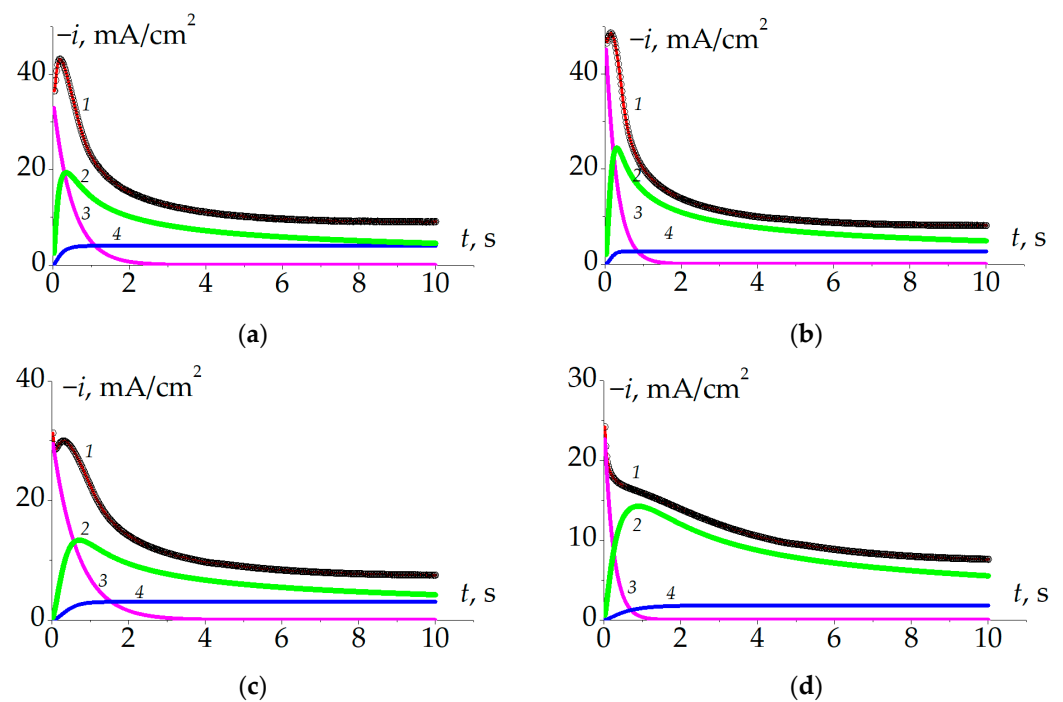


Figure 8. Comparison between experimental potentiostatic current transients (○) obtained during copper electrodeposition from solutions of type 0 (a), II (b), III (c), and IV (d), for an applied potential of -400 mV, and theoretical transients (continuous red line) obtained by non-linear fitting of the experimental data to Equations (1)–(4). Also, the three contributions to the overall current density are displayed individually: a 3D diffusion-limited nucleation process (2), an adsorption process or double-layer charging (3), and a hydrogen reduction process (4).

Table 2. Calculated copper ion diffusion coefficients $D \cdot 10^5$, $\text{cm}^2 \cdot \text{s}^{-1}$.

E_{dep} , mV	Solution				
	0	I	II	III	IV
-500	0.79	0.75	0.81	0.83	0.62
-400	0.70	0.78	0.80	0.60	1.03
-300	0.97	0.56	0.49	0.18	0.24

Table 3. Calculated nucleation active site densities on the surface $N_0 \cdot 10^{-7}$, cm^{-2} .

E_{dep} , mV	Solution				
	0	I	II	III	IV
-500	5.8	6.4	8.1	4.1	1.1
-400	2.1	3.3	5.7	1.9	0.5
-300	1.7	7.2	5.3	2.7	1.0

Table 4. Calculated nucleation rate A , s^{-1} .

E_{dep} , mV	Solution				
	0	I	II	III	IV
-500	23.8	9.8	5.8	3.4	2.6
-400	17.3	9.2	3.8	3.3	8.8
-300	1.5	1.5	1.6	1.8	3.8

The analysis shows that when organic additives are introduced into the electrolyte, regardless of their nature, the diffusion coefficient of copper ions does not change noticeably, decreasing at -300 mV in the presence of PEG and ABT. This can be explained by complexation, as well as the formation of a barrier layer on the electrode surface.

The dependence of N_0 on the nature of additives is more complex. With the introduction of DBDA and Cl^- , the density of nucleation active sites increases, which confirms the presence of their joint catalytic effect. The addition of PEG and ABT, on the contrary, significantly decreases the density of nucleation active sites, which is probably the reason for their inhibitory effect at the stage of electrocrystallization of copper in the studied systems.

The rate of nucleation A , as expected, increases with potential, but it decreases with the introduction of additives irrespective of their nature. It is known that depending on the nucleation rate value, the nucleation process may be classified as instantaneous (for very large $A \gg 1/t$) or progressive (for very small $A \ll 1/t$) [57]. According to the obtained values of the nucleation rate, it is hard to choose one of these limiting cases of nucleation. However, it is clear that the introduction of an additive into the copper deposition solution at comparatively negative potentials slows down the process and increases the probability of transition from the instantaneous to the progressive kinetics of copper electrocrystallization.

4. Conclusions

The introduction of the organic additive DBDA into the sulfate electrolyte of copper plating in a composition with chloride ions has an accelerating effect on the deposition of Cu. The additional introduction of polyethylene glycol and 2-aminobenzotiazole additives significantly inhibits the process.

The surface of copper coatings obtained in electrolytes without additives is characterized by a coarse-grained structure. The use of the DBDA additive leads to the formation of grains into crystals with clear edges. The influence of NaCl is manifested in a significant increase in the size of crystallites with partial blurring of the grain boundaries. The organic additive of polyethylene glycol significantly smooths the surface of copper coatings, and the smoothest and most defect-free copper coating is formed with the combined use of the additives DBDA, NaCl, PEG, and ABT.

According to the extended model of the metal electrodeposition process that occurs along the hydrogen reduction and EDL charging, the process of the electrocrystallization of copper in the studied electrolytes is controlled by the diffusion of ions to a growing three-dimensional nucleus of a new phase. The additives influence the rate and mechanism of nucleation, decreasing the nucleation rate at rather negative potentials, thereby increasing the probability of transition from instantaneous to progressive nucleation. The density of nucleation active sites increases with the addition of DBDA and significantly decreases in the presence of PEG and ABT, which can explain their significant smoothing effect.

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