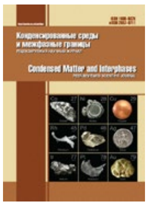

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Kinetics of electrocrystallization of copper from an acid sulfate solution in the presence of N-methylpolyvinylpyridine-methylsulfate

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Abstract

Objective: In this work, kinetic patterns are established and the main parameters of heterogeneous nucleation and the growth of a new phase during electrocrystallization of copper during cathodic deposition from an acid sulfate solution in the presence of *N*-methyl polyvinylpyridine-methyl sulfate of various molar masses are estimated. The polymers under study are quaternized polyvinylpyridine derivatives and are promising organic additives for use in the technology of electrochemical void-free filling of through holes (through silicon vias) of silicon wafers used in microelectronics in the manufacture of microcircuits.

Experimental: Using scanning electron microscopy, it was found that the use of *N*-methyl polyvinylpyridine-methyl sulfate additive leads to a noticeable decrease in the size of crystallites and blurring of grain boundaries, however, it can contribute to the localized formation of globular formations (if the molecular weight of the polymer is relatively small) or the formation of a layered structure (in the case of high-molecular derivatives). The introduction of a quaternized polymer into a copper plating solution significantly inhibits the electrodeposition process, which includes the stages of irreversible charge transfer and diffusion-controlled electrocrystallization.

Conclusions: It has been found that the activation process of heterogeneous nucleation sites in the presence of a polymer additive is instantaneous regardless of the molar mass. At the same time, as it increases, the density of active nucleation centers decreases significantly.

Keywords: Copper, Electrodeposition, Nucleation, Kinetics, Polyvinylpyridine, Quaternized derivatives

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1. Introduction

The electrochemical deposition of metals is widely used to obtain functional coatings. Particular preference is given to copper, which has high electrical conductivity, solderability, and ductility. In microelectronics, high demands are placed on the quality of the cathode copper coating when implementing TSV (through silicon vias) technology based on electrochemical copper filling of through-holes in a silicon wafer [1, 2]. This technology makes it possible to create vertical electrical connections between different levels of semiconductor devices in a compact package [3, 4]. Given that copper electroplated TSV coatings are characterized by a complex geometric configuration, high requirements for the morphological properties of their surface require careful selection of the composition of the copper electrolyte. Acid sulfate electrolytes containing two main components, copper sulfate and sulfuric acid, are most widely used in copper cathodic deposition, since they are stable and easy to prepare. However, such electrolytes have a low scattering capacity, which negatively affects the quality of the coating, especially if it is necessary to fill holes with an unusual geometric profile and/or characterized by a high aspect ratio. To ensure a high-quality copper coating acceptable for TSV technology, several additional components are introduced into the acid sulfate electrolyte of copper plating: a suppressor, an accelerator, and a leveler, which perform specific functions during deposition [5-7]. When adsorbed on the surface of the cathode, they have a certain effect on the kinetics and mechanism of the electrodeposition process, providing a synergistic effect on the structure, morphology, and other properties of the resulting precipitation. A suppressor (for example, polyethylene glycol in the presence of chloride ions [8, 9]) forms a blocking layer on the copper surface, thereby significantly reducing the rate of copper deposition on the planar sections of the electrode. In turn, the accelerator (most often organic disulfide [10, 11]) is adsorbed mainly in the holes of the silicon wafer and ensures their superconformal filling, reducing the polarization of the cathodic process. Levelers play a special role in TSV technology, which locally affect the rate of copper electrodeposition depending on the curvature of the surface, slowing down the process on the protrusions and accelerating in the depressions. As a result, the surface roughness of the copper deposit should decrease, however, it should be noted that the leveling effect is observed only in the presence of two other additives, a suppressor and an accelerator, since it is the result of competing adsorption of additives [12, 13]. It is in the combination of a leveler with an accelerator and a suppressor that more favorable conditions are created for copper deposition in the lower part of TSV holes compared to their upper part and side walls, which contributes to superconformal filling with copper without the formation of voids.

The levellers are, as a rule, heterocyclic nitrogen-containing compounds and polymers [14–18]. The electron-donating properties of nitrogen atoms contribute to their strong interaction with copper atoms. The molecular chains of the leveling additives contain tertiary and quaternary amines carrying a positive charge, which further enhances their adsorption on the negatively charged surface of the cathode. The leveler molecule must be large enough not to compete with the accelerator for adsorption sites inside the hole filled with copper and thus not disrupt its superconformal filling, and at the same time not too large so as not to interfere with the suppressor's operation on planar sections of the silicon wafer. In this regard, polymer levelers with variable molar mass seem to be the most promising. It has been shown [19] that compounds with a molar mass of 3500 g/mol are too small to fulfill the above requirement, and the necessary effect is manifested only when exceeding 60,000 g/mol. In addition, a leveler with an even larger molar mass is preferred, since it does not adversely affect the process inside the hole, even at high concentrations.

Polyvinylpyrrolidone of various molecular weights was used as a potential leveler in [20, 21], however, only minor improvements were noted after its addition. A stronger effect can be achieved not only by increasing the molar mass, but also by modifying the polymer molecule, including by quaternization. Indeed, it is quaternary ammonium compounds with cationic functional groups that are considered the most promising levelers due to their low cost, accessibility, and environmental friendliness compared to other organic additives [12]. Quaternized derivatives, as a rule, are more strongly adsorbed on the protrusions of the electrode surface and locally reduce the rate of copper deposition [13]. This effect has been confirmed by the example of a number of cationic nitrogen-containing polymers. Thus, electrochemical and spectroscopic studies of dodecyltrimethylammonium bromide, benzyldimethylhexadecylammonium chloride, and thonzonium bromide have shown that the deposition of copper electroplating in their presence is characterized by a decrease in the rate of Cu deposition [22]. A significant slowdown in the cathodic deposition of copper in the presence of benzetonium chloride was showed in [12]. Quaternary ammonium salts of 3,3'-bicarbazole also proved to be promising levelers during the electrodeposition of copper in through holes [23]: the leveling effect was observed in the combined presence of an inhibitor and accelerator, and kinetic analysis made it possible to establish an instantaneous nucleation. It was shown [24] that the quaternary ammonium salt based on anthraquinone has an excellent inhibitory effect on copper deposition and a high adsorption capacity. Using cyclic voltammetry, it was found in [25] that when the dodecyltrimethylammonium cation was added to the copper electrolyte, inhibition of the electrochemical reduction of copper due to adsorption was observed, regardless of the electrode material used. Quaternized porphyrin derivatives also exhibit a pronounced inhibitory effect [26].

Until now, the mechanism of action of quaternary ammonium compounds as components of copper electrolytes has not been fully established, and the study of the relationship between their structure, electrochemical process parameters in their presence, and filling efficiency needs further study, as it is of great importance for the targeted selection of highly effective leveling additives.

In this work, *N*-methyl polyvinylpyridine-methyl sulfate (MPVP-MS) is investigated as a potential leveling agent, which satisfies all the characteristics of an organic leveling additive: it is a cationic heterocyclic polymer with quaternized nitrogen and a sufficiently high (variable) molar mass.

To establish the role of MPVP-MS of various molar masses on the kinetics of copper deposition, it is necessary to investigate the effect of the additive on the patterns and parameters of the process at the stage of electrocrystallization of the galvanic precipitate, that is, at the stages of nucleation and growth of a new copper phase. It should be borne in mind that the process is often complicated by the adsorption of solution components on the electrode surface and the occurrence of a side reaction of hydrogen evolution [27], which requires a preliminary determination of the partial rate of the electrocrystallization stage. Non-stationary electrochemical methods such as chronopotentiometry and voltammetry allow us to identify the general effect of MPVP-MS on the kinetics of copper cathodic deposition. Chronoamperometry plays a special role, as it allows us to determine the effect of the additive on the quantitative characteristics of the electrocrystallization stage, which is responsible for the formation of a galvanic deposit and determines its structure and properties. A feature of the approach we use to identify the role of MPVP-MS in the kinetics of copper electrocrystallization is that in this work the differentiated effect of one additive is studied, which will reveal the behavior of MPVP-MS, unlike most similar works, which consider only the combined (synergistic) effect of several additives (accelerator, suppressor, leveler).

The purpose of the work is to establish the kinetic patterns of the electrocrystallization of copper in an acid sulfate solution in the presence of *N*-methylpolyvinylpyridine-methylsulfate.

The objectives were:

1. To determine the effect of N-methylpolyvinylpyridine-methyl sulfate on the morphology of electrodeposition of copper coatings.
2. To identify the role of *N*-methylpolyvinylpyridine-methyl sulfate in the non-stationary electrochemical deposition of copper from a sulfate solution.
3. To establish the nucleation parameters during electrodeposition of copper in the presence of *N*-methyl polyvinylpyridine-methyl sulfate of various molar masses.

2. **Experimental**

The electrodeposition of copper coatings was carried out from aqueous solutions of the following compositions: (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 analysis of the morphology of the obtained coatings, solution (2) was used for non-stationary electrochemical measurements and study of the kinetics of electrocrystallization of copper.

A copper electrode reinforced in polymerized epoxy resin was used as a working electrode in non-stationary studies. To determine the morphology of the coating and the current efficiency, deposition was performed on a copper plate. Before electrochemical studies, the working electrode was cleaned using 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, 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 (S.C.E.) 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 non-stationary electrochemical methods of voltammetry, chronopotentiation, and chronoammetry. The measurements were carried out using a computerized P-40X potentiostat-galvanostat. The potentials are given relative to the silver chloride electrode, the potential of which is 205 mV on the scale of a standard hydrogen electrode. The current density *i* was calculated per unit of the visible (geometric) area of the electrode, which was 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 scanning the electrode potential over time t from an open-circuit value to $E = -1000$ mV with a preset scan rate $\upsilon = dE/dt$. The kinetics of electrocrystallization was studied by chronoamperometry, recording *I-t* current transients at different E_{dep} deposition potentials in the region of the voltammetric maximum (−400 mV, −500 mV). 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.

N-methyl polyvinylpyridine-methyl sulfate (Fig. 1) with different molar weights (800, 35,000, 300,000, 600,000 g/mol) at a concentration of 0.025 g/l was used as an organic additive, the synthesis of which was carried out as follows [28].

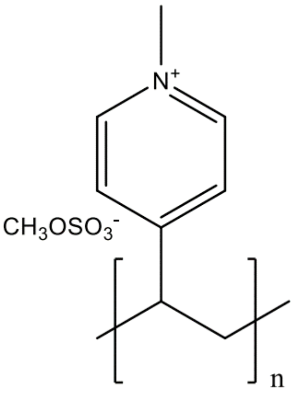


Fig. 1. Molecular structure of *N*-methylpolyvinylpyridine-methylsulfate

The monomer 4-vinylpyridine (4-VP) was purified by high-vacuum distillation at a temperature of 68 °C at 18 mmHg. Poly-4-vinylpyridine (P-4-VP) was obtained by radical polymerization by the lacquer method in the presence of azoisobutyronitrile (AIBN), previously purified by recrystallization from ethyl alcohol, in an inert gas atmosphere (nitrogen) with constant stirring under various conditions shown in Table 1.

Given the ability of 4-VP to oxidize in the presence of light when even small amounts of oxygen enter the reaction system (formation of pyridine oxides, cleavage of the cycle to form red-colored products), polymerization was carried out in a darkened chamber. The resulting polymers were reconstituted from isopropyl alcohol (IPA) into petroleum ether, filtered, and washed with hexane to remove the residual monomer, dried

Table 1. Synthesis conditions for poly-4-vinylpyridine of different molar weights

M, g/mol	4-VP, g	AIBN, g	IPA, g	*t*, °C	τ, hr	Efficiency, %
800	5	0.015	25	80	4	64
35000	5	0.01	25	70	5	57
300000	10	0.01	20	60	7	50
600000	10	0.01	20	50	9	50

at 55 °C (under vacuum) to a constant weight. The average molar mass (MM) of the resulting polymers was calculated using the viscometric method. 0.9 g of the obtained polymer was dissolved in 10 ml of methanol in a conical flask. About 5 ml of methanol was poured into a viscometer installed in a glass thermostat with distilled water, thermostated for 10–15 minutes at 25 °C, and the expiration time τ_0 was measured. The resulting polymer solution was placed in a viscometer, thermostated for 5 minutes, and the expiration time was measured at least three times. The concentration of the polymer solution was changed directly in a viscometer by successively adding 2, 3, and 5 ml of methanol. After each dilution, the solution was stirred by blowing through a viscometer tube, thermostated, and then the corresponding leakage time was measured. Further calculations were performed using the Kuhn-Mark- Houwink equation [29].

To obtain quaternized derivatives of P-4 VP, a mixture of 2.1 g of the obtained polymer, 50 ml of absolutized methanol and 5 mmol of dimethyl sulfate was mixed for 8–10 hours at a temperature not exceeding 40 °C. At the end of the reaction, the solvent was evaporated on a rotary evaporator in a vacuum of a water jet pump to ¼ volume. The resulting residue was cooled and 30 ml of toluene was added. The resulting suspension was thoroughly stirred and boiled for 5–10 minutes. The mixture was cooled and after ~1 hour, the precipitate was filtered, thoroughly rinsed with ether on a filter, crushed and dried at 70–80 °C. The resulting salts were kept at 60 °C (under vacuum) to a constant mass. The degree of quaternization reached 75% (titrimetrically determined).

3. Results and discussion

Analysis of cathodic chronopotentiograms obtained by galvanostatic deposition of copper (Fig. 2) shows that the introduction of *N*-methyl polyvinylpyridine-methyl sulfate into an acid copper sulfate solution leads to a noticeable

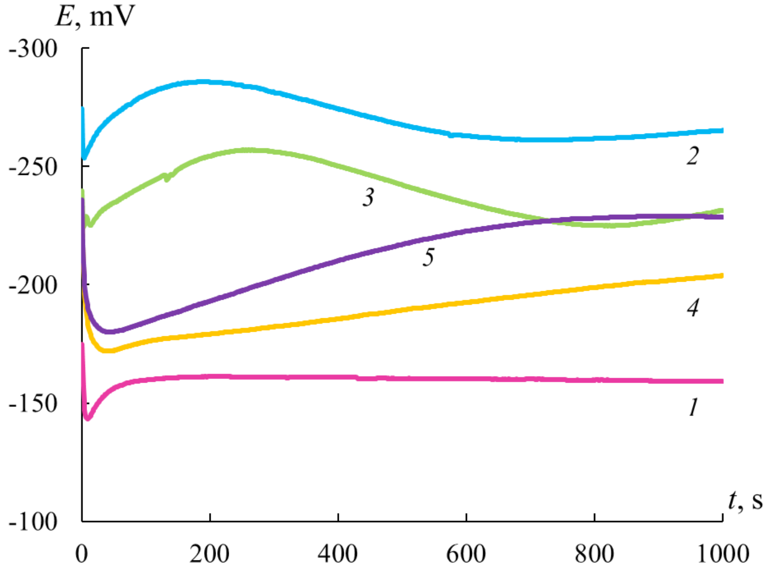


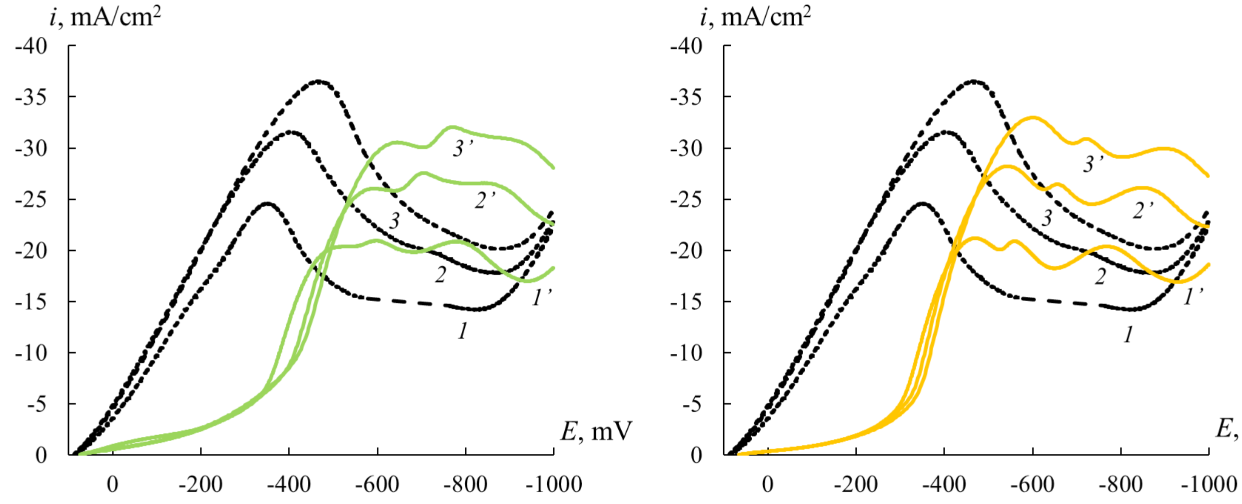
Fig. 2. Chronopotentiograms of copper deposition from solution (1) at *i* = –1.5 A/dm^2 in the absence of additives (*1*) and in the presence of *N*-methyl polyvinylpyridine-methyl sulfate with molecular weight 800 (*2*), 35000 (*3*), 300000 (*4*), 600000 (*5*) g/mol

shift in the deposition potential of copper towards more negative values compared with a solution containing no additives. This indicates an increase in the electrode polarization of the deposition process, i.e., an inhibition of the cathodic deposition of copper in the presence of MPVP-MS, regardless of its molar mass. In general, the lower the molar mass of the polymer, the more the potential shifts to the negative region, and the more pronounced its inhibitory effect.

The results of cathodic voltammetry of copper electrodeposition are consistent with chronopotentiometry data. Indeed, if, in the absence of MPVP-MS, potentiodynamic polarization leads to a sharp increase in current even at small overvoltages, then when an additive is added to the deposition solution, the current density increases much more slowly, and the maximum $i_{\max}$ on the polarization curve decreases significantly. In addition, the potential of the $E_{\max}$ peak is sufficiently shifted to the negative side (Fig. 3).

The observed changes in the voltammetric response indicate an inhibition of the deposition process in the presence of *N*-methyl polyvinylpyridine-methyl sulfate, but only at potentials more positive than the maximum potential. Indeed, at potentials $E < E_{\max}$, the potentiodynamic deposition in the presence of MPVP-MS in this potential range is characterized by higher current values. In an acid sulfate solution without additives, at more negative potentials E compared to $E_{\max}$, a decrease in current is observed, probably due to an increase in diffusion limitations. In solutions with polymer, current fluctuations are observed in the voltammograms in the same potential range and, as a result, several maxima are formed. In other words, at potentials more negative than the maximum potential, *N*-methyl polyvinylpyridine-methyl sulfate increases the copper deposition current. Current fluctuations observed at corresponding sufficiently high overvoltages are probably due to changes in surface roughness, for example, due to the formation of a coating with a morphologically heterogeneous or layered structure.

The dual effect of MPVP-MS on the deposition rate of copper in an acid sulfate solution observed on voltammograms is confirmed by the results of scanning electron microscopy (Fig. 4). The surface of the copper coating obtained from an acid sulfate electrolyte without additives is characterized by a coarse-crystalline structure. The use of the MPVP-MS additive with the lowest molar mass of 800 g/mol generally smooths the coating surface due to a significant decrease in the size of crystallites because of increased overvoltage and blurring of grain boundaries,



a b

Fig. 3. 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 *N*-methyl polyvinylpyridine-methyl sulfate (*1′, 2′, 3′*) with a molar weight of 35000 (*a*) and 300000 (*b*) g/mol

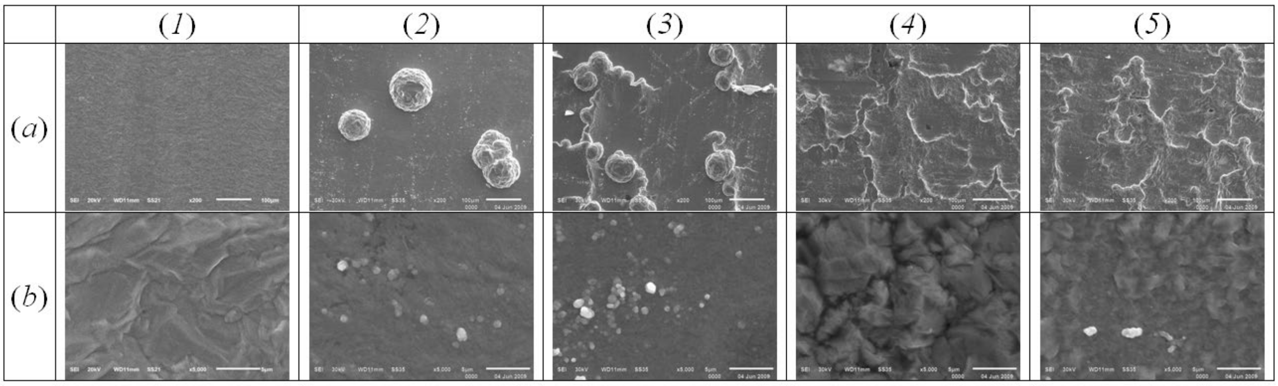


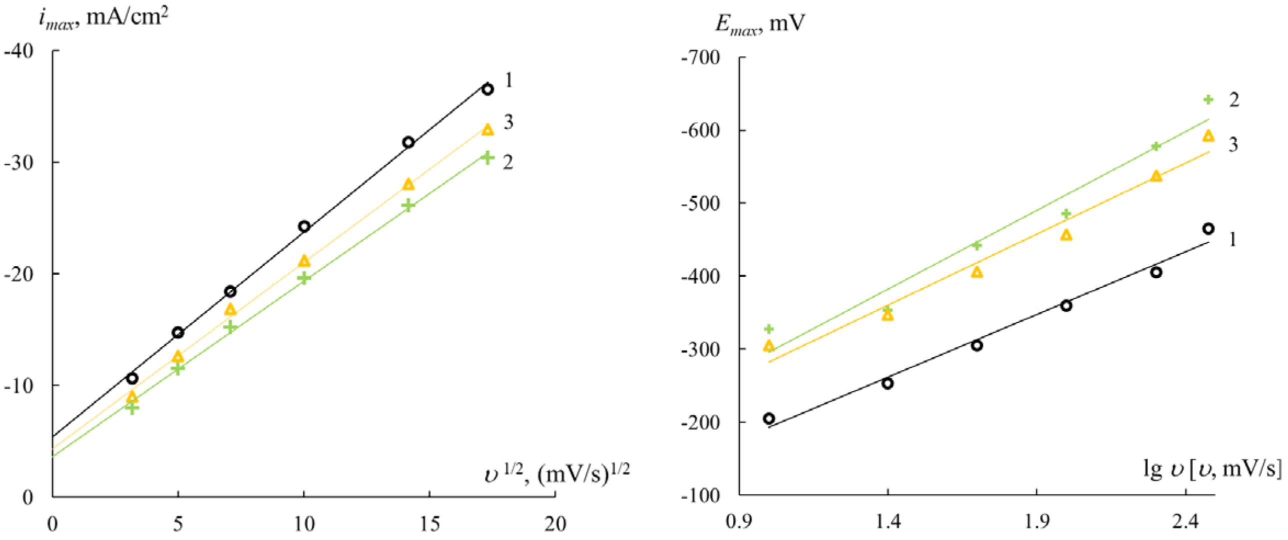
Fig. 4. SEM images obtained with magnification ×200 (*a*) and ×5000 (*b*) of the surface of copper coatings galvanostatically deposited (current density $i = -1.5$ A/dm^2, deposition time 1000 s) from solution (1) without additives (*1*) and in the presence of *N*-methyl polyvinylpyridine-methyl sulfate with a molar weight of 800 (*2*), 35000 (*3*), 300000 (*4*) and 600000 (*5*) g/mol

however, it leads to the localized formation of sufficiently large globular formations up to 100 microns in size. With an increase in the molar mass of the polymer to 35,000 g/mol, the size of both globular formations and crystallites decreases, there is a partial blurring of the grain boundaries and a decrease in the number of globules on the surface of the coating, the structure of which becomes layered. With a subsequent increase in the molar mass of the additive to 300,000 and 600,000 g/mol, the formation of globular formations is no longer observed, and the layered nature of the coating becomes the most pronounced, which is reflected in an increase in surface roughness. The observed morphological changes are most likely due to the pronounced adsorption of the polymer on the surface of the copper coating, which leads to localization of metal deposition and, as a result, uneven globular and/or layered growth. It should be noted that a similar heterogeneity of morphology with differentiated (i.e., in the absence of a suppressor and accelerator) introduction of levelers into an acid sulfate solution of copper plating was also observed in [14], which confirms the manifestation of the greatest leveling effect only in the presence of a complex of additives of all three types.

Obviously, the introduction of a polymer into a copper solution has a strong effect on the kinetics of the deposition process, in order to establish the patterns of which the data of non-stationary electrochemical measurements were analyzed.

The linearity of the dependence of the current density at the maximum of the voltammogram on the root of the potential scan rate confirms the presence of diffusion limitations of the process (Fig. 5a). The curves are not extrapolated to the origin, probably due to a parallel side process (most likely, the hydrogen evolution reaction). 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 the polymer 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 within the framework of instantaneous or continuous nucleation [30] within the framework of the 3D nucleation model proposed by Sharifker and Hills [31]. However, a preliminary comparison of the experimental chronoamperograms with the theoretical curves of the Sharifker–Hills model showed their significant discrepancy, which made it impossible to establish the nature of nucleation, much less to quantify the characteristics of the copper electrocrystallization process. 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 copper electrolyte. In this regard, for further analysis, we used an extended model of nucleation and growth of a new phase [27],



a b

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 (*1*) and with the introduction of *N*–methyl polyvinylpyridine-methyl sulfate with a molar weight of 35000 (*2*) and 300000 (*3*) g/mol

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:

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

Here, the current density i_H determines the rate of the proton reduction reaction [27] and can be described by the ratio:

$$i_H(t) = P_1S(t), \qquad (2)$$

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

$$S(t) = (2c_0M/\pi\rho)^{1/2}\theta(t) \qquad (3)$$

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

$$\theta(t) = \{1 - \exp\{-P_2[t - (1 - \exp(P_3t))/P_3]\}\}. \qquad (4)$$

Here, the parameters $P_2 = N_0\pi kD$ and $P_3 = A$ represent, respectively, the density of active nucleation sites on the electrode surface (N_0), the diffusion coefficient of copper ions (D) in solution, the rate constant of activation of nucleation sites (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, obeys the ratio [27]:

$$i_{Cu}(t) = P_4t^{-1/2}\theta(t), \qquad (5)$$

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 [27] as an exponential decrease in current:

$$i_{ads}(t) = K_1\exp(-K_2t). \qquad (6)$$

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

$$i(t) = \left\{P_1^* + P_4t^{-1/2}\right\}\times$$
$$\times\left\{1 - \exp\left\{-P_2\left[t - \frac{1 - \exp(P_3t)}{P_3}\right]\right\}\right\} + K_1\exp(-K_2t), \qquad (7)$$

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

To identify the effect of *N*-methyl polyvinylpyridine methyl sulfate on the stage of heterogeneous nucleation during cathodic deposition of copper, the kinetic parameters of the electrocrystallization process were obtained by the nonlinear approximation comparison of equation (7) and experimental chronoamperograms recorded at potentials in the vicinity of the voltammetric peak. 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 a constant value. The maximum current decreases with the introduction of additives, but increases with an increase in the molar mass of the additive. 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, partial *i*,*t*-curves were calculated for three parallel non-stationary processes (electrocrystallization, hydrogen evolution, and adsorption). The nucleation current is characterized by the formation of a maximum in the initial period of the process, the height of which depends on the molar mass of the additive in the same way as the height of the maximum of the total current density: an increase in current is observed with an increase in the molar mass of the additive. The nucleation current in the presence of MPVP-MS with a molecular weight of 300,000 and 600,000 g/mol is higher than in a solution without additives. The adsorption current is predominant at short process times, but it quickly decreases to zero. The adsorption current is higher in a solution without additives than in their presence. In addition, in solutions containing MPVP-MS, there is a smoother decrease in the current associated with the adsorption process. The current caused by the hydrogen release reaction increases and reaches a constant value, which does not significantly depend on the presence and molar mass of the additive. 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 MPVP-MS of various molecular weights (Fig. 7).

The analysis shows that *N*-methyl polyvinylpyridine-methyl sulfate has a noticeable effect on the parameters of copper nucleation, which depends on the electrode potential and the molar mass of the polymer. Regardless of the deposition potential, the density of nucleation sites decreases markedly (Fig. 7a) when MPVP-MS is introduced into the electrolyte solution, which can be explained by the strong adsorption

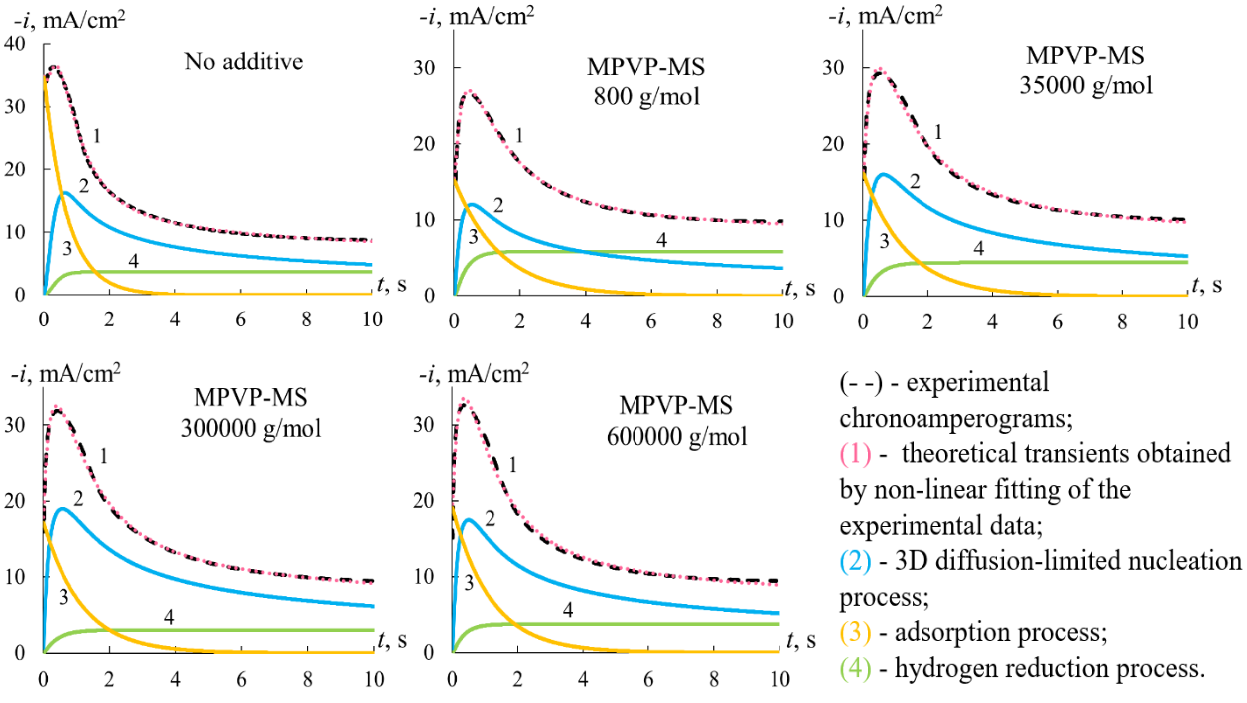


Fig. 6. Experimental and theoretically calculated chronoamperograms obtained by electrodeposition of copper at a potential of –500 mV

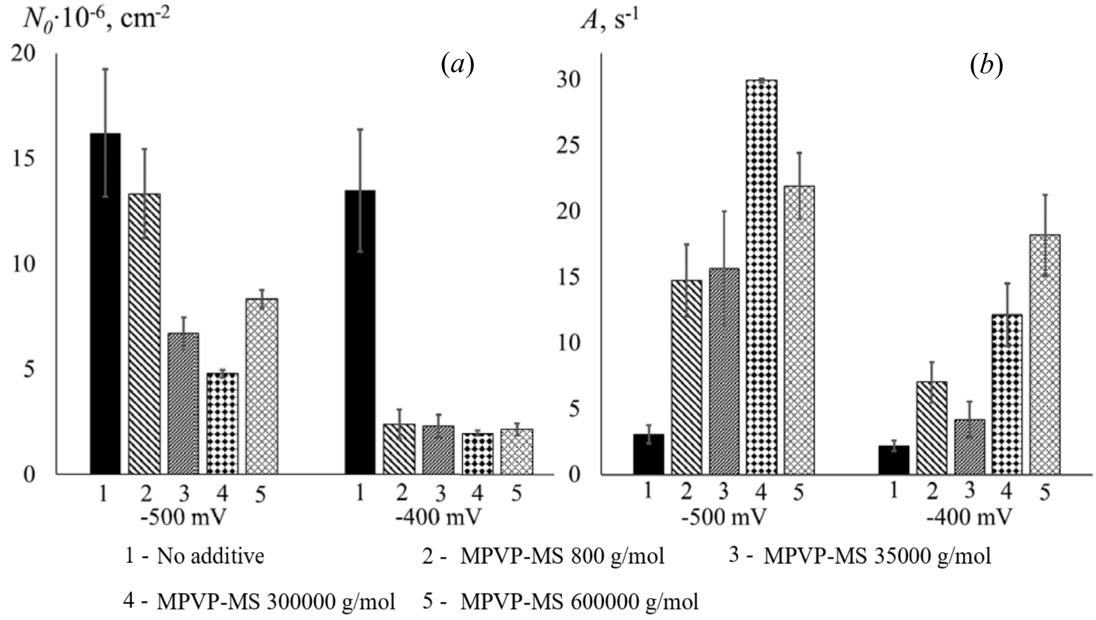


Fig. 7. Kinetic parameters of nucleation: (*a*) – nucleation active sites density (N_0), (*b*) – rate constant of nucleation sites activation (A)

of quaternized polyvinylpyrridine derivatives on the copper surface. Thus, the inhibitory effect of *N*-methylpolyvinylpyridine-methyl sulfate revealed by chronopotentiation and voltammetry methods is explained by a significant (up to 5-6 times) decrease in the concentration of active sites of copper nucleation in the presence of an organic additive.

In turn, the rate constant of nucleation sites activation (*A*) increases with the introduction of MPVP-MS into the solution (Fig. 7b) and, in general, the higher the molar mass of the additive. It is known that, depending on the value of parameter *A*, the process of activation of potential nucleation centers can be classified as instantaneous (at $At >> 1$) or continuous (at $At << 1$) [31]. The estimation of *At* by the time the maximum is reached on the partial nucleation curve ($t \approx 1$ s) results in the case of a solution without an additive to the value of $At \approx 3$, which does not allow the process under study to be attributed to one of the limiting cases of instantaneous or continuous nucleation. In the presence of MPVP-MS with a molar mass of 800, 35,000, 300,000, 600,000 g/mol, *At* takes the value ≈15, ≈16, ≈30, ≈22, respectively. According to the obtained values, the process of activation of nucleation sites in the presence of MPVP-MS in the plating solution is instantaneous. Probably, the introduction of quaternized polyvinylpyridine derivatives into an acid sulfate copper solution due to its adsorption on the electrode surface contributes to a more uniform potential distribution along the surface and the transition of nucleation sites activation to an instantaneous mode.

Thus, an analysis of the kinetic parameters of nucleation/growth of the new copper phase shows that the effect of *N*-methyl polyvinylpyridine-methyl sulfate is complex, depending on the potential and molar mass of the polymer. By varying the values of these parameters, it is possible to adjust the morphological state and surface roughness of the copper coating, as well as its structure. This is especially important when choosing the electrolyte composition for microelectronics, in which the additive under study could perform the universal role of a suppressor and leveler: the research of such electrolytes is an urgent task of TSV technology [32].

4. Conclusion

The introduction of N-methyl polyvinylpyridine-methyl sulfate into an acid sulfate solution of copper plating has a noticeable inhibitory effect on the process of copper electrodeposition at relatively low overvoltages, and this effect is higher the lower the molar mass of the polymer. The potentiodynamic deposition in the presence of the polymer additive under study at high cathodic overvoltages is characterized by higher current values compared to the electrolyte without the additive. As a result, *N*-methylpolyvinylpyridine-methylsulfate, depending on the molecular weight, makes it possible to obtain copper coatings of varying morphology. Electrodeposition of copper in the presence of *N*-methyl polyvinylpyridine-methyl sulfate is a diffusion-controlled process and involves a step of irreversible charge transfer. Within the framework of an expanded model of heterogeneous nucleation and growth of a new phase complicated by hydrogen reduction and adsorption of solution components, it was found that the activation of nucleation sites in the presence of *N*-methyl polyvinylpyridine-methyl sulfate is instantaneous, and the introduction of a polymer into a copper electrolyte significantly reduces the density of nucleation sites, which explains its inhibitory effect on copper electrodeposition.

Contribution of the authors

Ilina E. A. – conducting electrochemical research, text writing. Kozaderov O. A. – scientific guidance, research concept, methodology development, text editing, final conclusions. Sotskaya N. V. – conducting research, editing text. Vandyshev D. Y. – conducting organic synthesis, writing text. Polikarchuk V. P. – conducting organic synthesis. Shikhaliev Kh. S. – organic synthesis concept.

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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