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CHEMICAL PROBLEMS OF THE DEVELOPMENT OF NEW MATERIALS AND TECHNOLOGIES
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ELECTROLESS DEPOSITION AND ELECTROPLATING OF METALS

INTRODUCTION

Alongside with multipurpose procedures of low-temperature metal deposition by electrochemical reduction of their soluble compounds, there is a possibility for electroless reduction of various metals in solutions. In both cases the dispersity, structure and morphology of the product depend on the composition of a reaction medium and conditions. Chemical deposition of metals occupies an important place among the synthesis reactions of solids with the controlled structure. Unlike the processes of electrochemical reduction, the reaction of electroless reduction may proceed both on the conducting surface and within the solution bulk, as well as the dielectric surface provided it is catalyst-coated. Since the majority of electroless metal deposition reactions are autocatalytic in nature, their local proceeding on solid surfaces is greatly facilitated.

The chemical metal plating may be subdivided into three groups of processes according to the state of the product formed and its localization:

1) production of ultrafine powders with different dispersity as well as metal sols and alloys (when the reaction is not necessarily autocatalytic);

2) formation of metal films on solid surface (metallic or nonmetallic) containing the particles of an electroless plating catalyst or reactants suitable for the formation of such particles;

3) selective metal deposition on solid surface or within a thin polymeric layer as patterns of the predetermined geometry.

The results of the electroless metal plating studies conducted at the Institute for Physical and Chemical Problems (IPCP) and at the Inorganic Chemistry Department of the Belarusian State University (BSU) make an important contribution to numerous literature sources in this field [1–5]. Since the end of seventies of the last century, most of these studies have been concerned with the general features of chemical deposition processes for the production of continuous metal films, conductive patterns and photographic images. The investigation of a new photographic process with a nonsilver physical development using the reactions of chemical deposition (first conducted in BSU in 1968/1969) is one of the most important among these studies. In the last 25 years the emphasis has been made on the investigations in the peculiarities of the film formation via the processes of electroless metal and alloy deposition, composition, structure and properties of

thus obtained deposites. From the end of the eighties these studies have involved the processes of chemically reduced ultradispersed metal formation. At the same time, a lot of attention was focused at the solid-phase formation with comparison between the electroplating and electroless reduction methods. In parallel with these studies, the processes in which the products of electroplating cannot be produced by electroless reduction have been investigated.

These studies formed the basis for the development of a series of technological processes for electroless deposition and electroplating of many metals and their alloys, covered by the USSR authors certificates, Belarusian and Russian patents and introduced in commercial production at the industrial enterprises of Belarus and other NIS-countries.

1. ELECTROLESS METAL PLATING. MECHANISM AND KINETICS

Catalysis phenomenon. The data on different aspects of chemical metal deposition from solutions accumulated over the period of 30 years have clarified some peculiarities of the reactions associated with the process.

A character of the proceeding reactions and morphology of the product is greatly influenced by the presence or absence of catalytic activity of the formed metal particles in a reaction of the ion reduction. Though in the majority of cases these reactions are catalyzed by the solid product formed, i.e. they are autocatalytic in nature, it has been known that in some cases autocatalysis by solid product is weakly expressed or not exhibited at all (e.g. the reduction of lead ions by different reducing agents, of bithmus ions by boron hydride, of silver ions by hypophosphite, the reduction of cyanoaurate complexes by hypophosphite, etc.) [4]

In all cases the final solid product of the reduction (metal or oxide) consists of highly dispersed particles, the size of which strongly depends on the possibilities and conditions for aggregation of the initially formed nuclei. It should be noted that only autocatalytic reactions provide local deposition of metal and hence they are useful as for the formation of nanodispersed metal in the solution bulk and for the deposition of continuous metal films, so for the selective plating and production of conducting thin-film patterns or photographic images. To this purpose, most suitable are the reactions of nickel ions reduction by hypophosphite, boron hydride and different derivatives of boranes (dimethylamine borane, hydrazine borane, etc.), copper ions reduction by formaldehyde and boron hydride capable to exist for some time in an aqueous medium without the formation of a reduced product in the bulk of a solution. These reactions proceed being catalyzed by the forming solid product and some noble metals. To illustrate, the reduction reactions realized with boron hydride are catalyzed by palladium, platinum and to a lesser degree by silver, copper [6]; reactions with hypophosphite – by palladium and platinum (excluding silver); reactions with formaldehyde – by silver, palladium, platinum and copper. Our investigations [1,3] and published data [7] point to the fact that reduction by hydrogen-containing BH_4^- and $H_2PO_2^-$ ions actually represents dehydration reactions of reducer's ions and are well catalyzed by active catalysts for these reactions. At the same time, on the surface of silver the ions of hypop-

hosphite are not subjected to dehydration, so no catalytic deposition of this metal occurs under the effect of hypophosphite.

Characteristic feature of electroless solutions containing metal ions and a reducing agent is the possibility for concurrent catalytic reaction on the activated substrate and spontaneous ion reduction of the metal ions in the solution bulk with formation of metallic particles of colloidal sizes [3,8,9]. The process of metal ions reduction (nickel, copper) by reducing agents may be represented by the following stages: formation of isolated atoms or clusters of the partially reduced metal, formation of stable nuclei that is terminated at the end of induction period, growth of metal nuclei. It is believed that at first Ni_n^{m+} clusters are formed, subsequently reducing to Ni_n or undergoing to disproportion ($2Ni^+ \rightarrow Ni + Ni^{2+}$).

Low initial reaction rate of the spontaneous metal deposition under the effect of hydrogen-containing reductants and hence the stability of electroless solution in the absence of a catalytically-active surface are determined by significant kinetic difficulties in the formation of the initial catalytically-active nuclei of a reducible metal. The induction period for particle appearance in the solution bulk is dependent on the nature of reducing agent and metal, growing in the following sequence: hydrazine borane, boron hydride, dimethylamine borane in case of nickel ions or boron hydride > formaldehyde in case of copper ions (Fig. 1).

A drastic increase in the reduction rate of nickel and copper ions after the induction period is due to simultaneous appearance of new and growth of the earlier formed metal particles. Absolute quantity of the particles formed per unit volume of the solution and their accumulation rate are considerably higher for the reduction of nickel ions by hydrazine borane and boron hydride as compared to dimethylamine borane or in case of copper ions being reduced by boron hydride as compared to formaldehyde (Fig.1). Transmission electron microscopy with the use

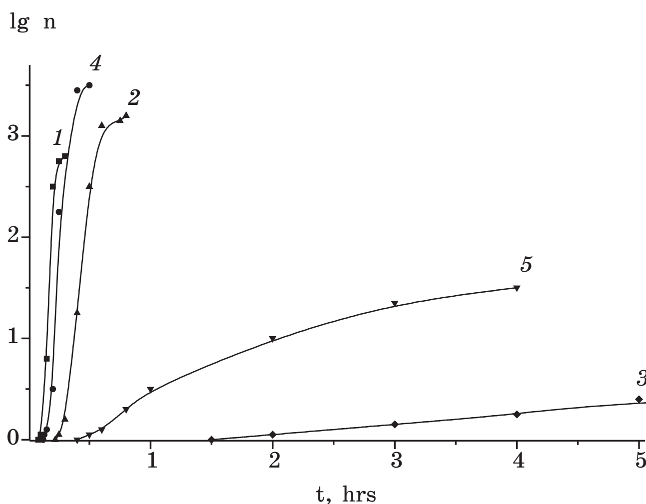

Fig. 1. Changes in concentration of nickel particles (*1–3*) and copper particles (*4*, *5*) in electroless solutions with hydrazine borane (*1*), boron hydride (*2*, *4*), dimethylamine borane (*3*) or formaldehyde (*5*) as a reductant

of frozen solutions has revealed that at the initial stages of the formation and growth of solid phase, fine metal particles (over 1 nm in size) appear in the solution at the end moment of the induction period [8, 9]. Further these particles are growing and some new particles appear. An average size of the particles forming by the end of the induction period for Ni(II) reduced by boron hydride is 5–8 nm, for Cu(II) reduced by boron hydride 3–5 nm, for Cu(II)) reduced by formaldehyde 9–15 nm. In 10–15 minutes their size grows to 10–15, 6–10 and 25–45 nm, respectively. However, instead of equally probable and homogeneously distributed metal particles spherical in shape, as it is observed at the initial stages of the reaction, at the degree of reduction exceeding 25% one observes the aggregates differing in the geometrical configuration and containing the aggregates of isolated particles spherical in shape [8–11]. The appearance of such aggregates results in the diminished interface, where the reduction process of metal ions is localized, and may be responsible for lower reaction rate at the later stages. However, the diminishing of the rate may be also provoked by decrease in concentration of the components.

Kinetics. At the initial stage the electroless plating of copper and nickel leading to the formation and growth of solid particles in the bulk of a solution may be described by kinetic equations for homogeneous autocatalytic reactions [12–14]:

$$\alpha = k \cdot t^n, \qquad (1)$$

or

$$\alpha = k \cdot (t - t_0)^n, \qquad (2)$$

where α is the degree of ion metals reduction, t_0 – duration of the induction period.

Equation (1) describes the initial stage of Cu(II) reduction by formaldehyde, until the degree of Cu(II) reduction is below 10–25 % (depending on the temperature) and n = 3.2–3.7. Provided the particles formed in the bulk of a solution are nonspherical in their shape or the reaction proceeds not over the whole surface of the growing particles, as it occurs in the presence of surfactants due to their adsorption at the active surface sites of metal nuclei, the growth rate of the latter may be described by equation (1), where $n = 2$ [12, 13]. It is impossible to describe «in-depth» stages of the reaction by equations (1) and (2) which neglect the expenditure of reagents and possible termination of particle growth caused by inhibition of their surfaces by the adsorbed medium components.

The kinetic reaction curves including the deep stages, proceeding in conditions when a reducing agent is in excess, so that no substantial changes of its concentration are observed during the reaction and concentration of the reducible ions is decreasing, may be described by the equation typical for autocatalytic reactions of solid phase formation:

$$\alpha \quad 1 \quad e^{\;kt^n} \qquad (3)$$

It has been found [12] that equation (3) gives the whole process over the temperature interval 4–50 °C up to the transformation degree of 75% at $n = 3.5 \pm 0.2$, i.e. as long as the reaction proceeds with a continuous rate of growth in time. Kinetics of the reaction leading to the formation of solid particles in the bulk of a solution may be described by other kinetic equations as well.

It should be emphasized that kinetic equations don't provide unambiguously interpreted information about the reaction mechanism due to complexity and versatility of the effects exerted by different factors on the metal particle growth at the deep stages of the reaction.

In case of the reaction proceeding on a solid surface after the period of free metal particles growth, previous to the formation of a continuous film, the reaction rate becomes constant, but its value is influenced by changes in the concentration of reagents during the reaction and by the usual inhibiting effects on the particle growth under the action of the solution components adsorbed on a growing metal surface. The reaction rate is dependent on the microstructure of a growing film that determines the reaction front value and hence may be varying with structural changes in the films.

The studies have been conducted into the effects exerted by the concentration of solution components, stabilizing additives, plating conditions, nature of ligands and catalytic surface on the deposition rate of copper from boron hydride [15, 16] and formaldehyde [12, 17–19] solutions, nickel from boron hydride [20–23] and dimethylamine borane [24] solutions. In extensive experimental studies a great body of data on the empirical-kinetic relationships between the copper and nickel deposition rates from solutions of their complexes and the concentration of reducing complexes, reductant, solution pH or other factors has been obtained [15, 21, 25]. Clarifying the reaction mechanisms, this information is important for optimization of the composition of usable electroless solutions and plating modes.

Electrochemical mechanism of metal deposition from electroless bathes. The mechanism of electroless metal plating is thoroughly studied only for relatively deep stages of autocatalytic reduction when the deposition process proceeds on a metal substrate [1, 7]. The latter provides electrochemical conjugation of the cathodic reduction of metal ions (e.g. nickel) and anodic oxidation of a reducing agent (e.g. boron hydride) [1]. In many cases anodic oxidation of a reducing agent is a limiting stage that determines the reaction rate of electroless plating. It has been demonstrated [26] that the effect of different factors on the rate of anodic oxidation of a reductant correlates with the rate of metal ion reduction, although there is no direct quantitative agreement between these two parameters. However, it goes without saying that a kinetic retardation of the cathodic process may also be responsible for the possibility of local metal ion reduction on the surface of the already formed metal particles, of the same or some other nature [27].

The consideration of the features of metal reduction reactions within an electrochemical model is complicated by the fact that the anodic reaction stage has a pronounced effect on the cathodic one and vice versa. So, it has been determined by us [26] that at the simultaneous presence of Ni^{2+} and BH_4^- ions in a solution, the partial processes of Ni^{2+} reduction and of boron hydride oxidation proceed not independently but influence each other. This effect exhibits in the retardation of boron hydride oxidation on the catalytic surface in the presence of Ni^{2+} ions, whereas BH_4^- ions facilitate the reduction of Ni^{2+} ions. It should be taken into acco-

unt that a nature of the catalytic surface, where the discharge occurs, is of great importance. Comparison between the catalytic activities of silver and nickel in the reaction of boron hydride oxidation has revealed that in this reaction nickel is a better catalyst [26].

Note that a character of this reciprocal influence of anodic and cathodic stages in the redox process in case of the reactions followed by deep destruction of reducing agent ions (molecules), e.g. reduction by boron hydride, formaldehyde and so on, may be much more complex than that in the reactions proceeding with a slight deviation from equilibrium, as it is seen for the reduction of silver ions by the redox couple Fe^{2+}/Fe^{3+}. Firstly, reciprocal influence of the anodic and cathodic stages has a uniform character for different reactions. Secondly, the electrochemical reaction mechanism may be affected by the other non electrochemical processes, proceeding in parallel and representing a rearrangement inside the complex ions adsorbed on the solid phase surface. The role of the latter may be particularly important at the initial stage of the formation and growth of fine metal particles in the solution bulk when the anodic and cathodic stages are hardly to occur due to the impossibility of their spatial separation. A complex character of the electroless metal deposition reactions and reciprocal influence of the cathodic and anodic stages when the electrochemical mechanism is realized are responsible for the fact that in the special cases only one is enabled to find correspondence between the reaction rate and its thermodynamic parameters.

It should be noted that electroless plating of metals at the stage of their catalysis by foreign metals (deposition centers) may produce galvanic couples which greatly influence the reaction kinetics, until the reagents have the access both to the surface of a reducing metal and to the particles of a catalyst metal. Just these galvanic couples determine the possibility for gold plating on nickel surface, when anodic oxidation of the reducing agent (hypophosphite) occurs on nickel surface and reduction of Au(I) proceeds on the surface of gold particles [4, 28].

The mechanism of electroless plating reactions is largely complicated by a specific behavior exhibited by fine metal particles (catalyst or nuclei of the plating product). Fine particles differ from the bulk metal in the catalytic action in the anodic oxidation of BH_4^- ions [29, 30]. High activity of fine metal particles in aqueous solutions seems to be responsible for the fact that at least some portion of the atoms on the surface of particles is in the oxidized state. In alkaline media such a state is associated with the formation of several Me–OH groups capable to interact with BH_4 ions initiating their oxidation. In this case anodic oxidation of BH_4 ions represents the repeated process, involving the stage of interaction between Me–OH groups and BH_4^- ions and subsequent regeneration of an oxidizer as a result of anodic oxidation of metal atoms on the surface. As sizes of the particles increase and their properties become close to those of the metallic phase, the number of easily oxidizable metal atoms decreases thus reducing the contribution of the above mechanism to the process of anodic oxidation of BH_4^- ions. In consequence of the differences in mechanisms of catalytic effect exerted by fine particles and metallic phase, for fine particles one observes no electrochemical conjugation between anodic oxidation of BH_4 ions and cathodic reduction of Ni^{2+} ions. It is possible that different mechanisms of Ni(II) autocatalytic reduction in the bulk of a solution and on the metal surface (where reduction of Ni(II) is a result of its

electrochemical conjugation with anodic oxidation of BH_4^- ions) may provide selective retardation of the reaction with introduction of different additives. The relationship between the initiation rate of autocatalytic reduction of Ni(II) by BH_4 ions in the solution bulk and the rate of the anodic reaction, not conjugated to the cathodic reduction of Ni(II), seems to be caused by the following. Ni^{2+} ions may react with the products from anodic oxidation of BH_4^- ions (H atoms and other active particles) with a probability dependent on the anodic reaction rate. In the absence of electrochemical conjugation between cathodic and anodic reactions, this nonequilibrium process seems to be responsible for the solid phase formation in the bulk of a solution. Owing to a rather nonequilibrium character of the process, the growth of fine and chemically very active nickel particles is realized in an aqueous medium fairly aggressive for them. At the same time, this may provide a means for effective decrease in the particle-growth initiation rate with the use of particular additives, inhibiting oxidation of BH_4 ions and hence the generation of active nonequilibrium particles [27, 29, 30].

It is believed that the difference in the reaction mechanisms on the surface of very fine and larger particles of a catalyst may be the cause for changes in the catalytic activity of the particles which fulfil the function of the deposition centers as well as the particles of a reducing metal after a certain size is reached. Besides, the existence of a minimum size of catalyst particles (below which they could not act as the localization centers for the products of reduction) is associated with instability of fine metal particles within the reaction medium. When the reactions proceed in conditions close to the equilibrium ones (e.g. reactions with redox Fe^{2+}/Fe^{3+} couple), the instability of fine particles may be determined by their chemical interaction (oxidation) with the oxidized form of a reagent used as a reducing agent. In case of reduction reactions proceeding in nonequilibrium conditions a system may exhibit equilibrium states with water, ligands present in the solution and oxygen. Consequently, the stability problem of fine metal particles could not be solved considering only the relation between the redox-potential of a fine (claster-size) particle of the formed metallic phase and that characteristic for a system «initial – oxidized form» of a reducing agent. Because of this, estimation (based on simple relations) of the effect exerted by the size of particles on their catalytic and autocatalytic activity in specific reactions is impossible without special experiments.

The situation is still aggravated by the fact that with increasing size of fine metal particles their activity in electroless plating reactions may decrease and even disappear due to the accumulation of inhibiting additives on the surface of the growing particles. Illustrative examples for the effect exerted by the particle sizes of silver and palladium on their activity in the above-mentioned reactions may be found in literature [31, 32].

Nature of ligands. The reaction rate is greatly influenced by the composition of the reduced metal complexes. It has been found [14, 33, 34] that reduction of nickel ions by boron hydride proceeds at a considerably higher rate when two ligands (of the acidic type and ammonia) are introduced simultaneously rather than separately. This is conditioned by a significantly higher electroactivity of mixed complexes as compared to $Ni(NH_3)_6^{2+}$ or complex ions containing acidic ligands only. Other results point to a specific role of the environment of reducing ions in electroless plating reactions [16].

It should be noted that several ligands not only affect the kinetic properties of the reduction process resultant in the end reaction product, but also may influence the composition of the end product. Reduction of copper by formaldehyde from glycerate, tartrate and some other solutions is accompanied by surface passivation of the growing copper films due to the formation of cuprous oxide apart from the main product. At the same time, no passivation occurs with the use of trilonate solutions [1, 7]. The components of electroless solutions, present from the start or formed as reaction products, are often responsible for passivation phenomena causing not only the rate of reduction but also complete termination of the reaction. Inhibition effects present difficulties in the formation of thick (on the order of 10^{-3} mm) metal films. Because of this, sometimes selection of a reaction medium for the production of high-quality thick layers of metal films is a complex experimental task necessitating studies of inhibition effects exerted by different components of the reaction medium, including ligands as a part of the reducing complexes.

In many cases the principal reaction of metal ion reduction is accompanied by the reactions proceeding in parallel, which influence the yield of the end product, its chemical composition and structure. Firstly, the stages leading to the production of hydrogen, the evolution of which is always followed by the reduction of chemically active metals found to the left of hydrogen in the contact series (reduction of nickel, cobalt, iron ions). Hydrogen is formed when the above metals are reduced by boron hydride, hypophosphite due to simultaneously proceeding catalytic reaction of boron hydride and hypophosphite ion decomposition. Hydrogen generation may be detrimental for the quality of metallic coatings due to nanopores formation. Because of this, it is essential to study this problem for the development of technological processes aimed at the production of metal films by electroless plating.

Apart from hydrogen, on reduction of nickel, cobalt and iron ions by boron hydride and hypophosphite a various but appreciable quantity of boron or phosphorus is deposited together with them. This involves difficulties in crystallization of metal and if a quantity of the above-mentioned nonmetals is sufficient, results in the formation of amorphous metals, essentially alloys of a metal with boron or phosphorus [20, 24, 33–35]. The proceeding of the above processes when the named reducing agents are used excludes the possibility for the production of pure nickel and its analogues, but is useful for the production of alloys with valuable properties.

The process of Ni^{2+} ion reduction at electroless plating of Ni-W and Ni-Mo alloys has a complicated and multistage character [36,37]. In this case W(VI) and Mo(VI) are reduced step-by-step, and the reaction may be terminated at the stage when WO_x or MoO_x oxide is formed ($x < 6$). Simultaneous deposition of nickel with tungsten and molybdenum in the process of their electroplating occurs similarly [37]. The films produced by simultaneous electroreduction of Ni(II) and WO_4^{2-} , in certain conditions contain tungsten with a degree of oxidation of +6, +5, +2, 0 according to the data [37] obtained at X-ray photoelectron spectral analysis of the product. All the afore-said points to the fact that simultaneous deposition may provide a means for the production of metals, their alloys and boron- or phosphorus-containing products as well as composites including metallic phases together with an ultradispersed oxide. Such a product is formed also in the pro-

cess of simultaneous electroplating of nickel and copper with tin [38-40], copper with zinc [40]. A rather great number of nickel and boron oxides may be observed in the electroplated nickel-boron alloys too [41]. In all cases the content of partially reduced compounds of polyvalent metals may be controlled by varying the composition of a reaction medium (electrolyte) and reduction conditions.

It should be noted that electroless and electrochemical reduction of WO_4^{2-} and MoO_4^{2-} ions is practically absent in the solutions which do not contain the reducible compounds of Ni(II) and some other metals, though these reactions are possible from the viewpoint of thermodynamics. It is believed that tungsten and molybdenum, and especially their oxides forming as intermediate or end products in the process of reduction, possess no adequate catalytic activity in the reaction associated with the oxidation of reducing agent ions. Involvement of these ions into the reduction process is largely determined by the presence in the reaction zone of nickel catalyzing the reaction. Besides, atomic hydrogen formed during the reaction seems to be of importance.

Stabilization of electroless solutions. Most essential for the application of electroless metal plating solutions in the production of continuous metal films and patterns on different substrates is the stability exhibited by these solutions in storage and particularly in service. Selection of ligands for the reducible ions to form more stable complexes is unacceptable, since it is detrimental for thermodynamic parameters of the proceeding reaction.

The problem of stabilization in case of electroless solutions may be effectively solved by the introduction of special inhibitors for the formation of fine metal particles, capable to catalyze the reaction of metal reduction without pronounced effect on the rate of a catalytic reaction at the substrate surface. The next three approaches may be suggested to improve the stability of electroless solutions:

1) Addition into a solution of organic compounds (in small quantities) capable of chemisorption on the surface of very fine particles which are the solid product of the reduction, without their decomposition or noticeable inhibiting the catalytic activity of fine particles of palladium, silver and some other metals catalyzing electroless deposition of metal on the substrate. Among the stabilizing agents in solutions containing boron hydride and formaldehyde as a reductants are particular organic compounds, which include sulphydryl and thiol groups and also N-containing compounds (nitrobenzimidazole, pyrimidine derivatives, triazenes, etc.) [20, 42].

2) Carrying out the reaction in the presence of some surfactants in electroless plating solutions in the concentration exceeding the critical one for the formation of micellae. In this case the reaction of electroless metal ion reduction in the solution bulk begins inside these micellae, where the access of one of the reagents is impeded. As a result, the metal particles are isolated and further catalysis of the reduction is excluded. As these particles become sufficiently exceeding the sizes of micellae, they cannot be located inside micellae and at this moment the inhibiting effect of surfactants is weakened considerably. However, the surface of the particles beyond the micellae may be inhibited by different components of the medium. Micellae are unable to retard markedly the catalytic reduction of metal ions at the surface of a growing film and do not preclude from deposition of the metal as a film or pattern. This deduction is supported by the data of electron microscopy for frozen solutions [10, 11, 13, 43].

3) The stability of the electroless metal plating solutions may be significantly improved by oxygen blowing through the solution bulk in service. An oxidizing activity of oxygen is sufficient to decompose small clasters of a reducing metal formed in the solution, while the reaction at the surface of a growing film is not appreciably retarded. The stabilizing effect may be exerted by some inorganic oxidizers too [44].

Many stabilizing additives for solutions containing strong reducing agents (e.g. boron hydride) are inactive in the solutions containing reversibly oxidizing reductants (in particular reductants used in electroless silver plating) that presents supplementary problems in selection of stabilizing agents for electroless metal plating solutions.

It has been found [15,44] that simultaneous introduction of two-three additives differing in nature, e.g. cationic surfactants and S- or N-containing compounds, or cationic surfactance, S-containing compounds and oxidizer, has a superadditive effect on inhibition of the metal particle formation in the bulk of a solution. The majority of the additives studied are distinguished by their ability to suppress the metallic-phase nucleation at the initial stage of the reaction leading to the increased induction period for the solid particles appearance and their decreased absolute numbers in the solution bulk (Fig.2). Addition of most effective stabilizing agents results in both a prolonged induction period of the solid particles formation and a decreased growth rate of the particles in the solution bulk. At the same time, the latter is not observed in all cases. To illustrate, the addition of some cationic surfactants into boron-hydride solutions of copper and nickel plating inhibits the formation of solid particles, whereas their growth rate remains practically invariable after the induction period (Fig.2).

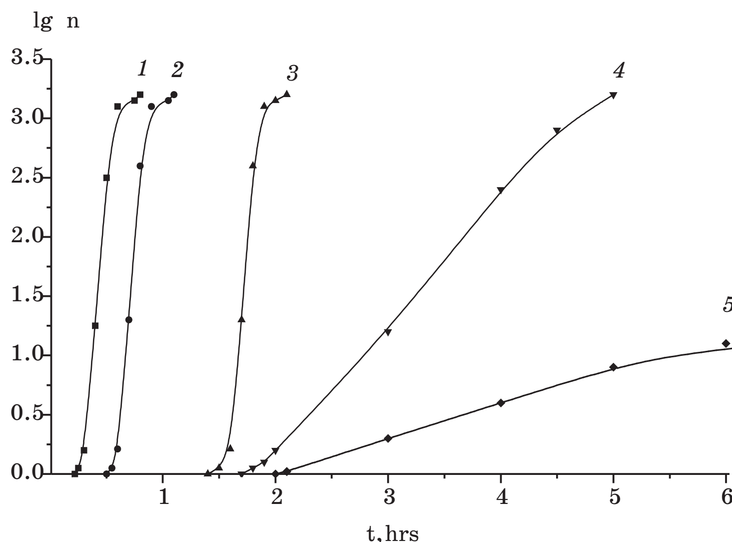

Fig. 2. Changes in concentration of nickel particles in the volume of boron-hydride solution (*1*) in the absence of the additives and in the presence of:
2 – alkyl dimethylamine oxide, *3* – 5-nitrobenzimidazole, *4* – 6-methyl dithiouracil, *5* – 2,4-dithio-1,2,3,4-tetrahydropyrimidine

The retarded growth of the particles may be due to the positively charged SAS micellae adsorbed at their surface that causes the recharging of metal particles, as observed in electrophoretic measurements [8, 11]. The surface of the particles beyond the micellae may be inhibited by S- and N-containing compounds or oxidizers present in the solution, facilitating the formation of a metal oxide layer at the particle's surface or sulfur- and nitrogen-containing substances [20, 33, 42, 44]. Owing to this, the presence of chemically different additives in the electroless solution at the same time influences the metal particle growth most effectively. The carried out electrochemical studies [9] have demonstrated that surfactants and sulfur-containing compounds inhibit the process of hydrogen-containing reducing agent oxidation (boron hydride, hydrazine borane, dimethylamine borane), but exert a weaker effect on cathodic reduction of Ni^{2+} ions. In such a manner stabilizers impede anodic oxidation of the reductant adsorbing on metallic surface of the particles.

Most of the stabilizing additives under study at a certain concentration in the solution inhibit the occurrence and growth of metal particles in the bulk of this solution little affecting the rate of metal deposition on the catalytic surface, and sometimes even increasing this rate [20,42,44].

The electroless solutions stabilized by certain additives differing in chemical nature have been used as nonsilver physical developers to enhance a weak silver image [10, 15–17, 21–24, 26, 43, 44] and to produce metal films with particular functional properties on different substrates [20, 45–47].

2. ELECTROLESS AND ELECTROCHEMICAL PLATING OF NICKEL-BASED FILMS

Owing to studies into the problem of deposition from water solutions of films and coatings based on metals and alloys from solutions, workers of the BSU IPCP have elaborated the physical, chemical and preparative principles and proposed special methods for deposition of particular metals and alloys on different substrates using the processes of electroless and electrochemical reduction. Investigations of film compositions, structures and properties, various effects produced on them provided the scientists with a great body of information, making it possible to forecast and to control these properties purposefully in order to create various high-quality coatings (protective, functional and decorative).

Whereas electroplating of metals may be realized on conductive substrates only, electroless plating may take place both at the conductive and nonconductive substrates. The ability of the substrates to catalyze the reduction reaction or react with the reducible ions (e.g. by substitution mechanism) is a requisite for the formation of such coatings without electric current. As a result of the substitution reaction, an active substrate metal with higher electronegativity is displaced into the solution and that with higher electropositivity is reduced yielding a thin-film product. The dielectric substrates require preliminary formation of special particles catalyzing the reduction reaction or adsorption of reagents providing a means for catalyst formation in contact with electroless solutions.

Chemically and electrochemically deposited films of copper, some copper- and nickel- based alloys with other metals, nickel-boron and nickel-phosphorus as well

as tin and gold have been the subject of investigations in the BSU IPCP. This section presents the results obtained when studying the electroless and electroplating of boron-containing coatings based on metals of the ferric subgroup (nickel, cobalt, iron) and phosphorus-containing coatings based on nickel, which are of special interest due to their properties.

Plating of nickel-boron films. Electroless plating of nickel-boron alloy on copper, steel or other substrates is performed from aqueous solutions with the use of such boron-containing reductants as hydrazine borane, dimethylamine borane [24, 48, 49] and sodium boron hydride [20, 50–53]. It has been found [20, 53] that Ni (II) is reduced by boron hydride to form thin metal films at temperatures of 80–90 °C in a strongly-alkaline medium (pH 13–14) in the presence of tartrate and ethylenediamine ligands. The electrochemical studies [20] have demonstrated that at a certain ratio (Ni(II) : tartrate : ethylenediamine = 1:4:1.5) the active mixed complexes formed are liable to reduce Ni(II) at a rather high rate (5–6 μm/h) forming uniform lustrous coatings under the effect of boron hydride. The necessity to carry out the reaction in a strongly alkaline medium (narrowing the scope of applicable substrates) is dictated by hydrolysis of sodium boron hydride proceeding in neutral solutions [1, 7]. The process of plating is only possible in the presence of the above-mentioned solution-stabilizing additives (sulfur- and nitrogen-containing substances). This stems from the fact that boron hydride solutions are characterized by spontaneous high-rate reduction of nickel ions in the solution bulk.

The content of boron in the films is mainly determined by the nature and concentration of the introduced substance and also by the plating conditions, varying from 12 to 26.5 at. % [20, 50–53]. Using dimethylamine borane as a reductant during the plating of nickel-boron alloy, one is enabled to conduct the process yielding a film in ammonium citrate solution at a relatively low temperature (60–70 °C) in neutral or weakly alkaline medium (pH 6–12). The nickel-boron plating rate grows with the increase in concentration of Ni(II), reducing agent, ammonia and with plating temperature. As regards the ammonia concentration, this may be explained by the formation of mixed ammonium citrate complexes able to dissociate with the generation of active ammonia complexes $[Ni(NH_3)_n]^{2+}$, where n = 1–4 [24]. The content of boron (3–16 at.%) in the films is growing with increase in the concentration of dimethylamine borane and is decreased with increase in the ammonia concentration. The latter seems to be determined by a relative change in the rates of simultaneously proceeding catalytic reactions, namely: reduction of Ni(II) by dimethylamine borane and dehydration of dimethylamine borane to form boron codeposited with nickel.

High plating temperature, alkalinity, instability in time determine a limited usefulness of boron hydride solutions for the production of boron containing metal films on different substrates. An alternative method worked out by us is electroplating with the use of sodium decahydridklozodekaborate ($Na_2B_{10}H_{10}$, DHKDB) as a boron-containing compound that has not been used with this purpose previously. Electroplating of nickel in the presence of this compound may be conducted at room temperature in neutral or alkaline as well as acidic medium. DHKDB belonging to the class of higher polyhedral klozoboranes is stable in alkaline and acid solutions. Unlike sodium boron hydride, it is not a strong reductant [54], and chemical reduction of Ni(II) both on a catalytic surface and in the bulk of solution is

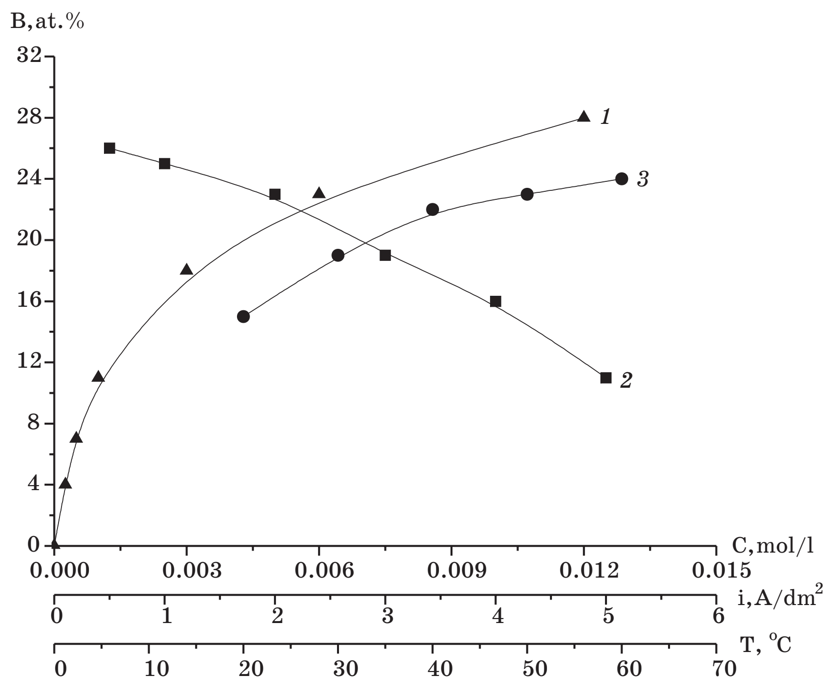

Fig. 3. Boron content in the nickel-boron film as a function of the (*1*) $Na_2B_{10}H_{10}$ concentration (T = 20 °C, pH 4.5, I_k = 2 A/dm^2), (*2*) current density ($C_{DHKDB} = 0.6 \cdot 10^{-3}$ mol/l, T = 20 °C, pH 4.5), (*3*) temperature (pH 4.5, I_k = 2 A/dm^2, $C_{DHKDB} = 0.6 \cdot 10^{-3}$ mol/l).

excluded. Electroplating of nickel in the presence of $Na_2B_{10}H_{10}$ leads to the formation of polycrystalline and amorphous films containing boron up to 30 at. % [55–58]. For the most part, the content of boron in them is determined by the concentration of $Na_2B_{10}H_{10}$, temperature and current density (Fig. 3).

Inclusion of boron into the nickel films at electrochemical reduction of Ni(II) from solutions seems to be a result of boron hydride adsorption on the deposited surface with subsequent catalytic decomposition to elemental boron. The catalytic DHKDB decomposition is indicated by boron deposition on the surface of nickel catalyst in the absence of an external current source [55]. Depending on conditions, the content of boron in nickel films is determined by the relation between the rates of cathodic reduction of Ni(II) and catalytic decomposition of $Na_2B_{10}H_{10}$. A study of the possibility for cooperative electroplating of boron with cobalt and iron has demonstrated that inclusion of boron into the films is dictated by the catalytic activity of metal during the decomposition reaction of DHKDB. To illustrate, plating of nickel-boron alloy yields the films with the content of boron close to 30 at. %, whereas on plating of cobalt-boron alloy this content is below 16 at. % [59]. It is impossible to realize codeposition of boron and iron electrochemically with $Na_2B_{10}H_{10}$ present in electrolyte. Thus, the results obtained give evidence to the fact that the catalytic activity of metals in the decomposition reaction of the above additive is diminished in the following sequence: nickel, cobalt, iron. It is interesting that the inclusion of boron into the films in case of nickel and iron

deposition is influenced by iron [60]. Maximum boron content in Ni–Fe–B alloys never exceeds 18 at. %. When iron ions occur in the solution with $Na_2B_{10}H_{10}$, the content of boron in the three-component alloy is reduced by a factor of 1.5–2.0 compared to the electroplated alloy of nickel and boron at the same concentration of the boron-containing additive. Increase in the concentration of this additive in the solution leads to higher concentration of boron in the films, while the content of iron in them is going down [60]. Since iron reveals no catalytic activity in decomposition of DHKDB with boron deposition, the alloy of iron and boron can be plated in the presence of a reducing agent (sodium boron hydride) only [61, 62].

X-ray diffraction analysis [56–58] has demonstrated that both electroless and electroplated nickel-boron films with the content of boron up to 6 at. % represent solid polycrystalline solution of boron in nickel. The films with high boron content are roentgen-amorphous and may be classified as so-called amorphous metals which are of great interest in nowadays. Owing to their specific properties, these metals are of great practical importance. By the X-ray diffraction method it has been found that the regions of coherent scattering in the films of crystalline nickel are diminished with growing boron content in them: from 30 nm (electroless plating) and 10 nm (electroplating) to 3–4 nm and less. Heating of the films at 300–400 °C invokes the crystallization processes leading to the formation of Ni_3B and Ni_2B borides in different ratios depending on the temperature and heating conditions [41].

Systematic studies [59–64] of the mechanical properties, contact electrical conduction and corrosion resistance of different films have enabled the authors to establish the means and conditions for variation of these characteristics in order to produce the films able to be applied as contacts, hard coatings, corrosion-resistant conductors. It has been found that the corrosion resistance of nickel-boron alloys is very high (being comparable to that of gold films during the printed board testing procedures) to allow using of Ni–B films instead of the gold ones in the production of boards.

Owing to the studies of electroless Ni(II) reduction by boron hydride in the solution bulk, the methods for plating of high-dispersed nickel powders have been developed, which allow to produce a product containing up to 43 at.% of boron, depending on the solution composition, ligand nature and reaction temperature [33, 34], and the additives for motor oils on their basis have been proposed [65]. The ability of the solutions in the process of spontaneous Ni^{2+} ion reduction by boron hydride to form a thin conductive layer on the catalytic surface at room temperature and at a high rate (1μm/10 s) provided a means for the development of the aerosol – jet dielectric plating technology used presently for the production of holographic marks. The worked out technological processes allow to produce nickel – boron coating on the bars of printed boards. Plated contacts replace gold and silver in series production in Belarus and other NIS-countries.

Of particular interest are the results [69–72] demonstrating that small amounts of ultra-dispersed diamonds (3–5 nm sizes) are capable to strengthen nickel coatings considerably offering better durability due to a change in the microstructure of the deposited nickel under the effect of simultaneously deposited diamond nanocrystals.

Plating of nickel–phosphorous films. Reduction of nickel ions by hypophosphite and the possibility for the formation of nickel coatings have been described previously [1, 7]. Unlike the reduction of Ni(II) by sodium boron hydride, hypophosphite enables reduction both in acid (pH 4.0–7.0) and alkaline medium (pH 8–11) at a temperature of 60 – 90 °C. It has been stated that plating of Ni – P films may be realized at room temperature from alkaline citrate-ammoniac solutions in a ratio Ni(II) : Cit : NH_3 = 1 : 2 : 1 at a plating rate of 2 –3 μm /h. The plating solutions with hypophosphite as a reductant are more stable than boron hydride solutions and may be in service for a long time without spontaneous reduction of Ni(II) in the solution bulk. However, in case of high-rate solutions (v = 20–25 μm/h) at high concentration of the reductant and plating temperature of 70–90 °C a search for adequate stabilizing additives, having practically no effect on the nickel plating on the substrate surface and at the same time inhibiting the reduction process of nickel ions within the solution, is a critical problem [1]. At the Laboratory of Chemistry of Thin Films IPCP the investigations of this problem are presently under way [73, 74]. The content of phosphorus in Ni–P solutions is dependent on the solution composition and plating conditions, amounting to 3–25 at.%. The Ni–P alloys containing 1.5–33 at.% of phosphorous may be electroplated from acidic solutions (pH 1–2) in the presence of hypophosphite [35]. Similar to boron, the presence of phosphorus in the films imparts high hardness, wearability and corrosion resistance to these films, motivating wide application of nickel coatings with boron and phosphorus.

The authors have conducted investigations of electroless Ni–P plating with the aim to obtain the data about the processes, to control the film structure on the surface of dielectrics containing the catalytically active particles, and to use this information for the elaboration of methods providing the formation of ultrafine-grained conductive films and locally deposited miniature conductors with good adhesion to the substrate. This task was essential for the development of techniques for pattern forming on dielectrics without the use of photoresists.

The studies of hypophosphite solutions (pH 4–11, temperature 30–60 °C) containing different ligands (pyrophosphate, citrate, acetate, chloride, sulphate ions, glycine or ammonia) have revealed extreme sensitivity of the electroless plating of nickel – phosphorus films to all the above-mentioned solution characteristics and to the nature, production prehistory and sizes of the catalytically-active particles. It has been found that the induction period of reduction, plating rate, film microstructure and hence the structure-sensitive properties (especially internal strains in the films and their adhesion to the substrate as well as selectivity of deposition at the specified sites of the dielectric surface, possibility of pattern forming) differ greatly depending on the composition of a plating solution, its pH, temperature and origin of catalyst particles [74].

It has been determined [32] that during the induction period of nickel plating the palladium centers of all sizes are partially dissolved with the result that small particles disappear completely and take no part in the catalytic reduction of nickel. Palladium particles 10 nm in size exhibit high catalytic activity in the reduction process of nickel, and the particles less than 4–7 nm depending on their prehistory dissolve completely whereas the plating of copper from formaldehyde solutions is associated with a minimum particle size that is one-third as great. Pla-

ting of nickel is very sensitive to inhibition of the catalyst particles by trace amounts of difficultly soluble compounds. The experience gained in forming the patterns of nickel on different substrates is indicative of the necessity to use for the development of these patterns (i.e. for selective deposition of thin, below 0.2 μm, nickel films on the palladium-activated sites) only weakly alkaline electroless-plating solutions [31, 32, 74]. This seems to be required to exclude the formation of hydroxo compounds of palladium with pH growth and to provide the decomposition of tin complex compounds with palladium, forming on the substrate surface after activation and being precursors of palladium particles. At the same time, the deposition of nickel patterns should be performed from weakly acidic solutions to prevent the appearance of trace amounts of nickel on the substrate between the pattern elements growing.

It has been demonstrated that nickel nuclei, as distinguished from copper particles, are able to grow two-dimensionally in the plane of the substrate without the formation of new nuclei. This feature involves a peculiar «healing» of the pores and fissures in the films, on the one hand, and growing of the pattern element sizes in the process of Ni–P plating, on the other hand. The latter is causing particular problems in the production of microconductors. The particles enlarging in the process of nickel film growth permit of a greater adhesion area and better adhesion at the interface between the forming Ni-P film and the substrate [74].

The data obtained have revealed that there is distinct correlation between the internal strain in Ni–P films and their adhesion to the substrate. However, the character of this relation is rather complex, since only in specific cases lowering of the internal strain results in greater adhesion of the films. To illustrate, the increase in the solution temperature, though causing reduction of the internal strains, leads to lower adhesion. The effect of common electroplating additives (saccharin, 1.4-butyne diol, etc.) introduced for diminishing of internal strains is similarly unpredictable.

The results obtained have been used for the development of the electroless plating process aimed at the formation of thick (up to 2–12 μm) patterns of nickel on polyimide film, that is a hard-to-plate polymer due to its very smooth surface, but is a widespread dielectric in production of printed boards and printed cables owing to its good dielectric properties and thermostability.

3. ELECTROLESS AND ELECTROCHEMICAL PLATING OF COPPER FILMS

There is a voluminous literature on the problems of the electroless copper film plating from solutions. A number of surveys are made and thesis works defended at the BSU IPCP [1, 5, 7, 18, 19, 45, 46, 47, 74–76]. It should be noted that in a most common method copper is plated from the solutions containing copper sulfate and formaldehyde in an alkaline medium (pH 12 and more) in the presence of such ligands as tartrate, trilonate, glycerol. Different particles (Pd, Ag, Au, Cu, etc.) may serve as plating catalysts. A side-product of formaldehyde oxidation is hydrogen.

When our investigations into electroless copper plating from solutions have been started, the authors encountered some challenging problems. Specifically, the production of sufficiently thick copper films (5–25 μm), the deposition of films with the demanded microstructure, the plating of conductive patterns on dielectrics with prespecified size, configuration and high adhesion to the substrate required particular attention.

The authors had to look out into the possibility and conditions for producing thick films of copper (a few tens of microns) on different surfaces. In so doing considerable difficulties have been experienced. Among them there are strong passivation of the film surface and the development of considerable internal strain at the interface film – substrate. Additional difficulties have been encountered due to the necessity to provide the solution stability both in storage, in service and at temperatures up to boiling. Owing to the results obtained during large-scale investigations, particular compositions of electroless plating formaldehyde baths enabling the formation of high-quality copper films at a rate of 1–7 μm/h with a thickness from a few to 30–40 μm have been proposed.

The passivation problem has been considered regarding to the fact that during the formation of individual metal films their structure and hence the properties are determined by the concentration of the main components in electrolyte, ligand nature, temperature and pH, the presence of stabilizing substances and compounds, modifying characteristics of the films. Our findings in this investigation and the results of other authors have been summarized in the monograph [1] and adequately illustrated in some papers [18, 19, 45] devoted to the study of electroless plating of copper. Experimentally it has been established that trilonate copper-plating solution stabilized by a salt of heavy metal and potassium ferricyanide is most useful for the production of thick (up to 30–40 μm) copper layers. It has been found that copper films with the desired parameters are formed at a certain reaction rate that is attainable by variation of the ligand's nature and concentration, concentration of the reducing agent, by introduction of special additives, by temperature and pH [18, 19, 45].

It has been stated that purposeful control of the rates for partial stages of metal film growth (nucleation, nuclei growth, coalescence of metal grains, recrystallization) makes it possible to obtain copper films with the required structure and properties.

For example, the rate of copper electroless plating from the trilonate–formaldehyde solution is critically dependent on its pH. The highest rate (up to 7 μm/h) is achieved at pH 12.5, and the rate diminishes with further increase in the solution alkalinity. With respect to the grain size in films, temperature growth of the solutions results in larger areas of coherent scattering. An increase in pH leads to a diminished size of the grains. These observations provided a means to realize the control of grain sizes in copper films within some limits and of coalescence even without the introduction of special additives into the solution for copper electroless plating.

Plasticity of copper films enabling multiple resoldering is one of the most important characteristics of copper films. In the works [18, 19, 45, 76] it has been demonstrated that electrolessly plated copper films of high-placticity are characterized by large grain sizes and regions of coherent scattering (up to 200 nm), as

well as insignificant microdistortions of the lattice. However, this is true only for the samples similar in tendency to absorb hydrogen, presence of impurities and other factors influencing the plasticity. Analysis of the tendency to hydrogen absorption and plasticity of copper films plated from solutions in the presence of special additives has shown that copper films, as a rule, exhibit low level of hydrogen absorption (to within 40–150 ppm). All other things being equal, the content of hydrogen in the plated copper films is lowering with the decrease in the plating rate. That is due to lower intensity of hydrogen production at low rates of the process and to the possibility for sufficiently complete desorption of the gas formed in these conditions. At the same time, with the addition of polypropylene glycol or 2,2'-dipyridyl into plating solutions the films with small hydrogen content are formed at higher rates as well. As a rule, the films containing less hydrogen possess higher plasticity. However, there is no complete correlation between the tendency to absorb hydrogen and relative film elongation (i.e. a measure of plasticity). It seems that the latter is determined mostly by the structure of a deposited copper film: its grain size, their packing density and the presence of structural defects or impurities.

On condition of its adequate correction, a trilonate electroless copper plating solution stabilized by ferricyanide and the salt of heavy metal is suitable for multiple use. The accumulation of different products of the main and side reactions together with SO_4^{2-} and Na^+ ions introduced into the solution to correct copper ion and alkaline concentration occurs at a prolonged period of the solution usage, as in case of any other plating bath. The accumulation of the above products results in an increased density of the solution and affects the properties of the forming films. In the work [76] consideration is given to the effect of a prolonged service life of the solution on the physical and mechanical properties of the films plated.

The developed procedures for the formation of copper films by electroless plating have found practical application in radio and electronic technology. The methods developed and proposed by the authors for copper deposition into through and blind holes in a wide range of the ratios of hole diameter to substrate thickness, especially for copper filling through holes in ceramic substrates (alumina and silicon nitride) are of particular interest. Actually, thick copper layers may be deposited in a selective way on the demanded parts of substrates stable in an alkaline media which are characterized by high conductivity and solderability [18, 19, 45, 47, 75, 76].

Quite specific problems arise when electroless copper plating is used for conductive copper films and especially copper patterns production on dielectrics with a smooth surface. Firstly, the difficulties have been found connected with copper to dielectric adhesion which are especially great if some parts of the substrate surface must not be covered by copper film and are exposed to the alkaline electroless copper plating solution. Secondly, the task to prevent copper deposition even in trace quantities on the dielectric surface between the conductive elements and to preserve the demanded form and sizes of miniature elements with verticality of conductive walls were quite new. Most of our results in the solving of the named problems are described in section 6. Here we note, that much emphasis was placed on the production of copper films with minimum internal strain, capable to retain small-grain structures invariable through the whole growth period [46, 74, 77–79]. The latter turned to be most important, since the differences in grain sizes on the

inside and outside surfaces of copper films result in the internal strains leading to peeling of the films from the substrate. The investigations performed have revealed that increase in the grain size during the growth procedure is observed both for the process of radial growth and for coalescence of the grains with each other. The latter is due to the formation of new fine copper nuclei on the surface of the earlier formed grains and at junctions between them. Because of this, it was essential to find the conditions of copper plating, suppressing the formation of new nuclei on the surface of the earlier formed ones and coalescence of the grains with each other. It was shown in a great series of experiments that only low speed electroless copper plating solutions with the rate of film deposition about 2 μm /h can satisfy these strict demands. It means the usage of solutions at room temperature and pH 12 with concentrations of copper ions and formaldehyde not high that contain a stabilizer not able to inhibit the catalyst particles and the growing copper grains at essential degree but oxidizing colloid copper particles in the solution volume (e.g., $K_3Fe(CN)_6$).

A special study has shown that the ligand's nature is of great importance. So, trilonate copper complexes cannot satisfy the demand of small grain sizes and to prevent the grain coalescence. Tartrate copper complexes appeared to be the best for this purpose that is most probable connected with Cu_2O formation in a trace quantities leading to the neglectively small but perceptible copper grain passivation. Besides, the rate of copper plating from tartrate-containing solutions is lower than in case of trilonate solutions [1, 7]. It was determined by us that an important role in the limitation of grain sizes plays the addition of small quantities of Ni^{2+} ions into the electroless copper plating solutions [46]. The authors have studied the effect of many sulfur containing stabilizing agents (sodium thiosulphate, different thioacids, thioaminoacids, etc.) and some quaternary ammonium bases [11, 13, 42, 80] on the solution stability, copper deposition rate, film microstructure and copper film adhesion to a smooth surface. It was estimated that thiosulphate ions only exert the demanded influence upon the copper plating rate and peculiarities of grain grows and coalescence.

In electroplating processes the problem of fine-grained metal coatings deposition is solved by the introduction of brighteners into the baths. However, this approach presents difficulties with catalytic electroless plating of copper in view of the necessity to maintain high catalytic activity of the growing surface. Proceeding from the afore-said, this problem in the case of electroless plating was solved by a complex way providing a moderate passivation of the growing grains and the exclusion of their effective coalescence with the help of such measures as thoroughly changed ligands and stabilizers, doping with traces of nickel, moderate concentrations of the main components, low pH (12) and temperature (18–22 ^oC) of the solution. It should be also noted that the required effect is achieved only in the case when on the dielectric surface there are homogeneously distributed catalytically active, nano-dimensional particles with high concentration (~10^3– 10^4 μm^{-2}) [46, 74, 77–79].

Unfortunately, this is inadequate for the production of copper films with a thickness above 0.5–1.0 μm on a very smooth surface of dielectric. In this case, despite all measures, expansion of the growing nuclei is taking place, and the surface of a polymer is exposed to alkaline solution when copper pattern is formed

with gaps between the conductive elements. The authors have found that in this situation one should carry out a two-stage copper plating process. At the first stage a thin copper film is formed at a low plating rate to provide high selectivity of plating, accurate replication of fine elements sizes in the patterns, high adhesion of copper films to the substrate. During the interval between the first and second stage, when the samples are dried, adhesion of copper to the substrate is strengthened and partial passivation of the copper surface occurs due to its oxidation by atmospheric oxygen, suppressing the expansion of the grains at least at the beginning of subsequent plating. The second stage enables retaining of the form and size of pattern elements but the plating is performed at a higher rate (4–6 μm/h) [74, 78]. Nevertheless, the growth of copper films to a thickness above 1 μm often requires the use of electroplating procedures.

A number of investigations was fulfilled by the authors aimed at the studies of the regularities of copper electroless deposition by boron hydride as a reductant [15]. This process is rather poorly elucidated in literature. As it was shown in the section 2 for nickel plating the boron hydride copper plating solutions are also alkaline (pH 10–11) for hydrolysis prevention, work at an elevated temperatures, contain trilonates and often ammonia as ligands for copper ions. The side products of copper ion reduction by boron hydride are unstable copper hydride (CuH), hydrodgen, but it is important to note that the copper films deposited by the named reductant are almost free of boron differing from nickel boron films. Copper plating boron hydride solutions are rather unstable and a lot of work was done by the authors to stabilize them [15, 44]. These solutions have found a limited utility for copper thin film plating and may used to obtaine photographic images.

Electrochemical copper deposition is realized from numerous copper plating electrolytes which may be subdivided into the following groups: weakly alkaline complex (pyrophosphate, ethylenediamine electrolytes), acid (sulfate, silicofluoride, boronfluoride electrolytes). Considering inadequate stability of polymeric substrates in alkaline solutions for the thick copper layers to be plated on them, the authors have used acid electrolytes. It has been established that «growing» of copper patterns on polymeric substrates up to 15–30 μm is possible only in conditions for the production of ultrafine-grained coatings. Just in this case the adhesion between metal and substrate remains high, whereas the expansion of the pattern elements is kept minimal. Most suitable are sulfate solutions with some brighteners or fast silicofluoride and boronfluoride electrolytes. Besides, most advantageous is the plating in the reverse mode allowing for the production of ultrafine-grained layers. As this takes place, no brighteners are required. The developed two-stage copper plating process have been introduced in to production of printed boards and cables on flexible polyimide dielectric [74, 78].

It is known from the literature that the electrochemical reduction of metal ions from aqueous solutions can provide the deposition of oxides in conditions of not full metal hydroxo compound reduction, for example, cathodic deposition of copper (I) oxide from copper (II) hydroxo compounds. These processes are still not clearly understood and the thin film product in spite of its decorative appearance has non-predictable properties and so is of no particular value. In our works we found the additives which can increase the cathodic current of Cu(II) to Cu(I) reduction and provide the electrolyte stability and reproducibility of film composition

and structure [81]. Besides, the nature of the deposited films, their structure and properties were studied.

Chemical composition of the coatings was determined by XPS and AES and it was shown that at low current density about 0.01–0.02 A/dm^2 the coatings include the products of incomplete copper reduction such as Cu_2O (the main product) and the admixtures of CuO, $Cu(OH)_2$, CuOH and Cu. The nature of the admixtures and their content are changing at film growth. The electron microscope investigation gives evidence that the films consist of compactly packed grains with sizes about 30–200 nm in diameter that increase inside these limits with the growth of film thickness from 0.1 to 2.5 μm. The changes in coating composition and the content of copper oxygen compounds during deposition are responsible to a large extent for the alternations in coating color. Thus, gold-like coatings have the thickness 0.13 μm, include Cu_2O, CuO, Cu and consist of the grains with the average sizes about 100 nm.

The coatings deposited on the smooth surface of copper or zinc and nickel have good corrosion stability. So, the alternation of the coating color and the appearance of corrosion spots at the treatment in camera with 100% humidity is observed much later than the analogous alternations of copper foil and thin electroless gold films 0.2 μm in thickness.

The results of investigations have allowed to work out the number of technologies for metal and metal alloy finishing by the deposition of protective and decorative thin coatings on the base of composite material including oxo and hydroxo Cu(I) and Cu(II) compounds that have the designated color (gold-like, crimson, bronze, red) and to use these technologies in production of furniture, clothes and different other accessories at belarussian enterprises [81]. We have found also, that the analogous phenomenon is inherent to a process of nickel-boron electrochemical deposition when the cathodic deposit includes metal oxides in rather large quantity.

It should be noted that copper plating from silico- or boronfluoride electrolytes is actually realized without overpotential, and possible at high current densities (10 A/dm^2 and more), as distinct from sulfate and slightly alkaline solutions, where the current density should not be higher than 2 A/dm^2. Consequently, the growth rate of the films differs greatly (ranging from 100 μm/h and higher to 10 μm/h). This fact was used by authors to derive some methods of copper electroplating from high-speed electrolytes on a number of metal substrates such as steel, foundry iron, zink and aluminium alloys which have found practical application in industry [82].

4. ELECTROLESS AND ELECTROCHEMICAL PLATING OF COPPER- AND NICKEL-BASED BINARY ALLOYS

Electroless and electrochemical plating of binary alloys and composites on their basis represent a rapidly advancing field of materials science that is competitive with a conventional metallurgy. The principal advantages are as follows: saving of nonferrous and precious metals, lower energy consumption in the production of individual metals and alloys, means for modifying the composition and

particularly the microstructure of solids and hence the possibility for rendering new properties; exclusion of labor-intensive processes of casting, extrusion and machining during the production and finishing procedures. Practical tasks associated with this field of material science are focused at the production of thin-film materials with the desired properties: anticorrosion, magnetic, optical, thermal, mechanical, antifriction, etc. The alloys and composites thus obtained allow to replace expensive and rare metals by other easily available and inexpensive ones, e.g. plating enables one to produce nickel alloys with zinc or tin that surpass nickel in corrosion resistance. However, not many of about 300 binary and ternary alloys known presently have found industrial introduction due to the problems with the control of the composition, its constancy, coating microstructure that is essential for the properties. The authors have conducted investigations aimed at the solution of these problems in the field of electroless and electrochemical alloy plating.

Electroless plating of binary alloys. The regularities of simultaneous electroless ion reduction of two metals from solutions are determined by a great number of factors such as concentration ratios of the reducing metal salts, ligand's nature and concentration, reductant nature and concentration, pH of solution, its temperature and stirring conditions, etc. Varying these parameters, one can change both the thermodynamic (redox potential) and kinetic (discharge rate of complex ions) conditions of the reduction processes for each of the ions, that in turn results in changes in the composition and structure of the produced alloys and hence of their properties.

Films of binary alloys deposited by electroless plating include crystalline intermetallic compounds, solid solutions and frequently amorphous phases. It is not unusual to find a discrepancy between the composition of the plated alloys and phase diagrams describing equilibrium systems as the alloys contain supersaturated solid solutions or intermetallic compounds characteristic for high (no less than 800–1000 °C) temperature range. Alloys plated from aqueous solutions differ from the metallurgical samples by their fine-grained character, i.e. grain sizes in the alloy coatings are primarily about a few tens of nanometer. As distinct from metallurgical alloys the composition of alloys produced by electroless plating from solutions is characterized by a great quantity of impurities as inclusions and their distribution mainly over the grain boundaries. The results obtained by the authors make a considerable contribution to data of the earlier published works.

The processes of simultaneous electroless plating of two metals may be subdivided into three large groups, namely: (1) simultaneous reduction of metals the ions of which are individually reducible by a given reductant; (2) simultaneous plating of metals, one of which is not individually reducible from aqueous solutions; (3) simultaneous ion reduction of two metals, one of which is a catalytic poison, i.e. it is not only nonreducible by a given reducing agent, but also inhibiting the process at an attempt of individual reduction [1, 5].

Cu – Ni – B alloy. Cu – Ni – B alloy provides an example of a group number one [83–89]. Individual ions of copper and nickel are easily reducible by boron hydride. In case when ions of both types are present in citrate ammonia solution the plating rate of the alloy is critically dependent on the concentration of copper salt. A maximum plating rate is observed at a relative concentration of the copper salt amounting to about 30–35 % of the total molar concentration of metal salts (Fig.4). A

partial reduction rate of each metal at the alloy plating is also extremely dependent on the concentration of their salts with approximately the same position of a maximum. The rate of copper ions reduction at a maximum exceeds the rate of individual copper deposition by a factor of seventy, while in case of nickel the difference is 2–3-fold only. This allows to conclude that the product formed as a result of simultaneous reduction is characterized by a rather high catalytic activity in the process of Cu(II) ion reduction. The composition of the alloy may be regulated not only by varying the concentration ratio of the salts of reducing metals, but also by varying the solution temperature and pH, by introducing the second reductant (e.g. sodium hypophosphite), and by the composition of ligands in the electrolyte. It has been found that without ammonia ions in the solution the reaction product contains mainly copper. When the ammonia ions are present in the solution, all other things being equal, the plated alloy contain considerable amounts of nickel (15–20 at.% and more). Electrochemical studies have demonstrated that with ammonia ions present in the solution the discharge of nickel ions proceeds with much greater depolarization than that of copper, as compared with the processes of cathodic ion reduction for these metals from solutions without NH_4^+ ions. The proportion of the alloy components is changing with a thickness of the films (Fig. 4).

The plating rate and composition of Cu – Ni alloys are also influenced by the character of catalytically active centers initiating the reaction of the electroless deposition. Comparison between palladium and silver centers formed in a similar

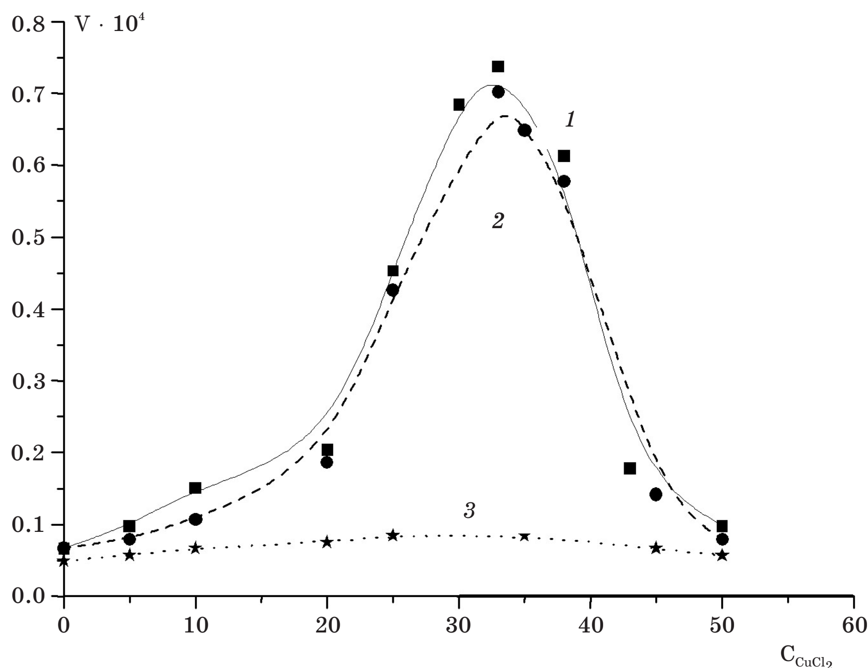

Fig. 4. The deposition rate V (g/(cm^2 min)) of Cu – Ni – B alloy (*1*), Cu (*2*), Ni (*3*) as a function of the copper salt concentration (mol.%) in solution. T = 20 °C

way has revealed that the plating rate in the second case is lower, whereas the content of nickel and boron is always higher.

According to the phase diagram, copper and nickel are mutually soluble without limits, and it could be expected that solid solutions should be formed at any proportion of these metals in alloys. However, a study of the alloy phase composition with different content of components has demonstrated that only the films containing 7 at.% of Cu and 14.5 at.% of B represent solid solutions of copper and boron in nickel. The films of other compositions may contain the second solid solution based on nickel as well as metallic copper and its oxides [88,89].

Ni – W – P and Ni – Mo – P alloys. With the second group one can classify Ni – W – P and Ni – Mo – P alloys produced by electroless plating from citrate-hypophosphite solutions considered in detail in [90-93]. The investigation showed that the tungsten content in the alloys Ni – W -P depended on temperature, solution pH and sodium tungstate and citrate contents. An increase in the solution temperature and concentration ratio of Na_2WO_4: nickel salt favors an enhanced tungsten content in the alloy. According to the chemical analysis data, thin alloy films (about 0.5–0.8 μm in thickness) deposited at 90 °C, pH 8 and the mole ratio of the nickel and tungsten salts in the solution equal to 3 : 7 contain 7–8 at. % W and 8–9 at. % P. In response to the increase of tungsten salt concentration in the solution from 0.07 to 0.09 mol/l (the mole ratio of tungsten and nickel salt in the solution being correspondingly changed from 2.3 to 9), tungsten content in the film is rather slightly increased, and the alloy deposition is significantly retarded (from 4 to 1 μm/h).

Freshly deposited Ni – W – P alloys containing 1 at. % W (13 at. % P) are crystalline and 8–9 at. % W (10.5 at. % P) are amorphous specimens. The heating at 250 °C for 6 hours does not effect phase composition of the alloys. Ni_3P phase is separated and solid solution of W in Ni formed on annealing the alloys which comprise 1 at. % W both at 600 and 900 °C. The comparison of the intensities of X-ray diffraction peaks for phosphide and nickel phases shows that even at 600 °C Ni_3P phase separation is essentially complete.

The annealing of tungsten enriched alloys (8–9 at. % W) at 600 °C results not only Ni – W solid solution formation and phosphide phase separation, but also the appearance of a third phase which is intermetallic compound Ni_4W. The comparison of X-ray diffraction peak intensities for phosphide, nickel and intermetallic compounds shows that their formation at 600 °C is not complete and it is continued during heating at 900 °C. Thus, it may be supposed that the increase in the content of tungsten in the alloy inhibits the process of phosphide phase formation, in spite of the fact that the Ni_4W intermetallic phase separation provides more favorable conditions for the formation thereof. The lattice spacing values for the solid solution coupled with the fact of the intermetallic compound phase separation, allow to suppose the microheterogeneous distribution of tungsten in as-deposited tungsten-enriched alloys.

It should be noted that, similar to other alloys under study, introduction of tungsten (molybdenum) salts into the solution and inclusion the refractory metals into alloys significantly affects the structure of a reduction product, grain size and content of the third (nonmetallic) component, e.g. phosphorus, and hence the properties of the metal film.

Cu – Cd alloy. Introduction of cadmium salts into the tartrate-formaldehyde plating solution results in the deposition of supersaturated Cu–Cd solid solution (assigned to the third group of alloys) containing up to 30 at. % of cadmium, the plating rate and corrosion resistance of which are much higher than the reduction rate of individual copper and its resistance in oxidation processes. An increased plating rate results in changes in the state of the surface of a growing metal particles, due to simultaneous plating of cadmium and copper leading to higher catalytic activity of these particles. Higher corrosion resistance of these films, as compared to copper, may be explained by possible formation at the initial stage of the alloy oxidation at corrosion tests of the dense cadmium oxide film that locks out further corrosion. It should be noted that cadmium is a catalytic poison in the processes of electroless reduction by formaldehyde. Consiquently, a marked growth of the plating rate in the presence of cadmium ions in the electroless copper plating solution may be attributed only to the effects of the alloy formation [94, 95].

Electroplating of binary alloys. Among the advantages of metal electroplating from solutions over electroless plating there are considerably higher rates of the processes and stability of solutions. At the same time, these processes are not universally applicable, e.g. they are of limited usefulness for plating on objects of complex geometry due to small scattering ability. Therefore, the researchers engaged in plating of metal coatings require information both about the mechanisms of electroless deposition and electroplating from solutions.

Electroplating of alloys from solutions is in many respects similar to the above processes of electroless alloy plating. The current density, at which the reduction process is realized, current polarity (unipolar, pulse, bipolar) and a nature of electrodes on the surface of which an electrolytic alloy is deposited are of great importance among the factors influencing the composition, structure and properties of a cathodic product. Owing to the absence of a reductant, catalytic effects essential for the processes of electroless plating become less important. Because of this, alloys associated with simultaneous electroplating of metals may be subdivided into two large groups: (1) alloys formed of the individually reducible metals and (2) alloys with only one of the components reducible individually.

Cu – Sn, Ni – Sn, Cu – Zn alloys. Cu–Sn alloys have been plated with the use of sulphate acid and pyrophosphate neutral electrolytes enabling the production of alloys with tin content from 3 to 50 at. %, depending on the current density (0.5 – 1.0 A/dm^2 is optimum), ion ratio of both metals in the solution (Cu(II): Ni(II) being from 1:10 to 1:1). The composition of the produced alloys includes intermetallic compounds (CuSn, $Cu_{10}Sn_3$, Cu_6Sn_5) and supersaturated solid solution of tin in copper containing up to 12 at. % of tin, and in some cases metallic copper and tin. The latter is in the amorphous state [38, 40, 74, 96, 97].

The formation of Ni – Sn films was performed from chloride- fluoride and pyrophosphate electrolytes providing the formation of alloys with the content of nickel from 30 to 70 at. % depending on the metal ions ratio in the electrolytes, pH and current density (0.5–2.5 A/dm^2). The films include intermetallic compounds of the type Ni_3Sn_4, Ni_3Sn_2, Ni_3Sn, and tin for the most part in the amorphous state [40, 74, 97, 98]. Plating of Cu–Zn films was performed from pyrophosphate electrolytes varying the ion ratio of copper and zinc from 1:1 to 1:10. The alloys

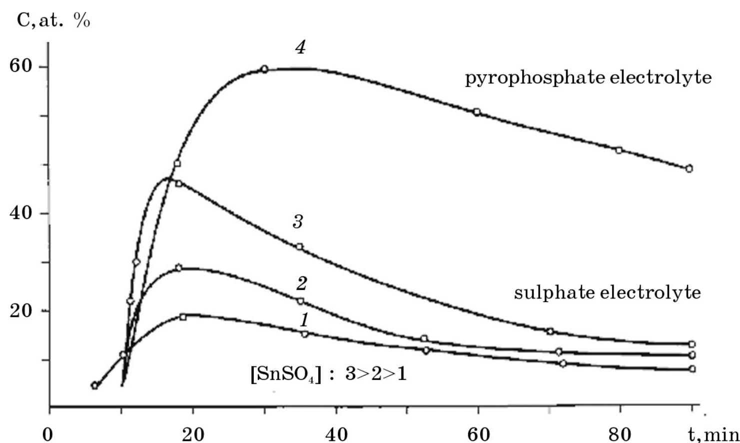

Fig. 5. Sn content in Cu – Sn films according to the results of atomic emission spectroscopy in dependence from the time of plating: 1–3 sulphate electrolyte, concentration $SnSO_4$ increased from 0.13 to 0.22 mol/l; *4*-pyrophosphate electrolyte

thus obtained included a solid solution of zinc in copper (up to 15–20 at. %) and also intermetallic compound Cu_5Zn_8 [40, 97].

In all three cases the content of more electronegative metal increases with the growth of its ion concentration in solution and current density. The latter is limited by formation of metal oxides as a result of hydrolysis occurring in proximity to the cathode and incomplete metal ion reduction. Chemical analysis of Cu – Sn, Ni – Sn, Cu – Zn alloys has revealed that an integral composition of the coatings is changing as the plating proceeds (Fig. 5).

At the early stages of plating the content of copper in Cu–Sn films is much greater than that of tin. For thickness ranging from 1,5 to 2,5 μm the total tin content is drastically increased, and with further thickness growth it reduces attaining the constant values at 10–12 μm. The content of tin and zinc in Ni – Sn and Cu – Zn alloys increases with film thickness growth to the constant values at 6–10 μm.

The phase composition of the above alloys (Table 1) is distinguished by the presence of the amorphous component that, as seen from the results of electron microscopy studies, is formed by the finest particles ranging in size from 1 to 100 nm. An interesting peculiarity of the composition of Cu – Sn alloys is also the formation of supersaturated solid solutions. The fine-grained structure is a characteristic feature of electrolytic alloys (especially Cu – Sn and Ni – Sn). The majority of grains have the size from a few tens to 100–200 nm, being one-tenth of the grain sizes in coatings formed of individual metals and even less.

It is important to note that the alloys (e.g. Cu – Sn, Ni – Sn) deposited from the solutions containing easily hydrolyzed tin compounds contain colloid particles of SnO_2 adsorbed from the electrolyte on the cathode surface or formed as a result of hydrolysis directly on the growing surface [97]. When these oxide content is limited (about 2–3% of the alloy mass), the alloys formed are characterized by better

microhardness and corrosion resistance than their metallurgical analogues. For example, we plated Cu – Sn and Ni – Sn coatings with a microhardness about 3.0–3.7 GPa and 3.7–4.2 GPa correspondingly. At the same time, their metallurgic analogues (not doped with the third element) have less microhardness about 2.5 GPa and 3.3 GPa accordingly. It has been demonstrated that unusual properties of the studied copper-based binary alloys plated from solutions are determined by the peculiarities of their phase composition and microstructure. These properties are the improved microhardness and corrosion resistance of the alloys, diffusion and recrystallization proceeding in the films (both in the process of film growth and on completion of electrolysis) at low temperatures within the interval 18–250 °C [40, 74, 96–98]. These processes are especially vigorous with the involvement of the liquid phase, i.e. electrolyte occluded into the films while their growth [74]. It has been found that the substrate metal takes part in the diffusion processes at electrolysis as well as on subsequent heating after the completion of plating. Accoding to Auger electron spectroscopy data, Cu – Sn film 5 μm in thickness heated at 250 °C includes about 20–30 % of nickel from the substrate [74,

Table 1

Composition of binary Cu-Sn and Cu-Zn alloy films 3 μm in thickness deposited in galvanostatic regime from combined pyrophosphate electrolytes

Mole fraction ratio of Sn (or Zn) and Cu in electrolyte	Current density, mA/dm^2	Mole fraction ratio of Sn (or Zn) and Cu in alloy	Crystalline phases in films		
			Freshly deposited	After heating 2 hours, 250 °C	After storage 18 month
Cu:Sn=1:10	80	1:9	Cu, Cu_6Sn_5, Sn*	Cu, Cu_6Sn_5, Sn*	Cu, Cu_6Sn_5, Sn*
	400	3:2	Sn, Cu_6Sn_5	Sn, Cu_6Sn_5	Sn, Cu_6Sn_5
Cu:Sn=10:1	80	1:49	Cu, solid solution Ni in Cu	Cu, Cu_2O, solid solution Ni in Cu	Cu, solid solution Ni in Cu
	600	3:7	Cu, solid solution Ni in Cu, solid solution Sn* in Cu	Cu, solid solution Ni in Cu, solid solution Sn*in Cu	Cu, solid solution Ni in Cu, solid solution Sn* in Cu
Cu:Zn=1:10	100	1:32	Cu	Cu,CuO, Cu_2O, Zn	Cu, CuO
	400	1:6	Cu, solid solution Zn in Cu, 15 at. %	Cu, solid solution Zn in Cu, 15 at. %, ZnO, Cu_5Zn_8	Cu, solid solution Zn in Cu, 15 at. %
	900	1:4	Cu_5Zn_8, Zn*	Cu_5Zn_8, ZnO	Cu_5Zn_8, ZnO, Zn*
Cu:Zn=2:1	50	1:99	Cu	Cu, Cu_2O, CuO, Zn*	Cu,CuO
	220	1:4	Cu, solid solution Zn in Cu, 20 ат. %	Cu, solid solution Zn in Cu, 20 at. %	Cu, solid solution Zn in Cu, 20 at. %

* phases, the content of which does not exceed several percents

97]. On completion of post electrolysis transformations,which continue 3–7 days the processes of recrystallization and phase changes in the films of binary alloys are drastically retarded, and the films behave themselves as metastable systems on storage and in service (Table 1).

The diffusion and recrystallization processes characteristic of nanostructured alloys have been purposefully used for deposition of Cu – Sn, Ni – Sn, Cu – Zn alloys by plating alternately the individual metals from solutions [40]. It has been shown that electrochemical synthesis of uniform ultrafine-grained films (including intermetallic compounds and/or solid solutions) may be realized by alternate plating of thin (20–200 nm) layers of the individual metals by two ways: eighther from electrolytes simple in formulation, each containing ions of one of the deposited metals, in the stationary mode or by plating from the solution containing the ions of both metals, varying the current density periodically. The latter method allows to deposit alternately the layers enriched in one or other metal. The films obtained in this way are also homogeneous, but not laminated and reveal high corrosion resistance and hardness. The latter is about 10–15 % superior to microhardness of the binary alloys produced in the stationary mode of electroplating. The possibility to vary the ratio of the both metals in extended limits (from 1:10 to 10:1) is of particular importance in these methods of alternative individual metal plating with an alloy formation. The other important feature of these methods is the possibility for the formation of fine-grained layers without special additives (e.g. brighteners). The novelty of this approach resides in the development of the procedures for metal alloy and composites synthesis with the controlled structure and properties.

Cu – Ni alloys. It is well known that copper and nickel can be codeposited into an alloy by electrochemical deposition. Most often pyrophosphate electrolytes are used for this purpose, but the coating thickness is limited by 5–7 μm because of cathod surface passivation inherent to this type of electrolytes. To exclude this phenomenon we worked out the way of buffering the solution and to prevent the reaction of hydrolysis in the near cathod zone of the electrolyte. This measure allowed to stabilize the work of the diphosphate electrolyte and to produce coatings with a thickness more than 60 μm. As it was shown for Cu-Sn, Cu-Zn, Ni-Sn alloys, the composition of Cu-Ni alloys also varies with their thickness. The nickel content diminishes usually at film thickening. It is important to emphasize that in spite of the integral alloy composition changes the both metal distribution in the coatings after the electrolysis finishing is uniform that gives evidence to the processes of low temperature diffusion in the alloys during their growth. Nickel content in the deposited Cu-Ni alloys can be changed up to 45 at. % and depends much on the current density. The results of X-ray diffraction analysis have shown the presence of only one phase which is the solid α-solution corresponding to the phase diagram.

The enthalpy of solid copper-nickel alloy formation has been determined at 298 K by reaction calorimetry of dissolution using the specially developed method and employing an isoperibol calorimeter for this purpose. The results obtained indicate that the model of subregular solution type still provide a reasonable description of the thermodynamic functions of the Cu-Ni system. Besides, the results

show that the product of electrochemical copper-nickel alloy plating from the worked out solution allows to produce an alloy which is the thermochemical analogue to a metallurgic alloy comparing their enthalpy of dissolution [99].

Zn – Ni alloys. Great interest in zinc-based films doped with metals of the iron-subgroup is determined by a continuing demand for the development of economically efficient and ecologically safe industrial plating processes, providing better corrosion resistance and protective ability than pure zinc coatings.

The results obtained for simultaneous electroplating of zinc and nickel or cobalt from aqueous solutions point to the fact that by varying the solution characteristics (ligand nature, molar ratio of the metals, pH) and electroplating conditions (current density, plating potential) one is enabled to change the proportions of zinc and nickel (or cobalt) over a wide range. To illustrate, the content of nickel may be ranging from below 2 at % (in case of a so-called anomalous codeposition plating with predominance of zinc in the alloy) to 90 at.% (normal cooperative plating when nickel is a predominant inclusion) [100–102]. Normal simultaneous plating of zinc and nickel in the process of the alloy formation is realized at the following conditions and with the following solution compositions: a) from ammonia diphosphate solution at the ratio [Zn(II)]:[Ni(II)] = 0.3 and i_k = 1A/dm^2, b) at [Zn(II)]:[Ni(II)] = 3 with the potentials ranging E = –0.95 ÷ –1.3 V vs. SCE or current densities ranging i_k = 0.05 ÷ 0.15 A/dm^2; c) from noncomplex chloride solution at [Zn(II)]:[Ni(II)] = 0.5 with the potentials ranging –0.75 ÷ –0.82 V or i_k = 0.05 A/dm^2. Low voltage or low current densities provide the proceeding of normal alloy plating. Growth in the voltage or current density lead to anomalous codeposition of zinc and nickel.

The formation of alloys with demanded composition and structure is greatly influenced by the formulation of an electroplating solution for the production of zinc-nickel films. It has been established that ammonia diphosphate solution provides the plating of homogeneous in phase composition films of Zn–Ni alloys over the whole range of the potentials and current densities under study. This seems to be conditioned by close approaching to each other of zinc and nickel potentials causing discharge of the ions of both metals already at low current densities. A chloride solution is characterized by the possibility to produce mainly two-phase films (phases of intermetallic compound Ni_5Zn_{21} and crystalline zinc or nickel) not excluding possible plating of single-phase alloys at quite definite conditions which are: the ratio [Zn(II)]:[Ni(II)] = 0.5 and current density <1 A/dm^2 or the plating potentials ranging –0.75 ÷ –1.3 V. Simultaneous discharge of zinc and nickel ions in a weakly alkaline chloride solution seems to occur only under the limiting diffusion current for the ions of a more electropositive metal (nickel) [101].

Based on the results of X-ray diffraction analysis [100], the conditions for production of the phases with nonequilibrium composition have been determined: roentgen-amorphous or poorly crystallized solid solutions of zinc in nickel are formed at low current densities (i_k = 0.05 A/dm^2), small voltage (E = –0.75 ÷ –1.15 V) or small film thickness (below 0.3 μm).

It has been found that the chemical and phase composition of Zn – Ni films is changing with their growth and grain sizes are smaller in films with the increased nickel content [100, 101]. This seems to be conditioned by the predominance of nickel reduction (as a more noble metal) at the initial stage. Further the forming

nickel monolayer may trap the ad-atoms of zinc or the products of zinc ion hydrolysis in the near cathod layer of the solution. Zinc phase deposition and its final reduction cause the inclusion of this metal into the alloy. The observed change in the chemical composition with the growing zinc-nickel film thickness is accompanied by changes in the phase composition too. The results obtained by X-ray diffraction, scanning and atomic-mass microscopy methods indicate the diminishing of the grain sizes in the films (from 120 to 2–5 nm) with growing nickel content (from 2 to 90 at. %).

Table 2

The effect of chemical and phase compositions of Zn–Ni films on their corrosion resistance

Solution	C_{Ni}, at. %	Phases in films	Dissolution potential, V	Corrosion current, $\mu A \cdot cm^{-2}$
Weak-acid chloride	–	Zn (crystalline)	−1.00 ÷ −1.02	12.0
	5.0–14.0	Zn (crystalline) Ni_5Zn_{21} (γ-phase)	−0.98 ÷ −0.96	5.0–5.5
	20.7–51.6	Ni (crystalline) Ni_5Zn_{21} (γ-phase)	−0.88 ÷ −0.85	2.0–2.5
Ammonia-diphosphate	12.0	Ni_3Zn_{22} (δ-phase)	−0.70	0.8–1.0
	19.0	Ni_5Zn21 (γ-phase)	−0.70	0.1–0.2
	33.4	Solid solution Ni in Ni_5Zn_{21}	−0.68	0.3–0.4
	68.0–76.4	Solid solution Zn in Ni (α-phase)	−0.65 ÷ −0.63	0.2–0.3

It has been determined that there is a correlation between such properties of Zn – Ni films as corrosion resistance, microhardness, contact electrical resistance and their microstructure, chemical and phase compositions. It has been shown that an increased content of nickel in films and the ultrafine grain structure are associated with better microhardness and contact resistance. The corrosion resistance of zinc-nickel films is growing with increasing uniformity of the structure. Zn – Ni films containing 19 at. % of Ni and the phase of intermetallic compound Ni_5Zn_{21} exhibit the highest corrosion resistance in 3 % solution of NaCl (Table 2). It has been found that doping of electroplated Zn layers with a small amount of Ni (up to 2 at. %) results in an unexpected increase in the corrosion resistance of these films, possibly being conditioned by the segregation of Ni atoms along the grain boundaries of zinc.

The results obtained have formed the basis for the development and commercialization of a technological process for plating of zinc – nickel films in instrument making and manufacture of fittings at the enterprises of Belarus.

Ni – W and Ni – Mo alloys. Electroplated alloys of nickel with tungsten or molybdenum possess some properties of great utility (high corrosion resistance, microhardness, wear resistance together with heat resistance). In particular conditions of plating the composition of these alloys differs from that corresponding to the phase diagram due to the formation of Ni-based solid solutions supersaturated with a refractory metal and their transition to an equilibrium state is hindered to some or other extent. The publications on the phase composition of such alloys are

merely confined to the statement of the fact that a crystalline or amorphous solid solution is formed, giving some information about the morphology, homogeneity of the doping distribution in a system and its valent state.

In the works [103–109] different approaches to the formation of nanostructured Ni – W and Ni – Mo systems are discussed. These approaches proceed from the effect of various factors (concentration ratio of the simultaneously reduced metal ions, nature and concentration of ligands, temperature and pH of the solution, current density, plating mode) influencing the formation kinetics of alloys, their chemical and phase composition, lattice constant of the deposited solid phases, film morphology and in-depth distribution profiles of the elements. It has been demonstrated that alloys with the limited content of tungsten (23–28 %) are formed from citrate solutions when the concentration of a tungsten salt in the solution is 2–3 times higher than that of a nickel salt, and with the concentration of NH_4^+ ions in the solution of no less than 1 mol/l as a critical requirement. The alloys formed without NH_4^+ ions contain below 13–15 at. % of tungsten. Auger spectroscopic studies have revealed in the samples plated from citrate solutions a considerable amount of oxygen along with nickel and tungsten. Together with the data on the morphology of the alloy film surface and lattice constants for the freshly deposited and heat-treated samples, this fact is indicative of the possibility for inclusion of tungsten into alloys in the form of a metal dissolved in the nickel lattice as well as in the form of oxides (valent states VI, V, IV, II) localized at the boundaries of nanograins in a solid solution. Oxygen-free and tungsten-enriched (above 24 at. % W), Ni – W alloys plated from the solution containing ammonium ions together with citrate ion are also nanoheterogeneous. The fact of intermetallic compound Ni_4W formed upon heating of the alloys and a character of changes in the lattice constant of the solid solution as a result of thermal treatment give evidence to formation while plating the sites with different tungsten content in the initial samples. The alloys formed from the same solutions and containing 24 at. % of tungsten that is above the solubility limit (11–13 at. %), according to the phase diagram represent homogeneous nanostructured systems with the grain sizes ranging from 10 to 170 nm.

X-ray diffraction studies have shown that the alloys plated out from the citrate-ammonia solutions with the content of tungsten from 11–13 to 23–26 at.% contain only one crystalline phase, i.e. supersaturated solid solution of tungsten in nickel with the lattice constant $a = 0.3585–0.3611$ nm. When plated with the use of pulse current, the alloys containing 27–28 at. % of tungsten are amorphous. The alloys plated from citrate solutions in the absence of NH_4^+ ions and containing below 15 at. % of tungsten are single-phase solid solutions with lattice constant $a = 0.3529–0.3531$.

It has been demonstrated that in case of Ni–Mo alloys, the peculiarities of homogeneous (metal – metal) and heterogeneous (metal – metal – metal oxide) nanostructured systems formation are very similar to the above-mentioned characteristic of Ni–W alloys. However, particular differences are also observed. The alloys with a limiting content of molybdenum (29–33 at.%) are formed from citrate solutions with the concentration of molybdenum salt that is lower by a factor of 1.5–2.0 than the concentration of nickel salt, and with the ammonium ions present in amounts of no more than 0.2–0.3 mol/l. Nanosized particles of molybdenum oxides are included into the films of Ni-Mo alloys in case when the solution

contains no ammonium ions and at the concentrations of the latter above 0.3 mol/l, and also with a rather high (as compared to the concentration of nickel salt) content of molybdate ions in the solution.

When plated out from citrate-ammonium solutions with a content of molybdenum up to 17–18 at.% , Ni – Mo alloys are nickel-based crystalline solid solutions with lattice constant a = 0.3538–0.3555 nm. With higher contents of molybdenum (up to 33 at.%) they are roentgen-amorphous (table 3). These alloys are also amorphous as being plated from solutions without ammonium ions.

Table 3

Composition of binary Ni-Mo alloy films

№	C_{Mo}, at. %	Oxygen content	Phase composition	
			Freshly deposited	After heating 2 hours, 900 °C
1	6	–	Solid solution Mo in Ni (lattice constant a= 0.3540)	Solid solution Mo in Ni (a = 0.3535)
2	8	–	Solid solution Mo in Ni (a = 0.3542)	Solid solution Mo in Ni (a = 0.3538)
3	24	Few percent	Amorphous	Two solid solutions Mo in Ni (a_1 = 0.3633 and a_2 = 0.3599), metallic molybdenum, few amount of MoO_2 and Ni_3Mo
4	31	> 10 at.%	Amorphous	Two solid solutions Mo in Ni (a_1 = 0.3625 and a_2 = 0.3578), metallic molybdenum, MoO_2 and few amount of Ni_3Mo

Annealing of Ni-Mo alloys with low molybdenum content leads only to regulating of solid solution's lattice. Crystallizing processes are much more complicated and complex in alloys with high molybdenum content and availability of oxygen (Table 3) [104,109].

Ni – MoO_3 and Ni – WO_3 composite films. The structural modification of solids by combining the components of different nature is a very promising approach to the creation of innovative materials with the desired properties. The electroplated composite coatings that include a metallic matrix with patches of fine-dispersed solid phase particles (organic or inorganic) are the example of such materials. These coatings possess the properties of a metal and a dispersed phase and are, as a rule, characterized by high corrosion resistance and microhardness, higher than usual wear and heat resistance. It should be noted that information about the methods for producing the composites «metal – dispersed inorganic particles» (oxides, borides, nitrides, carbides, silicides, carbon, diamond, etc.) and their properties is not adequately systematized and most commonly amounts to the formulations. Synthesis of dispersed particles with the desired sizes and properties still remains a complex problem.

So far the synthesis simplicity and availability of the initial reagents have been insufficient to motivate the investigators to use colloid solutions for the production of nanodispersed oxide particles intended as a dispersed phase of composite films «metal – metal oxide» electroplated from solutions. The data on the means of stabilizing the particles of these oxides within multicomponent solutions for

plating of composite films are lacking. There is little information about the quantity of oxide that may be included into the metal matrix, about changes in physical and mechanical properties of composite metal-oxide films compared to the metal films.

Owing our investigations [110–114], we have found the possibility for using nanosized particles of molybdenum or tungsten trioxide in the formation of composite films «nickel – oxide». It has been demonstrated that such composites are characterized by higher than usual wear resistance.

Trioxides of molybdenum and tungsten have been synthesized from solutions of the acids obtained by the ion-exchange method with the use of sodium tungstate or molybdate and high-acidity cationite. The samples of MoO_3 have been obtained by thermal treatment of the molybdic acid solutions in different conditions, depending on which amorphous and crystalline particles of oxide have been formed in a variety of shapes (spherical, needle- or parallelepiped-shaped) ranging in size from a few tens of nanometer to several micrometers. Sols of WO_3 formed under the mechanical or ultrasonic action on gels of tungstic acid (derived of its solutions in storage) contained large clearly-edged particles of fairly regular tetragonal shape, ranging in size from 0.3 to 1.5 mm as well as unconsolidated aggregations of fine particles, indefinite in form and ranging in size from 30 to 300 nm. Tungsten and molybdenum oxides were also produced with the use of hydrothermal treatment of the solutions of these metal acids at a pressure of 2–20 atm. In this case the formed particles were needle- or snow-flake-shaped varying in size and form over a wide range depending on the synthesis conditions. X-ray diffraction analysis has revealed that all the samples under study were crystalline formations, the content of water in which was determined by the treatment of the precursor solutions. Comparison between the thermographic results, IR spectra and data of X-ray phase analysis has revealed that, depending on the synthesis conditions, molybdenum trioxide is formed as a mixture of hexagonal anhydrous oxide and monoclinic dihydrate in different proportions, whereas tungsten trioxide is formed as monoclinic dihydrate or a mixture of hexagonal hydrate and ortho-rhombic $WO_3 \cdot 0.33\ H_2O$.

Being introduced into the nickel-plating electrolyte, the particles of both oxides are deposited simultaneously with nickel to form nanostructured composite films [113, 114]. The quantity of oxide incorporated into the nickel matrix is dependent on its concentration in the electrolyte, particle size and the process conditions (current density, temperature, presence of surfactant in the electrolyte, hydrodynamic factors), amounting to 1–9 mass %. When the amount of oxide in the electrolyte is low (0.1–3 g/l), its effect on the plating rate is insignificant. At higher concentrations the formation of coatings on the cathode is hindered. Wear resistance of the best samples of composite coatings with the incorporated particles of molybdenum or tungsten trioxides in conditions of dry friction is by a factor of 7–10 higher than that of nickel films, showing respectively of these oxides as dispersed phase for the use during the formation of $Ni – MoO_3$, $Ni – WO_3$ composite films.

Peculiarities of Alloying Deposition from Solutions. The peculiarities of simultaneous metal ion electroless and electrochemical reduction providing the formation of thin films or coating consisted of binary alloys and composites on their base were studied on a large series of binary systems (Cu – Sn, Cu – Ni, Cu – Zn, Cu – Cd, Ni – Sn, Ni – Zn, Ni – W, Ni – Mo), many mutual features were found in the both ways of solid film production when the electrons are supplied to the redu-

cing metal ions in a process of reductant oxydation or by the electrical current. Both methods provide the reduction of more noble metal with a larger probability. The increase in less noble metal content in the alloy may be achieved by the next ways: a) enlargement of a reducing agent concentration in a solution or an electrical current density; b) decrease in more noble metal ion concentration including binding its ions into complexes and the deposition under the limiting diffusion current, c) creating conditions of overvoltage for more noble metal ion discharge (e.g. adsorption of different substancies on the growing surface), d) elevating solution pH that provides the growth of reduction ability at electroless plating or the probability of hydroxocompound formation and adsorption on the growing surface at the electrochemical deposition, further this product plays the role of a precursor for unnoble metal deposition. A good way to enlarge the content of the less noble metal in an electrochemically deposited alloy is the raise in current density or voltage, but it is limited by formation of products of not full reduction. In all cases the concrete solutions formulations, ligands, pH, current density, the nature of different additives were found and the methods for deposition of alloys with the demanded ratio of the both metals were developed. The attention was paid at the mixed complex formation and synthesis of labile metal complexes, at the phenomenon of catalysis in the processes of electroless metal deposition.

It was found that the main features of metal codeposition and the binary alloy formation are the following: 1) the changes in the alloy composition while the film growth up to 6–8 μm, but the more thick films have the composition usually not changing with the increase in thickness; 2) the inclusion of a small quantity of oxo- and hydroxocompounds; as the result, the composites are deposited, containing some quantity of oxygen; in case when oxygen content does not exceed 2–4 at. % the alloys are characterized by high corrosion stability and microhardness; 3) the alloys deposited from solutions are ultrafine grained and the graines are not subjected to coalescence owing to trace amounts of admixtures surrounding the metal nuclei; these admixtures are concentrated at intergrain boundaries; 4) often the alloys deposited from solutions have the composition which does not correspond to phase diagram and are thermodinamically unbalanced, but phase transformations in these alloys are kinetically retarded; 5) hydrometallurgic alloys sometimes are thermodinamically identical to their pyrometallurgical analogues (e.g. Cu - Ni alloys deposited from solutions at conditions excluding hydrolysis.); 6) the processes of low temperature diffusion and phase conversion often are inherent to the alloys deposited from solutions. This fact was used to develope a series of methods for layer by layers deposition of thin individual metal films (not exceeding 0.1–0.2 μm in thickness) with subsequent alloying at low temperatures (100–300 °C) and production of coatings with rather uniform depth profile of component distribution.

5. ELECTROLESS GOLD AND SILVER PLATING

Plating of Gold. Electroless gold plating is commonly used in the microelectronics industry. Electroless processes are particularly useful for producing electrically isolated metal islands. However, a lack of understanding of the mechanism and a predominance of empirical data on the influence of plating conditions

and solution formulation on the film structure and properties retard a wide application of this technology.

There is no common agreement about the mechanism of electroless gold deposition from solutions. A number of researchers have concluded that the gold deposition occurs through the cementation reaction involving the metal of a substrate or that this reaction is a necessary initial stage of the process. These conclusions are based on the observation that substrate dissolution occurs during the electroless plating, that the coatings formed are porous and have unsatisfactory adhesion and limited thickness. Other researchers have considered that electroless gold plating is an autocatalytic process involving the oxidation of a reducing agent on the catalytically active surface of the metal being deposited. Such opinion is supported by the fact that the gold coatings can be formed without a limitation in thickness and without detectable substrate dissolution if specially adapted reducing agents (dimethylamine borane, borohydride) have been used. Besides, the assumption that the metal of a substrate can act as a catalyst of the gold deposition in a bath containing some reducing agents (for example, nickel in the process of the electroless gold plating involving hydrazine as a reductant) deserves special attention. Since hydrazine cannot provide an autocatalytic bath, this type of plating has been described as substrate-catalyzed plating.

Analysis of the literature indicates that electroless gold plating is a more complicated process than that for many other metals (Pd, Ni, Cu, etc.) exhibiting catalytic activity. To control this process, it is necessary to take into account different factors such as the high positive reversible potential of gold, the ease of gold reduction in the solution bulk and its low catalytic activity in a number of cases.

A purpose of our work was to study the peculiarities of gold film plating in processes of cementation and electroless reduction (it means, gold reduced by a more electronegative metal and by the dissolved reducing agent, respectively).

A number of gold plating solutions was investigated by us to find the conditions to stabilize the bath and to produce gold films of good appearance, protective ability, adhesion to a substrate and ability for soldering and ultrasonic welding. Some cementation solutions were tested [4, 28.] containing dicyanoaurate together with different ligands and buffering additives. It was shown that if no one of the additives fulfil the function of the reducing agent and there are no components in a solution which are aggressive towards the substrate than a thin and compactly packed fine grained gold film is plated about 0.07–0.1 μm in thickness. This film has nanopores but they are very small, so that the gold film prevents an atmosphere corrosion of the substrate. Besides, there are some few pores with micron sizes (1–4 por/cm^2 in quantity) which can fulfil the functions of microanodes during gold film cementation from solutions and which are the centers for corrosion of a substrate not only in solutions but also in a vapour phase. Mechanism of gold cementation from dicyanoaurate citrate solutions on nickel and copper had been studied. The methods of atomic absorption analysis of gold, nickel and copper ion concentration in cementation solutions at different stages of the gold film growth together with electrochemical investigations and the studies of the depth profiles of atomic distribution in gold films obtained by Auger electron spectroscopy had shown that gold ion reduction is accompanied by two side processes: 1) dissolution of the metal from the substrate which proceeds not only by the mechanism of the gold reduction with nickel or copper but by the mechanism

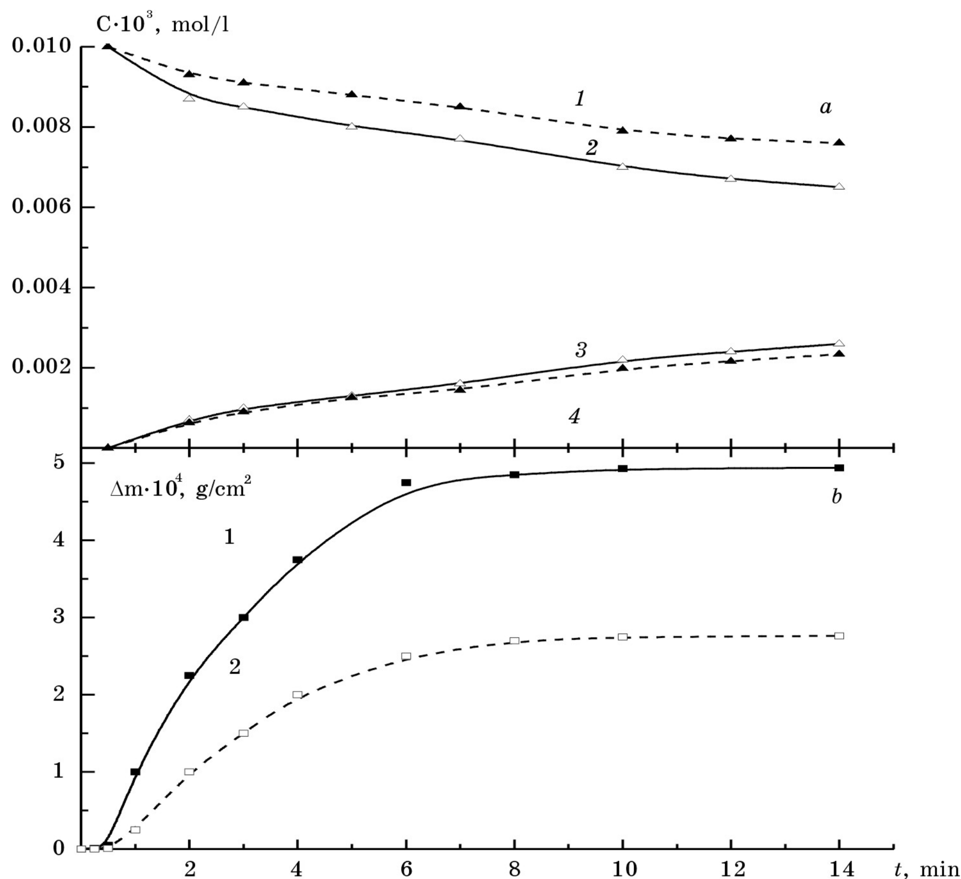

Fig. 6. Changes (*a*) in concentration of gold (*1*, *2*) and nickel (*3*, *4*) ions in solution and (*b*) in the sample mass during the gold plating in the cementation solution (--) and in the hypophosphite-containing bath (-)

of electrochemical corrosion with participation of molecular oxygen and H^+ ions in the case of nickel substrate and of only oxygen in the case of copper one; 2) codeposition of nickel or copper dissolved in solution together with gold (Fig. 6). The substrate metal dissolution is initiated by the formation of galvanic couples. Overstoichiometric nickel or copper dissolution and gold cementation are the coupled processes intensifying each other. Codeposition of the non noble metal with gold is demonstrated by Auger depth profiles and most probably proceeds owing to the electrochemical mechanism of cementation when the electrons on microcathods can transfer to any ion adsorbed at these sites.

Nickel or copper codeposited with gold in the working solution participate again in the cementation process. The codeposited copper gives the alloy with gold and is present all over the gold films, whereas the more reactive codeposited nickel has time to dissolve completely as the gold film is growing. As a result, nickel atoms are present in the near surface gold film at any stage of its growth but are absent in the film volume.

Side processes accompanying the gold cementation on Ni-P substrate favour the formation of gold films with specific structure and properties such as closely-packed ultrafine-grained structure, decorative appearance, rather high for such thin films wear resistance and corrosion-protective ability. The gold films on copper are of worse quality because of copper alloying with gold.

The properties of gold film could be improved much if to find the ways of more thick film production. For this purpose the reducing agents were introduced into dicyanoaurate solutions with buffering additives [74]. The named gold complex compound was used because of its great stability that is necessary to prevent the solution decomposition and the gold reduction in the volume of a solution. A series of solutions with different reducing agents such as formaldehyde, boron hydride, hydrazine and its derivatives, sodium hypophosphite were tried for electroless gold plating and it was found that solutions with hypophosphite ions were the best. They allowed to plate gold films about 0.3 μm in thickness with good appearance, adhesion to a substrate, protective ability and many other good qualities analogous to the qualities of the electroplated gold films ten times more thick [4, 115–117].

In order to study the reasons of such a quality of the electroless gold films we studied the peculiarities of gold deposition and its mechanism using the methods of atomic absorption analysis of solutions at different stages of film growth and the bath service (Fig. 6), the behavior of the gold and nickel electrodes in partial reactions of reduction and oxidation in the buffer solutions in hypophosphite presence and without this reducing agent, the phase composition of the films produced (X-ray and electron diffraction), the depth profiles of atomic distribution in films (Auger electron spectroscopy).

The data obtained allow us to suggest the following stages of the electroless gold plating on nickel which proceeds simultaneously by both mechanisms of cementation and catalytic reduction of a metal by hypophosphite.

1. Formation of microanodes and microcathodes on the nickel surface.
2. Oxidation of nickel and hypophosphite ions on microanodes and generation of electrons.
3. Reduction of the absorbed Au^{+}, Ni^{2+} and H^{+} ions on microcathodes.
4. Nickel incorporation into the gold film.
5. Hypophosphite oxidation which proceeds on the codeposited nickel only and coupled reduction of the adsorbed dicyanoaurate ions.
6. Gold cementation on the freshly deposited nickel.
7. Retarding of the gold film growth after 6–8 min of gold plating which can be provided by the diminution of the total area of Ni microanodes, by the increase in diffusion limitations (ion transport through the gold film), by the rise in ohmic losses in film pores and by the nickel passivation with the side products.

The peculiarities of the electroless gold plating onto nickel result in a fine grained structure, low porosity and improved characteristics (the resistance to abrasive wear and corrosion and the adhesion to the substrate) of the coatings deposited [4, 116, 117]. The thickness of electroless gold films having good properties is limited to ~ 0.3 μm. Besides, the nickel substrate dissolution through the largest pores provides the deterioration of the film appearance, adhesion and protective ability after 9–10 min of plating. The gold deposition is retarded due to diffusion limitations in the pores of the growing film and to the surface passivation. The technology of gold plating solutions from dicyanoaurate hy-

pophosphite solutions was worked out and used in production of printed boards for credit cards and in chips production at two enterprises of Belarus.

Many attempts were undertaken to work out the solutions with the other gold complexes such as $AuCl_4^-$ or $Au(S_2O_3)_2^{3-}$. It was found that it is very difficult to produce stable solutions. Most of them are colloid systems because of Au^{3+} partial reduction by the components of solutions. Nevertheless, it was shown that it is possible to plate thin gold films about 0.05–0.10 μm in thickness from these baths. The future investigation will be devoted to stabilization of gold colloid solutions.

Plating of Siver. Silver electroless plating proceeds from solutions containing a number of strong reductants such as formaldehyde, boron hydride, amino boranes, hydrazine and its derivatives, but it is also possible with the use of week reductants such as glucose, ascorbic acid, tartrate ions, metol, hydroquinone and complex compounds of metals able to change their degree of oxidation: Fe(II), Co(II), Cu(I) [1]. The reactions with week reducing agents are reversible. Most of them are used in traditional photographic procedure of silver image development and in not traditional photographic processes with so called «physical» development when silver ions are catalytically reduced from solutions [25]. The authors used these solutions to produce thin silver films on different dielectrics. It was shown that mirror-like films can be produced using glucose as a reductant, but in the presence of metol silver films are rather dark. These peculiarities are connected with different structure of the deposited silver films.

6. CONTINUOUS METAL FILM AND CONDUCTIVE METAL FILM ELEMENTS PLATING ON DIELECTRICS

The deposition of metals and metal film elements on the surface of dielectrics is very important in electronic and radio apparatus production and in decoration of plastics. It is needed in production of printed circuit boards and cables, multilayer circuit boards with high installation density, chips, wave guides, thermoelectric cells for heating devices and so on. The present-day hard requirements to the properties of metal coatings and functional metal patterns on dielectrics include: 1) the achievement of high metal-to-dielectric adhesion; 2) the ability to produce fine elements of micron sizes with the demanded configuration and the thickness from 0.1 to 25 μm or more and with the absence of metal traces (fog) on gaps; 3) the demanded properties of metal coatings, films and patterns such as the definite resistivity, corrosion and wear stability, the ability for welding and soldering, etc. All of these properties depend not only on the metal film composition but on film microstructure [1].

The fulfillment of these requirements is a very difficult problem and investigations in this field were carried out by the authors in the IPCP Belarussian State University for more than 20 years. Most of the results were published in [1, 5, 32, 46, 47, 118–142]. The difficulties in regulation of metal film adhesion, selectivity of metal film deposition in patterns and their microstructure are connected with a large number of physical and chemical processes which proceed in many stages and all of them are necessary to produce a continuous metal film or conductive metal film elements.

The main stages in the procedure of metal film deposition on dielectrics are: 1) the surface degreasing, cleaning and modification of the chemical nature and surface morphology; 2) the imparting a catalytic activity (deposition of small particles of a catalyst on a dielectric surface, usually palladium fulfills the function of a catalyst); 3) electroless deposition of thin (0.2–0.3 μm) metal film, copper or nickel most often; 4) electroless or electrochemical thick metal film plating. The production of electroconductive metal patterns without the usage of photoresists includes the stage of photochemical activation providing the catalyst particle formation on the demanded parts of the dielectric surface. For this purpose photosensitive substances are used that change their composition and state under the actinic exposure. As a rule, the photostimulated oxydation of Sn(II) compounds by the oxygen is used, so that the product of its oxidation (SnO_2) cannot reduce palladium ions to Pd^o and the metal deposits on the unexposed parts of the dielectric surface (the positive pattern). Besides, there are many not so often ways for photoselective activation which are described below.

The results of the studies concerning the beginning stages of nonselective and photoselective copper and nickel plating on dielectrics can be summarized as follows.

The first stage of surface nature and morphology modification is the main in obtaining good metal-to-dielectric adhesion. High adhesion strength is achieved most often by means of the mechanical interlocking of surfaces in contact. This is provided by the creation of a rough dielectric substrate topography with the help of mechanical, physical or chemical treatments. Sometimes it is possible to impart roughness without considerable diminishing the cohesive strength of the near surface layer of dielectrics. This may be done by etching away one of the phases which is finely dispersed in the matrix. The example is an epoxy adhesive with the dispersed butadiene-styrene rubber in which the rubber can be dissolved at the etching order to form so called ink-bottle contacts between the metal film and dielectric surfaces.

However, in the case of a single phase dielectric with a smooth surface, increasing the roughness enough to provide a high adhesion strength can lead to the deterioration of electrical parameters and the cohesive strength in the near surface layer and also to difficulties in the production of conductive elements with small dimensions [125, 134, 142]. That is why the problem of metal adhesion to dielectrics with a smooth surface is very difficult and it is necessary to find nontraditional ways of chemical modification to solve it.

Our investigations gave quantitative supplements that adhesion interaction in metal-polymer system may also have a chemical nature that is provided by the appropriate chemical modification of the dielectric surface. Prior to our works it was found that a high adhesion strength could be realized if the surface of the polymer has oxygen containing groups such as –COOH and $–CH_2OH$ with hydrogen ions capable of exchanging with metal ions. It was observed also that the internal surface of a metal coating plated onto a polymer is often oxidized. The penetration of a metal deposited from a solution into the near surface layer of a dielectric is also especially important to provide adhesion interaction. In our works we applied all these ways and evaluated their contribution into adhesion interaction [125, 138–140, 142].

Our evaluations of the adhesive strength and nature in a system «electroless copper film – epoxy rubber glass» had shown that the largest quota of adhesion strength belongs to mechanical deformation component and only 4–5 % of the adhesion strength has a chemical nature. The experimental studies of the adhesion

strength in a system «electroless copper film – polyimide film» where a dielectric is single phased and has a very smooth surface has shown that the quota of adhesion strength owing to chemical bonds Cu–O–C and Cu–N–C formation does not exceed 7–9 % in a sum [139, 142]. These bonds are formed in the result of copper ion exchange with carboxyl groups and the donor-acceptor interaction of copper atoms with the amido groups. Both types of the groups are produced at polyimide surface destructive hydrolysis during the etching that was confirmed by frustrated multiple internal reflection spectroscopy in the infrared region [136]. The results of the atomic absorption spectroscopic investigation showed that the polyimide surface contained 27.5 $\mu mol/m^2$ of functional groups able to exchange with metal ions from the solutions if optimum conditions of etching had been provided.

Besides, the swelled layer is formed on the polyimide surface at the etching the thickness of which is defined by the depth of diffusion of the etching components. Our observations show that the swelling of the polyimide surface layer at all stages of activation and at the beginning of copper film deposition is necessary to provide high copper-to-polyimide adhesion. This swelling provides the penetrating of metal ions from solutions into the near surface layer to a depth about 35 nm and that is very important for high adhesion of the deposited metal film (Fig.7) [125, 138, 139, 142].

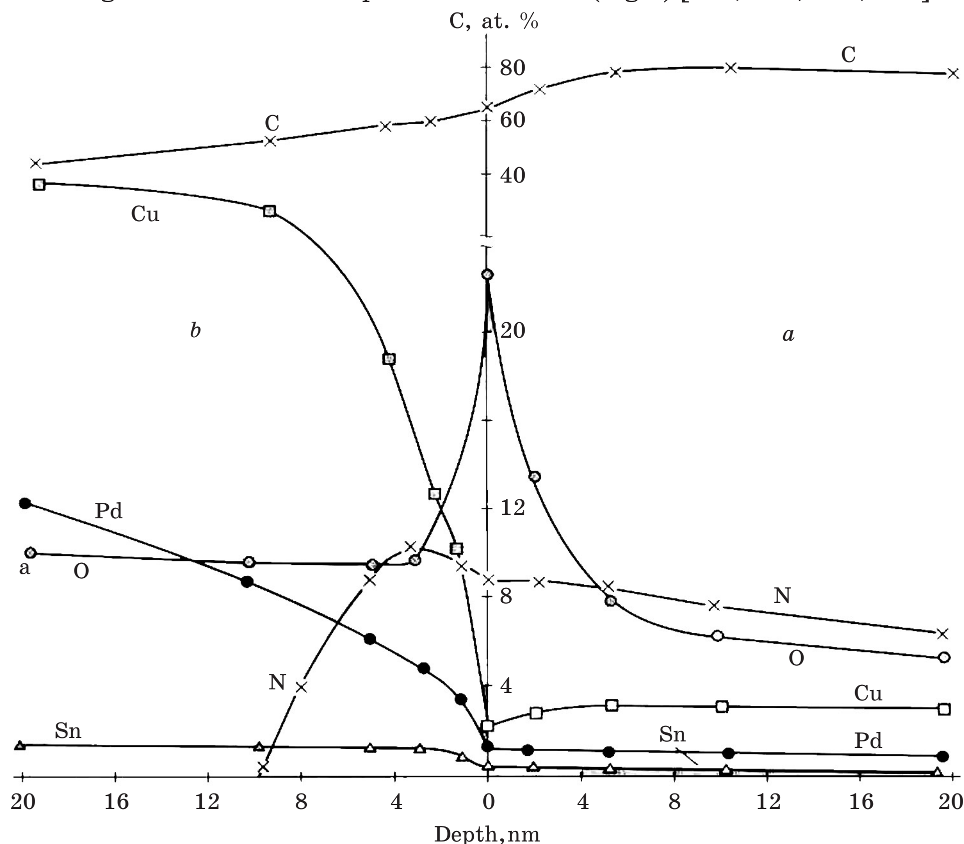

Fig. 7. Depth profile of a peeled Cu-PI system:
(*a*) polyimide films near-surface region; (*b*) copper internal near-surface zone

On drying, the polyimide surface hardens and the access of the solutions to the carboxyl groups into the junctions between polymer grains becomes impossible. This phenomenon causes a sharp decrease in hydrophilicity, and the adhesion of the deposited metal diminishes.

A number of the specific conditions necessary to provide high metal-to dielectric adhesion besides the named swelling which allows the treating solutions to penetrate into pores or capillaries at a depth of tens manometers are the following: the preservation of the sufficient cohesive strength in the dielectric subsurface layer, the creation of functional groups capable of chemical and donor-acceptor interaction, the formation of a fine-grained uniform surface topography with an area no less than 1.5 times the surface area of the initial polymer.

The investigations of numerous deposition variants for the formation of functional metal coatings on different substrates have enabled the development of methods intended for the surface preparation of various polymeric, ceramic and metallic materials before the metal plating procedure.

As mentioned above, the second stage in the procedure of metal plating consists in the substrate treatment by an activator solution to provide the formation of the catalytic particles either before the process of the metal deposition or at the initial stage of its reduction. The catalytically active particles are most commonly formed due to the step-by-step treatment in the solutions of tin (II) and palladium (II) compounds, that provides the formation of fine palladium particles by the reaction described by a scheme: Sn(II) + Pd(II) = Sn(IV) + Pd(0). Such processes have been thoroughly studied and there is a great body of published data [1, 2, 7, 47]. The substrate treated in tin chloride solution confine a layer of this solution in which the hydrolysis of Sn(II) compounds sharply intensifies by the aqueous washing. The hydrolysis products coagulate with the formation of a highly-adsorbed island film of Sn(II) hydroxo chlorides. The latter, upon adsorption of Pd(II) ions on their island provide the reduction of Pd(II) to Pd (0), whereas the formed palladium particles catalyze electroless plating from the solutions. The authors have found [125, 131–140] that the formation of island-like films of tin (II) compounds is more complex and involves both adsorption of colloidal particles from $SnC1_2$ solution and chemisorption as a result of ion exchange at the functional groups on a dielectric surface. It has been demonstrated that the colloidal particles formed in $SnCl_2$ solutions in the process of hydrolysis and Sn(II) oxidation by atmospheric oxygen fulfill the function of nucleation centers determining the microstructure of tin hydroxy-chloride layers. The authors have been first to establish the composition of colloidal particles (SnO_2, $Sn_4(OH)_6Cl_2$, Sn_3O_4, $Sn_{21}Cl_{16}(OH)_{14}O_6$, $Sn_3O_2(OH)_2$), their sizes (from 2–5 to 20–50 nm), concentration (optimum being 300–500 μm^{-2}), the relationship between these characteristics and the solution content, and storage life. Also it has been found that, even though the qualitative compositions of colloidal particles and adsorbed tin compounds are identical, the character of adsorption processes for Sn(II) compounds is greatly determined by a nature of adsorbent, i.e. dielectric surface. The quantity of adsorbed tin compounds may differ by an order of magnitude (from $8{\cdot}10^{-3}$ to $6.5{\cdot}10^{-1}$ mmol/m^2) depending on proceeding of ion exchange and donor-acceptor interaction on the dielectric surface (e.g., polyimide film) or the absence of chemical interaction with the surface (e.g., glass) [125, 135, 136, 142].

It has been shown that the film of tin hydroxy compounds applied to sufficiently smooth substrates in electroless plating of dielectrics serves as an adhesive and matrix determining the structure of deposited metal films. The highest adhesion of the letter is achieved by the deposition of a monolayer of closely adjacent nano-sized Sn(II) hydroxy chloride particles, which are confined to the surface owing to the chemical interaction with the formation of the C-O-Sn, Si-O-Sn type bonds. An optimum molar ratio between Sn(II) and Sn(IV) in this layer is 4:1 [129, 133, 138, 139].

The possibility of photochemical oxidation of Sn(II) to Sn(IV) provides a means to use a system based on bivalent tin for selective metal plating. Prior to the studies performed by the authors, it has been known that on UV irradiation (λ = 254 nm) of tin hydroxy chlorides Sn(II) is rapidly oxidized by atmospheric oxygen and looses its activity as a reducing agent [1]. As a result, no palladium particles are formed from the solution at the irradiated sites and the metal is not deposited. The studies conducted at the IPCP gave much more information on this question. It has been found that the rate of Sn(II) compound oxidation induced by UV irradiation in solutions is increased by hundredfold and more. At the same time, the reducing activity of tin hydroxy compounds in the adsorbed layers is completely lost in darkness in 60–90 minutes, while with UV irradiation the same effect is achieved faster by ten times [131–134]. It has been first established that tin (II) hydroxy chlorides possess the greatest light sensitivity compared to other tin compounds [137]. Their spectral sensitivity region is within 254–440 nm. The quantum efficiency of the light-induced oxidation of Sn(II) hydroxy chlorides in the far UV region is much more than unity, bearing witness to the chain mechanism of oxidation. At a wavelength of about 440 nm the quantum yield decreases to 0.3–0.4.

Photoselective plating may be provided by activation of dielectric substrates with the use of the solutions containing ferric oxalate or ferric potassium oxalate and ions of palladium and copper [47, 118–120]. Of great importance for the formation of palladium (copper) centers initiating subsequently the electroless plating process of metals is the ionic interaction of bivalent palladium (copper) and bivalent iron resultant from photolysis: $Pd^{2+}(Cu^{2+}) + 2Fe^{2+} = Pd^0(Cu^0) + 2Fe^{3+}$. The difference between these two systems is the necessity in case of copper (nano-particles of which are easily oxidized) to use additionally a dissolved reductant (e.g. formaldehyde in alkaline medium) for the irradiated sample treatment to realize complete transformation to metal.

Owing to the data offering possibilities of using the photo-generated ions of bivalent iron as a reducing agent for copper ions, the principles of nonselective surface activation for dielectric substrates with copper-containing compositions have been substantiated as well. The method is based on the use of activating solutions containing two salts of Fe(II) and Cu(II) with pH 2. The redox reaction in these conditions is not proceeding. After treatment in an activating solution the dielectric is dried and put into the solution with high pH. As a result, the reaction $Cu^{2+} + 2Fe^{2+} = Cu^0 + 2Fe^{3+}$ proceeds. Addition of formaldehyde into the alkaline solution causes shifting of the reaction equilibrium to the right. The formed particles of copper catalyze the reduction of copper ions from the plating solutions. Along with the reducible copper structures on the surface of the activated and dried sample put into the alkaline solution of formaldehyde, oxide-hydroxy compounds of iron (the composition of which is determined

by the concentration ratio of cupric and ferric salts) are also deposited with this activation method. It has been determined that the molar concentration ratio of Fe(II) and Cu(II) salts in the activating solution ranging from 10 to 5 (with fixed Fe(II) concentration) is associated with the formation of magnetite Fe_3O_4, and at greater concentrations of copper salts hematite Fe_2O_3 appears [121]. X-ray phase analysis has revealed that in the first case copper ions are reduced to metal and in the second one – to Cu(I) oxide. This suggests that for successive realization of the plating process the concentration of iron salts in the activating solution should be much greater than that of copper salts. To increase the particle concentration of the activator and decrease their sizes, one should introduce into activating solution small amounts of a water-soluble polymer inhibiting the growth process of crystals on drying [121].

A recently developed method of palladium-free activation provides the formation of the copper compound microcrystals and their subsequent reduction to metal on the dielectric surface. Microcrystals of the above compounds are formed in different ways: by hydrolysis process (from copper ammonium complex), by salting-out (from copper chloride dissolved in organic solution) or by drying. With these activation variants sodium boron hydride (E_{redox} = – 1.37V) is most suitable as reductant for copper compounds [121].

A special method has been developed for the activation of dielectric surface, allowing the direct electroplating of metal using electroconductive film of nonstoichiometric copper sulfide [122]. Conductive films of nonstoichiomentric copper sulfide Cu_xS are usually used in dielectric plating for direct deposition of nickel from nickel-plating electrolytes. Sulfide layers with the composition close to CuS exhibit the highest conductivity. The authors have developed a variant of sulfide

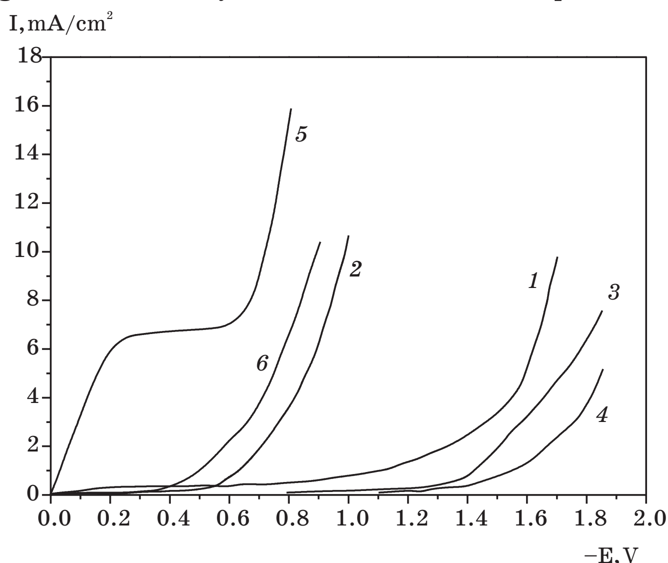

Fig. 8. Cathode polarization curves corresponding to reduction of copper sulfide (*1*–*3*) and copper ions (*4*–*6*) in ferrocyanide (*1*, *4*), fluoboric (*2*, *5*), ethylenediamine (*3*, *6*) electrolyte solutions

activation enabling the improved uniformity of the layers of nonstoichiometric sulfide and its reduced electric resistance [122–124]. It has been determined that sulfide layers stimulate the process of metal deposition in cases when the reduction is realized with great overvoltage (Ni, Fe, Co). However, copper plating from the most common electrolytes on the layer of nonstoichiometric copper sulfide in the form of a compact film, as a rule, does not proceed. Comparison of the polarization curves (Fig. 8) for the sulfide reduction processes in different electrolytes without copper ions presence with the analogous curves of cathodic reduction of copper ions [123, 124] has revealed that the curves are in the same range of potentials (–1.4 ÷ –1.8V) in ferrocyanide electrolyte only, pointing to concurrent proceeding of the processes in the second case.

The conditions are created therewith for the formation of compact copper films from a copper-plating electrolyte. In other solutions copper deposition is realized at much lower potentials than the reduction of nonstoichiometric copper sulfide that prevents plating of copper directly onto this layer. Since the voltages of the above processes are close only when copper ions in the electrolyte are forming a very stable complex (pK of ferrocyanide complex with copper ~ 34), so the lower is concentration of free copper ions in the solution, the greater is a probability of copper electroplating over the sulfide layer [123, 124].

In the processes of selective and nonselective metal plating electroless plating follows the stage of activation and the conditions of its realization are largely determining the quality of the formed films and coatings. To illustrate, it has been found that high adhesion of metal films, serving as conductive elements, to dielectrics with smooth surface is attainable owing to the control both over the structure of tin hydroxy compounds and the particles of palladium catalyst (desired concentration of palladium particles – 10^3–10^4 μm^{-2} and sizes 2–3 nm) and that of the metal films plated from the solution [74, 78, 126, 142]. The latter should retain nanostructure of the grains, their very compact packing, the absence of internal stresses at all stages of film growth. Adhesion interaction in a system metal – dielectric is greatly determined by the creation of a boundary between metal film and dielectric surface having a specific composition and a few tens of nanometer in length. Based on the obtained results, the process for the production of conductive patterns of copper and nickel on polyimide film without the use of photoresists has been developed and introduced into the industrial production of flexible boards.

The photoselective activation of a dielectric surface to produce metal conductive patterns can be also realized with the use of photosensitive semiconductors (TiO_2, SnO_2, ZnO, WO_3, PbI_2) [1, 31, 141]. The mechanism of photo-activation is based on the ability of the above mentioned semiconductors to generate photoelectrons under irradiation in a region of their own absorption with a division of a space charge; the photogenerated charge carriers are located on traps. At the subsequent sample processing by a solution containing noble metal or copper ions, the catalytic metal particles are formed on its surface. Processes of such type have found application for metal pattern production on TiO_2 film and include the following stages: 1) exposition by ultra-violet radiation; 2) processing in a solution containing ions of noble metal (palladium, silver) or copper ions in order to create

the latent image centers; 3) physical development, at which the deposition of a required metal (nickel, silver and more rarely copper) takes place on the these centers. Thus, a selective irradiation of dielectric with the help of a photomask gives the opportunities for selective metallization and production of metal conducting patterns on its surface [1, 31, 141].

The peculiarities of the photographic process with physical development (electroless thin film metal plating) on the TiO_2 photosensitive films 0.01–0.2 μm in thickness produced by polybutyl titanate hydrolysis in isopropyl alcohol were studied [141]. It was shown that the resolving capacity of such films is very high (up to 2000 mm^{-1}) when the thickness of the deposited metal film does not exceed 0.2 μm. The photographic sensitivity of TiO_2 layers in the region of titanium dioxide absorption equal to 340–380 nm can reach 10^7 $J^{-1}cm^2$ that is ten times higher than the sensitivity of electrophotographic layers. Besides, there are no problems with the adhesion of metal patterns on TiO_2 films, but the adhesion deteriorates with the further metal film thickness growth. The developed methods of selective metal plating with the use of TiO_2 photosensitive films were applied for industrial production of wear resistant high quality photo masks.

CONCLUSION

The results obtained in investigations of the films and coatings based on metals, alloys and composites make a considerable contribution to the preparative chemistry of the substances with the controlled structure, to chemistry of nonmetallurgical alloys of metals plated out of solutions, to the technology of selective metal deposition using photochemical activation of the substrate surface.

The problem of electroless deposition and electroplating of metals calls for further research. The future studies will be focused on the means and conditions for precise regulation of the composition (chemical and phase), structure and morphology of the thin-film nanostructured systems formed, the processes of metal alloy and metal composite deposition on the substrates of different nature and shape. The formation process, structure and properties of complex systems (powders and films) containing two and more metals, metal-oxide composites, composites including a polymeric component also deserve attention. The data obtained until the present time point to the strong possibilities of creation of nanostructured metal coatings, containing the phases of nonequilibrium composition which can not be obtained via the conventional alloy-production processes. An interesting and important problem is a possibility of prediction the composition of nonequilibrium phases showing a pronounced kinetic stability. The structure and properties of amorphous metallic systems and the structure-phase transformations in them are also of great interest.

It should be noted that the mechanisms of electroless and electrochemical reduction of the compounds of polyvalent metals and potentialities of formation of intermediate oxide phases that makes it possible to obtain nanostructured metal-oxide composites, are still not clearly understood. Photochemical studies associated with photoselective metal plating will be continued too.

Much remains to be done in the field of basic research in the processes of electroless deposition and electroplating and in the development of technological procedures for the formation of film structures and different coatings (protective, functional, decorative).

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