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ФОРМИРОВАНИЕ ТОПОЛОГИИ ПОВЕРХНОСТИ ПОКРЫТИЯ МЕТАЛЛОВ ТЕРМОХИМИЧЕСКИМ МЕТОДОМ В УСЛОВИЯХ ЛАЗЕРНОЙ АКТИВАЦИИ

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FORMATION OF THE SURFACE TOPOLOGY OF METAL COATINGS BY THE THERMOCHEMICAL METHOD UNDER LASER ACTIVATION CONDITIONS

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Аннотация. Исследованы структурные особенности осадков никеля, меди, олова и серебра, сформированные в процессе электролиза с использованием активирующего лазерного излучения. Показано, что введение лазерного излучения в процессы электролиза позволяет получать гальванические покрытия с улучшенными эксплуатационными характеристиками, в частности электропроводностью, при скорости формирования заданной субмикронной микрогеометрии до 5,69 мкм/с.

Ключевые слова: *субмикронная топология, атомно-силовая микроскопия, локальное электрохимическое осаждение.*

Abstract. The structural features of deposits of nickel, copper, tin and silver formed during electrolysis using activating laser radiation have been studied. It has been shown that the introduction of laser radiation into electrolysis processes makes it possible to obtain electroplated coatings with improved performance characteristics, in particular electrical conductivity, at a rate of formation of a given submicron microgeometry of up to 5.69 μm/s.

Keywords: *submicron topology, atomic force microscopy, local electrochemical deposition.*

Introduction

Electrochemical deposition of metals was carried out in liquid electrolytes, where, under the influence of an electric field and a concentration gradient, cations move to the cathode and are reduced. As a result, a deficiency of metal ions occurs near the surface on which the deposition is carried out, which causes relaxation inhibition of the process. When exposed to laser radiation (LR), the concentration of highly active particles – electrons, ions, excited molecules – corresponds to its nonequilibrium thermodynamic state, which is the reason for a significantly different course of processes than in conventional thermochemistry [1]–[5]. Although the study of the described processes has been actively carried out for several decades, the task of determining the optimal technological modes of coating production at a high rate of deposition is still relevant [5].

1 Methods and techniques of the experiment

We formed electrochemical coatings using continuous and pulsed LR sources. In each case, lasers and recording equipment of different types were used, the sizes and materials of the electrodes, as well as electrolytes, varied. The main purpose of the LR in accordance with the thermal mechanism of electrolysis activation is to transport the largest possible amount of radiant energy to the interface of the "electrolyte-electrode" phases. In contrast, when implementing LR exposure according to the photochemical mechanism, it is important that as much of the LR energy as possible is absorbed in the electrolyte, initiating dissociation reactions. When setting up an experiment under the conditions corresponding to both variants of the process, the information about the sorption and spectral properties of electrolytes is important.

When the LR passes through the electrolyte layer, its intensity decreases, and for this reason, the

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effective heat output of the heat source on the treated surface decreases. At the same time, it is assumed that the power density of the heat source W in the center of the zone of thermal influence of the LR is expressed through the intensity of LR I in accordance with the Bouguer – Lambert – Beer law [1], [2]:

$$W = (1 - R) I e^{-\varepsilon h},$$

where R – the reflection coefficient of the LR, ε – the spectral absorption coefficient of the precipitate material at the used wavelength LR; h – the thickness of the electrolyte layer.

In our research, the following types of electrolytes are most widely used in the technological processes of modern microelectronics [5]:

1) copper plating sulphate electrolyte ($CuSO_4 \cdot 5H_2O$ – 200 g/l, H_2SO_4 – 50 g/l);

2) nickel sulfate electrolyte ($NiSO_4 \cdot 7H_2O$ – 220 g/l, $Na_2SO_4 \cdot 10H_2O$ – 80 g/l, NaCl – 12 g/l, H_3BO_3 – 35 g/l);

3) silver plating ferrocyanide electrolyte ($AgNO_3$ – 40 g/l, $K_4Fe(CN)_6 \cdot 3H_2O$ – 150 g/l, K_2CO_3 – 25 g/l);

4) tin sulphuric acid electrolyte (SnSO4 – 40 g/l, H_2SO_4 – 100 g/l, OC-20 – 4 g/l);

5) silver cyanide electrolyte ($K[Ag(CN)_2]$ – 40 g/l, KCN – 50 g/l, K_2CO_3 – 40 g/l, KNO_3 – 60 g/l).

The spectral characteristics of these electrolytes in the wavelength range of 190–1100 nm were studied using the Cary-50 spectrophotometer (Varian, USA) of Agilent Technologies. The electrolyte absorption indicators presented in Table 1.1 were established.

Table 1.1 – Spectral distribution of extinction index ε (см$^{-1}$) of the electrolytes under study at the intensity of the LR 10^{11} W/m^2

Electrolyte type	Wavelength λ, nm			
	266	**355**	**532**	**1060**
1	0.010	0.083	0.017	0.617
2	0.753	0.213	0.057	0.587
3	0.015	0.293	0.087	0.097
4	0.012	0.162	0.041	0.323
5	0.011	0.305	0.093	0.105

In practice, it is difficult to provide ideal conditions for a positive effect on both the electrolyte and the surface of the metal at the same time, so compromise options for activating processes are most often used, and before starting the calculations, it is necessary to know exactly the intensity of the radiation both absorbed by the electrolyte and falling on the surface of the electrode.

The activation of electrolysis processes with an improvement in the useful properties of coatings is also facilitated by the methods based on the selection of the electrolyte composition, changes in its temperature and acidity, and the use of periodic currents of a special shape.

However, methods of modifying the composition of the electrolyte, for example, such as the introduction of gloss-forming, leveling and anti-pitting additives, have a number of drawbacks, starting with high cost, and ending with contamination of the electrolyte with the decomposition products of these additives. All these disadvantages are associated with the need to complicate galvanic equipment.

For the experiments, the most optimal laser in terms of type and parameters was selected, taking into account the dependence of the reflectance coefficients of various materials on the wavelength of the LI, the radiation attenuation coefficient of the electrolyte and the proportion of the radiant energy absorbed by the electrolyte and substrate. The radiation energy in the pulse, its duration, and the diameter of the light spot on the treated surface should be considered as the main parameters characterizing laser technological installations. Yttrium aluminum garnet was used as the active element of the laser (YAG, $\lambda = 1.06$ μm). Two types of laser systems were used:

1. «Квант–12». Working mode – pulse-periodic; pulse laser energy – 12 J; pulse duration – $(1–4) \cdot 10^{-3}$ s; pulse repetition rate – (1–60) Hz.

2. LS-2137U. Energy in pulse when generated for different wavelengths: 532 nm was (536–448) mJ, 355 nm – (140–222) mJ, 266 nm – (93–120) mJ, 213 nm – (18–21) mJ, pulse duration 6–8 ns, a pulse repetition rate: 0,1–10 Hz.

The schematic diagram of the experimental setup designed to study the effect of laser radiation on the process of electrolytic deposition of metals is presented in Figure 1.1 [1], [2].

The formation of electrochemical coatings took place as follows. After passing through the optical system, the LI was focused on the cathode, where, due to the surface heat source, a heat-affected zone appeared. The anode and cathode were connected to a power source, the current of which was stabilized by software. The coordinate system provides for the mutual movement of the laser radiation source and the cathode, as well as the focusing of laser radiation. The anode was made with a hole designed to allow laser radiation to pass through the electrolyte to the cathode.

The resulting coatings were studied by atomic force microscopy (AFM) with the use of a software and hardware complex «Solver P47 PRO». By means of AFM technology and subsequent computer processing of the resulting three-dimensional array in accordance with the methods of mathematical statistics, it is possible to determine the geometric characteristics of the nanorelief, such as the average size of nanocrystallites ("grains"), the direction of the normal to their surface, the average width and depth of the intergrain gap, and others. Based on this information, it is possible to predict what macroscopic properties (in particular, thermal and

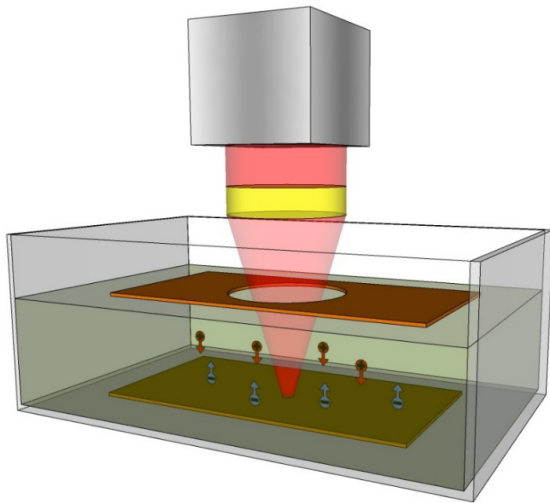electrical conductivity, microhardness) the surface under study will have.

Figure 1.1 – Schematic diagram of the laser activation process

2 Experiment results and discussion

The microtopology of the surface of nickel, tin, copper and silver coatings formed by laser electro-chemical method on non-conductive substrates made of sitall and silicon, on which conductive sublayers of copper, chromium, titanium and nickel were preliminarily applied in a vacuum, was studied by the AFM method. Deposition was carried out in various modes, varying the pulse repetition frequency f = 5–15 Hz and pulse duration τ = 1–8 10^{-3} c, at wavelength LI λ, corresponding to the minimum absorption for each of the electrolytes (Table 1.1), This ensured the optimal power density of the heat source on the cathode surface, which for different types of coating is a $W = 2,0$–$3,5 \cdot 10^{10}$ W/m^2. The studied samples are solid metal coatings applied in the process of electrochemical deposition, on which local precipitates have been formed under the influence of LI in an area commensurate with the diameter of the laser spot.

The experimental studies of the formation of local sediments in the stationary electrolysis mode were carried out for Ni, Ar, Cu and Sn at the optimal technological modes of stationary electrolysis using the types of electrolytes specified in Table 1.1. At the same time, different values of the intensity of the LI were taken I and the material of the conductive sublayer. The generalized experimental results characterizing the highest rate of coating growth without the effect of laser recrystallization and loss of coating quality are presented in Table 2.1.

A three-dimensional image, a histogram of inclination and an orientation diagram of nano-crystallites (grains) for a number of formed local sediments and their electrochemical background were obtained by the AFM method. For example, Figures 2.1 and 2.2 show the results of the AFM
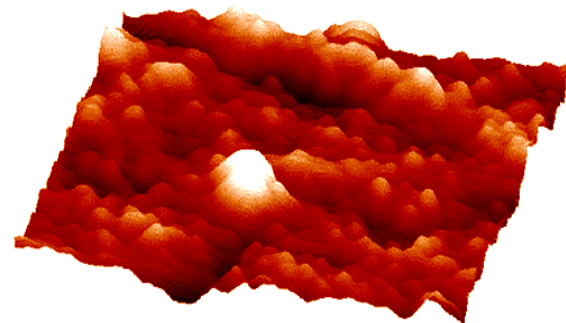
study of the silver coating formed on the copper substrate of the silicon substrate.

Table 2.1– Normal v_n and tangential v_τ growth rates of local precipitation

Sludge Material	Sublayer Material	I, 10^{10} W/m^2	v_n, μm /s	v_τ, Mm /s
Nickel (Ni)	Copper (Cu)	1.57	0.14	4.07
	Kovar	0.92	0.13	5.69
Silver (Ar)	Copper (Cu)	2.51	0.07	4.53
	Nickel (Ni)	2.32	0.06	4.51
Copper (Cu)	Molybdenum (Mo)	3.71	0.75	4.88
	Tungsten (W)	2.31	1.25	4.07
	Kovar	3.33	1.17	4.88
Tin (Sn)	Molybdenum (Mo)	3.51	1.19	4.88
	Tungsten (W)	2.73	1.22	4.07
	Kovar	3.33	1.14	4.88

The results of the AFM studies indicate that the topology of coatings of all the studied metaldles in the zone of local sedimentation differs significantly from the structure of the background coating. This trend is independent of the nature of the substrate material and subcoat.

The analysis of the structural features of the electrochemical coatings of all the studied metals showed that in the area of the electrochemical background, the samples in all the studied cases represent a homogeneous isotropic set of grains.
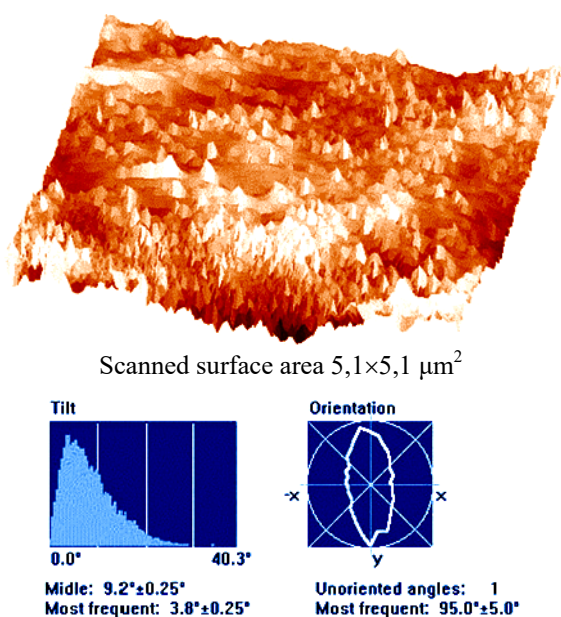

Scanned surface area 4,7×4,7 μm ^{2}
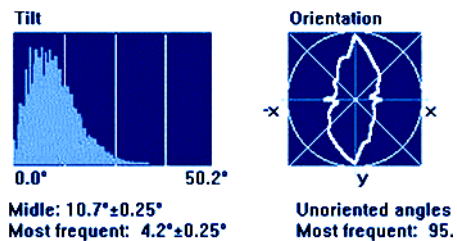
Tilt histogram and orientation diagram

Figure 2.1 – Results of the AFM study of the silver surface topology in the zone of local sediment deposited on the copper sublayer of the silicon substrate

Scanned surface area 5,1×5,1 μm²

Tilt histogram and orientation diagram

Figure 2.2 – Results of the AFM study of the topology of the silver surface in the zone of the electrochemical background deposited on the copper sublayer of the silicon substrate

At the same time, the average linear dimensions of such grains in 1.5–1.7 times less than on a similar substrate and sublayer for precipitates obtained under laser activation conditions. The surface of the crystallites of the local sediment has a fairly pronounced orientation along a certain direction. These facts are considered by us as confirmation that the impact of laser radiation activates recrystalliza-tion processes in the zone of local sediment, so a more accurate and regular crystal structure is formed, which causes increased wear resistance and electrical conductivity.

In addition, the following patterns have been revealed:

– When replacing the metal used as a sublayer, the size of crystalline grains and the degree of orientation of crystallites change; the structure of local metal sediments becomes more accurate.

– The structural features of local metal sediments (and, consequently, their operational properties) are significantly influenced primarily by the nature of the material of the conductive sublayer (in particular, the coefficient of conductivity, which determines the efficiency of thermal energy removal from the heat-affected zone).

When the intensity of the LI increases in the range $(1–6)\cdot10^{10}$ W/m² in local sediments of silver, copper and tin, there is a decrease in contact resistance by 20–40 % compared to the coatings formed without the use of laser activation. This is due to the fact that the local current density in the irradiated zone is 5 to 10 times higher than the local current density on an unirradiated surface. This leads to the formation of a fine-crystalline, densely packed coating structure with a minimum number of microdefects. In addition, with an increase in the intensity of the LI in the specified range, the coating heats up due to the absorption of laser energy. Under the influence of the described processes, the microhardness of thin-film layers and internal microstresses in them decrease. These effects ultimately contribute to a decrease in contact resistance with an increase in power density due to recrystallization, which is in good agreement with the results of the microhardness study.

However, with a further increase in the power density of the LI introduced into the heat-affected zone, the normal process of structure formation is disrupted due to the huge local current density and the large number of ions in this zone. As a result, the stable crystallization process is disrupted, and the perfection of the crystal structure decreases. On the surface of the coating, chaotically located large crystalline formations are formed.

Conclusion

The dependence of the stationary index of electrolyte extinction on the intensity of LI was analyzed. It has been established that with an increase in the power density of the LI values, the absorption indicators are stable up to the threshold level $W = 3\cdot10^{10}$ W/m², after exceeding which there is an increase in the value of ε, caused by scattering on convective flows, and at $W \geq 10^{12}$ W/m² relative energy losses are approaching 100%, as the electrolyte is heated to the boiling point.

The AFM method was used to study the topology of the surface of local sediments of a number of metals, as well as their electrochemical "background". It is shown that the crystal structure of the metal coating in the zone of local sediment is ordered and oriented in comparison with the electrochemical background. This is due to the fact that the effect of laser radiation activates the recrystallization processes.

It has been established that with an increase in the intensity of the LI, the average linear size of crystallites of the studied metals in the zone of local sediment increases by 1.5–1.7 times. Compared to the electrochemical background, the structure becomes more densely packed, the depth of the intergrain dips decreases in 1.8–2.0 times, which affects the electrically conductive properties of electroplating.

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