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BRIEF COMMUNICATIONS

EFFECT OF OPTICAL RADIATION IN LOCAL FORMATION OF THIN FILMS BY AN ELECTROCHEMICAL METHOD

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The most important problems in electrodeposition are the raising of the rate of metal deposition and the production of high-quality functional coatings. Various methods are used for their solution: preheating the electrolyte and mixing it, introduction of surfactants, deposition by a periodic current, and activation by laser radiation [1-4]. In local deposition of metal films methods using laser stimulation can find the greatest application since they eliminate preliminary masking of articles and provide the possibility of forming patterned layers with a high resolving power. However, at the present time the processes of interaction of laser radiation with both an electrolyte and the surface of a solid body in electrochemical systems are still not sufficiently well understood.

In our work we present results of an investigation of the spectral characteristics of a series of widely used electrolytes within the wavelength range 0.3-1.1 μm. As electrochemical systems, we selected (the concentration of the components is given in g/liter):

a) a sulfuric acid electrolyte for copper plating, solutions Nos. 1-9, differing in the concentrations of the substances involved (Table 1);

b) a sulfuric acid electrolyte for nickel plating, No. 10 ($NiSO_4 \cdot 7H_2O$, 220; $Na_2SO_4 \cdot 10H_2O$, 80; NaCl, 12; H_3B_3, 35; pH 5);

c) a ferrocyanide electrolyte for silver plating, No. 11 ($AgNO_3$, 40; $K_4Fe(CN)_6 \cdot 3H_2O$, 150; K_2CO_3, 25);

d) a phosphate electrolyte for gold plating, No. 12 (Au in the form of $K[Au(CN)_2]$, 15; $NH_4H_2PO_4$, 25; $(NH_4)_2HPO_4$, 40; pH 5.5);

e) a sulfuric acid electrolyte for tin plating, No. 13 ($SnSO_4$, 40; H_2SO_4, 100; OS-20, 4).

The electrolytes were placed in quartz cuvettes 1, 2, 3, and 5 cm thick.

To investigate the laser action on the solutions in the process of electrolytic deposition, we designed a setup consisting of a laser source, an optical focusing system made of quartz glass ($F1$ = 10 cm, $F2$ = 15 cm, $F3$ = 50 cm), a diaphragm, an IKT-1M laser radiation power meter, and an adjusting coordinate stand. As an optical radiation source, we used the following lasers: LTN-101 (λ = 0.337 μm), LTN-101-2 (λ = 0.537 μm), LGN-701 (λ = 0.632 μm), and GOS-301 (λ = 1.06 μm), which operated in a pulse regime. The spectral characteristics were recorded by Specord M40 and SF-46 spectrophotometers.

Figure 1 gives spectral dependences of the transmission coefficient for electrolytes Nos. 3, 10-13. As follows from an analysis of the figure, the spectral properties of the copper-plating electrolyte in the wavelength range investigated are virtually independent of the sulfuric acid concentration. For each of the electrolytes studied a linear dependence of the optical density on the cuvette thickness is fulfilled; this corresponds to the Bouguer-Lambert-Beer

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TABLE 1. Concentration of $CuSO_4 \cdot 5H_2O$ (C1) and H_2SO_4 (C2) in Copper-Plating Electrolytes

Componenet	Number of the electrolyte								
	1	2	3	4	5	6	7	8	9
*C*1	100	150	200	250	300	200	200	200	200
*C*2	50	50	50	50	50	25	150	75	100

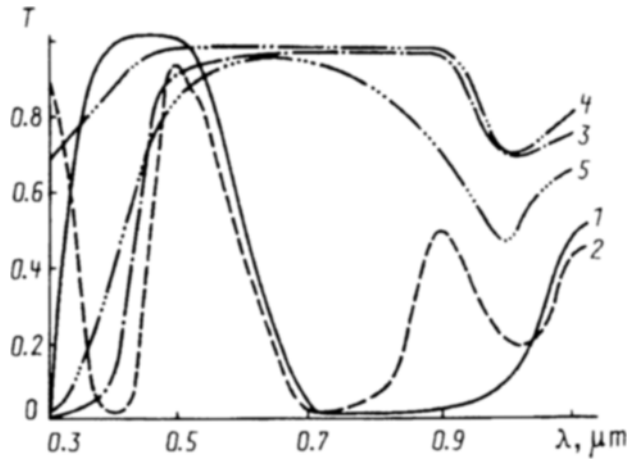

Fig. 1. Dependence of the transmission coefficient on the wavelength for electrolytes Nos. 3 (1), 10 (2), 11 (3), 12 (4), and 13 (5).

law. The dependence of the optical density of the electrolyte on the concentration of blue vitriol obtained for the series of electrolytes Nos. 1-5 at the wavelengths investigated also has a linear character. The different slope of the graphs indicates a substantial dependence of the absorption index of the solutions on the laser source wavelength.

On the basis of the spectra obtained we calculated the absorption indices K_n (cm^{-1}) of all of the investigated electrolytes at the generation wavelengths of the most widely used technological lasers (Table 2). The absorption indices of electrolytes Nos. 6-9 at all the wavelengths are virtually the same and coincide with the corresponding values for electrolyte No. 3. This indicates that the concentration of H_2SO_4 does not exert a substantial effect on the optical properties of the copper-plating electrolyte.

The data of Table 2 allow us to make a justified selection of a laser source whose radiation will exert the maximum effect on the electrolyte (which corresponds to the maximum value of the absorption index) or, hardly affecting the electrolyte properties, will exert an effect directly on the surface of the layer formed (which corresponds to the minimum value of K_n). Thus, for example, to exert the most effective influence on diffusion processes in a copper-plating electrolyte and on its electrochemical parameters, it is advisable to select a laser with $\lambda = 1.06\ \mu m$, and to stimulate and control the regularities of crystallization of thin films, a laser with $\lambda = 0.487\ \mu m$.

It is impossible to provide such ideal conditions in practice and therefore compromise variants are used. For this purpose it is necessary to know the radiation power exactly (both that absorbed by the electrolyte and that incident on the surface of the solid body). In the work we investigated the dependence of the attenuation factor K_0 of a copper-plating electrolyte on the power density P (W/cm^3) of a GOS-301 pulsed solid-state laser ($\lambda = 1.06\ \mu m$, $t = 0.8 \cdot 10^{-3}$ sec). After measurements of the power density at entry into the electrolyte and at exit from it with account for absorption by the cuvette, we calculated the values of the attenuation factor of the electrolyte for the laser radiation. At $P = 1.0$, 3.0, 4.0, 5.0, 6.7, 8.3, and $10.0 \cdot 10^5$ W/cm^2 the quantity K_0 had the values 0.61, 0.66, 0.68, 0.72, 0.78, and 0.80 cm^{-1}, respectively.

It is seen from the data presented that the value of the attenuation factor is stable up to some threshold level ($P = 3 \cdot 10^5$ W/cm^2) and that the optical properties do not change in the electrolyte under investigation. The increase in the attenuation factor with the power density in the laser radiation pulse is explained by the steadily

TABLE 2. Values of the Absorption Index K_n of Electrolytes at the Generation Wavelengths of Technological Lasers

Number of the electrolyte	λ, μm			
	0.337	0.487	0.537	1.060
1	0.084	0.002	0.016	0.610
2	0.133	0.004	0.028	0.642
3 (6-9)	0.193	0.008	0.046	0.666
4	0.210	0.011	0.054	0.676
5	0.268	0.018	0.072	0.711
10	0.203	0.021	0.061	0.590
11	0.300	0.062	0.091	0.100
12	0.061	0.004	0.006	0.113
13	0.157	0.031	0.037	0.319

Note. The averaged value of the radiation power density is $P = 1 \cdot 10^5$ W/cm^2.

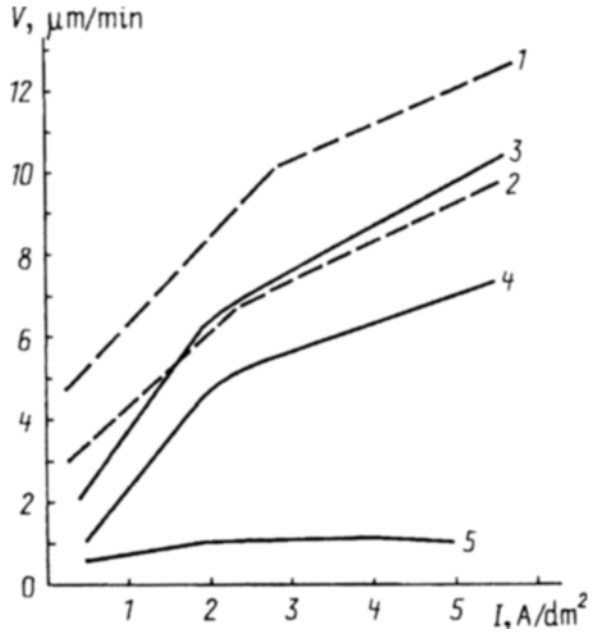

Fig. 2. Rate of deposition of tin as a function of the laser radiation parameters and the substrate material: 1) $\lambda = 0.537$ μm, $P = 5.15 \cdot 10^6$ W/cm^2, steel; 2) $\lambda = 0.537$ μm, $P = 5.15 \cdot 10^6$ W/cm^2, brass; 3) $\lambda = 1.06$ μm, $P = 1.56 \cdot 10^7$ W/cm^2, steel; 4) $\lambda = 1.06$ μm, $P = 1.56 \cdot 10^7$ W/cm^2, brass; 5) without laser stimulation, brass.

increasing heating of the electrolyte, which increases the radiation losses due to scattering. When the power density is $P \geq 10^6$ W/cm^2, during the time of action of a monopulse of duration $t = 0.8 \cdot 10^{-3}$ sec the electrolyte is heated to the boiling temperature and radiation losses in it on vapor bubbles approach 100%. Based on this, we established an admissible limit for the power density in the operation of a laser source in the pulse regime.

The investigations performed made it possible to select the optimum parameters for depositing thin tin films on substrates of brass and steel. The rate of deposition of tin from a sulfuric acid electrolyte is given in Fig. 2. It is seen from the graphs that upon exposure of the electrolyte to laser radiation ($\lambda = 0.537$ μm, $P = 5.15 \cdot 10^6$ W/cm^2) the efficiency of the process increases 12-fold. The coatings obtained are shiny and are attached well to the substrate. Upon changing the laser radiation parameters ($\lambda = 1.06$ μm, $P = 1.56 \cdot 10^7$ W/cm^2), the rate of the process decreases due to increased absorption of luminous energy by the electrolyte column.

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