Optimization of the solution composition for laser-induced chemical liquid phase deposition of copper

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Optimal compositions of autocatalytic solutions for laser-induced deposition of copper were established. The copper salt concentration range in which the process gives the best results was determined. It is shown that optical microscopy, as a means of controlling the topology of the deposited structures, has limited applicability. The results obtained by this method should be verified by alternative techniques, *e.g.*, electron microscopy or measurements of the electrical conductivity of deposited structures.

Key words: laser-induced chemical liquid phase deposition, copper, topology.

Interest in laser-induced chemical liquid phase deposition (LCLD) is due to prospects for its application in microelectronics since the method offers the possibility to deposit various metallic structures on dielectric surfaces without photomask. By scanning the surface of a dielectric immersed into a special solution with a focused laser beam one can locally initiate a chemical reaction of the reduction of metallic copper according to equation[1]

$$CuL^{(n-2)-} + 2\,HCHO + 4\,OH^- \longrightarrow$$
$$\longrightarrow Cu^0 + L^{n-} + H_2 + 2\,HCOO^- + 2\,H_2O, \qquad (1)$$

where L is the organic complexing agent (usually, salts of ethylenediaminetetraacetic acid (EDTA) or sodium-potassium tartrate); formaldehyde HCHO, a reducing agent, is introduced into the solution in a 6—7.5-fold excess. Copper sulfate or chloride are the most often used copper salts.

Laser treatment leads to activation of the dielectric surface[2] and to acceleration of the metallization reaction in the irradiated region due to an increase in temperature within the local volume confined by the focused laser beam.[3—5]

However, the existing regime of the LCLD process is far from being optimum;[1,6] it is characterized by a narrow laser power range, poor reproducibility, and topological defects (in particular, cracks and non-localized deposition nearby the irradiated area). The deposition of high-quality copper structures is reduced to controlled fabrication of continuous high-quality copper tracks. Topological defects can actually deteriorate the electrical properties of the deposited copper structures and thus lead to low conductivity (2—3 orders of magnitude lower than the conductivity of pure copper) or initiate the formation of electric contacts between neighboring copper tracks deposited on the dielectric substrate.

The results of an LCLD process are affected by three groups of factors[6]:

1) physical factors including the wavelength and power of laser radiation, the scan rate, and the temperatures of the environment and solution;

2) chemical factors including the solution composition, the concentrations of components, the pH value, and the chemical reactions in the solution; and

3) properties of the surface of the dielectric substrate, *viz.*, the structure, the presence of activated and catalytic sites, defectness, phase composition, and the chemical properties of the dielectric components.

At present, only the first group of factors was studied in detail, while the works on the other two groups are as yet scarce. In particular, the effect of the chemical composition of solutions (most often, these are solutions for conventional chemical metallization ignoring specific requirements of the LCLD process) is little studied as yet.

The aim of the present study was to optimize the composition of the "basis" solution in order to reveal the concentration ranges in which one can obtain copper conductors with the highest-quality topology (*i.e.*, having clearly defined edges, no cracks and other visible defects).

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Results and Discussion

Table 1 summarizes the results of our investigation of the dependence of the copper track topology on the compositions of autocatalytic solutions (in all solutions, the concentration of formaldehyde is 0.075 mol L^{-1} and that of NaOH is 0.05 mol L^{-1}). The results of deposition are illustrated in Fig. 1 by the results of optical examination of the metallic deposits. The role of "basis" solutions was played by conventional solutions for chemical metallization (see Table 1, samples *1* and *4*).[7,8]

The "basis" solutions containing a copper salt (0.01 mol L^{-1}) and sodium-potassium tartrate (0.03 mol L^{-1}) as complexing agent appeared to be inappropriate for effi-

Table 1. Compositions of solutions for laser-induced deposition of copper*

Sample	$CuCl_2$	Tartrate	EDTA	EDA	*para*-Benzoquinone	Comments
1	0.010	0.03	–	–	–	No reaction
2	0.010	0.03	–	–	0.005	Rapid aging of solution in the entire volume of the cell
3	0.010	0.01	0.0070	–	0.005	Bad topology
4	0.010	–	0.0110	–	–	No reaction
5	0.010	–	0.0110	–	0.005	High-quality copper track
6	0.001	–	0.0011	–	0.005	High-quality copper track
7	0.100	–	0.1100	–	0.005	No reaction
8	0.100	–	–	0.2	–	Dark structures precipitate

*For all solutions: formaldehyde concentration is 0.075 mol L^{-1} and NaOH concentration is 0.05 mol L^{-1}.

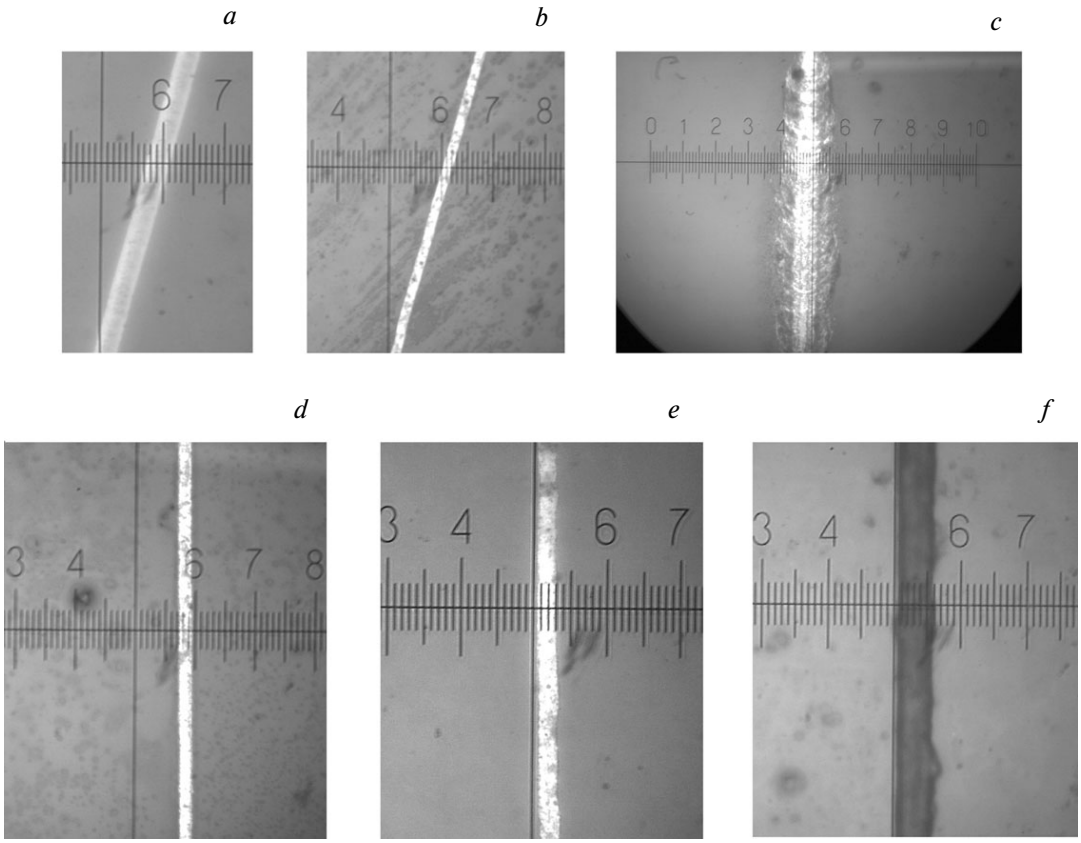

Fig. 1. Photomicrographs of copper structures obtained after laser-induced deposition of copper from solution according to optical microscopy data at *n*-fold magnification. The solution composition: 0.01 *M* $CuCl_2$ (*a*—*d*), 0.001 *M* $CuCl_2$ (*e*), 0.1 *M* $CuCl_2$ (*f*), 0.075 *M* HCHO (*a*—*f*), 0.05 *M* NaOH (*a*—*f*), 0.03 *M* Na—K tartrate (*a*, *b*), 0.04 *M* Na—K tartrate (*c*), 0.005 *M para*-benzoquinone (*b*, *c*, *d*), 0.07 *M* EDTA (*c*, *e*), and 0.011 *M* EDTA (*d*), 0.2 *M* EDA (*f*). Magnification, *n*: ×20 (*a*, *b*, *d*) and ×40 (*c*, *e*, *f*).

cient laser deposition of copper (Table 1, sample *1*). As a result, copper precipitated as a fine semi-transparent deposit (see Fig. 1, *a*).

The introduction of *para*-benzoquinone (0.005 mol L^{-1}) into the same solution (see Table 1, sample *2*) significantly improved the topology of copper conductors (see Fig. 1, *b*). At the same time, the autocatalytic reaction occurred not only within the laser beam focus point, but also extended spontaneously into the entire volume of the cell. As a result, the solution rapidly lost its properties and the cell was covered with copper deposit, which indicated a poor stability of the solution.

To stabilize the solution, the complexing agent, sodium-potassium tartrate, was partially replaced by a more stable complex of copper with EDTA characterized by an instability constant K_{inst} of $1.58 \cdot 10^{-19}$.[9] This led to significant stabilization of the solution and to termination of the sponaneous reaction in the bulk of the solution. However, the laser-induced reaction in this solution (see Table 1, sample *3*) resulted in a copper track with bad topology appeared as broad diffuse tail (see Fig. 1, *c*).

To improve the topology of deposits, we studied the possibility of complete replacement of the complexing agent sodium-potassium tartrate ($K_{inst} = 8.66 \cdot 10^{-6}$) by a conventional solution[7,10] with a more stable complex of copper with EDTA[9] (see Table 1, sample *4*). It was expected that the use of a more stable complex should slow down the autocatalytic reduction of copper outside the laser beam focus point, thus localizing it and improving the topology of copper structures. However, an attempt to initiate the reaction of laser-induced deposition failed probably due to a high activation energy of dissociation of the copper complex with EDTA, which suppresses the appearance of copper ions in solution in the amount necessary to overcome the activation barrier to crystallization.[11]

To compensate the kinetic retardation of the reaction by a stable complexing agent, *p*-benzoquinone (0.005 mol L^{-1}) was introduced into a series of solutions containing the copper complex with EDTA (see Table 1, sample *5*) by analogy with the sample *2*. In this case, a 20-μm wide copper track with high-quality topology and admissible geometry was obtained (see Fig. 1, *d*).

To investigate the effect of the concentration of the copper salt on the geometry of deposited structures, copper structures were deposited from a solution with a copper salt concentration of 0.001 mol L^{-1} (tenfold dilution). It was assumed that such a dilution will make it possible to obtain copper tracks whose width will be close to the diameter of the focus point (about 5 μm). Indeed, in this case an optical microscopy study revealed the formation of nearly 7-μm wide, high-quality copper tracks (see Table 1, sample *6* and Fig. 1, *e*).

Thus, in the salt concentration range from 0.001 to 0.01 mol L^{-1} one can obtain copper tracks with a high-quality topology and controlled geometry (see Table 1). The lower limit of the $CuCl_2$ concentration (0.001 mol L^{-1}) corresponds to the tracks with the highest-quality topology and a minimal width of 7 μm.

No deposition from a concentrated copper solution (0.1 mol L^{-1}) was initiated in the presence of *p*-benzoquinone with EDTA as a complexing agent (Table 1, sample *7*). This is probably due to a relatively high optical density of such a solution with a high concentration of copper chloride. As a result, laser radiation is to a great extent absorbed in the bulk of the solution and the remaining proportion of its radiation is too low to initiate the LCLD reaction.

The last complexing agent studied in this work was ethylenediamine (EDA). In conventional chemical deposition of copper, the introduction of EDA makes it possible to obtain a more smooth topology, a more uniform size distribution of copper grains, and a lower resistivity.[10] Our preliminary experiments revealed that after the introduction of a complex with EDA into the modified solutions for laser deposition their functional stability is more than five times higher than that of the tartrate complexes. Accordingly, the width of the deposited copper structures can be varied controllably in the range 20—50 μm. Note that the topology of the metallic structures obtained deserves additional investigations because the black color of the deposit suggests the presence of a large amount of crystallites of insoluble copper compounds. Both these effects caused by EDA are due to the fact that the instability constant of the copper complexes with EDA (see Ref. 12) in the second step ($K_{inst} = 3.98 \cdot 10^{-10}$) is lower than that of the complex with tartrate ($K = 8.66 \cdot 10^{-6}$). Therefore, using the EDA complexes in solution instead of the tartrate complexes, one would expect efficient control of the process of laser deposition *via* programming of the width of the deposited structures and the time interval of stability of the properties of the deposition solution.

Taking into account these factors, we studied a solution containing a copper salt (0.1 mol L^{-1}), EDA (0.2 mol L^{-1}), and sodium hydroxide (0.5 mol L^{-1}) (see Table 1, sample *8*). This composition was chosen with allowance for the fact that the copper complex with EDA has a two-step dissociation constant unlike the tartrate and EDTA complexes. In addition, the lower values of the stability constant compared with that of EDTA would allow copper to be deposited from more concentrarted solutions of the copper salt (0.1 mol L^{-1}). For this composition of the solution, the laser deposition reaction was initiated with ease and subsequent deposition proceeded without noticeable gas evolution. A large number of deposited structures was analyzed by optical microscopy (Fig. 1, *f*); dark color of the deposits (no copper glance) suggested the deposition of products of a copper reaction with an amino group of EDA rather than copper *per se*.

Summing up the results obtained (see Table 1, samples *1*—*8*) in our study on optimization of the composition of the solution for laser-induced deposition, the use of solutions containing copper (0.001—0.011 mol L^{-1}), EDTA (0.0011—0.011 mol L^{-1}) as complexing agent, sodium hydroxide (0.5 mol L^{-1}), and *p*-benzoquinone (0.005 mol L^{-1}) as a promoter of the laser deposition reaction seems to be an optimal choice.

All subsequent experiments on laser deposition of copper and copper alloys were carried out using the series of solutions outlined above in the specified concentration range.

To check and refine the results of our study of the deposited copper structures, we investigated the deposites using an electron microscope equipped with an accessory for energy dispersive X-ray (EDX) analysis. In some cases, EDX analysis makes it possible to carry out quantitative elemental analysis of a sample[13] and to determine which product is deposited during the laser-induced process (pure copper or copper compounds).

To analyze the deposits, copper tracks were deposited from four solutions of the copper complex with EDTA of different composition (Fig. 2). Having analyzed the SEM images of the tracks deposited from the copper solutions with concentrations of 0.010, 0.008, 0.006, and 0.004 mol L^{-1} (see Fig. 2), one can conclude that the decrease in the solution concentration below 0.01 mol L^{-1} by at least 20% causes the deposition of copper in the form of individual microcrystals with different surface coating density rather than continuous tracks. The amount of copper deposited abruptly decreases when using more dilute solutions, and only fragmentary deposition is observed at a copper concentration of 0.004 mol L^{-1}. This deposition pattern supports the idea that laser deposition begins at activated sites of the dielectric surface and then develops by heterogeneous centers of crystallization.[14,15]

The spectra obtained from the regions of the copper tracks and dielectric substrate (quartz glass, SiO_2) shown in Figs 2, *a* and 2, *c* are presented in Figs 3 and 4, respectively. The spectrum of the dielectric substrate (Fig. 3, *c*)

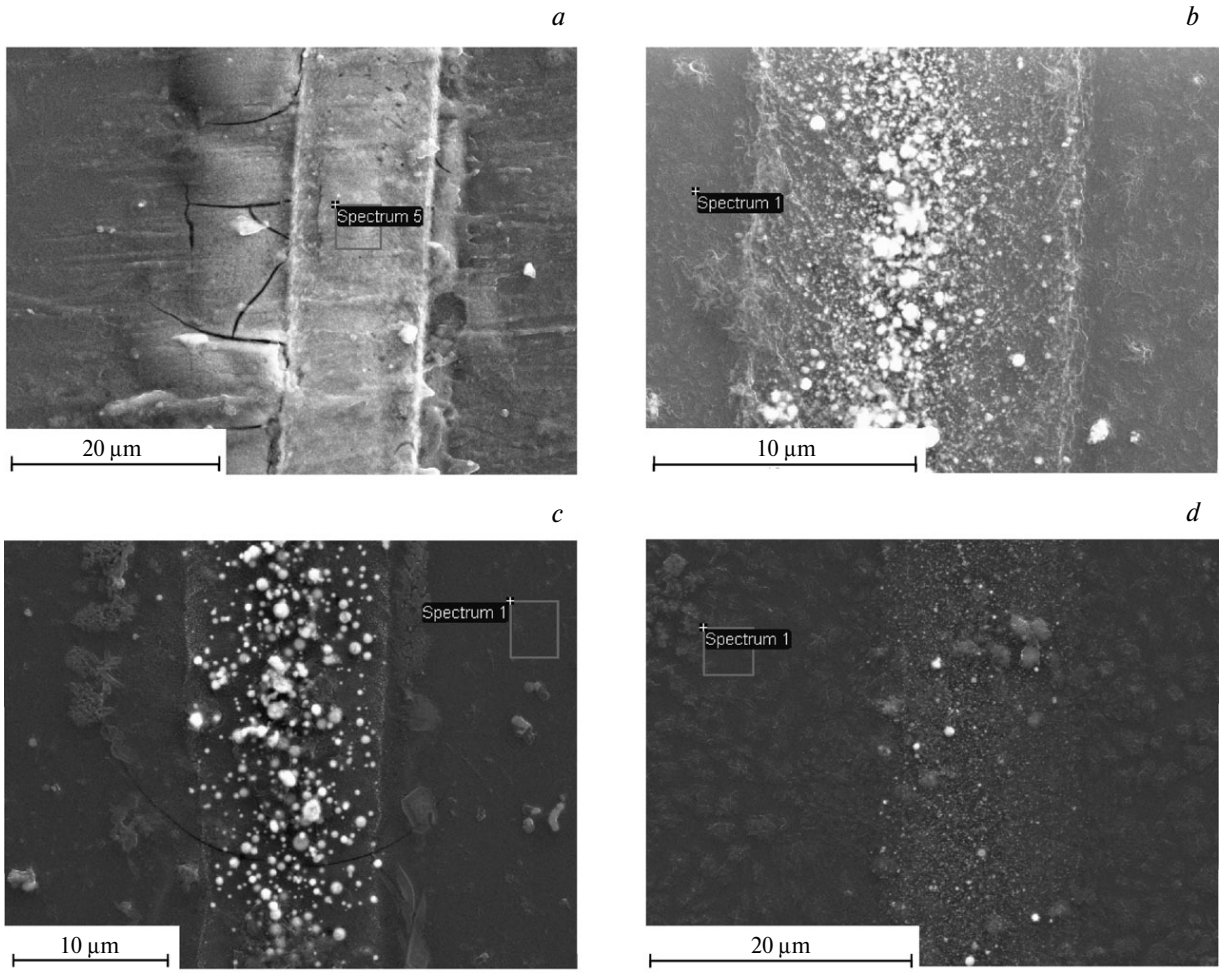

Fig. 2. SEM images of copper structures formed by copper deposition from solutions. The solution concentrations are 0.01 (*a*), 0.08 (*b*), 0.06 (*c*), and 0.04 *M* $CuCl_2$ (*d*).

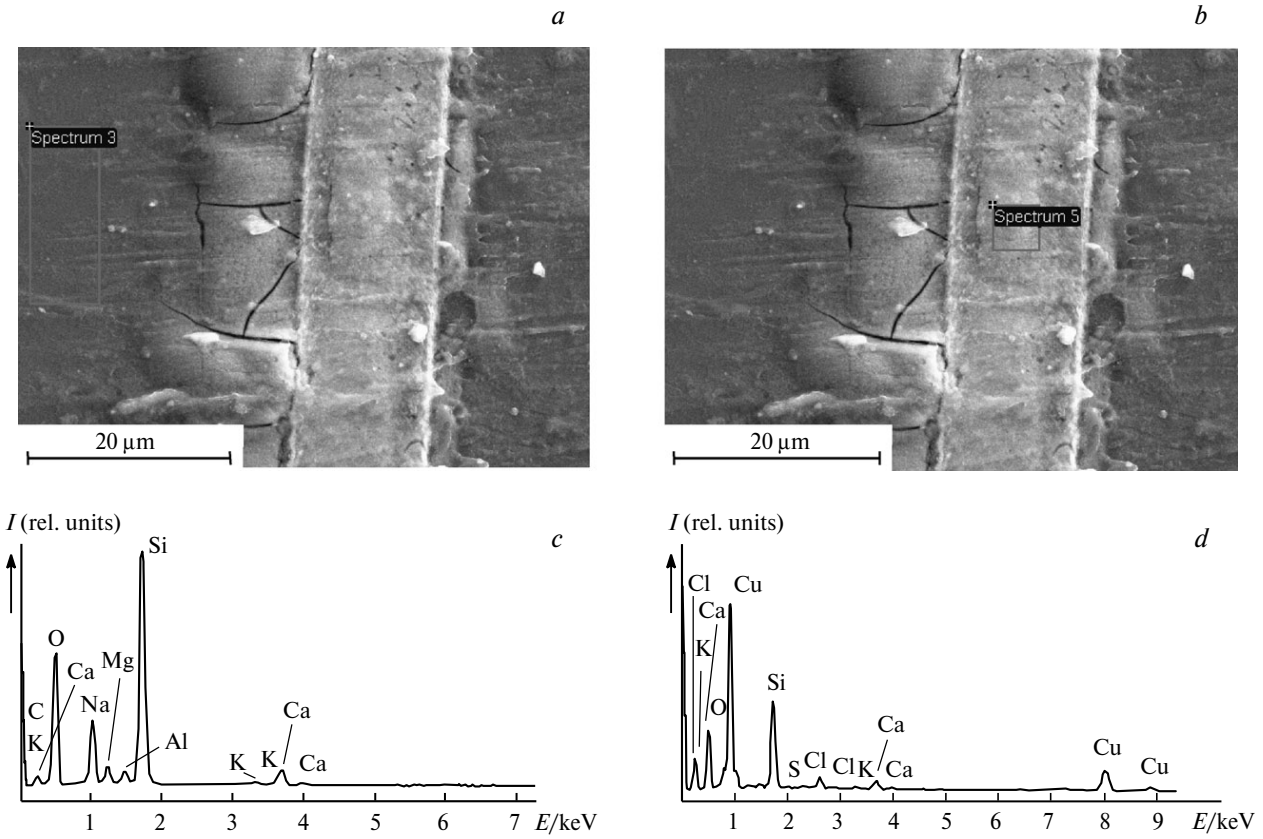

Fig. 3. SEM images of a copper track deposited from a 0.01 *M* $CuCl_2$ solution (*a*, *b*; rectangles denote the regions in which EDX spectra were recorded) and the EDX spectra of dielectric substrate regions without deposited copper (*c*) and with copper deposited on the cutter head (*d*).

corresponding to the 0.01 *M* $Cu(EDTA)^{2-}$ solution (see Fig. 3, *a*) exhibits signals of Si and O atoms of SiO_2, the major component of the substrate (oxide glass). Signals of Si and O atoms in the spectrum (Fig. 3, *d*) of the deposited copper structure (Fig. 3, *b*) suggest a small thickness of the deposited copper track. Namely, the energy of electrons accelerated in the electric field allows them to pass through the copper film and detach electrons from atoms of the dielectric substrate, thus initiating the characteristic emission of Si and O atoms. Weak signals of Mg, K, and Ca also probably originate from impurity inclusions into the dielectric substrate. In the second spectrum, the most intense signal is that of copper, which confirms the deposition of copper on the dielectric surface in the form of a continuous track. The only compositional defect is a weak peak attributable to chlorine (2.6 keV) which is apparently transferred from the $CuCl_2$ solution into microscopic defects of the copper deposit.

Figure 4, *b* shows the EDX spectrum of copper inclusions (see Fig. 4, *a*) and the corresponding region of point analysis. The results of point EDX analysis of individual microcrystals deposited from dilute solutions indicate that the crystals contain copper atoms, a small amount of oxygen (copper oxide surface layer), and a negligible amount of chlorine. Based on the spectrum, the content of oxygen and chlorine atoms in the sample is low. The Si peak is due to the substrate material and the C peak originates from a small amount of organic components of the solution adsorbed on the substrate surface. The peak of sulfur is probably due to a large error of the method in the region of analysis of light elements. Only weak peaks corresponding to Cu and Si atoms are observed at energies higher than 5 keV.

Figure 5 presents a SEM image of the surface and the EDX spectrum of the copper structure deposited from the solution of sample *3* containing a mixture of two complexing agents, copper tartrate and copper trilonate, with a copper concentration of 0.01 mol L^{-1} in the solution. The SEM image shows that copper deposition from the copper tartrate-trilonate solution occurs nonlocally and a rather large amount of copper is deposited outside the laser focus point, as was detected earlier by optical microscopy (see Fig. 1, *c*). Copper deposited from the tartrate-trilonate solution is of very high purity because only weak peaks of oxygen, potassium, and carbon atoms are detected. These peaks are probably due to adsorption of the solution components (tartrate and potassium ions) on the surface of the deposited copper. At a magnification

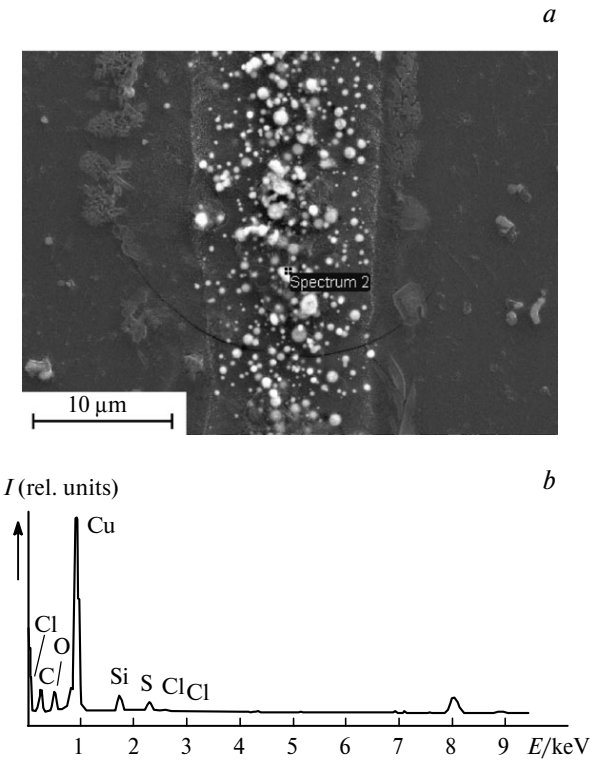

Fig. 4. SEM image of a copper track deposited from a solution containing 0.006 mol L^{-1} of copper complex (*a*) and the EDX spectrum of a copper microcrystal on the dielectric surface (*b*).

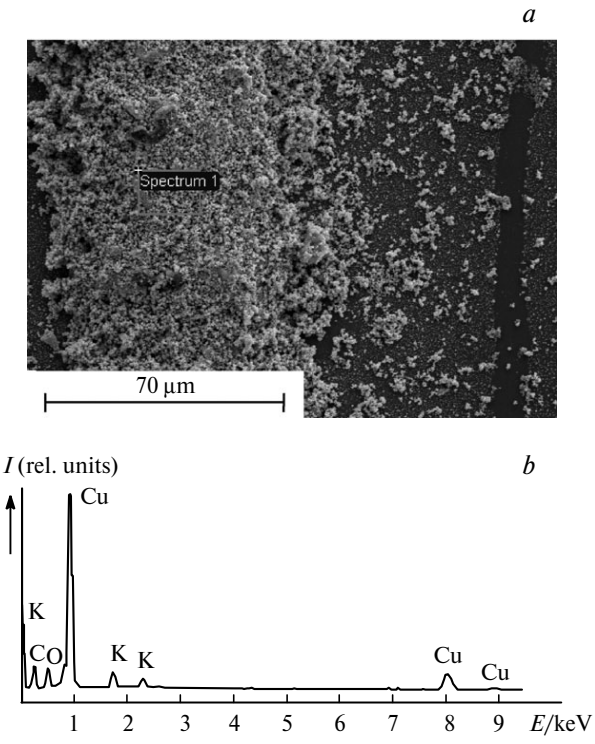

Fig. 5. SEM image of copper deposited from the tartrate-trilonate solution of copper (*a*) and the EDX spectrum of the central region of the copper track (*b*).

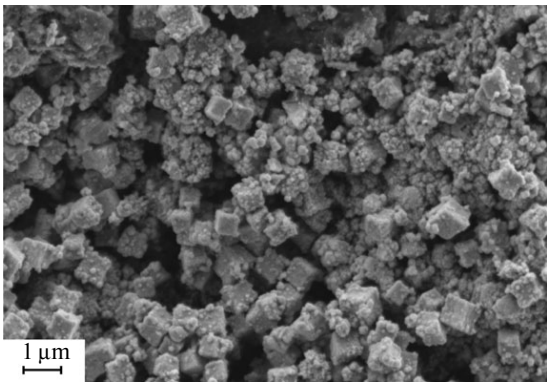

Fig. 6. SEM image of copper microcrystals deposited from 0.01 *M* copper tartrate-trilonate solution.

of ×8000, scanning electron microscopy allows one to observe the formation of individual copper microcrystals on the dielectric surface (Fig. 6). The SEM image clearly demonstrates individual cubic copper crystals from 100 to 1000 nm in size; this clearly illustrates the crystal growth in the copper deposit obtained by laser-induced deposition. An analysis of the SEM images (see Fig. 2) suggests that the solutions with copper concentrations of 0.01 and 0.008 mol L^{-1} can be used for the deposition of continuous copper structures with high electric conductivity. On the other hand, the solutions with the copper concentrations equal to 0.006 mol · L^{-1} and lower can be useful for predeposition of copper and activation of the desired regions of the dielectric substrate to conduct an electrodeless autocatalytic deposition of copper from heated solutions without using a laser. The regions with the predeposited copper can serve as catalytic areas for local deposition of copper.[2]

The intensity of a peak is proportional to the concentration of an element in the sample; therefore, the intensity ratio of the silicon and oxygen peaks in the spectra should specify the distribution of oxygen between silica and copper oxide (if the intensity ratio I_{Si}/I_O in the spectrum of the copper track is lower than in the spectrum of the glass, the track contains a large amount of copper oxide). However, a small decrease in the I_{Si}/I_O ratio will indicate the presence of a copper oxide surface film forming as a result of oxidation of the metal by atmospheric oxygen rather than deposition of copper in the form of CuO. The observed spectra (see Fig. 2—4) and the characteristic cubic shape of microcrystals (see Fig. 5) suggest that the deposit comprises crystals of pure copper with small amounts of impurities due to sorption of components of the solution.

Summing up, in the present study we determined the optimal compositions of autocatalytic solutions, which allow one to carry out laser-induced deposition of copper structures with a reasonably good topology, and found the concentration ranges of the copper salt in which the pro-

cess gives the best results. Also, we showed that optical microscopy is of limited use for controlling the topology of deposited structures and the results obtained by this method need to be verified indepedently by, *e.g.*, electron microscopy or by measuring the conductivity of deposited structures.

Experimental

Copper structures were deposited using a continuous multimode-operated Ar^+-laser (power range from 30 to 1000 mW). A laser beam ($\lambda = 488$ nm) was focused using an optical system on a flat dielectric substrate made of quartz glass. It was possible to move the substrate relative to the laser beam focus point on a motorized micrometric positioning actuator at a velocity of 0.01 mm s^{-1}.

The topology of deposited copper structures was analyzed using a MIKMED-6 reflection metallographic microscope (eyepieces with optical magnifications ×10, 20, and 40).

An electron microscopy study and recording of EDX spectra were carried out with a Zeiss Supra 40VP scanning electron microscope equipped with a field emission cathode, a GEMINI electronic optics column, and an oil-free vacuum system with a variable pressure (VP) operating mode at the Interdisciplinary Resource Center for Nanotechnology, Saint Petersburg State University. The spectra were recorded at *n*-fold magnification (up to ×8000).

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