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Laser-induced chemical liquid phase deposition of copper from aqueous solutions without reducing agents

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Abstract. **Laser-induced chemical liquid phase deposition of copper without a traditional reducing agent has been used for the first time to obtain conductive patterns on a dielectric surface having a reducing ability. It is shown that phenol-formaldehyde binder of the dielectric (glass fibre) can successfully play the role of a reducing agent in this process. The resulting copper sediments have low electrical resistance and good topology.**

Keywords: *laser-induced chemical liquid phase deposition, copper, solution, glass fibre, topology, conductivity.*

1. Introduction

Interest in the method of laser-induced chemical liquid phase deposition of metals is due to the prospects for its application in microelectronics and technology since the method offers a possibility to deposit a variety of metal structures on a dielectric surface without a photomask. Scanning the surface of a dielectric, immersed in a special solution, with a focused laser beam enables localised initiation of a reducing chemical reaction in metallic copper in accordance with the equation [1]

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

where L is the organic ligand [usually disodium salt of ethylenediaminetetraacetic acid (EDTA)]; HCHO is formaldehyde (the reducing agent, which is introduced in the 6–7.5-fold excess compared with the concentration of copper salt).

The process of laser-induced chemical liquid phase deposition of copper from a solution is hindered by the fact that reaction (1) proceeds not only on the deposited surface, but in the whole volume of the solution, which impairs its localisation in the focus of a laser beam and reduces the quality of the patterns [1–3]. Using the results of papers [4, 5] on the deposition of copper, equation (1) can be used to prepare patterns, whose electrical resistivity turns to be 2.5–4 orders of magnitude higher than that of pure copper [6]. In this case the length of continuously deposited copper patterns does not exceed 1–2 mm [4, 5].

One way to improve localisation of copper sediments in laser-induced chemical liquid phase deposition is the use of reducing agents, which are localised on the surface of the substrate and reduce the contribution of bulk processes. These reducing agents could be phenol-formaldehyde resins [7, 8], releasing in thermal hydrolysis formaldehyde, which is a reducing agent in reaction (1), and other molecules with reducing properties. In this case, the task is facilitated by the fact that among the dielectric substrates intended for electrical purposes, the most common is glass fibre, which contains phenol-formaldehyde resin as a binder. In addition, high local temperatures are produced in the focus of a laser beam and the hydrolysis of phenol-formaldehyde resin will proceed on the dielectric surface. Thus, in the process of laser deposition there are conditions under which a glass fibre binder can serve as a reducing agent.

In this paper we investigate the possibility of laser deposition of copper on glass fibre during reaction (1) in the absence of a reducing agent in the solution, phenol-formaldehyde resin contained between glass fibre serving as a reducing agent.

2. Experimental technique

Experiments on laser-induced chemical liquid phase deposition of copper were performed on a setup shown in [5]. To deposit copper patterns we used a cw multimode Ar^+ laser with an output power of 30–2000 mW at a wavelength of 488 nm. The power density in the reaction zone was $\sim 10^5$ W cm^{-2}. The laser beam was focused by an optical system on a flat dielectric substrate of STEF-1 glass fibre, which is moved relative to the focal point at 2.5 μm s^{-1}.

Analysis of the topology of the deposited copper patterns was carried out using a MIKMED-6 reflective metallographic microscope (eyepieces with 10-, 20- and 40-fold magnification). Electron microscopic study and energy dispersive X-ray spectroscopic (EDX) microanalysis were performed with a Zeiss Supra 40VP scanning electron microscope (SEM) (equipment of the Interdepartmental Nanotechnology Program of the Resource Centre at St. Petersburg State University). Registration was carried out at different magnifications (up to 8000-fold magnification).

Impedance spectra of copper patterns in the case of alternating current were recorded with an Z-2000 (LLS 'Elins') impedance meter (the frequency range, 20 Hz–2 MHz; the signal amplitude, 125 mV). The electrical resistance of the sediment was measured within 25 days after its deposition (with a 3-day interval).

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As a dielectric substrate with reducing properties, use was made of STEF-1 glass fibre, which is a frame made of fibreglass impregnated with a binder based on the phenol-formaldehyde resin.

The solution for the laser-induced deposition in the absence of a reducing agent had the following chemical composition: $CuCl_2$ (0.01 M), EDTA (Trilon B) (0.011 M), n-benzoquinone (0.005 M), NaOH (0.05 M).

3. Results and discussion

We investigated laser-induced chemical liquid phase deposition of copper on the glass fibre from a solution that differs from the standard one by the lack of formaldehyde [1]. The absence of a reducing agent in the initial solution eliminates the possibility of a reducing reaction (1) in the volume, i.e., outside the dielectric surface. To reduce the threshold of the laser-induced deposition reaction initiation, n-benzoquinone was added in the solution [3]. As a result of laser-induced deposition of copper under these conditions we obtained patterns, which according to optical microscopy (Fig. 1) have the characteristic copper luster and quality topology.

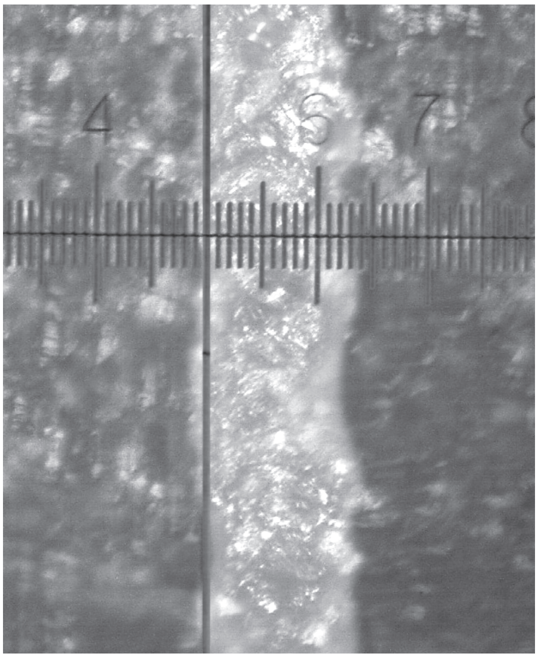

Figure 1. Microphotograph of a copper pattern formed by laser-induced chemical liquid phase deposition of copper on STEF-1 glass fibre, obtained with a MIKMED-6 microscope having an eyepiece with 20-fold magnification.

To test and refine the results we studied deposited copper patterns using a scanning electron microscope with an EDX attachment.

The SEM micrograph of the copper pattern (Fig. 2), deposited on the surface of the STEF-1 glass fibre, shows that the sediment has a spherical shape 30 to 70 μm in diameter. The EDX-analysis (Figs 3d–f) of different parts of the sediment (Figs 3a–c) showed that the composition of the sediment varies from pure copper (Fig. 3d) to silicate glass (Fig. 3e) that is used to reinforce glass fibre. In the sediment there are also intermediate regions with a mixture of these components (Fig. 3f).

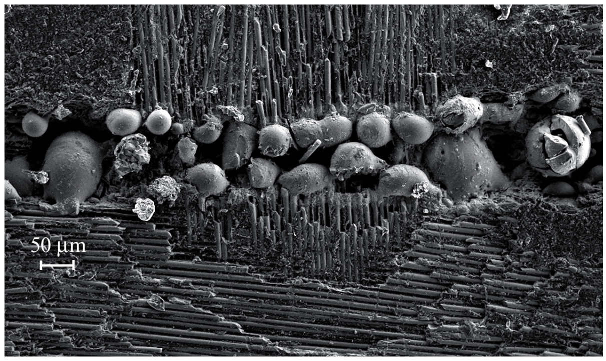

Figure 2. SEM microphotograph of the copper sediment formed as a result of laser-induced chemical liquid phase deposition on the surface of STEF-1 glass fibre. The width of the pattern is 80 mm.

Most likely, the sediment represents spheres of silicate glass coated with a layer of copper. Apparently, in the laser beam focus the silicate glass reinforcing glass fibre melts, resulting in a system of two immiscible liquids, i.e., an aqueous solution and glass melt, and copper is deposited in the form of a thin layer at the interface between two immiscible phases.

The study of electrical properties of the deposited patterns showed (Fig. 4) that the active electrical resistivity of the sediment is equal to $\sim$1.8 Ω cm^{-1}, which is close to the specific resistivity of pure copper. In addition, the magnitude of the active component of the impedance is almost unchanged over time (Fig. 4b). The length of the deposited continuous conductive copper patterns was at least 12 mm (it is limited by the setup capcity).

4. Conclusions

Thus, we have shown that laser-induced chemical liquid phase deposition of copper on the glass fibre which is impregnated with a binder based on the phenol-formaldehyde resin in the absence of a reducing agent in the solution allows one to obtain high-quality copper patterns with high electrical conductivity. It makes it promising to further study the possibility of using dielectrics having reducing properties in the reaction of laser-induced deposition of copper without a traditional reducing agent in the solution in order to employ the results obtained in microelectronics.

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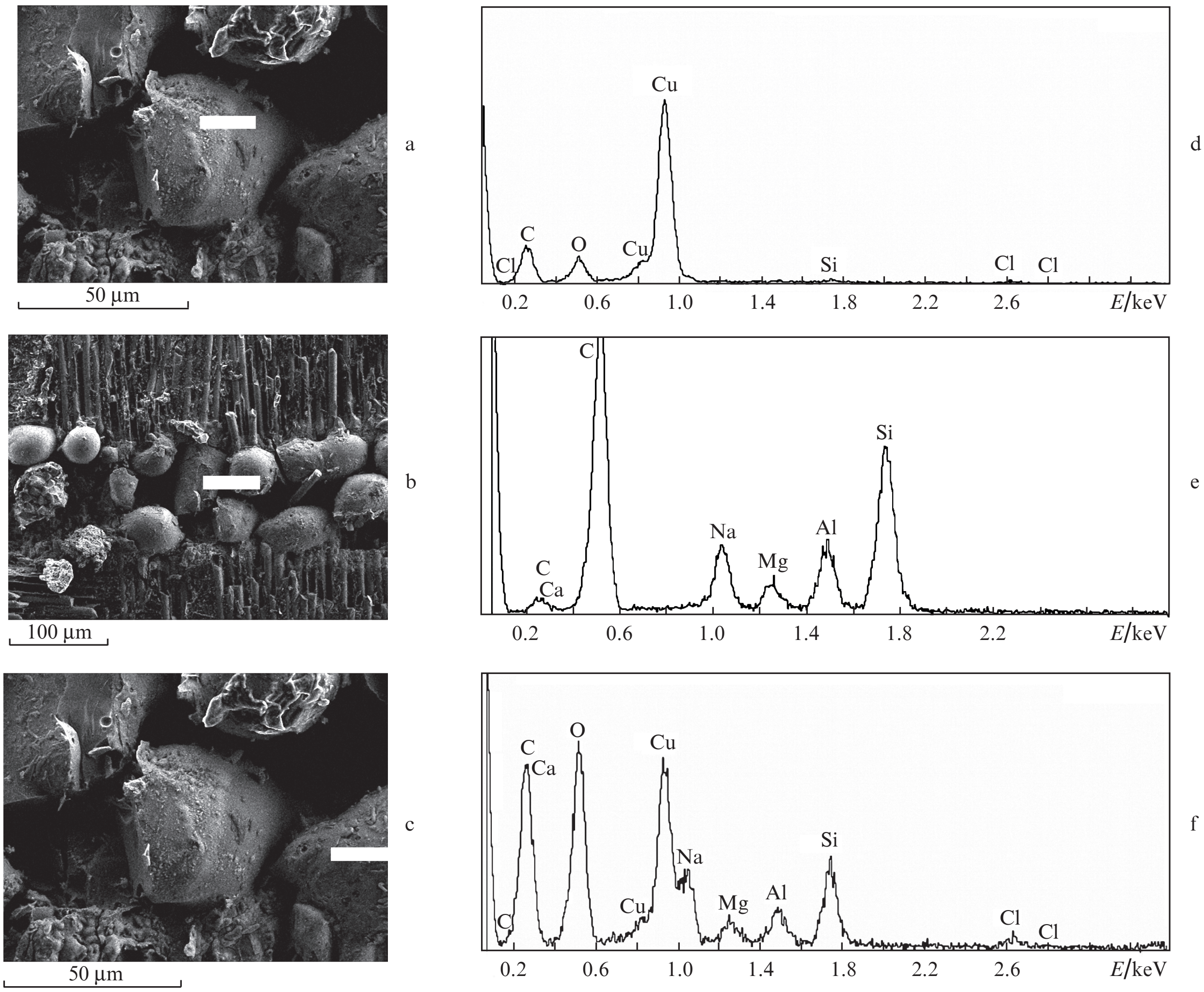

Figure 3. Microphotographs of copper sediments (a–c) and their EDX spectra (d–f) [white rectangles in the photographs (a–c) show the place of registration of the spectra], where the main components are copper (a, d), silicate glass (b, e) and a mixture of copper and glass (c, f); E is the energy of characteristic X-ray emission of the atoms.

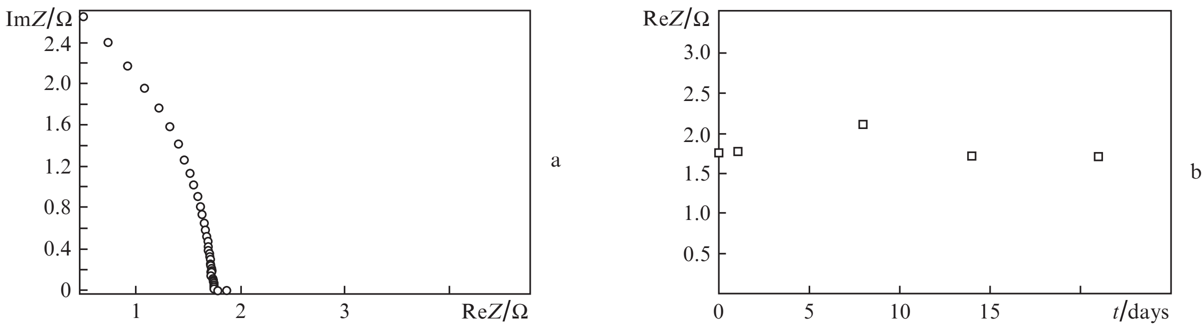

Figure 4. Hodograph of impedance Z of a copper pattern deposited on the surface of STEF-1 glass fibre (a), and time dependence of the active component of the electrical resistance (b).

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