Laser metallization of curved surfaces from deep eutectic solutions

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The development of electronics poses challenges that are difficult to solve using traditional methods, including obtaining metal coatings on a curved surface. One of the methods of solving this problem is presented — laser deposition of metallic copper on a curved glass substrate. A glass cylinder with a radius of 5 mm was selected as a demonstration substrate. The minimum width of the deposited track was 52 μm, the width deviation did not exceed 10% over the entire curved surface.The specific resistance of the track did not exceed $0.6\,\Omega \cdot \mathrm{mm}^2 \cdot \mathrm{m}^{-1}$, which allows the method to be used to create copper coatings — components of electronic devices. To demonstrate the capabilities of the method, grids with a cell size of 500 μm were deposited.

Keywords: curvilinearity, laser, deposition, metallization.

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The deposition of metal coatings with a complex geometry onto curved surfaces is one of the most formidable challenges in modern electronics. The traditional method (photolithography [1]) has significant limitations in application to substrates of a complex geometry. In addition, this method is extremely cost-intensive. Direct printing methods, such as inkjet printing and laser sintering [2–4], are used as an alternative. They are much more accessible and open up new opportunities for deposition of metal films onto curved substrates. Owing to its low electrical resistance and the feasibility of production of inks with a low oxide phase content, silver serves as the main metallization material in these methods. However, they require the construction of complex systems of several synchronized additive setups to obtain high-quality conductive coatings on surfaces of a complex geometry [5,6]. In addition, there is a need to switch from silver to copper in order to reduce the cost of fabricated devices.

Thus, no currently available methods combine relative simplicity and low cost with a high quality of the resulting coatings and their application directly to a curved substrate. In the present study, we propose to solve the indicated problem by producing copper coatings via laser-induced chemical deposition (LICD). The deposition process involves irradiating the working solution with a laser, which induces local heating and a chemical reaction of metal reduction from salt. This process and the results of fabrication of conductive coatings on flat substrates were discussed in more detail in [7–9].

Test tubes made of sodium silicate glass were used as substrates in the present study. Their height is 40 mm, and the radius of curvature is 5 mm. Surface cleaning was performed in several stages. The sample surface was first processed mechanically in an aqueous solution of sodium hydroxide. After that, the sample was washed in deionized water and isopropyl alcohol. Drying was performed by purging the tubes with atmospheric air at room temperature.

A deep eutectic solvent (DES) was used for the working solution. Compared to aqueous solutions of metal salts, it allows one to obtain higher-quality copper coatings at higher scanning rates. In addition, DES is more environmentally friendly and safer (see a more detailed comparison in [9]). DES is a mixture of choline chloride, citric acid, and copper acetate dihydrate in a molar ratio of 1:1:1. The needed weighed quantities of substances were mixed and heated at 100°C for 30 min. The mixture began to melt in the process. After this, the weighed sample was transferred to a magnetic stirrer and stirred for 8 h at 300 rpm and a temperature maintained at 100°C. For application to the substrate, DES was mixed with water in a ratio of 2.5:1 (DES:water) by weight in an ultrasonic bath. The obtained solution was applied to curved surfaces by dripping (100 μl of the working solution per a surface area of 20×20 mm). Following deposition, all samples were dried in a drying oven at a temperature of 70°C for 10 min with periodic (every minute) turning performed to achieve a uniform film distribution. This approach made it possible to fabricate reproducible films. A SOLAR LS PX 110 picosecond laser with a focal spot diameter of 20 μm was the radiation source. The power density was 127.3 kW/cm^2. The scanning rate was 7.5 mm/s. The beam was controlled by a galvanometer scanner. The transition from a planar surface to a curved one was made possible by the use of a medium-focal-length lens in the system, since it provides a sufficient depth of focus within a working field of 50 mm. This makes it unnecessary to design a complex laser focusing system for preserving the deposition parameters. The specifics of focus positioning are illustrated schematically in Fig. 1, *a*. The key feature is that the focal plane is positioned at half the curvature height (h). This is attributable to the need to

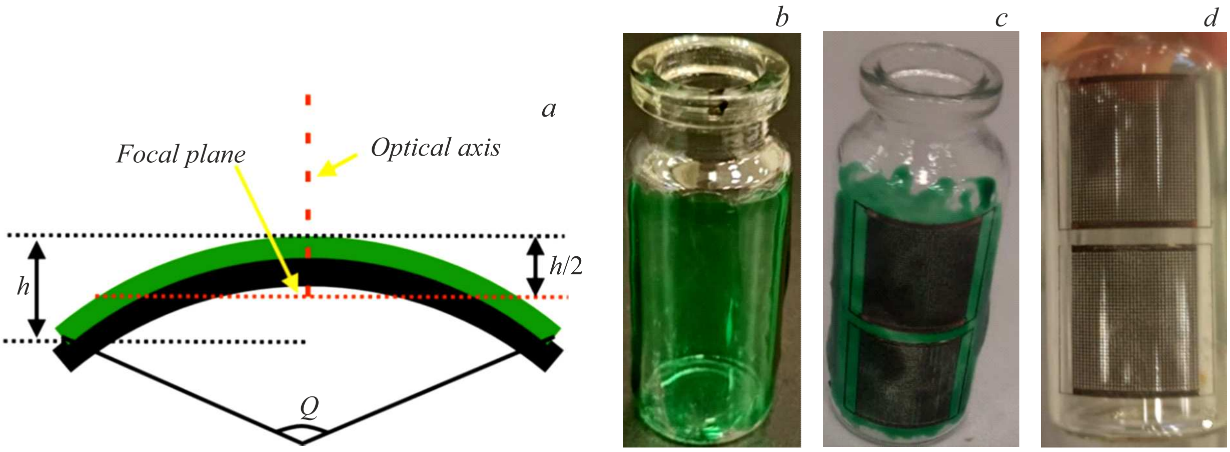

Figure 1. *a* — Specifics of focus positioning in the course of deposition; *b* — deep eutectic solvent applied to a tube; *c* — deposited grid before washing; and *d* — grid after cleaning.

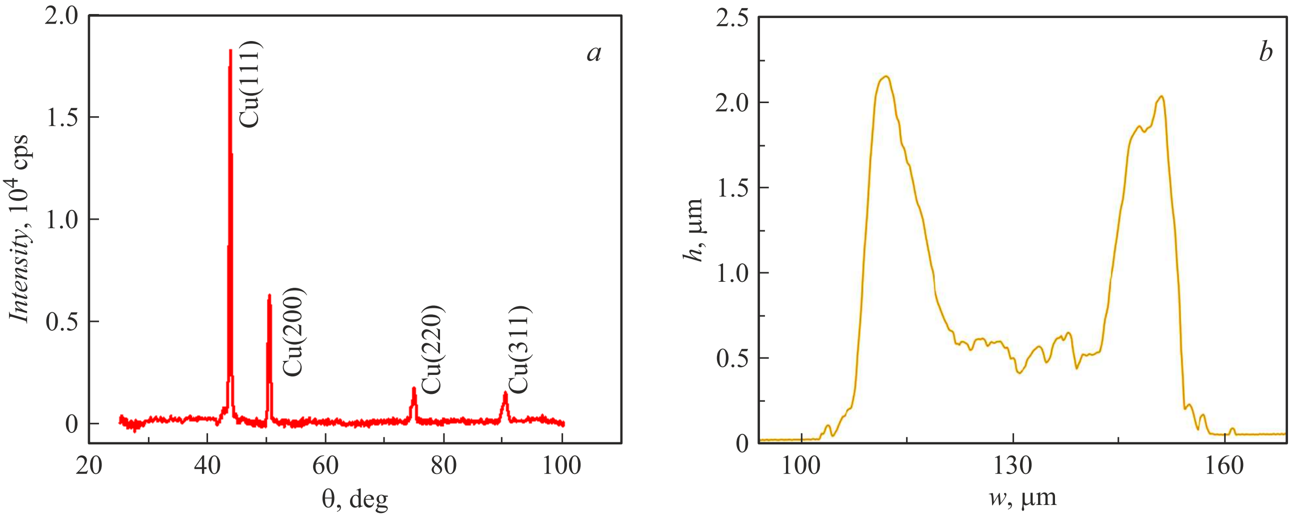

Figure 2. *a* — XRD spectrum (Shimadzu XRD-7000 setup); *b* — profile of the obtained tracks.

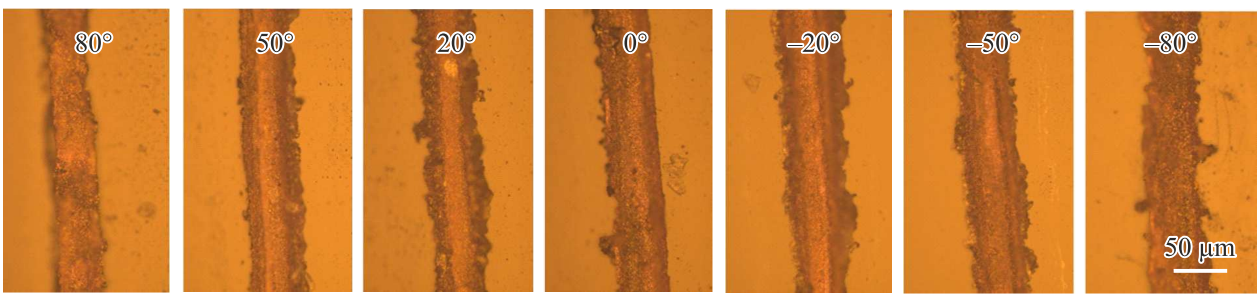

Figure 3. Photographic images of individual tracks obtained at different values of the half-central angle (the sign indicates the position of a track relative to the optical axis).

minimize the variation of area of a laser spot on the surface in the process of scanning of curved substrates, which, in turn, allows for a significant increase in central angle (Q) at which the coating is deposited (up to 160°). The experimental coatings are shown in Figs. 1, *b–d*. An example of DES application to a surface is presented in Fig. 1, *b*; owing to the specifics of the used application procedure, thickening of the solution is observed only at the DES coating edges. The produced grid with a cell size of 500 μm is completely electrically closed; the sheet resistance is 40 $\Omega/\square$.

Variation of width w of an individual track with central angle

$Q/2$, deg	w, μm
80	49
50	53
20	54
0	50
−20	54
−50	52
−80	53

X-ray diffraction (XRD) analysis (Fig. 2, a) revealed that the composition of tracks corresponds to metallic copper with reflection angles (111), (200), (220), and (311) and matches the results of previous studies [7]. Thus, the used method of application and deposition and the transition to curved substrates do not exert any significant influence on the composition.

The profile of the resulting tracks is typical of the LICD method. The measured track profile has a minimum in the center due to the Gaussian distribution of laser radiation power (Fig. 2, b). A KLA Tencor P-7 profilometer was used for profile measurements. The variation of central angle during deposition does not affect the nature of the profile. The widths of single tracks (Fig. 3) corresponding to different values of the half-central angle are listed in the table. Measurements were carried out with an Axio Imager Vario A2M microscope. The typical resolution was $52\,\mu$m. The width variation remains within 10% regardless of the angle of deviation from the optical axis, which is commensurate with the width drift of each individual track. Thus, the variation of central angle has virtually no effect on the geometry of deposited tracks. Measurements of specific resistance were performed in order to determine whether formed copper tracks are suitable for the production of optoelectronic device parts. A Keysight 34460A multimeter was used in these measurements. The specific resistance of the obtained tracks was $0.6\,\Omega \cdot \mathrm{mm}^2 \cdot \mathrm{m}^{-1}$, matching the results obtained on flat substrates [7] and verifying the suitability of the method for construction of optoelectronic device parts.

Thus, a method of laser metallization of curved surfaces from deep eutectic solutions was demonstrated. The minimum width of a single track was $52\,\mu$m within the entire area of a curved surface with a radius of curvature of 5 mm. The profile of the deposited track corresponds to the one typical of LICD. The width of a single track varies within 10%, and the specific resistance of a single track is $0.6\,\Omega \cdot \mathrm{mm}^2 \cdot \mathrm{m}^{-1}$. The developed technique allows one to deposit grids with a period up to $500\,\mu$m and a sheet resistance of $40\,\Omega/\square$.

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Conflict of interest

The authors declare that they have no conflict of interest.

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