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Composition of the gas phase formed upon laser-induced copper deposition from solutions

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Laser-induced copper deposition from solution is accompanied by the evolution of two types of gas objects that differ considerably in the geometric sizes of bubbles, optical properties and effects on the copper deposition process.

Interest in the laser-induced chemical liquid phase deposition (LCLD) stems from the prospects of its use in microelectronics due to the ability to create extended localized metal structures 5–100 μm in width on dielectric surfaces (Figure 1). Scanning a dielectric surface with a focused laser beam in an electrolyte solution allows chemical copper reduction to be locally initiated according to equation (1).[1,2]

$$\mathrm{CuL}^{(n-2)-} + 2\,\mathrm{HCHO} + 4\,\mathrm{OH}^- \rightarrow$$

$$\rightarrow \mathrm{Cu}^0 + \mathrm{L}^{n-} + \mathrm{H}_2 + 2\,\mathrm{HCOO}^- + 2\,\mathrm{H}_2\mathrm{O}, \qquad (1)$$

where L is an organic complexing agent, usually sodium potassium tartrate or EDTA, and HCHO is formaldehyde (reducing agent that is added to solution in 6–7.5-fold excess in the case of laser deposition). Copper sulfate or copper chloride is generally used.

An unsolved technical problem that prevents the practical application of LCLD is intense gas evolution occurring around the laser beam focus point on the dielectric surface.[3–6] The formation of gas bubbles in the laser beam path leads to its defocusing. As a result of this fact, metal deposition from solution is uncontrollably discontinued, or it occurs in a refracted or reflected irradiation zone. In such a case, diffuse edges, areas with unsatisfactory topology [Figure 2(*a*)], ruptures [Figure 2(*b*)], tails of the metal deposited in a non-localized way [Figure 2(*c*)], and other flaws are formed on the metal deposited structure. In order to develop methods for the efficient suppression of gas evolution, we need to know the reasons for the formation of gas phases during laser-induced deposition and their composition. In previous studies on LCLD, it was either assumed that only hydrogen was evolved as bubbles according to equation (1), or no assumptions concerning gas phase compositions were made.

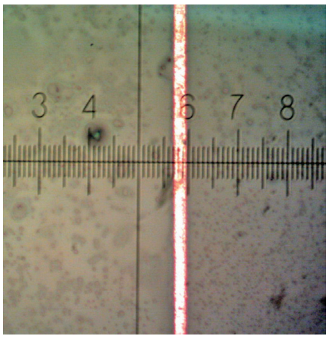

Figure 1 High-quality deposition in the absence of gas formation.

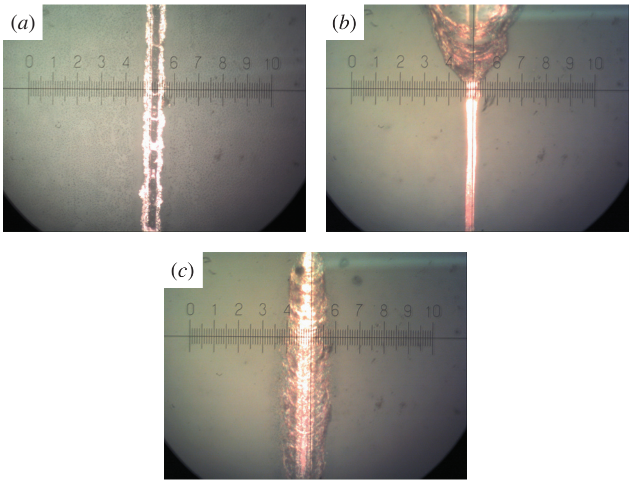

Figure 2 Defect types on deposited copper structures resulting from uncontrolled gas formation in the laser beam focus: (*a*) irregular topology, (*b*) path rupture and (*c*) metal tail deposited in a non-localized way.

We studied[†] the LCLD process using a 40$^\times$ optical microscope *in situ* with a CCD camera and found that two types of gas objects are formed in the system (Figure 3), which differ considerably in geometrical dimensions, optical properties and effects on the copper deposition. Some of the gas bubbles are small (up to 5 μm) and visually transparent (Figure 3, area *1*), while others are large (up to 200 μm in diameter) with an opaque surface layer and a transparent central part (Figure 3, area *2*).

The compositions of the two gas objects observed by means of a CCD camera were studied by mass spectrometry[‡] during laser deposition of copper and in the absence of laser irradiation. It was found that under a 488 nm laser irradiation, gas samples

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[†] Copper structures were deposited using a continuous multimode-operated Ar$^+$ laser in a power range from 30 to 1000 mW. An optical system was used to focus the laser beam immovably on a oxide glass planar dielectric substrate, which was moved at a rate of 0.01 mm s^{-1} relative to the focus point on a motorized micrometric positioning actuator.

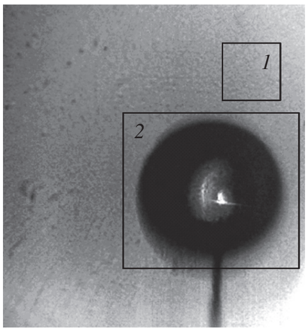

Figure 3 Photograph of gas objects: (*1*) transparent bubbles with diameters up to 5 μm (presumably hydrogen); (*2*) large gas bubbles with diameters up to 200 μm (presumably, by-products of reactions in the solution of organic components).

above the solution were characterized by a considerably increased carbon dioxide content (a peak at 44 a.m.u.). Comparison of the visual picture of deposition observed through a CCD camera with the mass-spectrometric data revealed that the appearance of the second-type gas phase in solution bulk distinctly correlated with the increase in the CO_2 peak intensity in the mass spectra of the headspace vapour.

Analysis of the fine structure of peaks at 28–31 a.m.u. also showed that these signals increased synchronously under laser irradiation. Based on the ratio of these peaks, one can assume that they are most likely due to the evolution of an appreciable amount of CO, as well as residual formaldehyde vapour that was not completely consumed in main reaction (1). The formation of CO- and CO_2-containing vapours may result from side reactions involving organic solution components that occur in the laser beam focus.

Note that the intensity of peaks at 1–2 a.m.u. in the mass spectra also increases during the laser induced reaction, which is apparently due to reaction (1). The evolution of hydrogen may also account for the formation of gas bubbles up to 5 μm in diameter.

Thus, the intense gas formation during LCLD, which results in the defocusing of a laser beam, is caused by the evolution of CO_2 and CO rather than hydrogen, as well as perhaps by evolution of other products of side reactions involving organic solution components and formaldehyde.

The occurrence of side reactions involving organic solution components was confirmed by blank experiments, *i.e*, irradiation of a solution containing all components of reaction (1) except for a copper salt. The formation of CO and CO_2 under laser irradiation was also detected in this case, both by optical observation and from mass-spectrometric data.

The formation of carbon oxides owing to laser irradiation should be accompanied by a decrease in the concentrations of organic solution components, both in the presence and in the absence of a copper salt. These concentrations were calculated by comparison of ^{1}H NMR spectra[§] of original solutions with those after the laser irradiation.

We also found that the decrease in the concentrations of organic complexing agents (both sodium potassium tartrate and EDTA) in the solution after laser deposition did not exceed 10–20%, even though these components were not consumed in reaction (1). The reducing agent, *i.e.*, formaldehyde (which was present in a 7.5-fold excess in the initial solution) was totally absent from the solution after the irradiation.

The experimental data were confirmed by the reported possible photoinduced oxidation of organic components in aqueous solutions under high-energy irradiation[7,8] and partial thermal destruction of organic solution components (in particular, EDTA).[8,9]

Thus, the intense gas formation during laser-induced copper deposition mainly results from side reactions involving organic solution components, to produce carbon oxides and perhaps residual formaldehyde in the gas phase rather than hydrogen alone, as it was believed previously. This opens a pathway to the development of efficient methods for the suppression of gas evolution during laser-induced copper deposition from solution.

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References

1 M. I. Shalauskas, *Metallizatsiya plastmass* (*Metallization of Plastics*), Znanie, Moscow, 1964 (in Russian).
2 K. M. Vansovskaya, *Metallicheskie pokrytiya, nanesennye khimicheskim sposobom* (*Chemically Deposited Metal Coatings*), Mashinostroenie, Leningrad, 1985 (in Russian).
3 K. Kordas, *Laser-assisted Chemical Liquid-phase Deposition of Metals for Micro- and Optoelectronics*, Academic Dissertation, Department of Electrical Engeneering and Infotech, University of Oulu, Finland, 2002.
4 A. Manshina, A. Povolotskiy, T. Ivanova, A. Kurochkin, Yu. Tver’yanovich, D. Kim, M. Kim and S. C. Kwon, *Glass Phys. Chem.*, 2007, **33** (3), 209.
5 A. Manshina, A. Povolotskiy, T. Ivanova, Yu. Tver’yanovich, S. P. Tunik, D. Kim, M. Kim and S. C. Kwon, *Appl. Phys. A*, 2007, **89**, 755.
6 A. Ouchi, Z. Bastl, J. Boháček, J. Šubrt and J. Pola, *Surf. Coat. Technol.*, 2007, **201**, 4728.
7 K. R. Rhoads and A. P. Davis, *J. Envir. Eng.*, 2004, **130**, 425.
8 G. S. Shcherbakova, *PhD Thesis*, D. I. Mendeleev RKhTU, Moscow, 2004 (RGB OD, 61:05-2/160) (in Russian).
9 A. E. Martell, R. J. Motekaitis, A. R. Fried, J. S. Wilson and D. T. MacMillan, *Can. J. Chem.*, 1975, **53**, 3471.

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[‡] A Techmas-200 quadrupole mass spectrometer with a mass range up to 200 a.m.u., a resolution of 1 a.m.u. and electron impact ionization (70 eV) was used as an analyzer. Samples were directly injected into the mass spectrometer ion source through a capillary from above the solution in the reaction cell.

[§] ^{1}H NMR spectra were recorded on a Bruker AM300 (300 MHz) spectrometer; solvent, D_2O.