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Laser-induced chemical liquid phase deposition of metals: chemical reactions in solution and activation of dielectric surfaces

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Abstract. Data on the factors affecting the result of laser-induced chemical liquid phase deposition of metals, first of all copper, are generalized and described systematically. The attention is focused on the chemical reactions in solution and activation of dielectric surfaces. The mechanisms of chemical and laser-induced deposition of local copper structures from solution onto dielectric surface are considered. The effect of the solution components on the result of deposition is discussed. The bibliography includes 92 references.

I. Introduction

The interest in the laser-induced chemical liquid phase deposition (LCLD) of metals is due to the prospects of application of this method in microelectronics and technology, as it allows maskless manufacture of metallic structures on the surface of dielectrics (Fig. 1).[1] From the practical standpoint, most interesting is the deposition of copper or, somewhat less, nickel. Focused laser beam scanning of the surface of a dielectric placed into a special solution results in local initiation of chemical reduction to give metallic copper according to Eqn (1):[2]

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

where L is an organic complexing agent [usually sodium potassium tartrate or ethylenediaminetetraacetate (EDTA) salts]; formaldehyde acts as the reducing agent and is added in a 6 – 7.5-fold excess. The copper salt used is most often sulfate or chloride.

Laser radiation activates the dielectric surface[3] and accelerates metal deposition in the irradiated area by increasing the temperature in the local volume located at the focus of the laser beam.[4–7] The high intensity of the focused laser beam, especially when pulsed lasers are used, creates locally highly non-equilibrium states with high temperature and concentration gradients.

The following specific features of laser-induced deposition may be noted.

1. The point localization of the reaction in a minor volume of the solution, which only slightly exceeds the laser beam focal spot (5 μm).

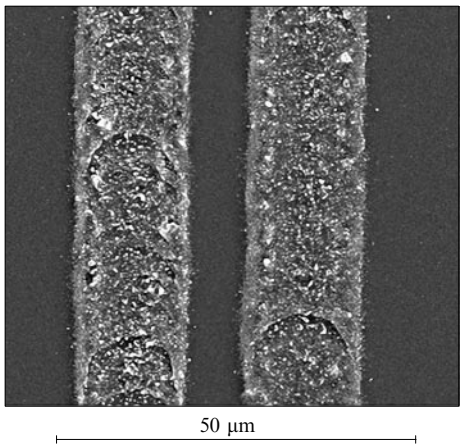


Figure 1. Spatial resolution of the laser-induced deposition technique illustrated by two copper lines deposited from a 0.001 M solution of $CuCl_2$ containing EDTA and *p*-benzoquinone onto a quartz glass substrate.[1]
The image was obtained by scanning electron microscopy (SEM).

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2. High temperature in the localization area, which is much higher that the temperature range normally used for the deposition (below 100 °C).

3. High temperature gradient between the reaction area and the solution bulk (more than 3×10^6 deg m^{-1}).

4. The presence of radiation with high energy flux (of about 10^5 W cm^{-2}) in the reaction zone.

5. Side reactions in the laser beam focal spot involving the same solution components as the main autocatalytic reaction.

As a consequence, for most known solutions with autocatalytic reactions, the result of laser-induced deposition differs appreciably from the outcome of the conventional chemical copper plating. The reasons and the mechanism of these differences have not been studied in detail as yet. It is usually assumed that the mechanism of the laser-induced reaction is similar to the autocatalytic mechanism,[5] or, alternatively, this issue is not considered at all, and the authors study only the effects of laser power and radiation wavelength,[3] the rate of laser beam scanning of the dielectric surface and the number of scans of the same area of the dielectric surface,[4] and other factors on the final result.

In addition, specific features of the laser-induced liquid phase deposition may open new chemical reaction pathways and also may enable reactions that are impossible in usual classical chemical systems close to chemical equilibrium.[8] The controlled laser-induced deposition of metallic structures is impossible without detailed investigation of the mechanisms of these chemical processes. Since these processes occur in the laser beam focal microvolume, they can hardly be investigated by the available physicochemical methods. It is necessary to model the processes relying on the concepts of the adjacent fields of chemistry: chemical and electrochemical metal plating, laser ablation, surface phenomena in dielectrics, adhesion, epitaxy, *etc*. This review generalizes and describes systematically the data that can conditionally be regarded as the chemical aspects of the LCLD process (the composition and reactions of the solution components, change in the chemical properties of dielectric surfaces under the action of activating factors).

The outcome of LCLD is affected by three main groups of factors:

— physical factors: laser radiation wavelength and power, scanning speed, temperature of the environment and the solution;

— chemical factors: solution composition, component concentrations, solution pH, chemical reactions taking place in the solution;

— surface properties of the dielectric substrate: structure, the presence of activated and catalytic sites, defectiveness, phase composition, and the chemical properties of the dielectric components.

Only physical factors have been studied to date in sufficient detail, while chemical factors and the effect of the substrate have been little studied. This review is focused on the works devoted to particularly these groups of factors. In numerous papers dealing with the laser-induced deposition, the discussion of chemical factors of the process is reduced, most often, to the list of reagents or dielectric substrates used for deposition. The attempts to optimize the process include only variation of the laser radiation wavelength and power and the scanning speed and the number of scans. Judging by the photomicrographs of the metallic structures thus formed (Fig. 2),[9] the vast majority of the deposited structures have a poor topology, which precludes their practical application.

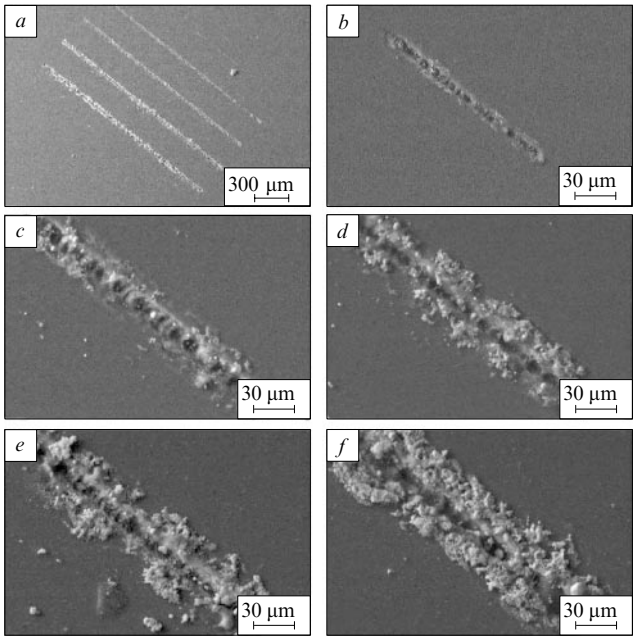


Figure 2. Photomicrographs of the copper precipitates obtained by laser-induced deposition upon N scans of the dielectric surface area.[1] General view for all lines (*a*) and enlarged images of some lines at $N = 1$ (*b*), 2 (*c*), 3 (*d*), 4 (*e*), 5 (*f*).

The final goal of the control of laser deposition is to create the optimal conditions for localized crystallization of the metallic deposit on the dielectric substrate. Copper crystallization is the final stage in the laser deposition sequence; therefore, the optimal conditions of deposition may be achieved only by addressing simultaneously all of the key aspects: modification of the composition of components of the autocatalytic solution to optimize the dissociation energy value of metal–ligand complexes; generation of chemically activated sites on the dielectric substrate and preparation of solutions with optimal optical characteristics; variation of the power, wavelength and dimensions of the laser beam focal spot; development of effective activation methods for dielectric surfaces.

It is clear that further progress in this field is possible only on the basis of investigations into the chemical mechanisms of laser-induced reactions and the mechanisms of surface activation, which constitute the subject of this review. Since the amount of theoretical and experimental studies of the chemical mechanisms of LCLD is still small, the mechanisms of laser-induced reactions are discussed resorting to the knowledge of related fields, in particular, of traditional chemical copper and nickel plating.

II. Chemical reactions in the solution during laser-induced chemical liquid deposition of copper

1. General characteristics of the process

In recent years, considerable attention has been devoted to the development of laser methods for the formation of metallic coatings and local elements on various surfaces

(Si, GaAs, SiO_2, Si_3N_4, Al_2O_3, *etc.*). These methods include laser-induced chemical vapour deposition (LCVD),[10] pulsed laser deposition (PLD),[11] laser-induced forward transfer (LIFT),[12] laser-induced pyrolytic decomposition of solids (LPDS)[13] and laser-induced chemical liquid-phase deposition (LCLD).[8,14–19]

These methods can be assigned to additive methods (as this term is applied to the printed circuit board manufacture), because they do not imply the continuous metal deposition followed by etching out of the needless areas but imply metal deposition directly onto the sites of metal contacts. Micron positioning of the laser beam makes it possible to produce conductors with small cross-section area and short distance between the metal lines. Using the existing laser-induced metal deposition techniques, it is possible to obtain conducting structures on metals, dielectrics and semiconductors. The methods are fairly effective but their extensive use is restricted by the need to use additional equipment. The key inconveniences of laser-induced chemical vapour deposition[10] and pulsed laser deposition[11] techniques are related to the use of vacuum and gas systems to generate the desired atmosphere above the substrate surface. Other problems are related to the high toxicity and low volatility of many organometallic compounds. In the chemical vapour deposition of a metal, laser radiation serves to destroy the metal-containing compound and then to deposit the metal on the substrate. For example, compounds such as $R'MPR_3$ and R'_3MPR_3 are used, where R, R′ = Me, Et and M is the metal being deposited.[10] Their vaporization starts at temperatures of 20–50 °C (4–1000 mTorr) and decomposition begins at 100–170 °C. Under these conditions, the deposited lines are several tens of micrometres wide and the deposition rate varies from several micrometres to several hundreds of micrometres per second,[20] which is quite suitable for some practical applications. The laser-induced forward transfer[12] or laser-induced pyrolytic decomposition of solids[13] do not require special atmosphere above the treatment area; however, LPDS requires special equipment for the application of a metal-containing solid on the substrate followed by the removal of the non-decomposed film.

The laser-induced chemical liquid phase deposition of metals[4–7] has a number of advantages over other methods: it does not require expensive complex equipment (as LCVD), does not produce a large amount of toxic wastes, which is the case for the lithographic process involving etching. Furthermore, this is a one-stage method if the surface being coated can exhibit catalytic activity during metal reduction or a two-stage method if the surface preactivation is required. The method simplicity and the efficiency of the use of materials are very important for practical applications.

Studies of LCLD deposition have been actively developed due to the fact that since the mid-1980s the search started for the ways of decreasing the dimensions of printed-circuit boards and their components used in various microelectronic parts.[21,22] Von Gutfeld *et al.*[23] showed for the first time that laser radiation can accelerate galvanic metal plating. Subsequently, it became possible to carry out laser-assisted metal deposition without external current sources.

Generally, laser-induced metal deposition includes treatment of a local area of a dielectric or a conductor in air or under a liquid layer (metal deposition solution) with a focused laser beam. Laser treatment activates the dielectric surface[3] and, in the case of laser treatment directly in the metal deposition solution, this accelerates the metal reduction in the irradiated area,[4–7,9,24–28] in particular, due to temperature rise in the local volume located at the laser beam focus.[1]

By laser-induced deposition, the following metals can be deposited on the surface of various dielectrics: copper,[4–7,9,25–28] silver,[6,29–31] palladium,[29,32–34] platinum,[34] nickel,[35,36] gold,[1,37] chromium,[38] tungsten.[38] However, it is copper deposition and, to a lesser extent, nickel deposition that are most important for practical purposes (nickel is used to apply a protective anticorrosion layer on copper conductors).

There are papers dealing with co-deposition of nanoparticles consisting of gold and platinum alloys using a femtosecond laser[39] and with the deposition of heterometallic Cu–Cr structures.[40] However, the list of co-deposited heterometallic structures is still short. As noted above, the problem of effective copper and nickel co-deposition to release the deposit as a solid solution, which is topical for microelectronics, has not been solved as yet. In our opinion, a possible way for solving the co-deposition problem in LCLD is to select a complexing agent the complexes of which with the metals to be co-deposited would have considerably different instability constants (for example, for the nickel and copper potentials to approach each other, the use of sulfosalicylic acid as the ligand, as in galvanic metal plating, might be a success).[41]

The copper plating of a broad range of dielectric and semiconductor materials has been reported: quartz glass,[3,9,42,43] crystalline silicon,[44] porous silicon,[35,36] diamond,[45] polyimide,[5,6,30,42] polyphenylquinoxaline,[33] polyethyleneterephthalate,[46] Al_2O_3 ceramics,[34,47] AlN ceramics.[48,49]

The methods of laser deposition of the metal from solution may be conventionally classified into three groups.

Single-stage process. The metal is deposited in one stage. The metal is deposited onto the substrate directly from the solution as a result of thermo- or photo-induced redox reaction in the solution at the interface with the dielectric.[8,35,36,46]

Two-stage process with laser-induced pre-deposition of a noble metal. First, laser-induced deposition of a mask of a noble metal (silver[50] or palladium[8]) is performed and this is followed by chemical deposition of copper. The noble metal serves as the catalyst for the redox reaction between copper(II) and the reducing agent in the solution. Copper is deposited only on the surface of the pre-deposited mask to form a conducting line.

Two-stage process with laser treatment of the material in air. First, the surface of the material to be metal coated is laser treated in air. Then the material is placed in a hot copper or nickel deposition solution. Due to the change in the surface properties upon irradiation, the metal is deposited only on the laser pre-treated areas.[34]

A considerable portion of the investigations of the laser-induced deposition of copper are devoted to analysis of the dependence of the width of deposited copper structures on the power of the laser radiation,[9,42,51,52] because this dependence gives a clue what is the predominant mechanism of the LCLD (either thermo- or photoinduced process).

A problem of principle that is still to be solved is what is the role of laser radiation during the deposition: either purely kinetic (accelerating the reaction in the laser beam

focal spot) or also thermodynamic (shift of the reaction equilibrium)? What are the process activation mechanisms?

The dependence of the difference of redox potentials (ΔE) of the half-reactions of formaldehyde oxidation and copper reduction from the ethylenediaminetetraacetate complex according to reaction (1) on the pH at various temperatures (this reaction is used for both chemical copper plating of dielectrics and the LCLD)[53] can be calculated from the Nernst equation:

$$\Delta E = E_{\mathrm{CuL/Cu}} - E^{\circ}_{\mathrm{HCHO/HCOO^-\ (pH=0)}} + \frac{4RT}{nF}\mathrm{pH},$$

where E is the reduction potential, R is the universal gas constant, T is temperature, F is the Faraday constant, n is the number of electrons involved in the process (in this case, $n = 2$).

A calculation based on the data of Kapitsa[54] and on the assumption of constant $\mathrm{HCHO:HCOO^-}$ concentration ratio for the solution macrovolume in view of localization of reaction (1) in the laser beam focal microvolume shows that the potential difference increases by approximately 0.1 V upon heating by every 50–60 degrees:

T/°C	25	60	95
ΔE/V	0.1	0.18	0.25

These data can be used to estimate the temperature dependence of the equilibrium constant:

$$\frac{K_{95\,^\circ\mathrm{C}}}{K_{25\,^\circ\mathrm{C}}} = \exp\left(\frac{\Delta E_{95\,^\circ\mathrm{C}}}{\Delta E_{25\,^\circ\mathrm{C}}}\right) = \exp\left(\frac{0.25}{0.1}\right) = 12.1.$$

Thus, laser heating may induce a 12-fold or even more pronounced increase in the equilibrium constant. In view of the relatively low concentrations of copper ions in the solutions normally used for laser deposition (0.01–0.001 mol litre^{-1}), this does not suffice for the formation of high-grade continuous copper deposits. Thus, initiation of the laser deposition of copper in the laser beam focal spot is due, in particular, to the kinetic factor, not only to the thermodynamic one.

As mentioned above, a laser-induced chemical reaction can follow two mechanisms — thermal and photochemical ones.

Thermochemical mechanism. The reaction occurs due to the local increase in the temperature upon radiation absorption by the matter. Since according to the Arrhenius equation, the rate constant exponentially depends on the temperature, even a small temperature gradient in the laser beam focal spot may contribute to acceleration of the chemical reaction in this area. The intense heating of the local reaction area initiates a number of side processes, first of all, a change in the substrate properties in the heated area (including activation of the substrate surface)[3] and chemical reactions (reactant decomposition, reduction or oxidation, and so on) at the substrate/liquid interface.[2]

The energy of some of the laser photons is transformed to the thermal energy. This process can be mathematically simulated.[55] Let N such photons per m atoms be present. Then, if the thermal exchange is ignored, the local temperature of an m-atomic fragment increases in proportion to the N value:

$$\Delta T \sim \frac{h}{3km} = 1.6\times10^{-11}\,\frac{\nu N}{m}, \qquad (2)$$

where h is the Planck constant, ν is the laser radiation frequency and k is the Boltzmann constant.

A substantial increase in the local temperature usually changes crucially the course of the chemical reaction. The following estimates are useful. For the frequency $\nu = 2.5\times10^9$ Hz of the microwave range, $\Delta T \approx 0.04\,(N/m)$. When $N = m$, the temperature rise is insignificant: $\Delta T \approx 0.04$ deg; considerable heating is possible only provided that $N \gg m$.

The situation is different for high frequencies. Thus for $\nu = 4.8\times10^{14}$ Hz of a helium–neon laser radiation, $\Delta T \approx 7.6\times10^3\,(N/m)$; when $N = 0.01\,m$, the local temperature jump is substantial ($\Delta T \approx 76$ deg). In this case, the reaction rate constant markedly increases.

Finally, in the steady-state mode with allowance for the heat exchange, the following estimate is valid for ΔT

$$\Delta T \sim \frac{W\tau}{C}, \qquad (3)$$

where W is the electromagnetic radiation energy absorbed per unit time, τ is the relaxation time, C is the heat capacity. The following estimate was proposed:[55] $W = 10$ W, $\tau = 300$ s and $C = 25$ J K^{-1}. In this case, we get $\Delta T \approx 100$ deg. Generally, the relations (2) and (3) demonstrate the role of the thermal factor.[55]

Photochemical mechanism. When a substance absorbs radiation, the photon energy is spent for the cleavage of chemical bonds and for the formation of new bonds. In addition, the action of radiation at particular wavelengths on some molecules or groups of atoms induces the formation of free radicals, electronically excited states, delocalized free electrons. This altogether stimulates photochemical reactions.[5]

The mechanisms of laser-induced photochemical reactions were considered in more detail by Kordás,[8] who formulated criteria for distinguishing between thermally or photo-induced reactions. A process has a thermal (or pyrolytic) mechanism if the photon energies are relatively low ($h\nu < 2$ eV). The photolytic or photochemical mechanism can be implemented if the energy of laser photons is commensurable with the chemical bond energy (2–5 eV).[8]

The general kinetic equation for the thermochemical reaction is as follows:

$$\upsilon(x,t) = A\,\exp\left(-\frac{E_\mathrm{a}}{kT(x,t)}\right)\prod_i X_i^{\omega_i},$$

where υ is the rate of the thermal reaction, A is the pre-exponential factor of the Arrhenius equation, E_a is the activation energy of the reaction, $T(x,t)$ is the time-dependent temperature of the point with coordinate x, X_i is the concentration of reactant i and ω_i is the partial order of the reaction with respect to component i. The exponential dependence of the reaction rate on the temperature provides a reasonable explanation for the pronounced change in the reaction rate during laser irradiation.

The rate of photolytic reaction depends on the number of excited or dissociated molecules and, broadly speaking, it does not depend on the system temperature:[56]

$$\upsilon^*(x,t) = k_0^* \prod \left[{}^{(n)}\sigma_i \left(\frac{I(x,t)}{h\nu} \right)^n \right]^{\omega_i} \prod_i X_i^{\omega_i},$$

where υ^* is the rate of the photochemical reaction, k_0^* is the reaction rate constant, n is the number of photons needed for excitation of the molecule, σ_i is the capture cross-section of component i, I is the radiation intensity. In the photolytic process, the heat conductivity can be neglected, as the chemical reaction is the result of interaction between photons and the matter. In other words, a purely photochemical process is confined to the laser-irradiated zone, and, thus, broadening of the deposited metal lines caused by thermal diffusion at the solution/substrate interface is minimized.

The above equations provide the conclusion that the simplest way to distinguish between laser-initiated photochemical and thermochemical reactions is to study the dependences of the width of the deposition zone on the laser spot diameter and laser beam power on the dielectric surface. If both mechanisms are realized simultaneously, it is rather difficult to estimate the contribution of each of them, because it is impossible to study the process by standard chemical kinetic methods to elucidate the true mechanism. The predominance of either photochemical [25] or thermochemical [3] mechanism can be considered only at a qualitative level.

As noted above, studies of the metal deposition from the liquid phase started with the process in which a laser was used to accelerate the reaction induced by external electric field.[23] It was found that the rate increases owing to the additional displacement of the electrochemical potential of the electrode in the illuminated area. Further studies showed that for metal deposition, one can do without external emf if the solution contains both a metal and a reducing agent. In this case, the liquid phase consists of the source of metal (the metal salt or organic metal complex), chelating agent (if the metal is not initially taken as a complex), acid/alkali or a buffer mixture to establish the desired pH and a reducing agent, all being dissolved in distilled water or in organic solvent.[8] Two mechanisms of charge transfer from the reducing agent to the oxidant are possible: chemical (in the solution bulk) and electrochemical ones (through the activated sites arising on the dielectric surface exposed to laser radiation).[57] The former of the two discussed mechanisms is determined by the composition of the solution components for the laser-induced deposition of copper.

2. Composition and functions of the solution components

The laser-induced liquid phase deposition of metals can be regarded, with some simplifications, as a modification of the chemical liquid phase metallization where chemical deposition occurs only in the laser-irradiated area according to Eqn (1). During the laser-induced deposition of a metal, chemical reactions occur, as a rule, due to simultaneous action of photo- and thermochemical factors. The kinetic features of the thermochemical processes following laser heating of chemically active media are mainly related to two factors, specific reactions and the mutual influence of the chemical state of the medium and energy and mass transfer processes in the laser radiation field.

After introduction of the ligands, the metal does not always precipitate in the bulk due to the little potential difference, which can, however, be locally increased by the temperature effect of laser radiation. Von Gutfeld [23] put forward the idea that a noticeable contribution is also made by the emf of the galvanic concentration cell related to the local changes in the activities of potential-forming ions in solution.[58] In turn, the change in the activities (a_i) is related to the change in the ion concentrations in the solution caused by thermal diffusion upon non-uniform laser heating. The sign of the thermal diffusion constant in solutions is such that positively charged metal ions move, most often, from less heated area to more heated area.[59]

As regards the photochemical constituent of the process, as noted above, its kinetics has little to do with the temperature factor and depends to a higher extent on the laser radiation parameters (power, wavelength).[56]

As noted above, a solution for chemical deposition of copper comprises a copper(II) salt, a reducing agent, a complexing agent, pH regulator and other additives.[53]

a. Copper(II) salts

According to the traditional cooper plating process for the manufacture of printed-circuit boards, $CuSO_4$ is used to build-up the copper layer.[60] As applied to laser deposition, the effect of the anionic composition of solutions on the deposition outcome was studied, and this effect was found [42] to be insignificant. Only the use of chloride ions gives copper structures with somewhat better electrical conductivity.[42]

The dependence of the rate (r) of copper metal deposition on the copper ion concentration in solutions [61] follows an empirical power-law dependence:

$$r \sim [\mathrm{Cu}]^{0.4},$$

where [Cu] is the concentration of copper(II) complex with EDTA in solution.

High deposition rate is good for preparing thick continuous coatings with low requirements to the deposited copper quality (inhomogeneous topology, porosity of the precipitate). For controlled preparation of a dense conducting deposit of copper with a specified thickness, it is better to use dilute solutions at relatively low deposition rates.[62]

b. Reducing agent

Formaldehyde is used traditionally as the reducing agent for copper, as copper catalyzes formaldehyde oxidation on its surface.[54, 62] Thus, owing to the use of formaldehyde as the reducing agent, the reduction of copper occurs mainly on grains and surfaces of pre-deposited copper rather throughout the solution bulk (autocatalytic reaction). The copper deposition rate increases with an increase in the formaldehyde concentration, this dependence having a complex pattern. At low copper concentrations (up to 0.01 mol litre^{-1}), the dependence of the reaction rate on the formaldehyde concentration starts to flatten out even at concentrations of >0.5 mol litre^{-1}. Hence, for copper deposition from dilute solutions, the use of high concentrations of formaldehyde is inappropriate. In the case of concentrated solutions of copper, the copper deposition rate increases monotonically at least up to formaldehyde concentration of 1 mol litre^{-1} (Ref. 54). Thermodynamically, formaldehyde can also be used for the reduction of nickel; however, for kinetic reasons, this reaction is inapplicable for the preparation of continuous nickel films.[63]

Of other reducing agents, sodium hypophosphite can also be used;[63, 64] nickel is reduced by sodium hypophosphite according to the following equation:

$$NiCl_2 + 2\,NaH_2PO_2 + 2\,H_2O \longrightarrow$$
$$\longrightarrow Ni^0 + 2\,NaH_2PO_3 + H_2 + 2\,HCl.$$

However, in this case, phosphorus (up to 21 mol.%) is co-deposited with the metal due to the side reaction

$$2\,NaH_2PO_2 \longrightarrow NaH_2PO_3 + P + NaOH + \frac{1}{2}H_2.$$

In order to obtain pure nickel, hydrazine is used as the reducing agent for the chemical deposition of nickel.[63, 64] Hydrazine can also serve as the reducing agent in the deposition of copper.[64] In some studies, copper deposition from solutions was carried out with other reducing agents. For example, isopropyl alcohol was used to reduce copper from copper(II) acetylacetonate.[25] In this case, photoinitiated reaction takes place. The absorption bands of copper acetylacetonate lie within the radiation regions of the ArF and KrF lasers applied.

c. Complexing agent

The complexing agent, which forms rather strong donor-acceptor bonds with the Cu^{2+} ion, performs a dual function. First, it prevents the precipitation of copper hydroxide, since reduction with formaldehyde occurs only in alkaline medium. The second function is to decrease the standard reduction potential of the Cu^{2+}/Cu^0 pair to prevent the uncontrolled reduction throughout the whole volume of the solution. The complexing agents applied in the chemical reduction of copper should also meet the following requirements:[54]

— ensure the sufficient solution stability during the process;

— not to react with formaldehyde and other reagents present in the solution (for this reason, primary and secondary amines are undesirable);

— not to retard the autocatalytic metal reduction process, *i.e.*, not to hamper the anodic oxidation of HCHO (for this reason, for example, cyanides and sulfides are inapplicable as ligands).

One more function of the complexing agent, namely, localization of copper deposition, has been reported.[65] By introducing complexes with high stability constants into the solution, one can obtain the thinnest copper conductors with sharp-cut edges and high-quality topology (Fig. 3).[1]

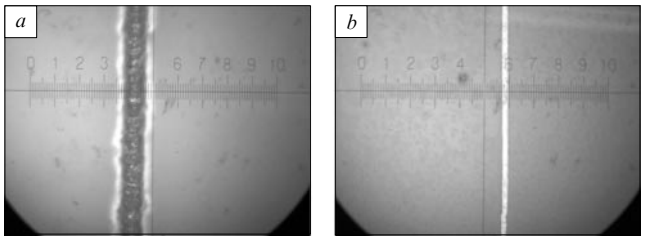


Figure 3. Comparison of the geometric parameters of the lines deposited from copper solutions with different complexing agents: EDA (*a*) and EDTA (*b*).[1]

It was found[65] that the geometric parameters (Fig. 4, 5) of the copper structures (line width, d) deposited from solutions with ethylenediamine (EDA) occupy an intermediate position between the lines deposited from copper tartrate and trilonate solutions:

$$d(\text{EDTA}) < d(\text{EDA}) < d(\text{tartrate}).$$

Furthermore, the degree of localization of the reaction decreases as the last instability constant of the copper complexes increases:

$$K_{n1}\,([Cu(EDTA)]^{2-})\,(1.6\times10^{-19}) <$$
$$< K_{n2}\,([Cu(EDA)_2]^{2+})\,(4.0\times10^{-10}) <$$
$$< K_{n3}\,([Cu(tartrate)_3]^{4-})\,(2.5\times10^{-1}).$$

The dependence of the deposited copper line width on particularly the last instability constant of the complex can be attributed to the steric factor: the electron transfer from the reducing agent to the copper ion (or from the deposited copper surface to the copper ion in solution in the case of the electrochemical mechanism) is hardly probable as all the coordination sites of the copper ion are occupied. The release of one of the ligands allows the reducing agent to

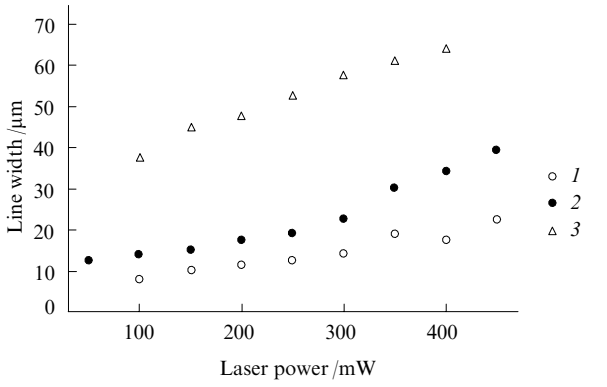


Figure 4. Width of the deposited copper line *vs.* laser power for various copper complexes.[1]
Ligands: EDTA (*1*), EDA (*2*), tartrate (*3*).

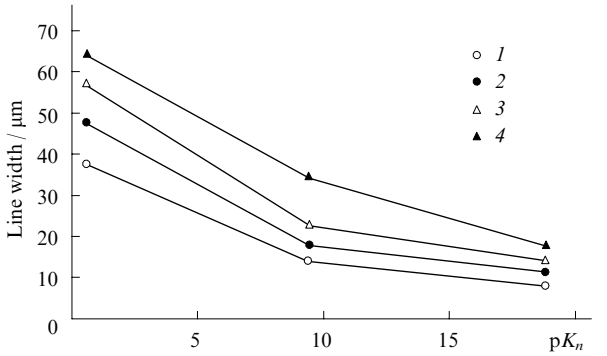


Figure 5. Width of the copper line *vs.* logarithm of the last instability constant of the copper complex in the solution at different laser powers (mW): 100 (*1*), 200 (*2*), 300 (*3*), 400 (*4*).[1]

give an electron to the copper ion and thus to initiate the autocatalytic deposition.

These assumptions are consistent with the theoretically predicted 'electrochemical' mechanism of the autocatalytic reduction of copper in solution.[58]

In the case of a strong complex, copper reduction occurs only at elevated temperature or on lowering of the activation barrier by the catalyst. The complexing agents used include oxalates, ammonia, glycerol,[64] but most often tartrates (potassium sodium tartrate) or disodium EDTA are used.[66] For autocatalytic deposition to proceed in solutions of strong metal complexes, it is necessary either to decrease the Gibbs energy or to increase the equilibrium constant of reaction (1).

A similar mechanism of action of complexing agents is also involved in the deposition of other metals, in particular, nickel.[64] The complexing agents usually introduced in nickel plating solutions include tartrates, citrates and malonates, which decrease the nickel reduction potential.[64]

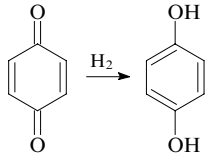
The search for techniques of copper and nickel co-deposition as a homogeneous solid solution is still in progress. The essence of the method is to bring the copper and nickel redox potentials closer to each other by selecting a complexing agent the copper and nickel complexes of which would have different stability constants, the nickel complex being more stable than the copper complex. In traditional chemical metal plating, sulfosalicylic acid salts have been proposed, for example, as such complexing agents.[46] However, this approach has not yet been used in the LCLD technique. Meanwhile, the problem is quite topical because nickel additives introduced in copper deposits can increase substantially the corrosion resistance of copper conductors with a minor increase in the specific electrical resistance. Copper and nickel form a continuous series of solid solutions over the whole concentration range;[67] nevertheless, it is quite difficult to obtain a solid solution with a nickel content above 4 mol.% by chemical or electrochemical co-deposition.[53, 54, 60, 62]

d. pH regulator

An alkaline medium is created in the solution to decrease the reduction potential of formaldehyde. Thus, as pH increases, the potential difference of the oxidant and the reducing agent becomes positive and copper reduction becomes a thermodynamically allowed reaction. The functions of the pH regulator are quite limited; therefore, its effect on the LCLD process has not yet been studied in detail.

e. Other additives

Some works consider the influence of some other additives on the LCLD. For example, the introduction of *p*-benzoquinone considerably (by several hundreds of milliwatts) decreases the initiation threshold of the laser-induced deposition of copper.[1] It was assumed that active absorption of hydrogen by reaction (4) would shift the equilibrium of copper reduction [reaction (1)] toward the formation of final products, including copper metal, and will also reduce the gas formation problem by chemically binding hydrogen.[1, 68]



(4)

An experiment showed that the introduction of *p*-benzoquinone into the solution is beneficial but the mechanism of its action is still obscure.[1, 68] For detailed understanding of the laser deposition process, it is necessary to find out what chemical reaction involving the quinone occurs during LCLD.

The effect of high concentrations of surfactants, which substantially improve the deposit quality in the chemical copper plating process, has been studied.[1] However, in the case of LCLD, the addition of surfactants had an adverse effect on the topology of the deposited copper structures. During the experiments of copper deposition from solutions containing various surfactants, the forces that support the gas bubbles on the dielectric surface were found to decrease, which facilitates the detachment of the bubbles from the surface. Simultaneously, the addition of surfactants decreases the surface tension at the liquid – gas interface, which facilitates the growth of bubbles and increases the bubble size. As a result of competition of the two processes, in some cases, the dependence of the width of the diffusion tail of the copper deposit tail on the laser radiation power passes through an extremum.

Note that the abundance of recipes for chemical copper plating (and nickel plating) solutions and some inconsistency of the published data on their compositions, deposition parameters and the properties of the deposited metal indicate that the search for the optimal formulation of this solution is still a topical task. For further development of the method, it is necessary to optimize the compositions of chemical copper plating solutions as applied to laser-induced deposition conditions.

3. Reactions giving gases in solution and their effect on the deposit topology

The uncontrolled effect of thermal factors during laser heating results in deposited metallic structures with low-quality topology. One of the adverse factors is the formation of a lot of gas bubbles at the site of contact of the laser beam with the dielectric substrate surface (Fig. 6).[2]

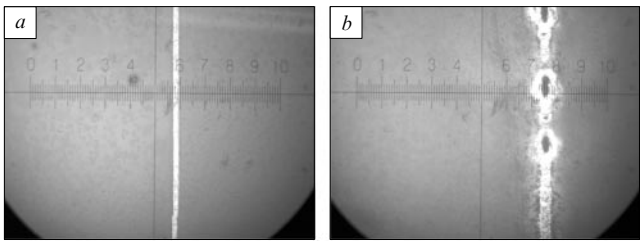


Figure 6. Copper lines obtained by laser-induced deposition.[2] (*a*) Deposition without formation of gas bubbles, (*2*) deposition with formation of gas bubbles.

It was believed for long that hydrogen formed by reaction (1) is the major gas-phase component in the laser-induced deposition of copper where formaldehyde is used as the reducing agent. However, later it was found[2] that two types of gas structures are present in the system (Fig. 7), and these differ considerably in the bubble size, optical

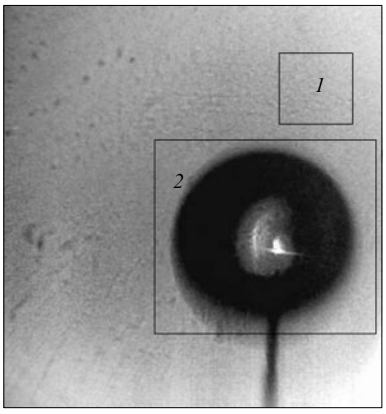


Figure 7. Photomicrographs of gas structures.[2]
(*1*) Transparent bubbles up to 5 μm in diameter (presumably, hydrogen), (*2*) large gas bubbles up to 200 μm in diameter (presumably, the products of side reactions of the organic components of the solution).

properties and the effect on copper deposition. It was found[2] that the vigorous gas evolution resulting in the laser beam defocusing during LCLD is related to CO_2 and CO (and probably other products of side reactions involving formaldehyde and other organic solution components) rather than to hydrogen.

Apart from the focusing problems, the interaction of laser radiation with the metallic deposit formed is also possible. This process may occur in different ways, in particular, as laser etching or ablation. This may be accompanied by local boiling of the solution, which also gives rise to gas bubbles.

A number of theoretical works on the mechanisms of laser etching and gas evolution processes in inert liquids were published. Ohara *et al.*[69] estimated the rate of bubble formation during laser etching of Al_2O_3 surface in solution. An increase in the bubble generation rate results in a higher etching rate. Empirical relationships between the weight of material carried away by ablation and the size of etched caverns were reported.[70] Good agreement was observed between the results of theoretical calculations and experiments, but in these experiments, laser radiation with atypically long pulses was used (140 μs).[71]

Thus, laser etching of materials is more intense in a liquid than in air, which may induce both side reactions in the radiation focal area and produce more activated sites towards metal deposition when the material is laser-irradiated directly in the copper plating solution.

4. Mechanisms of formation of crystalline phases in solutions for the laser-induced deposition of copper

The LCLD process may follow the classical nucleation mechanism in the solution bulk[72] or occur through the formation of atomic crystallization centres on defects or activated fragments of the dielectric surface followed by enlargement (coalescence) by an autocatalytic mechanism. The knowledge of the mechanism of formation of crystalline phase of the metal is needed in order to estimate the effect of solution components and optimize the LCLD process.

The probability of one or another mechanism can be estimated by a statistical calculation. It is known that laser-induced deposition can take place even at low concentrations of the copper complex (down to 0.001 mol litre^{-1}).[1] Consider a solution as a system in which fragments are located randomly.† Some of the fragments are identical (for example, the fragments of the hydrated Cu^{2+} ion). Due to lability of the solution, the geometry of the mutual positions of the fragments can be characterized only statistically, in particular, by specifying the probability density function $P_{AB}(r)$ for the distance r from fragment A to the nearest fragment B. Then the average value for this distance ($\bar{r}_{AB}$) is

$$\bar{r}_{AB} = \int_0^\infty r P_{AB}(r) \mathrm{d}r. \tag{5}$$

Of course, the function $P_{AB}(r)$ is individual for every solution, as various associates may form. However, if the concentrations of these fragments (C_A and C_B) are low, integral (5) can be estimated using the Poisson distribution.[73] In this approximation

$$\bar{r}_{AB} \approx 0.656 \sqrt[3]{\frac{1}{C_A + C_B}}. \tag{6}$$

The mean-square deviation $\Delta\bar{r}_{AB}$ for these distances is

$$\Delta\bar{r}_{AB} \approx 0.36\,\bar{r}_{AB}.$$

According to Eqn (6), even in a 0.01 M solution, the average distance between the neighbouring copper complexes is ~ 3 nm. The probability of occasional coming together of two copper-containing fragments is 2×10^{-4}. Further, the probability of formation of a critical-size nucleate comprising n copper atoms as a result of their simultaneous aggregation may be estimated as $2 \times 10^{-4(n-1)}$. It is obvious that under these conditions nucleation upon bulk fluctuations is statistically hardly probable, although cannot be ruled out completely. Moreover, it should be taken into account in the photolytic deposition processes. This was confirmed by publications[74, 75] in which the formation of the crystal phase of the metal in the autocatalytic solution according to the nucleation mechanism promoted by diffuse ultraviolet irradiation was proved by several independent methods, in particular, by X-ray diffraction.

Thus, without rejecting the possibility of the nucleation mechanism, it is necessary to study in detail the effect of the material of the surface to be metal coated on the laser-induced deposition process. The key point is the appearance of an activated site on the dielectric substrate; otherwise, crystallization will take place in the solution bulk by the nucleation mechanism to produce a loose precipitate, which may result in poor adhesion of the deposit to the dielectric surface.

III. Activation of the substrate material during the laser-induced liquid phase deposition of the metal

The outcome of LCLD (as in the case of classical chemical deposition of the metal) depends substantially on the properties of the dielectric substrate surface, first of all, on the presence and structure of the activated sites. The surface activation in LCLD is performed by two fundamentally different methods: traditional chemical (photo- or electro-

† Here a fragment refers to any species with an ordered local environment.

chemical) activation of the surface by pre-deposition of the catalyst and activation by physical treatment of the substrate. The focused laser treatment for liquid phase deposition of metals allows combining two methods into one thus creating the universal laser deposition mechanism.

1. The role of surface activation in the formation of metallic structures

The essence of activation of the dielectric surface is that an external treatment induces the formation of surface active sites that accomplish the electron transfer from the reducing agent to the metal ion (Fig. 8).[64] Then the reduced metal becomes the catalyst for further reduction. Usually this process is called autocatalytic deposition. The use of this term is supported by the fact that after deposition of some metal on the substrate, the process continues until the solution components are fully exhausted. Chemical metal plating studies show [53, 65] that high-quality deposited structures cannot be obtained without preactivation of the substrate surface.

The essence of the microscopic mechanism of the formation of active sites is as follows: laser radiation gives rise to defects (bond rupture, distortion of bond angles and bond lengths, dislocations, vacancies and so on) and to changes in the configuration of the electronic subsystem of the substrate surface, and this results in the formation of non-equilibrium, metastable structures. These are characterized by rather labile electronic subsystems that stimulate the electron transfer from the reducing agent to the oxidant.[76]

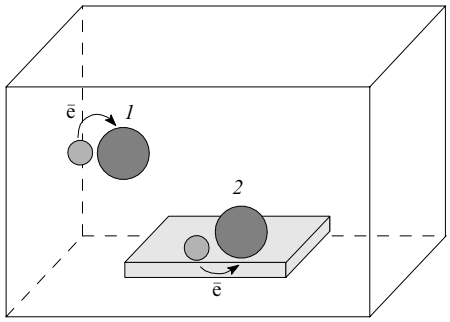


Figure 8. Schematic representation of the electron transfer from the reducing agent directly to the oxidant in the solution bulk (*1*) and electron transfer through the activated metal-coated surface (*2*).[64]

A promising new-generation material for microelectronics is polyimide (PI), which combines the dielectric properties and flexibility. Preactivation is widely used for LCLD deposition of copper on this material. Table 1 presents the results of studies dealing with metal plating

Table 1. Laser-induced deposition of copper on polyimide.

Laser used and its role	Irradiation mode [a]	Surface preactivation	Solution for chemical copper deposition [b]	Process temperature and time	Ref.
Nd : YAG photochemical pre-deposition of silver: $Ag^+ \rightarrow Ag^0$	pulsed λ = 266 nm, ν = 10 Hz, τ = 5 ns, Df = 20 μm	1) KOH (cleavage of imide bonds); 2) $AgNO_3$ ($K^+ \rightarrow Ag^+$ exchange); 3) laser irradiation ($Ag^+ \rightarrow Ag^0$); 4) annealing at 200 °C; 5) autocatalytic copper plating on Ag grains	$CuSO_4$ (0.05) NaOH (0.35) $NaKC_4H_4O_6$ (0.114) HCHO (0.16)	20–25 °C, 30 min	30
KrF ablation of the polyimide substrate	pulsed λ = 248 nm, ν_{max} = 100 Hz, τ = 25 ns	1) laser ablation of PI; 2) SDS;[c] 3) chemical activation; 4) 3% HNO_3 or acetone 5) autocatalytic copper plating	$CuSO_4$ (0.03) EDTA (0.06) HCHO (0.045) Py (5 ppm)	25 °C, 10 min	26
Nd : YAG generation of catalytic sites, solution heating	plsed λ = 532 nm, ν = 90 kHz, Df = 100 μm, N = 3–14, V = 0.02–0.3 mm s^{-1}	– (one-stage process)	commercial solution Coppermerse24 solution (the composition is not described)	–	5
HeCd photochemical pre-deposition of silver: $Ag^+ \rightarrow Ag^0$	continuous wave λ = 325 nm, P = 3 mW, Df = 15 μm	1) KOH (cleavage of imide bonds); 2) $AgNO_3$ ($K^+ \rightarrow Ag^+$ exchange); 3) polyethylene glycol coating; 4) laser irradiation ($Ag^+ \rightarrow Ag^0$); 5) annealing at 250 °C; 6) autocatalytic copper plating on Ag grains	$CuSO_4$ (0.01) NaOH (0.7) $NaKC_4H_4O_6$ (0.23) HCHO (0.16)	–	6
Ar^+ generation of catalytic sites, solution heating	continuous wave V = 60–80 μm s^{-1}, N = 8–24, P = 50–130 mW	–	$CuSO_4$ (0.1) NaOH (0.125) $NaKC_4H_4O_6$ (0.2) HCHO (6)	23 °C	42

[a] λ is laser radiation wavelength, ν is the pulsed laser frequency, τ is the pulse duration, Df is the focal spot diameter, V is the scanning rate, N is the number of scans, P is the laser power; [b] the value in parentheses is the concentration in mol $litre^{-1}$ unless otherwise specified; [c] SDS is sodium dodecyl sulfate.

Table 2. Laser-induced deposition of metals on the dielectric surface.

Substrate type	Deposited metal	Laser radiation wavelength /nm	Ref.	Substrate type	Deposited metal	Laser radiation wavelength /nm	Ref.
Al_2O_3	Ni, Cu, Pd, Pt	193, 248, 308, 337, 510, 690, 1060, 10 600	3	Si	Au	193, 248, 514, 633	8
					Cu	514	8
					Al	488	44
	Au	514	8		Pd	193, 248	8
	Pd, Pt	488	8	SiO_2	Ag	488	8
CeO_2	Pd, Pt	248, 308, 337	3		Cu	488	1, 9, 42, 51, 52
$SrTiO_3$	Ni, Cu	248	3				
$PbTi_{1-x}$	Ni, Cu	248	3		Cr	488	8
Zr_xO_3	Ni, Cu	193, 248, 308, 510, 10 600	3		Pd	308, 488	8, 77
ZrO_2				GaAs	Au	514	8
SiC	Ni, Cu	193, 308, 510	3		Pt	580 – 720	8
	Au	193, 248	8	InP	Au, Ni, Pt	580 – 720	8
	Pd	193, 248	8	TiO_2	Au	354 – 364 [a]	8
AlN	Ni, Cu	248, 308, 510	3		Sn	514.5	8
Diamond	Ni, Cu	248, 308, 510	3	Si_3N_4	Ag	488	8
$LiNbO_3$	Ni, Cu	248, 510, 10 600	3	Porous Si	Ni	488	35
						248, 308, 745.5, 1064	36
				Mn – Zn ferrite	Ni	514.5 [a]	8

Note. The following lasers were used for the indicated wavelengths: 193 — ArF; 248 — KrF; 308 — XeCl; 488 — Ar^+; 514 — Cu vapour; 532 — Nd : YAG; 580 – 720 — excimer dye laser; 745.5 — Ti : sapphire, 1060 — CO_2, 1064 — Q-switching Nd : YAG; 10 600 — CO_2; for 337 and 510 nm, the laser type was not indicated. [a] In these cases, Ar^+ laser.

on polyimide substrates. The data given in the Table confirm the statement about the mutual influence of the composition of the autocatalytic solution and the method of activation of the dielectric surface.

The most pronounced contribution to the development of the views on laser activation of the dielectric surfaces was made by G A Shafeev whose ideas and results formed the basis for many state-of-the-art experiments on laser-induced deposition. The data on laser-induced metal deposition reported by Shafeev [3] and Kordás [8] and the most recent publications on the considered problem are summarized in Table 2. These data confirm that the thermally induced laser deposition is less sensitive to the physical properties of laser radiation than to the chemical properties of the solution and the dielectric substrate, because deposition of one and the same metal is effective at different laser wavelengths.

Thus, preactivation of the surface on which copper is to be deposited is a common requirement, which also applies to usual chemical or electrochemical copper plating. It is not by chance that laser activation of dielectric surfaces is often used in conventional chemical deposition processes, while chemical activation is often used in the works on laser-induced deposition of metals.[3]

2. Mechanisms of activation of dielectric surfaces

The activation of dielectric surfaces is based on the processes involving restructuring at the atomic level and the change in the electronic configuration under the action of laser radiation. Three types of such processes are known.[3]

1) Formation of oxygen vacancies in oxide materials. On exposure to laser radiation, an oxide material loses some of the oxygen atoms as a result of fast heating. Since the laser irradiation time is short, the fast heating is quickly replaced by fast cooling, and the diffusion limitations preventing fast recombination of metal atoms with air oxygen result in the appearance of metastable oxygen vacancies. The metal atoms within the oxide structure serve as the crystallization centres.

2) The bending of the energy bands of the dielectric under the action of electromagnetic radiation. As a result of material quenching by laser radiation through successive expansion and compression, the band structure of the substrate material changes. This leads to bending of the valence and conduction bands of the dielectric, thus activating it.

3) The appearance of activation centres as metal clusters or other structures with high electrical conductivity, which allows easy charge transfer from the reducing agent to the positively charged metal ion.

However, not any dielectric surface can be activated. For example, Shafeev [3] points out that it is impossible to activate SiO_2 or MgO in air with subsequent immersion of the substrate into the metal plating solution (*i.e.*, a two-stage process is impossible). However, the possibility of one-stage copper plating process and SiO_2 activation was proved in experiments on laser-induced metal deposition on oxide and quartz glasses (Fig. 9, 10).[1, 9, 42, 51] In the SEM images (see Fig. 9), one can clearly see the separate cubic copper crystals with sizes of 100 to 1000 nm; this clearly illustrates the nucleation and crystal growth in the copper precipitate obtained by the laser-induced process. The energy dispersive X-ray (EDX) spectrum (see Fig. 10) shows that the crystals consist of pure copper. Moreover, the deposited copper structures have good adhesion to the surface, which attests to the formation of reaction initiation centres exactly on the activated surface sites.

Perhaps, the difference between the activation mechanisms in air and in solution [69 – 71] accounts for the observed different behaviours of the silica surface. The failure to

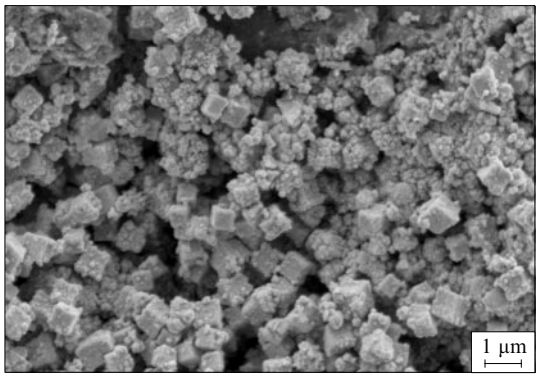


Figure 9. Copper microcrystals deposited from a 0.01 M solution of copper tartrate on a quartz glass surface.[1,9] The image was obtained by SEM.

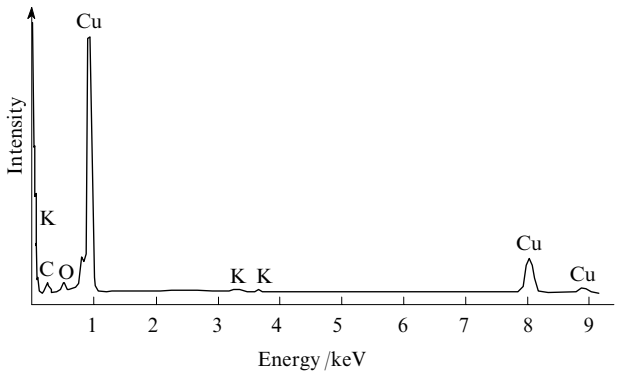


Figure 10. EDX spectrum of the deposit shown in Fig. 9.[1,9]

activate MgO is related, most likely, to its chemical instability in an alkaline copper plating solution where it is converted to $Mg(OH)_2$.

Also, one should take into account that many of Shafeev's works were performed for single crystals,[78] while most LCLD studies used polycrystalline, glassy and polymeric materials; and identical key chemical properties of single crystals and polycrystals or glass do not mean the identical results of laser activation of the surface. The mechanisms of physical and chemical activation of the surface for LCLD purposes are undoubtedly different and have not been ultimately studied as yet.

3. Activation by local physical treatment of the substrate

As noted above, activation by local physical treatment of the substrate is one of the two key methods utilized to prepare dielectric surfaces for copper plating.

The substrate areas treated mechanically or by a laser acquire special properties; they acquire either structural defects with enhanced free energy or surface charge. As a result, these areas become able to attract metal ions from solution and promote their electrochemical reduction with metal deposition only on the pretreated areas of the dielectric surface. The catalytic activity of the laser-treated areas of the substrate is determined by the degree of structural changes: the greater the number of defects arising on the substrate surface upon laser treatment, the higher the catalytic activity this surface exhibits. In the case of dielectric substrates made of oxide ceramics, for the activation of substrate surface, the laser radiation power should be higher than the ablation threshold.[79]

Laser ablation of some dielectrics causes surface activation even without producing additional metal centres. In particular, this is the case with AlN ceramics, which decomposes on exposure to an excimer UV laser to give Al metal even when the energy flow is several J cm^{-2} (see Refs 34, 48, 49).

It is at the energy density of 2–4 J cm^{-2} (XeCl, ArF, KrF lasers) that the irradiated areas of the ceramics become able to reduce Cu, Ni and other metals from the corresponding chemical metal plating solutions. The metal deposition starts at some sites of the ablated surface, the density of these sites being 10^7 cm^{-2}, and the continuous metallic film is produced upon coalescence of separate metallic islands on their lateral growth. It was shown that ablation with an XeCl laser in air gives rise to metal islands on the Al_2O_3 surface, and they activate the surface.[47]

It was found[3] that a dielectric surface can be activated by a laser even when no metal atoms on the surface are present. It is evident that the presence of Al film on the activated surface is inconsistent with the possibility of repeated deposition–dissolution of the metallic precipitate in acids[3] onto a once activated surface, as the Al film would dissolve together with the metal deposited from the solution. In addition, according to the authors cited,[3] Al metal is vigorously dissolved in the proper chemical copper plating solution because the latter has a high pH (>12). Similarly, as the Al film is dissolved away from the ablated surface of AlN ceramics, the surface catalytic activity is retained. This also indicates that the activation mechanism cannot be reduced to mere formation of metal-coated areas on the surface. Assumptions concerning the existence of some other activation mechanism were also put forward in other publications.[78–84] However, the copper deposition in the above-described case can easily be interpreted also from the chemical standpoint by considering competing processes in the solution: Al dissolution in alkaline solution and Al displacement from the surface by copper due to the lower standard electrode potential of Al compared with Cu [furthermore, the copper reduction (*i.e.*, displacement of Al by Cu) is faster than Al dissolution].

While developing this prospective line of research, Shafeev *et al.*[45] elaborated a two-stage laser-induced nickel deposition technique for dielectric and semiconductor surfaces. The area of a diamond surface activated by a copper-vapour laser (510 nm) or a KrF laser (248 nm) in air is selectively metal-coated when placed in a solution for chemical reduction of nickel by hypophosphite. The effect of laser activation of the surface is stable in time and disappears only on heating the sample for 3 h at 350–400 °C. It was also shown[85] that on laser etching either in air or at the contact with a liquid (DMSO, H_2O, N_2H_4), a SiC surface becomes catalytically active and favours selective deposition of both nickel and copper (from appropriate metal plating solutions). The irradiated area was found[85] to acquire a layered structure: the upper layer consists of SiO_x; then, from top down, there is a layer of Si clusters and a layer of amorphous SiC. The Si clusters are the catalytic sites initiating the chemical deposition of metals. A similar two-stage method[3] is suitable for metal

coating of $SrTiO_3$, $PbTi_{1-x}Zr_xO_3$, Al_2O_3, ZrO_2, AlN and $LiNbO_3$ surfaces.

One more explanation for the laser activation of a dielectric (*e.g.*, Al_2O_3) towards chemical deposition is mechanical stress that remains in the material upon ablation. This is confirmed indirectly by the possibility of activation by mechanical indentation of the sample placed in a chemical metal plating solution. It was found that in this case, Cu is deposited on the treated surfaces both on elastic (indentation with a glass rod at a pressure of 8–10 kbar) and on inelastic deformation (diamond scribing of the surface). However, unlike laser activation, metal coating of the indented area can be accomplished only once — after acid dissolution of the metal precipitate, the metal is not deposited once again on the treated areas. This is caused by the fact that mechanical stress exists in the sample only during indentation and is eliminated as the mechanical load is removed. The mechanical stress that remains in the sample after laser ablation can be eliminated only by sample annealing.

Meanwhile, the process of autocatalytic deposition of metals provides good visualization of the residual stresses, because 10^8–10^9 metal atoms can be deposited on several active sites of the surface, which corresponds to the minimum size of metallic particles that is reliably resolved by a scanning electron microscope at early stages of deposition.[34]

The class of dielectrics that can be locally metal-coated by laser ablation can be extended. Apart from the oxide materials, laser activation is possible for polymer surfaces.[86,87] In this case, it is most probable that the metal is deposited on the free carbon surface resulting from laser ablation of the polymeric material.

The methods of nickel deposition on the dielectric and semiconductor surfaces differ depending on the material used. In the case of ceramic and single-crystalline dielectrics resistant to laser radiation, direct laser irradiation of the surface in air in the contact with an inert solvent or directly with the nickel plating solution is applicable. For polymeric materials, indirect methods without direct laser irradiation of the polymer substrate surface are more suitable. Exceptions are provided by thermoplastics (stable on heating above 300 °C) and materials containing inclusions of 4 mass % to 12 mass % Al, As, Sn or Sb oxide powders.[88] For these substrates, local nickel or copper deposition can be performed by exposing the material to laser radiation at <350 nm in air and subsequent immersion of the substrate into chemical metal plating solution in order to deposit nickel or copper.

The one-stage method for nickel deposition[35,36] on the surface of porous silicon, a promising material for optoelectronics and sensors, is of particular interest. The deposition is performed by repeated laser beam scanning of the porous silicon substrate surface coated by a thin film of chemical nickel plating solution. However, although the nickel deposit is homogeneous for optical and electron microscopy, EDX analysis still shows that the deposit contains phosphorus (10 mol.%) and oxygen (5 mol.%) inclusions.[35,36] This results in low conductivity of the obtained nickel structures (the calculated specific electrical conductivity is 10–15 times lower than the conductivity of pure nickel). Attention is attracted by the similarity of the outcomes of the laser-induced and the usual chemical deposition; this is seldom the case for copper deposition. The use of hydrazine as a reducing agent, which does not result in co-deposition of impurities together with nickel, might be a good alternative to phosphorus-containing nickel plating solutions.[64]

The results of Kordás *et al.*[35,36] confirm once again the good prospects of the laser activation of dielectric surfaces, because it is potentially possible to develop a one-stage method of local metal deposition in which the surface activation, reduction and crystallization of the metal precipitate occur almost simultaneously.

The above arguments in favour of the laser mechanism of surface activation supplement the data on the thermal activity of laser radiation in the initiation of the laser-induced liquid phase deposition of the metal.

4. Chemical surface activation by pre-deposition of a metal catalyst

Apart from the activation by physical treatment, there is also the traditional chemical activation method. Unfortunately, the state-of-the-art knowledge in this field does not suffice to choose unambiguously the effective surface activation method from general considerations. This can be done only based on numerous experiments.

The most widely used method of chemical activation includes two successive stages, which were called 'sensitization' and 'activation'.[54,60,62,64] Sensitization (increase in the sensitivity) involves treatment of the surface with a solution of Sn^{2+}, Fe^{2+}, Ti^{3+} or Ge^{2+} salt. The most effective is surface treatment in a $SnCl_2$ solution. The activation consists in treatment of the sensitized surface by solutions of catalytically active compounds of metals (Pd, Pt, Ag, Au, Rh, Ru, Os, Ir). Solutions containing Pd(II) compounds have found the most extensive use.

According to the one-stage chemical activation method, dielectric substrate is coated by a thin layer of a solution containing a light-sensitive metal compound, which decomposes as the substrate surface is irradiated with a laser along a desired contour or illuminated with a lamp according to the exposure mask. As the metal catalyst, Ag or Pd is used, since the catalytic properties for deposition of, *e.g.*, copper can be exhibited only by metals that are located on the left of copper in the Allred–Rochow electronegativity scale. The catalytic activity of the pre-deposited metal grains is determined by their nature, size, surface condition, the persistence of the active sites in the course of time and resistance to dissolution and oxidation. In addition, the surface activity and the quality of the deposited coating depend on the pattern of distribution of the catalyst particles and the strength of their adhesion to the substrate.

These particles are either applied ready or are formed during chemical transformations. The ready finely dispersed catalyst particles are applied on the substrate as a suspension and are then dried. Often the metal catalyst particles are formed on the activated surface in a solution for chemical deposition of a metal. It is also possible to coat the surface meant for metal plating with a potent reducing agent, which would induce the chemical deposition of the metal.[63] There are also other methods that imply preliminary introduction of special additives into the substrate composition, which may become active sites on the external treatment.[89–91]

In recent years, so-called combined solutions that contain simultaneously $PdCl_2$ and $SnCl_2$ have found wide use for surface preactivation.[72]

The solutions known currently make it possible to deposit metals such as Cu, Ni, Co, Pt, Pd, Au, Ni/Co, Pb, Sn, *etc*.[63, 72]

An original approach to the deposition of nickel microstructures on the polymeric surface was proposed by Kikuchi *et al*.,[92] who used the reverse sequence of operations and, instead of the activation of the dielectric by metal-coated centres, they performed metal deactivation by applying the dielectric layer, *i.e*., an aluminium plate was subjected to anodic oxidation. As a result, an oxide layer was formed on the metal surface, the thickness of this layer being easily controllable by the rate and duration of the electrolysis. A focused Nd : YAG laser beam (532 nm) which scanned the sample surface destroyed the oxide layer. After laser irradiation, the layer of nickel metal could be electrodeposited only on the irradiated area. Then the metallic structure was attached to an epoxide resin surface at 120 °C, and the aluminium layer was dissolved in a concentrated solution of NaOH, leaving the nickel structure on the epoxide resin surface.

The chemical methods of activation of the dielectric surface towards LCLD are still seldom used and have been little studied, because the chemical aspect of the interaction of the preactivated surface with laser radiation is by itself an extensive field of scientific research.

IV. Conclusion

Analysis of the data presented in the review allows one to infer some general trends for the laser-induced deposition of copper and nikel.

The outcome of laser-induced deposition depends, first of all, on physical factors: the laser radiation power, the rate of scanning of the substrate surface by the laser beam, the number of scans and the solution temperature. On the other hand, the role of chemical factors is also pronounced. These include the presence of ligands that form complexes with different instability constants in the autocatalytic solution, the change in the copper salt concentration, the introduction of additives that control the energy threshold of the reaction initiation.

The gas evolution upon side reactions between organic components of the solution is an adverse factor, which hampers the preparation of deposits with high-quality topology. The deposition of high-grade metal structures is facilitated by effective activation of the dielectric surface; the nature of the activated sites is also significant.

Despite the fact that the data on the processes in question available from the literature are still scattered and sometimes contradictory, the development of exactly these lines of research may be expected to ensure the future progress of the LCLD method, and they would determine the contents of the scientific research into the laser-induced deposition of metals on dielectric substrates.

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References

1. Yu S Tver'yanovich, V A Kochemirovsky, A A Man'shina, A V Povolotsky, A V Povolotskaya, S V Safonov, I I Tumkin *Lazerno-indutsirovannoe Osazhdenie Zolota i Medi iz Rastvorov* (Laser-Induced Chemical Liquid Phase Deposition of Gold and Copper) (St Petersburg: A S Pushkin Leningrad University, 2010)
2. Y S Tver'yanovich, A G Kuz'min, L G Menchikov, V A Kochemirovsky, S V Safonov, I I Tumkin, A V Povolotsky, A A Man'shina *Mendeleev Commun.* **21** 34 (2011)
3. G A Shafeev *Kvant. Elektron.* **24** 1137 (1997) [a]
4. K Kordás, K Bali, S Leppävuori, A Uusimäki, L Nánai *Appl. Surf. Sci.* **154 – 155** 399 (2000)
5. X C Wang, H Y Zheng, G C Lim *Appl. Surf. Sci.* **200** 165 (2002)
6. J H-G Ng, M P Y Desmulliez, A McCarthy, H Suyal, K A Prior, D P Hand *DTIP MEMS/MOEMS* 360 (2008)
7. H Yang, C-T Pan *J. Micromech. Microeng.* **12** 157 (2002)
8. K Kordás *Acta Univ. Oulu* 168 (2002)
9. A A Man'shina, A V Povolotsky, T Yu Ivanova, A V Kurochkin, Yu S Tver'yanovich, D Kim, M Kim, S Kvon *Fiz. Khim. Stekla* **33** 297 (2007) [b]
10. H Moilanen, J Remes, S Leppävuori *Phys. Scr.* (T69) 237 (1997)
11. T Szörényi, Z Kántor, Z Tóth, P Heszler *Appl. Surf. Sci.* **138** 275 (1999)
12. Z Kántor, Z Tóth, T Szörényi, A L Tóth *Appl. Phys. Lett.* **64** 3506 (1994)
13. H G Müller *Appl. Phys. Lett.* **56** 904 (1990)
14. K Bali, T Szörényi, M R Brook, G A Shafeev *Appl. Surf. Sci.* **69** 75 (1993)
15. K Bali, T Szörényi, M R Brook, G A Shafeev, K I Grandberg *Mat. Sci. Eng., B* **17** 101 (1993)
16. G Tóth, K Kordás, J Vähäkangas, A Uuisimäki, T F George, L Nánai *J. Phys. Chem. B* **109** 6925 (2005)
17. M R Bruk, G A Shafeev, V S Petrosyan, V P Dyadchenko, K I Grandberg, E I Smyslova *Kvant. Elektron.* **18** 1088 (1991) [a]
18. F V Bunkin, K I Grandberg, B S Luk'yanchuk, E G Perevalova, G A Shafeev *Kvant. Elektron.* **13** 1321 (1986) [a]
19. G A Shafeev, Doctoral Thesis in Physical and Chemical Sciences, Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, 1999
20. J Messelhäuser, E B Flint, H Suhr *Appl. Surf. Sci.* **54** 64 (1992)
21. *Platy Pechatnye. Osnovnye Parametry i Konstruktsii. Gosudarstvennyi Standart SSSR 23751-86* (Plated Circuit Cards. Main Parameters and Constructions. State Standard of USSR 23751-86) (Moscow: State Committee on Standard, 1987)
22. D Dudek *Tekhnol. Elektron. Prom-ti* (5) 17 (2005)
23. R J von Gutfeld, E E Tynan, R L Melcher, S E Blum *Appl. Phys. Lett.* **35** 651 (1979)
24. H Esrom *Appl. Surf. Sci.* **168** 1 (2000)
25. A Ouchi, Z Bastl, J Boháček, J Šubrt, J Pola *Surf. Coat. Technol.* **201** 4728 (2007)
26. C T Pan *Microelectron. Eng.* **71** 242 (2004)
27. L Miní, C Giaconia, C Arnone *Appl. Phys. Lett.* **64** 3404 (1994)
28. H S Cole, Y S Liu, J W Rose, R Guida *Appl. Phys. Lett.* **53** 2111 (1988)
29. K Kordás, J Békési, R Vajtai, L Nánai, S Leppävuori, A Uusimäki, K Bali, T F George, G Galbács, F Ignácz, P Moilanen *Appl. Surf. Sci.* **172** 178 (2001)
30. D Chen, Q Lu, Y Zhao *Appl. Surf. Sci.* **253** 1573 (2006)
31. R Deng, J Li, H K Kang, H J Zhang, C C Wong *Thin Solid Films* **519** 5183 (2011)

32. K Kordás, L Nánai, K Bali, K Stépán, R Vajtai, T F George, S Leppävuori *Appl. Surf. Sci.* **168** 66 (2000)
33. G Shafeev, W Marine, H Dallaporta, L Bellard, A Cros *Thin Solid Films* **241** 52 (1994)
34. G A Shafeev *Adv. Mater. Opt. Electron.* **2** 183 (1993)
35. K Kordás, J Remes, S Leppävuori, L Nánai *Appl. Surf. Sci.* **178** 93 (2001)
36. K Kordás, S Leppävuori, J Békési, L Nánai, J Remes, R Vajtai, S Szatmári *Appl. Surf. Sci.* **186** 232 (2002)
37. B S Park, A P Malshe, A Muyshondt, W D Brown *Surf. Coat. Technol.* **115** 201 (1999)
38. H Yokoyama, S Kishida, K Washio *Appl. Phys. Lett.* **44** 755 (1984)
39. J L H Chau, C-Y Chen, M-C Yang, K-L Lin, S Sato, T Nakamura, C-C Yang, C-W Cheng *Mater. Lett.* **65** 804 (2011)
40. A Manshina, T Ivanova, A Povolotskiy *Laser Phys.* **20** 1532 (2010)
41. RF P. 2365683 (2009)
42. A A Manshina, A V Povolotskiy, T Y Ivanova, Y S Tver'yanovich, S P Tunik, D Kim, M Kim, S C Kwon *Appl. Phys. A* **89** 755 (2007)
43. J Xu, Y Liao, H Zeng, Y Cheng, Z Xu, K Sugioka, K Midorikawa *Opt. Commun.* **281** 3505 (2008)
44. L Nánai, I Hevesi, F V Bunkin, B S Luk'yanchuk, M R Brook, G A Shafeev, D A Jelski, Z C Wu, T F George *Appl. Phys. Lett.* **54** 736 (1989)
45. G A Shafeev, S M Pimenov, E N Loubnin *Appl. Surf. Sci.* **86** 392 (1995)
46. US P. 2010/0129566 (2010)
47. A J Pedraza, M J Godbole, M J DeSilva, D H Lowndes *MRS Symp. Proc.* **285** 203 (1992)
48. H Esrom *MRS Symp. Proc.* **204** 457 (1991)
49. H Esrom, J-Y Zhang, A J Pedraza *MRS Symp. Proc.* **236** 383 (1992)
50. J G Liu, C H Chen, J S Zheng, J Y Huang *Appl. Surf. Sci.* **245** 155 (2005)
51. A Manshina, A Povolotskiy, T Ivanova, A Kurochkin, Y Tver'yanovich, D Kim, M Kim, S C Kwon *Laser Phys. Lett.* **4** 163 (2007)
52. A Manshina, A Povolotskiy, T Ivanova, A Kurochkin, Y Tver'yanovich, D Kim, M Kim, S C Kwon *Laser Phys. Lett.* **4** 242 (2007)
53. M I Shalauskas *Metallizatsiya Plastmass* (Metal Plating of Plastics) (Moscow: Znanie, 1983)
54. M Kapitsa *Tekhnol. Elektron. Prom-ti* (6) 35 (2005)
55. M D Bal'makov, G M Muradova *Fiz. Khim. Stekla* **36** 140 (2010) [b]
56. L Nánai, K Kordás, S Leppävuori, T F George, in *Modern Topics in Chemical Physics* (Eds T F George, X Sun, G P Zhang) (Trivandrum, India: Research Signpost, 2002) p. 287
57. A M Kuznetsov *Elektrokhimiya* **27** 1516 (1991) [c]
58. N V Karlov, N A Kirichenko, B S Luk'yanchuk *Russ. Chem. Rev.* **62** 203 (1993); *Usp. Khim.* **62** 223 (1993)
59. N V Karlov, N A Kirichenko, B S Luk'yanchuk *Lazernaya Termokhimiya* (Laser Termochemistry) (Moscow: Nauka, 1992)
60. N F Melashchenko *Gal'vanicheskie Pokrytiya Dielektrikov* (Galvanic Coating on Dielectrics) (Minsk: Belarus', 1987)
61. M Ramasubramanian, B N Popov, R E White, K S Chen *J. Appl. Electrochem.* **28** 737 (1998)
62. M Kapitsa *Tekhnol. Elektron. Prom-ti* (1) 26 (2006)
63. V V Sviridov, T N Vorob'eva, T V Gaevskaya, L I Stepanova *Khimicheskoe Osazhdenie Metallov iz Vodnykh Rastvorov* (Chemical Deposition of Metals from Aqueous Solutions) (Minsk: Izd. Universitetskoe, 1987)
64. T P Petrova *Soros. Obrazovat. Zh.* **6** (11) 57 (2000) [d]
65. I I Tumkin, S V Safonov, V A Kochemirovsky, in *Trudy Mezhdunarodnoi Nauchno-tekhnicheskoi Konferentsii 'Nanotekhnologii Funktsional'nykh Materialov' (NFM'10)* [Proceedings of International Scientific and Technical Conference 'Nanotechnologies of Functional Materials' (NFM'10), St Petersburg, 2010] p. 280
66. N K Ivanov-Esipovich *Fiziko-Khimicheskie Osnovy Proizvodstva Radioelektronnoi Apparatury* (Physicochemical Fundamentals of Radio-Electronic Equipment) (Moscow: Vysshaya Shkola, 1979)
67. M Hansen, K Anderko *Constitution of Binary Alloys* (Second Ed.) (New-York, Toronto, London: McGraw-Hill, 1958)
68. V A Kochemirovsky, S V Safonov, I I Tumkin, Yu S Tver'yanovich, I A Balova, L G Menchikov *Izv. Akad. Nauk, Ser. Khim.* 1540 (2011) [e]
69. J Ohara, M Nagakubo, N Kawahara, T Hattori, in *Proceedings of the IEEE Tenth Annual International Workshop on MicroElectroMechanical Systems* (New York: IEEE, 1997) p. 175
70. V A Ageev, A F Bokhonov, V V Zhukovskii, A A Yankovskii *J. Appl. Spectrosc.* **64** 683 (1997)
71. A Kruusing *Opt. Lasers Eng.* **41** 329 (2004)
72. M D Mikhailov, Yu S Tver'yanovich, E Yu Turkina *Khimiya Stekol i Rasplavov* (The Chemistry of Glasses and Melts) (St Petersburg: St Petersburg State University, 1998)
73. M D Bal'makov *Fiz. Khim. Stekla* **15** 293 (1989) [b]
74. I I Roslov, Candidate Thesis in Chemical Sciences, Herzen University, St Petersburg: 2010
75. T B Boitsova, Doctoral Thesis in Chemical Sciences, Herzen University, St Petersburg: 2010
76. M D Bal'makov *Fiz. Khim. Stekla* **37** 210 (2011) [b]
77. K Kordás, A E Pap, V Lyöri, A Uusimäki, J Vähäkangas, S Leppävuori *Surf. Coat. Technol.* **155** 285 (2002)
78. S I Dolgaev, A A Lyalin, A V Simakin, G A Shafeev *Kvant. Elektron.* **23** 67 (1996) [a]
79. G A Shafeev *Dokl. Akad. Nauk* **332** 440 (1993) [f]
80. D H Lowndes, M J Godbole, G E Jellison Jr, A J Pedraza *AIP Conf. Proc.* **288** 321 (1993)
81. A J Pedraza, J W Park, M J DeSilva, D H Lowndes, D N Braski, H M Meyer III *AIP Conf. Proc.* **288** 329 (1993)
82. T J Turner, J H Crawford Jr *Phys. Rev. B* **13** 1735 (1976)
83. K H Lee, J H Crawford Jr *Phys. Rev. B* **19** 3217 (1979)
84. H H Tippins *Phys. Rev. B* **1** 126 (1970)
85. S I Dolgaev, V V Voronov, G A Shafeev, C Fauquet-Ben Ammar, J-M Themlin, A Cros, W Marine *Appl. Surf. Sci.* **109–110** 559 (1997)
86. G A Shafeev *Appl. Phys. A* **55** 387 (1992)
87. A A Lyalin, M S Nunuparov, A V Simakin, G A Shafeev *Adv. Mater. Opt. Electron.* **5** 299 (1995)
88. US P. 5599592 (1997)
89. EP P. 1367872 (2003)
90. R C Sausa, A Gupta, J R White *J. Electrochem. Soc.* **134** 2707 (1987)
91. M R Bruk, E A Morozova, G A Shafeev *Izv. Akad. Nauk, Ser. Fiz.* **54** 2480 (1990) [g]
92. T Kikuchi, M Sakairi, H Takahashi, Y Abe, N Katayama *Surf. Coat. Technol.* **169–170** 199 (2003)

[a] — *Quantum. Electron. (Engl. Transl.)*
[b] — *Glass Phys. Chem. (Engl. Transl.)*
[c] — *Russ. J. Electrochem. (Engl. Transl.)*
[d] — *Soros Educ. J. (Engl. Transl.)*
[e] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[f] — *Dokl. Phys. (Engl. Transl.)*
[g] — *Bull. Russ. Acad. Sci., Phys. (Engl. Transl.)*