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Laser-induced deposition of nanostructured copper microwires on surfaces of composite materials

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ABSTRACT

Microelectronics industry is growing fast and the rate of new devices' development increases every year. Therefore, methods for simple and high-precision metal coating on dielectrics are needed. Existing methods do not allow performing the high-precision metal deposition without using photomasks, while making a photomask for each prototype is a long and expensive process. One of the methods of maskless metal deposition is laser-induced chemical liquid-phase deposition (LCLD). In this work we show the effect of substrate surface type on a result of LCLD. Deposited copper structures were characterized by SEM, EDX and impedance spectroscopy. The results show that laser-induced copper deposition is highly affected by the surface being a homogeneous or composite material. It was found that the deposits with low resistivity and high quality metal localization mostly appear on the two-phase surfaces. In contrast, deposits on one-phase surfaces exhibited poor topology of copper material. Statistical modeling was involved to describe this phenomenon.

1. Introduction

The method of laser-induced chemical liquid-phase deposition (LCLD) is a promising approach to deposit metals on various substrates in the laser beam focus. The LCLD method makes it possible to create small-size metallic structures (with the width of a wire ranging from 1 to 200 μm) on surfaces of various dielectrics and semiconductors using no photomask [1–4]. Copper deposition is of the main interest, as copper has a high value of electric conductivity. Scanning the surface of a dielectric placed into the special copper plating solution with a focused laser beam allows the chemical reaction of copper (II) reduction to metallic copper to be initiated locally [4].

The activation process plays a crucial role in crystal phase formation on a dielectric surface by the LCLD method. This process depends on the nature of the dielectric surface used and surface defects of the dielectric. The essence of the dielectric surface activation process is that active sites, providing electron transfer from a reducing agent to a metal ion, are formed on the dielectric surface under the external effects [5]. Afterwards, the reduced metal becomes a catalyst for the further chemical reaction of metal reduction. Such process is referred to as autocatalytic deposition [6].

Upon laser irradiation [7], local changes in the electronic structure of ablated regions may occur due to residual mechanical stresses in the material. As a result, electron density in conduction band increases, making the electron transfer from the dielectric to metal ions in solution possible [1]. The considered model may find an original interpretation for two-phase composite materials with a broad interface. Double electric layer is always formed at interfaces. Negative charge formed on one of the surfaces also contributes to an increase in the local electron density. Being activated by laser radiation, an interface between two materials may serve as a set of activated sites, which have high catalytic activity in the metallization process. In work [8] the effect of surface tension at the solution–dielectric interface was studied and it was shown that changes in surface properties cause a significant effect on the metallization process. The aim of the present work is to investigate the surface effect on the LCLD process and, especially, laser-induced deposition of copper on composite surfaces. As we assumed above, surfaces to be metallized should have multiple active sites due to a redistribution of electron density at the interface. This assumption correlates with the data by other researchers [17]. It is shown in [9] that thermal treatment of a composite glass–ceramic material enhances the formation of point defects or electron-hole pairs in photoactive TiO_2. Laser irradiation combines thermal and photochemical effects on materials. Therefore, defects at the interface may form via both photochemical and thermal mechanisms. Possible occurrences of photoeffect in LCLD processes were discussed in paper [10]. One more possible mechanism of the formation of defects in composite materials under the laser effect, "laser doping" should be mentioned: the surface layer of one material penetrates in another material under the laser irradiation, leading to the formation of defects influencing electronic structure of the material.

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For instance, laser doping may cause the formation of donor or acceptor levels in solid semi-conductors [11].

Presented examples demonstrate that two-phase materials may be readily laser-activate through several different mechanisms and, consequently serve as prospective substrates for the laser-induced deposition of metals. In the present paper, two single-phase and two composite materials are investigated; the properties of the deposited copper structures are compared.

Four investigated materials include oxide glass (single-phase material), sitall (two-phase material, consisting of glass and ceramics), polycor (single-phase ceramic material), and fiber glass reinforced plastic (two-phase material, consisting of polymer and glass).

Manshina et al. reported that surfaces of oxide glasses may be activated for metallization [12–14]. However, the quality of obtained structures was unsatisfactory, and copper structures had high electric resistance. The series of investigations on this topic were carried out by our group [4,15]. However, electrically conductive copper structures were obtained only in one case, namely, upon deposition from surfactant-containing solutions [16]. The glass surface cannot be activated by laser beam without an additional surface modification. The surface of Al_3O_3 was metallized by the group of Shafeev using a pulse laser [17]. However, the two-step method was used in papers by Shafeev. In the two-step method the initial laser irradiation in air environment was followed by chemical metallization in solution. Fundamentally different results may be obtained in the case of a single-step metallization of Al_2O_3-based ceramic materials. No reports were found on the laser metallization of sitalls except investigations by our group [18]. Regarding the metallization of fiber glass reinforced plastics, with copper plating is a routine procedure, however, laser-induced deposition of metals on them is nearly not investigated.

In this paper experimental data presented earlier in work [18] was partially used to compare the whole range of materials investigated by our group.

2. Material and methods

The experimental setup used to deposit metals with the LCLD method is schematically depicted in Fig. 1.

Laser beam (1) was directed through a beam splitting cube (3) that diverted a portion of the laser radiation to the CCD camera for optical focusing and in situ monitoring of metal deposition. The sample-targeted beam was focused to produce a 5-μm spot at $1/e^2$ intensity using a 4× microscope objective lens (4) at the dielectric/solution interface. The dielectric was irradiated "from the solution side" for non-transparent substrates (glass–ceramics) and "from the substrate side" for transparent substrates. The dielectric and the electrolyte solutions were placed on a motorized translation stage (8) driven by the controller (12). Operating commands from the computer (11) were generated using original software. The same computer received data from the CCD-camera (10) that was used to monitor the deposition process in real-time mode.

Copper structures were deposited using a continuous diode-pumped solid-state Nd:YAG laser (DPSS) operated at power range from 100 to 2000 mW ($\lambda = 532$ nm). The laser beam was focused to a fixed spot of 10 μm in diameter on the dielectric surface. The substrate was translated on the motorized stage with respect to the focus point at the speed of 0.0025 mm/s for the glass–ceramics substrate. The laser power density in the experiments varied from $7 * 10^4$ to $1.5 * 10^6$ W/cm^2.

Copper was deposited on four different materials:

1. Oxide glass, 1 mm thick, the composition of oxide glass: 72% SiO_2, 15% Na_2O, 6.8% CaO, 4.2% MgO, and 2% Al_2O_3 with a single-phase glass surface with no interfaces or grain boundaries.
2. Ceramics polycor, consisting of a heat-proof α-Al_2O_3 also known as electrocorundum. α-Al_2O_3 is chemically inert due to its stable crystal lattice.
3. Sitall, which is widely used in microelectronics. The composition of sitall ST-50-1 is: SiO_2 (60.5%), Al_2O_3 (13.5%), CaO (8.5%), MgO (7.5%), and TiO_2 (10%). Sitall is a composite material containing a well-developed interface between the crystalline Al_2O_3 phase and oxide glass.
4. Fiber-reinforced plastic (FR-4). FR-4 is industrially used in microelectronics. Substrate is a glass-fiber fabric with an epoxyphenol binder. This is a composite material with a well-developed interface between the glass material and the polymer.

SEM images were collected using a Zeiss Supra 40 VP Field Emission Scanning Electron Microscope (FESEM) equipped with Energy Dispersive X-ray (EDX) Spectrometer that was used for chemical analysis. The impedance spectra of copper lines were recorded using an impedance meter Z-2000 by Elins Co. (Russia, Chernogolovka) employing the four-point probe method within the frequency range from 20 Hz to 2 MHz and a signal amplitude of 125 mV.

The composition of solution no. 1 for the formation of copper structures was 0.01 M $CuCl_2$, 0.05 M NaOH, 0.03 M potassium sodium tartrate (Rochelle salt), and 0.075 M HCHO.

The composition of solution no. 2 for the formation of copper structures was 0.01 M $CuCl_2$, 0.05 M NaOH, 0.03 M potassium sodium tartrate (Rochelle salt) ($KNaC_4H_4O_6 \times 4H_2O$), and 0.075 M sorbitol.

The composition of solution no. 3 for the formation of copper structures was 0.01 M $CuCl_2$, 0.05 M NaOH, and 0.03 M potassium sodium tartrate (Rochelle salt) ($KNaC_4H_4O_6 \times 4H_2O$), without a reducing agent.

All the used chemicals were of analytical grade of purity.

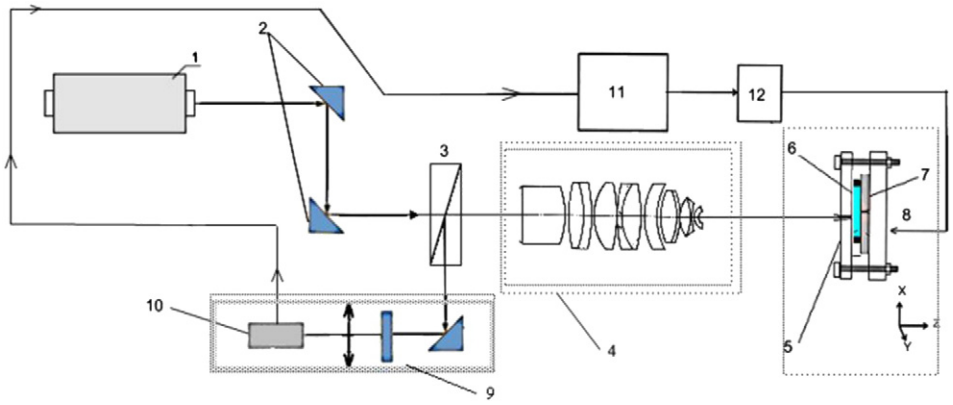

Fig. 1. Schematic representation of the device for the laser-induced deposition of metals from solutions: 1 — DPSS laser (532 nm), 2 — collimating mirrors, 3 — beam splitting cube, 4 — focusing objective, 5 — optical transparent quartz plate, 6 — plating solution, 7 — substrate to be plated, 8 — motorized translation stage, 9 — defocusing objective, 10 — CCD camera, 11 — PC, and 12 — controller.