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The influence of non-ionic surfactants on laser-induced copper deposition

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ABSTRACT

We describe the laser-induced chemical liquid phase deposition of copper using a solution containing a non-ionic surfactant on substrates comprising either an oxide glass or a glass-ceramic Sitall. Our results demonstrate that the addition of the surfactant to the deposition solution results in improved structural topology in the deposited copper layer. Our data confirm that the use of a non-ionic surfactant can reduce the negative influence of gas formation during the deposition process.

1. Introduction

Interest in the laser-induced chemical liquid phase deposition of copper (LCLD) stems from its possible applications in microelectronics and other technologies, as it allows the mask-less production of metallic structures on the surface of dielectrics. Scanning of the dielectric surface in a special copper solution with a focused laser beam locally activates copper reduction, resulting in the deposition of copper along the path of the laser [1–5].

The LCLD process is complicated by the accompanying gas formation [6,7], which can lead to the defocusing of the laser beam and prevents the diffusion of reagents into the reaction zone. One way to minimize unwanted gas formation is through the addition of surfactants. Surfactants reduce the surface tension at the boundary of the gas phase and the solution, thereby separating gas bubbles from the surface of the dielectric [8]. It is also known [9,10] that surfactants can enhance the nucleation process during the formation of the metallic deposit.

Previously, we demonstrated [8] that ionic surfactants negatively affect the topology of deposited copper structures in the LCLD process (Fig. 1a and b), despite their facilitation of bubble detachment from the surface of the dielectric. The use of ionic surfactants for chemical plating was found to exert an inhibitive effect on the phase boundary [11], leading to a deterioration of the copper structure topology.

In this study, we investigated the effect of a non-ionic surfactant (ethoxylated fat alcohol) on the laser-induced chemical liquid phase deposition of copper, as well as on the topology and other properties of the deposited copper structures.

2. Materials and methods

The investigation of laser-induced copper deposition from solution was conducted using the setup depicted in Fig. 2.

A laser beam (1) was directed through a beam splitting cube (2) that diverted a portion of the laser radiation to the CCD camera for optical focusing and *in situ* monitoring of the 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 (3) at the dielectric/solution interface. The dielectric was irradiated "from the side of the solution" for non-transparent substrates (glass-ceramics) and "from the side of the substrate" for transparent substrates. The dielectric and the electrolyte solution were placed on a motorised translation stage (7) driven by a controller (11). The operating

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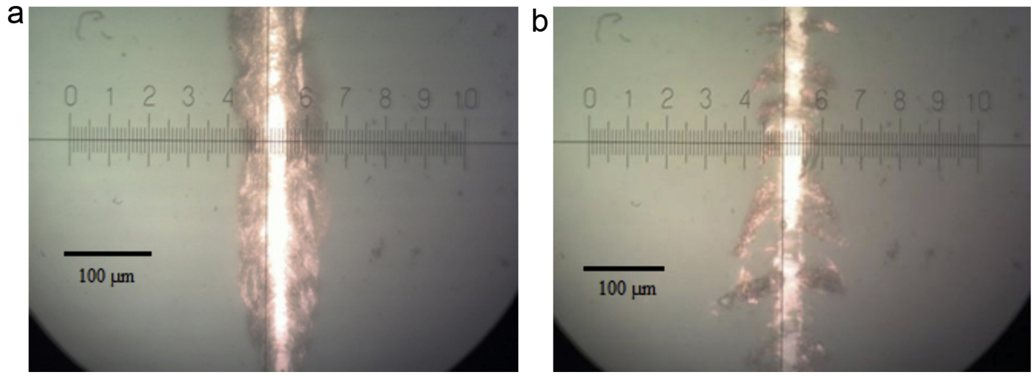

Fig. 1. (a) A copper structure on the surface of an oxide glass substrate, deposited from a standard copper trilonate solution with the addition of tetraethyl ammonium bromide (TEAB) surfactant [8]. (b) A copper structure on the surface of an oxide glass substrate, deposited from a standard copper trilonate solution with the addition of p-toluene sulphonic acid surfactant [8].

commands from the computer (10) were generated using original software. The same computer received data from the CCD-camera (9) that was used to monitor the deposition process in real-time.

The copper structures were deposited using a continuous diode-pumped solid-state Nd:YAG laser (DPSS) operated at a power ranging from 100 to 2000 mW ($\lambda = 532$ nm). The laser beam was focused to a fixed spot 10 μm in diameter on the dielectric surface. The substrate was translated on the motorized stage with respect to the focus point at a speed of 0.01 mm/s for the glass substrate and 0.0025 mm/s for the glass-ceramics substrate.

Copper was deposited onto dielectric substrates composed of either oxide glass (composition: 71.8% SiO_2, 14.8%, Na_2O, 6.7% CaO, 4.1% MgO, 2.0% Al_2O_3, 0.5%SO_3) or the crystalline glass ceramic material Sitall, which is widely used in microelectronics. The composition of Sitall ST-50-1 is as follows: SiO_2 (60.5%), Al_2O_3 (13.5%), CaO (8.5%), MgO (7.5%), TiO_2 (10%).

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

The non-ionic surfactant pentaethylene glycol monododecyl ether (C12E5) used in this study possesses the chemical formula $CH_3(CH_2)_{11}(OCH_2CH_2)_5OH$ (CAS Number 3055-95-6), HLB = 11.7.

The compositions of the solutions used for copper structure formation were as follows:

- 0.01 M $CuCl_2$, 0.011 M EDTA, 0.05 M NaOH, 0.075 M formaldehyde, 3×10^{-3} M 1,4-benzoquinone (Solution 1);

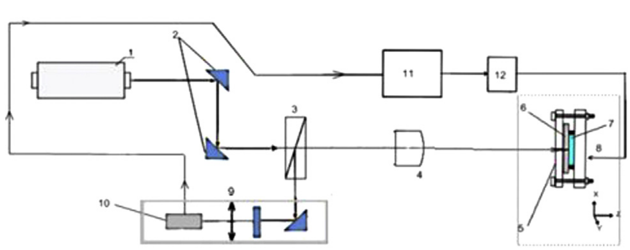

Fig. 2. Schematic of the device for the laser-induced deposition of metals from solution.

- 0.01 M $CuCl_2$, 0.011 M EDTA, 0.05 M NaOH, 0.075 M formaldehyde, 3×10^{-3} M 1,4-benzoquinone, 2×10^{-5} M non-ionic surfactant (Solution 2);
- 0.01 M $CuCl_2$, 0.03 M potassium sodium tartrate (Rochelle salt) ($KNaC_4H_4O_6 \cdot 4H_2O$), 0.05 M NaOH, 0.075 M sorbitol, 3×10^{-3} M 1,4-benzoquinone (Solution 3);
- 0.01 M $CuCl_2$, 0.03 M potassium sodium tartrate (Rochelle salt) ($KNaC_4H_4O_6 \cdot 4H_2O$),0.05 M NaOH, 0.075 M sorbitol, 3×10^{-3} M 1,4-benzoquinone, 2×10^{-5} M non-ionic surfactant (Solution 4).

Solution 1 is a standard chemical copper plating solution that employs formaldehyde as a reducing agent but has been modified by the addition of 1,4-benzoquinone [12]. The addition of 1,4-benzoquinone decreases the laser power required to initiate the chemical reaction [12].

Solution 2 possesses the same chemical composition as Solution 1 but has been modified by the addition of the non-ionic surfactant. Solution 3 includes sorbitol as a reducing agent, which we previously found [13] to act as a good substitute for formaldehyde in LCLD. Solution 4 is identical to Solution 3 with the exception of the addition of the non-ionic surfactant. In the cases in which surfactant was used, it was added in an amount below the critical micelle concentration.

3. Results

The addition of ionic surfactants (Fig. 1a and b) generally leads to unsatisfactory topology [8]. The laser-induced chemical liquid phase deposition of copper from Solution 2 onto the oxide glass substrate produced deposits that exhibited a typical copper lustre and topological qualities, as determined by optical microscopy (Fig. 3a). No breaks were observed and the deposits displayed clearly defined edges. For comparison, Fig. 3b presents the track deposited from a copper solution lacking the non-ionic surfactant (Solution 1). Numerous defects can be observed. The addition of the non-ionic surfactant to Solution 3 exerted similar positive effects on the topology of copper deposited on the ceramic surface Sitall ST 50-1 (Fig. 3c). For comparison, an optical image of copper deposited on Sitall without the addition of surfactant (Solution 4) [13] is displayed in Fig. 3d. These results demonstrate that adding a non-ionic surfactant to the deposition solution significantly improves the deposit topology.

To more completely characterise the topology and resistivity of copper structures deposited from Solution 2 onto an oxide glass surface, the deposit profile was measured (Fig. 4). The measurement revealed that the deposit had clearly defined edges and a rough surface, was continuous in length, and exhibited no breaks and a maximum height of 2.4 μm. Impedance spectroscopy data

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