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# LASER-INDUCED CHEMICAL LIQUID-PHASE DEPOSITION OF COPPER ON TRANSPARENT SUBSTRATES

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# Laser-induced chemical liquid-phase deposition of copper on transparent substrates

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### Abstract

Laser-induced chemical liquid phase deposition allows maskless manufacturing of metallic structures on the surface of dielectrics and is prospected to be a promising tool in the field of microelectronics and microfluidics. The aim of the work presented here is to combine this deposition method with a related micro-structuring method known as laser-induced backside wet etching. Fabricating both, microstructured surface structures and subsequent deposition of conducting patterns within the same setup would be an interesting tool for rapid prototyping.

To demonstrate the functional principle of this combined approach conductive copper lines were deposited at the backside of both polished and structured soda lime glass substrates by using a focused, scanning ns-pulsed Ytterbium fiber laser at 532nm wavelength. The deposition process is initiated by a photo induced reaction of a $CuSO_4$-based liquid precursor in contact with the backside of the substrate. The obtained metallic copper deposits are crystalline, stable under ambient conditions and have a conductivity in the same order of magnitude as bulk copper.

### Introduction

An interesting application for laser surface processing is the fabrication of metallic micro-structures with high lateral resolution. Such structures can find application in many fields of technology, such as in microelectronics, optoelectronics, micromechanics especially for sensor and actuator devices. One possibility to deposit such structures is laser-induced chemical liquid-phase deposition (LCLD) [1,2], a simple and cost-effective deposition method, where neither expensive vacuum exhaust and gas systems, nor spin-on, active site seeding or mask projection processes are required. In addition the components are affordable and easy to handle. LCLD is a well-known technique and is applied for a long time already [1-9]. In recent work, our group investigated an ablation technique called laser induced backside wet etching (LIBWE) [10,11]. This technique allows smooth and controlled ablation of transparent materials using related setup components like LCLD and also related $CuSO_4$-based solutions as absorber liquids. Since in LIBWE the ablation is done at the back side of the substrate, it would be interesting to perform LCLD at the backside as well, regarding the promising possibility to combine these two processes, i.e. ablation and deposition.

In this paper, copper structures fabricated at the backside of the substrate (i.e. with an “inverse” setup) are presented, as well as a qualitative example of a combination of the two processes (i.e. LCLD of a conductive copper line on a LIBWE-structured surface). The deposited copper features were investigated regarding their topography, composition and electrical properties.

### Experimental

For both the LIBWE and the LCLD process, the same experimental setup has been used (see Fig.1).

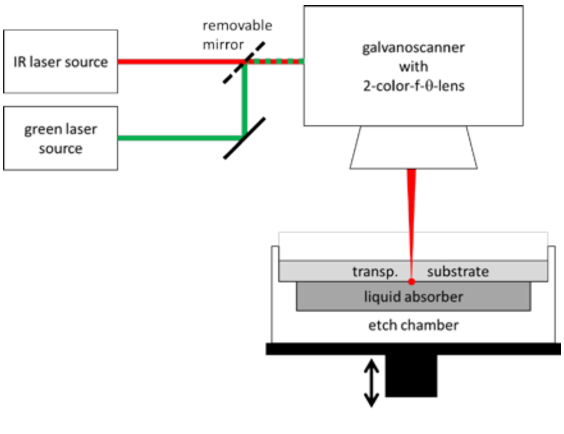


Fig.1: Experimental Setup for LIBWE and LCLD

A PTFE laser etch chamber with a reservoir for the $CuSO_4$-based liquid precursor of about 25ml and capable of fitting 50x50mm soda lime substrates was fixed on top of a height adjustable stage. The liquid precursor was placed in contact with the downside of the transparent substrate. Laser light was irradiated from the front side of the substrate and was focused onto the solid-liquid interface region. A galvano-scanner with a two-color-f-theta-lens of 163mm focal length has been used to control the scanning pattern and the lateral velocity of the laser beam.

However, several parameters, i.e. the wavelength of the laser or the composition of the liquid precursor differ between the two processes. Details will be specified in the following section:

***Ablation by LIBWE***

For the ablation process, a ns-pulsed ytterbium fiber laser with 1064nm center wavelength and a pulse width of 20ns has been used as laser source; as well as saturated aqueous $CuSO_4$-solution (1.25mol/l) as liquid absorber. The laser was focused onto the solid-liquid interface with a spot size of 45µm diameter.

Roughness and geometry of the etched structures can be controlled by laser and scanning parameters [11] and have been chosen appropriately in order to have a well-defined groove for subsequent copper deposition by LCLD.

***Deposition by LCLD***

For the deposition of copper features, a ns-ytterbium fiber laser with 532nm center wavelength and a pulse width of 1.4ns has been used as laser source. By coupling the laser source into the same beam path as the source for LIBWE, the same setup can be used subsequently. The composition of the liquid precursor was: 0.1mol/l $CuSO_4$, 0.2mol/l KNa-tartrate (Rochelle Salt, $KNaC_4H_4O_6$ x $4H_2O$), 0.125mol/l NaOH and 6mol/l formaldehyde ($CH_2O$). Laser light was irradiated from the front side of the substrate and was focused onto the solid-liquid interface region. Note that contrary to our setup, in most of the LCLD setups the precursor liquid is placed on top of the substrate.

For the LCLD experiments, focal plan positions from -3.5 to +3.5mm with respect to the solid liquid interface, scan velocities from 0.02mm/s to 10mm/s, pulse repetition rates from 50 to 300kHz, fluence values from a few $mJ/cm^2$ to $650mJ/cm^2$ and number of sweeps from 1x to 2400x have been analyzed systematically. It has been found that for the inverse setup used in our experiments, a two-step approach has to be applied. In a first step an initial “baseline” has to be written, followed by superposed multiple line scans using laser parameters different from the baseline parameters.

***Comparison between LIBWE and LCLD***

An overview of both processes is shown in Table 1:

Table 1: LIBWE versus LCLD

| **LIBWE** | **LCLD** |
|---|---|
| *laser source* | |
| ns pulsed fiber laser<br>1064nm<br>20ns | ns pulsed fiber laser<br>532nm<br>1.4ns |
| *process type* | |
| ablation process<br>single-step:<br>superposed multiple scans | deposition process<br>two-step:<br>1st: baseline (1 iterat.)<br>2nd: super-posed multiple scans |
| *liquid absorber* | |
| aq. $CuSO_4$-solution | aq.$CuSO_4$-tartrate-formaldehyde-solution |
| *focus plane position* | |
| at interface substrate/liquid | defocussed from interface |
| *rate* | |
| ablation rate:<br>app. $2*10^6 µm^3/min$ | deposition rate:<br>app. $1.5*10^3 µm^3/min$ |

## Results

***LIBWE – results***

A well-defined etching groove with trapezoidal cross section (width: 400µm, depth: 13µm) without micro cracks around the area has been fabricated as test structure for subsequent copper deposition. Laser scanning microscope measurements have been performed to analyze the topography ($500x500µm^2$-area) and the roughness ($180x100µm^2$ area at bottom of groove).

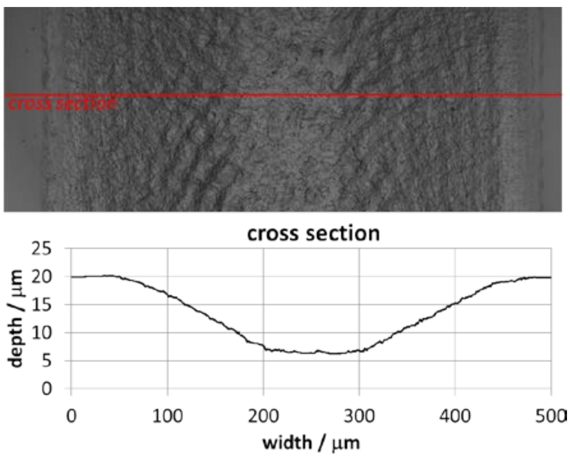


Fig.2: trapezoidal structure fabricated by LIBWE

The surface roughness is rather high ($R_q$: 0.193µm, $R_t$: 1.1µm, measured with LSM), since no optimization procedure concerning surface roughness has been done. To show the compatibility with LCLD, it is somehow appropriate not to use an idealized surface.

***LCLD – results***

*Topography*

As mentioned in the experimental section, the deposition of copper lines is done by a two-step approach.

For the first step of the deposition procedure (i.e. the "baseline") best results have been made by using a fluence of 55mJ/cm$^2$ per pulse, a scan velocity of 0.1mm/s and a focal plane in air 2.5mm above the liquid-sample interface. This resulted in a roughened surface with adhering metallic islands (see Fig. 3). The presence of pure copper has been confirmed by EDX measurements.

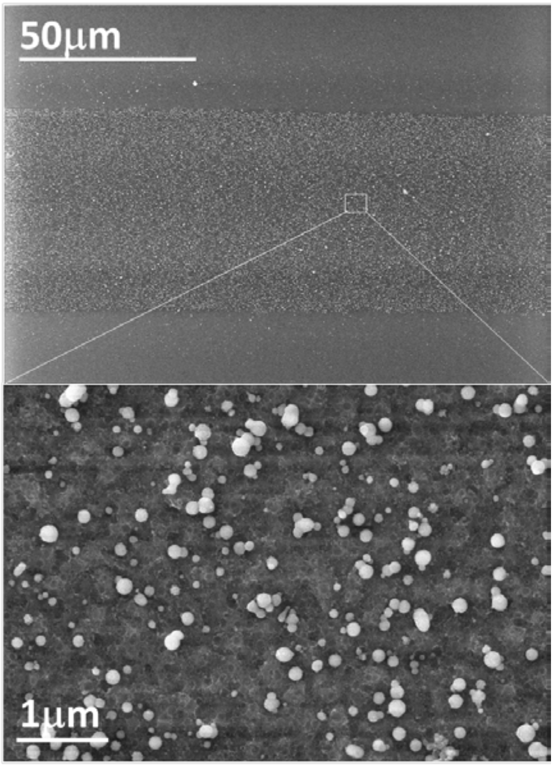


Fig.3: SEM-images of the initial baseline at a focus plane position at 2.5mm above solid/liquid interface, 55J/cm$^2$ fluence per pulse and 0.1mm/s scan velocity. The bright dot-like structures are initial Cu deposits.

By varying these parameters, one can observe very easy by eye, that a homogenous roughening and distribution of metallic clusters is disturbed, leading to uncontrolled ablation of the already deposited copper and parts of the substrate or to incomplete line features. In Figure 4, baselines fabricated with a) different scan velocities and b) different fluences per pulse are shown as example.

Since the metallic clusters even of the best result out of the baselines are randomly distributed and not in contact with each other, i.e. without forming a continuous conductive path, a second step inducing growth of the islands is needed. This is done by superposed multiple scans. Best results

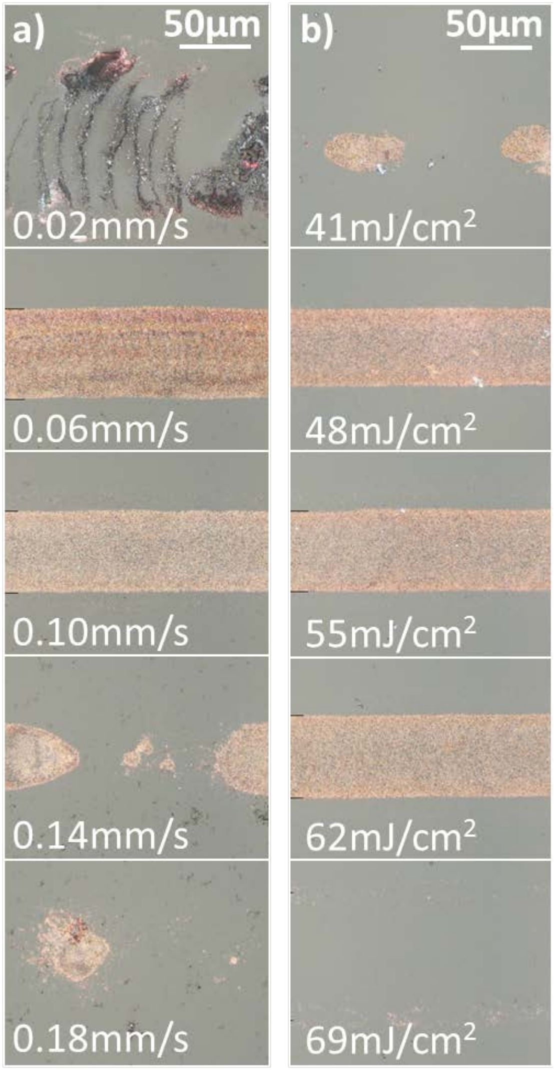


Fig.4: Optical images of different baselines, focus plane position at 2.5mm above solid/liquid interface, column a) with 55J/cm$^2$ fluence per pulse and different scan velocity, column b) with 0.1mm/s scan velocity and different fluences per pulse.

have been obtained by using a fluence of 7mJ/cm$^2$ per pulse (i.e., a factor 8 less than for the baseline), a scan velocity of 2mm/s (i.e., a factor 20 higher than for the baseline) and a focal plane in air 3.5mm above the liquid-sample interface. The further defocusing as well as the reduced fluence for the multiple scans is necessary again to avoid immediate laser ablation of the already deposited Cu-species. Note that the laser beam in our setup has to traverse the already deposited Cu.

Figure 5 shows the growth of well defined, crystalline copper structures over the whole roughened area with increasing number of sweeps. From Figure 5 it can be seen that rather compact and crystalline Cu deposits with grain sizes in the range of 1µm or below are formed. EDX measurements confirmed that the composition of the deposits is pure Cu.

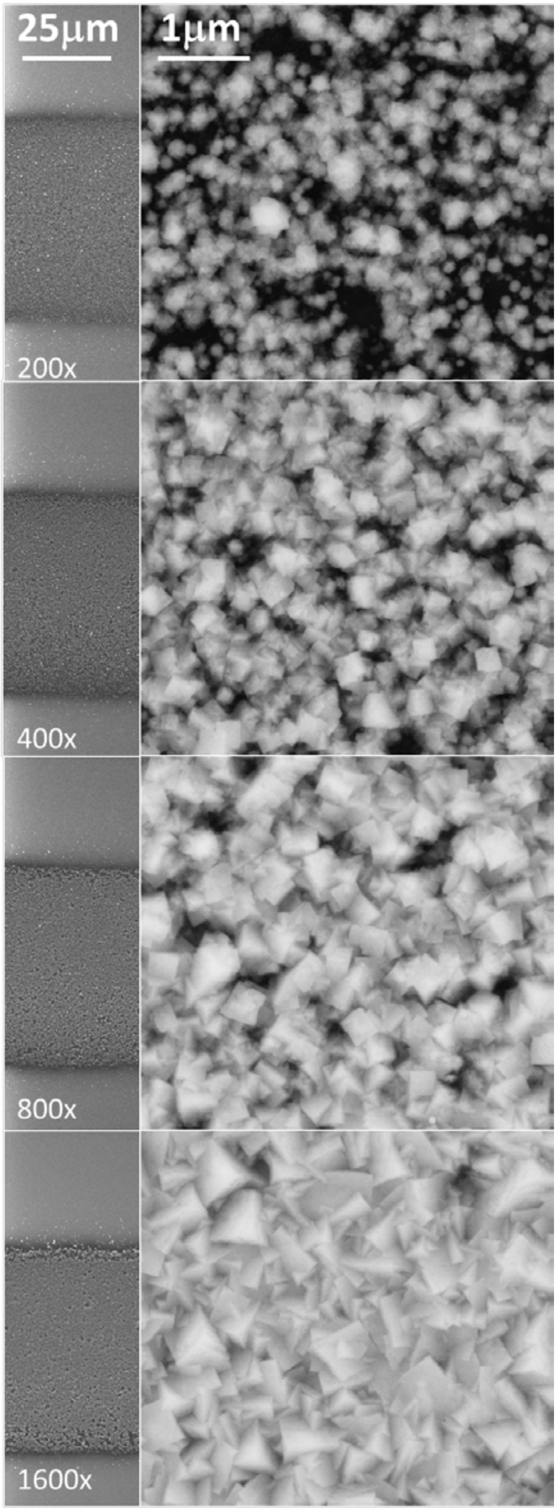


Fig.5: SEM-images of final copper lines, with different number of sweeps (overview on the left, detail on the right)

*Conductivity*

Estimations about the cross-section of the deposited lines have been made by means of AFM-measurements. While the width of the lines was constant (approx. 55µm), the height and shape were dependent on the number of sweeps of the multiple scan lines, which lead to a cross-sections areas of ca. 6µm$^2$ to about 30µm$^2$ for numbers of sweeps from 200x to 1600x. 4-Point-resistivity-measurements allowed calculating the specific conductivity of the deposited lines, taking in account the measured cross-sections areas for the corresponding lines.

Measurements with low current values (I < 5mA) showed a linear behavior of the voltage in function of the current, e.g., a constant conductivity value. Higher current values lead to a non-linear temperature dependent behavior of the measured voltage, e.g., a subsequent decrease of the conductivity in function of the current (see Fig. 6). Since the conductivity is temperature dependent, we assume that the copper features are heated due to the high current density, which leads to the decrease of the conductivity. Furthermore a rise of the conductivity Δσ of app. 10% was observed after a certain conditioning phase, where the conductivity value fluctuated arbitrarily (see Fig. 6). The higher value remained stable in subsequent measurements. We assume that local melting at narrow junctions between two copper crystals is the reason of the fluctuation and afterwards of the slightly higher conductivity value.

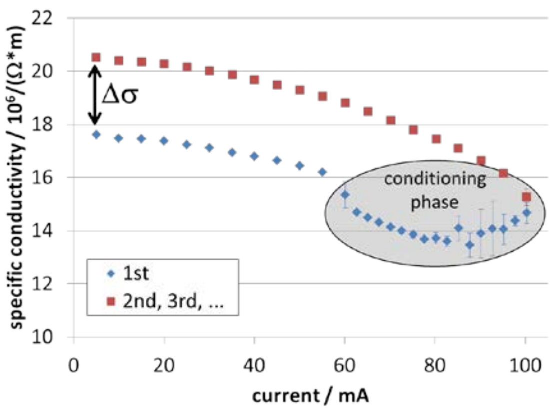


Fig.6: 4-point-measurement of one specific copper line as example, conditioning phase and rise of conductivity Δσ visible

The found mean value of 1.4x10$^7$ 1/(Ω*m) with a standard deviation of 0.4x10$^7$ 1/(Ω*m) corresponds approximately to a quarter of the specific conductivity of bulk copper. The conductivity remained stable after storage under ambient conditions for months.

***Combination of LIBWE and LCLD***

A conductive copper line was deposited on the trapezoidal structure etched with the LIBWE technique. This confirms, that principally the two processes are compatible (see Fig. 7).

The crystal habit of the copper lines deposited on a flat, unstructured surface is similar to the habit of the lines deposited on a rough, structured surface. Also the conductivity is to be found in the same magnitude.

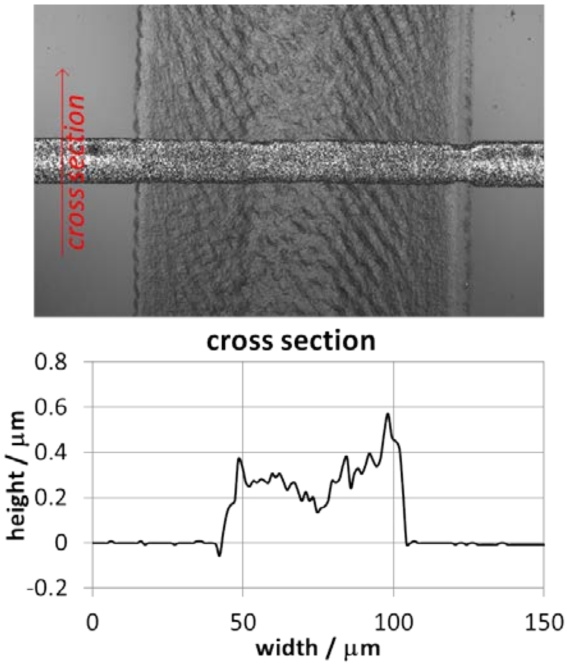


Fig.7: copper line deposited on structured surface (image: top view, diagram: cross section of copper line, position marked with red arrow)

Qualitative experiments showed that the flank angle of the etched groove is a critical parameter. Flanks which are too steep lead to interruptions of the deposition process, e.g., the homogenous deposition of the baseline already is disturbed.

### *Summary*

It has been found, that the laser-induced deposition process known as LCLD can be done using an "inverse" setup configuration: the copper features are deposited at the backside of the substrate. Due to the inverse setup, laser light is irradiated through copper structures, which are deposited during antecedent seeps, since multiple line scans are needed. Nevertheless, the copper lines have a conductivity of approx. a quarter of the specific conductivity of bulk copper. The conductivity remained stable for months under ambient storage.

Since the LCLD process can be done at the backside of the substrate, there is a possibility to combine it with a related micro-structuring process known as LIBWE, where the ablation is done at the backside of the substrate as well. It has been found, that the two processes are compatible. Well defined and conductive copper features have been deposited on a structured surface fabricated before using the same experimental setup.

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