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A novel Model for the Mechanism of Laser-Induced Back Side Wet Etching in Aqueous Cu Solutions using ns Pulses at 1064 nm

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Abstract

Laser induced back side wet etching has shown to be a promising tool for the micro-structuring of transparent materials. Detailed studies have been performed using UV excimer laser sources, aromatic hydrocarbon and liquid metal absorbers. Only little work is reported however using aqueous Cu solutions as absorbers and ns laser pulses at 1064 nm wavelength. We present a novel model for this specific setup. Our experiments indicate that physisorbed Cu^{2+} ions at the polar glass surface absorb the laser light. This leads to local thermal stresses in the glass and subsequent micro-ablation.

Keywords: laser induced backside wet etching (LIBWE), laser ablation, surface micro-structuring

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1. Introduction

There is a manifold need for micro-structured glass surfaces, such as micro-optical elements or components for micro-fluidics [1, 2, 3]. Established methods for manufacturing these kinds of structures already exist. The "classical" approach is to use conventional lithography and etching techniques. This method is well suited for mass production but not for rapid prototyping. In recent years an alternative approach has become more and more popular: Laser-induced back side wet etching (LIBWE). In a typical LIBWE experiment (see Figure 1a) laser light is directed through a transparent material and is absorbed in a liquid at the back side of the transparent material [4]. Depending on the used laser light and the absorbing liquid, thermal effects or shock waves lead to micro-ablation at the rear side of the glass surface. Most current applications of LIBWE use UV excimer lasers (ns pulse duration) and aromatic hydrocarbons or liquid heavy metals as absorbers [4, 5]. The desired structures are achieved by irradiating through a mask [6]. For rapid prototyping however, it would be interesting to use a scanning beam and the widely-used ns laser systems in the near infrared regime. Huang et al. presented LIBWE using 1064 nm laser pulses and aqueous copper (II) sulphate ($CuSO_4$) solution as an absorber [6]. They assume that metallic Cu is deposited on the glass surface due to a photochemical process. A subsequent laser pulse is then absorbed at the Cu deposit and leads to ablation of the glass. It is however not clear which species act as electron donors for the formation of metallic Cu^0. To further investigate this aspect we performed LIBWE experiments using 1064 nm laser pulses with 25 ns

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pulse duration and aqueous $CuSO_4$ and aqueous $CuSO_4$ in form of a tartrate-complex (labeled in the following as CuL_2) and with formaldehyde as electron donor. CuL_2 is known as precursor for photo-induced metal deposition [7].

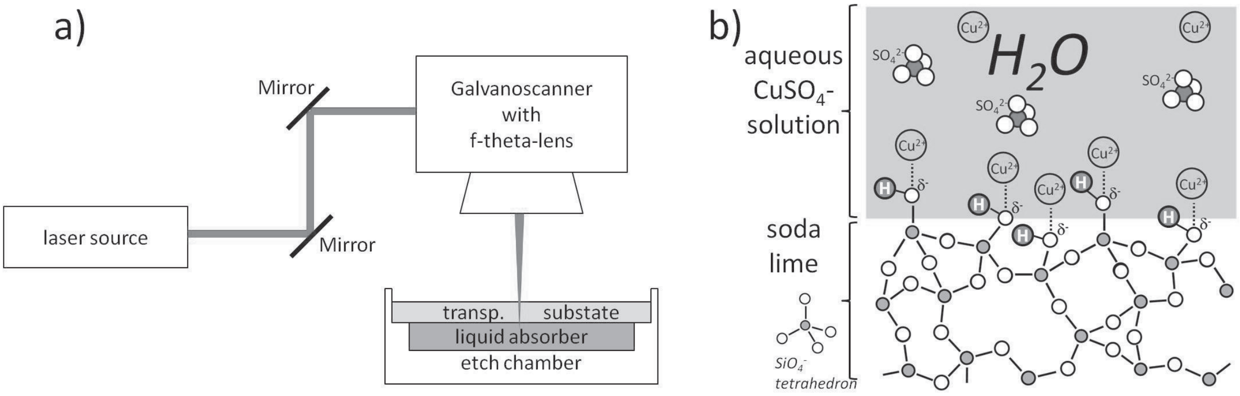

Figure 1: a) Experimental set-up for the LIBWE experiments; b) Schematic diagram of the physisorption of Cu $^{2+}$ ions at the polar soda lime surface.

For the two different absorbers two different ablation mechanisms are assumed. For the aqueous $CuSO_4$ solution Cu 2^+ ions are attracted by the polar glass surface due to Coulomb interaction and physisorb at the glass surface (see Figure 1b). This occurs without the need of a laser pulse. During the LIBWE experiment, the 1064 nm pulses are absorbed by the Cu^{2+} ions (at the glass surface and in the liquid). It is expected that for pulse lengths of 25 ns and for copper as absorbing material the absorbed energy is transformed mostly into heat [8]. In our case heat is transferred from the Cu^{2+} ions at the glass surface to the soda lime glass. This is followed by a local (only a few atoms are involved) micro-ablation due to thermally induced stress. The actual ablation is therefore a one-step process. Laser pulses that are absorbed by Cu^{2+} ions in the liquid transfer their energy also in form of heat to the surrounding liquid. Because the water acts as a heat sink, this has no further effect. Note in this context also that the specific heat capacity is 4.18 J/gK for H_2O at 25°C, whereas it is only about 0.8 J/gK for glass.

A different mechanism is assumed if the liquid absorber is aqueous $CuSO_4$ in form of a tartrate-complex (CuL_2) and with formaldehyde as electron donor. Here, ablation is expected to be a two-step process. First, electrically neutral metallic Cu species (Cu^0) are formed by a photo-induced process due to absorbed laser pulses according to equation (1).

$$[CuL_2]^{2-} + 2\,HCOH + 4\,OH^- \rightarrow Cu^0 + 2L^{2-} + H_2 + 2\,H_2O + 2\,HCOO^- \qquad (1)$$

In equation (1) L is the complexing agent, which is used to prevent the precipitation of the copper hydroxide. OH^- is needed for the redox reaction of formaldehyde (HCOH) and copper, and no excess OH^- is present that could interact with the glass surface. Cu^0 formed according equation (1) is likely to agglomerate to clusters of probably several hundred to thousand atoms and these clusters subsequently adsorb on the glass surface. Note that in this case the adsorption at the surface is not driven by Coulomb interaction since the Cu^0 clusters are apolar. However, similar to the Cu^{2+} ablation process the actual ablation for CuL_2 is a consequence of heat transfer from the Cu^0 to the soda lime glass. The ablation process using CuL_2 as an absorber is therefore a two step process whereas for $CuSO_4$ as an absorber a single absorption event is responsible for the ablation.

2. Experimental

The LIBWE experiments were performed using a pulsed Ytterbium fiber laser of 1064 nm center wavelength and with a pulse duration of 25 ns (YLPM series, IPG Laser GmbH). For all experiments presented in this work the pulse repetition rate has been set to 100 kHz. All results presented here have been obtained using soda lime glasses as a substrate. The soda lime specimens were cleaned with ethanol prior to the experiments (the label "untreated" will be used in the following for these substrates). For a second set of experiments soda lime glasses were treated with a dimethyldichlorsilane ($(CH_3)_2SiCl_2$) solution in toluene. The effect of this procedure is that the surface is more hydrophobic and less polar than untreated soda lime glass surfaces (see also Figure 2). For results obtained on these substrates the label "silanized" will be used in the following.

Line structures have been ablated using a galvanoscanner with different settings for fluence, scan speed and number of passes. The ablated structures have been investigated by using a confocal laser scanning microscope (LSM) and quantitative information about the ablated volume per laser pulse could be inferred from the topographical data.

To ensure that all observed effects in the LIBWE experiments are due to the aqueous $CuSO_4$ and CuL_2 absorber liquids, control experiments have been done on untreated and silanized soda lime glass and pure H_2O as liquid. In neither of the two cases ablation effects have been observed.

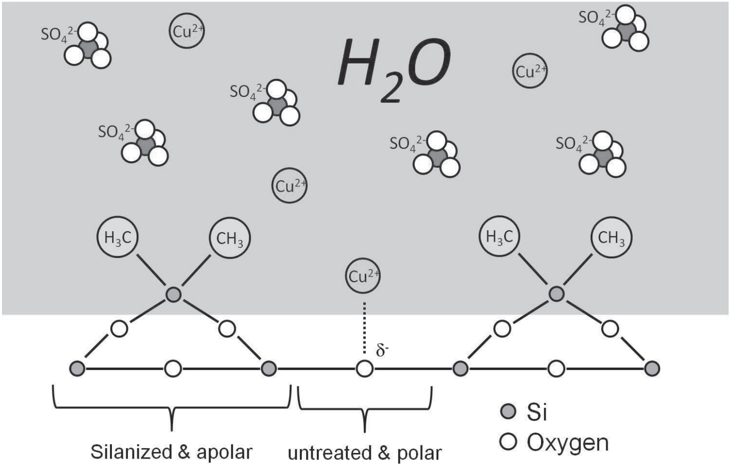

Figure 2: Effect of the treatment of the soda lime glass with a dimethyldichlorsilane solution. The silanized surface becomes partially apolar leading to less adsorption sites for Cu^{2+} ions.

3. Results and Discussion

3.1. Results on untreated soda lime glass surfaces

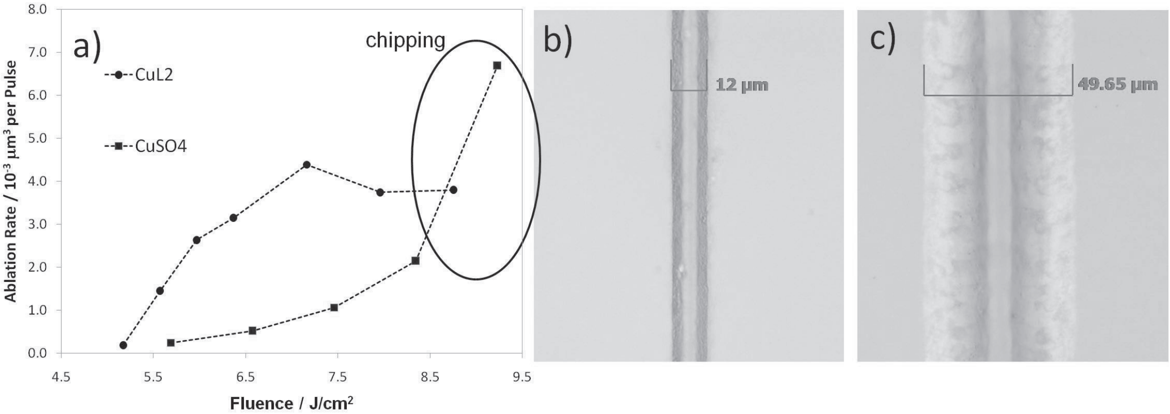

Figure 3: a) Volume ablation rates as a function of the fluence for $CuSO_4$ (squares) and CuL_2 (circles). The dashed lines serve as guide to the eye. For fluence values above 8 J/cm^2 chipping occurs; b) Ablation track in soda lime glass obtained with $CuSO_4$ and a fluence of 7.2 J/cm^2 and 100 passes; c) Same as in b) but with CuL_2 as adsorbing liquid.

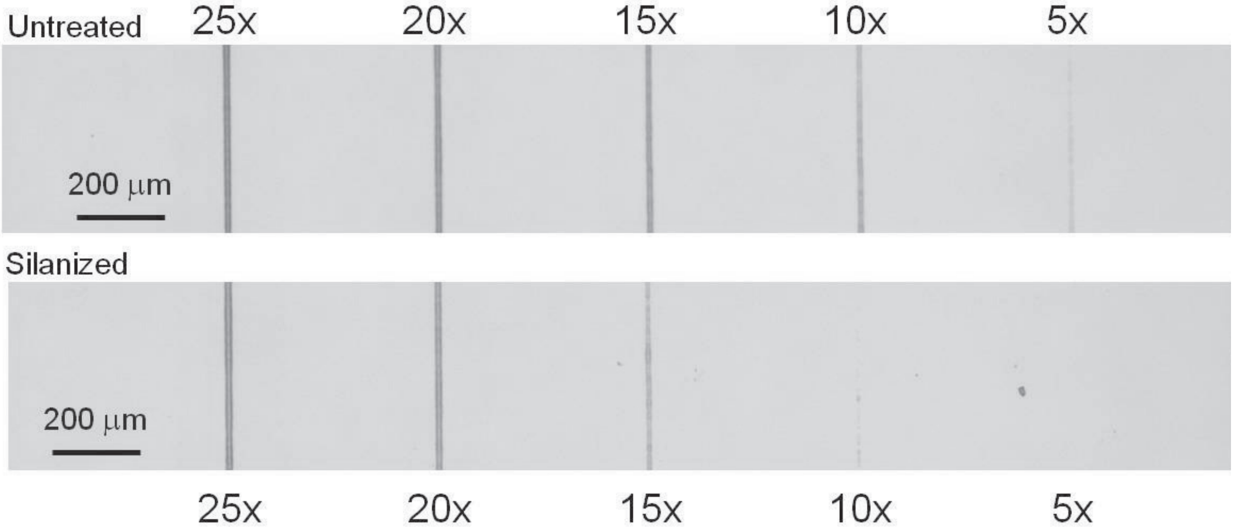

Figure 4: Optical micrographs of ablation tracks obtained with $CuSO_4$ for untreated (top) and silanized (bottom) soda lime glass. Ablation tracks for different number of passes are shown.

Figure 3a shows measured volume ablation rates in soda lime glasses for the aqueous $CuSO_4$ solution (squares) and for the CuL_2 solution (circles) as a function of the fluence. The absorbance was set to be 0.35 at 1064 nm wavelength for both solutions. Optical micrographs for a specific setup (7.2 J/cm^2, 100 passes) are shown in Figures 3b ($CuSO_4$ absorber) and 3c (CuL_2 absorber).

From the data in Figure 3 one can infer the following information: A minimal fluence for ablation exists. This threshold is lower for CuL_2 (5.2 J/cm^2) than for $CuSO_4$ (5.6 J/cm^2). Below these values no ablation was detectable.

The results in Figure 3 also indicate that ablation is more efficient for CuL_2 (deposited metallic Cu clusters) compared to $CuSO_4$ (physisorbed Cu^{2+} ions). For fluence values between the threshold and about 8 J/cm^2 it is observed that the ablation rate is increasing with the fluence with always higher rate values for the CuL_2 solution. For fluence values above 8 J/cm^2 (encircled data points in Figure 3a) prominent chipping of the soda lime glass has been observed, i.e. a smooth ablation is not possible anymore. An accurate determination of the ablation rate is in this case also delicate. The higher ablation efficiency for CuL_2 is reflected in the ablation tracks (Figures 3b and c), as well. For identical fluencies the ablated track is about 4 times wider for CuL_2. On the other hand a much smoother surface finish is observed with $CuSO_4$. Also consistent with our assumption for the different ablation mechanisms for $CuSO_4$ and CuL_2 is the observation of copper like deposits in the vicinity of the tracks for experiments with CuL_2. No such deposits have been observed on the other hand for $CuSO_4$.

The higher ablation rate in conjunction with the rougher surface of the ablated zones for CuL_2 compared to $CuSO_4$ is explained as follows: The Cu clusters formed by photo-induced decomposition of CuL_2 (see above) may absorb several subsequent laser pulses. The accumulated heat and, as a consequence the induced thermal stresses, are spread over a zone composed of several hundreds or thousands of atoms. This is assumed to lead to ablation within a region covered by the Cu cluster, i.e. several tenths of nm are affected. For the “isolated” Cu^{2+} ions on the other hand an absorbed laser pulse is assumed to lead to a very local (only a few atoms are concerned) microscopic ablation. Before the next ablation at the same position another Cu^{2+} ion has to adsorb first at the surface. This view of the ablation is – as mentioned above – corroborated by the experimental results shown in Figure 3.

3.2. Results on silanized soda lime glass surfaces

Figure 4 shows optical micrographs of ablation tracks obtained with $CuSO_4$ as absorber for untreated (top part of Figure 4) and silanized (bottom part of Figure 4) soda lime glass surfaces for different number of passes. For both glass surfaces the absorbance of the aqueous $CuSO_4$ solution was 7.47 (this corresponds to the maximal solubility) and the fluence of the laser was 5.0 J/cm^2. Figure 4 clearly indicates that the ablation process is delayed for the silanized surface (bottom of Figure 4) compared to the untreated surface (top of Figure 4). Similar conclusions can also be made if the depth of the ablation tracks as a function of the number of passes is measured. This is shown in Figure 5. Again the fluence was 5.0 J/cm^2 and the absorbance of the $CuSO_4$ solution 7.47. Measurable ablation is observed for a lower number of passes for the untreated surface. For 20 passes and more, however, the ablation rates approximately match for both surfaces.

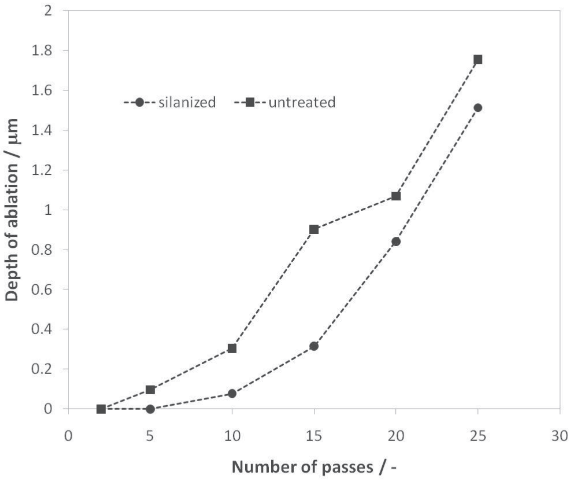

Figure 5: Depth of the ablation tracks as a function of the number of passes obtained with $CuSO_4$ as absorber for untreated (squares) and silanized (circles) soda lime glass surfaces. The dashed lines serve as guide to eye.

Figure 6 shows ablation tracks as a function of the number of passes obtained with CuL_2 as absorber for untreated (top part of Figure 6) and silanized (bottom part of Figure 6) soda lime glass. For these experiments the absorbance was 0.39 (corresponding to the maximal solubility) and the laser fluence 7.1 J/cm^2. In contrast to the findings for $CuSO_4$ (see Figures 4 and 5), no delay of the ablation due to the silanized surface is observed.

3.3. Discussion

The results presented above indicate that for 25 ns pulses at 1064 nm wavelength the ablation seems to be driven by absorption of laser light at species deposited at the back side of the soda lime substrate. In the case of aqueous $CuSO_4$ the absorption is made by Cu^{2+} ions, for CuL_2 solution by metallic Cu clusters. Whereas Cu-like deposits in the vicinity of the ablation tracks can be observed in experiments with CuL_2, a direct proof for the presence of Cu^{2+} at the surface is not possible. However, the fact that for $CuSO_4$ ablation is retarded on silanized soda lime glass (see Figures 4 and 5) and that the silanizing makes the surface partially apolar is a strong indication that our model is reasonable. A complete suppression of the ablation on the silanized surface incidentally cannot be expected because the applied surface treatment with dimethyldichlorsilane solution will not lead to a fully apolar surface. There will be still some polar adsorption sites for Cu^{2+} as also indicated in Figure 2. These sites act as seed locations for the ablation process and affect also the silanized surface atoms. After a certain number of passes (about 20 for the experimental settings used here, see Figure 5) all silanized sites seem to be removed such that the ablation is then similar to the ablation on an untreated surface. The adsorption of the Cu-clusters on the surface does not necessitate polar groups at the surface and therefore no significant differences between untreated and silanized soda lime glass is expected for CuL_2. Also this has been experimentally corroborated (see Figure 6).

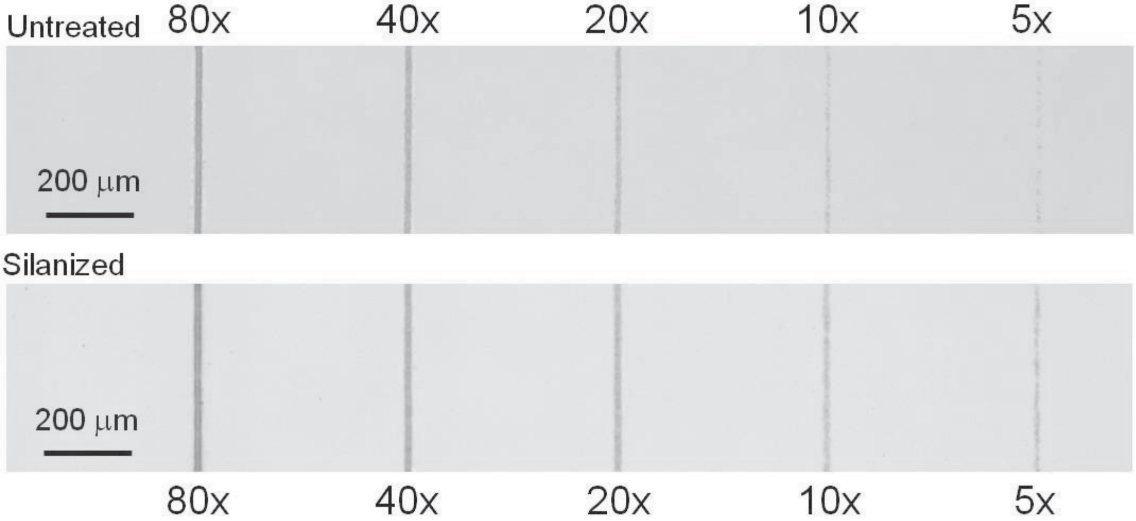

Figure 6: Optical micrographs of ablation tracks obtained with CuL_2 for untreated (top) and silanized (bottom) soda lime glass. Ablation tracks for different number of passes are shown. Note the significant difference compared to the ablation tracks shown in Figure 4.

4. Summary and Outlook

Our experiments indicate that – at least for 1064 nm pulses with a pulse length of 25 ns – the LIBWE process for aqueous $CuSO_4$ and CuL_2 is ruled by processes at the soda lime glass surface. For aqueous $CuSO_4$ a one-step process, i.e. laser pulse absorption at physisorbed Cu^{2+} at the glass surface is leading to a smooth ablation. For aqueous $CuSO_4$ in form of a tartrate-complex (CuL_2) a two-step process is present: First, formation of metallic Cu clusters that adsorb at the glass surface, followed by laser pulse absorption at the cluster. In both cases the absorbed energy is transferred to the glass in form of heat, leading to thermal induced stresses and finally to ablation. A detailed discussion of the effects of pulse duration and repetition rate, as well as for the quality of the surface finish is presented elsewhere [9].

The two different ablation models could be corroborated by comparing experiments made on untreated polar and silanized, partially apolar soda lime glass surfaces. Further experiments will consist in a modified and improved silanizing process that should be capable of inhibiting the adsorption of Cu^{2+} on an even larger fraction of the surface, thus further retarding the onset of ablation.

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