Backside Etching at the Interface to Diluted Medium with Nanometer Etch Rates

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The laser etching using a surface adsorbed layer (LESAL) is a new and promising method for precise etching of transparent materials such as fused silica. The etching process is based on the laser irradiation of the interface between a transparent solid and a diluted (vaporized) backside medium that forms an adsorbed layer. A KrF excimer laser ($\lambda = 248$ nm) with pulse duration of 25 ns is employed to study LESAL of fused silica. LESAL by means of toluene as adsorbate features outstanding attributes, e.g., low threshold fluences (< 1 J/cm²), an almost constant etch rate on the order of 1 nm/pulse over a wide fluence region, and very low, nearly optical grade surface roughness (~ 1 nm *rms*). As LESAL mechanism, the thermal ablation of a modified surface layer is discussed. The modification is caused chiefly by the deposition of decomposition products from organic molecules photolysis. The usage of halogenated adsorbate fluorobenzene (C_6H_5F), difluorobenzene ($C_6H_4F_2$), chlorobenzene (C_6H_5Cl), and dichlorobenzene ($C_6H_4Cl_2$) as diluted backside media reduces significantly the etching threshold and causes an additional characteristic fluence region with Angstrom/pulse etch rate and homogenous and smooth surface topography. The generation of halogen radicals close to the heated surface due to the decomposition of the solvent seems to be the most probably mechanism for a chemical erosion of the fused silica surface.

Keywords: laser, backside etching, LESAL, fused silica, halogen, organic, surface modification, adsorption, transparent material

1. Introduction

The high quality etching of dielectric materials with low roughness, high accuracy of the surface topography, and precise depth control is still a challenge of laser processing. For some applications, e.g., in micro optics, transparent materials such as fused silica, sapphire, and other dielectric materials have to be etched.

Due to the lack of sufficient high absorption, the laser ablation of transparent dielectric materials can be achieved using VUV, ps, or fs lasers [1-3] with micron or submicron resolution. Furthermore, some hybrid processing methods which make use of nanosecond UV laser pulses exploit the enhanced absorption at the backside interface by means of additional absorbing materials such as temporary plasmas [4], liquids [5,6], , or adsorbed layers [7-10].

J. Zhang et al. report on a laser ablation technique for glass machining named LIPAA [4] that exploits a laser-induced plasma to ablate fused silica at the backside of the sample. The plasma is generated by ablation of a metal target located near the backside surface after the laser beam passes the transparent sample.

The LIBWE technique uses organic solvents and solutions as absorbing media that are in contact with the backside of the transparent material to cause laser etching of the samples backside surface [5,6,11,12]. The etching process of the material is based on the rapid heating of the solid/liquid interface, material softening, and removing of softened material by thermo elastic stress of heated material and shock waves from the liquid [5,6,11,12].

Recently, a new technique called LESAL (laser etching at a surface adsorbed layer) was demonstrated [7-10]. This novel etching process makes use of a thin layer or organic solvent adsorbed at the backside of a transparent material that absorbs the laser radiation and causes the etching of the material surface. In comparison to LIBWE, LESAL offers similar low threshold fluences, less etch rates, and a distinctly reduced surface roughness on the order of 0.75 J/cm², 1 nm/pulse, and 0.3 nm *rms* (measured with AFM), respectively. In addition, the low etch rate is almost constant in a wide fluence range that allows, for instance, a very precise depth processing with accuracy in the nanometer range for the fabrication of binary optical elements [9]. Furthermore, secondary effects of the laser irradiation of an absorbing liquid, such as transient high pressures, liquid evaporation, or vapor bubble collapse [5,6,11,12], do not affect the backside etching at diluted backside medium.

In this work, the effect of halogenated hydrocarbons as adsorbed organic absorber is studied in comparison to toluene with respect to the etch rate behavior in LESAL processing of fused silica.

2. Experimental

The basic experimental set-up for the laser etching at a surface adsorbed layer (LESAL) was described elsewhere [8,10]. The laser beam first penetrates the transparent sample and is absorbed at the backside interface by a thin hydrocarbon layer. To create this thin adsorbed layer, the transparent sample is fitted into a laser-processing chamber equipped with an electric heater that evaporates the organic solvent. The details of the heating and evaporation procedure were described in [8]. The temperature of the actual set-up was set to 75°C.

To investigate the effect of halogenation on the etching process, molecules with similar structure and optical properties are required. Thus, different benzene derivates containing no, one, and two substituted species are used as adsorbate: toluene (C_7H_8), fluorobenzene (C_6H_5F), difluorobenzene ($C_6H_4F_2$), chlorobenzene (C_6H_5Cl), and dichlorobenzene ($C_6H_4Cl_2$). The respective linear absorption coefficients at a wavelength of 248 nm are determined with photo spectrometer and range from 1600 cm^{-1} (toluene) to 6900 cm^{-1} (fluorobenzene).

It is known that beside monolayer multi-molecular layers can be adsorbed from the vapor phase at surfaces according to BET theory [14]. Such multi-molecular films will support the etching process because the higher amount of absorbing molecules can absorb a larger part of the laser pulse energy. A thickness of the layer in case of toluene of about 2 nm is measured by means of ellipsometry.

LESAL has been accomplished using a commercial excimer laser workstation. The laser workstation is equipped with an excimer laser, beam shaping and homogenizing optics, a dielectric attenuator, and provides approximately 25 ns pulses at 248 nm with an overall energy deviation in the mask plane of below 5% *rms*. The laser-processing chamber is attached to a program controlled x-y-z stage. A Schwarzschild objective (15 x demagnification) with an optical resolution of 1 µm is used for projecting mask patterns onto the sample backside.

Double side polished fused silica plates with a thicknesses and a surface roughness of 0.38 mm and 0.23 nm, respectively, are used as received without additional cleaning. After etching the samples are cleaned by gentle oxygen plasma and ultrasonically in acetone/water bath to remove carbon residuals. Etch pits with an area of 100 µm x 100 µm are etched with 300 laser pulses at a pulse repetition rate of 10 Hz. The average etch rates are calculated from the depths of the etched features which are measured by a white light interference microscope (50 x magnification) having a depth resolution of better than 1 nm.

3. Results

The etch rate of fused silica in dependence on laser fluence is shown in Fig. 1 (a-c) for different organic absorbers with and without halogen content.

In Fig. 1a, the three characteristic fluence regions of LESAL known from former investigations [7-10] are discussed by means of toluene with considering the etch rates and the optically measured surface roughness. The threshold fluence for the etching of fused silica - the lowest fluence at which after 300 pulses a measurable etching occurs - is determined to be about 0.75 J/cm². This is more than one order of magnitude less than the ablation threshold of fused silica in air (> 10.0 J/cm²) [15].

The characteristic fluence regions are: (i) low fluence region (< 2.0 J/cm²), (ii) middle fluence region (2.0 … 5.0 J/cm²), and (iii) high fluence region (> 5 J/cm²). Strong incubation effects characterize region (i) and cause an enhanced surface roughness and slow growing etch rates below 1 nm per pulse [7,8]. In region (ii), the etch rates tend to be constant at about 1 nm/pulse (saturation region) and are accompanied by an optical-grade low roughness. For fluences in region (iii), the etching is characterized by high rates (up to

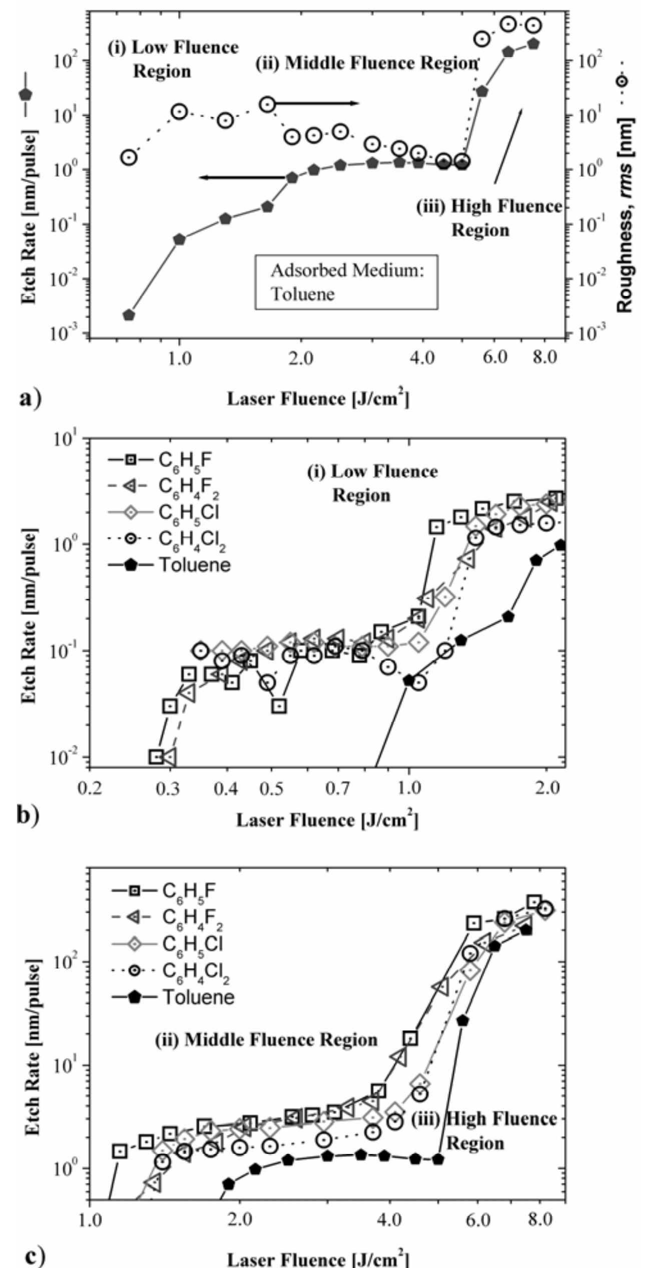

Fig. 1: Etch rate in dependence on the laser fluence for a) toluene and b), c) different halogenated hydrocarbons. The different fluence regions are designated. Additionally, in a) the optically measured roughness is depicted. (The lines are used to guide the eyes.)

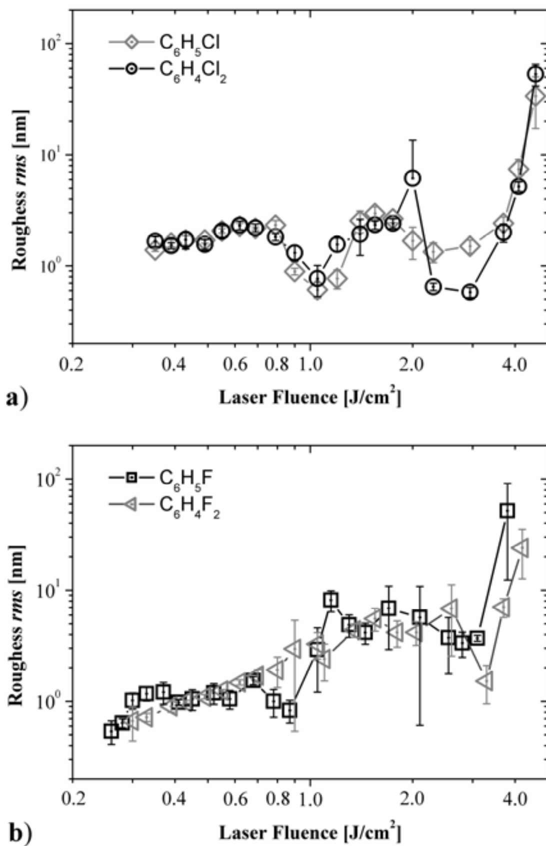

Fig. 2: Measured surface roughness by means of different halogenated adsorbate in dependence on the laser fluence. (The lines are used to guide the eyes.)

200 nm/pulse), a steep increasing etch rate, and a sudden rise of roughness that will be an indication for a more ablation-dominated mechanism compared with the gentle-etch behavior in the middle fluence range.

Fig. 1b) and c) present the etch rate behavior of fused silica using halogenated aromatic molecules. In principle, the etching shows - similar to toluene - the typical dividing into the different fluence regions. However, essential differences are found for the halogenated aromatic molecules in comparison to toluene in the low fluence region.

The threshold fluences by means of halogenated adsorbates are distinctly reduced. For C_6H_5F, $C_6H_4F_2$, C_6H_5Cl, and $C_6H_4Cl_2$, a starting surface etching after 300 pulses can be already observed at 0.26, 0.3, 0.35, and 0.35 J/cm², respectively. With rising fluence (0.4-0.9 J/cm²), the etch rate keeps almost constant at about 0.1 nm/pulse and the irradiated surface is characterized by a homogeneous and smooth etching (Fig. 2 and 3a) featuring a very low roughness at about 1 nm *rms*. By further increased laser fluence, the etch rate behavior and the roughness have the same etch rate and surface characteristics like the observed three fluence regions by means of toluene. But for C_6H_5F, $C_6H_4F_2$, C_6H_5Cl, and $C_6H_4Cl_2$, the etch rates slightly increase in the middle fluence range (ii).

In Fig. 3 images made by white light interference microscopy and SEM point out the different surface morphologies of the fluence regions by means of C_6H_5F that are representatively for all employed halogenated absorbing adsorbates. Fig. 3a shows a very homogeneous etch pit with an averaged depth of about 30 nm. It is fabricated with 300 pulses at a laser fluence of 0.65 J/cm². The SEM picture in Fig. 3b) depicts the origin of the higher roughness for fluences between 0.9 and 1.3 J/cm² (Fig. 2); a partially, inhomogeneous etching over the irradiated area enhances long wavelength surface topographic features. For fluences in the middle region, the surface quality is excellent (Fig. 3c). The etch pit has a depth of 980 nm and features well defined edges and a smooth and homogeneous etched bottom. For high fluences, e.g., 6.8 J/cm², beside the etch rate (Fig. 1) also the surface roughness (Fig. 2) is higher due to a visible surface topography (Fig. 3d) that resembles on ablation-like laser processes [15]. The depth of the pit after 30 laser pulses is 7800 nm.

4. Discussion

The etch mechanism at the solid/adsorbate/vapor interface using non-halogenated adsorbed molecules (toluene) is very complex but some processes involved in etching can be discussed.

The adsorbed layer absorbs the first laser pulse but a significant solid surface heating can be neglected due to the very low thickness and absorption coefficient. However, the absorption of the laser pulse energy results in fast heating of the adsorbate, desorption [16], and in decomposition of the organic molecules [17]. Due to the deposition of the decomposition products, a thin carbon-containing layer is formed after the laser pulse and covered again with adsorbate from vapor. The following laser pulse ablates the layer and causes fused silica surface etching. After the etching laser pulse, the preparative carbon layer is renewed due to the deposition of adsorbate decomposition products.

The film chiefly consists of amorphous carbon [18] as investigated by Raman spectroscopy. Such a carbon layer offers a high absorption for the subsequent laser pulse (~ 10^5 cm^{-1} [19]). As recently reported [18], the ablation of an adherent 20 nm carbon layer on the backside surface of fused silica is capable to induce an etching of the material due to the high laser-induced temperatures in the layer. Additionally, the high temperatures may cause the generation of shock waves [20], stress [21], and structural transitions [22] of the bulk material near the surface. An incorporation of carbon products into the fused silica surface similar to LIBWE [23] can also be expected and a respective study is on the way. Recapitulating the different mechanisms of surface modification in LESAL processing, an exact estimation of the thickness of the modified surface layer is not feasible yet and will be the subject of future investigations.

The etch rate behavior in the low fluence region by means of toluene resembles on the appearance of incubation effects similar to other incubation processes, such as laser ablation of fused silica in air [15]. The temperature due to the heating by the laser irradiated carbon layer is not sufficient to melt the fused silica surface overall in the irradiated area. Hence, the thermal etching mechanism starts preferable at intrinsic material defects or intensity peaks of the beam profile during

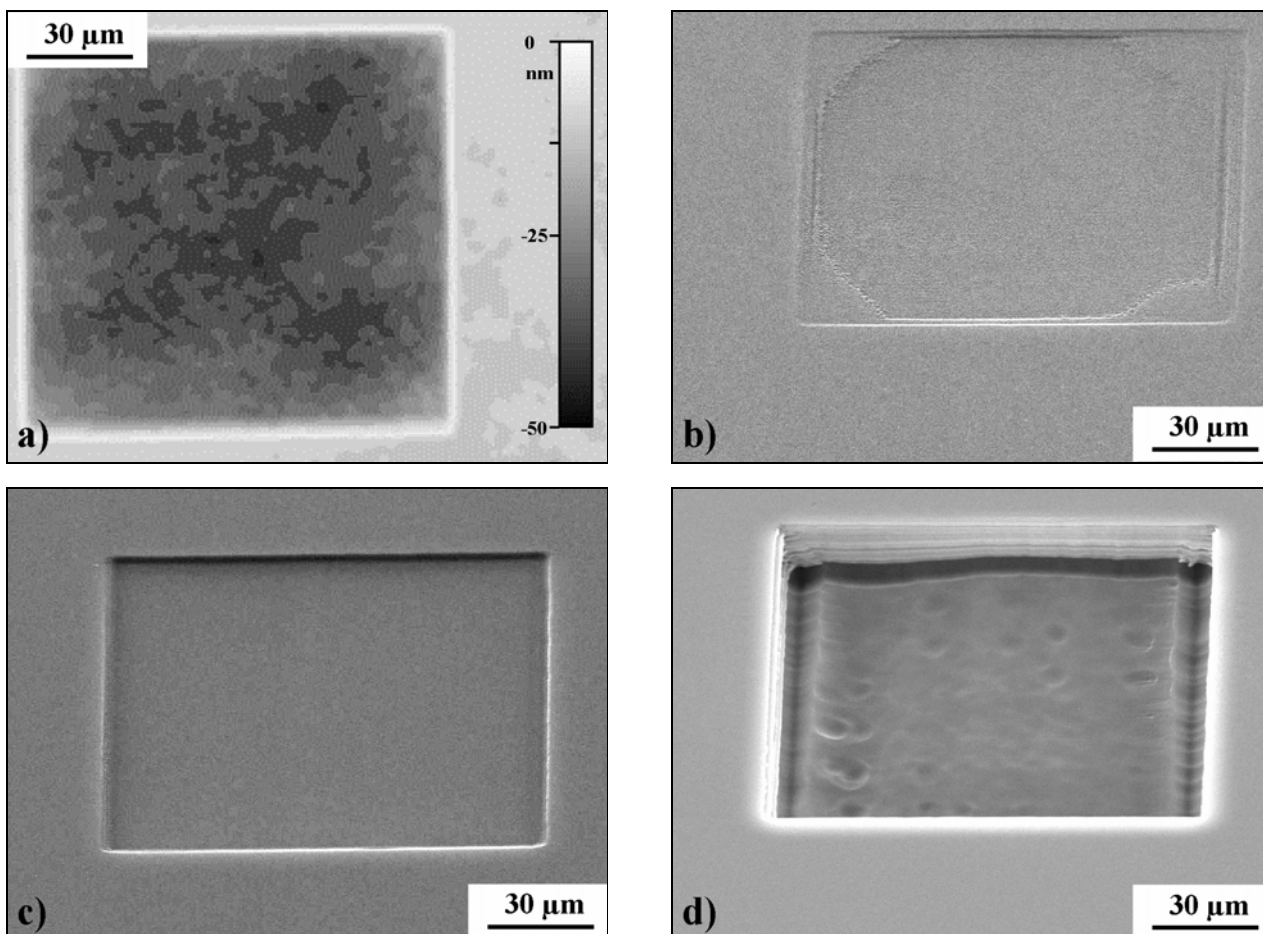

Fig. 3: Micrographs of etch pits in fused silica recorded by white light interference microscope (a) and SEM (b-d) representing the different etch regions by means of halogenated absorbers. The grooves in a) to d) were etched with C_6H_5F applying 300, 300, 300, and 30 pulses at fluences of 0.65, 1.15, 2.75, and 6.8 J/cm², respectively. The SEM images were received under a tilting angle of 34°.

prolonged laser irradiation and causes the partially etched surface topography [7,8].

For thermal driven processes, the increase of the laser fluence results in higher heating rates and temperatures that typically are the reason for higher etch rates. However, this is inconsistent with the observed rate saturation in the middle fluence region. As known from laser desorption studies [16,24], higher temperatures as consequence of higher fluences lead to higher removing rates of the deposited layer. Hence, the interaction time for heating the fused silica surface by the layer is limited to the time necessary to remove the layer by ablation. Assuming a certain temperature necessary for layer ablation, the further increase of the absorbed laser fluence reduces the time for the film removing without significant changes of the maximum fused silica surface temperature.

In the high fluence region, the laser fluences are high enough to induce direct laser ablation [15,25]. Here, the coupling of the laser energy with the material surface is facilitated by existing or generated (due to the deposition of carbon products) defects that allow the transfer of electrons to the conduction band making the near surface region opaque for the laser radiation.

LESAL by means of halogenated aromatic hydrocarbons - in contrast to toluene - features distinctly reduced threshold fluences and an additional fluence region at very low fluences. As been proposed in case of toluene, the laser-induced heating of the surface by the carbon layer is not capable of thermally etching the fused silica surface at fluences below 0.75 J/cm². Hence, the generation of halogenated radicals must obtain more importance.

The presence of halogen radicals such as Cl [24,26] at KrF laser irradiation of C_6H_5Cl and $C_6H_4Cl_2$ is proved. The estimated etch rates in the Angstrom range are typical for a laser-induced chemical corrosion of fused silica and is frequently described in [27] for chlorine as well as for fluorine. Due to the presence of intrinsic and laser-generated oxygen vacancies as defects (see Refs. cited in [25]), atomic halogen radicals (further abbreviated with *Hal*) can react with the fused silica surface by attaching to the free bond. As result, a photochemical etching mechanism described by $\mathrm{Si} + x\,Hal \rightarrow \mathrm{Si}Hal_x\ (\uparrow)$ with $x \leq 4$ will take place [27]. Because the used halogenated aromatic molecules are inert at room conditions, the temporary formation of halogen compounds near the interface and the short-term laser-induced temperatures at the interface lead to the observed etch effect.

5. Summary

The high quality processing of fused silica by means of laser etching at a surface adsorbed layer (LESAL) of

toluene and halogenated hydrocarbons is presented. The measured etch rate in dependence on the laser fluence and the induced surface roughness are basically similar to etching with non-halogenated molecules like toluene: (i) a low fluence region with enhanced roughness and nonlinear etch rate rise, (ii) almost constant etch rate and low roughness at middle fluences, and (iii) ablation-like surface characteristics and rates at high fluences. But at very low fluences, essential differences are found for the halogenated aromatic molecules in comparison to toluene: the etch threshold is distinctly reduced and an additional fluence region for low fluences with very small but constant etch rates in the Angstrom range is found. These differences give evidence for a chemical etch mechanism on base of a surface reaction of halogen radicals (as result of laser photolysis) with the fused silica that contribute to the thermal etch mechanism of LESAL.

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