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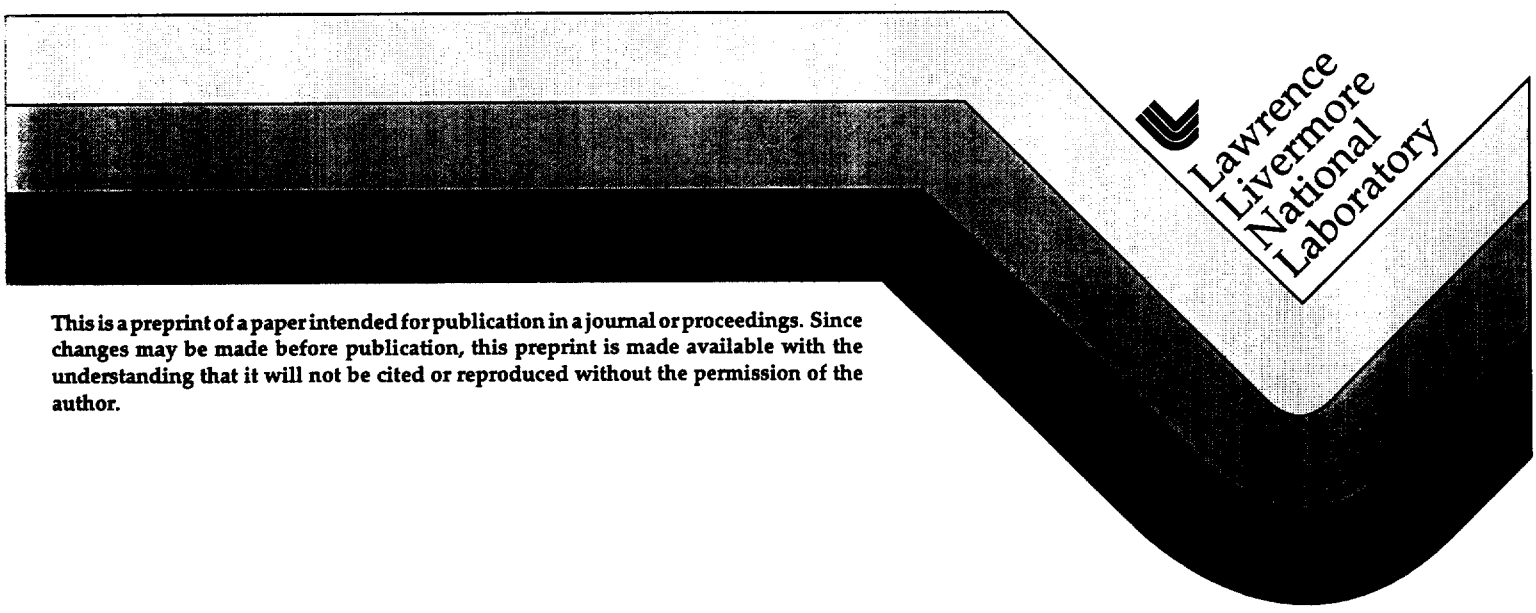

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A study of the effects of polishing, etching, cleaving, and water leaching on the UV laser damage of fused silica

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ABSTRACT

A damage morphology study was performed with a 355 nm, 8-ns Nd:YAG laser on synthetic UV-grade fused silica to determine the effects of post-polish chemical etching on laser-induced damage, compare damage morphologies of cleaved and polished surfaces, and understand the effects of the hydrolyzed surface layer and water-crack interactions. The samples were polished, then chemically etched in a buffered HF solution to remove 45, 90, 135, and 180 nm of surface material. Another set of samples was cleaved and soaked in boiling distilled water for 1 second and 1 hour. All the samples were irradiated at damaging fluences and characterized by Normarski optical microscopy and scanning electron microscopy.

Damage was initiated at micro-pits (smaller than 1 μm in diameter) on both input and output surface of the polished fused silica sample. At higher fluences, the micro-pits generated cracks on the surface. Laser damage of the etched fused silica surface showed that the areal density of micro-pits decreased with etched thickness. SIMS analysis of the polished surface showed significant trace contamination levels within a 50 nm surface layer. Micro-pits formation also appeared after irradiating cleaved fused silica surfaces at damaging fluences. Linear damage tracks corresponding cleaving cracks were often observed on cleaved surfaces. Soaking cleaved samples in water produced wide laser damage tracks.

Key words: laser-induced damage threshold, fused silica, 355 nm, damage morphology, sub-surface damage, micro-cracks, etching, surface contamination, environmental effects.

1. INTRODUCTION

Laser-induced damage in fused silica has been linked to energy absorbing defects (e.g. surface contamination,[1] surface scratches,[2] and bulk imperfections like bubbles or inclusions[3]). If damage initiation is to be prevented, the major contributors and conditions leading to damage must be identified. Experimental laser testing is a method where known laser irradiation parameters are used to damage fused silica substrates and the resulting morphological changes are observed.[4-6] Through the use of Nomarski microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM) we can characterize the basic damage morphologies.[7] Secondary ion mass spectrometry (SIMS) can also be used to determine the elemental constituents in the polished surface layer.

This paper addresses several fundamental questions to determine where and how damage in polished fused silica initiates. The assumption is that the electric field is enhanced or that the energy is absorbed at surface contamination particles,[3,8,9] surface scratches,[2] or sub-surface structures[10,11] to initiate damage. To understand the role that these defects play and separate the effects of chemical defects from mechanical defects, we examined the effects of post-polish chemical etching, compared the damage morphology in polished (contaminated) and cleaved (clean) surfaces, and characterized the influence of water on the damage behavior of cleaved surfaces.

2. EXPERIMENTAL PROCEDURE

2.1 Fused silica samples preparation

Three 2-inch diameter polished UV grade fused silica samples were tested. The first sample was UV damaged as received. The second was etched with buffered HF (1% HF, 15% NH_4F; pH 5) and then UV damaged. The third was cut into six pieces using a cleaving knife. One piece of the cleaved sample was UV damaged without any prior

treatment while the two other pieces were soaked in boiling distilled water for 1 second and 1 hour respectively and then UV damaged.

2.2 Laser test conditions

The laser damage tests were performed with a Nd:YAG laser at 355 nm in "P" polarization. The beam shape was Gaussian both spatially and temporally with a $1/e^2$ beam diameter of 0.9 mm and a pulse length of 8 ns. To damage the surface, all sites were irradiated with a single 35 J/cm^2 pulse. The polished and etched samples were irradiated at 10° incidence angle. Cleaved and hydrolized samples were irradiated at 5° incidence angle (input surface) and about 45° incidence angle (output surface).

2.3 Characterization of the surface damage morphologies

Damage on the fused silica samples was characterized by Nomarski optical microscopy, SEM and AFM. SIMS analysis of the polished fused silica surface was performed to determine the concentration of trace contaminants as a function of depth.

3. RESULTS AND DISCUSSION

3.1 Surface damage on polished fused silica

As the fluence is increased during a damage test, the first observed change in surface morphology consists of a set of ellipsoidal micro-pits that are less than 1 μm in diameter (see Figs. 1 and 2). These pits are not detectable on the surface prior to irradiation. The morphology of damage in UV grade fused silica at 355 nm is discussed more thoroughly in Ref. 12.

The input surface fracture first develops along the long axis of the ellipsoidal micro-pit, in a direction perpendicular to the electric field.[13] Higher fluence shots produce higher stresses and crack the surface in a star-like pattern where the center often looks molten. The output surface typically damages with a shell-like morphology due to localized compressive and shear stresses. The center of the cluster of shells (generated at higher fluences) also shows evidence of melting.

The micro-pit density (i.e. the number of pits per μm^{-2}) after damaging the polished surface can vary from $14x10^{-3}$ to more than 0.1 μm^{-2}. The pits are found on both input and output surfaces. The pit density is strongly dependent on the polishing process and the amount of surface contamination (Fig. 2). Increasing the laser fluence increases the pit density and the number of cracks. When the pit density is high (i.e. greater than $50x10^{-3}$ μm^{-2}), the pits and the damage debris scattered on the surface form a gray haze that can be detected by visual inspection.[10] The higher the pit density and the higher the fluence, the more heavily damaged the surface. Linear patterns due to mechanical defects located either on the surface (scratches) or under the surface (sub-surface micro-cracks) are sometimes observed.

3.2 Surface damage of etched fused silica

Four polished fused silica samples were etched in buffered HF (1% HF, 15% NH_4F; pH 5) to remove a surface layer 45, 90, 135, and 180 nm thick. After irradiation, the micro-pit density of the unetched sample is $26x10^{-3}$ μm^{-2}. For the etched samples, the density decreases to $4.7x10^{-3}$, $1.9x10^{-3}$, $0.9x10^{-3}$, and less than $0.2x10^{-3}$ μm^{-2} for 45 nm, 90 nm, 135 nm, and 180 nm thickness removal, respectively (see Fig. 3). The damaged area decreases as more silica is etched off the surface prior to irradiation (see Fig. 4 and 5). Since the spatial profile of the beam is Gaussian, the edge of the damaged area defines a cut-off fluence below which the surface stays undamaged. At a fixed fluence, the smaller the diameter of the damaged area, the higher the damage threshold of the surface. The data shows that the removal of a 200 nm thick silica layer makes the surface more resistant to UV radiation. The effect of etching could be due to the removal of surface and sub-surface mechanical defects caused during the polishing process.[14-17] It has been shown that etching can improve the mechanical strength of glass by removing surface flaws. Hata et al.[18] measured a four-fold increase in bending strength of glass slabs after a 50 to 300 μm chemical etch, in agreement with work by Marion[18] who reported an increase in the mechanical strength of laser glasses after chemical etching.

A SIMS analysis of a typical polished fused silica surface was performed to characterize the residual contamination from the polishing process. The results on the samples studied here show high concentrations of Al,

B, Ce, and Zr (elements that are commonly found in the polishing slurry; see Table 1 and Fig. 6). The concentrations of the surface contaminants decrease rapidly with depth, most falling to less than one tenth of the respective maximum values at a depth of about 50 nm. Ce decreases less rapidly, requiring ~100 nm to decrease to 10% of the maximum value. The depth profile of contaminants shows that etching exposes cleaner surface than the original polished one. This could be another explanation for the observed improved damage resistance of etched surfaces.

Element	Concentration (ppmw)
B	15
Na	6
Mg	3
Al	80
Ca	8
Cr	0.1
Fe	6
Ni	5
Cu	0.3
Zr	11
Ba	<0.1
Ce	23

Table 1: Peak concentration of trace contamination on the polished surface.

3.3 Surface damage of cleaved fused silica; effects of surface cracks

After irradiation at damaging fluence, the output surface of a freshly cleaved surface shows two different damage morphologies: I) micro-size pits typically found on polished surfaces (see Fig. 7.a) and II) large circular conchoidal pits more than 5 μm in diameter (see Fig. 7.b). Since a cleaved surface is never in contact with the polishing medium, surface contamination from the polishing slurry cannot be the only reason why micro-pits form. Moreover, a damage mechanism specific to cleaved surfaces seems to be revealed since larger craters are not observed on polished surfaces.

Cleaved surfaces show damage oriented in linear patterns (see Fig. 8) probably due to linear mechanical defects (cleavage planes or Wallner lines). Cleaving can also produce residual stresses and permanent mechanical damage in fused silica since crack propagation is quite rapid. Etching the cleaved surfaces after laser-damage revealed the complex underlying post-damage crack structure along these linear patterns (see Fig. 9). This information will be used in the future to model crack initiation and growth.

3.4 Surface damage of hydrolyzed cleaved fused silica

To separate the influence of water on damage from effects due to other contamination materials (e.g. from the polishing slurry), cleaved fused silica samples were soaked in boiling distilled water for 1 second and 1 hour. The micro-pit damage followed linear patterns (see Fig. 10). Both input and output surfaces showed similar linear tracks. Longer soak times in water seemed to increase the width of the damage tracks. It is well known that water tends to enhance crack growth in glass.[19,20] Water can either diffuse as a molecular specie in glass or react with the Si-O-Si network.[21] The reaction product is usually silanol (Si-OH).[22,23] The ratio of unreacted water to silanol depends on the environmental conditions. For example, it is proved that exposing silica to steam produces hydrated layers.[24] It is safe to assume that the soaked samples contain Si-OH as a reaction product. Water may thus influence the damage mechanism in two ways: silica hydrolyzes and can become more absorbent to UV light or water weakens existing micro-cracks which could then couple with light and lower the strength of the surface. Water seems to have penetrated cracks that were produced during cleaving: both input and output surfaces showed linear tracks (see Fig. 10) that decorate the mechanical damage caused by cleaving. Moreover, longer soak times allow for more water to

penetrate the sample causing thus wider damage tracks. Further study will try to determine whether water induces a higher UV absorption in fused silica or reduces the strength of the glass.

4. CONCLUSION

Polished, etched, cleaved and hydrolized fused silica samples were damaged with a 355 nm laser. The damage morphology characterization showed that ellipsoidal micro-pits initiate in the area illuminated by the laser beam at the onset of damaging threshold fluences. The density of micro-pits decreased from $26x10^{-3}$ μm^{-2} for the polished sample to less than $0.2x10^{-3}\mu m^{-2}$ after etching a 180 nm thick layer off the surface. This is a strong evidence that etching within 200 nm improves the resistance of the surface to UV laser irradiation. Micro-pits formation appeared also on freshly cleaved samples after irradiation which proved that trace polishing slurry contamination was not the only cause for absorption. Damage could also initiate at existing mechanical defects. Finally, soaking the cleaved samples in boiling water decreased the strength of the surface to laser radiation. The laser damage followed linear patterns (probably sub-surface damage caused by cleaving) and seemed to be deeper for samples with longer soak times. These observations provide further evidence that mechanical defects play a major role in the damage of high damage threshold UV optics.

6. ACKNOWLEDGMENTS

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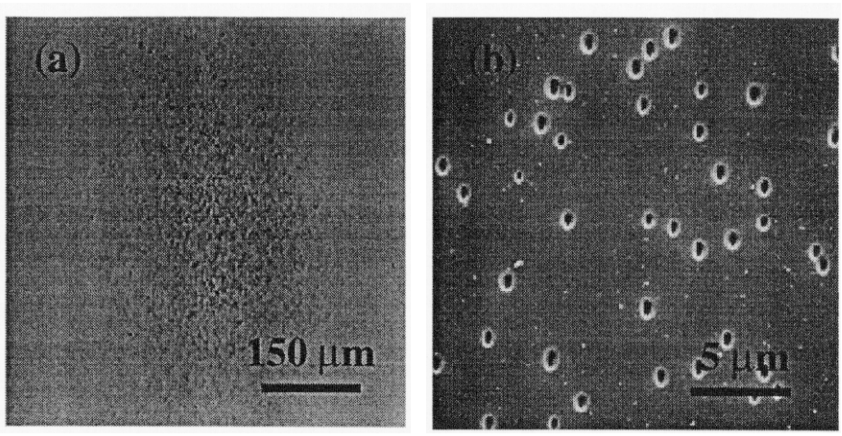

Figure 1: a) Normarski optical micrograph of the surface damage, b) SEM micrograph of the micro-pits that appear at the onset of damage. These pits and the damage debris produce a cludy surface. These changes on the surface can be detected by visual inspection.

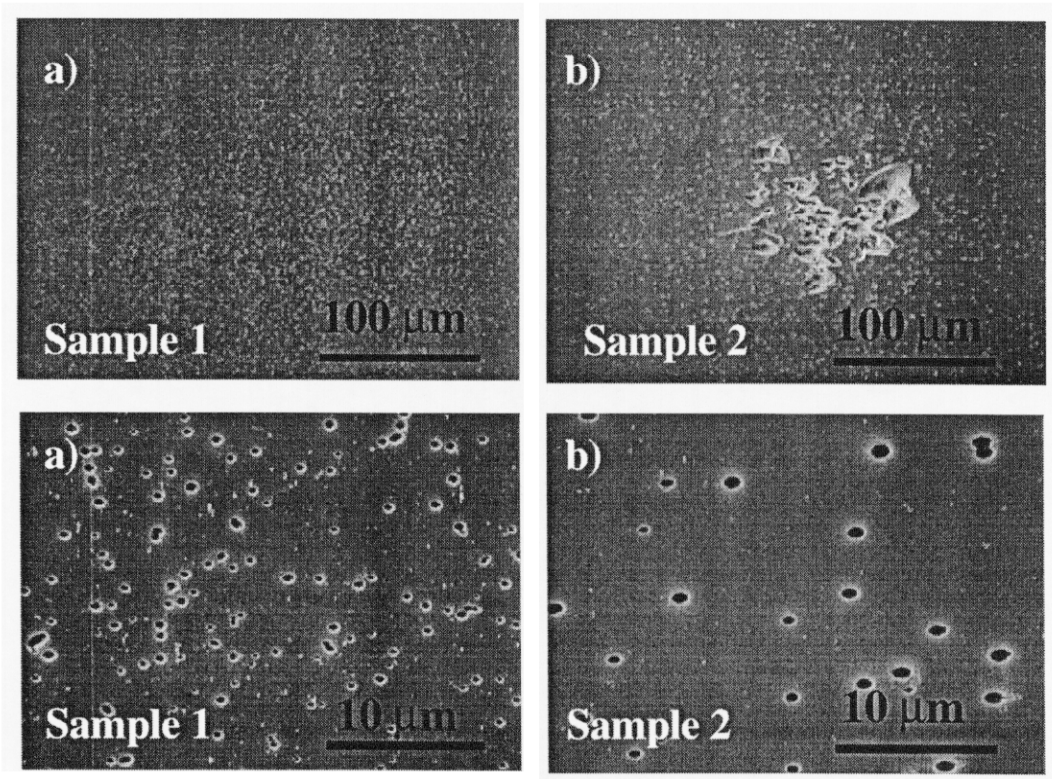

Figure 2: SEM micrographs of surface damage of two samples polished with different processes leading to a) a high density of pits and damage debris, and b) a medium density of pits.

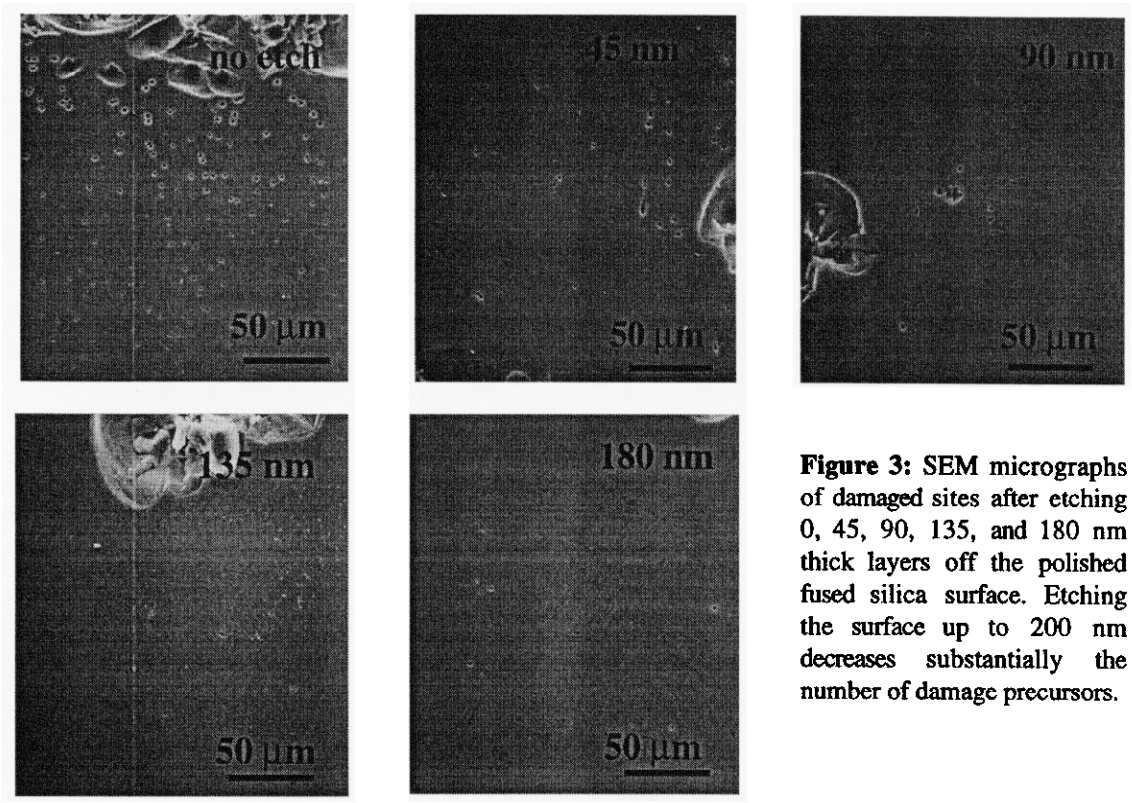

Figure 3: SEM micrographs of damaged sites after etching 0, 45, 90, 135, and 180 nm thick layers off the polished fused silica surface. Etching the surface up to 200 nm decreases substantially the number of damage precursors.

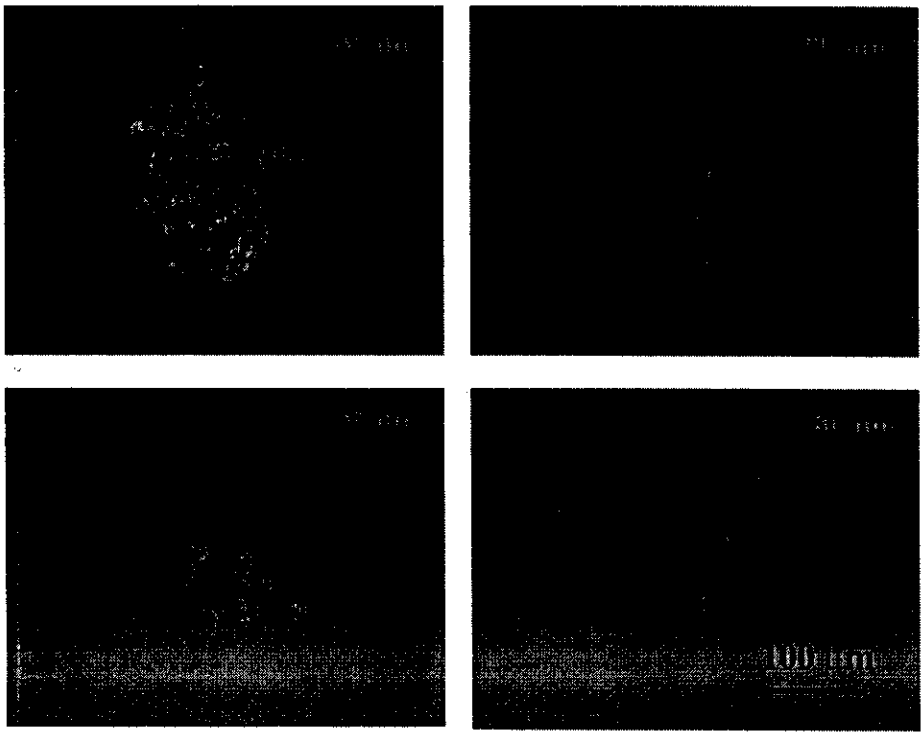

Figure 4: Nomarski micrographs of damaged sites. Each sample was etched for 3, 6, 9 and 12 minutes (etch rate: 15 nm/min) prior to irradiation.

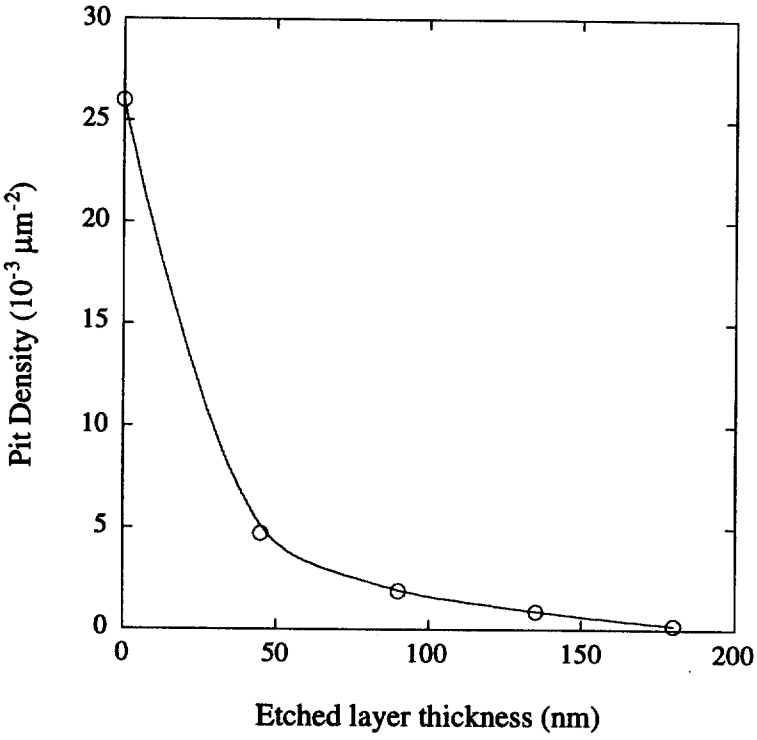

Figure 5: Plot of surface micro-pit density after laser irradiation vs. etched depth.

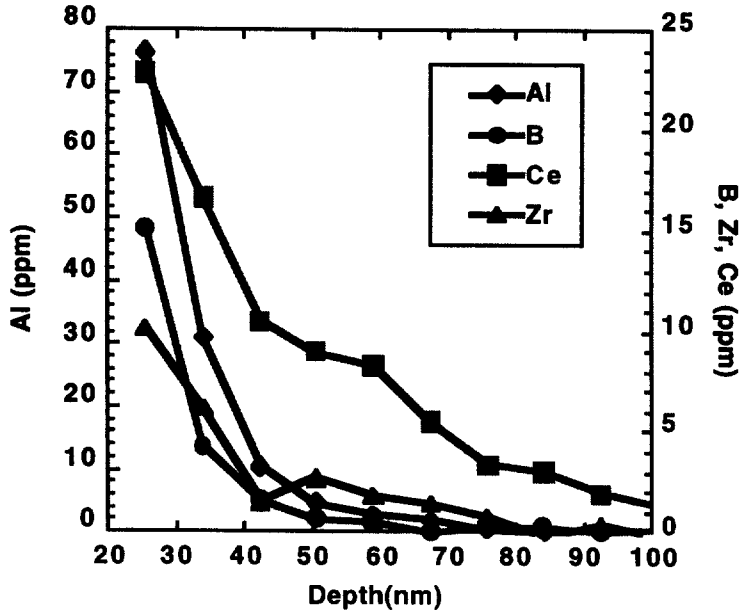

Figure 6: Concentration vs. depth of the four elements with the highest surface concentration.

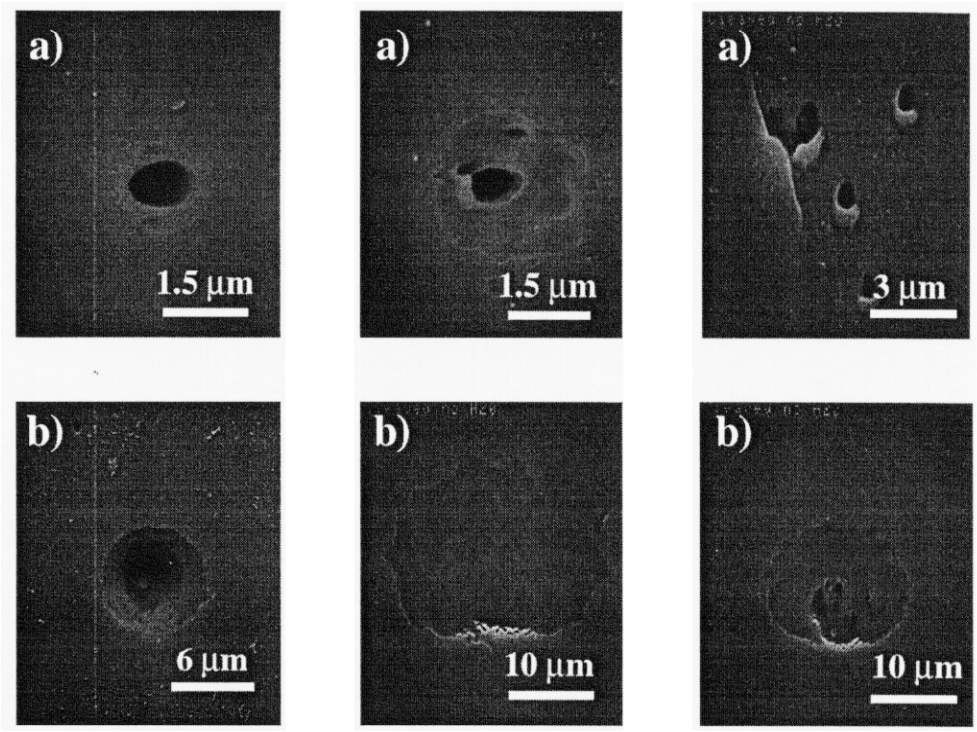

Figure 7: SEM micrographs of laser damage on a cleaved silica output surface; a) micro-pit damage and b) larger craters .

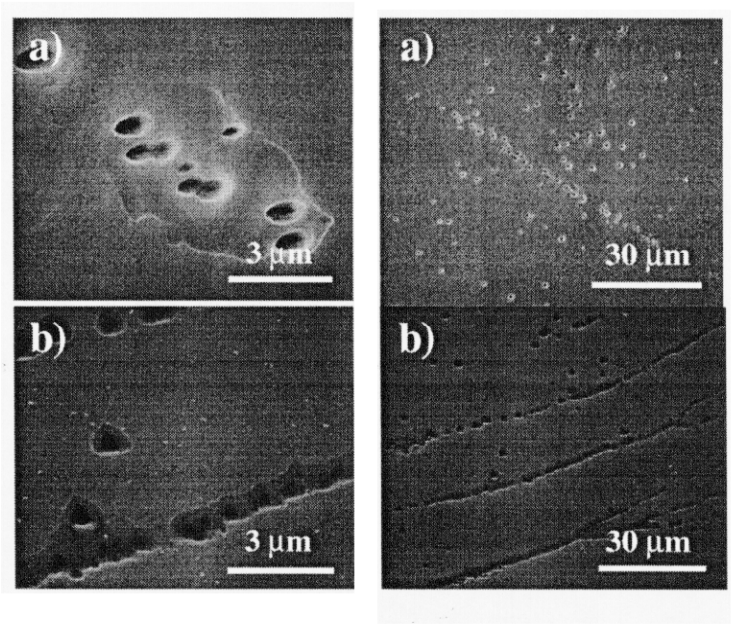

Figure 8: SEM micrographs of linear micro-pit tracks on the surface of a) polished and b) cleaved fused silica.

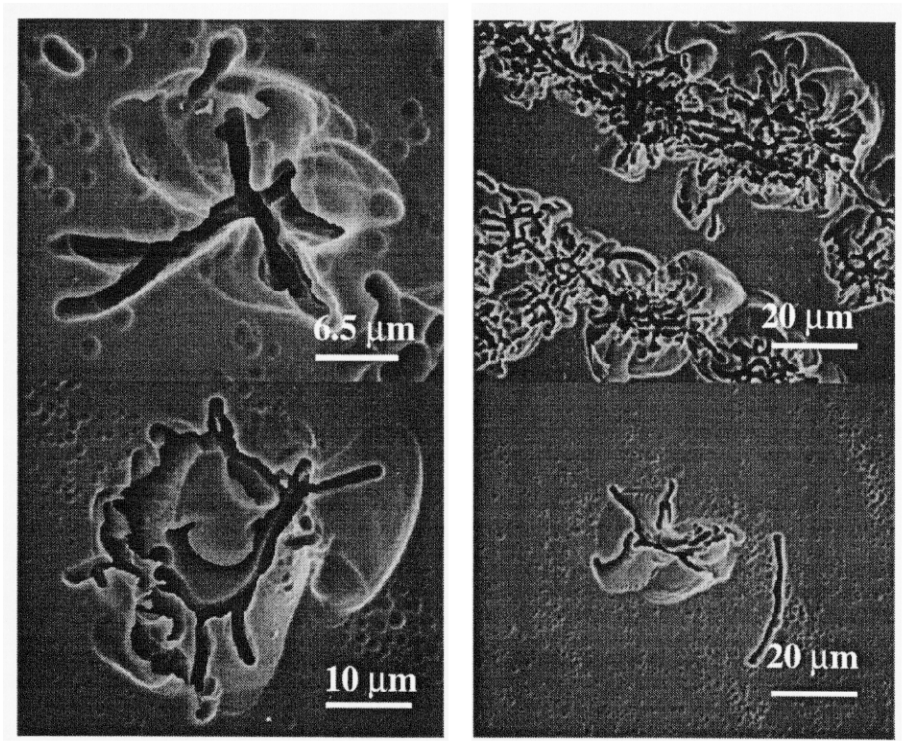

Figure 9: SEM micrographs of chemically etched sites after laser-induced damage of a cleaved output surface.

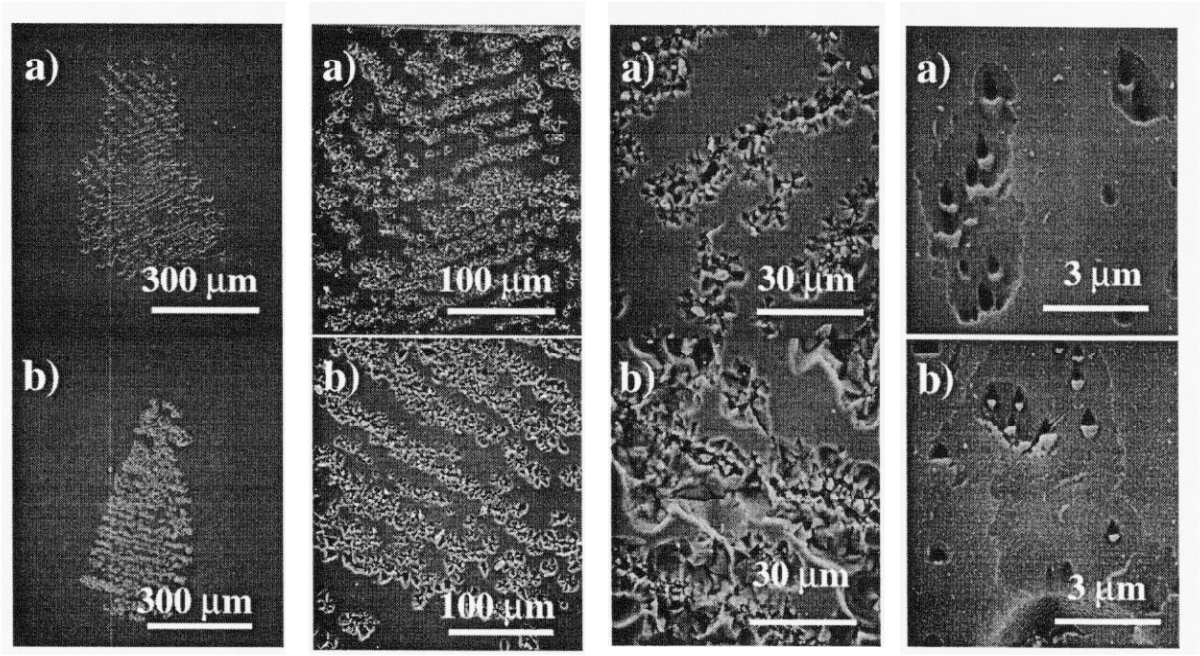

Figure 10: SEM micrographs of irradiated areas (8-ns; 35 J/cm^2) of cleaved silica input surfaces that were soaked in water for a) 1 second and b) 1 hour.