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Synchrotron radiation infrared microscopic study of non-bridging oxygen modes associated with laser-induced breakdown of fused silica

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Nanosecond pulse laser-driven optical breakdown at SiO_2 surfaces as probed by synchrotron-based Fourier transform infrared (SRFTIR) and photoluminescence (PL) microscopies is presented. SRFTIR mapping of laser damage identified localized non-bridging Si-O vibrational modes at ~950 cm^{-1} which became stiffer as 355 nm laser pulse lengths were increased from 5 to 20 ns. The bridging Si-O-Si transverse optic mode frequency varied significantly across damaged regions indicating a wide range of average bond angles, softening slightly with increasing pulse length. 355 nm-excited PL images of laser modified regions could be directly correlated with the structural modifications identified through SRFTIR.

Due to its unique optical and thermal properties, industrial applications of fused silica (a-SiO_2) are wide spread. For example, a-SiO_2 is a critical element in ultraviolet (UV)-resistant optical component in inertial confinement fusion (ICF) laser systems.[1-2] However, the details of damage resistance and the associated physical mechanism occurring in a-SiO_2 are still poorly understood. A time-dependent runaway absorption process is thought to take place with collapse of the ~9eV band gap[3] and transient temperatures and pressures as high as 10,000 K and 10 GPa, respectively.[4] Phase transformations,[5] shock-induced densification,[6] and the creation of electronic defects[7-10] have been observed following a laser-breakdown event. Because the onset of breakdown is strongly coupled to laser pulse characteristics,[11] additional insight might be achieved by probing a-SiO_2 as a function of laser pulse length τ.

In this letter we present synchrotron-based Fourier transform infrared spectromicroscopy (SRFTIR) micro-reflectance measurements of a-SiO_2 surfaces subjected to 5 - 20 ns 355 nm laser pulses. As compared with pristine fused silica, the laser damage event produces a high concentration of non-bridging SiO^- groups as evidenced by a peak at ~950 cm^{-1} which stiffen with pulse length corresponding with changes in local electronic environment. Shifts in the transverse optic (TO) asymmetric stretch mode are also observed, consistent with laser-induced densification and residual strain.

Damage sites were initiated in 2.5 torr of Ar on high purity Corning 7980 a-SiO_2 using a 351 nm laser system previously reported.[12] Laser pulse lengths (intensities) were 5 (5), 10 (3.6), 15 (3.5) and 20 (2.25) ns (GW/cm^2) yielding individual damage sites of approximately 20 to 100 μm in diameter, scaling with τ as 0.4 μm/ns.[13] SRFTIR measurements were performed at the Advanced Light Source on beam line 1.4.3 under ambient conditions. Synchrotron IR light was directed through a Nicolet Magna 760 FTIR bench (spectral resolution ~4 cm^{-1}) with a KBr beam splitter and a Spectra Tech Nic-Plan IR microscope (32×/0.65NA) before being detected with a LN-cooled HgCdTe detector. Spatial resolution was diffraction-limited (~10 μm), and step sizes for scanning were 2.5 (15 ns) or 5 (5, 10, 20 ns) μm.

Broadband, 355 nm-excited PL imaging of damage sites was carried out using instrumentation previously reported.[7]

Typical SRFTIR micro reflectance spectra of pristine and laser damaged a-SiO_2 are presented in Fig. 1. The pristine IR reflectance spectrum of silica is characterized by three broad features corresponding to the Si-O-Si symmetric stretching vibration (ν_{SS}~790 cm cm^{-1}) and a pair of LO-TO split asymmetric stretch modes ($\nu_{AS\text{-}TO}$~1120 cm^{-1} and $\nu_{AS\text{-}LO}$ ~1220 cm^{-1}).[14] In contrast, a-SiO_2 following laser breakdown yields spectra with additional peaks below 1100 cm^{-1}, as well as relative frequency and intensity shifts of $\nu_{AS\text{-}TO}$ and $\nu_{AS\text{-}LO}$. A peak near ~950 cm^{-1} was observed and assigned to the non-bridging oxygen vibration ν_{NB},[15] which shifted to higher frequencies with increasing τ. A weak shoulder appears in the range 1000-1050 cm^{-1}, most prominent in the 10 ns spectra, most likely due to the A_{2u} mode of (pressure induced) stishovite.[5] An increase and ~10-20 cm^{-1} blue shift of $\nu_{AS\text{-}LO}$ mode relative to that of the $\nu_{AS\text{-}TO}$ mode is attributed to an E-field enhancement and oblique angle scattering on (irregular) micro-structured surfaces.[14]

The spatial variation of the reflectivity peaks across laser-damaged regions was probed by raster-scanning the IR beam and least-squares fitting a sum of Gaussians to each spectrum (see Fig. 1). The fits were comprised of two narrow peaks ($\Delta\nu$<50 cm^{-1}) and two broad background peaks ($\Delta\nu$ >100 cm^{-1}), the former of which we associate with primary spectral contributions from non-bridging (ν_{NB}) and bridging ($\nu_{AS\text{-}LO}$) structural units. The micrograph of Fig. 2a shows a 15 ns pulse damage site morphology characterized by a molten-like inner core surrounded by a fractured periphery,[16] and is representative of the other τ raster scans. Figure 2b displays variations $\nu_{AS\text{-}TO}$ corresponding to Fig. 2a indicating $\Delta\nu_{AS\text{-}TO}$ shifts of -10 cm^{-1} and +7 cm^{-1} in the core and periphery, respectively, relative to pristine a-SiO_2 (~1124 cm^{-1}). Using central-force network models, $\nu_{AS\text{-}TO}$ has been expressed in terms of average Si-O-Si bond angles[17] and corresponding variations in density for thermally-quenched[18] and neutron-irradiated[19] a-SiO_2. Micro-Raman scattering of laser damaged a-SiO_2[6, 20] showed a higher concentration of 3- and 4-membered Si-O

rings, consistent with our damage core measurements. However, the stiffening of the $\nu_{AS\text{-}TO}$ mode is more difficult to interpret and somewhat unexpected, since quasi-static tensile and compressive strains both lead to a decrease in $\nu_{AS\text{-}TO}$ phonon frequencies due to dominant bond length or bond angle changes, respectively.[21] It is natural to expect a region of tensile strain surrounding a densified region; therefore, the observed mode stiffening might be due to differences in the transient relaxation of Si-O-Si bond angles and Si-O bond lengths, in favor of faster bond angle relaxation.

Shown in Fig. 2c is the relative variation of the ν_{NB} mode intensity normalized to that of $\nu_{AS\text{-}TO}$. We note that the relative contribution of non-bridging Si-O to the reflectivity appears somewhat higher at the periphery. Since 355 nm (3.5 eV) photoexcitation preferentially excites both laser-induced defects (LID)[6, 9] and NBOHCs,[6, 22] it is instructive to spatially correlate the ν_{NB} mode intensity PL maps under this excitation. Figure 2d shows the PL emission > 420 nm under 355 nm excitation from the damage site shown in Fig. 2a, exhibiting reasonable correlation with ν_{NB} mode intensity. Because the PL signal from laser damage tends to be dominated by the LID,[6, 10] we propose here that both NBOHC and LID electronic species may be related, to some degree, to non-bridging oxygen lattice defects. Figure 3 displays the intensity-weighted peak frequencies and associated standard deviations of the ν_{NB} and $\nu_{AS\text{-}TO}$ modes as a function of τ. The dashed line in Fig. 3 indicates the pristine peak value for $\nu_{AS\text{-}TO}$. The $\nu_{AS\text{-}TO}$ mode frequency shift and standard deviation appear to increase somewhat with τ. The ν_{NB} mode shifts from ~910 cm^{-1} at 5 ns to ~980 cm^{-1} at 20 ns, with a more narrow distribution of frequencies than $\nu_{AS\text{-}TO}$. Comparing this range of ν_{NB} with non-bridging oxygen surface modes in silica nanoparticles,[23] one might infer that shorter τ leads to SiO^- structures (ν_{NB}~900 cm^{-1}) that are predominantly bulk in nature[24] while the longer pulses lead to those (ν_{NB}>920 cm^{-1}) that are localized at the surface.[23] Alternatively, the electronic environment around a dangling Si-O bond may be modified not only by adjacent SiO_4 tetrahedral groups, but by non-bridging SiO^- bonds on the same SiO_4 tetrahedron. For example, in binary alkali-silicate melts[25] ν_{NB} decreases with increasing Li or Na concentrations due to a decrease in local T_d

point group symmetry (splitting into C_{3v} and C_{2v}) and to a softening of ν_{NB} mode.[26] In the case of nanosecond laser damage thresholds which scale as $\tau^{1/2}$, high thermal gradients could lead to faster cooling rates for shorter pulses, resulting in a higher concentration of C_{2v} tetrahedra as compared with a-SiO_2 exposed to longer τ. The interaction of nearest neighbor SiO^- bonds would also be expected to lead to very short excited electronic state lifetimes as compared with bulk NBOHCs, which might explain recently been reported metallic-like states observed in laser-damaged a-SiO_2.[10]

In conclusion, SRFTIR micro-reflectance measurements of a-SiO_2 surfaces subjected to varying 355 nm laser pulse length τ is presented. Laser breakdown in a-SiO_2 produces a high concentration of non-bridging SiO^- groups at the damage periphery as evidenced by the observed peak at ν_{NB}~950 cm^{-1} which stiffens with increasing τ. ν_{NB} mode intensities correlated well with broadband PL emission images associated with electronic defects. The asymmetric stretch TO phonon mode $\nu_{AS\text{-}TO}$ softens slightly with τ in damage core regions, but stiffens at the periphery, indicating a complex variation in bond angle changes from laser shock.

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FIGURE CAPTIONS

Figure 1: Micro-IR reflectance measurements of central damaged regions of 5, 10, 15 and 20 ns pulse damage initiations as compared to pristine silica, along with a least-squares fit (dot-dash) using peak ($\nu_{AS\text{-}TO}$:blue, ν_{NB}:red) and background (not shown) Gaussians. The arrow indicates the peak location of the ν_{NB} mode.

Figure 2: (a) Back-illuminated microscope image of 15 ns damage initiation and (b) corresponding false-color images of $\nu_{AS\text{-}TO}$ mode frequency, (c) ν_{NB} mode intensity, and (d) broadband photoluminescence emission under 355 nm excitation.

Figure 3: Frequency shifts of $\nu_{AS\text{-}TO}$ (top) and ν_{NB} (bottom) modes as a function of laser pulse length.