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Metallic-like photoluminescence and absorption in fused silica surface flaws

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Using high-sensitivity confocal time-resolved photoluminescence (PL) techniques, we report an ultra-fast PL (40ps–5ns) from impurity-free surface flaws on fused silica, including polished, indented or fractured surfaces of fused silica, and from laser-heated evaporation pits. This PL is excited by the single photon absorption of sub-band gap light, and is especially bright in fractures. Regions which exhibit this PL are strongly absorptive well below the band gap, as evidenced by a propensity to damage with 3.5eV ns-scale laser pulses.

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Despite high overall transparency, even the highest quality optical materials such as fused silica can absorb enough laser energy near the surface to damage at fluences and intensities far below their bulk breakdown limits.[1,2] The creation of surface flaws by scratching or indentation, previous laser-damage, or the redeposition of silica vapor surrounding CO_2 laser-heated evaporation pits creates laser damage precursors – regions susceptible to surface damage from ns-scale high fluence laser pulses.[2] These damaged regions are susceptible to exponential growth upon exposure to further laser pulses. Such regions with low laser-induced damage thresholds limit the performance of high fluence laser systems, such as laser-based inertial confinement fusion systems considered for nuclear energy production.[3]

The nature of the laser damage precursors has proven elusive for many years.[4] Damage precursors absorb sub-band-gap light, raising the temperature around the precursor high enough (in excess of the boiling point[1,5,6]) to result in explosive ejection of material from the surface. Typical laser fluences for silica surface damage range from 1 J/cm^2 (for poor surfaces) to 40 J/cm^2 (for excellent surfaces) for a 3 ns, 3.5 eV laser pulse; however, the bulk damage threshold under these conditions is over 160 J/cm^2. This absorption occurs over a broad range of photon energies as low as 1eV, much lower than the 9eV silica band-gap; for example, the damage threshold for silica surface flaws can be below 10 J/cm^2 at 2.3eV (532nm).[7] For the intensities involved, multi-photon ionization is extremely unlikely.[1] The absorptivity required to produce damage, estimated from the boiling point (2500K) and heat capacity of silica ($C_p \approx 2.6$ J/cm^3–K) to be >1000cm^{-1},[8] is surprisingly high, approaching the absorptivity of metals. Contamination by metallic impurities certainly leads to damage – the damage threshold for 12nm gold nano-particles imbedded near the silica surface has been measured to be 4.6J/cm^2 for 355nm, 0.5ns pulses.[6] However, impurity-free surface flaws like the static indentations studied here often damage at thresholds below those observed for the imbedded gold nanoparticles.

We introduce the use of high-sensitivity Confocal Time-resolved Photoluminescence (CTP) imaging, often used in single molecule biophysics, to probe the light-matter interactions in near surface regions of

optical materials (Fig. S1[8]). CTP enables high resolution three-dimensional PL imaging (2-3μm along optical path, submicron in transverse directions) in dielectrics. A 3.1 eV pulsed laser (400 nm, LDH-P-C-405B, Picoquant) is focused using a high numerical aperture objective (UMPLFL 100X, NA=0.95, Olympus) onto a fused silica sample. Scattering and luminescence excited by the laser are collected by the same objective and focused onto a confocal pinhole (100μm; excluding out-of-focus luminescence). Two spectral channels (550-610 nm, >665 nm) and a scattering channel are monitored by avalanche photodiodes (Micro Photon Devices PDM 50CT). Each detected photon is time-stamped with its absolute arrival time (50 ns resolution) and its arrival time relative to the laser pulse (measuring PL lifetime with 150-300ps resolution) using a time-to-digital converter (PicoHarp 300, Picoquant). The sample is scanned in 3 dimensions using a piezo scanner (Nano-LP-200, MadCityLabs). Data acquisition and analysis are performed using custom software written in LabVIEW.

The use of CTP for studying laser damage precursors is motivated by the fact that optically active transitions involved in absorption must also luminesce, even if weakly. The observed PL lifetime τ_{PL} results from a competition between the rates of radiative pathways k_{PL} and non-radiative pathways k_{NR}: $\tau_{PL}=1/(k_{PL}+k_{NR})$. Known silica point defects[9] have PL lifetimes ranging from 2ns to milliseconds; only the non-bridging oxygen hole center with τ_{PL} =13μs and the oxygen deficiency center II with τ_{PL} =10ms are excited at or below 3.5eV.[10] In order to raise the temperature of surface flaws to the silica boiling point within a 3ns laser pulse, we expect much shorter-lived electronic excitations with τ_{PL} <3ns. Electrons excited into continuum electronic states, such as those in a metal, decay very rapidly through non-radiative, single phonon emission, so that the perceived PL lifetimes, $\tau_{PL} \approx 1/k_{NR}$, are very short, and PL emission very weak.[11] The strong absorption (>1000cm^{-1}) of silica surface flaws suggests a high density of electronic states typical of metals. Consequently, we look for PL which behaves more like a metal than point defects. Although a true continuum of electronic states in silica surface flaws is not expected due to the wide band gap, a high density of absorbing electronic states would lead to PL

considerably faster than point defects (<<1ns). CTP has the sensitivity and resolution necessary to detect such small regions of absorbing material emitting weak, fast PL, as well as the ability to determine the lifetime of the luminescence transitions.

In this letter, we report CTP measurements of a variety of silica surface flaws (Fig. 1) and measure their laser damage threshold with 3ns, 355nm laser pulses. We identify a fast PL that correlates strongly to regions with a propensity for laser damage. This PL is not from any known defects in silica.[9] The flaws measured here were produced on optical grade Corning 7980 fused silica samples: laser damage sites (Fig. 1a) were produced by focused 3ns Gaussian laser pulses at 355nm with a $1/e^2$ diameter of about 100μm; static indentations were created with a Vicker's indenter with various loads (2N, Figs. 1b-c; 0.5N, Fig. 1d). Surface features were also created through local heating using a focused 10.6μm CO_2 laser (Fig. 1e); the surface was heated to about 2200K, creating a 200μm wide, 5μm deep, damage-resistant evaporation pit surrounded by a ring of damage-prone redeposited material formed by condensation of silica vapor.

Figure 1 shows time integrated PL images along with the corresponding optical scattering images of the surface flaws studied here. All show PL with a variety of strong lifetime components from 40ps-5ns (e.g. red and green lines in Fig. 2), hereafter referred to as "fast PL". By modulating the laser intensity with an electro-optic modulator, we found in all cases that the PL was linear in excitation intensity, and hence involves only single-photon processes. Polished silica surfaces show very weak fast PL. In contrast to the fast PL, all known silica point defects have PL lifetimes which are ≥ 2ns;[10,12] in many of the flaws, we have identified the non-bridging oxygen hole center by its lifetime (blue line) and spectrum (narrower than that of the fast PL; see Fig. S2[8]). The PL from silver nano-particles (black line) is faster than our time resolution (~150ps) and is used as an instrument response function, convolved with the exponential decays, for lifetime fitting. Figure 2 shows that the fast PL lies between the extremes of the PL from metallic nanoparticles and the known point defects of fused silica.

Fast PL in silica originates within several hundred nm of the surface and is strongly enhanced near fracture surfaces. Large fracture networks can form around 2N indentations, including cone fractures which extend up to 10μm below the surface;[13] strong fast PL clearly follows these fractures, and weak fast PL is associated with the polished surface (Fig. 1b-c). The deep fractures were not in contact with the indenter, hence fast PL cannot be caused by contamination from the indenter. Although a 0.5N indentation forms a layer of densified silica beneath it,[13] the fast PL is only observed along the edges of the indentation (Fig. 1d).

By extracting the total strengths of each lifetime component over an image, we can separate the fast PL components which correlate to damage propensity from the slow PL components which do not. Four lifetime components from 0.04ns to 5ns are required to fit the fast PL measured here (Fig. S3[8]); we interpret this to mean there is a distribution of lifetime components, rather than four specific values. For image extraction, we fit the total number of photons for each lifetime component, with fixed lifetimes of 0.04ns, 0.2ns, 1ns, and 5ns, and a constant component for PL >25ns. In the CO_2 laser-heated pits, two rings of luminescence are observed (Fig. 1e,Figs. 3a-b). The bright, inner ring of the CO_2 laser pit is dominated by long lifetimes. The outer ring of redeposited material has stronger fast components, and is where laser damage occurs upon exposure to a high fluence 3ns laser pulse (green arrow). Fast PL dominates the luminescence from indentations, so that images separating fast PL components from slow PL components are nearly identical to the total PL images (cf. Fig. 4a and Fig. 1d). Central regions of laser damage sites contain slow PL (Fig. S4[8]), matching the regions where the non-bridging oxygen hole center is observed with a 633nm laser (Fig. S2[8]).

Fast PL is directly linked to areas that exhibit strong absorption leading to laser damage. After CTP imaging the surface features above, we measured the laser damage threshold with focused 3ns Gaussian laser pulses at 355nm with a $1/e^2$ diameter of about 100μm (Fig. 4).[8] The 0.5 N indentations damage at the edges, precisely where the fast PL is observed (Fig. 4a). By performing a short etch (5 minute

buffered oxide etch-BOE[8]), we remove about 200nm of material, and also remove the PL (Fig. 4b); annealing of 0.5N indentations for 48 hrs at 750C removes the luminescence even more dramatically (Fig. 4c). Both processes significantly increase the damage threshold (Fig. 4d). The CO_2 laser heated sites damage on the redeposit where the fast PL is found, but not where the bright, slow PL is found (green arrow, Figs. 1e, 3a). Figure 4d shows the correlation between maximum fast (<1ns) PL and laser damage thresholds for the features measured here. This correlation holds for the surface treatments measured here; for our measurement conditions, the discrimination sensitivity is greater for damage thresholds below 20 J/cm^2. Also shown is the slow (>>25ns) point-defect-like PL extracted from the CTP for these surface regions; slow PL shows no direct correlation to damage. Understanding the physics which drives this unexpected fast PL will lead to a deeper understanding of the electronic structure and optical properties of dielectric surface regions.

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Figure Captions

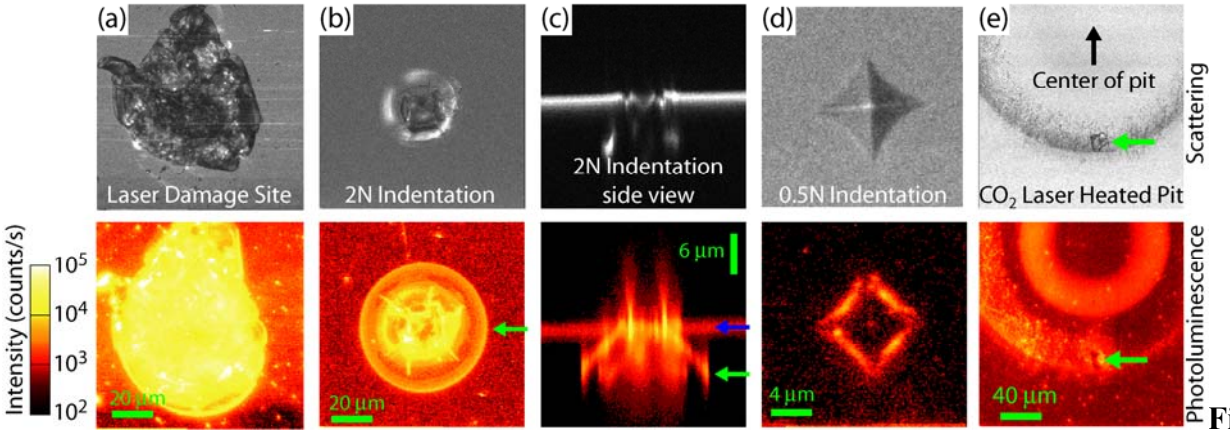

Figure 1: CTP images of scattering and photoluminescence from damage-prone silica surface flaws. **(a).** Laser damage site. **(b).** 2N silica indentation (surface view). **(c).** Plane through surface along green arrow in (a). Blue arrow: surface; green arrow: sub-surface fracture. **(d)**. 0.5N silica indentation. **(e).** CO_2 laser-heated pit (after damage testing). Green arrow: laser damaged area.

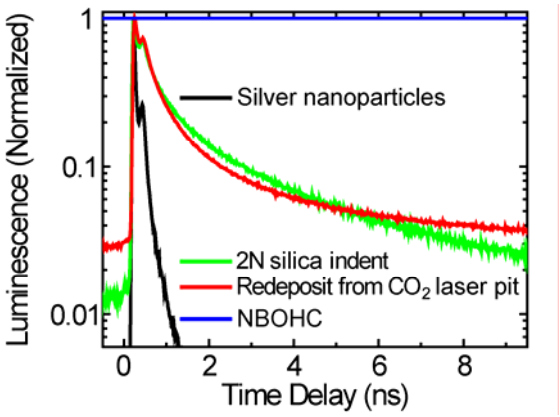

Figure 2. Photoluminescence lifetime decays of damage-prone silica surface flaws (integrated over entire flaw; red, green), silver nanoparticles (black), and the non-bridging oxygen hole center (NBOHC) (calculated from fit; blue).

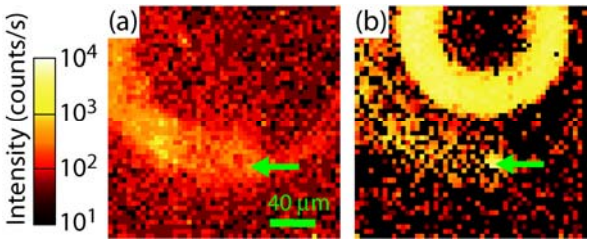

Figure 3: **(a).** Image of fitted amplitudes of fast PL (0.04 ns and 0.2 ns components) in CO_2 laser-heated pit; formed from image in Fig. 1e. Green arrow: laser damaged area. **(b)**. Long lifetime components (>25ns) from feature in **(a).**

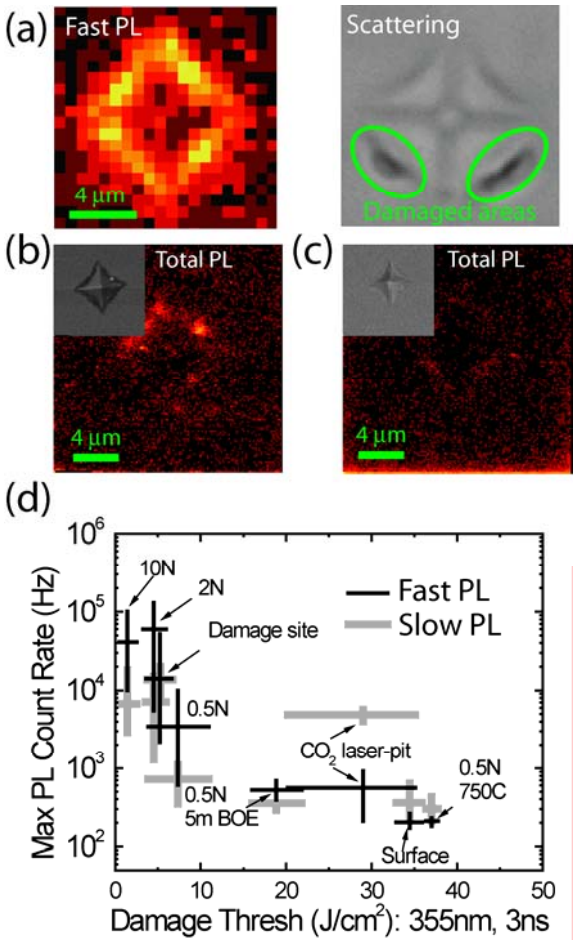

Figure 4: Laser damage measurements using a 3ns, 351nm laser demonstrate the link between strong absorption and the fast PL. **(a)**. 0.5N silica indentation before (left, fast PL image formed from image in Fig. 1d) and after (right, light microscopy) laser damage. **(b-c)**. Total PL images of treated 0.5N silica indentations after: 5 min BOE etch (**b**), 750C, 48 hour anneal **(c)**. Compare with Fig. 1d. **(d)**.

Maximum fast PL count rate vs. laser damage thresholds for the silica surface flaws with the range of values shown as width and height, intersecting at the mean (black). Indentation loads from 0.5N to 10N and BOE etch or 750C anneal are noted on graph. Maximum slow PL count rate shown in gray.