Ion emission from fused silica under 157-nm irradiation

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Abstract. We present a summary of initial work on the etching of silica at 157 nm. At fluences well below the threshold for plasma formation, we have characterized the direct desorption of atomic ions from fused silica surfaces during 157-nm irradiation. The ion identities and kinetic energies were determined by time-resolved mass spectroscopy. The principal ions are Si and O. The emission intensities are dramatically increased by treatments that are expected to increase the density of surfaces defects. Molecular dynamics simulations of the silica surface suggest that silicon ions bound at surface oxygen vacancies (analogous to E' centers) provide suitable configurations for emission. We propose that emission is best understood in terms of a hybrid mechanism involving both antibonding chemical forces (Menzel-Gomer-Redhead model) and repulsive electrostatic forces on the adsorbed ion after laser excitation of the underlying defect.

1. Introduction

The interaction of laser radiation with wide band gap materials, particularly at sub-band gap wavelengths, is an important area of research. Several investigators have demonstrated excellent, damage free surface modification of fused silica (band gap 9 eV) using 157-nm excimer lasers (7.9 eV photons), despite relatively poor quality etching at the longer excimer wavelengths [1]. In this work, we describe a preliminary investigation of ion emission from fused silica during 157-nm irradiation at fluences below the threshold for laser ablation. Ultimately, we hope to clarify the factors responsible for high-quality etching of silica at 157-nm. We observe both Si and O, with kinetic energies of several eV. The emission intensities are strongly enhanced by treatments expected to produce surface defects, and significantly decreased by treatments expected to remove surface defects. We attribute these emissions to a hybrid mechanism involving both antibonding chemical forces and electrostatic forces produced by laser excitation of surface defects.

2. Experiment

Samples were cut from UV grade fused silica rod obtained from Heraus-Amersil (Suprasil 2) and mounted on a 3D translation stage mounted directly in front of and normal to the axis of a UTI 100C quadrupole mass spectrometer (QMS). All experiments were performed in a vacuum chamber with a base pressure of about 2 x 10⁻⁶ torr. 157-nm laser radiation (20-ns pulses) was provided by a Lambda Physik LPF200 (F₂ eximer) laser running at 5 Hz. The beam was focused into a 0.009 cm² spot with a CaF₂ lens. Mass-selected time-of-flight (TOF) measurements were performed with the QMS Channeltron detector mounted 28.8 cm from the sample and operated in the pulse-counting mode. Time resolved signals at individual mass settings were acquired to
determine TOF distributions. The output of the detector was amplified, discriminated, and pulse counted over 200-ns intervals with an EG&G PARC 914P multichannel scalar. The results presented below represent a sum over 200 successive pulses.

A variety of surface treatments were employed. Samples were cut from a bar of fused silica using a diamond saw. Sanded samples were abraded with 600-grit sandpaper. Polished samples were sanded and polished to a 0.25-μm surface finish with diamond paste. Plastically deformed samples were prepared by uniformly indenting polished surfaces with a diamond scribe. Annealed samples were prepared by heating polished samples to 1100 °C for eight hours.

3. Results
The principal ions observed during 157-nm irradiation are Si\(^+\) (amu/e=28) and O\(^+\) (amu/e=16). The most intense emission is Si\(^+\) as shown in figure 1. The emission intensities are strongly affected by surface treatment. Figure 2 shows the total Si\(^+\) counts produced by 300 laser pulses on the surfaces studied in this work. Annealed surfaces show the weakest emission and the plastically deformed surface show the strongest emission. Polishing and annealing treatments remove surface defects, consistent with the weak emissions from these surfaces. Conversely, intense emissions are observed from the sanded and plastically deformed surfaces, where high defect densities are expected.

![Figure 1](image1.png)

**Figure 1.** Histogram of ion intensities observed at three fluences.

![Figure 2](image2.png)

**Figure 2.** Comparison of Si\(^+\) intensities for various surface treatments at 1.75 J/cm\(^2\).

The fluence dependence of the integrated Si\(^+\) intensity from an as-cut surface is plotted on a log-log scale in figure 3. The fluence dependence is non-linear and can be described by a power law with exponent of 1.7.

4. Discussion
Ion emission during UV laser irradiation has been observed from several wide band gap materials and attributed to an electrostatic emission mechanism [2]. Typically a positive ion is adsorbed on top of a surface electron trap and desorbed when the underlying trap is photoionized. The resulting net repulsive force on the adsorbed ion (adion) can eject it with kinetic energies of several eV. The observed Si\(^+\) emission depends nonlinearly on fluence, is strongly directed normal to the surface, and displays a consistent kinetic energy (almost independent of fluence)—consistent with electrostatic ejection. A surface dangling bond terminated with an adion would provide a suitable defect configuration for electrostatic emission. However, a purely electrostatic emission mechanism is not consistent with the strongly covalent bonding in this material.

Significant Si\(^+\) and O\(^+\) emissions have been observed during the fracture of silica in vacuum [3]. In principle, ions that do not escape during fracture can adsorb back onto the surface. These ions should preferentially adsorb at surface electron traps due to the localized negative charge at
these sites [4,5]. In the case of silica these sites would most likely be dangling bonds also created during fracture [6]. These adions would be well situated for emission after photoionization of the underlying electron trap.

**Figure 3.** Si+ ion intensity from an as-cut surface vs. laser fluence. **Figure 4.** Energy estimates for molecular orbitals in Si_{12}O_{12}(OH)_{15}^{+} cluster.

In this scenario, treatments that produce more adions and dangling bonds are expected to yield more intense ion emissions. Abrasion and plastic deformation both require extensive bond breaking and thus are expected to yield intense emission. Polishing removes gross surface defects and apparently reduces the number of adions available for emission. Annealing further reduces the number of surface defects, consistent with the weak emission from annealed material.

The plausibility of the proposed defect configuration for emission was explored by Hartree Fock calculations on SiO\textsubscript{2} clusters with attached silicon ions. Much of this work employed a cluster of 12 silicon ion and 28 oxygen ions arranged in four, six-member rings connected in a tetrahedral fashion. All silicon ions except the adion were bonded to four oxygen ions. Several of the oxygen ions were bonded to only one silicon ion (nonbridging oxygens—NBOs) and were terminated with hydrogen. To simulate the precursor defect, one NBO was replaced with a silicon adion. The resulting defect can be viewed as a silicon ion adsorbed atop an oxygen vacancy, or Si-Si\textsuperscript{+} dimer at the surface. Calculations assumed a positive charge on the cluster as a whole, consistent with a neutral cluster with one adsorbed, positive silicon ion. The simple STO-3G basis was used for equilibrium geometry calculations.

Mulliken charge analysis of the Hartree-Fock molecular orbitals showed that over half of the single positive charge of the cluster appears on the adion. Thus a Si\textsuperscript{+} ion adsorbed on such a cluster would retain most of its charge after interacting with an oxygen vacancy. This positively charged initial state helps account for ion, as opposed to neutral, emission.

The clusters of orbital energies near -5.73 eV and +3.41 eV in figure 4 correspond to the valence and conduction bands of the bulk material; the difference in these energies may be compared to the expected 9-eV band gap of bulk SiO\textsubscript{2}. The highest occupied molecular orbital (HOMO) has an energy of about -5.0 eV and is highly localized on the surface Si-Si\textsuperscript{+} dimer, consistent with a defect state within the band gap, not far above the top of the valence band. The energy of the lowest unfilled molecular orbital (LUMO) is about +0.5 eV and is highly localized on the silicon adion.

The energies and geometries of the derived molecular orbitals constrain the kinds of excitations that can lead to emission. Excitations to the LUMO and LUMO+1 state are not likely to yield emission, as the excitation renders the adion negative and thus electrostatically bound to...
the underlying silicon ion. However, excitations to the LUMO+2 state at +2.7 eV change the character of the Si-Si⁺ dimer bond from bonding to antibonding, while leaving both the adion and the underlying silicon positively charged. This excitation is likely to yield emission. Excitations to this higher state require about 7.7 eV, consistent with emission due to the absorption of 157-nm photons (7.9 eV). Significantly, ion emissions are not observed at 248 nm (5.0 eV), where absorption is sufficient to produce the LUMO and LUMO+1 excitations.

The antibonding character of the excited state is consistent with the Menzel-Gomer-Redhead emission mechanism [7,8], often discussed in the context of electron-stimulated ion and neutral emission. Conversely, the electrostatic repulsion between the adion and the underlying silicon is typical of electrostatic emission. We propose that ion emission from silica under 157-nm radiation is best viewed in terms of a hybrid of the two mechanisms—reflecting both the covalent character of silica and the ionic character of the emission. We note that Hartree-Fock energy calculations will reflect contributions from both antibonding and electrostatic effects.

The Hartree-Fock calculations suggest that single photon excitations are sufficient for emission. This contrasts with the nonlinear fluence dependence in figure 3. One simple explanation would involve a quenching mechanism. For instance, rapid charge transfer from bulk states to the adion could prevent emission. Simulations of ion ejection suggest that charge transfer on subnanosecond time scales can prevent ion escape. If increasing the laser fluence reduces the quenching efficiency, a supra-linear fluence dependence would be reasonable.

Preliminary attempts to detect neutral atomic and molecular emissions from fused silica under the conditions probed in this work were not successful. Improved neutral emission measurements are in progress. Previous work with ionic materials suggests that both neutral and ion emissions play a role in the onset of optical breakdown and laser ablation [2].

5. Conclusion
Si⁺ and O⁺ are emitted from fused silica during 157-nm irradiation at fluences well below the ablation threshold. These emissions depend strongly on the density and character of surface defects. Hartree-Fock calculations suggest that a surface Si-Si⁺ dimer displays appropriate initial and final states for photon absorption and Si⁺ emission. Single photon absorption within this complex produces a strongly antibonding excited state with repulsive electrostatic character. Therefore the emission process is usefully described as a hybrid of Menzel-Gomer-Redhead and electrostatic mechanisms. The sensitivity of ion intensities to surface defects suggests that they may serve as a sensitive probe of flaws and defects on fused silica optical components.

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