Ion Emission of Fused Silica with 157nm Irradiation

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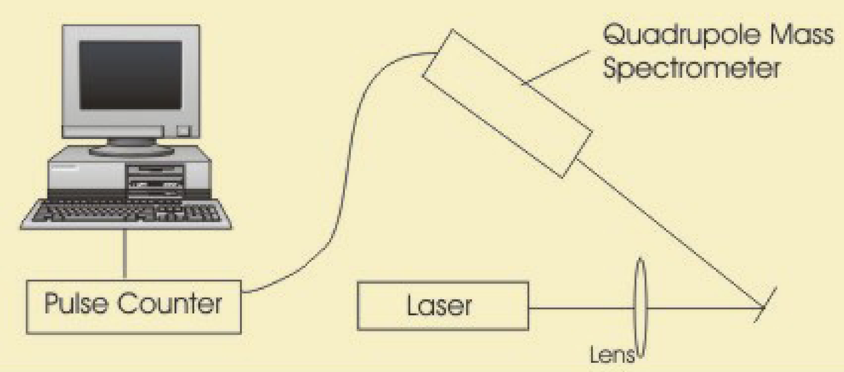
Introduction

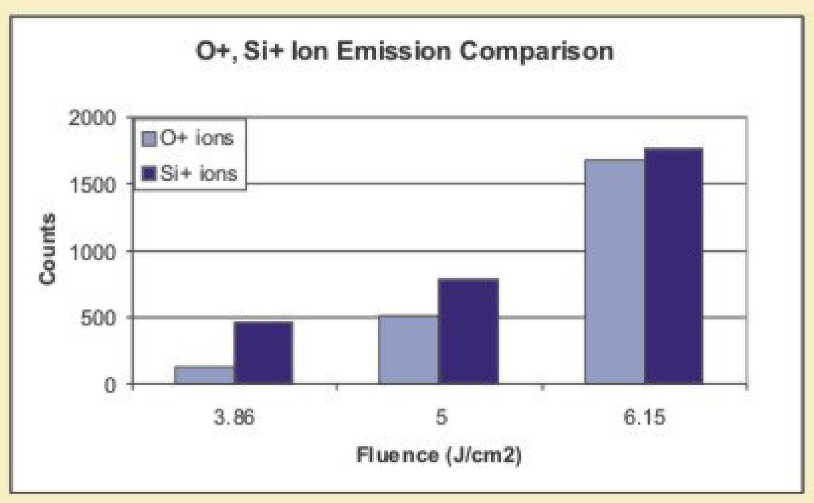
Particle emission from a variety of wide-band gap materials upon sub-band gap laser excitation is frequently observed. Most previous work on SiO_2 under157 nm irradiation (7.9 eV photosn) involve etching and machining, though the mechanism of material removal is unknown. Knowledge of material removal mechanisms could lead to a better understanding of the behavior of surface defects on silica, a material often used in optical devices. Our results demonstrate that 157 nm irradiation can be employed to locate surface defects in SiO_2. This experiment investigates laser induced ion emission from fused silica at laser fluences below the threshold for laser ablation. Strong correlations are observed between the ion emission intensities and defect concentrations. Experimental and theoretical evidence is presented for the possibility of a hybrid emission mechanism, with a character intermediate between the Gomer-Redhead and electrostatic emission mechanisms.

Experiment



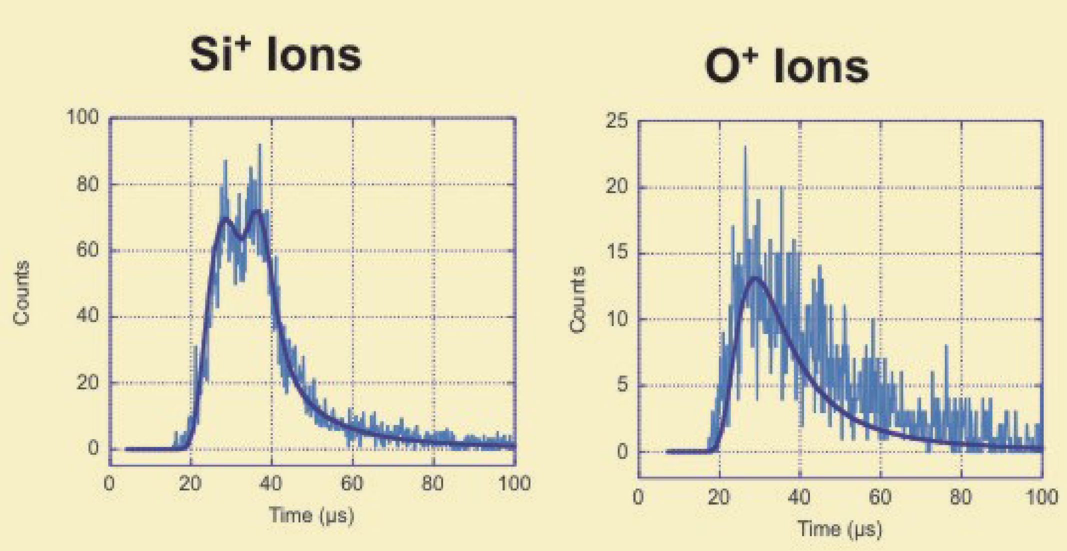
The beam of a 157 nm laser was focused with a 30 cm CaF_2 lens onto a silica surface in vacuum. The intensity of the beam was varied by attenuating it with a series of sapphire slips and/or changing the laser high voltage. The defect densities and character were varied by controlled surface treatments. Particle detection was accomplished using a UTI Precision Mass Analyzer for mass spectrometry. An MCS pulse counter was used to count the pulses supplied. Experiments were performed at room temperature in vacuum.

Observed Particles



The source of Si^+ and O^+ ions in fused silica could be due to fracture. Ion emission accompanying fracture has previously been observed by Dickinson et al. Ions that cannot escape the surface fall back onto the surface. These ions should adsorb at electron traps due to the coulomb attraction between the ions and the localized negative charge. This would account for intense emission from fracture surfaces. Candidate traps for fused silica include oxygen vacancies, which in various geometries have been denoted E' centers.

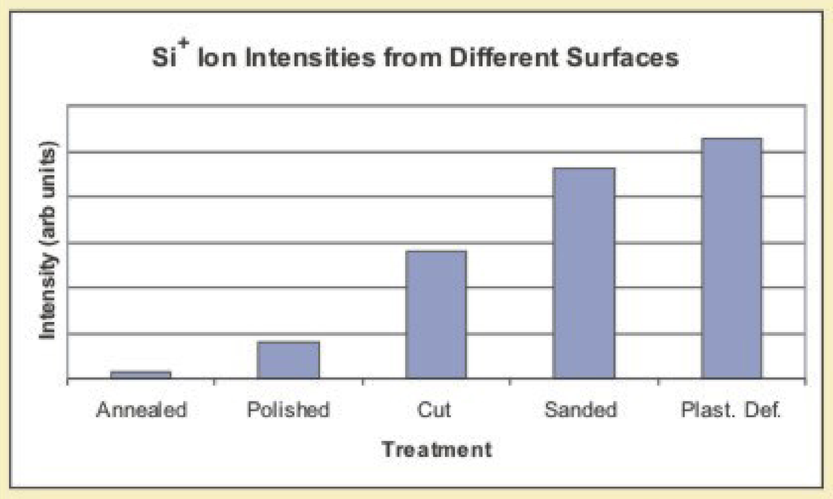
Time of Flight



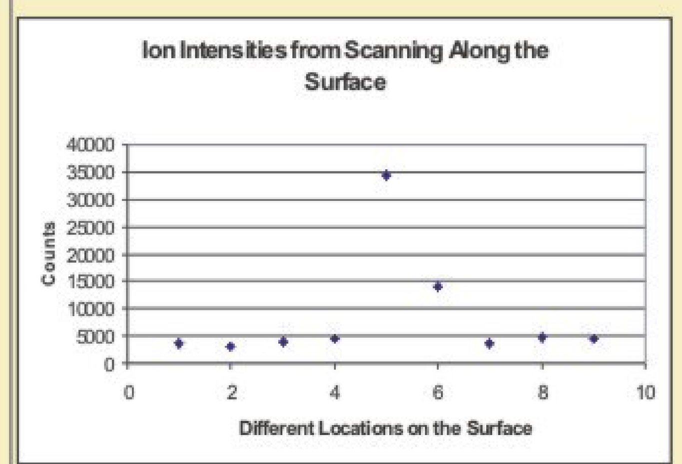
The above graphs are time of flight signals of Si^+ and O^+ fitted with double and single gaussian energy distributions.

Results

Surface Treatments

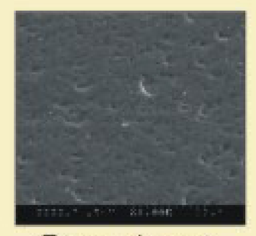


- Surface treatment strongly affects the ion emission of fused silica.
- By Polishing and annealing samples many of the surface defects are removed.
- The more defects present on the surface, the more ions observed (see graph)



SEM image of mechanically induced scratch on a polished fused silica surface.

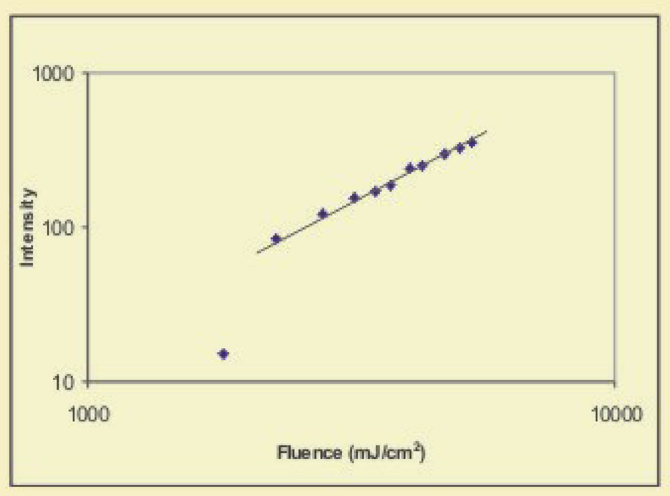
Zoom in on the scratch.



Zoom in on undamaged material.

Fluence

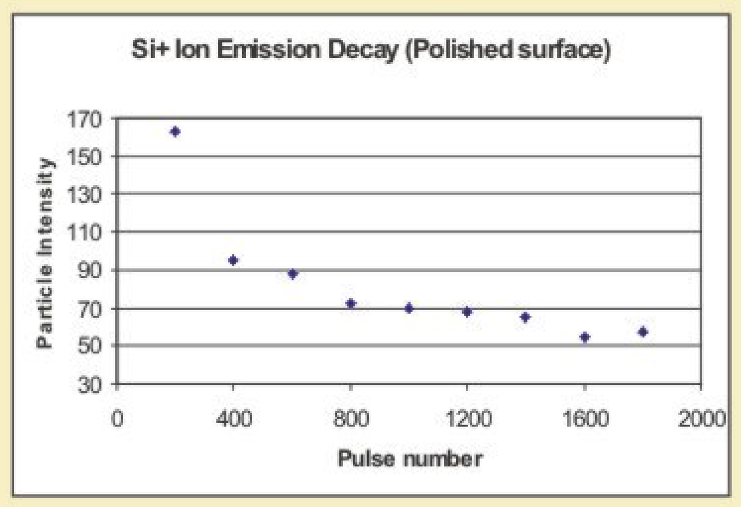
The fluence dependence of the emission intensities typically indicates how many photons are required for emission.



Log (I) α N= slope~1.6

- The power-law behavior, with a slope of 1.6, suggests that, on average, more than one and less than two photons are required for emission.

Ion Emission



- The decay in ion emission indicates surface defects are being removed.
- The emission never decays to zero, indicating that the defect sites are being repopulated.

Discussion

The double peak distributions of Si^+ ions were fit well with the sum of two Gaussian energy distributions. These fits indicate the most probable energies of Si^+ were found to be 8.6 and 10.0 ±1 eV.

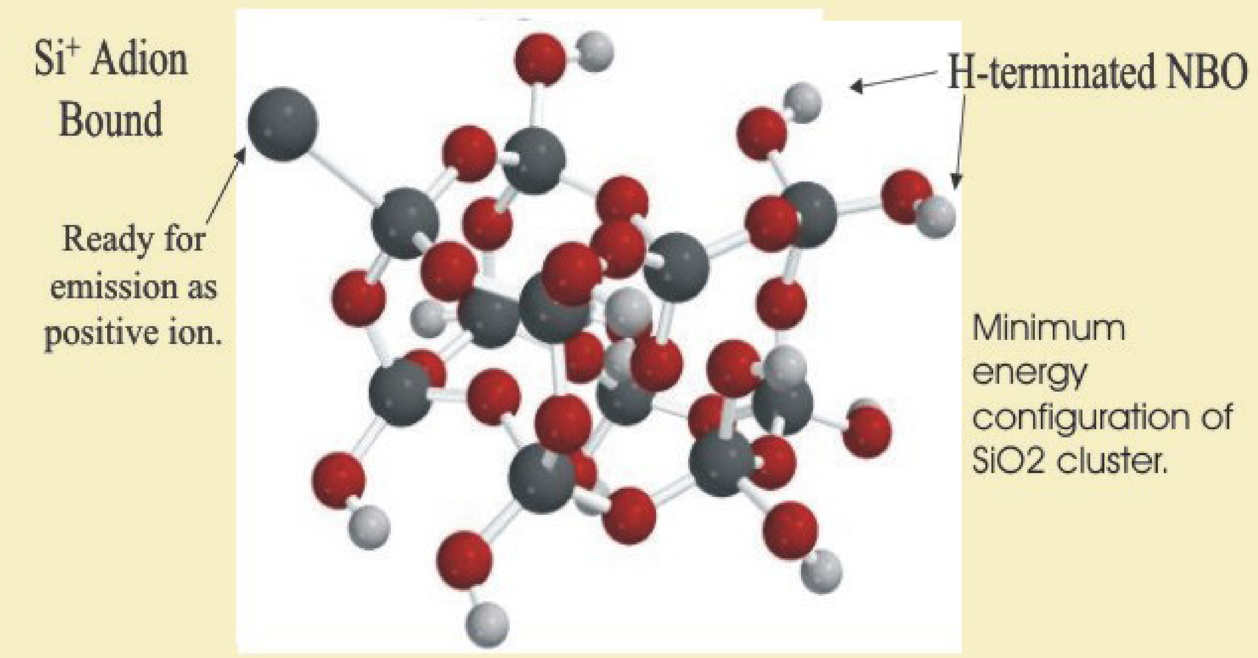
The behavior of the silica ions demonstrates properties characteristic of an electrostatic mechanism: Strong nonlinear fluence dependence, emissions normal to the surface, and high kinetic energies.

The observed behavior supports an electrostatic ion emission. This would entail a sequence of trap-to-trap charge transfer events, which ionize an underlying electron trap in the presence of the adsorbed ion (adion). The Coulomb repulsive force between the adion and the ionized trap causes the adion to be emitted with an energy corresponding to its Coulomb potential.

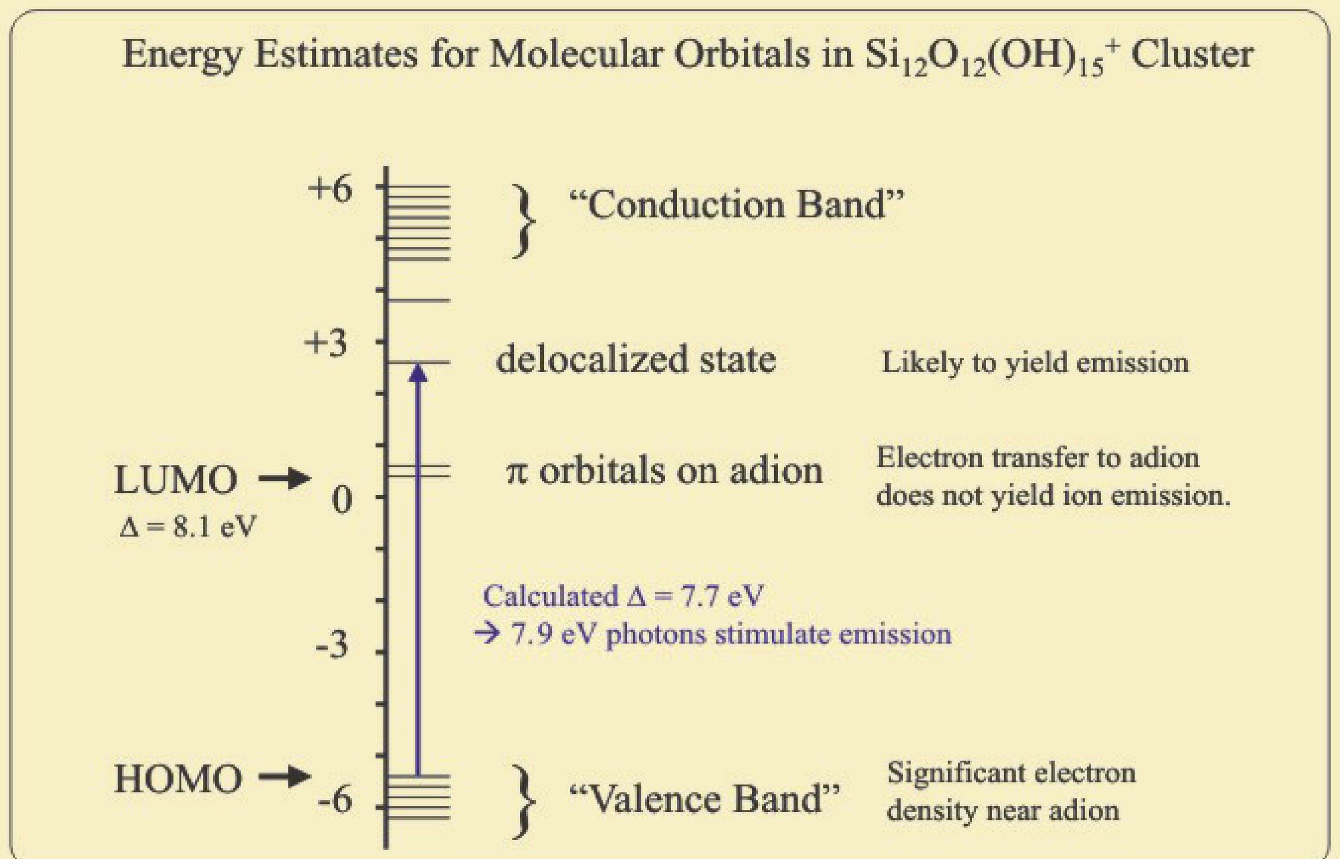
Assuming emission mechanism to be electrostatic and using the Coulomb potential as 8.6 eV predicts a distance of 1.67 Angstroms between an ion and a defect site. Since Si-O bond length in bulk silica is 1.617 Angstroms, an electrostatic mechanism is plausible.

Hartree-Fock Calculations

The plausibility of the expected emission mechanism was explored through Hartree-Fock Calculations on SiO_2 Clusters with adsorbed silicon ions. Most of this work employed a cluster of 12 silicon atoms and 28 oxygen ions arranged to form four, six-member rings connected in a tetrahedron fashion. Oxygen ions with one unsatisfied bond (non-bonding oxygens- NBO's), were terminated with hydrogen. To simulate the precursor defect, one NBO was replaced with a silicon adion. Calculations assumed a positive charge on the cluster, consistent with a neutral cluster with an adsorbed, positive silicon ion.



- The minimum energy configuration supports a Si^+ ion adsorbed at a defect site.
- The proximity of the actual accepted band gap value (9 eV) and that predicted by the calculation (9.14 eV) indicates the model is accurate.



- Emission is not probable due to excitations to the LUMO (Lowest unfilled molecular orbital state) and LUMO +1 states, as this renders the adion negative and thus electrostatically bond to the underlying silicon atom.
- This excitation would require an energy of 5 eV. Calculations are supported by a lack of emissions irradiation with 248 nm (5 eV photons).
- Excitation to the LUMO +2 State not only causes an antibonding orbital, but also is responsible for some delocalized negative charge. This indicates that the emission mechanism may be Menzel-Gomer-Redhead/electrostatic hybrid mechanism.

Conclusion

Ion emission of Fused silica was observed under 157nm irradiation at sub-ablation threshold. The observed species were Si^+ and O^+. We showed that ion emission is strongly dependent on surface defects. The energies obtained from Hartee-Fock calculations are in agreement with a Si^+ adion sorbed to a model defect structure. Single photon absorption within this complex leads to a necessary charge separation for emission of the adion. This model is a hybrid of the previous electrostatic model and the well known Menzel-Gomer-Redhead model. Further Calculations and experiments are being performed to confirm this mechanism as well as to explain the observed O^+ emission. One potentially practical use of this technique is the high sensitivity detection of flaws and defects on important fused silica optical components.

Acknowledgments

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