UV-induced modification of fused silica: Insights from ReaxFF-based molecular dynamics simulations

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Atomic structural modification and defect processes of fused silica resulting from UV-laser irradiation are studied by a combination of molecular dynamics (MD) simulations and the Reactive Force Field (ReaxFF). Bond state transitions by laser excitation are modeled as the result of localized recoils during energy deposition. Computations of pair distribution functions and bond angle distributions of the irradiated structure reveal that fused silica undergoes significant changes in terms of Si-O, Si-Si pair distances and Si-O-Si bond angles, which are attributed to the formation of silicon and oxygen coordination defects. It is found that nonbridging oxygen is responsible for the decreased Si-O bond length, while laser-induced five-coordinated silicon leads to small Si-O-Si bond angles in 2-membered rings. © 2016 Author(s). All article content, except otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).[http://dx.doi.org/10.1063/1.4963204]

Excellent transparency and damage resistance in the ultraviolet (UV) region have led to broad applications of fused silica in the final optics assemblies of inertial confinement fusion laser systems, such as the National Ignition Facility in the United States and the Laser Megajoule in France.1,2 However, current operational conditions often expose the silica components upstream from the fusion target to nanosecond, 351-nm pulse sequences with fluences near the laser-induced damage threshold, resulting in optical degradations that severely hinder the capability of laser output. Despite extensive studies of radiation effects on fused silica, details of the associated material response are still not fully understood.3,4 It is believed that low fluence laser can induce irreversible structural changes without destroying material integrity.5 In this work, molecular dynamics (MD) simulations were performed to present evidence that silica structure in both short and medium ranges is directly modified by UV-induced defects.

In recent years, MD simulations have been devoted to understanding laser-matter interactions at the atomic level. Due to the lack of electronic degrees of freedom for this methodology, which complicates direct correspondence of the quantum nature of ionization to a classical picture, most relevant MD research preliminarily considers the effect of laser radiation as exciting the potential or kinetic energy of atoms by energy conversion. For instance, Wang modified the Coulomb potential by changing atom charges to study the ultrafast laser ablation of silica films.6 Wootton and Zheng modeled laser absorption as adding extra kinetic energy to bonded Si-O pairs to produce densifications.7,8 In the latter approach, laser excitation functions as a highly localized recoil, in which process the absorbed energy initiates an instantaneous disruption in the lattice and allows the atoms to move towards the nearest minima of the ground state potential energy surface through subsequent

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relaxation. The concept of bond breaking is thus plausibly introduced, which shares similar characteristics to laser-induced radiolysis, the dominant mechanism occurring upon exposure.\textsuperscript{9,10} The simulations were performed with the LAMMPS code,\textsuperscript{11} using a similar model to that proposed by Wootton, i.e., depositing the absorbed laser energy into the thermal vibrational motions of the constituent atoms.\textsuperscript{7} A key factor hindering this treatment is that the MD empirical force field must provide reasonable predictions of bond state transitions as occur with radiolysis. The aforementioned studies chose the partial charge pairwise BKS potential because it can reproduce the static structure of fused silica. Such potential, however, is not optimally suited for situations involving bond breakage and reformation for low-energy excitations as the potential assumes unphysical values at low internuclear distances. To address this challenge, a bond order Reactive Force Field (ReaxFF)\textsuperscript{12} recently reparametrized for silica-water systems was used instead. Prior to conventional force fields, the ReaxFF potential has been validated to enable reactive bond computations in \textit{ab initio} qualities by numerable studies.\textsuperscript{12–15}

The amorphous structure of fused silica was prepared by the conventional simulated melt and quench process in steps of 0.5 fs. The initial configuration contains 3000 atoms (1000 SiO\textsubscript{2} units) that were randomly positioned in a periodic cubic cell with a density of 2.2 g/cm\textsuperscript{3}. After being fully melt at 4000 K, the liquid was gradually quenched to 300 K at 5 K/ps in an NVT ensemble. The silica system was then relaxed for 100 ps at 300 K, 1 atm in an NPT ensemble, followed by another 100 ps in an NVE ensemble to obtain the final structure. A Nose-Hoover thermostat/barostat was used in the NVT and NPT simulations to control temperature and pressure, with coupling constants of 50 fs and 500 fs, respectively. The resulting density of the system is 2.19 g/cm\textsuperscript{3}, in good agreement with the experimental value of 2.20 g/cm\textsuperscript{3}. FIG. 1 compares the simulated structure factor with the results obtained from neutron diffraction. The observed agreement indicates the well reproduced silica structure, a snapshot of which is also shown in FIG. 1.\textsuperscript{16}

Once the bulk structure was generated, coordination defects can be classified by the coordination number of each atom. A stoichiometric fused silica is known as a continuous random network formed by silicon atoms tetrahedrally bonded to bridging oxygen (BO) atoms. Given a bond order cutoff of 0.3, the simulation sample contains very low concentrations of coordination defects, including 0.03\% nonbridging oxygen (NBO, an O atom only bonded to one Si atom), 0.37\% three-coordinated silicon (Si\textsuperscript{3}, a Si atom bonded to 3 O atom) and 0.40\% five-coordinated silicon (Si\textsuperscript{5}, a Si atom bonded to 5 O atoms).

To simulate UV-induced excitations at 351 nm (3.5 eV), the absorbed laser energy was added to the kinetic energy of Si and O atoms. For simplicity, the energy released from non-radiative electron-hole recombination contributes exclusively to one atom in each excitation. Since an ionization event requires three photons at a time to surpass the wide band gap of fused silica (\textasciitilde 9 eV), a fixed

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Comparison of structure factor $S_N(Q)$ calculated from MD simulations (line) and neutron diffraction experiments (circle).\textsuperscript{16} A snapshot of the simulated silica structure (Si: red. O: blue) is shown in the corner.}
\end{figure}
energy of 10.5 eV was used to rescale atom velocity without changing its direction. The subsequent recoil thus had a chance to initiate defects by permanently knocking out the target atom that otherwise would have been recaptured from its neighboring atoms. FIG. 2 is an example of the two displacement categories of oxygen atoms, both of which were excited with 10.5 eV. In support of the recoil model, the displacement probability which depends mainly on atom orientation for amorphous solids was calculated by testing every atom in a smaller cell of 100 SiO$_2$ units. Because electron rearrangement occurs much faster than thermal conduction, the atoms within the recoil range (~3.2 Å as shown in FIG. 2) of the excited atom were allowed to move freely while all else were thermostated by the Brownian dynamics to maintain the system at room temperature. In this way all involved Si-O bonds around the excited atom have been taken into account instead of a random one. As with the example shown in FIG. 2, most of the target atoms are found to rearrange within about 200 fs. In this regard, an excited atom is defined to be permanently displaced if the atom has not returned to its original balance position within 1 ps after recoil. Considering thermal vibration at 300 K, the amplitude of which is about 0.4 Å (FIG. 2), a larger cutoff distance of 0.8 Å was set to classify the displacement. In the sample, 15.5% of the oxygen atoms and 2% of the silicon atoms were permanently displaced, leaving vacancies at their respective original positions. It is also found that smaller time steps of 0.1 and 0.2 fs do not significantly change the simulation results. The significant distinction in the displacement probability between oxygen and silicon confirms the observation that radiolysis in fused silica is oxygen-related only.

To check the accumulated radiation effect of multiple laser pulses, 600 excitations were successively applied in the 3000-atom simulation system. The 5 ps interval between two adjacent excitations was more than enough to dissipate the induced energy and regain thermal equilibrium. For a pulse duration of several nanoseconds, a large interval is essential because the weak UV absorption of fused silica is unlikely to initiate correlating excitations inside a small bulk of the simulated size. To reduce the simulation cost and guarantee uniform absorption, each excitation was imposed on a random oxygen atom. Since 2/3 of the atoms in fused silica are oxygen, the result was roughly equivalent to the radiation effect of 900 excitations regardless of atom type. After every 50 excitations, the configuration was abstracted to collect structure statistics individually in an NVE ensemble.

The defect number is plotted in FIG. 3 versus the number of excitations. As precursors to nonbridging oxygen hole centers (NBOHC), NBO increases at a rate similar to Si$^3$, the typically assumed precursors to $E'$ centers. Such defect pairs indicate the presence of the established radiolytic process, wherein a Si-O bond in a Si-O-Si group is fractured during electron excitation, as illustrated in FIG. 4. Apart from the preexisting defects, three-coordinated oxygen atoms (TBO, an O atom
FIG. 3. The number of coordination defects in the silica bulk during 600 excitations.

FIG. 4. Atomic view of the radiolysis scheme. After excitation with 10.5 eV, a Si-O bond linking a BO and a four-coordinated Si ($\text{Si}^4$) in FIG. 4(a) is fractured, forming an NBO/$\text{Si}^3$ pair in FIG. 4(b).

bonded to 3 Si atoms) appear and exhibit a comparable growth rate to $\text{Si}^5$ for the first 400 excitations. In previous studies, $\text{Si}^5$ are believed to be native defects in fused silica, and TBO are hypothesized as intermediate products of silicon oxidation during the formation of the amorphous network.\textsuperscript{19} For the case of UV-laser radiation, $\text{Si}^5$ and TBO correspond preliminarily to an oxygen-excess and oxygen-deficiency environment, respectively, which may generate Frenkel-type defects as reported elsewhere.\textsuperscript{20} Note that FIG. 4 does not provide quantitative predictions of the realistic defect yield, which indeed necessitates an accurate estimation of the ionization cross section other than the displacement probability for comparison with experiments. Besides, laser-induced defect evolution remains controversial, and distinctive growth behavior has been reported.\textsuperscript{20,21} However, since the effect of the radiolytic process was properly represented, the defective structure thus sharing basic features of irradiated silica is still useful for a qualitative investigation despite a different defect concentration.

Insight into the short-range structure is obtained by calculating pair distribution functions (PDF) for the Si-O, Si-Si and O-O pairs. After 600 excitations, substantial distinctions were identified in the primary peaks, as shown in FIG. 5. The slight decrease in the magnitude of each PDF peak indicates a decreased average coordination number for each atom species. For the Si-O PDF which primarily peaks at 1.58 Å (FIG. 5(a)), a conspicuous protrusion occurs in the 1.35 ~ 1.45 Å region. Direct measurements of the distances between neighbored Si-O atoms show that the average length of Si-NBO bonds is 1.38 Å, approximately 0.2 Å shorter than that of Si-BO. Hence, the protrusion around 1.4 Å is introduced mainly by NBO defects. Such phenomenon is important because it has not been identified from BKS-based MD studies.\textsuperscript{8} On the other hand, the decrease of Si-O bond length has been experimentally confirmed in 355-nm irradiated silica samples.\textsuperscript{20} For the other PDFs, the primary peak of the Si-Si PDF (FIG. 5(b)) exhibits a left shift of 0.02 Å from 3.1 Å, whereas the O-O peak position in FIG. 5(c) remains at 2.57 Å. Since the Si-Si and O-O pair distances in $\text{SiO}_4$...
tetrahedrons are determined by Si-O-Si and O-Si-O bond angles, respectively, the shift of their peak positions thus indicates the change of medium-range order.

As a further validation, the Si-O-Si and O-Si-O bond angle distributions (BAD) are plotted in FIG. 6(a) and (b), respectively. The Si-O-Si BAD peak shifts from 154.5° to 153.5° while the O-Si-O peak slightly decreases in magnitude only. After irradiation, an extra peak at 108° emerges in the Si-O-Si BAD. This peak associated with much smaller Si-O-Si bond angles than the most probable value originates from 2-membered rings, i.e. two SiO$_4$ tetrahedrons share edges to form the smallest closed paths, which are apt to generate in silica surfaces through atom reorganization after cleavage.\textsuperscript{22,23} Unlike those located in surfaces, wherein silicon remains regularly coordinated, a 2-membered ring in the irradiated bulk usually contains a Si$_{5}$ defect. This unique observation indicates that the formation of such 2-membered rings is caused by laser-induced Si$_{5}$ (not the native ones), which divided the network rings into smaller ones, resulting in small Si-O-Si bond angles and thus decreased Si-Si pair distances. However, some experiments suggested that the Si-O-Si bond angles will increase after 355-nm irradiation.\textsuperscript{20,21} The discrepancy may arise from the sub-bandgap absorption of some specified structures or defects that can furtherly overwrite the silica backbone.

In conclusion, MD simulations have been carried out with the ReaxFF potential to investigate UV-induced structural modification of fused silica. After initial validation, the enhanced recoil model developed to mimic the effect of radiolysis has confirmed that successive laser excitations can give rise to an increased number of coordination defects. In the irradiated silica structure, the Si-O bonds linking NBO defects have been identified to be significantly shorter than those between regularly
coordinated atoms. The change of Si-O-Si bond angles due to the formation of Si\textsuperscript{5} is responsible for the decrease of Si-Si pair distances. By providing atomic level details of laser-induced structural response, the simulation results may contribute to understanding the role that defects play in radiation effects on fused silica.

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