Free energy molecular dynamics simulations of pulsed-laser-irradiated SiO$_2$: Si Si bond formation in a matrix of SiO$_2$
Free energy molecular dynamics simulations of pulsed-laser-irradiated SiO₂: Si–Si bond formation in a matrix of SiO₂

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The calculations are based on the density functional approach, which allows to simulate the dynamics of ions and electrons upon laser excitation. The excitation energy \( h\omega \) is distributed among electrons within fs, a time scale much shorter than the electron-ion relaxation time, so that the adiabatic approximation holds. The calculations identify the \( h\omega \) range at which either LS or ESS occurs, and also how the diffusivities of O and Si differ upon high electron excitations. Occupation numbers are given by \( f_i = \left[ e^{(E_i - \mu)/k_B T_e} + 1 \right]^{-1} \) and valence wave functions are expanded in plane waves with a cutoff of 70 Ry with the Brillouin zone sampled at the \( \Gamma \) point. The core–valence interactions are described by Troullier–Martins pseudopotentials. The system is a well assessed formula unit \( \alpha \)-quartz supercell of 9.832 \( \times \) 8.514 \( \times \) 10.811 A\(^3\) with experimental lattice parameters and periodic boundary conditions. We inspected \( T_e = 20 \) 000, 25 000, and 30 000 K, corresponding to excitation energies \( h\omega \) of 1.72, 2.16, and 2.59 eV, respectively. However, these are not strictly related to the experimental excitations, due to the energy gap underestimated inherent in DFT.

Starting with a geometry-optimized SiO₂ system [Fig. 1(a)], we set \( T_e = 20 \) 000 K and performed a FEMD for 1.2 ps. The ionic temperature \( T_I \) was found to equilibrate around 304 K (Fig. 2). However, no structural changes occurred, as clearly shown by the pair correlation functions (PCF) (Fig. 3).

In a second simulation at \( T_e = 25 \) 000 K, the ionic forces \( \mathbf{F} \) change as a response to the enhanced \( T_e \). After initial large oscillations, a new equilibrium is attained in about 1.9 ps with \( T_I = 367 \) K, below \( T_{melt} \) (Fig. 2). Nevertheless, \( T_e \) is now sufficient to induce a weakening of several Si–O bonds, with large structural oscillations that in some cases result in a Si–O bond breaking. The longer equilibration time, in this case, reflects the structural modification, involving breaking and formation of chemical bonds and, although \( T_I \) is not too different from the former case, these chemical processes suppress or enhance \( T_I \) oscillations. Since it is easier for O to break its two bonds, rather than for Si to break...
all its four bonds, O atoms can be dislodged. This intuitive image is supported by the computed\textsuperscript{16} diffusion coefficients\textsuperscript{17} (Table I): $D_O$ is more than twice larger than $D_{Si}$. Interestingly, the weakening of the Si–O bonds occurs in regions where the electron excitations localize. In fact, by monitoring, the weakening of the Si–O bonds occurs in regions inside the SiO\textsubscript{2} gap, and are characterized by occupation numbers $f_{i}$ when an O atom diffuses away, it leaves behind two Si \textit{sp}\textsuperscript{3} DBs similar to $E'$ centers in SiO\textsubscript{2}.\textsuperscript{3,14,15} These are located in energy at $\sim$2.7–3.0 eV above the valence band of SiO\textsubscript{2}, i.e., inside the SiO\textsubscript{2} gap, and are characterized by occupation numbers $f_{i}=0.86$ and 0.82, respectively. These values are much larger than $f_{i}=4 \times 10^{-2}$ corresponding to antibonding eigenvalues. Thus, the disruption of the bond network and the formation of Si–Si bonds cannot be ascribed to a simple randomization caused by antibonding states occupation. Since the two DBs are close, a Si–Si dimer of average length $2.54 \pm 0.08$ Å is quickly formed and remains stable on the time scale of the simulation. The gap states corresponding to the DBs disappear and the resulting electron wave functions is a typical Si–Si covalent bond. The final equilibrated structure is shown in Fig. 1(c). The total number of Si atoms forming stable Si–Si bonds, with lengths ranging from 2.51 to 2.64 Å, is $\sim$20\% of the total number of Si. This results in nonzero values around 2.6 Å of the Si–Si PCF (Fig. 3). The presence of $\equiv$Si–Si–O– structures is responsible for a shift toward 1.78 Å and a broadening of the first peak of the Si–O PCF. The broad peak at $\sim$3.4 Å in Si–Si PCF, absent in other simulations at different $T_e$, originates from $\equiv$Si–Si–O–Si= and $\equiv$Si–Si–Si= structures. Interestingly, although $T_f < T_{melt}$ the formation of Si–Si structures occurs via lattice distortions promoted by the weakening of the chemical bonds and results in a local phase separation induced by electron excitations. Since we are working here in the $\mu$-canonical ensemble, the departing O sits elsewhere and forms a three-membered ring\textsuperscript{15} where a threefold O atom and a Si floating bonds (FB) coexist.

In our third simulation, at $T_e$ = 30 000 K, the ionic forces become so large that many Si–O bonds break and the system heats above $T_{melt}$ in $\sim$0.3 ps. The ions equilibrate at $T_f$ = 2870 K (Fig. 2) and with a random distribution of Si and O atoms. The PCFs become almost structureless with only a signature of a dynamical short range order (Fig. 3). Bonds are continuously broken and reformed, lots of unbound atoms wander around and the energy gap is filled by a large population of unsaturated bonds. This is a typical LS of SiO\textsubscript{2}, as confirmed by the enhancement of $D_{Si}$ and $D_{O}$ (Table I).

Finally, we inspected an oxygen deficient center (ODC) by removing the O atom in $\equiv$Si(1)–O–Si(2)<= [see Fig. 1(a)]. For $T_e$ = 20 000 K, the two Si atoms facing the O vacancy form a Si–Si dimer of $\sim$2.53 Å, as expected,\textsuperscript{14} with no

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**Table I.** Ionic temperatures ($T_f$) and O/Si diffusion coefficients ($D_O$, $D_{Si}$) for the simulated $T_e$. Error bars refer to dynamical oscillations of $T_f$.

<table>
<thead>
<tr>
<th>$T_e$ (K)</th>
<th>$T_f$ (K)</th>
<th>$D_O$ (cm$^2$/s)</th>
<th>$D_{Si}$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 000</td>
<td>304±118</td>
<td>$1.00 \times 10^{-9}$</td>
<td>$1.26 \times 10^{-9}$</td>
</tr>
<tr>
<td>25 000</td>
<td>367±112</td>
<td>$4.09 \times 10^{-9}$</td>
<td>$8.49 \times 10^{-9}$</td>
</tr>
<tr>
<td>30 000</td>
<td>2870±220</td>
<td>$1.42 \times 10^{-7}$</td>
<td>$3.40 \times 10^{-7}$</td>
</tr>
</tbody>
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FIG. 1. (a) SiO\textsubscript{2} supercell: Si and O atoms are the gray and white balls, respectively; (b) detail of an intermediate configuration at $T_e$ = 25 000 K with two DB (DB\textsubscript{1}, DB\textsubscript{2}) ready to form a Si–Si bond (the two black Si). Isosurfaces (gray): $|\langle \psi \rangle|^2 = 5 \times 10^{-3}$ Å$^{-3}$; (c) equilibrated SiO\textsubscript{2} structure at $T_e$ = 25 000 K (Si–Si bonds in black); (d) equilibrated ODC structure at $T_e$ = 25 000 K (Si–Si bonds in black).

FIG. 2. Ionic temperature evolution for the three electronic temperatures simulated.

FIG. 3. Si–O (upper panel) and Si–Si (lower panel) pair correlation functions (PCF) for $T_e$ = 20 000 K (dashed line), 25 000 K (solid line), and 30 000 K (dot-dashed line). The inset shows the details between 2.0 and 3.5 Å of the Si–Si PCF.
major modifications. On the contrary, when $T_r=25,000$ K Si(1) and Si(2) initially form a dimer that undergoes a very quick breaking. Si(2) moves beyond the plane of its neighbor O atoms forming a threefold O with a nearby oxygen site, while Si(1) carries an unpaired DB. This corresponds to a (meta)stable puckering configuration observed in ODCs. From this point on, the evolution of the system follows a pathway similar to the case of the nondefective α-quartz, eventually stabilizing as in Fig. 1d. In the whole system, four stable Si–Si bonds (∼25% of the total number of Si) with average distances ranging from 2.56 to 2.39 Å are formed in the regions where localized excitations induce a Si–O bond breaking and O diffusion. In the process, Si(1) loses its DB by forming a stable bond with one of the diffusing O atoms that, in turn, binds to another nearby Si. No DB survives, as seen by inspecting the electronic and atomic structures, but three-membered rings e.g., close to Si(1) in Fig. 1(d)] and FBs arise. The amount of Si–Si bonds formed around an ODC (25%) is larger than in pristine SiO$_2$ (20%), suggesting that defects promote the formation of Si nano-crystals.

Summarizing, we provided a microscopic picture of the creation of Si–Si bonds in SiO$_2$ upon electron excitation, clarifying the issues of LS/ESS formation and Si/O diffusivities.

The authors acknowledge computer facilities at Tsukuba University and ISSP and support from Special Nanoscience Project-Tsukuba University and ACT-JST Program.