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Molecular dynamics simulation of ultrafast laser ablation of fused silica

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Abstract. Ultrafast laser ablation of fused silica is studied using molecular dynamics simulations. Ionization and generation of free electrons, absorption of the laser energy by free electrons and energy coupling between free electrons and ions are considered. The BKS potential is used to describe molecular interactions and is modified to include the effect of free electrons. Temperature, density, and material removal are computed, and the thermal and non-thermal mechanisms of ultrafast laser ablation of fused silica are discussed.

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1. Introduction

Fused silica is an important material that has been widely used in industry. However, it is very difficult to machine with traditional abrasive tools because of its mechanical and thermal properties. In the recent decades, ultrafast lasers have been used to successfully fabricate wide bandgap dielectrics, including fused silica [1-3]. The machining results are clean, precise and reproducible, which shows that ultrafast laser is capable of microscale fabrication of glass.

The process of "laser ablation" or "dielectric breakdown" is usually involved in ultrafast laser machining of dielectrics. Common dielectric materials are transparent to longer pulse or continue-wave laser beams. However, during ultrafast irradiation, the high intensity of the laser pulse first excites valence electrons in the material to the conduction band via photoionization and avalanche ionization. The excited free electrons will absorb laser energy, and transfer its energy to the lattice, resulting in the temperature rise. When temperature is raised to a certain degree, volumetric phase change and material decomposition will occur. This process is considered as "thermal" ablation because it is caused by the high temperature in the material. On the other hand, because of the free electron generation, Coulomb forces exist among the atoms. This will result in internal repulsive force and may cause separation of the target material, which is the "non-thermal" ablation. Both thermal and non-thermal (Coulomb explosion) ablation processes have been discussed in the literature [e.g., 4].

Recently, molecular dynamics (MD) has shown its potential in the investigation of femtosecond laser ablation [5–7]. MD tracks the motion of each molecule or atom at every time step, so the detailed ablation phenomenon is traced and captured. In this work, MD simulations are performed to study the ablation of fused silica. Interactions among atoms in fused silica are modeled using the BKS potential [8]. Generation of free electrons inside the material and re-combination of free electrons with ions, and energy transfer from free electrons to the lattice are considered. The main goal of this work is to illustrate the ultrafast laser ablation process of fused silica, and to reveal the mechanisms leading to the material's removal.

2. Numerical Approach

2.1 MD model

In MD calculation, all atoms interact with each other via a potential function, and the motion of each atom is governed by the Newtonian motion law. Positions, velocities and forces of all atoms are tracked at each time step, and are used to evaluate macroscopic parameters such as temperature, pressure and density from statistical data processing. The potential function applied in this work to simulate fused silica is the widely-used BKS potential [8] expressed as

$$\Phi_{ij,BKS}(r) = \frac{q_i q_j \varepsilon_0^*}{r} + A_{ij} e^{-b_{ij} r} - \frac{C_{ij}}{r^6} \tag{1}$$

Here, atoms *i* and *j* can be Si or O atom. r is the distance between atoms, and *A*, *b* and *C* are constants with values $A_{Si\text{-}Si} = 0$, $A_{Si\text{-}O} = 18003.8$ eV, $A_{O\text{-}O} = 1388.8$ eV, $b_{Si\text{-}O} = 4.8732$ Å^{-1}, $b_{O\text{-}O} = 2.76$ Å^{-1}, $C_{Si\text{-}Si} = 0$, $C_{Si\text{-}O} = 133.5381$ eV Å^{-6}, and $C_{O\text{-}O} = 175$ eV Å^{-6}. q is the charge of an atom in a SiO_2 molecule as $q_{Si} = +2.4$ and $q_O = -1.2$. ε_0^* is the constant for Coulomb energy calculation with the value 1602.19/(4π8.8542) eV Å. To correct the well-known drawback of BKS potential [9] that the potential energies of Si-O and O-O bonds fall to negative infinity when *r* is small, the original potential is modified by a Lennard-Jones 18-6 term [9]

$$\Phi_{ij,M}(r) = \Phi_{ij,BKS}(r) + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{18} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] \tag{2}$$

2.2 Free electron effect

During femtosecond laser ablation of fused silica, valence electrons in the material will absorb photons in the laser beam and become free electrons in the conduction band. These free electrons have two effects to the ablation process: thermal and non-thermal. For thermal, free electrons absorb laser energy and transfer the energy to the lattice so that the temperature of the material is increased and the phase change occurs. At the same time, the negative changes of free electrons change the force acting on atoms. When free electrons are not generated evenly (particularly in the direction along the laser propagation direction), they form an electronic field. These effects may influence the material's removal process and need to be considered in the MD simulation.

The processes of laser energy absorption and generation of free electrons are calculated by solving a 2D axisymmetric wave propagation equation coupled with a rate equation of free electron generation [10]. The transient distributions of absorbed laser energy and free electron density obtained from that calculation are used in this work. Due to the generation of free electrons, the net charge of the Si and O atoms in a SiO_2 molecule is changed, modifying the Coulomb interaction among atoms. To account for this modification, in the first term in the BKS potential (Equation 1), the q value of the Si atom is changed from +2.4 to +2.8, while that for the two O atoms is changed from -1.2 to -0.9. These values are chosen so that the summary of the change of the SiO_2 molecule becomes +1, corresponding to the unit positive charge due to the absence of a free electron. The number of free electrons and the number of SiO_2 molecules whose potentials need to be modified with respect to depth and time are obtained from the wave equation calculation and are randomly distributed into the x-y plane (the plane perpendicular to the laser propagation direction) of the MD computational domain.

Since free electrons are not distributed evenly along the laser propagation direction, they form an electronic field which exerts an extra force to all charged particles (atoms or ions). This extra force can be estimated by adding up the electrostatic force vectors from all electrons, and is calculated as:

$$Fc = 2e^2 q_A \left(\sum_{k>k_A} \frac{n_k}{r_k} - \sum_{k<k_A} \frac{n_k}{r_k}\right) \tag{4}$$

where q_A is the charge of the particle, k is the index of the structure layer, n_k is the number of free electrons in layer k, and r_k is the distance of the particle from the center of layer k. k_A is the structure layer where particle A is located. Recombinations between free electrons and ions are considered as decaying exponentially with time, with a time constant of 5 ps. After recombination, q values are changed back to

the normal values (from +2.8 to +2.4 for Si atoms and from -0.9 to -1.2 for O atoms). Accordingly, the energy in free electrons is transferred to the lattice with a time constant of 5 ps.

3. Results and discussions

In this work, the initial thickness of the target is 198 nm, while the lateral dimension is 3.42 nm x 3.42 nm together with periodic boundary conditions. The laser beam has a uniform spatial distribution and a temporal Gaussian distribution of 100 fs FWHM centered at 10 ps. The wavelength is 800 nm. The absorption depth of the laser pulse in fused silica is assumed to be 300 nm. Before laser heating, the material is first equilibrated at 300 K.

First, the snapshots of the target at different time steps are shown in Figure 1. Each Si or O atom is represented by a black dot. The laser beam is incident perpendicularly onto the right surface. The bottom of the target is always located at x = 0 nm. The absorbed fluence is calculated as 0.5241 J/cm^2 from Reference [10]. Note that the scale in the *x* direction is 3 times smaller than that in the other direction so that a bigger length can be shown. It is seen that at 110 ps, a void occurs at *x* = 141 nm, about 95 nm below the surface. This void grows larger at later time steps and separates the material into two parts. The surface part on the right is ejected at a speed of about 600 m/s, causing the material ablation. Materials separation under the surface has been seen in laser ablation of other materials such as metal [11] due to a combination of thermal and thermomechanical effect, although here the electronic effect also plays a role as will be shown below.

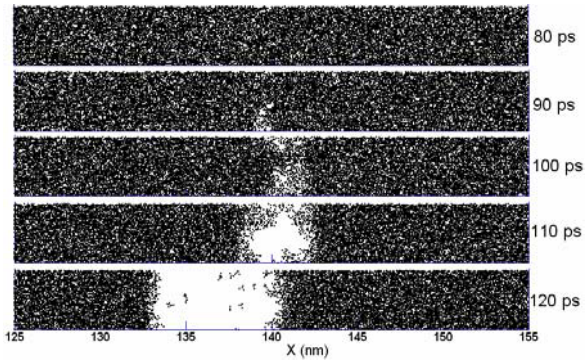
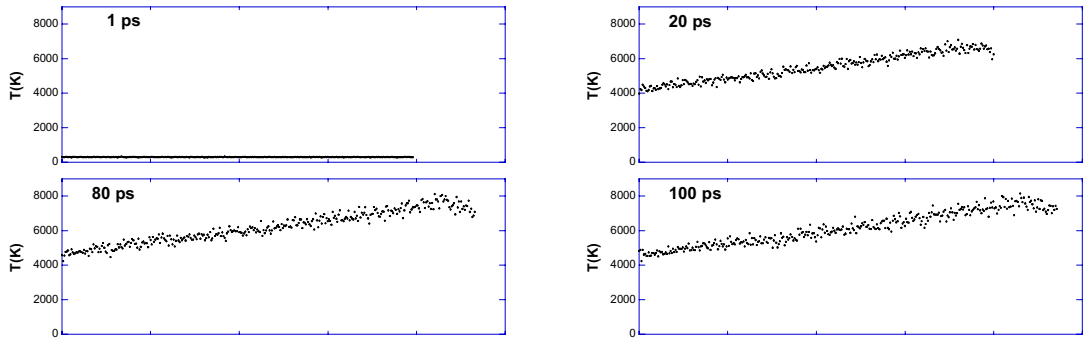


Figure 1. Snapshots of material. Laser energy: 0.5 μJ.

The temperature distributions at different time steps are shown in Figure 2. The fluctuation of temperature at the location around 140 nm at 120 and 160 ps is due to the existence of the void demonstrated in Figure 1.



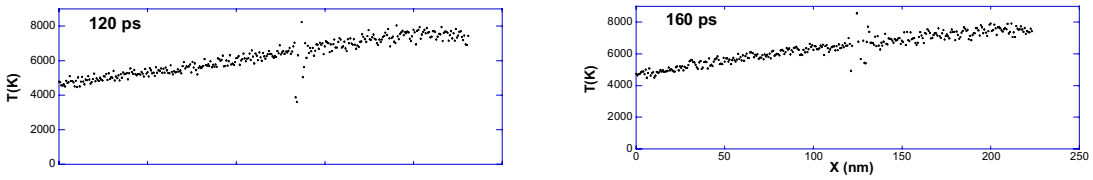


Figure 2. Temperature distributions.

To further reveal the mechanism of the void generation and ablation shown in Figure 1, a related calculation is performed where free electron effects are excluded. Specifically, the generation and recombination of free electrons are *not* considered, which means all atoms do not change their q values in their potentials, and the extra force from electron density gradient expressed in Equation 4 is not applied. The incident and absorbed laser fluences are the same as in the previous case. Results of snapshots of the atomic distribution at different time steps are shown in Figure 3.

The most significant difference between Figure 1 and Figure 3 is that a void is generated when the free electron effect is considered; while no void is seen when free electron effects are excluded. Further, we can compare the temperature distribution for these two cases: the temperature distributions at two time steps are shown in Figure 4. It is seen that the temperature distributions are almost the same regardless of the free electron effect. Therefore, it can be concluded that the free electron effects play a significant role in material's separation. Generation of free electrons changes the net charge carried by Si and O atoms in fused silica, causing repulsive Coulomb force between them. This additional repulsive interaction contributes to the separation of the material which is heated by the laser beam.

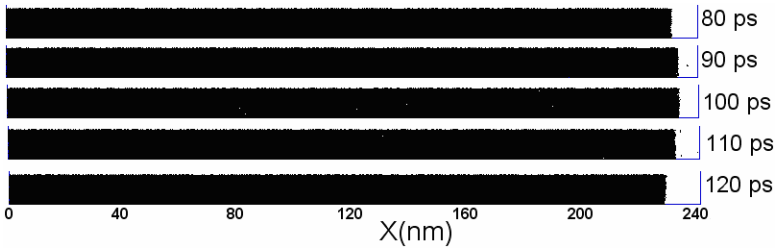


Figure 3. Snapshots of material. 0.5 μJ, no electron effect considered.

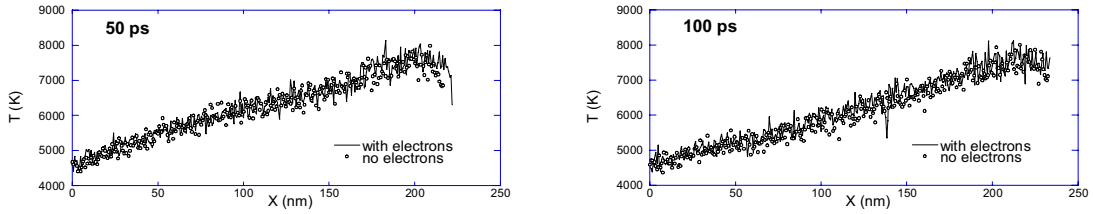


Figure 4. Comparison of temperature distribution with and without considering the free electron effects.

The above computations and discussions focus on a laser fluence (4.5 J/cm^2) that is found to be right above the ablation threshold from experiments [10, 12]. More analyses on laser ablation at higher fluences are being conducted in order to obtain a more complete picture of ultrafast laser ablation of fused silica.

4. Conclusion

Femtosecond laser ablation of fused silica is simulated using the molecular dynamics technique, with the consideration of free electron generation and recombination. The electrostatic force caused by free electrons is considered in MD calculations, and is found to play an important role in material's separation.

From calculation results, the non-thermal (Coulomb) effect is clearly shown for a laser fluence right above the ablation threshold.

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