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Molecular dynamics simulation of ultrafast laser ablation of fused silica film

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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 applied and modified to describe molecular interactions and the effect of free electrons. Smooth particle mesh of the Ewald method (SPME) is adopted to calculate the Coulomb force. It is found that the electrostatic Coulomb force, which is caused by the ionization, plays an important role in the laser ablation process.

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1 Introduction

In recent decades, ultrafast lasers have been used successfully to machine fused silica, demonstrating its capability for microscale fabrication. The high intensity laser pulses first excite valence electrons to the conduction band via photoionization and avalanche ionization. The excited free electrons further absorb laser energy, and transfer their energy to ions, resulting in the temperature rise. Because of the free electron generation, Coulomb forces exist among the atoms. Both the thermal and non-thermal (Coulomb explosion) ablation processes have been discussed in the literature [1]. This work applies molecular dynamics technique to study the interaction between ultrafast laser pulses and fused silica and the resulting ablation. The main goal of this study is to investigate the ultrafast laser ablation process of fused silica, and to reveal the mechanisms leading to the material's removal. Laser heating and material removal processes are simulated. The ionization of the material and the energy coupling between the laser beam and free electrons and ions are considered. Thermal expansion and material removal are shown, and the thermal and non-thermal mechanisms of fused silica ablation are discussed based on the calculation results.

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2 Numerical approach

In MD calculation, all atoms interact with each other via a given potential function, and the motion of each atom is governed by the Newtonian motion law. The MD simulation has been used successfully to compute many laser ablation problems (e.g., [2, 3]). The potential function applied in this work to simulate fused silica is the widely-used BKS potential for fused silica [4] expressed as

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

Here, atoms i and j can be Si or O atoms, r is the distance between atoms, and A, b, and C are constants for different bond types, q is the charge of an atom in a SiO_2 molecule as $q_{\mathrm{Si}} = +2.4$ and $q_{\mathrm{O}} = -1.2$. ε_0^* is the constant for Coulomb energy calculation. To correct the well-known drawback of BKS potential, the original potential is modified by a Lennard-Jones 18-6 term [5]

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

Because of the slow convergence of the Coulomb term (the first term in (1)), *Smooth Particle Mesh of the Ewald method (SPME)* [6–8] is applied to compute the Coulomb term efficiently.

The high intensity of femtosecond laser pulses produces free electrons from the valence band. These free electrons have three effects: (1) the thermal effect: free electrons absorb laser energy and transfer the energy to ions so that the temperature of the material is increased and the phase change occurs, (2) the non-thermal effect: 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. Specifically, in our approach, the first term in the BKS potential (see (1)), the q value is changed from +2.4 to +2.8, and from −1.2 to −0.9 for the Si and O atom, respectively. This is to make sure that the total charge of the molecule becomes "+1". There are other ways of making the total charge "+1", and this calculation can be considered as an initial attempt. (3) When the generated free electrons have an uneven distribution along the direction of laser propagation, they form an electronic field which exerts an extra force on ions. This extra force can be estimated by adding up the electrostatic force vectors from all electrons, and is calculated as:

$$Fc = 2\varepsilon_0^* e q_\mathrm{A}\left(\sum_{k>k_\mathrm{A}} \frac{n_k}{r_k} - \sum_{k<k_\mathrm{A}} \frac{n_k}{r_k}\right), \quad (3)$$

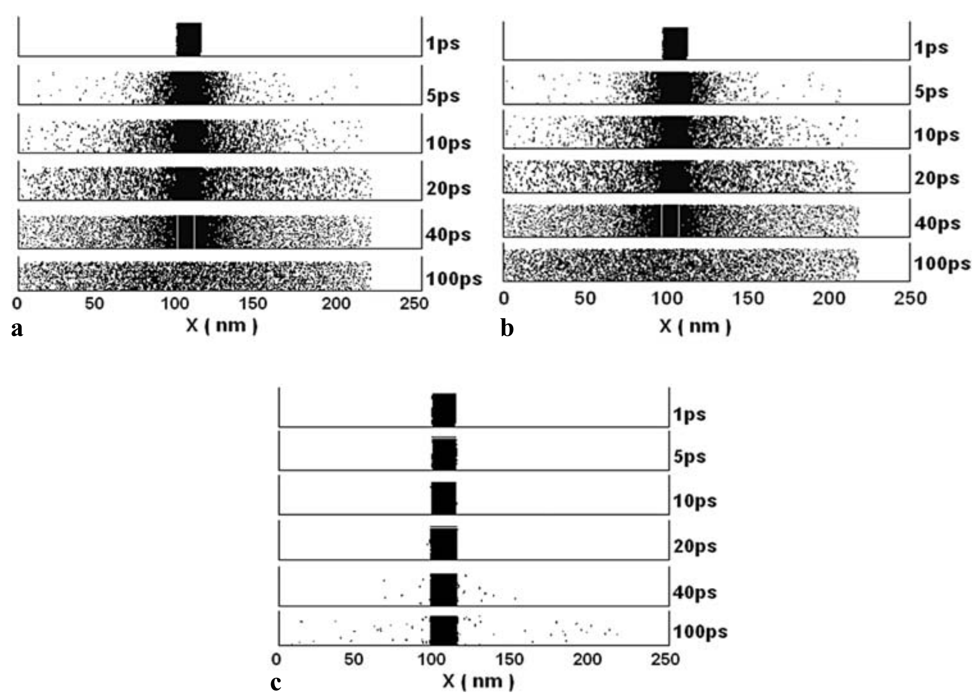
where ε_0^* is defined as in (1), q_A is the charge of the ion, k is the index of structure layer, r_k is the distance between the ion and the center of layer k, and n_k is the number density of free electrons in layer k.

The transient distributions of absorbed laser energy and free electron density are obtained by solving a wave propagation equation coupled with a rate equation of free electron generation [9]. 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 also obtained from the wave equation calculation [9] and are randomly distributed into the y–z plane (the plane perpendicular to the laser propagation direction) of the MD computational domain. Collisions between free electrons and ions result in transfer of energy from electrons to the ions. In this study, a time constant of 5 ps is used. We also assume the same time constant of 5 ps for recombination, i.e., for q values changed back to the values in a neutral molecule.

3 Results and discussions

MD calculations are first performed to obtain the equilibrium amorphous structure of fused silica at 300 K through a so-called "quenching" procedure [10]. The structure of the

Fig. 1 Snapshots of material at different time steps: (**a**) electrons stay in the sample, (**b**) electrons go out of sample, (**c**) no ionization



obtained fused silica is analyzed and agrees well with that reported in the literature [11]. A thin film of fused silica is considered. The initial thickness of the target is 16.8 nm, while the lateral dimension is 4.2 nm × 4.2 nm with periodic boundary conditions. The top and bottom surfaces are subject to free boundary conditions. The laser beam has a uniform spatial distribution and a temporal Gaussian distribution of 100 fs FWHM centered at 1.1 ps. The wavelength is 800 nm. Both the pulse width and the wavelength are chosen to be close to the values of the commonly used Ti:sapphire femtosecond laser. (Because the film studied here is thin, the phase change process is entirely volumetric. Therefore, the term "ablation" used here is different from the traditional meaning of ablation which is commonly used to describe material removal from a target surface.)

Figure 1 displays the snapshots of the target at different time. The incident laser fluence is 4.5 $\mathrm{J/cm^2}$, and the absorbed fluence is calculated as 0.055 $\mathrm{J/cm^2}$ (the majority of laser energy absorption is due to free electrons generated by multi-photon ionization) [9]. The laser pulse irradiates the target from the right. Ionization happens just after the peak of the laser pulse and the Si, O atoms change their charge values. Once the electrons are generated, free electrons either stay inside the target, or leave the target. The percentage of electrons leaving the target is unknown. In our calculation, we compute the two extreme cases, i.e., either the electrons all stay in the target or all leave the target. Also, for comparison, we compute the case that no ionization is considered, in which same amount of energy is deposited into the system through velocity scaling. This is done artificially for the purpose of this paper.

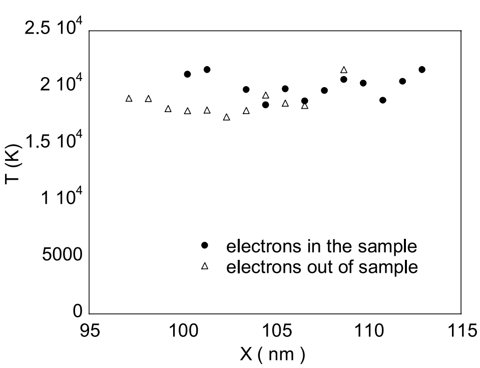


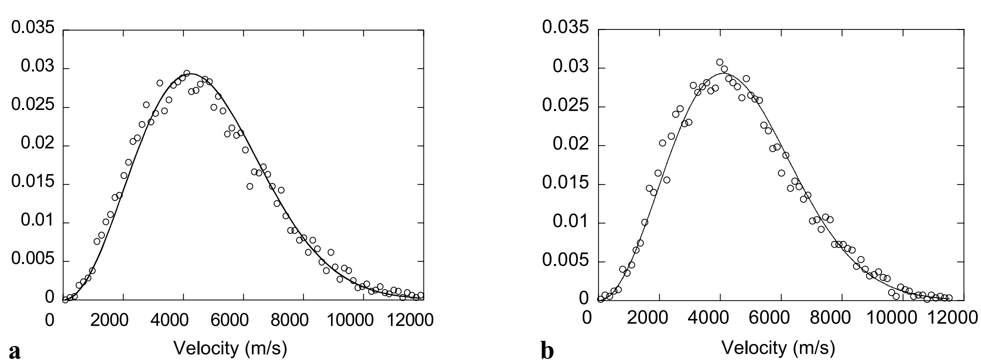
Fig. 2 Temperature distributions in the fused silica film at 40 ps

In the first case as shown in Fig. 1a, the produced free electrons stay in the sample, which give an extra Coulomb force (Fc in (3)) in addition to the static force described by (2). Strong ablation can be seen at about 5 ps and the material continues to expand. For the second case (Fig. 1b), the free electrons all leave the material after they are generated. There is no extra Coulomb force (Fc in (3)) in the system. It is seen that the snap shots of the molecular distribution are similar to what is shown in the first case. This is because the electrons are generated quite uniformly inside the thin fused silica film (a 7% difference of free electron density between the top and the bottom of the thin film), and perhaps the ablation is influenced more by the changes in the charges in Si and O. The forces caused by this difference could be small compared with other Coulomb terms in (2). More analyses are being performed to clarify this point. Figure 1c shows the result when no ionization is considered. All atoms do not change their q values in their potentials. No ablation but only small thermal expansion is seen.

In Fig. 2, the temperature distributions in the fused silica film at 40 ps (only for the central parts between gray lines in Fig. 1a and b) are shown, considering both electrons staying in and leaving the material. The two cases have similar temperature distributions. It is noted that temperatures of the material can still be defined. This can be seen by the Maxwellian velocity distribution shown in Fig. 3 (mass center velocity removed). In fact, the temperatures shown in Fig. 2 are found by Maxwellian fitting.

The most significant result from the calculations is that there is no strong ablation without the free electrons effect. Therefore, it can be concluded that the free electron effects play a significant role in material's removal. The threshold laser fluencies for ablation is 4.14 $\mathrm{J/cm^2}$ (absorbed fluence 0.03 $\mathrm{J/cm^2}$) when the free electron effect is considered. If the electron effect is not considered, strong ablation is only observed when the laser influence is higher than 5.4 $\mathrm{J/cm^2}$. Figure 4 shows the snapshots of the molecular distributions

Fig. 3 Velocity distribution and Maxwellian fitting for (**a**) electrons staying in the sample, (**b**) electrons going out of the sample (only for the central parts between gray lines in Fig. 1a and b)



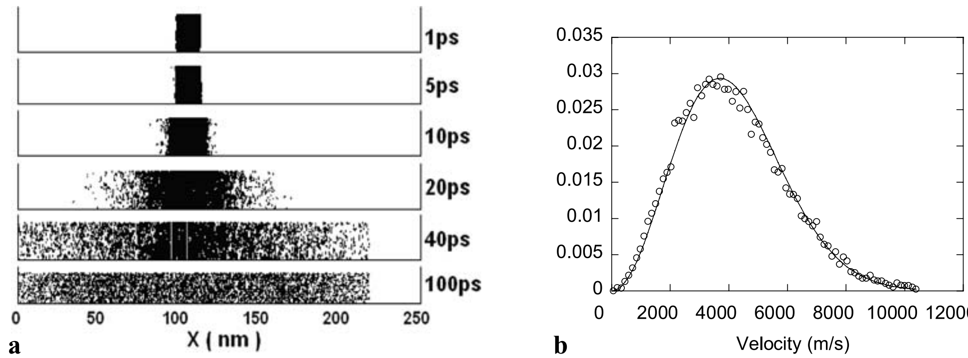


Fig. 4 (**a**) Snapshots and (**b**) velocity distribution at a laser fluence 5.4 J/cm^2 when no ionization is considered (only for the region between *gray lines*)

at a laser fluence of 5.4 J/cm^2 (absorbed fluence 0.1 J/cm^2). The temperature at 40 ps is about 16,000 K, as shown in Fig. 4b (mass center velocity removed).

4 Conclusion

In conclusion, ultrafast laser ablation of fused silica is simulated using the molecular dynamics technique. 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 smooth particle mesh of the Ewald method (SPME) is adopted to calculate the electrostatic Coulomb force, which is found to play an important role in material's ablation.

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