Swift heavy ion track formation in nanoporous Si: Wave packet molecular dynamics study

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Abstract. In this article we study the process of silicon relaxation after swift heavy ion (SHI) irradiation using first-principles-based electron force field eFF. We show that early stages of so-called nonthermal melting take place in the nanometric vicinity of SHI trajectory in both bulk Si and Si nanolayer, but result in structural modifications only for the last one. Our results shed light on recent experimental evidence of significant reduction of threshold for SHI-induced damage creation in nanoporous Si.

1. Introduction

Silicon is known to be resistant to single-ion swift heavy ion (SHI) irradiation. Only with C⁶₀ ions threshold value of the stopping power \( S_{\text{thres}} \approx 32 \text{ keV/nm} \) for damage formation was obtained [1]. Its resistance is usually explained by the fast hot-carrier diffusion that results in energy leakage from the SHI-trajectory zone and fast decreasing of \( T_e \) on the timescale of tens of fs, whereas electron–ion relaxation lies in picosecond timescale. Due to the high speed of relaxation processes in electron subsystem, ion lattice maintain its unperturbed structure. More distinct picture of this phenomenon is observed in metals, where conducting electrons are highly mobile, which makes most metals resistant to SHIs in electronic regime.

Recently it was found that, in contrast to the bulk Si, nanoporous crystalline silicon (PSi) could be easily amorphized with the threshold for damage creation \( S_{\text{thres}} \approx 3 \text{ keV/nm} \) [2], which is approximately one order lower than that for the bulk Si. Porosity of experimental samples was 56 and 75%. Modification of Si under the SHI-irradiation was also observed in nanolayered Ni–Si structures [3].

This situation with significant decreasing of \( S_{\text{thres}} \) for PSi still does not have appropriate explanation. In [4] it is assumed that low PSi electrical conductivity could play a major role localizing deposited energy. Here we question this hypothesis proposing a more detailed and sophisticated picture of the damage formation in nanoporous Si, based on the concept of nonthermal melting and subsequent fast expansion of material in a vicinity of a free surface.

Modeling of SHI-induced damage formation is a very complicated and nontrivial task, requiring description (at least qualitative) of the atomistic structure of material, its basic mechanical properties and nonadiabatic electron dynamics within a single framework. The last one (i.e. electron dynamics) is the most crucial during the first several hundred femtoseconds
Figure 1. (a) Atomistic structure of crystalline Si: grey spheres represent ions; red—electrons. (b) Radial distribution of energy per electron deposited around the path of SHI for ion with electron stopping power $S_e = 10$ keV/nm.

and includes such processes as electron–electron relaxation, scattering of fast electrons on ions, secondary ionization and cascading, covalent bond weakening due to electron excitations, Auger recombination. In case of porous Si it is also desirable to describe electron emission from the surface. In this article we study the process of silicon relaxation after swift heavy ion (SHI) irradiation using first-principles-based electron force field (eFF [5]). It was previously successfully applied to model non-adiabatic processes in Si [6], showing good agreement with experimental data on both mechanical (elastic modulus, yield strength) and quantum (potential of ionization, bond energy) properties. All calculations were performed using LAMMPS package.

2. Model and calculation method

The eFF potential is based on the model of wave-packet molecular dynamics (WPMD), which provides the combination of particle dynamics for ions with wave packet dynamics for electrons representing them as floating Gaussians. Unlike the more complex antisymmetrized approach [7–9], interactions between electrons in the eFF model are restricted to pairwise components only and the total energy of the system is evaluated as in classical force field methods. This simplification makes eFF model much more computationally efficient than traditional ab initio approaches and capable to perform computations of nm-size systems within reasonable time.

To accelerate calculations we use the effective core potential (ECP) modification of eFF: every Si atom is represented by a Si$^{4+}$ ion and four electrons, while ten core electrons are considered implicitly using pseudo-potential. It allows increasing the integration timestep significantly (from 0.0001 fs in all-electron representation to 0.002 fs for the ECP representation) and reducing the total number of particles in the system. The parameterization of electron-core interactions is based on DFT calculations. eFF ECP model for Si was previously applied to the case of electron excitation and emission in Si crystal under mechanical strain and fracturing [6].

The detailed description of ECP eFF validation for Si is presented in supplementary materials of paper [6].
3. Results and discussions

Depending on the amount of energy (e.g. the laser power or electron stopping power $S_e$ of SHI) deposited into the electron subsystem there can occur two scenarios of lattice melting in covalently-bonded semiconductors: so-called thermal and non-thermal melting. Thermal regime is characterized by direct transfer of energy from excited electrons to ions via the process of electron–ion relaxation, which takes place on picosecond timescales. Non-thermal regime occurs when excited electrons are transferred from the valence to the conduction band, changing the potential energy surface between atoms and reducing the energy of bonding interactions between them, which leads to a fast atomic relocation. Nonthermal melting requires higher levels of deposited energy and typically takes place on the timescale of several hundred femtoseconds [10]—much faster than the thermal melting.

To check the capabilities of eFF we first demonstrate the transition from thermal to nonthermal melting in Si by changing the dose of deposited energy. From the computational point of view, the early subpicosecond stages of material relaxation after SHI bombardment (in electronic regime) and after ultrafast fs-laser irradiation represent very similar tasks for modeling. The main difference is that SHI deposits energy in a nm-size cylinder along its trajectory, while after laser irradiation energy is spread over much larger zone. Also, lasers typically excite electrons from a particular energy level, while SHI interaction is less specific in this way.

Results from the next chapter therefore could also be applied in the analysis of femtosecond laser-induced Si melting, highly discussed in literature [11].

3.1. Two regimes: thermal vs nonthermal

To show the transition between thermal and nonthermal regimes and—more importantly—the ability of eFF to describe both of these processes we start with several tests. The cubic unit cell with size $21.7 \times 21.7 \times 21.7$ Å$^3$ shown in figure 1(a) contains 512 atoms (512 ions and 2048 electrons). The lattice constant of cubic diamond lattice was equal to 5.4 Å. During the
heating stage, that lasts for 25 fs, electron velocities are gradually rescaled increasing electron non-translational kinetic energy. Heating was performed isotropically without any artificial gradients inside the unit cell. The energy input from the SHI was modeled by setting the initial electron temperature profile $T_e = \text{Dose}(r)/k_B$ (where $r$ is the radial coordinate, $k_B$ is the Boltzmann constant), which was calculated using the Waligorski et al model [12], figure 1(b). In figure 2, the evolution of electron and ion temperatures for different doses of the deposited energy is shown.

One can see that in the case of nonthermal melting there is no direct transfer between electron kinetic energy and ion kinetic energy, figure 2(a): on 100 fs timescale $T_e$ is nearly constant, while $T_{\text{mi}}$ increases rapidly. Therefore, this process could not be directly associated with electron–phonon coupling. Instead, ions gain their velocity during rearrangement within a new sufficiently perturbed atomic potential energy surface (which was changed due to the excitation of electrons). The picture resembles much one shown in [10]. The insets show lattice structure at corresponding time. On the contrary, thermal melting shows much slower $T_i$ increase, figure 2(b).

3.2. Dissipation of energy due to electron–electron relaxation

Next we compare relaxation processes after SHI-irradiation in both bulk Si and Si nanolayer. For the bulk sample values of electron stopping powers $S_e = 15$ and 24 keV/nm were examined, and $S_e = 15$ keV/nm for Si nanolayer. Geometrical parameters of the computational cell were as followed: $13 \times 13 \times 2.2$ nm$^3$ with 3D periodic boundary conditions (PBC) for bulk Si and $13 \times 13 \times 7$ nm$^3$ for Si 2.2-nm-thick nanolayer without periodicity along $z$ direction (nanolayer
Figure 4. Thermograms of energy dissipation within electron subsystem ($T_e$) for 2.2-nm-thick Si layer (a) and bulk Si (b).

was surrounded by 2.4-nm-thick vacuum layers on each side along $z$ direction. Simulations were carried out with the SHI trajectory directed along the [1 0 0] direction of the Si crystalline lattice. To imitate the energy radial flow from the irradiated area to the bulk crystal in PBC, temperature $T = 300$ K was kept in 2-nm layers on the side surfaces which were parallel to $z$ direction using Nose–Hoover thermostat, while in the central part which had size $9 \times 9 \times 2.2 \text{ nm}^3$ microcanonical ($NVE$) ensemble was set.

First we give brief overview of the processes appear in the bulk Si during the first picoseconds after SHI-irradiation with sufficiently high $S_e = 24 \text{ keV/nm}$, figure 3(a). At $t = 5$ fs, figure 3(b), all of the deposited energy is accumulated in the electron subsystem, which leads to electron excitations and covalent bond breaking within approximately 2.5 nm radius around the SHI trajectory. As the deposited energy flows out of the irradiated zone and electron temperature decreases, atoms tend to return back (into the non-excited state) recovering bond structure in the outer region of the irradiated zone, figure 3(c). Nevertheless, if $T_e$ stays high long enough (e.g. in the central part of the cell), ion lattice undergoes rapid disordering and its density decreases (nonthermal melting is known to cause a volume expansion in Si [10]). One can also see elastic deformation of the crystal lattice around the heated zone due to its expansion. At $t = 600$ fs
low-density zone collapses to its initial density, figure 3(d), and the process of recrystallization starts.

In figure 4 thermograms representing energy dissipation within electron subsystem for bulk Si and Si nanolayer at $S_e = 15$ keV/nm are shown. In both cases the dynamics of electron subsystem relaxation is nearly identical: $T_e$ drops to the levels of 20000–3000 K within 50 fs. This relaxation time is not sufficiently large to increase $T_i$ significantly, figure 5(b), and to cause damage formation in the ion lattice for the bulk sample. Different situation is observed for the Si nanolayer: central region of the simulation cell undergoes fast heating during the nonthermal melting stage, figure 5(a).

Properties of matter with high $T_e$ differ much from that with unperturbed electron subsystem [13, 14]. Silicon in the central part stays with still high $T_e$ [15] and, as a consequence, high electronic pressure $P_e$ [16]—so-called warm dense matter (WDM). In the case of the bulk Si this jump of the pressure results in the generation of phonons, which are then completely absorbed by the crystal lattice around the track. General parameters of this process were discussed in [17]. But in the case of PSi fast ions do not experience any resistance toward their movement in the $z$ direction. At high levels of $S_e$ it even results in material ejection (figure 6).

\[\text{Figure 5. Thermograms of heating of ion lattice ($T_i$) for 2.2-nm-thick Si layer (a) and bulk Si (b).}\]
Figure 6. Si layer 250 fs after $S_e = 15$ keV/nm energy deposition.

It should be additionally clarified why SHIs do not modify the surface of bulk crystal through the process discussed above, but easily modify one in nanoporous. The peak level of energy deposition (i.e. highest values of electron stopping power $S_e$) is usually reached in the depth starting from 100 nm, when SHI becomes sufficiently ionized, while in the surface layer $S_e$ is much lower than its maximum value in the bulk. In the case of nanoporous Si SHI can interact with the surfaces of pores in the depth of the material being already highly ionized and depositing peak levels of energy into the electron subsystem along its trajectory.

4. Conclusions
In order to analyze the process of SHI-irradiation of nanoporous silicon we have performed WPMD calculations of electron–electron and electron–ion relaxation in Si using eFF potential. Our results show that electron subsystem relaxation has similar time characteristics in both bulk and nanolayer systems, despite the difference in geometry. In both cases system undergoes sharp increase of electronic pressure and covalent bond weakening in the vicinity of the SHI trajectory. But in bulk Si the possibility of subsequent lattice rearrangement and expansion is prevented due to stabilization by surrounding material. On the contrary, in PSi material ejection from the open surfaces and lattice disordering is observed well below the bulk damage threshold. Our results clarify the experimental data obtained in [2] for SHI-irradiated nanoporous Si, showing that the actual reason of material modification is related to the complex combination of such effects as nonthermal melting and jump of electron pressure.

Acknowledgments
The present work is supported by grant No. 14-50-00124 from the Russian Science Foundation. The authors acknowledge the Supercomputer Centre of JIHT RAS for providing computing time.

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