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Molecular Dynamics simulations of the formation and crystallization of amorphous Si

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ABSTRACT

Encouraged by the good performance of the MEAM-L potential for Si in Molecular Dynamics simulations of 500 eV Ar bombardment of Si (0 0 1) surface [M. Timonova, B-J. Lee, B.J. Thijsse, Nucl. Instrum. Methods B 225 (2007) 195], we continue to investigate the amorphous phase formed during this bombardment and compare it with the amorphous phase formed in the same way using the Stillinger–Weber potential [F.H. Stillinger, T.A. Weber, Phys. Rev. B 31 (1985) 5262] and with the amorphous phase produced by high-energy ion self-implantation experiments [K. Laaziri, et al., Phys. Rev. B 60, (1999) 13520]. By submitting the computational amorphous phases to high-temperature treatments we follow the kinetics of the crystallization process. The purpose of the study is to analyze the amorphous structure, to identify the atomistic details of relaxation and crystallization dynamics, and to validate the potentials.

1. Introduction

Silicon is one of the most used materials in the modern technological world. The ability to model Si on different scales improves our understanding of its properties and helps in developing new technologies based on Si. For semiconductors, the covalent type of bonding makes a realistic description of many important phenomena at the atomic scale difficult, at least more difficult than, for example, for metals. Many classical potentials have been developed for atomic interaction in silicon. Very popular are the Stillinger–Weber (SW) [1] and Tersoff (T3) [2] potentials. In a previous paper [3] we have reported on the performance of a new Modified Embedded Atom Method potential, indicated as MEAM-L, in describing properties of crystalline, liquid and amorphous Si phases. It was shown that the MEAM-L potential describes various fundamental physical properties of the crystal and some molecules better that many other empirical potentials. Elastic and structural properties of the crystal, energies of point defects and the (0 0 1) surface, and thermal expansion calculated using MEAM-L are in good agreement with *ab initio* calculations or experimental values. The melting temperature is an exception. Liquid silicon is also well described and its properties are quite comparable with the experiment [4]. However, it was not clear if MEAM-L is superior to SW in describing the amorphous phase, since the amorphous structure depends on the formation process, and an accurate description therefore requires realistic simulations that can reproduce experimental conditions of amorphous phase formation.

Our earlier Molecular Dynamic (MD) simulations of sputter erosion of Si (0 0 1) by 500 eV Ar ions have shown that with the MEAM-L potential the steady state sputter yield is close to the experimental value and the dimer/monomer ejection ratio has a reasonable magnitude [5]. This steady state is reached at Ar fluence (dose) of 1.33×10^{15} cm^{-2}. These were important results, since they showed that the MEAM-L potential acts reliably under conditions, where silicon atoms have locally different geometries than in the diamond cubic (dc) crystal structure, and, where a substantial range of interaction energies are probed. One of the points of this simulation was that the amorphous phase at the surface of the system was formed in a similar way as in an amorphization experiment by Si self-implantation [6]. Apart from differences in the energy and flux of the incident ions, a direct comparison of the results would therefore be interesting, as both in the experiment and in the simulation amorphization is accomplished by ballistic mixing processes rather than by rapid quenching of the liquid. Earlier, the simulation of sputter erosion was performed using the SW potential [7], so a comparison of the abilities of the MEAM-L and SW potentials to produce a realistic amorphous phase is now also possible. An advantage of the simulation of amorphization by sputter erosion is that the amorphous phase formed at the surface during bombardment is in a natural contact with the crystal phase, i.e., without a constructed or forced interface. This is a good starting point for high-temperature recrystallization studies using the MEAM-L and SW potentials.

In this paper we present results of amorphization simulations of Si (0 0 1) by 500 eV Ar sputter erosion using the two different

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potentials, MEAM-L and SW. We compare the amorphous phases produced by the two potentials with each other and with the amorphous phase generated by high-energy ion self-implantation experiments. By submitting the computational amorphous phases to high-temperature treatments we following the kinetics of the crystallization process. The purpose of the study is to analyze the amorphous structure, to identify the atomistic details of relaxation and crystallization dynamics, and to validate the potentials.

This article is organized as the follows. Computational details are given in Section 2, and a brief summary of the results for 500 eV Ar sputter erosion using the MEAM-L and SW potentials is presented in Section 3.1. The properties of the amorphous phases produced by the MEAM-L (Sections 3.2 and 3.3) and SW (Section 3.4) potentials are presented, discussed, and compared with experiment. Finally, in Section 4 we show results of the high temperature annealing, leading to crystallization of the amorphous phase.

2. Computational details

Si–Si interactions are described by either the recently developed MEAM-L potential [3] or the SW potential [1]. The Firsov–Molière pair potential [11] is used for Ar–Ar and Si–Ar at all distances and for Si–Si at short distances.

MD simulations of the sputtering of the Si crystal were performed for 500 eV Ar bombardment at room temperature. The initial silicon target of 27,000 atoms had a Si (0 0 1) surface area of 81 Å × 81 Å, and contained 60 monolayers (ML) of Si (thickness 81 Å), of which the lowest 2 ML were harmonically bound to their crystal locations. The simulations were performed at constant volume and with automatic time step adjustment (limiting the largest atomic displacement in each iteration step to 0.02 Å). The overall temperature of the system was controlled using Berendsen damped velocity scaling with a time constant of 18 fs, applied to all atoms that interact with other atoms. Periodic boundary conditions were applied only in the two directions that are parallel to the surface.

The surface plane became fully dimerized almost immediately after bringing the simulation to room temperature. Every 7 ps a new Ar atom was introduced from a randomly chosen location above the surface area and directed with 500 eV energy towards the surface, at a polar angle of 45° and an azimuthal angle of 0° with respect to the [1 0 0] direction. In the MEAM-L simulation the temperature control was switched off during the first half of the time interval between Ar atom impacts (3.5 ps). This guarantees that the heat cascade can develop naturally by phonon diffusion, defect creation, and projectile ejection. During the second half of the time interval, the temperature of the system was controlled at 300 K by scaling velocities in all MD time steps. In the SW simulation a slightly different thermostat mechanism was applied. Here velocity scaling towards 300 K was not suspended for fixed time intervals but was suspended for as long as the velocity distribution of the atoms in the system was noticeably non-Maxwellian. An Ar arrival period of 7 ps implies a flux of 2.13×10^{23} cm^{-2} s^{-1}. Such a high Ar flux was chosen in order to finish the simulation in a feasible amount of time. As will be shown later, this choice is justified, as the system has a negligible tendency to relax at 300 K (Section 3.3), so that a longer time interval between Ar impacts would not have led to substantially different results.

The product of Ar sputtering is, apart from ejection of Si atoms and Si_2 dimer molecules, an amorphous Si phase formed at the top of the eroding surface of the crystal. We study its recrystallization of during annealing at different temperatures.

3. Results of 500 eV Ar sputtering of Si

3.1. Sputtering

Ar beam sputtering involves particle removal, incorporation of Ar atoms under the surface, and amorphization at the surface. Side snap-shots of the systems at the end of bombardment are presented in Fig. 1a and b. For the MEAM-L potential, the system is shown after 7.2 ns of bombardment (4 ML removed) [5] and for the SW potential after 21.3 ns (9.7 ML removed) [7]. We will call these the "sputtered systems".

In Table 1 the two potentials are compared after sputter removal of the same number of monolayers (4 ML). For the MEAM-L potential, after 7.2 ns of bombardment the Ar fluence was 1.53×10^{15} cm^{-2} and the average sputter yield 1.78 (Table 1), close to the experimental value 1.63 [8]. In the SW simulation, after 8.4 ns, the Ar fluence was 1.79×10^{15} cm^{-2} and the average sputter yield 1.52, also not far from the experimental value. Table 1 also shows the average ratio of the sputtered Si_2 dimers and Si_1 monomers. The SW potential produced a low dimer yield (only 4.5% of the monomer yield). The MEAM-L potential gave rise to a somewhat higher yield ratio (14.5%), which is probably a more reasonable value. The exact comparison with SIMS experiments is difficult here, because of the unknown ionization probabilities. More details about the simulations can be found in Refs. [5,7]. As a conclusion, both potentials perform well in predicting the sputter yield. As we will see in the following, the structures and properties of the MEAM-L and SW amorphous phases are in some ways different.

3.2. Sputtered system using the MEAM-L potential

Local density properties of the sputtered MEAM-L system versus *z*-coordinate (height) are shown in Fig. 2a. At the moment

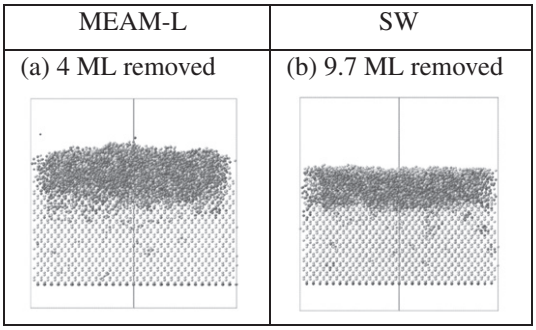

Fig. 1. (1 1 0) side views of the (0 0 1) oriented Si crystal, with free top surface and constrained bottom surface, after (a) Four monolayer sputter removal modeled by the MEAM-L potential, and (b) 9.7 monolayer Ar sputter removal modeled by the SW potential. The argon bombardment energy and flux are 500 eV and 2.13×10^{23} cm^{-2} s^{-1}. Bombardment times are 7.2 ns for MEAM-L and 21.3 ns for SW. The term "sputtered system" is used for either of the configurations shown. The *z*-direction points upward.

Table 1
Simulation results of 500 eV Ar sputtering of Si (0 0 1) at 45° incidence after 4 ML silicon removal modeled with the MEAM-L and SW potentials. The average sputter yield covers the entire 0-4 ML sputtering period.

	MEAM-L	SW
Incident Ar fluence (10^{15} cm^{-2})	1.53	1.79
Average sputter yield Si/Ar	1.78	1.52
Experimental 1.63 [8]		
Si monomers sputtered (ML)	1365 (3.03)	1632 (3.63)
Si dimers/monomers ratio	0.145	0.045
Ar implanted in film (10^{15} cm^{-2})	0.28	0.39