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Melting of crystalline silicon thin films

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ABSTRACT

Melting of crystalline silicon thin films is studied by molecular dynamics (MD) simulations using Stillinger–Weber potential. Models are heated up from a crystalline to a normal liquid state. Temperature dependence of total energy and the Lindemann ratio exhibits a first-order-like behavior of the transition at a melting point. Heat capacity of the system exhibits a single peak at around the melting point. Atomic mechanism of melting is analyzed via monitoring spatio-temporal arrangements of the liquidlike atoms occurred during heating process. We find the formation of a quasi-liquid surface layer containing both solidlike and liquidlike atoms, i.e. at temperature around the melting point (T_m), there is a mixed phase of the solidlike and liquidlike atoms in the surface layer. The mechanism of melting of crystalline silicon is different from that of Lennard–Jones crystals and monatomic glass with free surfaces due to the potentials used in simulation and due to sizes of models.

1. Introduction

Melting of crystalline solids is one of the most important phase transformations in materials science and engineering and it is still not well understood [1–3]. In particular, melting of crystals with free surfaces has been under intensive investigations by experiments, computer simulations and theoretical models. It is found that it exhibits a heterogeneous behavior, i.e. liquid surface layer of a few atoms/molecules thick is forming at temperature far below T_m (e.g. surface melting) and it gradually penetrates into the interior with further heating [3–11]. However, simulations and experiments indicate the existence of the interplay between heterogeneous and homogeneous meltings in some materials, i.e. heterogeneous melting starts first at the undercoordinated sites in the surface shell while homogeneous one starts a bit later throughout the interior since it requires a relatively higher degree of heating which enhances the local instability of crystal lattice for a homogeneous nucleation of liquidlike atoms [11–13].

It is well-known that surface melting contributes a significant part in the melting process. However, nature of the melted surface layer occurred in the pre-melting stage is still under debate, i.e. it is commonly thought that it should be a liquid skin [14–17]. However, experimental evidences show that the melted surface layer should be different from the equilibrium liquid and it is called a quasi-liquid layer which exhibits structural, dynamic and transport properties that are intermediate between those of the solid and the liquid (see [6,17,18] and references therein). Moreover, the surface melting is crystal-face dependent [19] and the surface quasi-liquid layer thickness grows at temperature far below melting point [20].

Recently, Vo Van Hoang et al. have studied the melting of mesoscale Lennard–Jones crystals with free surfaces [21] using MD simulations. They found that melting proceeds by two different mechanisms: the heterogeneous one in the surface shell and the homogeneous one in the interior leading to the fast collapse of crystal lattice. Liquidlike atoms do not form a purely liquidlike layer at the surface but a quasi-liquid one is formed which contains both liquidlike and solidlike atoms with equal concentration. It is well-known that Lennard–Jones potential is applied for simple model that approximates the interaction between a pair of neutral atoms or molecules. It is of great interest to expand the research in this direction by computer simulations for various realistic materials including those with more complicated atomic interactions. Therefore, we would like to carry out the MD simulations of melting crystalline silicon thin films in order to clarify the situation.

In addition, silicon has been under intensive investigation for a long time. In particular, several potentials including two- and three-body terms have been used to compute the structural energies of covalent crystals such as silicon [22–24]. However, for silicon as well as the covalent materials, pair potentials alone are insufficient to describe the equilibrium diamond lattice. In particular, the Stillinger–Weber (SW) potential [25] has nine parameter that were adjusted to fit the silicon properties of condensed phases

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such as bond length, cohesive energy, melting temperature to satisfy qualitatively the Lindemann melting criterion for solids and to produce the property of shrinking when silicon melts. There are numbers of studies focusing on simulation of silicon using SW and other potentials [26–36]. While experiments mainly focus on studying zone melting and the mechanism of formation of grains using laser energy [26,28–32], some simulations study the velocity of melting on the (1 1 0) silicon with free surface [27]. Moreover, Zhang et al. focus on the volume change from solid to liquid and the curvature of the interface between the solid and the liquid phases [35]. However, none of them gives the whole picture about the atomic mechanism of melting of crystalline silicon thin films. Therefore, it motivates us to carry out the MD simulations of melting of crystalline silicon thin films via analyzing spatio-temporal arrangements of the liquidlike atoms occurred during heating process. We also present corresponding changes in various thermodynamic quantities related to the melting. Details about the calculations can be seen in Sec. II. Results and discussions related to the thermodynamics and atomic mechanism of melting of crystalline silicon thin films can be found in Sec. III. Conclusions are given in the last section of the paper.

2. Calculation

The initial object is diamond cubic structure of crystalline silicon. We use SW potential for describing the interaction between atoms in the models. The SW potential is given below [25]:

$$E = \sum_i \sum_{j>i} \phi_2(r_{ij}) + \sum_i \sum_{j\neq i} \sum_{k>j} \phi_3(r_{ij}, r_{ik}, \theta_{ijk}) \quad (1)$$

$$\phi(r_{ij}, r_{ik}, \theta_{ijk}) = \lambda_{ijk}\varepsilon_{ijk}[\cos\theta_{ijk} - \cos\theta_{0ijk}]^2 \times \exp\left(\frac{r_{ij}\sigma_{ij}}{r_{ij} - \alpha_{ij}\sigma_{ij}}\right) \exp\left(\frac{r_{ik}\sigma_{ik}}{r_{ik} - \alpha_{ik}\sigma_{ik}}\right) \quad (2)$$

where $\phi_2(r_{ij})$ and $\phi_3(r_{ij}, r_{ik}, \theta_{ijk})$ are two-body and three-body term, respectively; r_{ij} – the distance between the atoms i and j; θ_{ijk} – the angle between the vectors r_{ij} and r_{ik}; A_{ij}, B_{ij}, p_{ij}, q_{ij}, λ_{ijk}, γ_{ij}, and a are the dimensionless parameters, the parameter ε has a dimension of energy, the parameter σ has a dimension of length. Parameters were chosen based on the properties of crystalline and liquid silicon.

To perform the calculations we use the software package LAMMPS (Large-Scale Atomic/Molecular Massively Parallel Simulator), designed to solve various problems by the methods of classical molecular dynamics [37].

Our simulation scenario includes 3 stages.

Stage 1: The initial crystalline silicon models containing 32,678 identical atoms of Si in a cube of the size of 86.896 Å × 86.896 Å × 86.896 Å at the density $\rho = 2.3290$ g/cm^3 under periodic boundary conditions (PBCs) have been relaxed in NVT ensemble for 10_5 MD steps at $T_0 = 50$ K. Note that 1 MD step takes 0.001 picoseconds.

Stage 2: After that PBCs are applied only along the x and y Cartesian directions, while along the z direction the non-periodic boundaries with an elastic reflection behavior are employed after adding the empty space of $\Delta z = 20$Å at both side at z = 0 and at z = 86.896 Å. The system is left to equilibrate further for 2×10^5 MD steps at $T_0 = 50$ K using *NVT* ensemble simulation corresponding to the new boundaries of the simulation cell.

Stage 3: A temperature $T_i (T_i = 2500$ K) is chosen. It is higher than the melting point of Si to guarantee that at temperature T_i all atoms become liquid. The system is heated from temperature T_0 to T_i in the Nosé–Hoover canonical (*NVT* ensemble). The heating rate is 1.225×10^{11} K/s.

In order to improve the statistics, we average results over two independent runs.

3. Results and discussions

In the low temperature region, total energy linearly increases with temperature since the system remains in solid state and vibrational motion of atoms around their equilibrium positions dominates in the system (see Fig. 1a). At $T \geqslant T_x$, contribution of anharmonic motion of atoms is strong enough leading to massive collapse of a crystalline matrix that exhibits homogeneous melting process [9,10] and total energy starts to deviate from the linearity at $T_x = 1608$ K. Location of a sharp peak of the heat capacity is an equilibrium melting point, $T_m = 1779$ K. This is a bit higher than experimental result, i.e. $T_m^{\exp} = 1685$ K [38] and it is also higher than that obtained in other simulations due to the bigger number of atoms in the present work [25,39,40]. The heat capacity at a constant zero pressure is approximately calculated via the simple relation: $C_p = \frac{\Delta E}{\Delta T}$. Here, ΔE is a discrepancy in total energy per atom upon heating from T_1 to T_2 with $\Delta T = T_2 - T_1 = 12$ K. The transition from crystal to liquid upon heating can be seen via evolution of radial distribution function (RDF, see Fig. 1b), i.e. the peaks in RDF related to the diamond cubic structure of crystal become weaker with temperature and almost disappear at around $T = T_m$. At $T > T_m$, RDF exhibits a liquid like behavior. We also calculate important quantity, the Lindemann ratio, which is given for the ith atom [41–43]: $\delta_i = \langle \Delta r_i^2 \rangle^{1/2}/\overline{R}$. Here, $\langle \Delta r_i^2 \rangle$ is the mean-squared displacement (MSD) of the ith atom and $\overline{R} = 2.33$ Å is a nearest neighbor distance in our diamond cubic structure of crystalline silicon at low temperature. In the atomic motions, there are two kinds of contributions to the MSD: the first one is vibrational motion and the second one is diffusive displacement. The diffusive motions (liquidlike motion [44]) are thought to be related to the local instability in the system, which play the key-role of the melting mechanism [44,45]. Therefore, the best relaxation time for identifying ε_L is proposed to be not larger than several picoseconds [46]. In present work, the value for ε_L is calculated via relaxation of model for 5000 MD steps (or 5 ps) at a given temperature, i.e., the time is large enough for atoms to diffuse if they are liquidlike [47]. The mean Lindemann ratio ε_L of the system is defined by averaging of ε_i overall atoms, $\varepsilon_L = \sum_i \delta_i / N$. As shown in Fig. 1c, temperature dependence of ε_L is similar to that of total energy indicating a close correlation between two quantities. At $T = T_x$, critical value for the Lindemann ratio is $\delta_C = 0.19$. Critical value for ε_L is taken as 0.15 or from 0.05 to 0.20 of the nearest neighbor distance depending on the crystal structure, nature of the interparticle interaction and magnitude of quantum effects (see [48] and references therein). One can see that temperature dependence of total energy, heat capacity and the Lindemann ratio exhibit a first-order-like behavior of the transition at a melting point.

We also present the size-dependent melting via temperature dependence of total energy per atom of different sizes of models: 216, 8000 and 32768 atoms (see Fig. 2). One can see that the model with 216 atoms has almost the same behavior as found in [25]. Melting point of this model is about 1689 K (very close to the experimental one, $T_m^{\exp} = 1685$ K). When the number of atoms is increased to 8000 (red color) and 32768 atoms (black color), melting point is about 1755 K and 1784 K, respectively. Fig. 2 clearly shows the size-dependent melting point. One can see that the statistical noise increases with decreasing size of models as presented in Fig. 2.

Melting process can be monitored via analyzing spatio-temporal arrangements of liquidlike atoms occurred in the models during heating [48,49]. Liquidlike atoms can be detected via using the Lindemann melting criterion, i.e. atoms with $\delta_i < \delta_C$ are classified