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Phase transformations of mono-crystal silicon induced by two-body and three-body abrasion in nanoscale

Jiapeng Sun [a,*], Liang Fang [a,*], Jing Han [b], Ying Han [a], Huwei Chen [c], Kun Sun [a,*]

[a] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, Shaanxi Province, PR China
[b] School of Mechanical and Electrical Engineering, China University of Mining and Technology, Xuzhou 221116, Jiangsu Province, PR China
[c] Department of Applied Physics, School of Science, Xi'an Jiaotong University, Xi'an 710049, Shaanxi Province, PR China

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ABSTRACT

This article is focused on understanding the structural phase transformations of mono-crystalline silicon induced by nanoindentation, two-body and three-body abrasion at the nanoscale using the large-scale molecular dynamics simulation. The evolution and distribution of the possible phases are discussed in terms of coordination number (CN), radial distribution function (RDF), bond angle distribution function (ADF) and atom type tracking. The results show a new phase transformation route that is an initial diamond cubic silicon turns into high density amorphous (HDA) beneath the moving particle and then transforms into low density metastable amorphous (LDMA) behind the particle in both two-body and three-body abrasion. Considering the different phase transformation between nanoindentation and two/three-body abrasion, a stress criterion is proposed to predict the phase transformation, which can be generally applied to hydrostatic pressure experiment, nanoscale uniaxial compression and nanoindentation. For nanoindentation, a common misunderstanding of a metastable phase is clarified, which is also observed in front of the moving particle in two/three-body abrasive.

1. Introduction

Motivated by the extensive application in continuously shrinking modern electronic devices, the single crystal silicon has been investigated intensively in the past few decades in order to deeply understand its mechanical behavior at the micro/nanoscale. In particular, the phase transformation mechanisms of the mono-crystalline silicon under various mechanical loadings, led by hydrostatic pressure, nanoindentation, nanoscratching and nanotribology, have been attracting considerable attention. Since the pioneering work of Minomura and Drickamer [1], earlier studies are focused on the high-pressure phase transformation under the hydrostatic pressure using the diamond-anvil cell (DAC) experiments. It has been well known that the bulk silicon undergoes first phase transformation of the diamond cubic phase (Si-I) to the dense body-centered-tetragonal metallic β-tin phase (β-Si or Si-II) at ~10–13 GPa [2–4]. Larger hydrostatic pressures, then, lead to a sequence of transitions to other high-pressure phase, such as, Si-V, Si-VI, Si-VII, Si-X and Si-XI. During depressurization process, the high-pressure phases do not recover to the ground-state Si-I structure, but to other denser metastable phases with fourfold coordination depending on the pressure release rate. Slow pressure release from the Si-II results in the rhombohedra r8 phase (Si-XII) at ~10 GPa, which then transforms into the body-centered-cubic bc8 phase (Si-III) at ~2 GPa [5,6]. For fast unloading, the Si-II turns into amorphous silicon on the contrary [7–9].

As a standard tool for probing the nanoscale mechanical behavior of materials, the nanoindentation has been extensively applied to understand the phase transformation mechanism of mono-crystalline silicon. A unique high load by the nanoindentation is applied to a very small local region, which makes it possible to understand the mechanical deformation at the nanoscale. In contrast to the DAC experiments, nanoindentation induces not only hydrostatic pressure but also high shear stress which has been reported to lower the threshold for the onset of the phase transformation [10] and promote a new phase not observed under hydrostatic conditions [11,12]. *In situ* electrical measurements show that the semiconductor like Si-I transforms into a material with more metallic character during loading [13–15], which is believed to the β-Si recorded by hydrostatic pressure tests. The molecular dynamics simulations, however, indicate that the Si-I transforms into two types of body-centered-tetragonal phase i.e. β-Si and bct5 with fivefold coordination [16–18]. Recently, the *in situ* Raman microspectroscopy experiment confirms the formation of mixture of β-Si and bct5 during nanoindenation [19]. The only suggested β-Si by the electrical measurements could be attributed to the similar metallic structure between bct5 and β-Si phase. During unloading, the bct5 and β-Si all could be transformed into a

* Corresponding authors.
E-mail addresses: sun.jiap@gmail.com (J. Sun), fangl@xjtu.edu.cn (L. Fang), sunkun@mail.xjtu.edu.cn (K. Sun).

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mixture of metastable bc8 (Si-III) and r8 (Si-XII) at a slow release rate. But most amorphous silicon is detected in the residual contact impressions for fast unloading rates [19–22]. The presence and distribution of residual phases after nanoindentation could be related to the crystallographic anisotropy and in homogeneity of the stress distribution [22,23].

Comparing with the considerable understanding of the phase transformation induced by the nanoindentation and hydrostatic pressure, the phase transformation and deformation mechanism is still an open question on the nanotribology, including two-body abrasion and three-body abrasion. With the aid of the molecular dynamics, Zhang and Tanaka [24] reports that amorphous phase transformation is the main deformation mechanism during two-body and three-body abrasion. Wu et al. [25] suggest an alternative phase transformation route under the nano-grinding conditions: the initial Si-I phase transforms into amorphous silicon, which is in turn partially transformed into a mixture of metastable bc8 (Si-III) and r8 (Si-XII) embedded in amorphous silicon. Apparently, the phase transformations are related to the loading status and velocity. From the nanoscratching experiments, Huang et al. [26] reports that amorphous silicon is the only phase at a low stress, but the amorphous silicon can be recrystallized into Si-I nanocrystal, metastable bc8 (Si-III) and r8 (Si-XII) embedded in amorphous silicon at a sufficient stress. Gassilloud [27] finds that Si-XII can appear within the amorphous silicon region at a low loading speed, but only amorphous silicon exists at a high loading speed after nanoscratching. At a large load, dislocations can be initiated. The molecular dynamics simulations [28] confirm the amorphous transformation at a relatively small load, and suggest that nanotwins will be emerged at a large load. However, there is no direct evidence that confirms the transformed metastable bc8 (Si-III) and r8 (Si-XII) from the amorphous silicon in the previous experiments or simulations.

Two/three-body abrasion induced phase transformation at the nanoscale is not only the basic science, but also related to engineering applications. Besides the Micro-Electro Mechanical Systems (MEMS), the specific applications, where the abrasion at the nanoscale becomes critical, include chemical–mechanical polishing (CMP), probe-based data storage devices and semiconductor processing equipment. From above short review, it follows that the structural phase transformation as well as the mechanism are far less clear in two-body abrasion and three-body abrasion. Even until now, we almost know nothing about three-body abrasion induced phase transformation, compared to abundant research on nanoindentation and DAC experiment. Hence, investigations on the deformation and phase transformation of mono-crystalline silicon induced by two/three-body abrasion are still interesting, and a promote understanding of the possible phase transformation as well as the mechanism is required.

This article is intended to evaluate the structural phase transformation and deformation of mono-crystalline silicon induced by nanoindentation, two-body and three-body abrasion at the nanoscale. Large-scale molecular dynamics simulations are carried out on the (1 0 0) surface of mono-crystalline silicon based on Tersoff potential as described in Section 2. The techniques of coordination number (CN), radial distribution function (RDF), bond angle distribution function (ADF) and atom type tracking are used to monitor and elucidate the phase transformation. The detailed phase distributions and structure characteristics in nanoindentation and two/three-body abrasion are described in Section 3. The possible experiment and theoretical evidences are also provided. The phase transformation route in two/three-body abrasion, stress mechanisms and criterion to predict the phase transformation are presented in separate subsections of Section 4. The possible phase transformation in three-body abrasion is also investigation. Finally, generalization and conclusions are presented in Section 5.

2. Methods

Large scale molecular dynamics simulations are performed based on the Tersoff potential [29] for silicon atoms. Because the Tersoff potential gives the correct cohesive energies for the different phase, it has been extensively employed to predict the phase transformation. The interactions between the silicon atoms and the diamond atoms as abrasive particle are modeled by the Morse potential [30]. All of the simulations are performed utilizing the Verlet integration algorithm with a time step of 2.5 fs by LAMMPS [31] molecular dynamics simulation code.

A commonly used model of two-body abrasion is adopted as illustrated in Fig. 1(a), where a spherical diamond particle with radius ~10.86 nm slides with constant velocity in (1 0 0) silicon substrate surface. Because of the large hardness compared with silicon, the diamond particle is considered as a rigid body. To avoid the boundary effect a large silicon substrate consists of 2, 834, 079 atoms in total with a dimensions of $70.60 \times 16.29 \times 32.59$ nm along x-, y-, and z-directions. The sliding is along the x-directions, and the indenting is along the y-directions. Periodic boundary conditions are applied in both x- and z- directions, but free boundary is set along the y-direction. A ~1 nm thick layer on the bottom of the substrate is fixed to provide structural stability. To dissipate excessive thermal energy generated by loading and sliding, Langevin thermostat [32] is applied to a ~1.6 nm thick layer of atoms adjacent to the rigid layers. All the remaining layers are free moved according the Newton motion equations.

The silicon atoms are initially arranged in a diamond cubic structure with a constant lattice parameter of 0.5431 nm and then equilibrated at 300 K for 50 ps using the Nose–Hoover thermostat [33,34]. Subsequently, the particle is moved toward the silicon substrate to the defined indentation depth with a constant velocity of 100 m/s along the y-direction. After 50 ps relaxation, the particle is scratched along the crystal orientation of [1 0 0] in the (0 1 0) crystal plane with a constant sliding velocity of 100 m/s. The normal and lateral force is timely calculated by accumulating all the vertical and horizontal interaction forces where the substrate atoms contact with the particle atoms during simulation.

Since the pioneering work of Zhang and Tanaka [24], the existing molecular dynamics simulations of three-body abrasion all utilize the modified two-body abrasion model by adding the

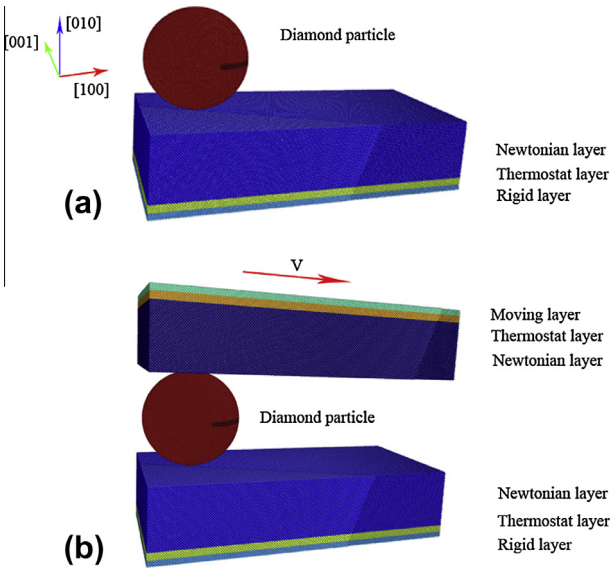

Fig. 1. The atomic model of the (a) two-body abrasion and (b) three-body abrasion.