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Effect of indentation speed on deformation behaviors of surface modified silicon: A molecular dynamics study

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ABSTRACT

To explore the effect of indentation speed on the deformation behaviors of silicon (Si) surface coated with silica (SiO_2) in chemical mechanical polishing process, the nanoindentation test is performed by molecular dynamics (MD) simulation. It is found that the force and indentation depth at which the force drops for high speed are lower than those for low speed, implying the mechanical strength of the bilayer composite increasing with a reducing indention speed. The percentage variations of atom number of coordinated silicon and Si-O bond number consistently indicate that the SiO_2 film at higher speed tends to fracture preferentially without sufficient densification and the amount of deformation is also larger. As amorphous SiO_2 film tends to fracture during indentation, the original Si-I and newly generated Si-II phases induced by indentation within underlying silicon begin to transform to a Si amorphous structure, which reveals the reason for why the CN5 number for higher indentation speed are larger than those for lower speed at the same indentation depth but with lower CN6 number when indentation depth grows from 4.0 nm to 8.2 nm. Stress analysis indicates the much higher shear stress subjected to silicon at higher speed facilitates the crystalline-to-amorphous transformation.

1. Introduction

Monocrystalline silicon, as one of the most popular semiconductor materials, plays an important role in the manufacture of the micro-electro mechanical systems (MEMS), precision optics elements and electronic products [1]. Prior to the fabrication of such devices, crystals of bulk silicon are usually sliced, ground, and polished using high precision machining technologies to achieve an atomic level flatness. Chemical mechanical polishing (CMP) now is generally considered as the only planarization technique to produce an atomically flat and defect-free surface based on the complicated polishing mechanisms coupled with a synergistic action of both chemical and mechanical effects [2]. Due to the synergistic effects, the silicon surface is usually oxidized and an amorphous SiO_2 layer with a thickness of several nanometers forms on the top surface, which can alter the mechanical properties of the substrate, like hardness and plastic deformation [3,4]. Therefore, it is necessary and interesting to explore the deformation behaviors of silicon substrate covered by the SiO_2 coating.

It is generally accepted that the phase transformation of silicon is the dominant deformation mechanism during contact loading at room temperature [5–10]. The diamond anvil and nanoindentation experiments indicated that displacement uncontinuity appears in loading section of load-depth curve, namely, "pop-in", which is a signature of phase deformation of pristine diamond cubic silicon (Si-I) to metallic dense body-centered-tetragonal β-tin (Si-II) by flattening the tetrahedral structure [11] and leads to a volume reduction by ~20% [12]. Upon pressure release, the generated Si-II phase converts to a mixture of crystal Si-XII/Si-III at slow retraction speed or amorphous α-Si phase at high retraction speed, which causes the occurrence of characteristic "pop-out" or "elbow" in unloading curve [13–15], respectively. Jang [16] and other researchers [5,17] attempted to study the effects of indenter angle and maximum load systematically characterized from nanoindentation load–displacement data in conjunction with micro-Raman imaging spectroscopy. They reported that a sufficiently large transformed volume of Si-II phase is needed to form the metastable Si-XII/Si-III crystalline phases during unloading, and the sharper indenter and higher maximum load individually enhance this formation. Whilst, the blunt indenter and lower maximum load tend to produce α-Si in indent after completely unloading. Chang et al. [18] studied the influence of loading rate on the shape of loading curve and presented that a lower loading rate favors appearance of pop-in but a rapid loading process tends to generate a gradual slope change of the

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load–displacement curve, indicating the formation of amorphous α-Si. A pop-in event is induced by phase transformation upon ultra-low load and represents the onset of incipient plasticity [18], and the phase transformation becomes the single deformation mode at shallow indentation depth [8]. Furthermore, nanoindentation experiments expressed that the pop-in load level decreases with the increasing loading rate in materials of phase transformation-governed plasticity, which is opposed to that of dislocation-governed plasticity [19,20]. With the increasing indentation load, the crystalline defects, including slip bands, planar defects and dislocations, and cracks, commonly coexist with phase transformation determined by transmission electron microscope (TEM) [5,17]. Fortunately, Sun and coworkers [8] reported the occurrence of multiple pop-in events in the load-indentation strain curve. They also established the one-to-one relationships between the pop-in events and the versatile deformation modes, including high pressure phase transformation, dislocation, median and surface crack, based on the combined studies using experiments and MD simulations of nanoindentation on Si (1 0 0). Additionally, another new body-centered-tetragonal phase (bct-5) with 5-coordinated number is observed in the MD simulations during nanoindentation, which has never been detected during anvil cell experiments. The prediction has been confirmed by in situ Raman microspectroscope, providing evidence for both the existence of bct-5 phase and the possibility of generating it under indentation tests [21,22].

On the other hand, amorphous SiO_2 is an inorganic material which has various applications in many nanotechnology areas, such as nanoelectronics, microfluidics, and nanopore sensors [23]. Over past decades, a variety of experimental and theoretical studies have been performed to probe the structure and properties of amorphous SiO_2 [24–27]. Jin et al. [28–30] tried to clarify the microscopic structure of deformed SiO_2 via experiments and simulations. Wu [31] provided the comprehensive relations between the structure and physical and electronic properties, he also confirmed that the compression mechanism relates to the occurrence of 5- and 6-fold coordinated silicon. Mott [32] proposed that the broken Si-O bond linked to 4-coordinated silicon leads to plastic flow through its capacity to change the number of silicon atoms in a –Si-O-Si-O- ring. Lu et al. [33–35] investigated the origin of crack nucleation and propagation by MD simulations and atomic force microscope (AFM) experiments, and the results indicated that damaged nanocavities around the precrack coalesce with kinks to form crack nanocolumns which finally develop into a crack. Recently, Ebrahem [36] studied the influence of Si-O ring distribution on the deformation and fracture behaviors of amorphous SiO_2 by varying quenching rate and demonstrated that the mechanical behavior is closely associated with ring statistics. Despite of extensive investigations of amorphous SiO_2, the specific features of restricted SiO_2 film during nanoindentation process, especially at atomic scale, are still unclear and extremely difficult to realize in the present experimental conditions.

Although these experiments and simulations have offered us a wealth of information, the atomic scale structure transformation of restricted amorphous SiO_2 film and the plastic deformation of monocrystalline silicon coated with SiO_2 film are still unclear. Fortunately, The MD simulation due to its ability of high spatiotemporal processes enables one to study the mechanical behaviors and structure transformation clearly at atomic scale. We hence in this work perform a MD simulation of nanoindentation to investigate the effect of nanoindentation speed on the deformation behaviors of surface modified silicon on the base of our previous work. Emphasis is put on deformation process and deformation characteristics of amorphous SiO_2 film and underlying monocrystalline silicon substrate.

2. Methods and simulation details

In this work, the MD simulations are performed using the large-scale atomic/molecular massively parallel simulator (LAMMPS) [37]. The nanoindentation system is composed of a spherical diamond indenter and a bilayer substrate (monocrystalline silicon substrate covered by amorphous SiO_2 film), as shown in Fig. 1. The composite substrate has a size of 30.0 nm × 30.0 nm × 26.0 nm. The amorphous SiO_2 film with a thickness of 0.8 nm is carefully prepared by quenching melted beta-cristobalite, similar to the methods reported by Chowdhury [38]. The underlying silicon substrate with a thickness of 25.2 nm contains 1,130,976 silicon atoms, which are initially arranged in a diamond cubic structure with a lattice of 0.543 nm. Its crystallographic orientations along X, Y and Z axes are [1 0 0], [0 1 0] and [0 0 1], respectively. The boundary layer with a thickness of 1.0 nm at the bottom of the bilayer substrate is frozen to restrict the motion of the specimen. The next layer of atoms with a thickness of 1.5 nm adjacent to the boundary atoms are set to be the thermostatic atoms to imitate the heat dissipation. All the residual atoms in bilayer substrate are Newtonian atoms, which are freely moved according to the Newton motion equations. The spherical indenter contains 159,024 carbon atoms with a radius of 6.0 nm, which is deliberately positioned 0.9 nm above the center of the bilayer substrate. The periodic boundary conditions are employed in X and Y directions while non-periodic boundary conditions are imposed in Z direction.

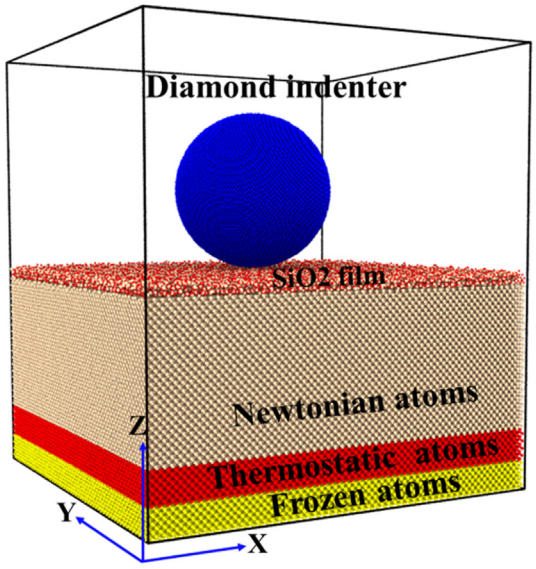

Fig. 1. Schematic of the MD simulation for nanoindentation on the Si (0 0 1) surface covered by an amorphous SiO_2 film.

The interatomic Tersoff potential function that considers the effects of bond angle and covalent bond has been widely used in predicting silicon phase transformation [11,12]. The developed Tersoff potential for Si-O system [39] determined based on *ab initio* calculations, which has been successfully applied in amorphous SiO_2 and α-Si [40,41], is employed in this work to describe the interactions between Si-Si, O-O and Si-O atoms within bilayer substrate. The relations between Si atoms of bilayer substrate and C atoms of diamond indenter are described by Morse potential, with the parameters cohesive energy D_0 = 0.435 eV, elastic modulus α = 4.6487 $Å^{-1}$ and interatomic equilibrium distance r_0 = 1.9475 Å [42]. The interactions between C atoms of indenter and O atoms within amorphous SiO_2 film are depicted by Lennard-Jones potential with the parameters ε = 0.1 eV and σ = 3.275 Å. The nanoindentation simulations consist of three stages: relaxation, loading and unloading. Prior to perform the nanoindentation, the designed bilayer substrate is first relaxed to local energy minimum by the steepest descent algorithm and then equilibrated using NVT ensemble with Nose-Hoover thermostat for 90 ps at a constant temperature of 300 K. After equilibration, the MD simulation of nanoindentation is conducted in which the spherical indenter moves along -Z direction, and finally the unloading process occurs. In both loading and unloading stages, the NVE ensemble with the Langevin thermostat to maintain the