Amorphization-assisted nanoscale wear during the running-in process

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A B S T R A C T

Atomistic simulations were used to study the nanoscale wear of crystalline silicon with a native oxide sliding against amorphous silicon dioxide. The size, shape and crystallographic orientation of the model were defined to be comparable to those in a corresponding atomic force microscope experiment, where the tip was imaged before and after 40 nm of sliding using *ex situ* transmission electron microscopy. Tip wear was quantified in the simulation as the volume of silicon atoms removed from the tip at intervals up to 40 nm sliding distance. We also quantified amorphization during sliding as the change of tip material from crystalline to amorphous. Amorphization was analyzed in the context of a previously-proposed analytical model for crystalline-to-amorphous transitions and related qualitatively to local strain distributions within the tip. Finally, wear and amorphization rates were found to exhibit similar trends, which suggests that amorphization may play an important role in nanoscale wear during the running-in process.

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1. Introduction

Since its invention, atomic force microscopy (AFM) has been widely used for studying surface features and manipulating materials from the atomic to the micron scale. The quality of AFM-based measurements and manufacturing processes are critically dependent on the reliability and durability of the AFM tip itself [1–5]. However, contact between the tip and sample, and the associated high mechanical stress and/or chemical reactions, can result in wear of the tip during use [6–13]. Tip wear is undesirable because it can result in an inability to resolve fine structures during AFM implementation [14]. These wear processes are necessarily nanoscale, suggesting that standard, macroscale wear theories may not always be applicable to describe or predict tip wear. Thus, a fundamental understanding of wear mechanisms at the nanoscale is a critical first step towards ensuring the structural and chemical integrity of an AFM tip during instrument use.

Recently, a number of experimental studies have used AFM to characterize nanoscale wear on a variety of different material systems [6,7,9,15]. These studies have been complemented by molecular dynamics (MD) simulation of the AFM tip apex sliding on well-defined substrate surfaces [12,13,16]. One observation from such studies is that a crystalline-to-amorphous transition may contribute to nanoscale wear. Experimental measurements of sliding on nanocrystalline diamond revealed that amorphous

carbon was formed by the wear process [17,18]. This observation was explained theoretically by an MD study of a diamond-diamond interface that showed mechanical amorphization drives wear [19]. These studies suggest that wear at the nanoscale may not be a simple process of material removal, but rather may be assisted by material change during sliding. Further complicating the issue is that wear rate is not only a material- and condition-specific property, but is also dependent on how long sliding has progressed. At the onset of sliding, the system is "running-in" and the wear rate can be orders of magnitude higher than that during steady state wear [9]. During running-in, the two sliding partners adjust to each other in terms of stress, surface roughness or crystal orientation [20–22]. The chemical and mechanical processes that occur during running-in are expected to play an important role in steady state wear [20]. This means that understanding the processes that leads to material removal in the first tens of nanometers of sliding is critical to understanding nanoscale wear in general.

In this work, MD simulations were used to study the nanoscale wear of a crystalline silicon AFM tip with a native oxide due to sliding against an amorphous silicon dioxide substrate. The size, shape and crystallographic orientation of the tip apex in the MD model were defined to be comparable to those in a corresponding AFM experiment, where the tip was imaged before and after 40 nm of sliding using *ex situ* transmission electron microscopy (TEM). Tip wear was quantified in the simulation as the volume of silicon atoms removed from the tip at intervals up to the same 40 nm sliding distance as in the experiment. We also quantified tip amorphization as the change of amorphous tip volume due to

sliding. The amorphization process was analyzed in the context of a previously-proposed model for sliding-induced amorphization and considered in terms of local strain within the tip. Lastly, the wear and amorphization rates were evaluated together to determine how these two processes are related and better understand the running-in process at the nanoscale.

2. Methods

2.1. Experiments

In the experiment, a silicon tip was slid against a freshly-annealed amorphous SiO_2 substrate (1050 °C, 15 h in air) under dry nitrogen (0.026 bar above ambient) and stabilized temperature (28 ± 5)°C. Non-contact AFM images and force distance curves (maximum load of 5 nN) were obtained immediately before sliding. The tip was brought into contact with the surface maintaining the silicon crystallographic direction [1 1 7] perpendicular to the sample surface and loaded to 100 nN. Then the tip was slid, in contact with the surface, along the [1 $\bar{1}$ 0] silicon crystallographic direction at constant normal load of 100 nN and speed of 2.5 μm/s. The tip was imaged using high resolution TEM (HRTEM) before and after sliding 40 nm. Experimental tip wear volume was calculated by overlaying the HRTEM images obtained before and after wear experiment, measuring the difference in area of those 2D projections and assuming tip was circularly symmetric in the third dimension (truncated cone approximation).

2.2. Simulations

In the simulation, consistent with the materials in experiments, we modeled a Si tip with an oxidized surface and an amorphous SiO_2 substrate. From the high-resolution tip image obtained from TEM before sliding, shown in Fig. 1(a), the tip profile was extracted and fit with a parabola, indicated by a dashed red line in the figure. Based on this profile, a corresponding parabolic tip was cut from a cubic model of crystalline silicon. The radius of curvature of the tip profile was estimated to be 1 nm, and the model tip height of 10 nm was sufficient to capture the wear mechanisms expected under the conditions explored here. Then the tip was placed in an atmosphere of atomic oxygen. After the reaction between silicon atoms and oxygen atoms, unbonded oxygen atoms were removed from the simulation box. A cross section of the oxygen-terminated tip is shown in Fig. 1(b).

The amorphous SiO_2 substrate was created using Visual Molecular Dynamics (VMD), in which crystalline silicon dioxide was annealed by increasing the temperature to 8000 K and then decreasing it to 300 K [23,24]. The dimensions of the substrate were $23.2 \times 11.4 \times 3.5$ nm in the x-, y-, and z- directions, respectively. To maintain computation efficiency, we did not initially create a substrate long enough to accommodate the entire target sliding distance, i.e. 40 nm. However, when the tip was about to exceed the right boundary during sliding, we removed the worn part of the substrate near the left boundary and added a newly prepared amorphous SiO_2 block to the substrate at the right boundary. The new block of material was added to the model when the tip was at least 5 nm away from the right boundary to ensure there was initially no interaction between the tip and the extended block. The surface roughness of the SiO_2 substrate was 0.18 nm in the simulation, comparable to 0.22 nm in the experiment. A perspective-view snapshot of the entire model system is shown in Fig. 1(c).

In the simulated system, the top 2 nm of the tip and the bottom 1.5 nm of the substrate were held rigid. Adjacent to the rigid layer, thermostatted layers were created and held at 300 K using the Langevin thermostat. The Langevin thermostat was applied only in
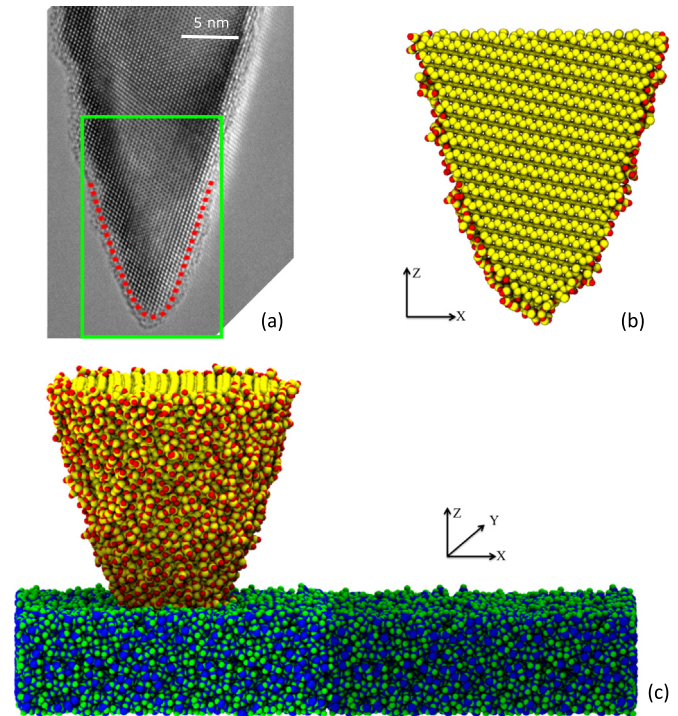
Fig. 1. (a) TEM image of the silicon AFM tip before sliding, where the dashed line represents a parabola fit to the traced profile of the tip; (b) xz cross section of the model tip, which represents the Si (1 $\bar{1}$ 0) plane; (c) Snapshot of the simulation setup. The brightness change of the substrate indicates that the substrate can be extended along its sliding direction. Silicon atoms in the tip are shown in yellow, oxygen atoms in the tip in red, silicon atoms in the substrate in blue, and oxygen atoms in the substrate in green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the directions perpendicular to the direction of tip movement. The remaining atoms in the model were free to evolve according to Newtonian dynamics. Periodic boundary conditions were applied in the x- and y- directions. The charge-optimized many-body (COMB) potential for Si/SiO_2 [25] was used with a time step of 0.2 fs to describe all atomic interactions. This potential includes many-body effects that allow for the breaking of existing bonds and the formation of new bonds and has been successfully applied to model a Si/SiO_2 interface [25]. Simulations were run using the large-scale atomic/molecular massively parallel simulator (LAMMPS) [26].

Indentation simulations were performed to partially validate the model. A load of 5 nN was applied to the rigid layer of the tip in the z [1 1 7] direction. After the potential energy of the system was stable, which indicates that the system was at equilibrium, the tip was pulled away from the surface at a constant velocity of 20 m/s. The pull off force was identified as the minimum force during tip retraction. The pull off force measured in the simulation was 12.4 ± 4.1 nN, which was reasonable, although somewhat larger than the 3.93 ± 1.27 nN measured in the experiment. From the Derjaguin–Muller–Toporov (DMT) contact model [27], the work of adhesion in the simulation and experiment were estimated to be 2.0 ± 0.7 J/m^2 and 0.6 ± 0.2 J/m^2, respectively. The difference between experiment and simulation may be attributed to the existence of water in the experiment. In a previous study, it was observed that water adsorbed on silicon dioxide surface can change the adhesive strength of nanoscale contacts [28].

Sliding simulations were then performed to observe tip wear due to shear. A constant normal load of 100 nN was applied on the rigid top layer of the tip and then the system was relaxed for 40 ps, after which the potential energy was stable. Then, the tip was slid along either the x- or the y- direction at a constant speed of