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## A molecular dynamics analysis of the effect of surface passivation on the adhesion, deformation behavior and structure stability of amorphous carbon ultrathin films

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#### 1. Introduction

Amorphous carbon (a-C) films represent an important class of low-friction protective overcoats used in many applications where intermittent or continuous contact interactions may lead to the development of high friction traction and chemomechanical wear, leading to device dysfunctionality [1]. The mechanical properties of a-C films mainly depend on the prevailing carbon atom hybridization state and can strongly influence the tribological behavior [2]. In addition, the atmospheric conditions may activate tribochemical reactions that can profoundly influence the friction of *a*-C films [3]. Ambient gaseous species may chemically bond to free dangling bonds, inducing surface passivation of interacting solid bodies that can dramatically alter the adhesion and friction characteristics. For example, hydrogen surface passivation of *a*-C films may reduce the coefficient of friction from approximately 0.7 to 0.01 [3-5]. Atomic-scale friction is a manifestation of surface adhesion forces generated by atomic interactions that greatly depend on surface passivation [6]. Consequently, basic understanding of the effect of surface passivation on the tribomechanical behavior of ultrathin films at the atomic level, necessitated by the extremely small film

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#### ABSTRACT

Basic knowledge of the interfacial interactions, contact deformation, and structure changes in amorphous carbon (*a*-C) ultrathin films due to irreversible deformation is of critical importance to the protective effectiveness of these films. This paper presents a molecular dynamics (MD) analysis that reveals the role of surface passivation on the contact deformation and adhesion characteristics of ultrathin (<30 Å) *a*-C films possessing a layered structure consisting of intermixing, bulk, and surface layers. MD simulations reveal much higher interfacial adhesion, destabilization of the film structure resulting in partial *sp*<sup>3</sup>-to-*sp*<sup>2</sup> rehybridization, and film delamination in the intermixing layer for unpassivated compared to hydrogen-passivated diamond surfaces. The results of this study illuminate the adhesion and contact deformation behaviors of ultrathin *a*-C films with layered structures, which are impossible to track experimentally due to the extremely small spatiotemporal scales.

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thickness and very low external forces, is critical to the reliability and performance of contact-mode micro/nanodevices.

Molecular dynamics (MD) is a powerful computational method for investigating atomic-scale surface interaction phenomena and structure changes in ultrathin films. For example, previous MD studies have provided important insight into the shear, tension, and scratch deformation behavior of tetrahedral *a*-C films [7] and the evolution of the structure of *a*-C films during growth and thermal annealing [8]. Consequently, the objective of this study was to introduce a comprehensive MD analysis that can elucidate the effect of surface passivation on the adhesion, deformation characteristics, and structure stability of ultrathin (<30 Å) *a*-C films synthesized by deposition processes that use energetic particles as film precursors.

#### 2. Modeling methodology

A 23  $\times$  23  $\times$  125 Å simulation box with periodic *x*- and *y*boundary conditions that contained ~4700 particles was used in this study (Fig. 1). Convergence studies have shown that the results were not affected by the dimensions of this simulation box [8]. The red silicon atoms at the bottom of the substrate were fixed to mimic a semi-infinite substrate, whereas the unconstrained green silicon atoms were assigned to a Berendsen thermostat that main-









**Fig. 1.** MD model of *a*-C film on a Si substrate and a diamond substrate with (a) unpassivated and (b) hydrogen-passivated surface.

tained the system's temperature at 300 K. All of the grey carbon atoms of the diamond substrate were fixed to model a rigid structure. The growth of <30-Å-thick *a*-C film with 48% overall  $sp^3$  content was simulated by randomly injecting a total of 2000 carbon atoms with a kinetic energy of 80 eV, one-by-one in 2 ps intervals to allow the system to equilibrate between consecutive injections. Under these simulation conditions, the *a*-C film exhibited a layered structure consisting of an intermixing layer at the interface with the silicon substrate, an intermediate bulk layer rich in  $sp^3$ hybridization, and a predominantly  $sp^2$  hybridized surface layer, which is typical of the structure of *a*-C films synthesized by energetic carbon particle bombardment. More details about the simulation procedure of *a*-C film growth by energetic carbon atoms can be found elsewhere [8].

Full passivation of the diamond surface was accomplished by allowing free hydrogen atoms to attach to all of the surface atoms (Fig. 1(b)) before contact with the *a*-C film. The initial gap between the diamond and *a*-C film surfaces was 17 Å. The diamond substrate was advanced toward the film at a constant speed of 10 m/s until the surface interference reached 6 Å. After allowing the system to equilibrate for 10 ps, the diamond substrate was retracted at the same speed as for the loading until it fully separated from the film. Interatomic force interaction was modelled with the Brenner's second-generation reactive empirical bond-order (REBO) potential [9]. All of the MD simulations were performed with the LAMMPS code [10].



**Fig. 2.** Normal force versus surface interference of *a*-C film deformed by a diamond substrate with (a) unpassivated and (b) hydrogen-passivated surface.

#### 3. Results and discussion

Fig. 2 shows representative normal force versus surface interference plots for unpassivated and hydrogen-passivated diamond surfaces. The different loading and unloading paths indicate irreversible deformation. Hydrogen surface passivation reduced the maximum normal force by ~31.5%, presumably due to the weaker carbon-hydrogen atomic forces than the carbon–carbon atomic forces. Compared to the unpassivated diamond surface, the hydrogen-passivated diamond surface exhibited compliance due to the free hydrogen atoms, leading to a lower normal force. The most profound difference is the remarkable decrease (by a factor of ~6.4), the earlier commencement (~17 times smaller surface interference), and the gradual decrease to zero of the adhesion force for surface-passivated diamond. These results indicate a first-order effect of surface passivation on interfacial adhesion and film deformation during surface separation.

The large number of unsaturated atoms at the *a*-C [11,12] and diamond [13] surfaces, where  $sp^2$  and sp were the predominant atomic carbon hybridizations, formed carbon–carbon bonds [14] at the contact interface (dashed–line boxed region in Fig. 3(a)). The intense film stretching during unloading instigated by the

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**Fig. 3.** (a) Film delamination at the bottom of the intermixing layer of the *a*-C film induced by the high attractive (adhesion) force during the retraction of a diamond substrate with an unpassivated surface. Bond formation at the contact interface for a diamond substrate with (b) unpassivated and (c) hydrogen-passivated surface.

strong adhesion force led to the extensive breakage of bonds in the intermixing layer of the *a*-C film (solid-line boxed region in Fig. 3 (a)), ultimately causing film delamination. Considering the infinitely large model (periodic boundary conditions), film delamination is attributed to the large attractive (adhesion) force generated at the contact interface. In fact, film delamination commenced at the bottom of the intermixing layer, presumably the weaker region due to the damage of the crystalline silicon structure by the implanted carbon atoms during film growth. The formation of carbon-carbon and carbon-silicon bonds at the unsaturated diamond/a-C film contact interface (Fig. 3(b)), which are responsible for the strong adhesion force that caused film delamination, was prevented by hydrogen passivation of the diamond surface (Fig. 3(c)). Additional insight into the deformation of the a-C film induced by unpassivated and hydrogen surfacepassivated diamond substrates can be obtained from the animations of the loading/unloading process shown in videos A and B of the Supplementary Data section, respectively.

The effect of irreversible deformation due to compressive loading and unloading on the film structure can be interpreted in the light of  $sp^3$  depth profiles computed by averaging the  $sp^3$  content of 1-Å-thick slices through the film thickness, shown in Fig. 4. The *sp*<sup>3</sup> depth profiles reveal the formation of a layered film structure consisting of an intermixing layer with rapidly decreasing sp<sup>3</sup> fraction towards the film/substrate interface (0 < depth < 10 Å), an intermediate bulk layer with relatively high  $sp^3$  fraction of 50–60%  $(\sim 10 < \text{depth} < 20 \text{ Å})$ , and a surface layer with sharply decreasing sp<sup>3</sup> fraction towards the film surface (~20 < depth < 28 Å), in agreement with experimental evidence [15]. All cases show that the bulk layer exhibited the highest sp<sup>3</sup> fraction before and after loading. However, a more pronounced decrease of the  $sp^3$  content occurred during the retraction of the unpassivated diamond substrate compared to the hydrogen surface-passivated diamond substrate. This difference is attributed to the development of a much stronger attractive (adhesion) force in the case of the unpassivated diamond substrate, as seen in Fig. 2, which destabilized the film nanostructure by introducing a tensile mechanical environment that activated partial  $sp^3$ -to- $sp^2$  atomic carbon rehybridization.



**Fig. 4.** Through-thickness  $sp^3$  distribution before deformation and after halfway retraction and full surface separation (maximum attractive (adhesion) force) for a diamond substrate with (a) unpassivated and (b) hydrogen-passivated surface. (The zero depth corresponds to the bottom of the intermixing layer.)

#### 4. Conclusions

An MD analysis of ultrathin *a*-C films possessing a layered structure was performed to elucidate the effect of surface passivation on the adhesion and contact deformation behavior of these films. The formation of strong carbon-carbon bonds at the contact interface of the *a*-C film with the unpassivated diamond substrate yielded a high attractive (adhesion) force, film delamination at the bottom of the intermixing layer, and structure destabilization due to the high attractive (tensile) stresses generated during the retraction of the diamond substrate that activated a partial  $sp^3$ -to- $sp^2$  atomic carbon rehybridization, mainly in the sp<sup>3</sup>-rich bulk layer. Alternatively, the six fold decrease of the interfacial adhesion due to hydrogen passivation of the diamond surface prevented film delamination and significant sp<sup>3</sup>-to-sp<sup>2</sup> atomic carbon rehybridization during the surface detachment. The present MD model can also be used to analyze more complex systems, including surface passivation of both contacting surfaces and the effect of sliding traction on the adhesion and deformation characteristics of ultrathin a-C films, which are difficult, if not impossible, to capture experimentally due to the ultrasmall length and time scales.

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#### Appendix A. Supplementary data

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