

Experimental and molecular dynamics simulation studies of friction behavior of hydrogenated carbon films

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Abstract

Hydrogenated carbon (CH_x) films were grown by reactive magnetron sputtering of graphite in an argon–hydrogen plasma. Pulsed d.c. bias was applied to both the carbon target and the substrate to maintain a stable process and reasonable deposition rate. The resulting films were smooth and stress-free. The influence of hydrogen concentration and relative humidity on friction properties of the films was investigated. At 5% relative humidity, the lowest friction coefficient of 0.01 was obtained at a sputter-gas composition containing 25% hydrogen. Excessive incorporation of hydrogen produces softening and degrades its friction performance at high contact stresses. Molecular dynamics simulation studies showed the reduction of friction coefficient with surface hydrogenation. These studies indicate that pulsed d.c. magnetron sputtering can produce hydrogenated carbon films with friction properties similar to those prepared by chemical vapor deposition methods.

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1. Introduction

Friction properties of diamond-like (hydrogenated) carbon films have been investigated extensively. Earlier work showed that the friction coefficient varies between 0.001 and 0.5, depending on the synthesis methods, counterface materials and testing conditions [1–5]. Recent studies by Erdemir and co-workers showed that hydrogenated carbon films grown using plasma-enhanced chemical vapor deposition with methane–hydrogen mixtures attain friction coefficients as low as 0.001 [6,7]. Generally, such ultralow friction performance was achieved when three conditions were satisfied: (i) hydrogenated carbon surfaces sliding against each other; (ii) smooth surfaces; and (iii) dry environment. Using time-delay friction measurements, Heimberg et al. [8] demonstrated the sensitivity of these carbon films towards the environment, mostly due to the adsorption of water vapor. There were indications from the work of Erdemir et al. [6,7] that friction depends on the

hydrogen concentrations in these carbon films, but no quantitative information was given.

Magnetron sputtering provides a flexible deposition method that can be readily scaled up for industrial applications. We would like to explore if this deposition technique can produce hydrogenated carbon films with friction properties comparable to those produced by plasma-enhanced chemical vapor deposition. In this paper, we report the growth of hydrogenated carbon films (CH_x) by pulsed d.c. magnetron sputtering at ambient substrate temperatures (approx. 350 K). We explored the effect of hydrogen concentration, relative humidity and applied load on friction in these CH_x films. In addition, we performed molecular dynamics simulation studies to determine how surface hydrogenation affects friction coefficient.

2. Experimental

CH_x films were grown using pulsed d.c. magnetron sputtering in a single-cathode deposition chamber. The base pressure of the chamber was below 2.7×10^{-6} Pa. We used a 2-inch carbon target (99.999% purity) in an unbalanced magnetron. The target voltage was pulsed at

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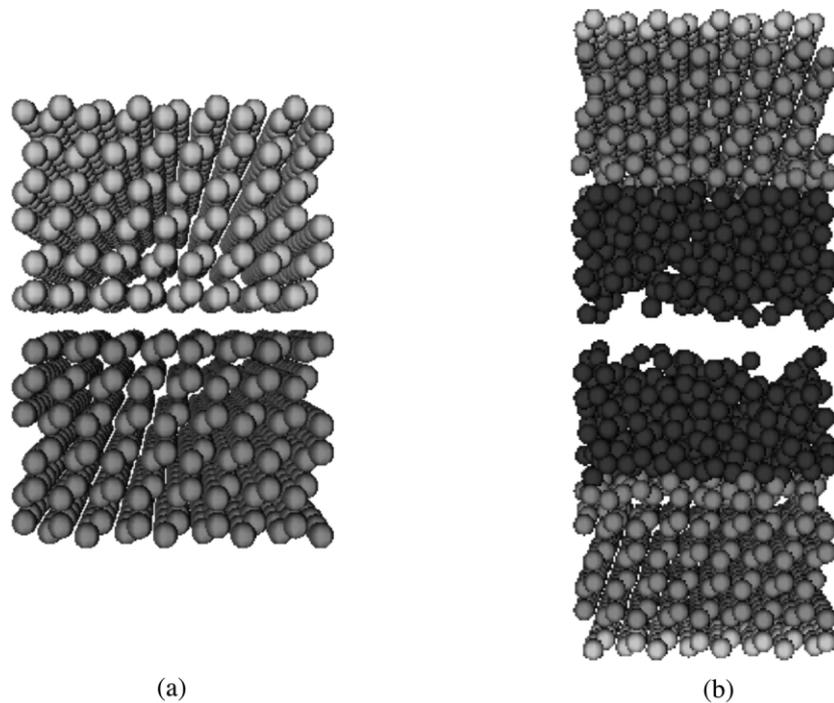


Fig. 1. (a) Two diamond surfaces and (b) amorphous carbon films grown on diamond.

50 kHz (80% duty cycle), with the positive voltage set at 10% of the negative voltage, (e.g. at a set target bias of -400 V, the actual target voltage is a rectangular wave cycling between -400 and $+40$ V). The target power was set at 100 W. The sputter-gas was argon–hydrogen mixture at a total pressure of 0.67 Pa, with hydrogen concentration ranging from 3 to 35%. Si (100) wafers were used as substrates. They were first cleaned in acetone and 2-propanol, then transferred into the chamber and reverse-sputter-etched in argon plasma at 10.7 Pa. A 20 kHz pulsed d.c. bias (pulse shape similar to that applied to the target) was applied to the substrate during deposition for low-energy ion bombardment of the growing film and eliminating charging. The d.c. bias voltage was -50 V. The thickness of all films was approximately 550 nm.

Friction properties of these CH_x films were determined using a ball-on-disk tribotester at room temperature. In this test, a coated 3.2-mm diameter steel ball was loaded onto a coated Si wafer rotated at 50 rev./min. The friction force was measured as a function of time. The surface topography was obtained by atomic force microscopy. The film hardness was measured using a Hysitron nanoindenter, analyzed by the Pharr–Oliver method [9]. In the latter case, the penetration was kept at less than 15% of the film thickness to minimize substrate effects. Film stress was measured using the wafer curvature method.

3. Molecular dynamics simulation

3.1. Film deposition

The first step in the MD simulation is to grow an amorphous carbon film on diamond. The interatomic potential is of the Tersoff–Brenner form [10]. The initial substrate is a diamond lattice consisting of 672 carbon atoms with 56 atoms per layer as shown in Fig. 1a. Prior to deposition, the lattice is quasi-statically relaxed to its minimum potential configuration, using a conjugate gradient method. Carbon atoms are then deposited at 40 eV sequentially into the substrate at normal incidence and randomly chosen locations. Periodic boundary conditions are applied in the plane perpendicular to the film growth direction. The bottom two layers of the substrate are held fixed to mimic the infinite dimension of the substrate, while atoms of the next four layers are coupled to an external heat bath at 300 K employing the method developed by Berendsen et al. [11]. Based on the actual maximum velocity of the atoms, a varying time-step strategy is introduced to accelerate the simulation. Between two successive depositions, the system is thermally equilibrated for approximately 10 ps. The amorphous film consists of 1037 carbon atoms, as shown in Fig. 1b.

To study the effect of surface hydrogenation on friction, hydrogen atoms are deposited onto the amor-

phous carbon film at random impacting locations. Carbon–hydrogen and hydrogen–hydrogen interactions are described by a Brenner potential. Not all deposition attempts are successful. In many cases, the depositing hydrogen atom bounces back from the carbon surface due to bond saturation. The maximum number of available bonds of surface carbon atoms determines how many hydrogen atoms the surface can receive. For the film shown in Fig. 1b, the maximum number of deposited hydrogen atoms is 68. This is defined as 100% surface hydrogenation.

3.2. Sliding friction

Two carbon films of the same kind (with or without hydrogen atoms on the surface) are brought into sliding contact with each another. The intralayer interaction of each film is described by a Brenner potential, while the interlayer interaction is described by a Lennard–Jones (L–J) potential [12] as

$$\Phi_{L-J} = 4\varepsilon \left\{ \left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right\}$$

The classically known parameters for the L–J potential for carbon–carbon, carbon–hydrogen, and hydrogen–hydrogen interactions are:

$$\varepsilon_{CC} = 1.663 \text{ meV}, \sigma_{CC} = 3.191 \text{ \AA}$$

$$\varepsilon_{CH} = 2.762 \text{ meV}, \sigma_{CH} = 3.179 \text{ \AA}$$

$$\varepsilon_{HH} = 3.180 \text{ meV}, \sigma_{HH} = 2.918 \text{ \AA}$$

Periodic boundary conditions are applied in the two dimensions parallel to the surface plane. In the third dimension, two outermost layers (112 atoms) of each film are held rigid. The distance between the static atoms defines the separation between the two films. The next ten layers in each film are coupled to an external heat bath at 300 K, employing the method introduced by Brendsen et al. [11]. All other atoms are allowed to dynamically evolve in space and time according to Newton's equations of motion without any constraints. At each time step, numerical integration of the equations of motion is realized using an explicit time integrator based on the Gear algorithm, a fifth-order predictor-corrector method. For simplicity, constant separation, rather than constant load, is applied when sliding the two films in the simulation. The separation determines the applied normal load. To avoid numerical instability, a relatively large separation between the films is assigned prior to sliding. The two films are then brought into the target distance by moving the top film down

step-by-step. Between two sequential steps, the system is relaxed for approximately 5 ps to attain thermal equilibrium. The load ranges between 0 and 8 nN.

Sliding is realized by displacing the rigid layers of the top film in the sliding direction at each time step, while maintaining a constant separation between the films. The displacement and the time step determine the sliding velocity (0.1 nm/ps). At each time step, the frictional forces are calculated by summing up the L–J forces over the atoms in the top film. At least five different starting configurations are constructed by changing the relative position of the films in the y-direction. The resultant frictional force and the normal force are averaged over these configurations [13].

4. Results and discussion

4.1. Surface roughness and internal stress

Atomic force microscopy shows that all CH_x films are smooth, with r.m.s. surface roughness of 0.13–0.17 nm over sampling areas of $5 \times 5 \mu\text{m}^2$. This compares favorably with the r.m.s. surface roughness of 0.07–0.1 nm for the silicon substrates. The compressive stress in these films is minimal, ranging from 0.19 to 0.26 GPa.

4.2. Friction vs. hydrogen concentration

Fig. 2 shows a typical friction trace as a function of time. Typically, it takes approximately 30–60 s to obtain low steady-state friction. Fig. 3 shows the dependence of friction coefficient on hydrogen concentration in the sputter-gas, measured at a relative humidity of 8%. The minimum friction coefficient is approximately 0.01 at a hydrogen concentration of 25%. As a reference, elastic recoil measurements using 2.2 MeV helium ions show that carbon films deposited with 6 and 12% hydrogen in the sputter-gas contain 18 and 27 a/o hydrogen. In agreement with earlier work by Erdemir and co-workers, large amounts of hydrogen in the carbon films are needed to obtain low friction. Note that with further increase in hydrogen, the friction begins to increase. We will discuss this point later.

4.3. Friction vs. relative humidity

Fig. 4 shows the variation of friction coefficient as a function of relative humidity, obtained from carbon films grown at a hydrogen concentration of 25%. There appears to be an abrupt decrease of friction below 10% relative humidity. Again, this is consistent with the results of earlier studies [2,4–7], demonstrating the sensitivity of friction coefficient towards the testing environments.

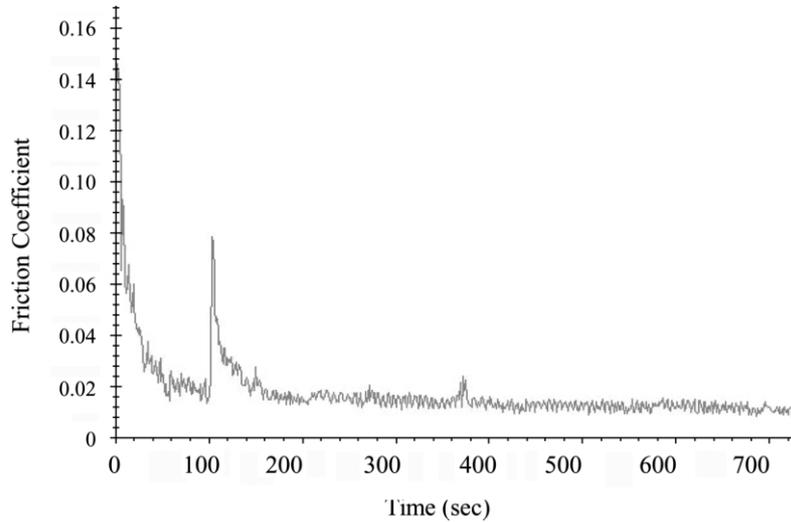


Fig. 2. A typical friction trace vs. time.

4.4. Load dependence of friction

Fig. 5 shows the dependence of friction coefficient on applied load obtained from a CH_x film grown in 25% hydrogen. At low loads, the friction coefficient appears to vary as $L^{-1/3}$, where L is the applied load. This is consistent with the notion that friction is controlled by adhesive interactions within the real area of contact. At higher loads, plastic deformation and possibly film fracture begin to dominate, thus increasing friction. This also explains the trend shown in Fig. 3, in which CH_x films grown in 35% hydrogen have higher friction—these films are somewhat softer (Fig. 6) and more prone to plastic deformation. Assuming elastic Hertzian contacts with a composite modulus of 100

GPa, loading at 20 gm results in a maximum Hertzian contact stress of almost 600 MPa. Asperity contact pressures will definitely be much higher and therefore account for the observed load dependence.

4.5. MD simulation results and time-delay effects

Not surprisingly, MD simulation shows that surface hydrogenation reduces the friction coefficient (Fig. 7). One may argue that surface hydrogenation of carbon atoms creates a methane-like surface, thus weakening the adhesive interaction and hence reducing friction. Experimentally, it is not clear why it takes 30–60 s of sliding to attain low friction (Fig. 2).

Fig. 8 shows the evolution of the friction trace after different delay times. In the first test, it took approxi-

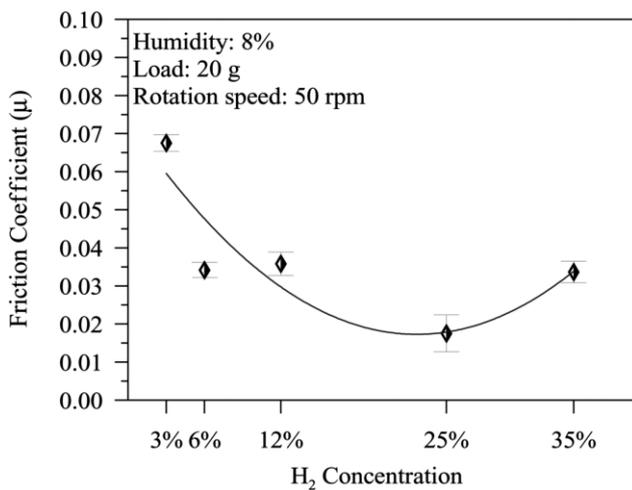


Fig. 3. Effect of hydrogen concentration on friction coefficient of CH_x films (relative humidity=8%, load=20 g, rotation speed=50 rev./min).

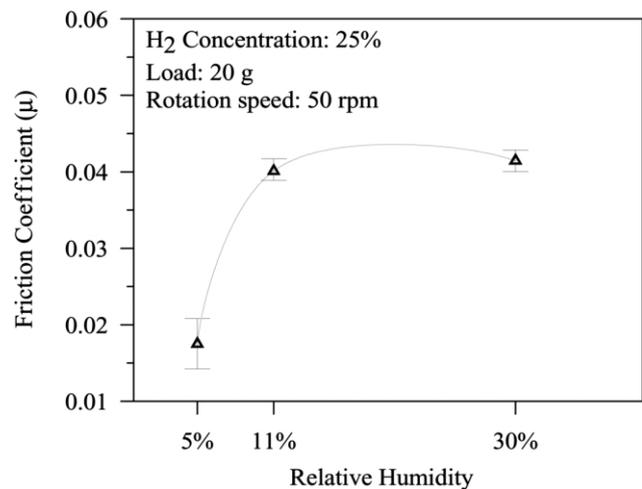


Fig. 4. Effect of humidity on friction coefficient of CH_x films (H_2 concentration=25%, load=20 g, rotation speed=50 rev./min).

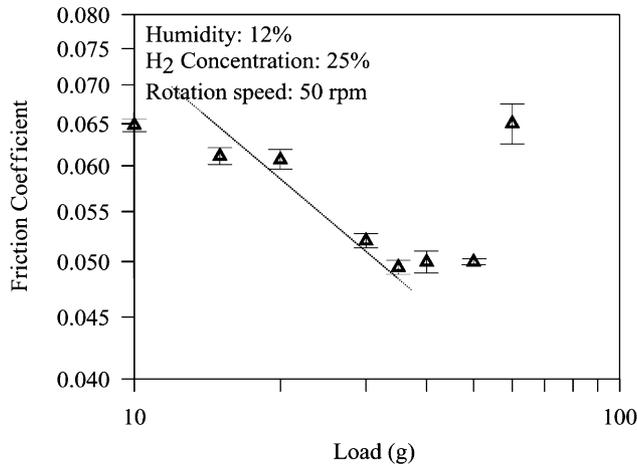


Fig. 5. Load effect on friction coefficient of CH_x films. The dotted line has a slope of $-1/3$ (relative humidity = 12%, H_2 concentration = 25%, rotation speed = 50 rev./min).

mately 40 s to reach the steady-state friction coefficient of 0.04. The rotation was stopped for different periods from 15 to 100 s, with the ball still in contact with the surface. Qualitatively, the recovery time to steady state appears to scale with the delay time. Heimberg et al. [8] made similar observations. They suggested that repeated wiping of the test track is needed to remove the adsorbed gases (presumably water vapor) and that time-dependent effects are due to the combined effects of gas adsorption and removal (by wiping).

5. Conclusions

Smooth and stress-free CH_x films were synthesized by reactive magnetron sputtering with pulsed d.c. power to the target and the substrate. Ball-on-disk tribotesting

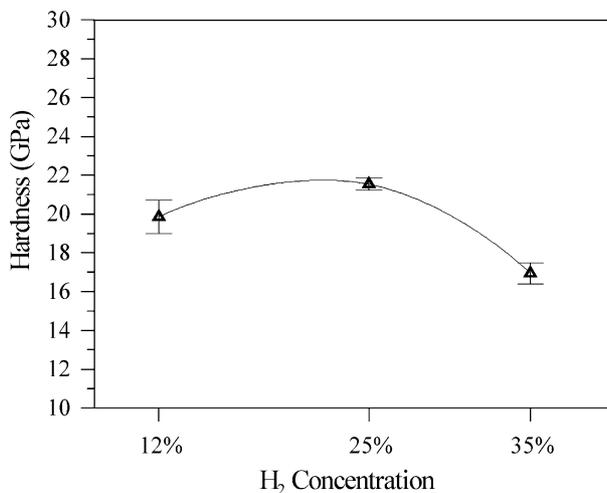


Fig. 6. Nanoindentation hardness versus hydrogen concentration of CH_x films.

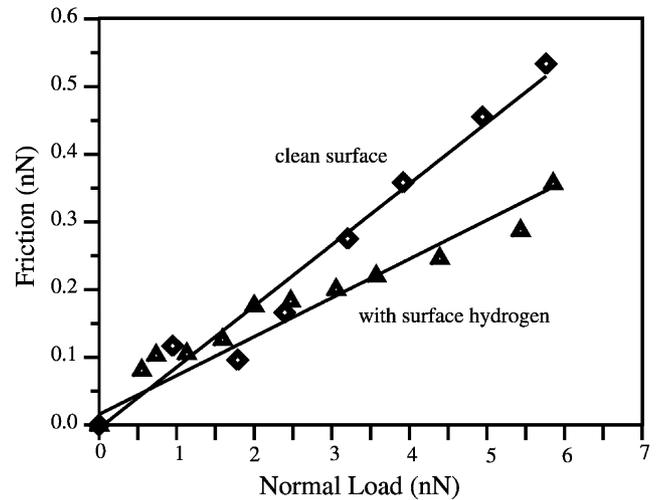


Fig. 7. Friction vs. load during sliding between two carbon surfaces, with and without surface hydrogenation, from MD simulation.

at room temperature showed that CH_x films grown in argon + 25% hydrogen attain friction coefficient in the 0.01 range at relative humidity of 5%. Excessive incorporation of hydrogen produces softening and degrades its friction performance at high contact stresses. Molecular dynamics simulation studies showed the reduction of friction coefficient with surface hydrogenation. These results suggest that pulsed d.c. magnetron sputtering can produce CH_x films with friction properties similar to those obtained by plasma-enhanced CVD. This provides a flexible avenue to explore the effect of dopants for the possible suppression of moisture effects.

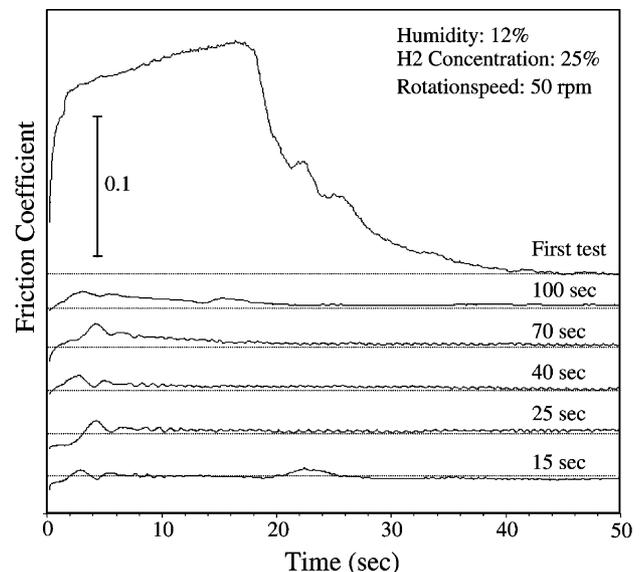


Fig. 8. Effect of delay-time on friction coefficient of CH_x films. The steady state value is 0.04 for all cases. The transient in the initial 2–4 s is due to the startup of the motor (relative humidity = 12%, H_2 concentration = 25%, load = 50 g, rotation speed = 50 rev./min).

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