High temperature nanotribology of ultra-thin hydrogenated amorphous carbon coatings

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The present study utilizes a high-temperature nano-mechanical system to perform shallow tribology experiments on an ultra-thin (3 nm) hydrogenated amorphous (a-C:H) coating at elevated temperatures up to 300 °C. The nano-scratch experiments (single scratch) provide *in-situ* measurement of the friction coefficient and material deformation of the carbon film. The nano-wear experiments (repeated scratches over an area) investigate the extent of wear under multiple scratches. The two groups of experiments reveal the temperature dependence of the tribological behavior of the coating. Raman analysis is performed to compare the chemical structure of the carbon film before and after heating. The spectrum reveals both the hydrogen and sp^3 content of the carbon film decrease after the high-temperature experiments, which contribute to deterioration of the wear resistance of the coating.

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1. Introduction

Amorphous Diamond-like carbon (DLC) is widely used in industry as protective coating material because of its high hardness, low friction coefficient and good wear resistance [1,2]. Composition-wise there are different types of DLC including hydrogen-free amorphous carbon (a-C), hydrogen-free tetrahedral amorphous carbon (ta-C), hydrogenated amorphous carbon (a-C:H) and hydrogenated tetrahedral amorphous carbon (ta-C:H) [3]. Also, there are amorphous carbon films with metals as additives such as tungsten (a-C:W, a-C:H:W), or with non-metal elements such as silicon (a-C:Si, a-C:H:Si). Their mechanical properties vary to satisfy different industrial needs [4].

In some electronic devices with miniature systems, such as Microelectromechanical systems (MEMS) or Nano-electromechanical systems (NEMS), amorphous DLC coatings are widely applied to protect functional thin films from mechanical wear and chemical corrosion. For example, in magnetic storage hard disk drives (HDD), a hydrogenated carbon (a-C:H) overcoat with a thickness of about 3 nm is typically deposited above the magnetic media. Comparing hydrogen-free a-C films and

hydrogenated a-C:H films, the absence or presence of hydrogen is critical in determining their tribological properties [5]. It was found that tribo-chemical wear is more dominant for a-C films where dangling bonds of carbon are saturated by oxygen from the environment [6] or gradual graphitization can be induced by shear stress [7]. The addition of hydrogen in a-C:H films is found to greatly reduce friction and wear, as observed in experiments [5,7—9]. There are debates on the mechanisms for how hydrogen reduces friction and wear of amorphous carbons. One explanation, the graphitization mechanism, believes that hydrogen promotes the formation of a self-lubricating graphitized tribo-film under sliding motions [5,9]. Another one, the passivation mechanism, believes that hydrogen saturates dangling bonds of carbon atoms at the sliding interface that may be otherwise oxidized [10,11].

Other than investigating the effects of hydrogen, extensive research has been carried out to study nano-wear and nano-mechanical properties as well as wear mechanisms and modelling of ultra-thin a-C:H coatings [12—15]. In recent years, durability of ultra-thin a-C:H coatings at high temperature is drawing increasing attention. For example, in the HDD industry, with the development of the heat assisted magnetic recording (HAMR) technology [16], there is increasing interest in the durability of coatings and thin films at high temperature. Meanwhile, MEMS/NEMS devices applying a-C:H films are also confronted with challenges at high temperatures due to overheating. Experiments using

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XPS and Raman Spectroscopy on thermally annealed a-C:H films have captured sp^3-to-sp^2 conversion, sp^2 clustering, hydrogen loss and carbon loss [17—21]. There have been some high-temperature tribology experiments conducted on thicker a-C:H films (150—500 nm) in the literature [22—24]. Van der Donck et al. performed *in-situ* high-temperature tribology experiments up to 150 °C and observed significantly increased wear of a-C:H films at 100 °C [22]. Thermal annealing tests found that wear of a-C:H films becomes severe at temperatures of 300 °C [23] and 400 °C [24]. The above mentioned high-temperature tribology tests were conducted on rougher and thicker a-C:H films of ~150—500 nm thickness which are not suitable for MEMS/NEMS applications. In addition, the tribology properties of a-C:H films exhibit thickness dependence [25—27]. Therefore, it is necessary to perform well-designed and independent tribology experiments at high temperatures to measure friction and wear of thinner a-C:H films (<10 nm).

In the present study, a high temperature nano-mechanical system and its evaluation of thermal drift rates, as well as the geometry of the probe are first presented. Then results from nano-scratch and nano-wear experiments at temperatures ranging from 25 °C to 300 °C are presented and discussed. An empirical relationship obtained from curve-fitting of the experimental data is proposed to reveal the temperature dependence of the wear rate. The deterioration of the wear resistance of the films is discussed based on Raman spectra analysis performed before and after the high-temperature experiments.

2. Experimental

2.1. Samples

The sample is a 3-nm thick hydrogenated amorphous carbon film (a-C:H) deposited on Nickel-Phosphorus (NiP)-plated Aluminum (Al) substrate using Plasma-Enhanced Chemical Vapor Deposition (PECVD). The sample surface is extremely smooth, having an RMS roughness of 0.2 nm, similar to that reported in the literature [14]. The PECVD technique uses a hot filament cathode to create a plasma from a hydrocarbon gas precursor. Substrate bias was used to modify the carbon properties during growth.

2.2. High-temperature tribology experiments

The experiments are conducted on a high temperature nano-mechanical stage (TI Premier, Hysitron Inc.). Inert gas (Argon) is introduced in the chamber to minimize graphitization of the diamond probe whose tip radius is calibrated and found to be 124.5 nm. The stage is enclosed with insulating materials to ensure thermal stability. The thermal drift rate of the system increases with temperature, being 0.08 nm/s at 25 °C and 0.17 nm/s at 300 °C, based on calibration experiments. Detailed description and calibration of this instrument is given in the supporting information. The present tribology experiments were performed sequentially at 25 °C, 100 °C, 200 °C, 300 °C and back to 25 °C. That is, the sample experiences gradual heating from 25 °C to 300 °C and then cooling down to 25 °C. At each testing temperature, the sample is retained for 15 min to ensure it is thermally stable.

2.3. Raman spectroscopy

A Raman confocal microscope made by Horiba Ltd (Jobin-Yvon LabRam) is used to take measurements over two a-C:H samples, one pristine and one following heat treatment at 300 °C. The laser wavelength is 633 nm and the exposure time is 15 s with 5 accumulations for each test.

3. Results and discussion

3.1. Nano-scratch experiments

For hard coatings with weak viscoelasticity, their mechanical behavior shows very small time dependence and ramp-load scratch is an effective and convenient method to evaluate their tribological properties. In the literature, there are applications of ramp-load scratch in investigating tribological properties of carbon coatings [14,28,29].

Fig. 1 (a) shows a schematic of the ramp-load scratch experimental set up. The transducer controls both the lateral sliding distance and the normal load that is applied on the diamond probe. In general, there are three steps for the ramp-load scratch experiments, namely: (a) the pre-scan, (b) the scratch and (c) retrace (or post-scan), see Fig. 1(b). In the pre-scan step, the probe is moving laterally on the sample surface with a small contact force of 2 μN to ensure contact and tracing the surface topography. The pre-scan step is used for data correction that removes any misalignment of the normal displacement due to tilt or gradient of the sample surface. In the scratch step, the transducer applies the ramp load increasing linearly from zero to the peak load, while moving the probe laterally with a constant speed for a specified sliding distance. In the present experiments, we use a peak load of 30 μN corresponding to a sliding distance of 5 μm, and the duration of the experiment is 15 s. The resulting loading rate is 2 μN/s and the scratch velocity is 0.33 μm/s. The scratch step measures the in-situ scratch depth and the in-situ friction force (converted to friction coefficient). In the retrace step the probe moves backward from the peak-load point back to the beginning point of the ramp-load scratch, with a small contact force (2 μN), in order to measure the residual depth of the scratch groove.

3.1.1. In-situ and residual scratch depths

Fig. 2 plots the in-situ scratch and residual depths at room temperature before heating (a), 300 °C (b) and room temperature after heating (c). The in-situ scratch depths increase almost linearly with the load and shows "jump points" at depths of about 3—4 nm where the probe is penetrating through the 3 nm thick coating.

Fig. 3 shows the scanning probe microscopy (SPM) images and cross-sectional profiles at the maximum-load points after the scratch experiments at 25 °C (before heating), 300 °C and 25 °C (after heating). The ramp-load scratch experiments cause a groove after the probe plowing on the sample. With the same height scale, the grooves provide visual characterization of the extent of wear. Before heating, the carbon film shows very slight wear near the peak load, while at 300 °C, the scratch mark is deeper and initiates at smaller force. Note that in both cases the scratch is initiated at 0.5 μm away from the top of the image and completes at the bottom of the image (5 μm long).

Fig. 4 displays the extracted quantitative results for the in-situ and residual depths at the peak load. Both in-situ and residual depths show similar variation trends. They increase with temperature and cannot recover after heating, implying irreversible reduction of wear resistance. Please note that NiP has a higher hardness and constant elastic modulus at elevated temperature of 400 °C [30]. Thus, the increased in-situ and residual depths could be attributed to softening of the carbon film.

3.1.2. Friction coefficient

Low friction resistance is an important advantage of a:C—H films as coating materials. Fig. 5 reports the in-situ friction coefficient during the ramp-load scratch experiments. All friction coefficients are high at the beginning and then tend to be constant. At the initial stage of nano-scratch experiments, the friction coefficient is usually