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Effect of feed gas composition effects on the nanotribological properties of diamond-like carbon films

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ABSTRACT

A series of experimental nanoindentation, nanowear and nanoscratch tests was conducted to investigate the relationship between the nanotribological characteristics of diamond-like carbon (DLC) and feed gas composition used for the deposition. The DLC films were deposited on silicon substrates in radio-frequency plasma enhanced chemical vapor deposition system with a mixture of hydrogen and methane gases. Raman spectroscopy results show that the integrated intensity ratios (I_D/I_G) of each profile correlate with sp^2/sp^3 ratios. The result also indicates that the hydrogen content in the source gas has a significant influence upon the sp^2/sp^3 ratio and hydrogen-to-carbon ratio in DLC films. It is demonstrated that the sp^2/sp^3 ratio decreases with increasing hydrogen content in the DLC film. Our result also reveals that a significant relationship between the hydrogen content and the nanotribological characterizations of the DLC films, namely lower hydrogen-to-carbon ratio leads to higher hardness, elastic modulus, friction coefficient, and lower wear depth. The surface reinforcement can be attributed to the fact that variation of surface energy arises from the different carbon hybridized states (sp^2/sp^3 ratio), which improve the surface properties via the hydrogen content in the source gas and associated nanotribological characteristics.

1. Introduction

For decades, diamond-like carbon (DLC) films have attracted a desirable interest from both industry and the scientific community. DLC is a unique coating material for hardening the surface of moving mechanical parts, especially for tribological applications. DLC coatings are attractive for tribological applications because of their favorable properties including low friction coefficient, high mechanical hardness and excellent chemical inertness. DLC coatings have been the subject of growing attention within tribological applications as a result of their high hardness, high wear resistance, low friction coefficient, excellent chemical inertness, and their potential for use in a variety of energy-saving applications. Previous studies show that preparation methods can result in different compositions and rations, hence affect the film properties (composition, carbon bonding, surface roughness, mechanical strength, tribological behavior and electrical resistivity) [1–10]. In general, the sp^3- and sp^2-bonded carbons have been revealed to coexist in amorphous or crystalline carbon microstructures and nanostructures [11–17].

Fontaine et al. [17] studied the effect of the hydrogen contents on the friction coefficient of DLC films. Their results showed that the friction coefficient for lower hydrogenated DLC films rises up to 0.6. By contrast, in the case of DLC films with the higher hydrogen content, the friction decreases down to lower values (less than 0.01). Therefore, the hydrogen content of the DLC films and the nature of the carbon–hydrogen bonds are now widely recognized to play a paramount role on the friction coefficient observed. A similar performance has also been reported for the tribological behaviors of hydrogenated and hydrogen-free DLC coatings by Ronkainen et al. [18]. Recently, many research works have been published on tribological phenomena of DLC films using a pin-on-disk tester or ball-on-disk tribometer [19–22]. However, such conventional tests based on continuum theory might break down when the physical dimension falls in the nanometer regime. Recent development of nanotechnology provides a unique opportunity to microscopically manipulate various nano-mechanisms to achieve desirable tribological performances and good interfacial behaviors. In this study, we have employed nanoindentation to characterize tribological properties of DLC thin films for which a depth-sensing technique also was utilized to determine mechanical properties through the analysis of the load-depth curve. These DLC films have been deposited on a silicon substrate using radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) method with pure methane gas (CH_4)

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or a mixture of H_2 and CH_4 gases as the source gas. The nanotribological and nanowear properties for the DLC films were investigated by the nanoscratch tests. The topography of the wear tracks of samples prepared using various H_2 contents in the fed gas was examined by scanning probe microscopy (SPM). Moreover, the role of H_2 content in the deposition process on the properties of DLC films was examined using Raman spectroscopy, which has proven to be a powerful method to characterize DLC films.

2. Experiments

In this present study, the DLC films were deposited on a silicon substrate using the capacitively-coupled radio frequency (RF) plasma enhanced chemical vapor deposition (RF-PECVD) method [23]. The substrates were mounted on the RF-powered electrode with a negative dc self-bias of 220–250 V. The electrode was cooled in flowing water to keep the substrate near room temperature during the deposition of DLC films, and the substrate temperature was measured using a K-type thermocouple. The substrate surface was always cleaned by argon ion bombardment for 30 min before DLC deposition. The hydrogen and methane mixture was used as the gas precursor for the deposition at 1.4 Pa pressure. With the methane flow rate fixed at 20 sccm, the H_2 flow rate was varied to adjust the H_2 composition. The DLC films were deposited at a fixed RF power of 200 W, and the resulting DLC films of thickness up to 1.4 μm were achieved after 50 min of RF-PECVD method. The sp^2/sp^3 bonding states and integrated intensity ratios (I_D/I_G) of the DLC films with different amounts of hydrogen have been estimated using the Renishaw inVia micro-Raman spectrometer. The Raman system employed was an argon ion laser with a wavelength of 532 nm [14,21]. The spectra were recorded by the computer and analyzed with the Gauss-curve fitting method to find out the characteristics of D band and G band, including the peak position, FWHM (full width at half maximum), and integrated intensity. The Raman spectra of the DLC films prepared from various source gases revealed broad Raman features at 1560 cm^{-1} and shouldered features at 1350 cm^{-1}. The Raman curves are fitted by the two Gaussian profiles: one corresponds to the D-band related to the disordered structure and the other corresponds to the G-band related to the graphite structure.

A Hysitron nanoindenter (Hysitron Inc.) has been employed to measure mechanical and tribological characteristics, including the hardness and reduced modulus. The theory for nanoindentation proposed by Oliver and Pharr [24] was adopted to characterize the hardness and Young's modulus. For the determination of hardness and Young's modulus, the relation of the contact area and indentation depth for a Berkovich indenter with a face angle of 65.3° can be expressed as

$$A = f(h_c) = 24.5h_c^2 + c_1h_c^1 + c_2h_c^{1/2} + c_3h_c^{1/4} + \cdots + c_8h_c^{1/128} \quad (1)$$

where A is the projected area of contact, and h_c is the indentation depth. The first term in Eq. (1) represents the area function of a perfect Berkovich indenter, and the other terms represent the correction for tip wear due to usage. We can calculate the hardness of a material by dividing the maximum indentation load P_{max} by the projected area of contact A

$$H = \frac{P_{max}}{A}. \quad (2)$$

In the depth-sensing nanoindentation, the projected area of contact can be substituted into Eq. (3) to calculate the reduced Young's modulus E_r

$$S = \frac{2}{\sqrt{\pi}}E_r\sqrt{A} \quad (3)$$

where the stiffness, $S = dp/dh$, is obtained as the slope at the very beginning of the unloading load–displacement curve [21]. Note that by curve fitting, we can express the unloading load–displacement curve as a polynomial function and take the derivative of this polynomial function to obtain the slope. The Young's modulus of the specimen E_f is then obtained from the E_r by following equation,

$$\frac{1}{E_r} = \left\{\frac{1-2\nu_f^2}{E_f}\right\}_{specimen} + \left\{\frac{1-2\nu_i^2}{E_i}\right\}_{indenter} \quad (4)$$

where ν and E are Poisson's ratio and Young's modulus, respectively, and the subscripts f and i refer to the specimen and indenter material. The coefficient of friction is calculated as

$$\mu = \frac{F_L}{F_N} \quad (5)$$

where F_L is the lateral friction force and F_N is the normal force measured.

A conical indenter was used to scratch the DLC film for the measurement of friction coefficient. Both the applied normal force and friction coefficient were determined by dividing the friction force with the normal force. In this study, various normal forces of 500, 1000, 2000, 3000, and 4000 μN have been applied, respectively. In general, the error due to the substrate effect increases with increasing indentation depth and with increasing elastic mismatch between film and various substrates [25–27]. To minimize substrate effects in the nanoindentation test, the proper indentation depth has been limited to less than 10% of the film thickness [28,29] and, furthermore, reasonable mechanical properties of thin film can be extracted. A series of ten indentations was performed for each sample. For the interfacial adhesion measurement, the normal force was slowly increased during indentation with a constant indentation velocity of 125 μN/s. Nanocrystalline DLC films have strain- and strain rate-dependent properties and show substantially different behaviors when the indentations are produced under various indentation velocities [30–33]. Therefore, a constant indentation velocity has been chosen to load on the DLC samples in order to avoid strain-rate hardening and creep susceptibility on the measurements [34]. Simultaneously, the friction force also was measured, in which a sudden jump in the friction force indicates the delamination of DLC film. This critical normal load provides an indication of the interfacial adhesion of DLC film with the substrate. For the nanowear test, the conical indenter with a tip radius of approximately 2 μm was moved back and forth within an area of 1×1 μm to scratch the DLC film surface with the applied normal load of 50 μN and speed of 4 μm/s. After the nanowear test, a SPM (Shimadzu SPM-9500J2) apparatus is used to measure the wear depth of the specimens. The measurement tip is made of Si_3N_4 with a tip radius of approximately 20 nm mounted on a cantilever of lower stiffness, thereby yielding greater sensitivity in measurement. A constant scan speed of 1 μm/s is used and a constant load of 10 nN is applied to the cantilever.

3. Result and discussion

The Raman analyses are performed for various DLC films derived from pure methane and various hydrogenated methane gas discharge plasmas. The results, shown in Fig. 1, indicate that the film structure contains both G-band and D-band, in which the two peaks in the curves correspond to peaks for G-band and D-band, the former being centered at 1560 cm^{-1}, the latter at 1350 cm^{-1}. In general, the shift of G band to a lower wavenumber usually reflects the increase of sp^3 bonds, in which the I_D/I_G ratio is related with the bond angle disorder and nature binding and thus decreasing with the increase of sp^3 bonds [35–38]. Specifically, the G band was shifted to lower wavenumber by increasing the hydrogen composition of the source gas, which implies the increase