Research article

Ultra-low friction of fluorine-doped hydrogenated carbon film with curved graphitic structure

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Fluorine-doped hydrogenated carbon film was grown by chemical vapor deposition technique using CH_4 and CF_4 as feedstock, with a pulse DC-bias power supply. The structure of as-deposited film was characterized by transmission electron microscopy and Raman spectra. The results suggested that the film could be considered as composite thin film with curved graphitic structures embedded in amorphous carbon matrix. The mechanical properties and friction coefficient were tested by TI 950 TriboIndenter and UMT-2 at humidity of 30%, respectively. The results showed that the film exhibited high hardness (~11.04 GPa), good elasticity recovery(~83%) and ultra-low coefficient of friction (~0.01). Copyright © 2013 John Wiley & Sons, Ltd.

Keywords: fluorine-doped hydrogenated carbon film; curved graphitic structure; tribological property; mechanical property

Introduction

Amorphous hydrogenated carbon (a-C:H) films have attracted much attention, because they can afford both low friction and high wear resistance, and thus are promising for a wide range of tribological application, such as high precision bearing, biomedical implants, hard disks and molds.[1] However, there are also some problems for a-C:H films, such as high compressive stress and environmental sensitivity. These shortcomings can be improved by the incorporation of elements, such as silicon,[2,3] fluorine,[4,5] nitrogen[6,7] and metals.[8] Among them, considerable attention has been given to the fluorine-modified a-C:H films, because fluorine-doped a-C:H films could greatly improve the inertia and reduce the surface free energy. Moreover, the passivation of surface carbon atom's dangling bonds by fluorine is thought to hinder interaction with the environment and counterface materials, resulting in a stable surface with a low coefficient of friction. However, when the fluorine content is lower than 20 at%, the fluorinated carbon films have possessed good tribological property, while the fluorine content is higher than 40 at %, the films appear to be soft with poor wear resistance.[9] The hydrogenated amorphous carbon films(a-C:H) containing at least 40% hydrogen can reach to the ultra-low coefficient of friction.[10] That is to say, for ultra-low friction of the fluorinated carbon film, the passivation of surface carbon atom's dangling bonds by fluorine is not enough since the fluorine content is required to be lower than 20 at% for getting good tribological behavior. Furthermore, the incorporation of fluorine causes many terminations of C–C bonds and less cross-linking, because the coordination number of carbon is four and that of fluorine is one.[11] This reduction in cross-linking leads to a diminution in hardness, elasticity recovery and wear resistance. Hence, how to obtain the ultra-low friction and improve the hardness and elasticity recovery of fluorinated carbon film is a problem to be solved.

The hardness of the carbon films is not only related to the amount of sp^3 C, but also dominated by the microstructure. Some amorphous carbon films showed high hardness though containing a high number of sp^2 C, such as amorphous carbon films with graphite crystal microstructure, carbon and carbon nitride films with fullerene-like microstructure.[12–14] They all showed high hardness and super elasticity. The reason was attributed to the interlinking of graphene planes by sp^3 bond.

In our previous work, a new kind of fullerene-like hydrogenated carbon (FL-C:H) film has been prepared,[15,16] which has not only high hardness (up to 19 GPa) and good elasticity (elasticity recovery of 83%), but also super low friction coefficient in air (drop to 0.009). Moreover, it was proved that nano-scale allotropes of carbon in carbon matrix, such as multilayer graphene, C_{60} and carbon nanotube, can endow the films outstanding mechanical and tribological performance.[14,17,18]

In this work, we try to introduce nanostructure to fluorine-doped hydrogenated carbon film to gain good mechanical and low friction properties. The results indicate that the fluorinate-doped hydrogenated carbon film with curved graphitic structure possesses high hardness, high elastic recovery and low friction.

Experimental

The fluorinate-doped hydrogenated carbon film with curved graphitic structure (CG-C:H:F) film was deposited on Si(100) substrates by chemical vapor deposition (CVD). The chamber was pumped down to 1.0×10^{-3} Pa. Prior to deposition, the substrates were cleaned by argon discharge with 300 sccm gas flow at 5.8 Pa working pressure and a discharge voltage of -800 V for 30 min. Then, feedstock of the mixture of CH_4 and CF_4 were introduced into the chamber to reactive for 120 min. The flow rate of CH_4 and CF_4 were kept at 10 sccm and 20 sccm, respectively. The deposition pressure was 15 Pa. The film was deposited by a DC-bias accompanied with a pulsed constant current power supply, DC-bias dc power

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was −800 V and the parameter of the dc pulse constant current power (as the auxiliary power) was set as: voltage: 500 V; pulse frequency: 100 KHz; duty cycle: 60%. The substrate was not heated. In this paper, a-C:H film was deposited as a reference sample; the differences of the deposition parameters were that it substituted H_2 for CF_4, no auxiliary power, other parameters were the same.

Microstructure characterization of the films were performed by high-resolution transmission electron microscope (HRTEM), and the samples with thickness of up to 20 nm for HRTEM analysis were grown on freshly cleaved NaCl wafers, and placing the freed fragments of the film onto Cu grids. The HRTEM images were obtained using a JEOL2010 TEM and operated at 200 KV with a point resolution of 0.19 nm. Further investigation on the structure of as-deposited films was collected by micro-Raman with a LABRAM HR 800 microspectrometer at an excitation wavelength of 532 nm (2.3 eV). TI 950 TriboIndenter was used to obtain the mechanical propertied of the films; the indentation depth was 100 nm. The tribological performances of the films were tested by a UMT-2 at humidity of 30%. The Al_2O_3 ball with a diameter of 5 mm was used. All frictional tests were performed under a load of 30 N. The amplitude was 5 mm, and the frequency was 15 Hz. XPS has been carried out on a Perkin-Elmer PHI-5702 system using monochromated Al K_α irradiation to investigate the chemical states of carbon in films.

Results

Microstructure

The HRTEM was used for microstructure investigation, the a-C:H film was produced for comparison. The plan-view TEM micrograph and area electron diffraction (SAED) of the CG-C:H:F film are shown in Fig. 1, that there are some agglomerated nano-particles with a diameter of about 20–30 nm in the film (Fig. 1(a)), and the SAED shows three diffuse rings, a, b and c, corresponding to ~1.23 Å, ~2.13 Å and ~3.45 Å interplanar spacing, respectively. The innermost and brightest ring with ~3.45 Å lattice spacing matches the graphite d002 spacing and the spacing between the carbon layers in bucky onion structures;[19,20] the other rings with ~1.23 Å and ~2.13 Å lattice spacing coincide with the graphite d110 spacing and d100 spacing, respectively.[18] HRTEM image of the plan-view specimen is shown as Fig. 1(b). The film is amorphous, but some curved graphitic features are revealed. The interplanar spacing of the carbon layers equals 3.45 Å,[21] which is larger than that of graphite (3.35 Å).[22] The increase of the interplanar distance in this film, as compared with that of graphite, is probably due to the curved graphitic planes, since this increase has been observed in carbon nanotube structures.[23,24] The plan-view TEM micrograph and SAED of the a-C:H film were shown in Fig. 1(c) and Fig. 1(d), neither a cross-linking network nor curved graphitic structure was observed in the a-C:H film.

The nano-structured carbon species are many, such as diamond, graphite, C_{60}, etc. Raman spectroscopy is the useful non-destructive technique that distinguish the differences among the various carbon structures. Figure 2 shows the micro-Raman spectra for the films. For the CG-C:H:F film, besides a broad overlapped D (graphitic) and G (disorder induced) band similar to that of a-C:H, broad weak peaks near 430 cm^{-1}, 720cm^{-1} and 860 cm^{-1} can be also observed; these peaks were caused by the phonon density of states and phonon dispersion curves of graphite.[25] While no peaks near 430 cm^{-1}, 720 cm^{-1} and 860 cm^{-1} could be observed in the visible Raman spectrum of the a-C:H film.
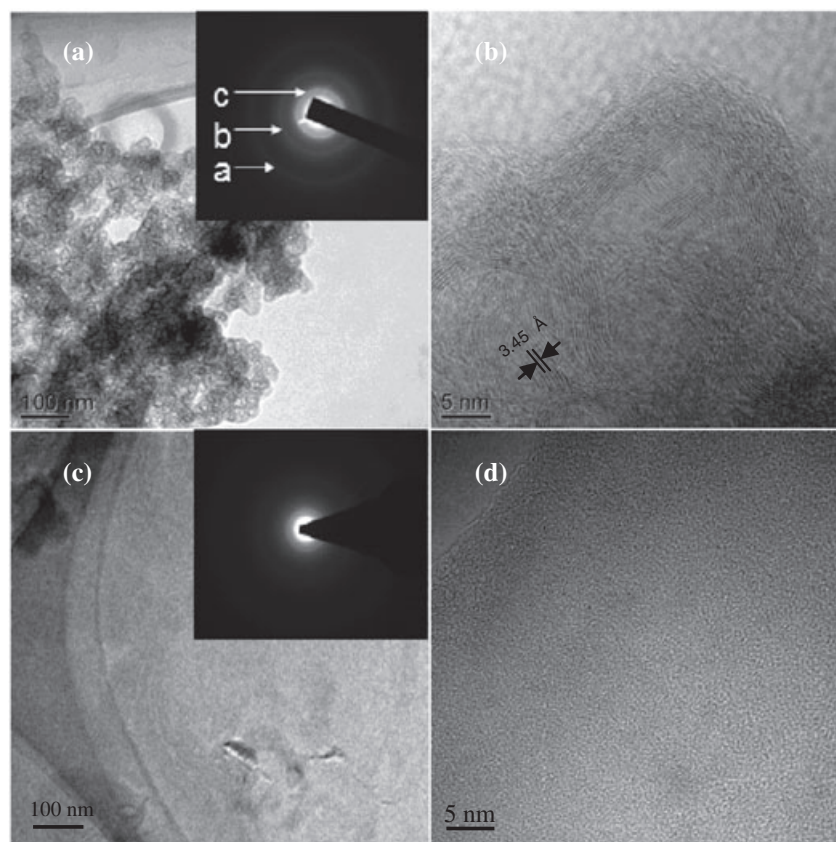

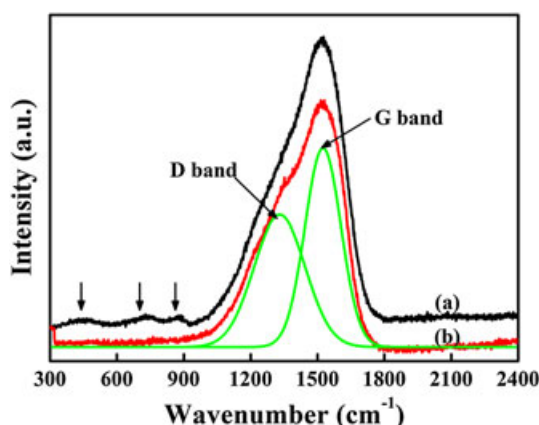**Figure 1.** TEM images and SAED pattern of the CG-C:H:F (a, b) and a-C:H (c, d).

Figure 2. Raman spectrum of the CG-C:H:F film(a) and a-C:H film(b) in the range of 300 cm^{-1}–2400 cm^{-1}.

Figure 4. The coefficient of friction (COF) of the CG-C:H:F film (a) and the a-C:H (b).

Hence, it can be believed the structure of carbon nanoparticles with curved graphitic structure embedded in an amorphous matrix was present in the fluorinate doped hydrogenated carbon film.

Mechanical and tribological properties

Figure 3 shows the load–displacement curves obtained from the nanoindentation measurement for the CG-C:H:F film and a-C:H film. The elastic recovery R is as high as ~83% for the CG-C:H:F film compared to ~74% for the a-C:H film. At the same time, the hardness is as high as 11.4 GPa for the CG-C:H:F film compared to 5.6 GPa for the a-C:H film.

The frictional behavior of the CG-C:H:F film against Al$_2$O$_3$ ball was described in Fig. 4. An a-C:H film was also presented for comparison. It can be found that the CG-C:H:F film exhibited a ultra-low friction coefficient ($\mu = 0.01$) in ambient atmosphere with 30% relative humidity, while the friction coefficient of the a-C:H is higher, 0.03.

Discussion

From the above experimental results, it can be concluded that it is possible to improve the mechanical and tribological properties of the films by the incorporation of curved graphitic structure.

Generally, high hardness and elasticity recovery have been attributed to the presence of a high percentage of sp^3 C in
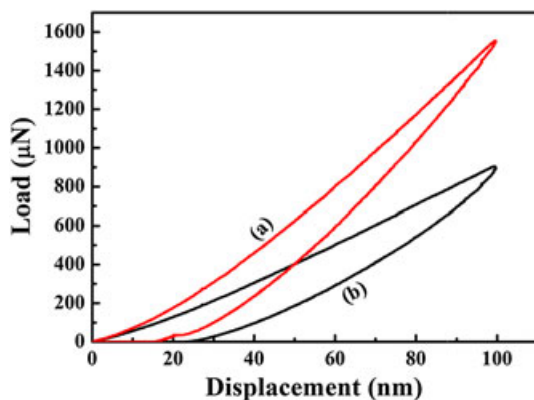

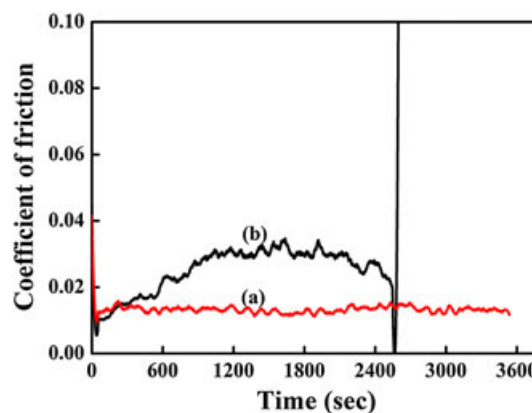**Figure 3.** Nanoindentation load–displacement curves for the CG-C:H:F film (a), and a-C:H film (b).

amorphous carbon films. However, the CG-C:H:F film has a lower content of sp^3 bonded carbon than the a-C:H film, as proved by the XPS analysis (Fig. 5). The C1s spectrum of CG-C:H:F (Fig 5(a) was decomposed into three Gausian-distributing curves; the two main curves with the peak position at 284.3 eV and 285.1 eV indicated C=C bonds and C–C bonds, on which C were sp^2 and ap^3 hybridized, respectively. Another minor curve with the peak position at 286.8 eV indicated C–CF bonds, and the F content was 4.04%, the sp^3/sp^2 was 0.78; The C1s spectrum of the a-C:H film was decomposed into two Gausian-distributing curves, the peak position at 284.3 eV and 285.1 eV indicated C=C bonds and C–C bonds, and the sp^3/sp^2 was 1.36. These results indicate that the mechanical properties of carbon films are strongly dependent not only on the amount of sp^3 bonding but also on the fabricated nanostructure in the film. It is believed that the good mechanical properties of fluorinate doped hydrogenated carbon film, caused by the existence of curved graphitic embedded in the amorphous matrix. These micro-clusters of curved graphite interconnected closely, and formed a network structure by sp^3 bonds linking,[26] and it extends the extraordinary strength of a planar sp^2-coordinated carbon network into three dimensions and prevents interplanar slip and bond breaking by reversible bond rotation and bond angle deflection, so the film exhibits good mechanical property. Moreover, the unique structure that curved graphitic dispersed in amorphous carbon phase might restrain dislocation migration, assist the relaxation of stress and also improved the mechanical property.

The results also demonstrated that the CG-C:H:F film had ultra-low friction in air. Various mechanisms have been proposed to explain the friction and wear behaviors of fluorinated carbon films. Alpas[27] investigated the material transfer mechanisms between aluminum and fluorinated carbon interfaces and indicated that the formation of AlF$_x$ is the main reason of the low coefficient of friction, but in other researches, the coefficient of frictions for fluorinated carbon films tested against steel surface and Si$_3$N$_4$ in air were also low.[28,29] Miyamoto[30] investigated the tribological properties of the fluorinated carbon films by molecular dynamics and quantum chemical calculation and concluded that the general low coefficient of friction of fluorinated carbon films was mainly attributed to the high chemical inertness of the fluorinated carbon films by fluorine passivating the surface dangling bonds; the friction coefficient of the fluorinate-terminated diamond carbon film was obtained to be 0.07. However, when it comes to investigate the deep cause of ultra-low friction of
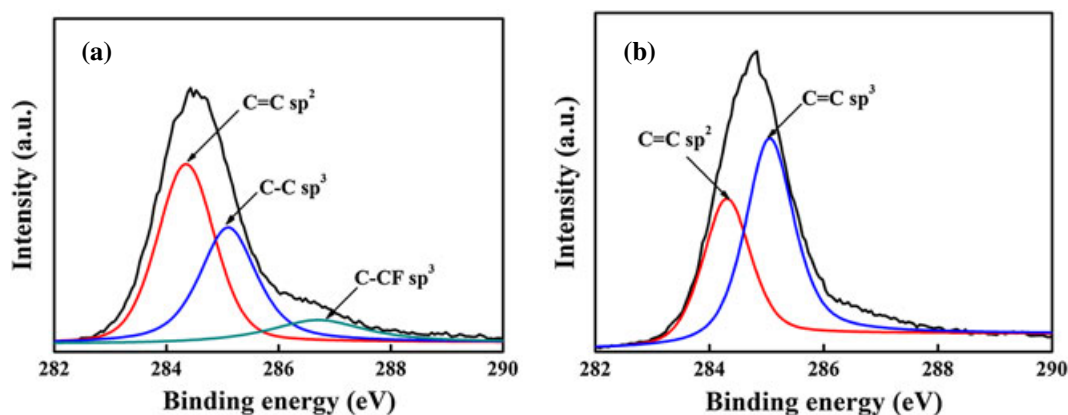
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Figure 5. XPS C1s core-level spectra for the CG-C:H:F film (a) and a-C:H film (b).

fluorinate doped hydrogenated carbon film, both standpoints could not explain it well. The surface passivating model might give some effect, but the deep cause of super-low friction need further study.

In order to get clear confirmation of this super-low friction behavior of the CG-C:H:F film, the Raman spectra of the wear track was employed. Figure 6 shows the Raman spectra collected surface, inside the wear track and on the debris of the GC-C:H:F film after tested at 30 N load. Near 430 cm^{-1}, 720cm^{-1} and 860 cm^{-1}, broad weak peaks can be all observed in these three curves. Besides, on the debris, there's a broad peak at 1200 cm^{-1}, and it's more obvious than the surface's. This peak originates from seven-member carbon rings of curved graphite. From the result, it can be seen the structures after friction have no obvious changes. Hence, it can be believed that the super-low friction of the CG-C:H:F film in this paper may be caused by the formation of curved graphite. Formation of the curved graphite interfacial layers diminished interlayer bonds, which provides a near-frictionless sliding plane. This view was proved by Tianbao Ma.[31] He investigated the shear-induced phase transition from disorder to lamellar ordering in amorphous carbon films by molecular dynamics simulations. A super-low friction or super-lubricity regime with coefficient of friction of approximately 0.01 originates from the extremely large repulsive and low shear interactions across the sliding interface. Moreover, it is well known that the friction of carbon films mainly arises from the chemical interactions caused by the strong free σ-bond at the sliding interfaces. Therefore, the elimination of free σ-bonds on sliding surfaces of carbon films is an essential

requirement for achieving ultra-low friction. The surface of the film with curved graphite was rich in saturated π-bond, which reduced the adhesion of the friction surface caused by unsaturated σ-bonds. Furthermore, high hardness and excellent elastic recovery of the film bestowed the good wear resistance to the film, assuring the good load-bearing and immediate recovery of friction-induced deformation during friction, which is beneficial to achieve long-term ultra-low friction. Hence, such graphite nanostructure might be responsible for the significant change of the properties, which induced the improvement of the tribology.

Conclusion

The CG-C:H:F film was obtained by CVD in CH$_4$ and CF$_4$ atmosphere without heating. This curved graphitic structure fluorinated carbon film exhibited high hardness, good elasticity recovery and ultra-low friction in 30% humid. The reasons for the good mechanical properties and super-low friction could probably attribute to the unique structure that curved graphitic dispersed in amorphous carbon phase, which restrains dislocation migration, assists the relaxation of stress and reduces the interfacial shear force in the sliding process.

Figure 6. Raman spectra collected surface, inside the wear track and on the debris of the CG-C:H:F film after tested at 30 N load.

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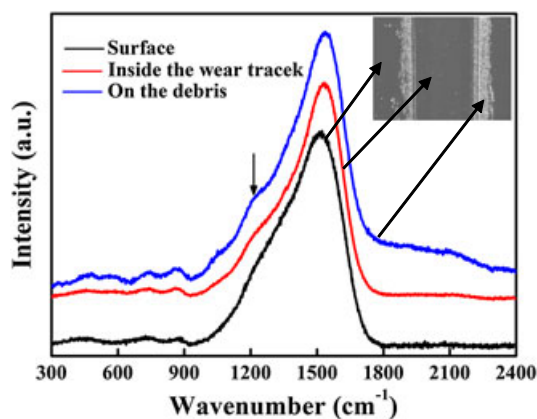[11] R. Hatada, K. Baba, *Nucl. Instrum. Meth B.* **1999**, *148*, 655.

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