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Featured letter

Synthesis of fullerene-like hydrogenated carbon films containing iron nanoparticles

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ABSTRACT

Fullerene-like hydrogenated carbon films deposited by plasma enhanced chemical vapor deposition (PECVD) as compared with other methods can attain super-low friction and wear. But they often have bad adhesion to steel substrate and their structures are tailored by non-metal elements as F, N etc. In this work, we have prepared the films on steel balls by the combination of PECVD and plasma nitriding, among which iron nitride particles are sputtered and introduced in the films. The films have longer wear life and better adhesion to the steel substrate due to the N diffusion from iron nitride particles to the atom matrix of the ball.

1. Introduction

Special carbon nanostructures are introduced into hydrogenated amorphous carbon (a-C:H) films and thus significantly enhance the material properties at the macroscale. Fullerene-like (FL) a-C:H films, named for the presence of highly curved graphitic structures as in C_{60} fullerenes [1–12], are unlike traditional a-C:H films that have the presence of sp^3 hybrids with tetrahedral coordination. However, the films without hydrogen incorporation have shown poor friction behavior. Recently, hydrogenated FL carbon (FL-C:H) films exhibit excellent mechanical and frictional properties [13–15]. Nowadays, different chemical vapor deposition (CVD) techniques have been used to improve film performances, such as plasma enhanced CVD (PECVD) [13–15], ECR-CVD [16], magnetron sputtering [17] etc. And some non-metal elements such as F, N etc. have been doped to tailor FL structures [18,19]. By comparison, the films deposited by PECVD can attain lower friction and wear, for example, the films [13] have shown super-low friction in humid air and N_2 gas. Moreover, the introduction of metal elements has been rarely reported. In this work, we have prepared FL-C:H films on steel balls by the combination of PECVD and plasma nitriding, among which iron nitride particles are sputtered and introduced in the films.

2. Experimental

FL-C:H films with thickness of 500 nm were deposited on steel balls (Φ5) by the PECVD as Si substrates in previous studies [15]. In the PECVD, the substrate was ultrasonic cleaned in ethanol and acetone for 10 min and thus placed in the deposition chamber (1.0×10^{-3} Pa). The PECVD was carried out in the chamber with a precursor of pure methane, and the deposition parameters were set at the pressure of 12 Pa and the substrate bias of 1000 V (depositing time: 180 min). Another films (~500 nm) were prepared on steel balls (Φ5) by combining the PECVD with plasma nitriding. The plasma nitriding (depositing time: 2 h) was used after Ar+ etching, and the deposition conditions included the negative voltage of 1200 V (pulsed frequency: 80 kHz; duty cycle: 0.8) and the N_2 gas flow rate of 90 SCCM. The process could form iron nitride particles which were considered to be the nitrogen carrier, and resulted in the formation of iron nitride layer on steel substrates and thus enhanced the adhesion of carbon films. After the process, the PECVD was carried out for 1 h. Then, the plasma nitriding (depositing time: 30 min) and PECVD (depositing time: 1 h) were alternately operated and repeated 3 times. The film structures and chemical elements were evaluated with the combination

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of transmission electron microscopy (TEM, FEI Tecani F30), Raman spectroscopy (Jobin-Yvon HR-800 with an excitation wavelength of 532 nm), and Energy Dispersive X-Ray spectroscopy (EDX, JSM-5600LV). For TEM analysis, the films (~20 nm) were deposited on a single crystal NaCl wafer, and then placed on a Cu grid by dissolve the wafer. Friction properties of the films against FL-C:H films on Si substrates were assessed on a reciprocating ball on-disc tribotester (relative humidity: 35%; Load: 10 N; frequency: 8 Hz). The surface morphologies and wear scars on steel balls were investigated by a 3D surface profilometry (ZYGO Nexview, USA).

3. Results and discussion

FL-C:H films were deposited on steel balls by the PECVD as Si substrates in previous studies [15]. Fig. 1a shows the TEM image of the films, which display curved and frequently intersected graphite planes with the layer spacing of about 0.34 nm. The layer spacing accords with the graphite face (0002) [20]. The curvature observation is due to the introduction of pentagonal and heptagonal rings distributed randomly throughout a hexagonal network as C_{60}. The film structure is further confirmed by Raman spectroscopy, which is an effective way to distinguish FL structure in a-C:H films. Compared with the graphite-like (GL) films containing two D and G peaks (Fig. 2), the spectrum shows three additional peaks at ~700, 860 and 1200 cm^{-1} apart from a bulging peak at ~1530 cm^{-1}. These peaks are due to the curved graphite planes in FL-CNx [18] and FL-C:H films [14,15]. Moreover, compared with the GL films, the downshift of G peak and the disappearance of D peak indicate the decrease of I_D/I_G (from ~0.84 of GL to 0.69 of FL-C:H). The difference is caused by bond angle distortion and other topological disorders, as well as by the introduction of sp^3 bonds in the graphite structure [21,22]. Topological disorders like pentagons are introduced into the graphite planes, and then the planes curve to trigger bond angle distortion and other disorders which cause the softening of the vibration frequencies. I_D/I_G reflects the average aromatic cluster size [21], and decreasing I_D/I_G means that aromatic clusters become smaller and more disordered. Compared with the GL films, the sample includes mainly sp^2 sites in some chain-like configurations and puckered ring-like configurations that consist of five-, six-, and seven-C ring. In other words, mainly sp^2 phase for the FL-C:H is not organized in sixfold aromatic rings as the GL films, but organized in chains or in rings that are distorted.

In order to enhance the adhesion of the carbon films to steel, plasma nitriding was introduced prior to the PECVD of forming FL-C:H films. Iron nitride particles would be sputtered from the top electrode plate by plasma nitriding, and wrapped by subsequent carbon films. The plasma nitriding and PECVD were alternately operated and repeated 3 times. Fig. 1b shows the chemical element of the films deposited by PECVD and plasma nitriding. The Fe element is uniformly distributed in the films (the set in Fig. 1b) and its content is 15.8 wt% (mass percent). The sample has a similar profile with the FL-C:H films deposited by PECVD. Usually, the Raman spectra for carbon-based films are fitted by G (~1560 cm^{-1}) and D (~1380 cm^{-1}) peaks. For example, the method is used to fit the spectrum of graphite-like films (Fig. 2). However, the simple two symmetric-line fits are difficult to analyze the FL carbon films, owing to the presence of ~700, 850 and 1200 cm^{-1} peaks which are related to the presence of pentagonal and heptagonal rings [18,23]. Based on the model suggested by Doyle and Dennision [24] in the case of FL carbon films, the symmetric multipeak fits [18,25] can provide a much better fit quality, which include four peaks at ~1200, ~1360, ~1470 and ~ 1560 c m^{-1}. The films show a strong signature of odd rings, meaning the

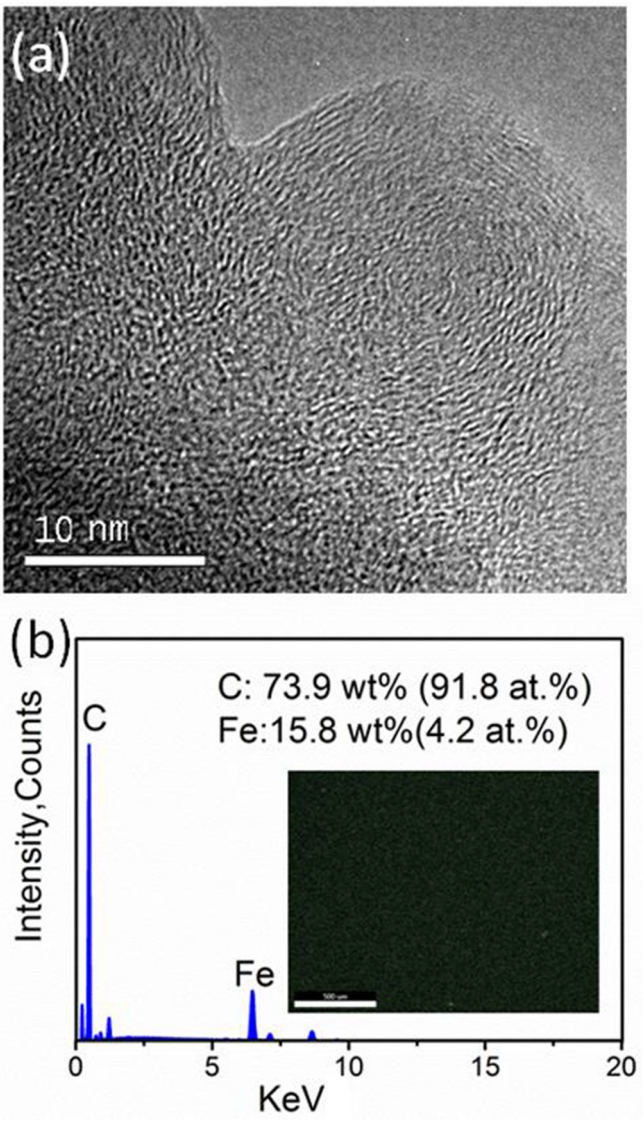

Fig. 1. (a) TEM of FL-C:H in PECVD; (b) EDX of FL-C:H in PECVD + plasma nitriding.

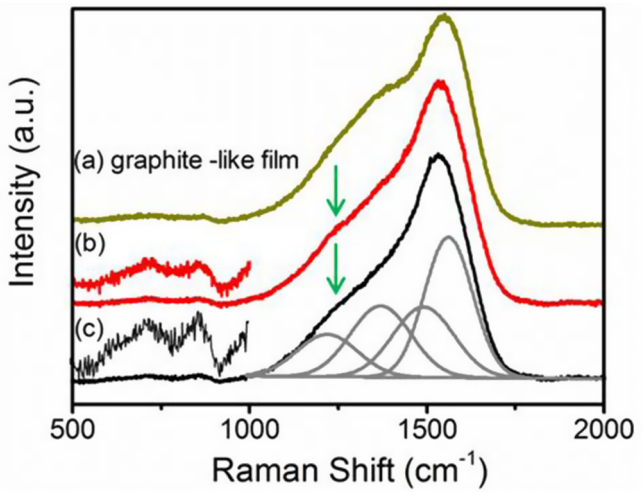

Fig. 2. Raman spectra of GL and FL-C:H films in PECVD and PECVD + plasma nitriding.