



Research paper

The correlation between nano-hardness and elasticity and fullerene-like clusters in hydrogenated amorphous carbon films

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ABSTRACT

Fullerene-like hydrogenated carbon films have outstanding mechanical and frictional properties, but their structures have never enjoyed elaboration. In this study, we investigate the relation between nano-hardness and elasticity and fullerene-like clusters by changing energy supply form (direct current and pulse) and H₂ concentration in the feedstock. It is found that the films have a network of H-rich amorphous carbon and H-poor or -deficient fullerene-like carbon, and the network change can affect hardness and elastic recovery. This is due to the energy minimization process of the film growing system in a very short pulse period at low temperature.

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1. Introduction

Hydrogenated amorphous carbon (a-C:H) films have shown very interesting properties which can be ideal in various applications such as optical, mechanical, and tribological applications etc [1,2]. To produce special carbon nanostructures in a-C:H films is the focus to significantly enhance material properties at the macroscale. Fullerene-like (FL) carbon materials [3–12] are unlike traditional a-C:H films that have the presence of sp³ hybrids with tetrahedral coordination. Recently, fullerene-like hydrogenated carbon (FL-C:H) films exhibit mechanical and tribological properties over a wide range, such as 15–35 GPa of nano-hardness, 75–89% of elasticity, and 0.08–0.005 of coefficient of friction. The variation are achieved by tuning such films' preparation methods [13–17], additional element [18–20] or carbon nanostructure incorporations [21]. Among them, the films prepared by plasma chemical vapor deposition show super-low friction (frictional coefficient < 0.01) and wear in both dry N₂ and open air [22]. The method because of its own advantages [13] is also used to explore another possibility for applying for nanoparticles [23,24]. However, an initial consensus is made that the variation originates from unique FL

structures. Nevertheless, the detailed structure changes as the degree of curvature and cross-link of graphitic basal planes, and the role of H in the changes have never enjoyed elaboration. In the FL-CN_x films [4,11], doped nitrogen atoms replace carbon atoms in the graphitic planes, and promote some bending and crosslinkage. The curvature in the basal planes introduces high elastic recovery, and cross-linking between the curved planes induces the hardening mechanism. Thus, it is very necessary to further reveal the relation between H bonded sites and degree of curvature and crosslinkage in graphitic basal planes.

In this study, we clarify the relation between nano-hardness and elasticity and fullerene-like clusters in a-C:H films by changing ex-situ energy supply form (direct current (dc) and pulse) and H₂ concentration in the feedstock. First, majority of H atoms are distributed in a-C, and a small amount are distributed in FL structures. Second, the H distribution causes a carbon network composed of H-rich a-C and H-poor or -deficient FL, which is tailored by ex-situ energy supply form and H content. The network change can affect hardness and elastic recovery. Low H promotes the formation of FL arrangement, and inhibits the development of a-C, attaining higher hardness and elastic recovery. Dc supply form easily leads to the formation of large graphitic layer stacks, and whereas pulse form tends to induce the curvature and crosslink of graphitic layers each with shorter sizes. The structural differences result from the energy minimization process of the film growing system in a very short pulse period at low temperature.

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2. Experimental section

2.1. Film preparation

All the samples were produced on Si (0 0 1) substrates by using plasma chemical vapor deposition (CVD). Prior to the deposition, the distance between the two electrodes was fixed at about 5 cm, and the deposition chamber was pumped down to 10^{-4} Pa. They were derived from the mixed gases of methane and hydrogen with different energy supply form (dc and pulse) and different partial pressure ratio (2:1 and 1:2) in the feedstock. The samples were thus called as dc 2:1, dc 1:2, pulse 2:1 and pulse 1:2 for short. The other deposition conditions such as negative voltage, duty cycle and pulsed frequency were shown in Table 1. For comparison, an a-C:H film was produced at the same deposition system (dc, bias voltage -1200 V, CH_4 30 SCCM, and H_2 20 SCCM). The films were about 500 nm thick.

2.2. Characterization

The structures of these films were characterized by high resolution transmission electron microscopy (HRTEM, FEI Tecani F30), Raman spectra (Jobin-Yvon HR-800), Reflection fourier-transform infrared (FTIR) measurement (Nexus 870), and X-ray photoelectron spectroscopy (PHI-5702, operating with Al-K α radiation and detecting chamber pressure of below 10^{-6} Pa). The samples for HRTEM observation were deposited on a freshly cleaved NaCl wafer followed by dissolution of the NaCl wafer with water. Prior to XPS detection, Au thin films about 0.2 nm thick were deposited on the tested carbon film surfaces. The surface treatment method minimized the charging effect in the XPS analysis, and helped to detect the changes of C 1s peaks. When the films were detected in Raman spectrometer, the power on the films was kept below 0.5 MW m^{-2} to avoid their unintentional damage, Nanoindentation was employed to explore nano-hardness and elastic recovery (R). R was defined as $R = (d_{\text{max}} - d_{\text{res}})/d_{\text{max}}$, where d_{max} and d_{res} were the maximum displacement at maximum load and the residual displacement after unloading, respectively.

3. Results and discussion

3.1. Nano-hardness and elastic recovery of FL-C:H films

Fig. 1 shows the nano-hardness and elastic recovery of a-C:H, dc 2:1, dc 1:2, pulse 2:1 and pulse 1:2 samples. All experimental data are performed more than five times, and are averaged. FL-C:H films (dc 2:1, dc 1:2, pulse 2:1 and pulse 1:2 samples) exhibit higher hardness and elastic recovery than a-C:H film. The result further confirms that the excellent mechanical properties are in close relation with the FL generation. However, two differences can be observed: (1) both the hardness and elastic recovery decreased with the increasing H_2 gas ratio; (2) pulse-method has better mechanical properties than dc-method at the same gas ratio. Therefore, it is very necessary to reveal the reason causing the differences.

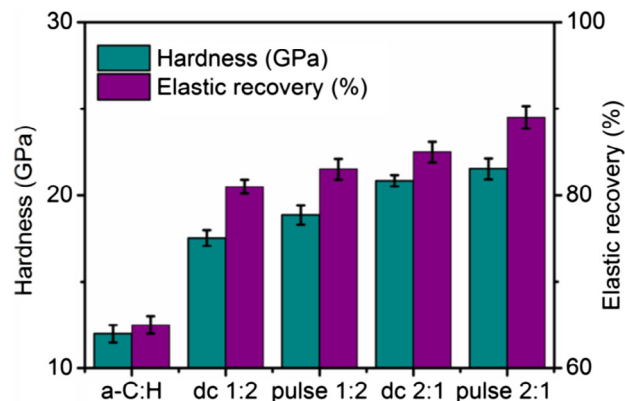


Fig. 1. Hardness and elastic recovery of a-C:H, dc 2:1, dc 1:2, pulse 2:1 and pulse 1:2 samples.

3.2. Basic structure features of FL-C:H films

Fig. 2a can show the coexistence of amorphous carbon (red lines) and cross-linked or curved graphitic sheets (yellow lines) in the dc 2:1 sample, as compared with the a-C:H film (Fig. 2e). This is confirmed by corresponding selected area electron diffraction (SAED) pattern, which displays two rings at 1.15 and 2 Å from the a-C, and an innermost diffuse ring at 3.50 Å. The 3.50 Å ring matches the interlayer (0002) spacing of graphite and the spacing between the carbon layers in bucky onion structures (Fig. 2b) [25,26]. The observed curvature results from the presence of both pentagons and heptagons distributed randomly throughout a hexagonal network. Evidence for pentagons and heptagons in the sample can be obtained using its Raman spectrum due to the presence of a weak peak at $\sim 1200 \text{ cm}^{-1}$ [22,27,28]. In the early Raman fit model, G (graphitic) and D (disorder induced) bands are used to fit a-C spectra based on the active vibrational modes of disordered nanocrystalline graphite, or glassy carbon. The references have proposed the four peaks' fit method, which involves A_{1g} at 1360 cm^{-1} and E_{2g} at 1569 cm^{-1} for six C-atom rings, A_{1g} at 1470 cm^{-1} for pentagons, and A_{1g} at 1200 cm^{-1} for heptagons. The fit method is realized by fixing the position of four Gaussian peaks and the fractional contribution of each vibrational frequency to the Raman spectra is obtained by the intensity ratio of each bands (Table 2). The Raman fit shows that the odd ring content is about 38.9% and the hexagonal ring content is about 61.1% (Fig. 2c). Thus, the dc 2:1 sample has a carbon network with a-C and FL.

However, additional bonding information is obtained by IR spectrum of the dc 2:1 sample. Always, the $sp^1 \equiv \text{C-H}$ mode centres on 3300 cm^{-1} , the $sp^2 = \text{CH}_n$ mode lies from 2975 to 3085 cm^{-1} , and $sp^3\text{-C-H}_n$ mode lies from 2850 to 2955 cm^{-1} [1]. In Fig. 2d, there are no obvious peaks corresponding to $sp^2\text{-CH}_n$ stretching mode above 3000 cm^{-1} , as compared with the a-C:H film. In other words, majority of hydrogen atoms in the sample are predominantly bonded to sp^3 -bonded carbon atoms. Two peaks at 1580 and 1640 cm^{-1} can be seen, which are respectively assigned to vibrations due to sp^2 carbon bonding in aromatic rings and olefinic chains [1]. The presence of sp^2 carbon mixtures induce

Table 1
The deposition conditions of FL-C:H films.

	CH_4/H_2 ratio	Gas pressure (Pa)	Power supply	Bias voltage	Duty cycle (%)	Pulsed frequency
dc 2:1	2:1	15	dc	-850	–	–
dc 1:2	1:2	31	dc	-850	–	–
Pulse 2:1	2:1	18	Pulse	-900	50	60 kHz
Pulse 1:2	1:2	35	Pulse	-900	50	60 kHz

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