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Research paper

Bond topography and nanostructure of hydrogenated fullerene-like carbon films: A comparative study

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ABSTRACT

Fullerene-like nanostructural hydrogenated amorphous carbon (FL-C:H) films were prepared by dc- and pulse- plasma enhanced chemical vapor deposition technique (PECVD). Both the films exhibit relatively stresses (0.63 GPa) in spite of their FL features and nanostructural bonding configurations, especially the pentagonal carbon rings. The creation of pentagonal rings is not fully driven by thermodynamics, but is closely related to compressive stress determined by the ion bombardment at the discharged state of the pulse- and dc- discharged plasmas methods. The dc method leads to FL's basal planes which contain less cross-linkages, and causes amorphous strongly hydrogenated structures.

1. Introduction

Fullerene-like carbon materials present outstanding mechanical properties that, unlike traditional diamond-like carbon, cannot be attributed to the presence of sp^3 hybrids with tetrahedral coordination but to the highly sp^2-based FL structures. The so-called FL arrangements stem from the curvature and interconnection of the graphitic basal planes [1]. The inducement, function and nanostructure (referring to the orientation, corrugation and crosslinking of the basal planes) of the FL arrangement have been detailed reported in the FL carbon nitride (FL-CN_x) films [2–4]. In the FL-CNx films, the doped nitrogen atoms, replacing carbon atoms in the graphitic planes, promote some bending and cross-linkage, and thus the incorporated nitrogen is confined in the FL structures. These films exhibit a large variation in basal plane curvature and therefore extension and alignment of sheets, providing possibilities for tailoring its mechanical and tribological properties over a wide range. In the recent decades, hydrogenated FL structures produced from the hydrogen containing environment have been emerged and well developed, due to their tribological applications achieving super-low friction and near wear-less [5,6]. Despite this move toward application, there is still much that is not understood about the topology, or nanostructural bonding configurations, within the hydrogenated FL films. For example, hydrogen atoms, unlike incorporated nitrides, may prefer to be bonded to amorphous carbon atoms since they cannot be incorporated in a fullerene network and is difficult to be stored in a fullerene cage in the form of molecules [7]. Thus, the variations in the basal plane's curvature, extension and cross-linking may lead to changes of hydrogen distribution or topography within the hydrogenated FL films.

In this letter, we have prepared two FL-C:H films by dc- and pulse- PECVD, and then discussed their nanostructural characterizations about the orientation, corrugation and cross-linking of FL's basal planes and the topography such as hydrogen distribution. Both the films exhibit low stress by introducing FL structures with pentagonal and heptagonal rings. However, the dc- FL-C:H film contains different FL structural features such as nearly parallel plane stacks with less cross-linkages and large bending radii, as compared with the pulse- film. Their structure analysis by Raman spectra and Fourier transform infrared spectra, reveals a close relationship between the different FL features and the distribution of their bonding structures such as five-, six- and seven C-atom rings, and hydrogen bonding. Combing the films' growing environments, we can assume that the creation of pentagonal rings is not fully driven by thermodynamics, but is closely related to compressive stress, which can be associated with the ion bombardment at the discharged state of the pulse- and dc- discharged plasmas methods.

2. Experimental details

FL-C:H films were deposited onto Si (100) substrates at room temperature using a PECVD system (Fig. 4(a)). The diameter and the height of the cylinder chamber were both 450 mm. The

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diameter of the top circularly electrode upper electrode and the sample holder were 300 and 200 mm, respectively. Their distance was set as 50 mm. The deposition feedstock has the mixed gas of methane and hydrogen with a partial pressure ratio of 1:2. A pulsed (duty cycle of 50%) bias of −1000 V or a dc bias of −1000 V was applied to the substrate holder for the films. Prior to the deposition, the deposition chamber was pumped down to 10^{-4} Pa followed by introducing mixed gas to 15 Pa. The substrate temperature heated by plasma bombardment did not exceed 120 °C. The structures of as-deposited films were revealed by high resolution transmission electron microscopy (HRTEM, FEI Tecani F30), Raman spectra (Jobin-Yvon HR-800) and Fourier transform infrared spectra (Nexus 870). The sample for HRTEM observation was deposited on a freshly cleaved NaCl wafer followed by dissolution of the NaCl wafer with water.

3. Results and discussion

Fig. 1(b) and (c) shows SEM images of hydrogenated carbon films' cross section deposited with pulse- and dc-PECVD, respectively. The thickness of the pulse-film is 60% of the dc-film, which is consistent with the study [8] that the thickness of the FL-C:H film has decreased with the decreasing pulse duty cycle or decreasing plasma discharging time. Their residual stresses were calculated from the curvature of the film/substrate composite using Stoney's equation. Both the stresses reach to a very low value (Fig. 1(a)). As we known, the stresses of FL-C:H films are correlated to their own nanostructural characterizations. Representative topologies of FL structural- and amorphous- carbon atom clusters now exist, and their distribution within a given film is known to be inhomogeneous. Therefore, it is necessary to perform other detections to reveal the spatial distribution of two types of carbon clusters above, and the correlation between stress and structure characterizations.

The plan-view HRTEM micrographs of pulse- and dc- FL-C:H films are shown in Fig. 2(a) and (c), respectively. It is observed that curved graphitic planes are embedded in an amorphous carbon matrix. The observation indicates that odd member rings such as five- and seven-member carbon rings are present in the structure, which induce the curvature in the basal planes and form fullerene-like structures [9–12]. Notice that, distinctive basal planes with less cross-linkages and large bending radii are observed in the dc-film, as shown in Fig. 2(c). Raman spectroscopy is also used to probe the quality of the two samples due to its ability to distinguish different carbon structures. The data in this letter were collected by Raman spectrometer with an excitation wavelength of 532 nm. The power on the samples was kept well below 0.5 MW m^{-2} to avoid unintentional damage of the samples. Considering the presence of curved graphite structures as shown in Fig. 2(a) and (c), it is rational to use four Gaussian peaks with wavenumbers of 1230, 1383, 1470, and 1560 cm^{-1}, respectively [13–17]. As can be seen from Fig. 2(b) and (d), the peaks at 1230 cm^{-1} (originates from seven-member carbon rings of curved graphite) and 1470 cm^{-1} (comes from five-member carbon rings of curved graphite) confirm that the two films have high volume of pentagonal and heptagonal rings. The high content odd rings' production can lead to structural relaxation of the C–C network, resulting in the films lower stress. Furthermore, compared to the dc-film, the pulse-film contains fewer pentagonal rings, which needs further discussion.

FTIR spectroscopy is performed to identify the nanostructural characterizations of the films. Generally, hydrogen easily enters into sublayer and causes higher compressive stress in depositing a-C:H films [18,19]. While for the case of FL-C:H films, hydrogen atoms may prefer to be bonded to amorphous carbon since they cannot be incorporated in a fullerene network. Thus, the hydrogen distribution or topography of the FL-C:H films would change along with the change of the nanostructure existing in the FL-C:H films, such as the curvature, extension and cross-linking of the FL basal plane. In order to understand the role of hydrogen atoms in determining the structure of a carbon network, FTIR is worth to be considered. Fig. 3 shows the changes of approximate hydrogen bonding in pulse- and dc- FL-C:H films. Both the films show very weak intensity of C–H absorption at 1450 and 2950 cm^{-1}. This is consistent with our previous study [20] that the creation of high content of pentagonal and heptagonal rings need a lower hydrogen surroundings in depositing FL-C:H film. But, the dc-film shows stronger intensity of C–H absorption than the pulse- film, which means that there is higher hydrogen bonding in the dc-film. We attribute higher hydrogen bonding surroundings in the dc-film to its growing continuity. According to the view suggested by Chen et al. [8], the thickness of FL-C:H film is observed to increased linearly with the increased pulse duty cycle, Namely, the film only grow during the discharging process of pulse-discharged plasma. The pulse plasma's undischarged process can provide an opportunity for film annealing, which is often associated with hydrogen removal from the films. For the dc-film, it grows in a continuous discharged plasma environment and can't be annealed. Since hydrogen cannot be incorporated in a fullerene network, the

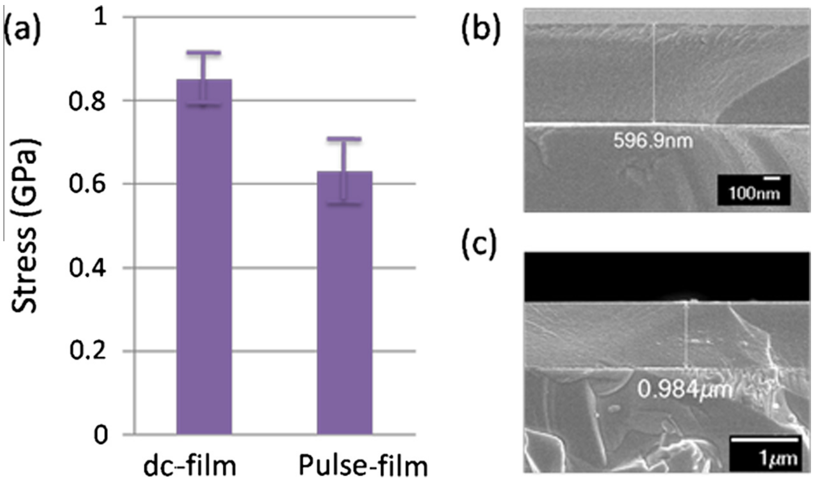

Fig. 1. Thicknesses (a) and corresponding compressive stresses of pulse- (b) and dc- (c) FL-C:H films.