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Stress relief patterns of hydrogenated amorphous carbon films grown by dc-pulse plasma chemical vapor deposition

Qi Wang [a,b], Chengbing Wang [b], Zhou Wang [b], Junyan Zhang [b], Deyan He [a,*]

[a] Department of Physics, Lanzhou University, Lanzhou 730000, China
[b] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

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ABSTRACT

Hydrogenated amorphous carbon films were prepared on Si (1 0 0) substrates by dc-pulse plasma chemical vapor deposition. The nature of the deposited films was characterized by Raman spectra and the stress relief patterns were observed by scanning electron microscope. Besides the well-known sinusoidal type and flower type patterns, etc., two different stress relief patterns, ring type and peg-top shape with exiguous tine on the top, were observed. The ring type in this paper was a clear ridge-cracked buckle and unusual. Two competing buckle delamination morphologies ring and sinusoidal buckling coexist. The ridge-cracked buckle in ring type was narrower than the sinusoidal buckling. Meanwhile peg-top shape with exiguous tine on the top in this paper was unusual. These different patterns supported the approach in which the stress relief forms have been analyzed using the theory of plate buckling.

1. Introduction

Diamond-like carbon (DLC) has been used as protective coatings in various tribological and optical applications for their mechanical behavior and stability [1,2]. But the reduction of stress in this material is still a technological challenge and many efforts have focused on this field [3–5]. Normally, it has been observed that there is strong contradiction between enhanced diamond-like characteristics and a tendency to delaminate or crack the film.

Usually, delamination or cracking of the films occurs due to excessive stress in these films and poor adhesion between the films and substrates. Some very interesting buckling patterns have been reported in carbon films deposited by other deposition technique [6–15]. Weissmantel and co-workers [8,9] first reported sinusoidal stress relief patterns of DLC films on glass and NaC1 substrates. Their study was, however, limited to the observation itself. Later, Nir [14] investigated the shapes of stress relief patterns such as sinusoidal buckling, straight cracking, strings of beads and cracking after buckling with theoretical analysis based on the linear theory of thin plates. Gioia and Ortiz [15] have compiled most of these patterns in their paper on delamination of compressed thin films. Buckling forms such as wavy wrinkles with definite shapes and widths were observed. Although buckling in these films is undesirable, the study of buckling is quite useful in estimating mechanical properties such as the Young modulus, adhesion energy, etc.

We prepared hydrogenated carbon films onto Si (1 0 0) substrates with a dc-pulse plasma chemical vapor deposition (CVD) system. This hydrogenated carbon films deposited with dc-pulse plasma CVD system showed excellent properties, such as ultra-low friction coefficient, high hardness and elastic recovery, etc. [16]. The residual internal stress plays an important role in determining and controlling the microstructures, surface morphologies and physical properties of thin films. In order to study the influence of stress on the properties of carbon films, hydrogenated carbon films were deposited with the introduction of Ar to the traditional mixture of methane and hydrogen as feedstock. The stress in the hydrogenated carbon films decreased with the content of Ar in the feedstock. The stress relief behavior of the hydrogenated carbon films took different patterns such as sinusoidal type, flower type, ring type and buckle type, etc. To our knowledge, even if there were some similar patterns like clock type, the ring type in this paper was a clear ridge-cracked buckle and unusual. Two competing buckle delamination morphologies ring and sinusoidal buckling coexist. The ridge-cracked buckle in ring type was narrower than the sinusoidal buckling. Meanwhile peg-top shape with exiguous tine on the top in this paper was unusual.

* Corresponding author. Fax: +86 931 4968295.
E-mail address: hedy@lzu.edu.cn (D. He).

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2. Experimental

In this paper, hydrogenated carbon films with thickness of 1 μm were deposited onto Si (1 0 0) substrates using a dc-pulse plasma CVD system. The feedstock CH_4 gas flow rate was kept constantly at 10.3 sccm. The whole H_2 and Ar gas flow rate was kept at 20 sccm. The Ar gas flow rate in the mixture was set to 0 sccm (0%), 5 sccm (25%), 10 sccm (50%), and 15 sccm (75%). Before deposition, the chamber was pumped down to 10^{-4} Pa and then argon plasma was fed into the chamber to etch the silicon surface for 30 min in order to remove the native oxides and residual contamination at dc-pulse negative voltage of 1000 V (pulse frequency: 20 kHz) with a duty cycle of 0.6 at pressure of 3 Pa. After that, the working gas was introduced into the chamber and the pressure was kept at 13 Pa. During deposition, the distance between the two electrodes was fixed at about 5 cm, and dc-pulse negative voltage of 1000 V (pulse frequency: 20 kHz) with a duty cycle of 0.4 was applied on to the substrate holder. The substrate was not heated. After deposition, Raman spectrum was introduced to reveal the structure of the films, and scanning electron microscope (SEM) was performed to analyze the stress relief patterns.

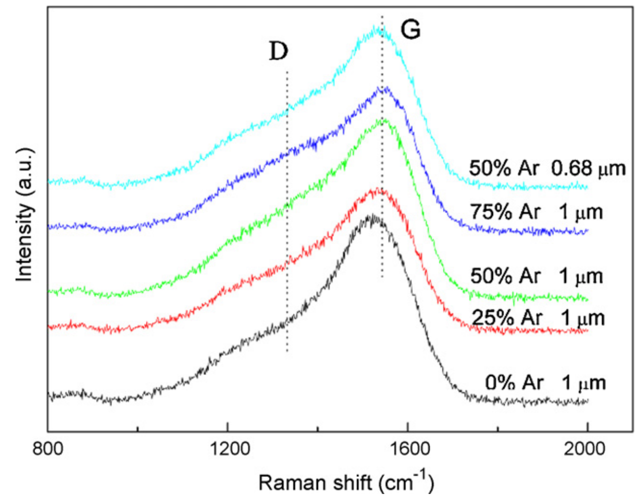

Fig. 1. Raman spectra of hydrogenated carbon film deposited by dc-pulse plasma CVD with different Ar content in feedstock and different film thickness at 50% Ar content in the feedstock of H_2 and Ar.

3. Results and discussion

3.1. Structure of the film

Raman spectrum is widely used to probe the qualities of carbon base films due to its ability to distinguish different microstructures. Raman scattering from π bonding is 50 times stronger than that from σ bonds [17]. Therefore, there are different degree resonances of the G (graphitic) and the D (disorder induced) bands, [18] and it limits direct estimation of the sp^3 and sp^2 bonding. Generally speaking, the G peak and D peak in a conventional hydrogenated carbon film will shift towards higher wavenumber and the D peak intensity will increase with decreasing sp^3 bonding in the films, which corresponds to the decreased diamond-like characteristics of the films. In this paper Raman data were collected by micro-Raman spectra with a LABRAM HR 800 micro-spectrometer at an excitation wavelength of 532 nm (2.3 eV). The power density on the sample was controlled carefully at 0.3 MW m^{-2} to avoid unintentional damage of the samples. The micro-Raman analysis was performed on local of film without cracks and delamination.

Fig. 1 shows the Raman spectra acquired from the deposited hydrogenated amorphous carbon films. There was a typical character of DLC films in the region of 1000–2000 cm^{-1}: a G peak around 1560 cm^{-1} originated from optical zone center vibrations (E_{2g} mode) of all pairs of sp^2 C atoms, in aromatic rings and olefinic chains; a D shoulder peak around 1380 cm^{-1} originated from the breathing modes of sp^2 atoms in clusters of sixfold aromatic rings [19,20]. The curves corresponded to the films deposited with 0%, 25%, 50% and 75% Ar in the mixture gas of Ar and H_2 within 80 min, and 50% Ar in the mixture gas of Ar and H_2 with 50 min. As the Ar glow content increased in the mixture, the D peak became more prominent, reflected with increase in D peak intensity.

Table 1 shows the Raman spectra fitting results that the increase of Ar flow led to the I_D/I_G ratio increase. Also, the position of G peak shifted to higher wavenumber and the width of G peak became narrow with the Ar flow content increase. This behavior could be attributed to stronger graphitic character, due to the large number or size of the carbon sp^2 units. At the same time, when the Ar glow content was kept at 50%, the I_D/I_G ratio decreased with the thickness of the film decreased from 1 μm to 0.68 μm. The position of G peak shifted to lower wavenumber and the width of G peak broadened with the thickness decrease, which could be attributed to stronger graphitic character in the thick film.

In as-deposited films, stress relief patterns appear promptly. Therefore, it is very difficult to measure the film stress before the relief patterns appeared. Meanwhile, some of the film cracks or peels off; the stress value from curvature radii according to the Stoney's equation is not real stress of the film. In this paper, we just try to give qualitative analyses on the stress of the films with Raman spectroscopy. Since micro-Raman spectra can detect the structure from local film. From the local of film without cracks and delaminations, micro-Raman spectra can reflect the relationship between the stress and deposition condition. According to the paper [21,22], the decrease of the compressive stress accompanied the decrease of ΔG in amorphous carbon films, and the decrease of the internal stress accompanied the increase of ΔG in amorphous carbon films. We can know the stress in our films decreased as the increased Ar in mixture gas, and the stress in our films increased as the increased thickness of film.

3.2. Patterns of stress relief

Many patterns of stress relief behavior have been found in DLC films [6–15]. Considerable effort has been made to understand the stress relief patterns, particularly in hard carbon films, and there have been attempts to study the thickness dependence of the buckling patterns by Matuda et al. [11] and Nir [14]. These include the well-known sinusoidal type, string of beads pattern, etc. In most cases, the buckling of the films extended from the outer edge of the substrate towards its interior over a distance proportional to the thickness of the film.

Table 1
Fitting result data of Raman spectra

Sample	Raman peak position (cm^{-1})		Raman (cm^{-1})	FWHM	I_D/I_G
	D-band	G-band	D-band	G-band	
0% Ar 1 μm	1338	1535	268	157	0.79
25% Ar 1 μm	1362	1545	281	148	1.18
50% Ar 1 μm	1377	1553	292	138	1.61
75% Ar 1 μm	1376	1555	293	130	1.80
50% Ar 0.68 μm	1362	1546	285	146	1.22