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Ripple surface generated on hydrogenated amorphous carbon nitride films

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Abstract

It is reported for the first time that the periodical ripple surface feature at micrometer-scale was observed on hydrogenated amorphous carbon nitride films deposited by pulse plasma chemical vapor deposition (CVD) technique. Nitrogen incorporation to hydrogenated amorphous carbon films and the different growing environments of pulse dc plasma discharge perhaps played crucial role in the surface morphology transformation of hydrogenated amorphous carbon nitride films.
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Keywords: Carbon nitride films; Ripple morphology

1. Introduction

Recently there has been much interest in understanding the size and shape dependent properties of low-dimensional structures, which are different from those of their bulk counterpart. Great effort has been devoted to fabricate unique film surfaces, which presents a rich gallery of engrossing patterns such as dots, wires, ripples, etc., during film deposition or postsputtering [1–5]. However, it remains a difficult challenge to fabricate functional film materials with desirable surface structures.

Amorphous carbon nitride (a-CN$_x$) films exhibit significant characteristics, such as high hardness and high elasticity [6,7], low friction coefficient [8,9], and infrared transparency [10], which reversely stimulate further study of carbon nitride films. One of the challenges is to achieve low surface roughness, which is concerned in practical application [11,12], On the other hand, few studies have been done to investigate the surface aspects of this kind of material [4,5,13].

Plasma chemical vapor deposition (CVD) is generally employed to produce hydrogenated carbon nitride films [14]. In plasma of continuous discharge, however, the densities of active species are almost in steady state and it is somewhat difficult to control their ratios as desired. Just after turning on or turning off the discharge, the density of each specie changes dramatically due to its production or loss with individual time constant. A repetition of transitional reaction stages makes it possible to control the ratio of radicals and to provide quite different growing environment in the continuous discharge plasma [15]. So, one may synthesize the films with larruping characteristic by pulse plasma CVD compared to by a plasma of continuous discharge. Some interesting results for material processing have been also reported [16–18].

We deposited hydrogenated carbon nitride films by pulse dc plasma CVD, and the results showed that the surface morphology of the films are strongly dependent on the pulse negative bias voltage, and for the first time, we found that a periodical ripple surface feature was generated on the hydrogenated amorphous carbon nitride films with large negative bias voltage applied during the film deposition process. By changing pulse negative bias voltage, a surface morphological transformation from periodical ripples to mounding coarsening was realized.

2. Experimental details

Hydrogenated carbon nitride films were deposited on Si (1 0 0) substrates by pulse dc plasma CVD using a mixture of
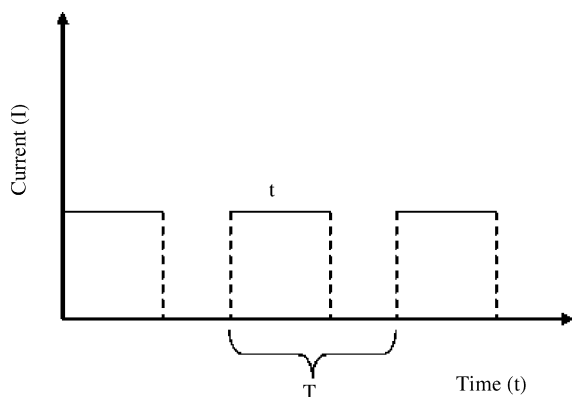

Fig. 1. The schematic diagram of pulse dc power current character.

methane and nitrogen as feedstock. The deposition conditions were as follows: (1) applied pulse dc negative voltage: 600–1000 V; (2) pulse frequency: 20 KHz; (3) duty cycle: 60%; (4) gas flow rate: CH_4 = 14 sccm and N_2 = 10 sccm; (5) deposition pressure: 20 Pa. The character of pulse dc power is shown in Fig. 1.

Here, the duty cycle in percentage is defined by the following equation:

$$\tau = \frac{t}{T} \times 100$$

where τ is the duty cycle, t the pulse ON power duration and T is total pulse period.

Prior to deposition the chamber was pumped down to 10^{-4} Par firstly and then the working gas was introduced into the chamber. The substrate was not heated and the temperature increase, which is less than 100 °C, in the chamber was mainly caused by the plasma heating effect. After the deposition, the films were analyzed by micro-Raman spectroscopy and 3D profilometer instrument. Micro-Raman spectra were recorded at room temperature using the 514 nm line of Ar^+-ion laser.

3. Results and discussion

Raman spectroscopy is popularly used to probe the quality of carbon base films due to its ability to distinguish between different bonding types and domain sizes. When nitrogen is introduced into a carbon network, the CN vibration frequencies for chainlike molecules and ringlike molecules are very close to those of pure carbon [19]. The modes are delocalized over both C and N sites due to the capability of N to acquire the same hybridizations as C atoms. Following this, the same approach as used for various carbon films can be applied to carbon nitride films.

Fig. 2 depicts Raman spectra of the amorphous carbon nitride films deposited at three different pulse dc negative bias voltages applied to substrate. Usually, disorder graphite has two significant Raman lines, so-called G peak and D peak. The major features of Raman spectra of amorphous carbon nitride films can be derived from corresponding features in the spectrum of graphite. The Raman spectrum of the film deposited at pulse dc negative bias voltage of −600 V shows
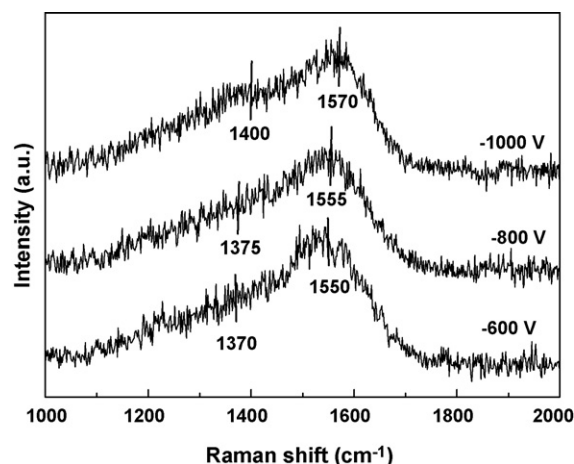

Fig. 2. Raman spectra of carbon nitride films deposited at pulse dc negative voltage of −600, −800, and −1000 V, respectively.

typical character of diamond-like carbon films: a G peak at around 1550 cm^{-1} due to optical zone center vibrations (E_{2g} mode) of pairs of sp^2 C atoms in aromatic rings or olefinic chains, and a D shoulder peak at around 1360 cm^{-1}, arises from the breathing modes of sp^2 atoms in clusters of six-fold aromatic rings [20,21].

In carbon films the position of the G mode can vary between 1500 and 1600 cm^{-1}. In sp^2 bonded a-C, the G mode is around 1520 cm^{-1}, lower than graphite due to bond angle distortions and other disorders which cause a softening of the vibration frequencies [22]. However, the G mode moves up with increasing sp^3 bonding in ta-C ($\sim$1575 cm^{-1}) since the remaining sp^2 sites change their configuration from rings to short chains and the vibration frequency moves toward the frequency of the C=C dimer embedded in the C–C sp^3 matrix. The C=C bond length in the chains is shorter, so the modes lie at higher frequency [22]. However in conventional a-C:H, an increased sp^3 content correlates with an increased H content. H saturates the C=C bonds, mainly converting sp^2 C sites into sp^3 =CH$_2$ and to ≡CH, rather than increasing the number of C–C bonds, as occurs when sp^2 a-C becomes ta-C. Thus, the change in the sp^2 configuration is not as ta-C. The a-C:H with maximum H content has a high sp^3 content and the D peak is very weak and the sp^2 sites are organized in very small clusters. As a-C:H retains some aromatic ordering of sp^3 sites, the increase in sp^3 fraction has an alloying effect, which causes the G wavenumber to move down. Furthermore, there is also a down-shift in the G peak at olefinic sites because H bonded to chains begins to resemble polyacetylene. This lowers the G frequency. Thus, the G peak moves down with increasing sp^3 content in a-C:H, the opposite direction to that in ta-C.

The peak positions of the D and G line signals were determined by fitting the Raman spectra using two Gaussian distributions. From the spectra, it can be seen that as the applied pulse bias is changed from −600 to −1000 V, the G peak position shifts towards higher wavenumber from 1550 to 1570 cm^{-1}, and the D peak position also shifts upwards from 1370 to 1400 cm^{-1}. So we think pulsed dc increasing promote the short C=C chains change to rings. That is to say, the

variation of the Raman spectra reflected the transition in carbon nitride films structure from diamond-like to graphite-like as the dc bias increased from −600 to −1000 V. This can be explained using the subsurface implantation model [23,24]. Accordingly, at a certain relative high applied bias voltage (−600 V), the ion species will have sufficient energy to penetrate into the subsurface leading to the formation of dense C–C networks, thus the film has the most diamond-like character. However, at too high dc bias voltage (−1000 V), the dissipation of the excess heat generated by the impinging ion could relax the high compressive stress or excess density phase leading to loose carbon networks and inducing an order increase of sp^2-bonded clusters, i.e., graphitization.

We employed non-contact 3D Laser-Profilometer instrument (Micro XAM) to examine the surface morphologies of the prepared hydrogenated amorphous carbon nitride films. Fig. 3 shows topography images of carbon nitride films fabricated at different pulse negative bias voltage of −600, −800 and −1000 V, respectively. The interesting finding is an apparent periodical ripple film generated at the deposition negative bias voltage of −1000 V. Similar surface feature was also seen in the case of the film deposited at negative bias voltage of −800 V although the ripple's height is not as high as that found in the case of negative bias voltage of −1000 V. However, no ripple feature was observed at the negative bias voltage of −600 V, and reversely, irregular growth mounds appear on the film surface.

Furthermore, a few pyramid-like particles were observed on a-CN$_x$:H films surface at the deposition negative bias voltage of −1000 V. As discussed above in the section of Raman spectra (Fig. 2), sp^3 carbon dominated the deposited films at relatively low negative bias voltage. With increasing the negative bias voltage to −1000 V, however, higher G peak and D peaks wavenumber, suggesting more sp^2 phase, graphite, generated. In this case, it is very likely that an intrinsic mechanism is responsible for the formation of graphitic particles in the center region, which is similar to the extrinsic model of seed–cone formation proposed by Robinson and Rossnagel [25]. This intrinsic model is based on the surface phase transition. High pulse dc negative bias voltage promotes great amount of small graphitic clusters generation, these clusters tend to gather into islands due to surface diffusion.

The formation of ripple feature implies an unstable growth mode that is not yet well understood experimentally and theoretically. This kind of unstable surface commonly appears after postsputtering of the films. Bradley and Harper first proposed a theory (BH model) [3] that ion bombardment induced this kind of periodical surface aspect. BH model predicts that ripple topography appears as an amorphous solid is bombarded by off-normal incidental ion beam. The ripple orientation depends on the projection of the ion beam. This theory is based on the fact that the power deposition that causes sputtering is maximized below the surface. Almost all the ripple theories were base on the off-normal incidental ion beam. But different from previously reported, we used PECVD system in which the direction of ions are heterogeneous and no off-normal incidental ion beam to fabricate carbon film. The traditional theory (BH model) is not able to explain clearly the interesting phenomenon
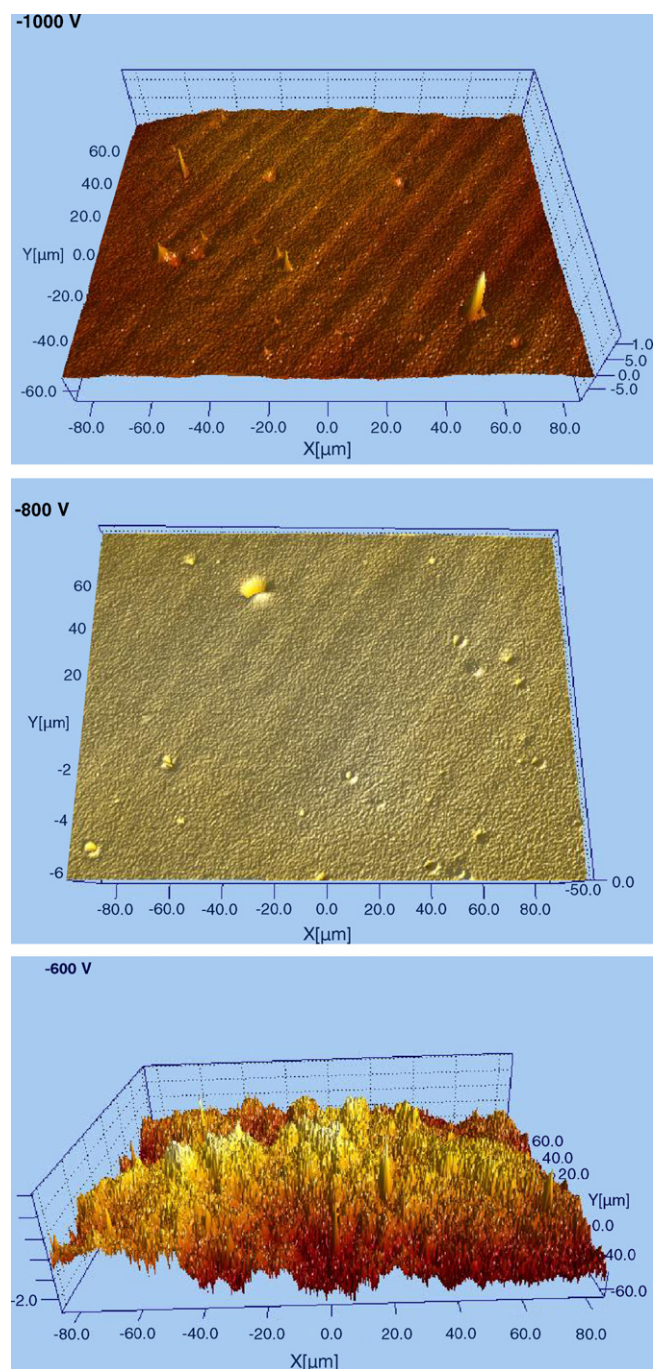

Fig. 3. The topography images of carbon nitride films fabricated at different pulse negative bias voltage of −600, −800 and −1000 V, respectively.

observed in this study. Therefore, it is reasonable to deduce that the C–N bonding structure, which is a function of applied negative bias voltage, in the amorphous carbon nitride films and the character of pulse dc plasma discharge probably dominate the morphological transformation.

In order to study the role of nitrogen in the deposition process, methane and argon instead of hydrogen were also used as working gases while other deposition conditions were kept constantly. Finally, no ripple morphology was observed on the film surface with dc–rf plasma system, no ripple morphology formation was observed either (use methane and argon or

hydrogen as feedstock). Therefore, it is definite that the ripple feature is associated with nitrogen in the film and the character of pulse dc plasma. The detail investigation of the effect of nitrogen and pulse plasma discharge on the formation of ripple morphology is undergoing.

4. Conclusions

In summary, we have investigated topography of hydrogenated carbon nitride films deposited by pulse dc plasma CVD. At certain pulse dc negative voltage (−600 V), the periodical ripple morphology was observed. Nitrogen incorporation in the film and the pulse dc plasma discharge are necessary for the appearance of ripple structures. The chemical bonding configurations in the amorphous carbon nitride films should be taken into consideration for elucidating the surface morphological transformation.

Acknowledgements

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