

# Effect of Nitrogen Ion Beam Irradiation on Diamond-like Carbon Films

Yoshihisa Watanabe\* and Nobuaki Kitazawa

Department of Materials Science and Engineering, National Defense Academy,  
1-10-20 Hashirimizu, Yokosuka, Kanagawa 239-8686, Japan

(Received 25 January 2005; accepted 17 May 2005)

**Key words:** diamond-like carbon films, nitrogen ion beam, carbon nitride, AFM, XPS

Diamond-like carbon (DLC) films were deposited on silicon single crystal substrates from toluene vapor using rf plasma. After deposition, the DLC films were irradiated with a nitrogen ion beam and the effects of this irradiation on surface morphology and composition were studied. Nitrogen ion irradiation was performed using a nitrogen ion beam of 0.2 keV for 10 min under a constant ion current density of approximately  $70 \mu\text{A}/\text{cm}^2$ . Surface morphology was observed by atomic force microscopy (AFM). Changes in composition and carbon-nitrogen bonding states were analyzed by X-ray photoelectron spectroscopy (XPS). Carbon structures were examined by Raman spectroscopy. AFM observations revealed that the DLC film surface became smooth after nitrogen ion beam irradiation. XPS studies showed that nitrogen was absorbed near the surface of the DLC films after nitrogen ion irradiation, and carbon-nitrogen bonding was confirmed in  $\text{C}_{1s}$  and  $\text{N}_{1s}$  photoelectron spectra. Carbon structures did not change remarkably after nitrogen ion irradiation. These results show that irradiated nitrogen ions are absorbed into the DLC films to form carbon nitride layers near the surface.

## 1. Introduction

Since its theoretical prediction by Liu and Cohen,<sup>(1)</sup> crystalline carbon nitride ( $\beta\text{-C}_3\text{N}_4$ ) has attracted considerable attention and many scientists have tried to prepare this material using various techniques including laser ablation deposition, ion-beam-assisted deposition, reactive sputtering and hot-filament chemical vapor deposition.<sup>(2-5)</sup> In addition to these deposition methods, nitrogen ion irradiation into carbon materials was proposed as an effective technique for preparation of carbon nitride ( $\text{CN}_x$ ).<sup>(6)</sup>

---

\*Corresponding author: e-mail: ywat@nda.ac.jp

Hoffman *et al.* irradiated graphite and diamond using 500 eV nitrogen ions in the temperature range from room temperature to 800 K and studied the effects of irradiation temperature, post-irradiation annealing and ion dose.<sup>(6)</sup> According to these authors, the nitrogen concentration increased and implanted nitrogen was present in three different bonding states of nitrogen and carbon.<sup>(6-8)</sup> Galán *et al.* studied X-ray photoelectron spectroscopy (XPS) of CN<sub>x</sub> films grown by nitrogen ion implantation on graphite and hydrogenated amorphous carbon in the ion energy region from 250 to 5000 eV.<sup>(9)</sup> They found that higher nitrogen concentration is obtained by consecutive implanting from higher to lower energies and that the N<sub>1s</sub> line shape is due to the presence of four chemical species. Husein *et al.* prepared CN<sub>x</sub> films by implanting amorphous carbon films with nitrogen using plasma immersion ion implantation and conventional ion beam implantation.<sup>(10)</sup> Their Raman spectra indicated that the structure of implanted CN<sub>x</sub> films becomes more amorphous than the as-deposited amorphous carbon films.

More recently, we prepared CN<sub>x</sub> layers by irradiating amorphous carbon substrates with a nitrogen ion beam.<sup>(11)</sup> In a previous work, the effect of nitrogen ion beam energy on the formation of CN<sub>x</sub> layers in bulk amorphous carbon was studied.<sup>(11)</sup> It was found that 0.2 keV ion irradiation is more effective for CN<sub>x</sub> formation than 1.5 keV ion irradiation. Since the previous work was limited to bulk amorphous carbon, studying the irradiation effect for amorphous carbon films using the nitrogen ion beam and comparing the irradiation effect to that of bulk amorphous carbon are both of interest.

In this paper, diamond-like carbon (DLC) films are deposited from toluene vapor using rf plasma, and the DLC films are irradiated with the nitrogen ion beam after deposition. The effect of nitrogen ion irradiation on the surface morphology and composition of the DLC films is examined.

## 2. Experimental Procedures

### 2.1 Film deposition

DLC films were prepared on silicon single crystal substrates from toluene vapor using rf plasma. The gas was introduced into the reaction chamber and 180 W of 13.56 MHz rf power was used to produce a discharge. The working pressure was kept at 10 Pa and the deposition was carried out for 5 min at room temperature.

### 2.2 Ion beam irradiation

A nitrogen ion beam was generated with a bucket-type ion gun. The nitrogen ion beam energy was fixed at 0.2 keV and the nitrogen ion beam current density was kept constant at approximately 70  $\mu\text{A}/\text{cm}^2$ . After the vacuum chamber attained a base pressure of  $1.3 \times 10^{-4}$  Pa, nitrogen gas was introduced into the chamber and nitrogen ions were generated by arc discharge. The pressure was then maintained at about  $4.7 \times 10^{-3}$  Pa during ion beam irradiation. Irradiation was carried out for 10 min at room temperature.

### 2.3 Characterization

Surface morphology was observed with an atomic force microscope (AFM) (NanoScope III, Digital Instruments) with a commercial silicon tip using a tapping mode. Film

composition and chemical bonding states between carbon and nitrogen were analyzed by X-ray photoelectron spectroscopy (XPS) (ESCA 1600, Physical Electronics) with a non-monochromatic Mg  $K_{\alpha}$  X-ray source. Depth profiles of carbon and nitrogen in the DLC films after irradiation were obtained by sputtering the specimens with 2 keV argon ions. Raman spectroscopy (NR-1800, Japan Spectroscopic) was performed by backscattering from the DLC films using an argon-ion laser operating at 514.5 nm.

### 3. Results and Discussion

#### 3.1 *As-deposited films*

Figure 1 shows a typical AFM image of the surface of the as-deposited film. From this figure, it can be seen that the surface of the film is covered uniformly with small protrusions. The root-mean-square roughness ( $R_{\text{RMS}}$ ) is calculated from several different AFM scans of  $1 \mu\text{m}^2$ . The value of  $R_{\text{RMS}}$  is approximately 0.25 nm for the as-deposited films.

In the XPS wide spectrum for the as-deposited film, only the carbon peak is observed and extraneous peaks are not discerned. Thus, the deposited film is a contamination-free film.

The Raman spectrum from the as-deposited films, as displayed in Fig. 2, shows typical features of DLC films: a broad peak around  $1550 \text{ cm}^{-1}$  (G-band) and a shouldered peak around  $1350 \text{ cm}^{-1}$  (D-band).<sup>(12)</sup> From these results, it is concluded that the as-deposited films are contamination-free DLC films with smooth surfaces.

#### 3.2 *Effect on surface morphology*

Figure 3 shows a typical AFM image of the DLC film after irradiation with the 0.2 keV nitrogen ion beam for 10 min. In contrast with the as-deposited films, although the surface is still uniform, the shape of the protrusions is not well defined and the top of the protrusions looks as though it has been melted. For the DLC films after irradiation with 0.2 keV nitrogen ions, the average roughness is evaluated from several different AFM scans of  $1 \mu\text{m}^2$  and the value of  $R_{\text{RMS}}$  is approximately 0.16 nm.

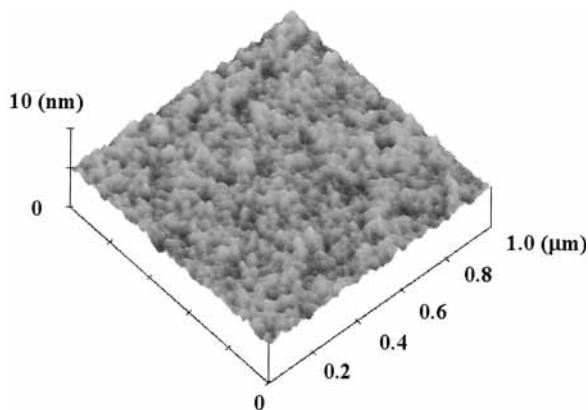


Fig. 1. AFM image of the as-deposited DLC film.

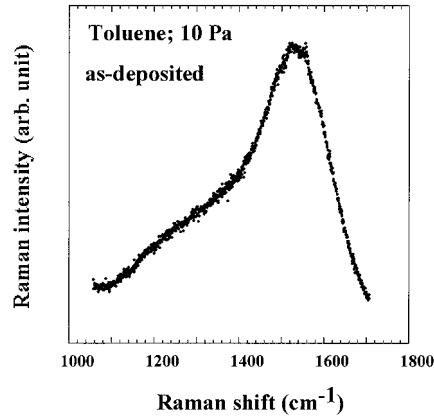


Fig. 2. Typical Raman spectrum of the as-deposited DLC film.

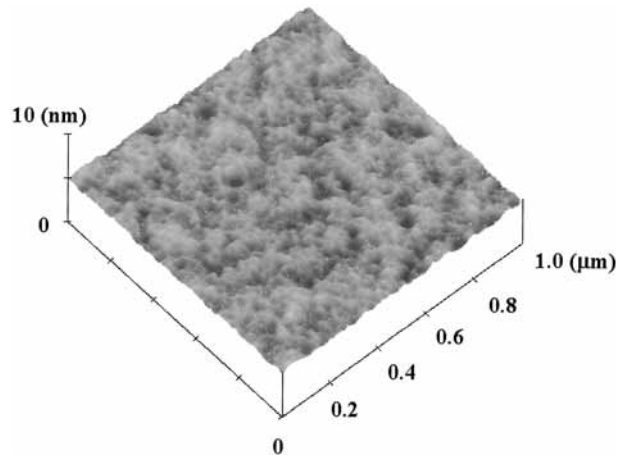


Fig. 3. AFM image of the DLC film after irradiation with a nitrogen ion beam of 0.2 keV for 10 min.

When the bulk amorphous carbon was irradiated with 0.2 keV nitrogen ions for 10 min, the protrusions that covered the initial surface seemed to be aggregated, and the value of  $R_{\text{RMS}}$  increased from approximately 2.0 to 2.5 nm.<sup>(11)</sup> This tendency is different from that of the nitrogen ion irradiated films. From the smooth and uniform surface after irradiation, we consider that the surface of the DLC films was etched uniformly by nitrogen ions. In contrast, the bulk amorphous carbon seems to be selectively etched by nitrogen ions, because the peak-valley structures are formed after irradiation. The Raman spectrum of the bulk amorphous carbon shows the D and G bands more sharply than the DLC films.<sup>(13)</sup> This indicates that the structure of the bulk amorphous carbon is closer to graphite than to DLC film.

Gouzman *et al.*<sup>(7)</sup> studied the irradiation effects of low-energy nitrogen ions on graphite. Based on the measurements of C (KVV) Auger line shape before and after irradiation, they found that a high degree of structural disorder is induced in the near-surface region of graphite. They considered that disruption of the graphite structure by ion irradiation leads to the formation of dangling bonds and point defects. According to their results, it is reasonable to surmise that the surface morphology of ion-irradiated graphite is modified associated with structural disruption and this may be responsible for the difference in the surface morphology after ion irradiation between the bulk amorphous carbon and DLC films.

### 3.3 Effect on composition and carbon structure

Carbon, oxygen and nitrogen peaks were clearly observed in the wide XPS spectra from the DLC films after irradiation with 0.2 keV nitrogen ions for 10 min. However, after the surface was sputtered with 2 keV argon ions for 30 s, the oxygen peak disappeared while the nitrogen peak remained. From these results, it can be inferred that oxygen is adsorbed onto the surface and nitrogen is absorbed into the DLC films.

Typical depth profiles of nitrogen and carbon in the DLC films are shown in Fig. 4 for films after irradiation with 0.2 keV nitrogen ions for 10 min. Because the surface morphology of the DLC films changes very slightly after the depth-profile measurements, it is difficult to estimate the sputtering rate of the DLC films during the depth-profile measurements. Instead, the bulk amorphous carbon was sputtered with argon ions under the same conditions as the depth-profile measurements, and it was found that the sputtered depth was approximately 20 nm after 9000 s sputtering, which indicates that approximately 4 nm was sputtered after 2000 s sputtering. In this figure, it can be seen that the nitrogen concentration was approximately 15% near the surface. In addition, the carbon concentration rapidly increased with the sputtering time with a concomitant decrease in the nitrogen

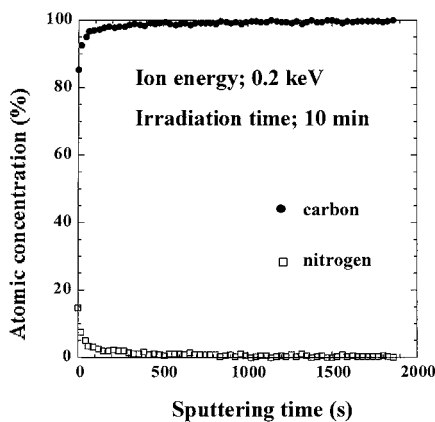


Fig. 4. Depth profiles of carbon and nitrogen in the DLC films after irradiation with the 0.2 keV nitrogen ion beam for 10 min. Atomic concentration was calculated from the XPS spectra and the sensitivity factor of the apparatus.

concentration. The atomic ratio of nitrogen to carbon (N/C) near the surface was calculated to be 0.18 for the film irradiated with 0.2 keV nitrogen ions for 10 min. This value is lower than that for the bulk amorphous carbon irradiated with 0.2 keV nitrogen ions for 10 min, which is about 0.25.<sup>(11)</sup> As discussed in the effect on surface morphology, disruption of the graphite structure by nitrogen ion irradiation leads to the formation of dangling bonds and point defects. These defects are partly compensated by chemical bonding between implanted nitrogen and displaced carbon atoms.<sup>(7)</sup> This phenomenon may be related to the higher N/C value observed in the bulk amorphous carbon than in the DLC films.

To study the bonding state between carbon and nitrogen,  $C_{1s}$  and  $N_{1s}$  spectra were observed in detail. Figures 5(a) and 5(b) show typical results of  $C_{1s}$  and  $N_{1s}$  spectra from the DLC film after irradiation with 0.2 keV ions for 10 min, respectively. Based on the model proposed by Marton *et al.*,<sup>(3)</sup> the  $C_{1s}$  spectrum can be separated to four components, C-C at 284.6 eV,  $sp^2$ C-N at 285.9 eV,  $sp^3$ C-N at 287.7 eV and C-O at 289.5 eV. The high-energy tail in the  $C_{1s}$  spectrum is attributed to the bonding of carbon and nitrogen. Based on the same model as the  $C_{1s}$  spectrum, the  $N_{1s}$  spectrum can be separated to three components, N- $sp^3$ C at 398.3 eV, N- $sp^2$ C at 400.0 eV, and N-N/N-O at 402.0 eV,<sup>(3)</sup> and a combination between carbon and nitrogen is also confirmed in the  $N_{1s}$  spectrum. This observation is consistent with the results of peak separation for the  $C_{1s}$  spectrum.

Figure 6 shows a typical Raman spectrum from the DLC film after irradiation using the 0.2 keV nitrogen ions for 10 min. The difference in the spectra before and after ion irradiation is hardly remarkable. This suggests that the carbon structure in the DLC films does not change significantly. As described in the introduction, Husein *et al.* prepared  $CN_x$  films by ion implantation into carbon thin films deposited by anodic vacuum arc dis-

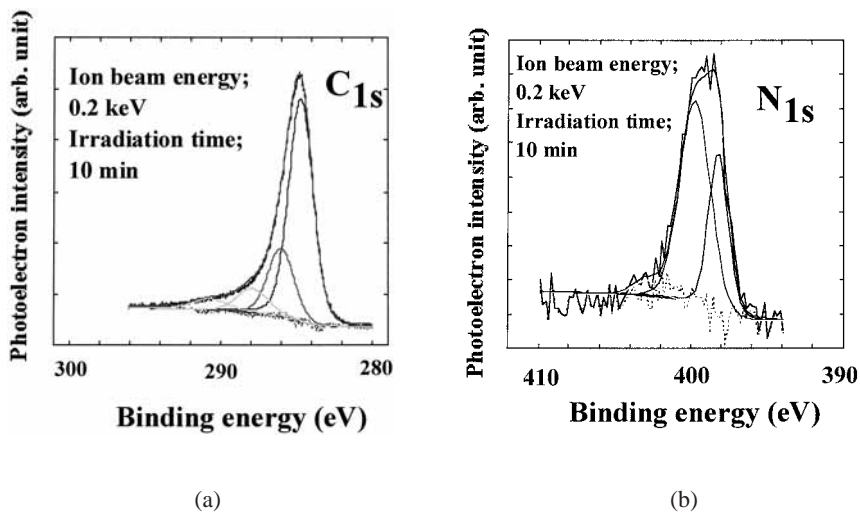


Fig. 5. Typical spectra of (a)  $C_{1s}$  and (b)  $N_{1s}$  photoelectrons obtained from XPS studies for the DLC films after irradiation with a 0.2 keV nitrogen ion beam for 10 min.

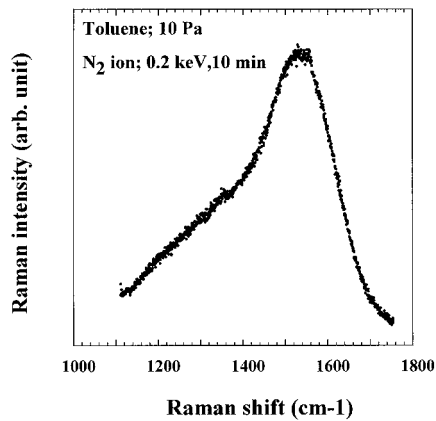


Fig. 6. Typical Raman spectrum of the DLC film after irradiation with the nitrogen ion beam at 0.2 keV for 10 min.

charge.<sup>(10)</sup> They immersed the carbon films in a nitrogen plasma, and nitrogen ions diffused into the films between the high voltage (1 to 2 kV) pulses via thermal diffusion. After immersion, they found the N/C ratio to be between 0.135 and 0.25 in the film. In addition, they observed a broad asymmetric peak at approximately 1500 cm<sup>-1</sup> in the Raman spectrum of the ion immersed films, and they concluded that the film structure became more amorphous after ion immersion.

Comparing our results with those of Husein *et al.*, we notice that the carbon structure of the films after ion treatment is different, although the N/C ratio is similar. The reason for the difference may be due to the film structure itself. Husein's Raman spectrum shows two broad peaks (D and G bands) for the as-deposited film, while the D peak in our spectrum has a shoulder as shown in Fig. 2. This suggests that the carbon structure of the as-deposited films is different. Furthermore, the kinetic energy of nitrogen ions in the method used by Husein *et al.* is higher (1 to 2 keV) than in our method (0.2 keV). This difference may also be related to the different behavior due to carbon structure change after nitrogen ion treatment.

#### 4. Conclusions

Diamond-like carbon (DLC) films were deposited on silicon single-crystal substrates from toluene vapor using rf plasma. After deposition, the DLC films were irradiated with a 0.2 keV nitrogen ion beam for 10 min. AFM observations reveal that the film surface becomes smooth after nitrogen ion irradiation. XPS studies show that irradiated nitrogen ions were absorbed into the DLC films and combined with carbon to form CN<sub>x</sub> layers near the surface. Additionally, the carbon structure did not change remarkably after 10 min of ion irradiation.

## Acknowledgments

The DLC films were prepared using the plasma deposition apparatus in the Advanced Materials Laboratory of the National Defense Academy. The nitrogen ion beam irradiation was performed using the ion vapor deposition apparatus in the Advanced Materials Laboratory of the National Defense Academy.

## References

- 1) A. Y. Liu and M. L. Cohen: *Science* **245** (1989) 841.
- 2) M. Okoshi, H. Kumagai and K. Toyoda: *J. Mater. Res.* **12** (1997) 3376.
- 3) D. Marton, K. J. Boyd, A. H. Al-Bayati, S. S. Todorov and J. W. Rabalais: *Phys. Rev. Lett.* **73** (1994) 118.
- 4) H. Sjöström, W. Lungford, B. Hjörvarson, K. Xing and J. E. Sundgren: *J. Mater. Res.* **11** (1996) 981.
- 5) Y. Chen, L. Guo and E. G. Wang: *J. Phys.: Condens. Matter* **8** (1996) L685.
- 6) A. Hoffman, I. Gousman and R. Brener: *Appl. Phys. Lett.* **64** (1994) 845.
- 7) I. Gousman, R. Brener, C. Cytermann and A. Hoffman: *Surf. Interface Anal.* **22** (1994) 524.
- 8) I. Gousman, R. Brener and A. Hoffman: *J. Vac. Sci. Technol., A* **17** (1999) 411.
- 9) L. Galán, I. Montero and F. Rueda: *Surface and Coatings Technique* **83** (1996) 103.
- 10) I. F. Husein, Y. Zhou, C. Chan, J. I. Kleiman, Y. Gudimenko and K.-N. Leung: *Ion-Solid Interactions for Materials Modification and Processing, Materials Research Society Symposium Proceedings* **396**, Eds. D. B. Poker, D. Ila, Y.-T. Cheng, L. R. Harriott and T. W. Sigmon (Materials Research Society, Pittsburgh, 1996) p. 255.
- 11) C. Iwasaki, M. Aono, N. Kitazawa and Y. Watanabe: *Scientific and Engineering Reports of the National Defense Academy* **42** (2004) 125 (in Japanese).
- 12) T. Ohana, M. Suzuki, T. Nakamura, A. Tanaka and Y. Koga: *New Diamond and Frontier Carbon Technology* **14** (2004) 207.
- 13) C. Iwasaki, M. Aono, N. Kitazawa and Y. Watanabe: *Surface Engineering 2004 - Fundamentals and Applications, Materials Research Society Symposium Proceedings* **843**, Eds. D. J. E. Krzanowski, S. N. Basu, J. Patscheider and Y. Gogotsi (Materials Research Society, Warrendale, 2005) (in press).