Formation of C-N-Si Film for Interlayer of Hard Material Coating by Pulsed Discharge Plasma CVD

Mikio Noda
Pulse Plasma Technology GK
Higashisango 222, Owariasahi, Aichi 488-007, Japan
E-mail: m_noda2003@ybb.ne.jp

Abstract. Carbon nitride (C-N) and Si added C-N (C-N-Si) films were deposited on SKD61 steel plate by pulsed discharge (PD) plasma chemical vapour deposition (CVD). When the films were deposited with N$_2$ and H$_2$ diluted CH$_4$ source gases, the deposition rate increased and the hardness decreased with increasing CH$_4$ concentration. By means of adding mono-methyl-silane (MMS) gas to the source gases, the C-N-Si film having high hardness of 10 GPa and low Young’s modulus of 80 GPa could be deposited. The FT-IR spectrum of the films showed a peak of graphitic ring and peaks of terminating with H and N were observed. Raman spectra showed D and G peaks at around 1350 and 1590 cm$^{-1}$, respectively. The intensity of D peak compared to G peak decreased when MMS was added. Ball on disk test of the C-N-Si film against SUJ2 ball showed the friction coefficient was about 0.2. These results shows that the C-N-Si film having high hardness and low Young’s modulus, which is suitable for interlayer of hard film coating, can deposit by the PD plasma CVD, and suggest that the film is composed of fullerene-like structure which forms resilient and fracture tough materials.

1. Introduction
Formation of high hardness and low Young’s modulus film is desired for use as interlayer of hard coatings. Furthermore, it is desirable that the interlayer material is mainly composed of C and N because the typical hard coating materials such as diamond, diamond like carbon (DLC), TiN and c-BN contain C and N. For this point of view, fullerene-like allotrope of carbon nitride (FL-CNx) is suitable for the interlayer material. As reviewed by Broitman et al. [1], FL-CNx is a predominantly sp$^2$-hybridized material with nitrogen structurally incorporated either substitution in a graphite sheet or in a pyridine-like manner. The substitution of nitrogen results in bending by formation of pentagon structure and cross-linking. The nitrogen-induced bending and cross-linking between the sheets contributes considerably to the strength of FL-CNx by preventing inter-planar slip, and results in an extremely fracture tough and elastic material, where deform occurs with reversible bond rotation and bond angle deflection.

The N incorporation into the carbon network is a complicated procedure since carbon and nitrogen form multiply bonding configuration [2-4]. Therefore, it is necessary to excite the carbon and nitrogen to form the pentagon structure, where the N atom is three-fold coordinated through three σ bonds and two electrons consist a lone pair orbital. Deposition at low temperature below 550°C is also necessary when the film is deposited on heat treated materials such as SKD 61 and SKD11 steel. In the present experiments, pulsed discharge (PD) plasma chemical vapour deposition (CVD) method was used to
resolve these requirements. The film having high hardness and low Young’s modulus could be deposited by using high peak power, after glow effect and low mean power of the PD plasma CVD.

2. Experimental procedure

The carbon nitride (C-N) and C-N-Si films were deposited on SKD61 steel by means of the PD plasma CVD method by using pure N$_2$ gas, hydrogen diluted CH$_4$ gas (CH$_4$/H$_2$) and hydrogen diluted mono-methyl-silane (MMS) gas (MMS/H$_2$). The concentration of CH$_4$ of (CH$_4$/H$_2$) gas was changed from 10 to 30 %, and that of MMS of (MMS/H$_2$) was 5 %. These gases were prepared by a company and their purity was assured more than 99.9 %. Figure 1 shows the schematic diagram of the PD plasma CVD system fabricated for the present experiments. The source gases were introduced into the chamber after pre-evacuation by a rotary pump. The flow rate of the N$_2$, CH$_4$/H$_2$ and MMS/H$_2$ gases were 100, 100 and 10 mL/min, respectively. The total gas pressure during the deposition was kept constant as 1 kPa by adjusting the evacuating speed by the rotary pump. A SKD61 steel plate of about 2 cm in diameter was used as substrate. The distance between the Mo electrode and the substrate used as cathode was about 10 cm. When the discharge was produced between the electrode and substrate by using the pulse power supply, the plasma was produced between the electrode and substrate, and the film was formed on the substrate.

![Figure 1. Schematic view of the deposition system.](image1)

![Figure 2. Schematic view of the pulse power supply.](image2)

![Figure 3. Typical waveforms of the pulse generator (a), discharge voltage (b) and current (c).](image3)

The pulse power supply was fabricated by means of chopping the output of the DC power supply with IGBT and elevating the voltage by the transformer as shown in Figure 2. Detailed description of the pulsed discharge was reported before [5-8]. Frequency and duty ratio of the pulsed discharge in the
present experiments were 1 kHz and 20%, respectively. Figure 3 shows typical waveforms of the pulse generator (a), discharge voltage (b) and current (c). The peak voltage ($V_p$) was about 4 kV, and voltage of glow discharge ($V_g$) was about 700 V. The peak current of the discharge ($I_p$) was 4 A. The deposition time was changed from 30 to 120 min. The substrate was heated with lamp heater and the substrate temperature was from 400 to 500°C. The hardness test of the deposited film was performed by using a nano-indenter made in Elionics INC. The hardness was calculated from the road-displacement curves. The load was chosen 1 or 10 mN so that the penetration depth was less than 10 % of the film thickness. Raman analysis of the films was performed using a 532 nm line of a green laser.

3. Results and discussion

Table 1 shows changes of deposition rate, hardness and Young’s modulus when the source gases are changed. When the CH$_4$ concentration of (CH$_4$/H$_2$) gas is increased from 10 to 30 %, where the flow rate of the (CH$_4$/H$_2$) and N$_2$ gases are 100 mL/ min, the deposition rate increases, and the hardness and Young’s modulus decreases as shown for sample 1 to 3 in table 1. These decreases of hardness and Young’s modulus are probably due to decrease of elimination of weak bonds by atomic hydrogen as well known for diamond and DLC depositions [9].

Table 1. Changes of deposition rate, hardness and Young’s modulus of the C-N and C-N-Si films when CH$_4$ concentration of the CH$_4$/H$_2$ gas is changed and Si is added.

| Sample     | CH$_4$ concentration of CH$_4$/H$_2$ gas (%) | Deposition time (min) | Thickness (nm) | Deposition rate (nm/min) | Hardness (GPa) | Young’s modulus (GPa) |
|------------|--------------------------------------------|-----------------------|----------------|--------------------------|----------------|-----------------------|
| 1 (C-N)    | 10                                         | 120                   | 100            | 0.8                      | 11.1           | 268                   |
| 2 (C-N)    | 15                                         | 120                   | 250            | 2.1                      | 5.3            | 239                   |
| 3 (C-N)    | 30                                         | 60                    | 500            | 8.3                      | 4.1            | 181                   |
| 4 (C-N-Si) | 30                                         | 30                    | 1,140           | 38.0                     | 10.0           | 80                    |

When the MMS/H$_2$ gas was added to the source gases of the sample 3, the hardness of the film is increased from 4.1 to 10 GPa and the deposition rate is increased from 8.3 to 38 nm/min as shown for sample 4. Whereas, Young’s modulus is decreased from 180 to 80 GPa. These extreme increases of the deposition rate and the hardness, and the extreme decrease of Young’s modulus suggest that the structure of the film changes to the FL-CNx by the adding of Si.

In the case of DLC prepared from CH$_4$, H$_2$, Ar and Si(CH$_3$)$_4$ source gases by means of DC plasma CVD, it has been reported that adding of small amount of Si prevent the formation of sp$^2$ nano-clustering structure and polycarbosilane of Si-CHx-Si bonds are formed [10]. In the present experiments, the flow rate of MMS/H$_2$ gas was 10 mL/min and considerably smaller than that of N$_2$ and CH$_4$/H$_2$ of 100 mL/min. Therefore, the adding of small amount of Si in the present experiments is probably effective to the formation of basal plane of the FL structure. Furthermore, it can be considered that Si in the basal plane forms cross-linking between the basal planes because Si has sp$^3$ configuration. Therefore, it can be speculated that the significant increase of hardness and extreme decrease of Young’s modulus by adding Si are caused by enhancing the formation of FL structure and cross-linking between the basal plane.

Figure 4 shows optical photograph of the surface of the sample 3 and 4 denoted in table 1. The structure of the sample 3 is grain-like and comes to smooth with adding Si, suggesting that the structure changes to FL by adding Si.

Figure 5 shows FT-IR spectra of the sample 3 and 4. A peak of 1530 cm$^{-1}$ due to C=N graphitic ring denoted by Laskarakis et al [3] is observed. A broad peak at around 2100 cm$^{-1}$ due to terminating with
N appears for the sample 4, reflecting that the size of the aromatic clusters become smaller and more disordered.

Figure 4. Optical photograph of the surface of the sample 3 denoted in table1 (C-N) and sample 4 (C-N-Si) which is deposited with adding Si to the sample 3.

Figure 5. FT-IR spectra of the sample 3 (C-N) denoted in table 1 and sample 4 (C-N-Si) which is deposited with adding Si to the sample 3.

Figure 6. FT-IR spectra of the sample 3 (C-N) denoted in table 1 and sample 4 (C-N-Si) which is deposited with adding Si to the sample 3.

Figure 6 shows Raman spectra of the sample 3 and 4 shown in table 1. Two main peaks positioned at around 1350 and 1590 cm$^{-1}$, which are denoted by D and G respectively, are observed. The intensity of D peak ($I_D$) compared to that of G peak ($I_G$) decreases when Si is added to the sample 3. The decrease of ($I_D$ / $I_G$) ratio means the size of the aromatic clusters become smaller and more disordered as reported by Ferrari et al [4]. This result coincides with the results shown in Figure 4, which shows the film surface becomes smooth due to the decrease of the cluster size by adding Si. Furthermore, the G peak is caused by in-plane bond stretching vibration and can be present in aromatic clusters [11]. Therefore, the increase of $I_G$ suggests that FL structure of graphite is enhanced by the adding of Si.
Figure 7 shows ball on disk test of the sample 4 shown in table 1 against SUJ2 ball, where the load was 500 g and the rotational speed was 120 rpm. The friction coefficient is about 0.25 until about 55 m sliding distance. This value of the friction coefficient is almost same as that of FL-CN films [1].

4. Conclusion

The C-N and C-N-Si films were deposited by PD plasma CVD by using N₂, CH₄/H₂ and MMS/H₂ source gases. In the case of C-N films deposited by using N₂ and CH₄/H₂ gases, the deposition rate increases with increasing the CH₄ concentration of CH₄/H₂ gas. Whereas, the hardness decreases, and Young’s modulus also decreases. In the case of C-N-Si films, where MMS/H₂ gas is added to the N₂ and CH₄/H₂ gases, both the deposition rate and the hardness are extremely increased, and significant decrease of Young’s modulus is also observed in comparison with those of the C-N films. As a result, the C-N-Si film of high deposition rate of 38 nm/min, high hardness of 10 GPa and low Young’s modulus of 80 GPa can be deposited. These extreme changes due to adding of Si to the C-N films suggest that the film comes to contain fullerene-like structure composed of pentagon configuration which forms resilient and fracture tough materials by inducing the curvature in the basal plane and inter-planar cross-linking. The results of FT-IR, Raman spectra and friction coefficient measurements support this consideration. The C-N-Si film having high hardness and low Young’s modulus is suitable for interlayer of hard material coatings.

5. References

[1] Broitman E, Neidhardt J and Hultman L, 2008, Tribology of Diamond-Like Carbon Films: Fundamentals and Applications, ed C. Donnet and A. Erdemir (Springer, 2008) P. 620-653.
[2] dos Santos M. C. and Alvarez F, 1998, Phys. Rev. B 58 13918.
[3] Laskarakis S, Logothetidis S and Gioti M, 2001, Phys. Rev. B 64 125419.
[4] Ferrari A. C., Rodil S. E. and Robertson, 2003, Phys. Rev. B 67 155306.
[5] Noda M, 2001, J. Indian Inst. Sci. 81 627.
[6] Noda M and Umeno M, 2005, Diamond Relat. Mater. 14 1791.
[7] Noda M, Shinagawa T, Kawai S and Umeno M, 2008, Diamond Relat. Mater. 17 646.
[8] Kawai S, Shinagawa T, Noda M and Umeno M, 2008, Diamond Relat. Mater. 17 676.
[9] Spear K. E and Frenklach M, Synthetic Diamond: Emerging CVD Science and Technology, ed H. E. Spear and J. P. Dismukes (John Wiley & Sons, 1994) P. 243-304.
[10] Iseki T, Mori H, Hasegawa H, Tachikawa K and Nakanishi K, 2006, Diamond Relat. Mater. 15 1004.
[11] Abrasonis G, Gago R, Vinnichenko M, Kreissig A, Kolitsch A and Moller W, 2006, Phys. Rev. B 73 125427.