SYNTHESIS OF CARBON NITRIDE THIN FILMS BY PLASMA PROCESSING

Osamu Takai, Yusuke Taki and Toshihisa Kitagawa

Department of Materials Processing Engineering, Nagoya University, Chikusa-ku, Nagoya 464-01, Japan

ABSTRACT

Carbon nitride is one of the new carbon materials which show interesting properties. After the theoretical calculation by LIu and Cohen, many researchers are trying to prepare β-C_3N_4 which may be harder than diamond. Many carbon nitride films synthesized till now by various methods are amorphous and the N/C ratios in the films are usually below 0.5. First we review shortly the synthesis of carbon nitride thin films by plasma, ion and laser processing. Second we report on the preparation of amorphous carbon nitride thin films by shielded arc ion plating and the structural and mechanical properties of the films.

INTRODUCTION TO CARBON NITRIDE SYNTHESIS

After the theoretical calculation about hypothetical covalent carbon-nitrogen solid, β-C_3N_4 which has the same structure as β-Si_3N_4 by Liu and Cohen[1,2], many researchers have been tried to synthesize β-C_3N_4. They calculated the bulk modulus of β-C_3N_4 using the first-principle pseudo-potential theory and reported the hardness of β-C_3N_4 might be greater than or equal to that of diamond. Hence the synthesis of β-C_3N_4 is attracting many researchers' interest.

Recently Liu and Wentzcovitch[3] proposed β-C_3N_4 and zincblende-like cubic C_3N_4 as metastable phases comparable to diamond. On the other hand, Guo and Goddard III[4] calculated that α-C_3N_4 was more stable than β-C_3N_4 and both α-and β-C_3N_4 were about half as hard as diamond. Now it is unclear that

which compound really exists or not.

From the experimental viewpoint many carbon nitride thin films have been prepared by using plasma, ion and laser processing. We summarize the preparation methods, and the structure and harness of the prepated films in Table I[5-31]. Plasma processing is most widely used to synthesize carbon nitride films. Until now crystalline carbon nitride films detectable by X-ray diffraction have not been prepared except the report by Zhang et al.[31]. Almost all the films are amorphous. By transmission electron microscopy Yu et al.[15]. Niu et al.[21], Narayan et al.[22] and Yen et al.[30] obtained the diffraction ring patterns probably corresponding to β-and/or α-C_3N_4. Carbon nitride crystallites were included in amorphous carbon matrix of the films. About the nitrogen contents in the prepared films, the ratio of nitrogen to carbon(N/C ratio) is almost below 0.5, which is much lower than

Table 1 Processes used for the synthesis of carbon nitride thin films and the properties of the films prepared.

Process	Max. N/C ratio	Structure	Hardness	Ref. No.
Reactive sputtering	0.5(1.0)	amorphous	hard(soft)	5–17
Nitrogen implantation	······	······	······	18–20
Laser ablation	0.8	amorphous	hard	21.22
Capactively coupled plasma CVD	0.2	amorphous	hard	23.24
Ion–assisted dynamical mixing (ion and vapor) deposition)	2.0	amorphous	very hard (Knoop 6500)	25.26
Arc ion plating)	0.5	amorphous	hard	27–29
Arc plasma jet CVD	0.6	amorphous	hard	30
Inductively coupled plasma CVD	1.6	amorphous (crystal ?)	hard	31

1.33 of C_3N_4. Only the ion-assisted dynamical mixing[26] gave the high C/N ratio (0.3-2)

About the hardness of the prepared films, many films are as hard as or softer than usual DLC films. The hardest amorphous carbon nitride film was prepared on a WC substrate by the ion-assisted dynamical mixing mentioned above and its Knoop hardness was 6500 (thickness:1um, N/C ratio:above 1))[26]. The carbon nitride films (thickess:150 nm, N/C ratio:about 0.2) prepared by arc ion plating on Si substrates also showed high hardness and were two or more times harder than Si substrates (Knoop hardness of Si:about 1400)[29]. Recently hard carbon nitride thin films have prepared by several techniques. Optical and electrical properties also vary according to N/C ratio. Therefore the mechanical, optical and electrical properties of the amorphous carbon nitride thin films synthesized are interesting in spite of their amorophous structure and less content of nitrogen.

SYNTHESIS OF CARBON NITRIDE THIN FILMS BY SHIELDED ARC ION PLATING INTRODUCTION

Preparation of amorphous carbon nitride thin films has been studied by cathodic are ion plating[27-29]

Generally high deposition rate and high ionization are achieved by the cathodic arc ion plating (cathodic arc evaporation). Therefore this method is adequate technique for the synthesis of carbon nitride. Moreover this is easily applicable to industrial coatings. On the other hand, the deposition of macroparticles (0.1-100 μm) is a problem in the cathodic arc ion plating Hence we avoided the deposition of the macroparticles by setting a shielding plate between a cathodic target (evaporation source) and a substrate. Using this shielding plate we can synthesize carbon nitride thin films and obtain a smooth surface. We call this ion plating technique "shie-lded

arc ion plating". We report on the synt-hesis of carbon nitride thin films by shielded ion plating. The structure, chemical composition and chemical bonding states of the films are investigated fully with reference to substrate bias voltage. The mechanical properties, microhardness and internal stress, are also studied.

EXPERIMENTAL

Film deposition

The apparatus used for film preparation is shown in Fig. 1. A high purity sintered graphite target(ϕ64mm×32mm) was mounted on a cathode as a carbon source. Nitrogen gas was introduced into a chamber through a mass flow controller. After the initiation of nitrogen arc plasma at 60 A and 1 Pa, the target surface was heated and evaporated by the plasma. Carbon atoms and clusters evaporated from the target were ionized partially and reacted with activated nitrogen species, and a carbon nitride film was deposited onto a Si (100) substrate (10mm×35mm×0.5mm). The surface of the growing film also reacted with activated nitrogen species. Carbon macroparticles evaporated from the target at the same time were not ionized and did not react fully with nitrogen species. These macroparticles interfered with the formation of the carbon nitride film. Therefore we set a shielding plate made of stainless steel between the target and the substrate as shown in Fig. 1 to trap the macroparticles. The distance between the target and the shielding plate was 120mm and that between the plate and the substrate was 40mm. The substrate was negatively biased during deposition in the range
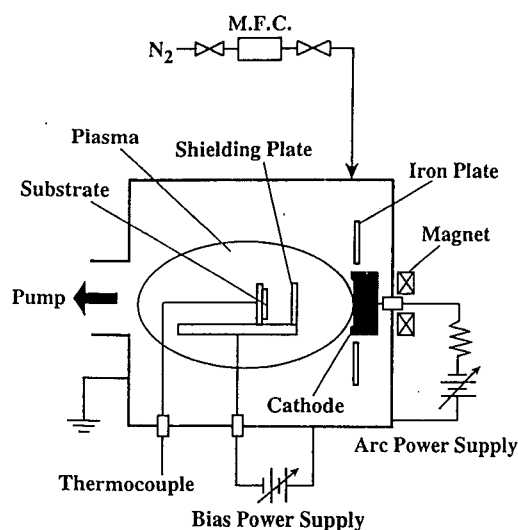

Fig.1 Schematic diagram of the shielded ion plating system.

of 0–700V. The substrate temperature was not maintained constant in this experiment and increased from room temperature to 330 ℃ during depostion according to the bias voltages.

Film characterization

Film structure was studied by X–ray diffraction (XRD) with Cu Kα radiation and Raman spectroscopy with Ar laser at 514. 5nm. Chemical composotion and chemical bonding states of the films were measured with X–ray photoelectron spectroscopy(XPS) with unmonochromated Mg Kα radiation. Film surfaces were analyzed without Ar ion etching, since this etching destroyed metastable carbon structure and caused denitrification from the surfaces. All the spectra were referenced to the C 1s peak of saturated aliphatic carbon ($-CH_2^-$) at 285.0 eV. Chem-ical bonding states were also investigated by Fourie transform infrared spectroscopy (FTIR).

Film thickness and substrate curvature were measured with a stylus instrument. Atomic force microscope (AFM) was used for the observation of film surface. Film microhardness was determined with a dynamic ultra-microhardness tester. A trigonal pyramidal diamond indenter with an edge angle of 115 degrees was used at a maximum load of 0.50 gf.

Internal stress in a deposited film was calculated from the difference in substrate curvature between an uncoated substrate and a coated substrate[32].

RESULTS AND DISUSSION

Carbon nitride films were deposited at various bias voltages. The structure of all the films was found to be amorphous by XRD. Figure 2 shows Raman spectra of the amorphous carbon nitride films prepared at various bias voltages. Each Raman spectrum co-ε∈mposes of two broad bands at 1570-1565cm^{-1} (G band) and 1370-1360cm^{-1} (D band). The G band is assigned to the E_{2g} symmetric vibrational mode of graphitic layers in the sp^2 domains, whereas the D band is attributed to the bond-angle disorder in the graphic layers induced by the linking with sp^3 carbon atoms[33] as well as the luck of the long distance order in the sp^2 domains[34].

Some nitrogen atoms are substituted for carbon atoms constituting aromatic rings in sp^2 graphitic domains in the films. Namely aniline-like C-N bonding is formed. There-fore the bond-angle of the sp^2 domains is disordered much more than DLC films because of the bonding with nitrogen atoms, and the D bands in the spectra of the amorphous carbon
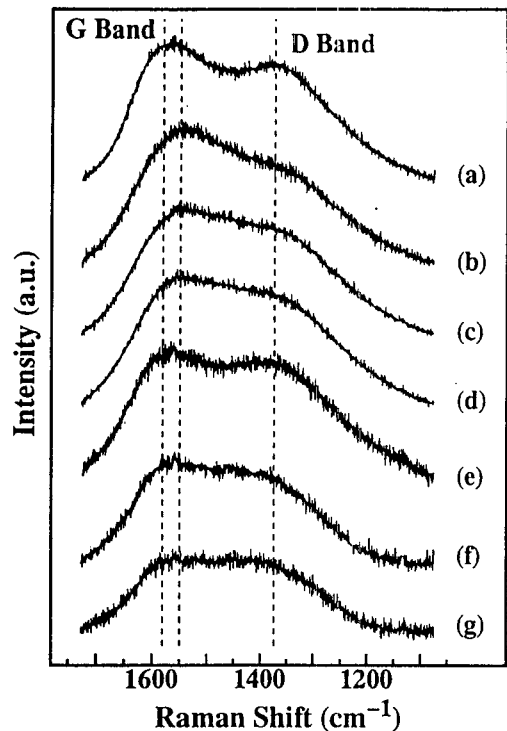

Fig.2 Raman spectra of the films prepared at the bias voltages of (a) 0V, (b) -100V, (c) -200V, (d) -300V, (e) -500V, (f) -600V and (g) -700V

nitride films become larger than the D bands for the DLC films[29]. In addition, carbon-nitrogen stretching vibrations in the pyridine-like and aniline-like structure are included in the spectra.

The formation of carbon-nitrogen bonding in the films was confirmed by XPS. The film surface was smooth and no ma-croparticles were detected by AFM observation. The effect of the shielding plate is significant on the preparation of the carbon nitride films.

The deposition rate and the N/C atomic ratio measured by XPS of the films are shown in Fig. 3 as a function of bias voltage. The de-

position rate indicates minimum at -300V. The N/C ratio decreases with negative bias voltage below -200V. This will be related to the substrate temperature. Nitrogen atoms are considered to be released from carbon-nitrogen bonding in the films owing to the increase in substrate temperature induced by the positive ion bombardment.

We measured the microhardness of the films by a dynamic ultra-microhardness tester. By recording load versus displacement of an indenter we get information of both elastic and plastic degormation of a sample. The hardness corresponding to only plastic deformation is called "permanent depth hardness" and the hardness due to the sum of elastic and plastic deformation is called "total depth hardness"[35]. In the case that a film is harder than a substrate and the penetration depth of the indenter is deeper than one tenth of the film thickness, the measured film hardness will be lower than the intrinsic film hardness. Additionally the total depth hardness is more affected by the substrate than the permanent hardness. In this study we fixed the film
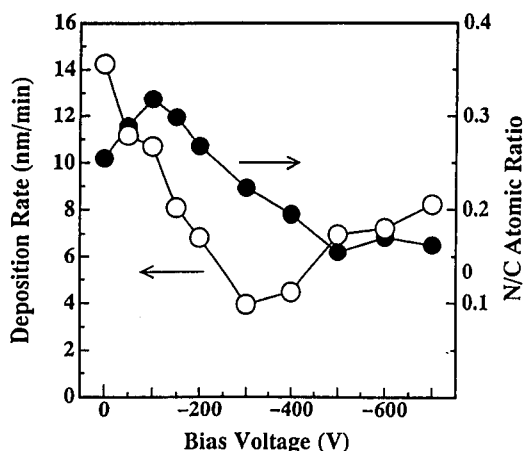
thickness at 150 nm and the penetration depth of the indenter was almost half of this thickness. Consequently the Si substrate affects the measurement of the film hardness and the measured hardness will be lower than the intrinsic film hardness. We, therefore, use the permanent film hardness in this paper. Figure 4 shows the permanent depth hardness of the films as a function of negative bias voltage. The hardness of an uncoated Si (100) substrate measured under the same condition is also indicated in Fig. 4. For reference, the Knoop hardness of the Si (100) substrate is about 1400. The film deposited at 0 V is softer than the Si substrate. Film hardness increases with decreasing substrate bias voltage because of the effect of positive ion bombradment. This ion bombardment promotes fourfold coordinated carbon domains in amorphous network. The optimumvoltage to make the hardest film is -300V. The amorphous carbon nitride prepared in this experiment is about twice as hard as silicon. Below -300V the film hardness decreases,
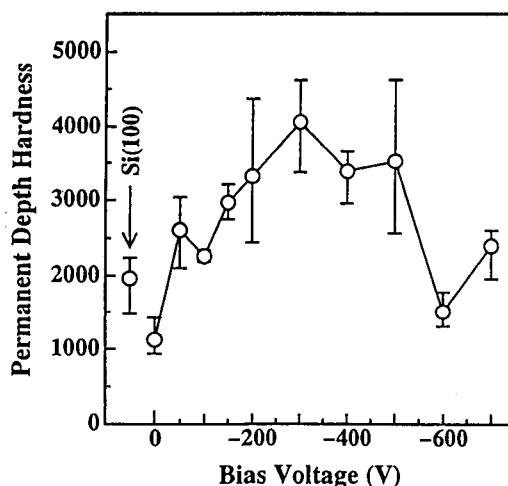
Fig. 3 Deposition rate and N/C ratio as a function of bias voltage.

Fig. 4. Permanent depth hardness as a function if bias voltage.

since excess ion bombardment induces the growth of sp² domains instead of sp³ domains. From Figs. 3 and 4, the N/C ratio is not directly related to the film hardness. The deposition rate was relatively low at the voltages suitable for hardening the films. This is probably related to the density of the films deposited. It is considered that hard films grow slower than soft films.

The relation between the residual stress in the film and the bias voltage is shown in Fig. 5. The compressive stress remained in all the films. The maximum stress, 4 G Pa, is obtained at −150V. The increase in compressive stress is related to flim hardening by ion bombardment.

Figure 6 shows the XPS N 1s spectra of the films deposited at various bias voltages.In the film deposited at 0V, some nitrogen atoms are substituted for the carbon atoms constituting aromatic rings in sp² graphitic domains in the films, and some of graphitic domains change to pyridine-like (P) domains.
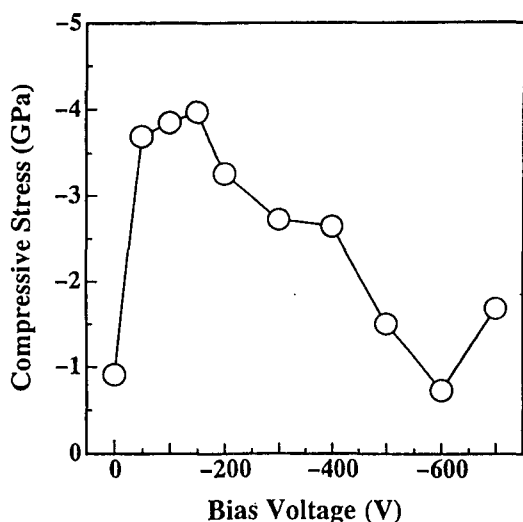
Other nitrogen atoms link the carbon atoms constituting aromatic rings in graphitic and pyridine-like (P) domains, and aniline-like (A) C-N bonding is formed.

Because this film takes sp² plain structure, it is softer than the Si substrate. The components of the pyridine-like (P) and aniline-like (A) C-N bonding decrease with negative bias voltage. The component of the nitrile-like (N) C-N bonding alsodecreases. These phenomena correspond well with the FTIR results. Moreover, as the substrate is negatively biased, the N 1s spectrum becomes to be divided into two peaks. The higher energy
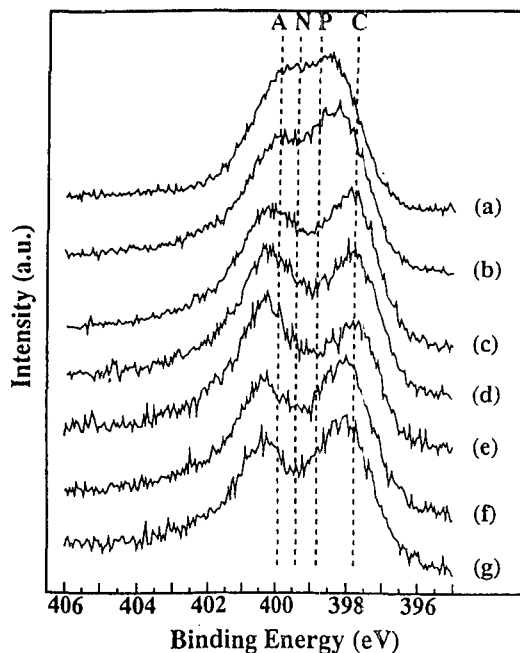

Fig. 6 XPS N 1s spectra of the films prepared at the bias voltages of (a) 0V, (b) −100V, (c) −200V, (d) −300V, (e) −500V, (f) −600V and (g) −700V. A indicates the peak position for polyanilineorigomer, N does that for benzonitrile, P does that for polyvinylpyridine and C does that for cleavage of pyridine ring[36].

Fig. 5 Residual stress as a function of bias voltage.

peak is due to nitrogen atoms which have lower electron density than the nitrogen atoms in the aniline-like (A) structure. Hence this peak is considered to be related to film hardness, that is, three-dimensional C-N bonding, since this peak increases at the voltages suitable for hardening films. On the other hand, the lower energy peak corresponds to polarized ionic bonding to cleavage (C) of pyridine ring.

CONCLUSIONS

Hard amorphous carbon nitride thin films were deposited onto Si substrates by shielded arc ion plating with a graphite target in a nitrogen plasma at the negative substrate bias voltage of about -300 V. The shielding plate is very important to prepare cabon nitride films because of the trapping of carbon macroparticles evaporated from the target. The microhardness of the films prepared under proper conditions is about twice as much as that of silicon. The three-dimensional C-N bonding will be developed in the hard carbon nitride films by XPS analysis. The amorphous carbon nitride films are useful for hard coatings like DLC films.

ACKNOWLEDGMENTS

REFERNCES

1. A. Y. Liu and M. L. Cohen, Science, 245, 841 (1989).

2. A. Y. Lin and M. L. Cohen, Phys. Rev. B 41, 10727 (1990).

3. A. Y. Liu and R. M. Wentcovitch, Phys. Rev. B 50, 10362 (1994).

4. Y. Guo and W. A. Goddard III, Chem. Phys. Lett. 237, 72 (1995)

5. D. Li, Y. W. Chung, M. S. Wong and W. D. Sproul, J. Appl. Phys. 74, 219 (1993).

6. M. Y. Chen, X. Lin, V. P. Dravid, Y. W. Chung, M. S. Wong and W. D. Sproul, Tribol. Trans. 36, 491 (1993).

7. M. Y. Chen, D. Li, X. Lin, V. P. Dravid, Y. W. Chung, M. S. Wong and W. D. Sproul, J. Vac. Sci. Technol. A 11, 521 (1993).

8. D. Li, E. Cutiongco, Y. W. Chun, M. S. Wong and W. D. Sproul, Surf. Coat. Technol. 68/69, 611 (1994).

9. H. Sjöström, I. Ivanov, M. Johansson, L. Hultman, J. E. Sundgen, S. V. Hainsworth, T. F. Page and L. R. Wallenberg, Thin Solid Films 246, 103 (1994).

10. J. J. Cuomo, P.A. Leary, D. Yu, W. Reuter and M. Frich, J. Vac. Sci. Technol. 16, 299 (1979).

11. J. H. Kaufman, S. Metin and D. D. Saperstein, Phys. Rev. B 39, 13052 (1989).

12. C. J. Toring, J. M. Sivertsen, J. H. Judy and C. Chang, J. Mater. Res. 5, 2490 (1990)

13. S. Kumer and T. L. Tansley, Solid State Commun. 88, 803 (1993).

14. N. Nakayama, Y. Tsuchiya, S. Tamada, K. Kosuge, S. Nagata, K. Takahiro and S. Yamaguchi, Jpn. J. Appl. Phus. 32, L1465 (1993).

15. K. M. Yu, M. L. Cohen, E. E. Haller, W. L. Hansen, A. Y. Liu ans I. C. Wu, Phys, Rev. b 49, 5034 (1994).

16. F. Rossi, B. Andre, A. van Veen, P. E.

Mijnarends, H. Schut, F. Labohm, H. Dunlop, M. P. Deplancke and K. Hubbard, J. Mater. Res. 9, 2440 (1994).

17. F. Rossi, B. Andre, A. van Veen, P. E. Mijnarends, H. Schut, F. Labohm, M. P. Deplancke, H. Dunlop and E. Anger, Thin Solid Films 253, 85 (1994).

18. G. L. Doll, J. P. Heremans, T. A. Perry and J. V. Mantese, J. Mater. Res. 9, 85 (1994).

19. A. Hoffman and I. Gouzman, Appl. Phys. Lett. 64, 845 (1994).

20. Gouzman, R. Brener and A. Hoffman, Thin Solid Films 253, 90 (1994).

21. C. Niu, Y. Z. Lu and C. M. Lieber, Science 261, 334 (1993).

22. J. Narayan, J. Reddy, N. Biunno, S. M. Kanetkar, P. Tiwari and P. Parikh, Mater. Sci. Eng. B26, 49 (1994).

23. H. W. Han and B. J. Fedman, Solid State Commun. 65, 921 (1988).

24. P. Wood, T. Wydeven and O. Tsuji, Thin Solid Films 258, 151 (1995).

25. F. Fijimoto and K. Ogata, Jpn. J. Appl. Phys. 76, 3791 (1994).

26. K. Ogata, J. F. D. Chubaci and F. Fujimoto, J. Appl. Phys. 76, 3791 (1994).

27. Y. Taki, T. Kitagawa and O. Takai, Proc. Symp. Plasma Sci. Mater. 8, 39 (1995)

28. Y. Taki, T. Kitagawa and O. Takai, Favric ation and Characterization of Advanced Materials (eds. S. W. Kim and S. J. Park), Materials Research Society of Korea (1995), p.613.

29. Y. Taki, T. Kitagawa and O. Takai, Proc. Symp. Plasma Sci. Mater. 9, 21 (1996).

30. T. Yen and C. Chou, Appl. Phys. Lett. 67, 2801 (1995)

31. Y. Zhang, Z. Zhou and H. Li, Appl. Phys. Lett. 68, 634 (1996).

32. N. Maréchal, E. Quesnel and Y. Pauleau, J. Vac. Sci. Technol. A 12, 707 (1994).

33. D. Beeman, J. Silverman, R. Lynds and M. R. Anderson, Phys. Rev. B 30, 870 (1984).

34. H. C. Tsai and D. B. Bogy, J. Vac. Sci. Technol. A 5, 3287 (1987).

35. K. Kanazawa, J. Precision Eng. Soc. Jpn. 55, 1342 (1989).

36. G. Beamson and D. Briggs, High Resoution XPS of Organic Polymers-The Scienta ESCA 300 Database, John Wiley & Sons. Inc., Chichester (1992), p.222.