Preparation of carbon nitride films from g-C₃N₄ by ion-beam-assisted deposition

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Abstract

Carbon nitride has noteworthy properties including high hardness levels. If the c-C₃N₄ or β-C₃N₄ structure can be synthesized, then hardness levels higher than that of diamond can be obtained. It is important to clarify the effect of ion impact on the growth of crystalline carbon nitrides on the synthesis of super-hard carbon nitrides. The ion beam-assisted deposition (IBAD) technique provides independent control over parameters, such as ion energy, temperature, and arrival rate of the atomic species during deposition. In this study, we investigated the structure and composition of a carbon nitride film prepared using graphitic carbon nitride as the evaporation source for the IBAD. The graphitic carbon nitride was formed into a pellet by press molding. The film deposited without nitrogen ion beam was obtained by evaporation using the pellet molded at 200 °C and 300 °C as the evaporation source. An amorphous carbon nitride film was obtained by IBAD using g-C₃N₄ as the evaporation source. The main chemical bonding in the carbon nitride film changed from C-N=C to C-C by varying the acceleration voltage of the nitrogen ion beam. Accordingly, the hardness of the film was increased. The hardness of the film at an acceleration voltage of 500 V was 23 GPa. This is due to the breaking of the CN bond by the ion beam, depending on the acceleration voltage of the ion beam.

Keywords: Carbon nitride film, IBAD, Electron beam deposition, Ion beam, Hardness

1. Introduction

Carbon nitride (C₃N₄) has noteworthy properties including high hardness levels and high current density of field emissions. If the c-C₃N₄ or β-C₃N₄ structure can be synthesized, then hardness levels higher than that of diamond can be obtained (Liu and Cohen, 1989; Liu and Wentzcovitch, 1994). Many studies on the synthesis of carbon nitride from the vapor phase have been conducted using various chemical vapor deposition (CVD) and physical vapor deposition (PVD) methods. Films prepared using PVD are generally amorphous carbon nitrides (CN_x) containing a small amount of nitrogen (Sjostrom, et al., 1994). The c- or β- C₃N₄ phase in the amorphous matrix has been obtained by the implantation of low-energy nitrogen into graphite (Yamamoto, et al., 1997) and unbalanced magnetron sputtering (Wei, et al., 1999). These studies showed that ion impact is important for the growth of super-hard carbon nitrides. Some reports showed that crystalline deposits are obtained when using CVD. α-C₃N₄ was obtained from a mixture of CH₄-N₂ reaction gas systems using microwave plasma CVD (Tanaka and Sakamoto, 2016), and graphitic C₃N₄ (g-C₃N₄) was obtained by thermal CVD (Tanaka and Sakamoto, 2017). Nevertheless, a super-hard carbon nitride film has not been realized. It is important to clarify the effect of ion impact on the growth of crystalline carbon nitrides on the synthesis of super-hard carbon nitrides. The ion beam-assisted deposition (IBAD) technique provides independent control over parameters, such as ion energy, temperature, and arrival rate of the atomic species during deposition.

Graphite has been used as the evaporation source in the synthesis of carbon nitride (Hayashi, et al., 2000). It is necessary to control the complex chemical reaction between the carbon vapor and the nitrogen ion beam occurring on the substrate surface. The conventional method using graphite is insufficient in terms of clarifying the effect of nitrogen

ions on the synthesis of super-hard carbon nitride. Hence, we propose g-C₃N₄, which is a type of carbon nitride compound, as the new evaporation source for the synthesis of carbon nitride by IBAD. The g-C₃N₄ has a layered structure similar to graphite. The preparation of g-C₃N₄ involves heating melamine, urea, or dicyandiamide at a temperature ranging from 550 °C to 700 °C, yielding a yellowish-brown or yellow powder (Liu, et al., 2011; Thomas, et al., 2008; Komatsu, 2001; Ge, 2011). The deposition of carbon nitride by IBAD with the evaporation of g-C₃N₄ can help clarify the effect of ion beam on the structure and chemical bond of CN films. Hence, stable evaporation of g-C₃N₄, the powder form of which is molded to pellets using a die, is necessary.

In this study, we synthesized a carbon nitride film by IBAD using g-C₃N₄ as the new evaporation source. First, we investigated the evaporation stability of the g-C₃N₄ pellet molded by press molding. We then demonstrated the deposition of the carbon nitride film by IBAD using g-C₃N₄ as the evaporation source. The effects of the acceleration voltage of the ion beam on the structure and composition of the carbon nitride film were studied.

2. Experimental procedure

2.1 Preparation of g-C₃N₄ pellet

Melamine (purity; 98.0%) was used as the feedstock. g-C₃N₄ was synthesized by directly heating the melamine in an alumina crucible with a cover. The melamine was heated at 600 °C for 1 h in an electric furnace. g-C₃N₄ was subjected to pulverization in a mortar and then formed into a pellet by press molding. Figure 1 shows the schematic of the press molding apparatus. The g-C₃N₄ powder was molded at 238 MPa for 1 h in a stainless die. During the press molding, the die was heated at room temperature (R.T.), 150 °C, 200 °C, and 300 °C. The density of the pellets was estimated by electronic balance. The structures of the pellets were determined using X-ray diffraction (XRD, Rigaku Co., Ltd., RINT-2100HK/PC) with Cu α radiation.

Fig. 1 Schematic of press molding apparatus.

2.2 Deposition of carbon nitride film

The carbon nitride films were deposited using the IBAD system. Figure 2 shows a schematic of the IBAD system (IVD 20/30E2/80-DE, Nissin Electric Co., Ltd.). Table 1 lists the deposition conditions. The substrate is a Si wafer (10 × 10 mm). The surface orientation of the Si wafers is (100). The substrates were cleaned by successive rinsing in an ultrasonic bath containing acetone. After cleaning, the Si substrates were fixed on a holder, and the chamber was evacuated to a base pressure of 5×10^{-3} Pa. The substrates were sputtered using an Ar-ion beam at an accelerating voltage of 2 keV for 10 min.

The g-C₃N₄ pellets molded at different temperatures were used as the evaporation source. An electron beam evaporation (EBE) of the g-C₃N₄ pellets without the ion beam was performed. The pressure during the evaporation was measured. For comparison, graphite was used as the evaporation source.

The carbon nitride film was deposited by IBAD with the EBE of the g-C₃N₄ pellets, and simultaneously, nitrogen ion beam bombardment was witnessed. The g-C₃N₄ pellet molded at 300 °C was used as the evaporation source. The ion current and the substrate temperature were fixed at 30 mA and room temperature, respectively. The acceleration voltage was varied to 200, 500, and 1000 V.

The structures of the deposits were characterized using an X-ray diffractometer. The diffraction was measured using the 2θ method (with an incident angle of 1.5°). The chemical bonds of the deposits were measured by X-ray photoelectron

spectroscopy (XPS, PHI 5000 VersaProbe, ULVAC-PHI, Inc.). The X-ray source was a monochrome Al $K\alpha$ with a photoelectron energy of 1486.6 eV. The films were referenced to the C-C peak at 284.5 eV to compensate for surface charging. The hardness of the deposits was estimated using a nanoindentation tester (ENT-1100a, ELIONIX Inc.). The tests were performed using a Berkovich indenter made of a single crystalline diamond. The maximum load was fixed at 50 mN. The time for loading and unloading was the same (10 s).

Fig. 2 Schematic of the IBAF system.

Table 1 Deposition conditions.

Substrate			Si
Evaporation source			g-C ₃ N ₄ pellet
Electron beam	Current	mA	9–23
	Background pressure	Pa	5.0×10^{-3}
	Deposition rate	nm/s	0.1
Ion beam	Assist gas	Gas	N ₂
		Flow rate	cm ³ /min
			2.0
	Acceleration voltage	V	200, 500, 1000
	Ion current	mA	30
Substrate current			mA
			1–9
Deposition time			h
			1

3. Results and discussion

3.1 Preparation and deposition of g-C₃N₄ pellet

Figure 3 shows the appearance and compact density of the g-C₃N₄ pellets molded at different temperatures. The pellets are yellow in color with a cylindrical column shape. The compact density of the pellets increases with the increase

in the molding temperature. The theoretical density of g-C₃N₄ is in the range of 1.59–2.20 g/cm³ (Kroke and Schwarz, 2004). The compact density of the g-C₃N₄ pellets is lower than the theoretical density because of the voids in the pellets.

Figure 4 shows the XRD patterns of the pellets molded at different temperatures. Only g-C₃N₄ peaks are observed in all the patterns. The difference in the diffraction pattern with respect to the molding temperature is not confirmed. The peaks of g-C₃N₄ are observed at positions of 13.0, 27.6, 44.8, and 57.8°. The XRD patterns were assigned based on the data from previous studies (Yan et al., 2009; Yang et al., 2011). The strongest peak at 27.6° is a typical interlayer stacking peak, assigned to g-C₃N₄ as the (0 0 2) peak.

Figure 5 shows the relationship between the pressure during evaporation and the evaporation time. The pressure at the start of evaporation is in the range of 10⁻² to 10⁻³ Pa. For the pellets prepared at molding temperatures of R.T. and 150 °C, the pressure suddenly increases during 5–10 min. On the other hand, the pressure is stable when using pellets prepared at molding temperatures of 200 °C and 300 °C. Therefore, the pellets molded at 200 °C and 300 °C were used as the evaporation source for the synthesis of the film. The reason for the increased pressure could be evaporated moisture or unreacted substances in the pellet. The XRD pattern, shown in Fig. 4, indicates that there are no unreacted substances in the pellet. This suggests that the increased pressure is due to the evaporation of the moisture in the pellet.

The electron beam currents applied to the g-C₃N₄ pellets and graphite at a deposition rate of 0.1 nm/s were in the ranges of 9–23 mA and 94–165 mA, respectively. The g-C₃N₄ evaporated with an electron beam current less than 1/18 that required for graphite. Because g-C₃N₄ has a lower evaporating temperature (Yan et al., 2009) and thermal conductivity than graphite. This result shows that a high-speed coating of the carbon nitride can be realized using g-C₃N₄ as the evaporation source.

	Molding temperature (°C)			
	R.T.	150	200	300
Appearance
Compact density (g/cm ³)	1.14	1.30	1.32	1.38

Fig. 3 Appearance and compact density of g-C₃N₄ pellets molded at different temperatures.

Fig. 4 X-ray diffraction patterns of pellets molded at different temperatures.

Fig. 5 Relationship between pressure during evaporation and evaporation time.

3.2 Preparation of carbon nitride film by IBAD

Figure 6 shows (a) XRD pattern and (b) Raman spectra of the deposits fabricated at different acceleration voltages of the ion beam. No peaks are observed in the patterns shown in Fig. 6(a). This result indicates that the deposits have an amorphous structure. The broad peaks at 1350 and 1580 cm^{-1} corresponding to amorphous carbon are observed in the Raman spectra (in Fig. 6(b)) of all the substrate deposits. However, these peaks are weak at an acceleration voltage of 1000 V . The background slope of the deposits fabricated via EBE is high; the slope at an acceleration voltage of 200 V is higher than those at acceleration voltages of 500 and 1000 V . The peaks of $g\text{-C}_3\text{N}_4$ in the range of $1000\text{--}1800\text{ cm}^{-1}$, based on the data from another study (Zinin et al., 2009), are not found.

Figure 7 shows the composition of the deposits fabricated at different acceleration voltages of the ion beam. The deposit including nitrogen (56 at.%) is obtained by EBE. The nitrogen content in the deposit decreases with the increase in the acceleration voltage of the ion beam and is 23 at.% at acceleration voltages of 500 and 1000 V . The Si content (12 at.%) at 1000 V indicates that the deposit is not film-like.

Fig. 6 (a) XRD pattern and (b) Raman spectra of deposits fabricated at different acceleration voltages of the ion beam.

Fig. 7 Composition of deposits fabricated at different acceleration voltages of the ion beam.

Figure 8 shows the XPS (a) C1s and (b) N1s spectra of the deposits fabricated at different acceleration voltages of the ion beam. The C-C (284.5 eV), C-N $\equiv$ C (286.7 eV), and C-N=C (288.1 eV) peaks are observed in the C1s spectra (a). The main peak of the deposit by EBE can be attributed to C-N=C. The main peak shifts from C-N=C to C-C with the increase in the acceleration voltage of the ion beam. The C-N=C (398.5 eV), C-N (399.5 eV), and -NH (401 eV) peaks are observed in the N1s spectra (b). The C-N peak is higher at an acceleration voltage of 500 V. Figure 9 shows the peak area ratio deconvoluted (a) C1s and (b) N1s spectra of the deposits. With the increase in the acceleration voltage, the area ratio of C-C increases and that of C-N=C decreases, as shown in Fig. 9(a). The area ratio of C-N $\equiv$ C is maximum at 200 V. The area ratio of C-N=C, shown in Fig. 9(b), decreases with the increase in the acceleration voltage to 500 V, whereas that of C-N increases. The area ratio of NH is minimum at 500 V.

Fig. 8 XPS (a) C1s and (b) N1s spectra of deposits fabricated at different acceleration voltages of the ion beam.

Fig. 9 Peak area ratio deconvoluted (a) C1s and (b) N1s spectra of the deposits fabricated at different acceleration voltages of the ion beam.

The structural and chemical bonding analyses indicate that the films deposited using the g-C₃N₄ pellet as the evaporation source are CN_x. In addition, the results of the Raman and XPS measurements indicate that hydrogen is present in the films. The slope of the background correlates with the CH bond (Marchon et al., 1997). The Raman spectra, shown in Fig. 6(b), suggest that the films deposited by EBE and IBAD at 200 V include hydrogen. Moreover, the existence of hydrogen can be confirmed from the NH peak in the N1s spectra shown in Fig. 9(b). The hydrogen content in g-C₃N₄ powder is reported to be 17 at.% (Zhao et al., 2005). Taking this result into account, the existence of hydrogen in the films can be attributed to that in the g-C₃N₄ pellet. On the other hand, the slope of the Raman spectra (Fig. 6(b)) of the film deposited by IBAD at 500 V is low, and the corresponding NH area ratio is also low (Fig. 9). It is suggested that hydrogen is sputtered from the films by the impact of the nitrogen ion beam. Because of the decrease in the nitrogen with the increase in the acceleration voltage, hydrogen is vaporized as NH. Additionally, the nitrogen ion beam leads to a change in the chemical bonds such as C-N and C-N=C. The C-N/C-N=C ratios of the peak area ratio for EBE and IBAD at 500 V are 0.25 and 0.55, respectively. This result indicates that the C-N bond ratio is increased by the impact of the nitrogen ion beam.

Because the ion beam at 1000 V has a high energy, the deposit by IBAD at 1000 V could not form a film. The nitrogen ion beam enhances the C-N bond formation and decreases the nitrogen content in the films.

Figure 10 shows the relationship between the displacement and the load from the indentation test. Figure 11 shows the hardness of the deposits fabricated at different acceleration voltages of the ion beam. The maximum film thickness is approximately 360 nm, and the indentation depths under all the conditions are greater than the film thickness. The hardness of the deposits is considered to be influenced by that of the substrate. The hardness of the deposit increases with the increase in the acceleration voltage; the maximum value is 23 GPa at 500 V. The hardness decreases at 1000 V.

Fig. 10 Relationship between displacement and load during indentation test.

Fig. 11 Hardness of deposits fabricated at different acceleration voltages of the ion beam.

The hardness of the deposit by IBAD at 1000 V is the same as that of the Si substrate because the deposit by IBAD at 1000 V is not film-like, and the hardness of the substrate was 14.0 GPa. These results show the same tendency as those of the IBAD applied at various acceleration voltages using graphite as the evaporation source (Tokoroyama et al., 2011). Although the hardness of the deposit by IBAD at 500 V is similar to that of the deposit by IBAD using graphite, the hardness under other conditions is low. This is due to the effect of the chemical bond and the atomic concentration of the films. Figure 12 shows the atomic ratio of the peak area (a) C1s and (b) N1s as a function of the hardness. The atomic ratio of the peak area was calculated by multiplying the peak area with the atomic content obtained using XPS. The deposit by IBAD at 1000 V is not included in Fig. 12 because the deposit does not form a film. Generally, the hardness of diamond-like carbon (DLC) depends on the hydrogen content; an increase in the hydrogen content in DLC leads to a decrease in its hardness (Tamor and Vassell, 1994).

The hydrogen in CN_x has the same effect as DLC. The correlation between NH, shown in Fig. 12(b), and the hardness is low. On the other hand, the hardness correlates with the ratio of C-C, C-N, and C-N=C bond. Moreover, the deposits by EBE and IBAD at 200 V include CH bonds, as shown in Fig. 6(b). The higher hardness at higher acceleration voltages of the ion beam can be attributed to the decreased hydrogen content in the films and a greater number of C-C and C-N bonds. Therefore, CN_x with various hardness values can be obtained by carefully selecting the acceleration voltage of the ion beam with g-C₃N₄ pellet as the evaporation source. Additionally, IBAD using g-C₃N₄ as an evaporation source can be used to obtain a high-speed coating of hard CN_x because the g-C₃N₄ pellet can evaporate at low electron beam currents.

Fig. 12 Atomic ratio of the peak area (a) C1s and (b) N1s as a function of hardness.

4. Conclusions

This study demonstrated that a CN_x film can be obtained by IBAD using a g-C₃N₄ pellet as the evaporation source. Although the CN_x films contain hydrogen because of the hydrogen in the g-C₃N₄ pellet, the IBAD method using g-C₃N₄ as an evaporation source was found to be effective in realizing a high-speed coating of hard CN_x. The main chemical bonding in the CN_x film changed from C-N=C to C-C and C-N by varying the acceleration voltage of the nitrogen ion beam. Moreover, the nitrogen content in the film decreased with the increase in the acceleration voltage of the ion beam; thus, increasing the hardness of the film. The deposit fabricated using the IBAD at an acceleration voltage of 500 V exhibited maximum hardness, i.e., 23 GPa.

References

- Ge, L., Synthesis and photocatalytic performance of novel metal-free g-C₃N₄ photocatalysts, *Materials Letters*, Vol.65, No.17-18 (2011), pp.2652–2654.
- Hayashi, T., Matsumoto, A., Muramatsu, M., Kohzaki, M. and Yamaguchi, K., Wear resistance of carbon nitride thin films formed by ion beam assisted deposition, *Thin Solid Films*, Vol.376 (2000), pp.152–158.
- Komatsu, T., Attempted chemical synthesis of graphite-like carbon nitride, *Journal of Materials Chemistry*, Vol.11 (2001), pp.799–801.
- Kroke, E. and Schwarz, M., Novel group 14 nitrides, *Coordination Chemistry Reviews*, Vol.248 (2004), pp.493–532.
- Liu, J., Zhang, T., Dawson, G. and Chen, W., Simple pyrolysis of urea into graphitic carbon nitride with recyclable adsorption and photocatalytic activity, *Journal of Materials Chemistry*, Vol.21 (2011), pp.14398–14401.
- Liu, Y. A. and Cohen, L. M., Prediction of new low compressibility solids, *Science*, Vol.245 (1989), pp.841–842.
- Liu, Y. A. and Wentzcovitch, M. R., Stability of carbon nitride solids, *Physical Review B*, Vol.50, No.14 (1994), pp.10362–10365.
- Marchon, B. Gui, J. Grannen, K. Rauch, C. G. Ager, W. J. Silva, P. R. S. and Robertson, J., Photoluminescence and Raman spectroscopy in hydrogenated carbon films, *IEEE Transactions on Magnetics*, Vol.33, No.5 (1997), pp.3148–3150.
- Sjostrom, H., Ivanov, I., Johansson, M., Hultman, L., Sundgren, E. J., V. Hainsworth, S., Page, F. T. and Wallenberg, R., Reactive magnetron sputter deposition of CN_x films on Si(001) substrates: film growth, microstructure and mechanical properties, *Thin Solid Films*, Vol.264, No.1-2 (1994), pp.103–109.
- Tamor, A. M. and Vassell, C. W., Raman “fingerprinting” of amorphous carbon films, *Journal of Applied Physics*, Vol.76, No.6 (1994), pp.3823–3830.
- Tanaka, I. and Sakamoto, Y., Low-temperature synthesis of carbon nitride by microwave plasma CVD, *Japanese Journal of Applied Physics*, Vol.55, No.1S (2016), pp.01AA15-1-01AA15-4.
- Tanaka, I. and Sakamoto, Y., Synthesis of graphitic carbon nitride films from melamine by thermal CVD, *TANSO*, Vol.276 (2017), pp. 8–14 (in Japanese).
- Thomas, A., Fischer, A., Goettmann, F., Antonietti, M., Muller, O. J., Schlogl, R. and Carlsson, M. J., Graphitic carbon nitride materials: variation of structure and morphology and their use as metal-free catalysts, *Journal of Materials Chemistry*, Vol.18 (2008), pp.4893–4908.
- Tokoroyama, T., Saito, R., Umehara, N. and Fuwa, Y., The effect of substrate temperature, nitrogen ion beam acceleration voltage, and deposition rate on hardness of carbon nitride coating, *The Japan Society of Mechanical Engineers*, Vol.7, No.772 (2011), pp. 624–630[in Japanese].
- Wei, J., Hing, P. and Mo, Q. Z., Structure and tribological behaviour of carbon nitride films, *Wear*, Vol.225–229, No.2 (1999), pp.1141–1147.
- Yamamoto, K., Koga, Y., Yase, K., Fujiwara, S. and Kubota, M., Formation of cubic phase carbon nitride solid by low energy nitrogen implantation into graphite, *Japanese Journal of Applied Physics*, Vol.36, No.2B (1997), pp.230–233.
- Yan, C. S., Li, S. Z. and Zou, G. Z., Photodegradation performance of g-C₃N₄ fabricated by directly heating melamine, *Langmuir*, Vol.25, No.17 (2009), pp.10397–10401.
- Yang, J., Wu, X., Li, X., Liu, Y., Gao, M., Liu, X., Kong, L. and Yang, S., Synthesis and characterization of nitrogen-rich carbon nitride nanobelts by pyrolysis of melamine, *Applied Physics A*, Vol.105 (2011), pp.161–166.
- Zhang, P. Y., Gu, S. Y., Chang, R. X., Ti, Z. Z. Shi, X. and Zhang, F. X., On the structure and composition of crystalline carbon nitride films synthesized by microwave plasma chemical vapor deposition, *Materials Science and Engineering: B*, Vol.78, No.1 (2000), pp.11–15.
- Zhao, C. Y., Yu, L. D., Zhou, W. H. and Tian, J. Y., Turbostratic carbon nitride prepared by pyrolysis of melamine, *Journal of Materials Science*, Vol.40 (2005), pp.2645–2647.
- Zinin, V. P., Ming, C. L., Sharma, K. S., Khabashesku, N. V., Liu, X., Hong, S., Endo, S. and Acosta, T., Ultraviolet and near-infrared Raman spectroscopy of graphitic C₃N₄ phase, *Chemical Physics Letters*, Vol.472 (2009), pp.69–73.