SPUTTER-DEPOSITION OF CARBON NITRIDE FILMS WITH HIGH NITROGEN CONCENTRATION

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ABSTRACT

The synthesis of carbon nitride thin films with high nitrgen concentration was accomplished by reactive supttering at relatively high working pressure. In conventional reactive sputter-deposition of carbon nitride films, working pressure was 0.3-5Pa and the ratio of nitrogen to carbon(N/C ratio) in the films was less than 0.5. In this study, amorphous carbon nitride films with the N/C ratio $\approx$ 1.0 were prepared on Si(100) substrates at higher pressure, 20-60 Pa. Structural analyses with Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy revealed that the films prepared consisted of triazine-like plain network.

INTRODUCTION

In recent years, several hypothetical covalent carbon-nitrogen solids were suggested as candidates for super hard materials by theoretical calculations. Liu and Cohen[1,2] reported that the bulk modulus of the theoretical covalent carbon-nitrogen solid, β-C$_3$N$_4$, which had the same structure as β-Si$_3$N$_4$, might be greater than or equal to that of diamond. Liu and Wentzcovitch[3] also proposed β-C$_3$N$_4$, and zinc-blende like cubic C$_3$N$_4$ as metastable phases comparable to diamond. Conversely, Guo and Goddard III[4] showed that α-C$_3$N$_4$ was more stable than β-C$_3$N$_4$, and both α-and β-C$_3$N$_4$ were about half as hard as diamond. These calculation triggered off the studies on preparation of carbon nitride thin films.

The current popular processes to synthesize carbon nitride thin films are de[5-9], rf[10-15] and ion beam-assisted[16,17] reactive sputtering, nitrogen implantation into graphite[18-20], laser ablation of graphite combined with atomic and/or ionic nitrogen[21,22] and capacitively coupled rf plasma chemical vapor deposition(CVD)[23,24]. In addition, ion-assisted dynamic mixing(ion and vapor deposition)[25,26], shielded are ion plating (shielded cathodic are evaporation)[27-29], are plasma jet CVD[30] and inductively coupled rf plasma assisted hot filament CVD[31] have also been used for preparation. To date, cry stalline carbon nitride films detectable with X-ray diffraction have not been synthesized except for the report by Zhang et al.[31] Transmission electron microscopy investigation of the carbon nitride films prepared by Yu et al.[15], Niu et al.[21], Naray an et al.[22] and Yen et al.[30] showed the dif-

fraction ring patterns corresponding to α-and /or β-C_3N_4. C_3N_4 nanocry stallites were included in amorphous carbon matrix of the films prepared by them. Further, with the exception of ion-assisted dy namic mixing, the ratio of nitrogen to carbon(the N/C ratio) in prepared films was almost up to 0.5, which was a very low value compared to 1.33 of the hypothetical β-C_3N_4.

Reactive sputtering is the most popular process to prepare amorphous carbon nitride films. In usual reactive sputtering, working pressure was 0.3-5 Pa and the N/C ratio was less than 0.5. In this paper, we report on the preparation of amorphous carbon nitride films with high nitrogen concentration, the N /C ratio $\approx$ 1.0, by reactive sputtering at relatively high pressure.

EXPERIMENTAL PROCEDURE

FILM PREPARATION

A high purity sintered graphite (Toyo Tanso IG510, ash:10 ppm) was used as a sputtering target. The target voltage was-1000 V(dc). A substrate holder was located opposite to the target. A Si(100) substrate was set on the substrate holder. The distance between the target and the substrate was 40 mm. N_2gas was introduced into a chamber. Carbon nitride films were prepared on Si (100) substrates (size:10mm×35mm, thickness:0.5mm) by reactive dc sputtering. Working pressure and substrate temperature were kept at fixed values in the ranges of 20-60 Pa and 50-400°C.

FILM CHARACTERIZATION

Chemical bonding states and composition in the films were measured with X-ray photoelectron spectroscopy(XPS) (Shimadzu-Kratos AXIS). The pressure inside the analytical chamber was in the 10^{-8} Pa range. Unmonochromated Mg $K\alpha$ radiation (1253.6 eV) was used at 12 kV and 10mA. The pass energy of the photoelectron detector was kept at 10 eV. Deposited film surfaces were investigated without Ar^+ ion sputtering, since this sputtering technique destroyed metastable carbon network and caused the denitrification from the film surfaces. All spectra measured were referenced to the C ls peak of staturated aliphatic carbon(-CH_2-) at 285.0 eV. Chemical composition in the films was calculated using each peak area with the sensitive factor for each element.

The thickness of the films was estimated with a stylus instrument (Mitutoyo SV-600). Fourier transform infrared (FT-IR) spectroscopy (Jasco FT/IR-5300) was also used to reveal chemical bonding states in the films. the crystallinity of the films was investigated with X-ray diffraction (Rigaku RINT).

RESULTS AND DISCUSSION

The measurement with X-ray diffraction indicated that all carbon nitride films prepared were amorphous.

The N/C atomic ratios in the films prepared at the substrate temperature of 50°C and the pressures of 20, 40 and 60 Pa were beyond 0.8. Contaminant oxygen concentration was below 10 at.%. Almost of this amount was considered to be due to oxygen atoms adsorbed on the film surfaces because of unused Ar^+ion sputtering during the XPS measurement. These films had twice as high

N/C ratio as amorphous carbon nitride films synthesized by conventional sputtering at 0.3 -5 Pa. Higher pressure deposition leads to the decrease in mean free path of species and the enhancement of collisions and chemical reactions among species. Chemical vap or reaction in the space between the target and the substrate are important in order to increase nitrogen concentration in carbon nitride films deposited.

Figure 1 shows the N/C ratio and deposition rate of the films prepared at 20 Pa as a function of substrate temperature. The N/C ratio more than 0.8 was achieved at temperature range of 50-300℃ and the maximum ratio was 1.0 at 200℃. Deposition rate decreased with rising substrate temperature and film formation was impossible beyond 400℃. Namely, volatile resultants like cyanogen $(CN)_x$ are produced in gas phase between the target and the substrate, these species reach the substrate surface, and a car-

bon nitride film is formed on the substrate. These volatile species are considered to revaporize from the substrate surface with rising substrate temperature after they deposit on the substrate.

Figure 2 shows a IR spectrum of the film prepared at 20 Pa and 50℃. The spectra of the films prepared at other temperatures were almost the same as that shown in Fig. 2. the most remarkable feature in the spectrum is a non-distinguished strong broad band at 1800-1100 cm^{-1}. A peak at 1630 cm^{-1} is identified with N-H deformation vibration. Two shoulders at 1537 cm^{-1} and 1381 cm^{-1} are assigned to inplain stretching vibrations of triazine ring. A weak peak at 986cm^{-1} is due to the interactions between C=C and C=N stretching vibrations of pyridine ring. A peak at 791cm^{-1} is attributed to out-of-plain deformation of triaxine ring. An azine ring is a six-membered hetero aromatic
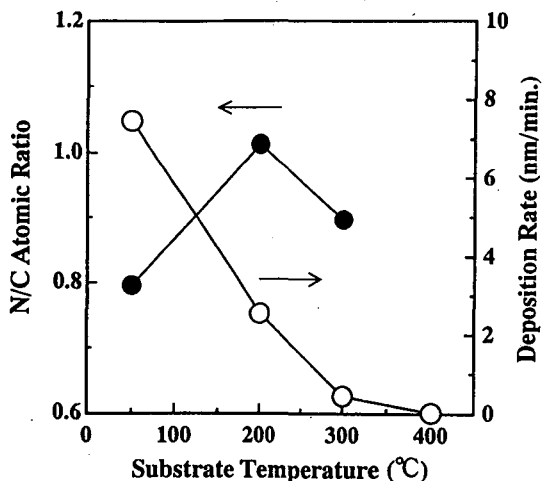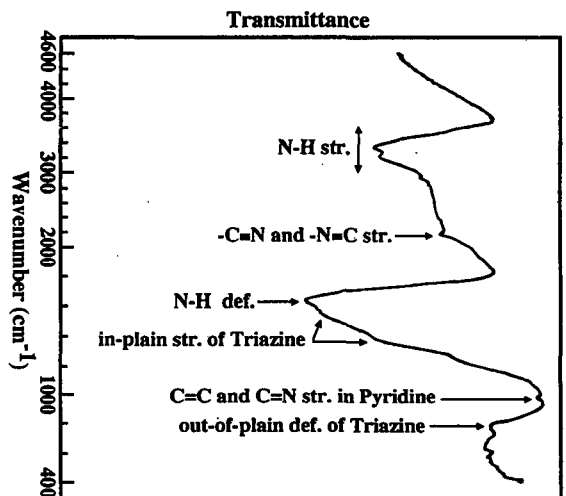

Fig 1. Effects of the substrate temperature on the N/C atomic and deposition rate of the amorphous carbon nitride films prepared at the working pressure of 20 Pa.

Fig 2. IR spectrum of the amorphous carbon nitride film prepared at the working pressure pressure of 20 Pa and the substrate temperature of 50℃

ring where nitrogen atoms are substituted for carbon atoms. The azine where carbon and nitrogen atoms are located alternatively is called triazine. And specially, mono azine is usually named pyridine. The existence of a little amount of pyridine rings in the film is consistent with the N/C ratio of 0.8 slightly less than 1.0.
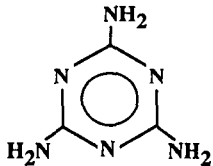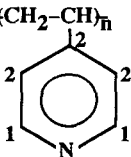
A weak but relatively sharp peak at $2182cm^{-1}$ is attributed to nitrile($-C\equiv N$) and isonitrile ($-N\equiv C$)groups. A medium broad band at $3300-3000cm^{-1}$ is assigned to N-H stretching abosorption. The origin of hydrogen is considered to be residual moisture in the experimental chamber.

Structural analysis with FT-IR reveals that aromatic sp^2 plain carbon-nitrogen bonding like triazine is dominant in all the films prepared.

Chemical bonding states in carbon nitride films were also investigated with XPS. As referential organic compounds, the structural formulas and XPS core level peak positions of triazine, melamine and polyvinylpyridine[32, 33] molecules are summarized in Table 1. The C 12 peak position of a triazine molecule is 288. 7 eV, whereas the peak position of a melamine molecule where carbon atoms are bonded with amino groups is 288.3 eV. The carbon atoms in a triazine ring of a melamine molecule have a little higher electron density than the carbon atoms in a triazine molecule, because of plus resonance (+R) effect of - NH_2 groups which act as electron donor groups in the resonance structure of a melamine molecule. The peak due to the carbon atoms in the triazine ring of a melamine molecule, therefore, appears at a little lower binding energy side than that due to the carbon atoms in a triazine molecule. In the case

Table 1 The structural formulas and XPS C ls peak positions of triazine, melamine and polyvinytpyridine.

Organic Compound	Structural Formula	Binding Energy (eV)	Symbol
Triazine		288.7	T
Melamine		288.3	M
Polyvinylpyridine		1. 285.99 2. 285.48	P1 P2

of polyvinylpyridine, the C ls peak is spearated into two compon4nts according to the distance teween carbon atmos and a nitrogen atom in the molecule. On the other hand, the N ls spectrum for a melamine is not divided into two components of -NH₂ groups and nitrogen atoms in a triazine ring because chemical shifts of these two components are not seriously different each other. The symbols representative of these substances shown in Table l are used in Fig. 3.

Figure 3 shows XPS Cls spectra of referential melamine powder and the carbon nitride films prepared at 20 Pa and 50, 200 and 300 ℃. The spectrum of melamine separates into
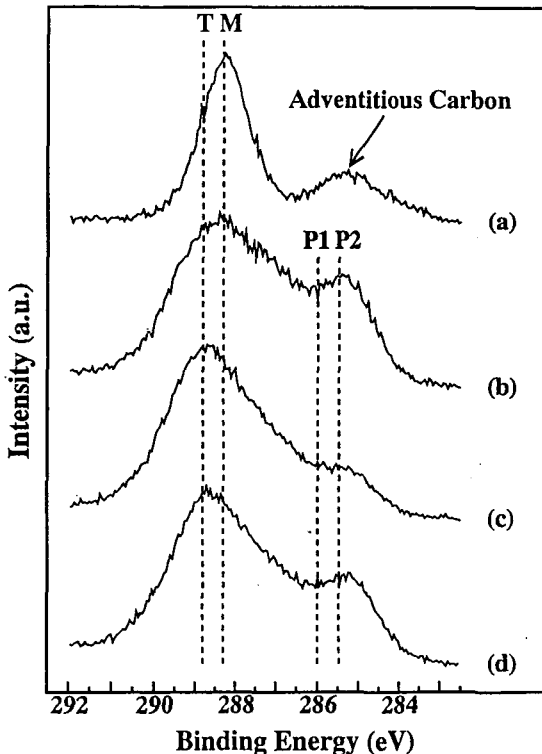

Fig 3. XPS C ls spectra of (a) referential melamine powder and the amorphous carbon nitride films prepared at the working pressure of 20 Pa and the substrate temperatures of (b) 50℃, (c) 200℃ and (d) ℃

two peaks at 288.3eV and 285.3 eV. A main sharp peak at 288.3 eV is indentified with the carbon atoms in a triazine ring of a melamine molecule and a weak broad peak at 285.3 eV is assigned to adventitious carbon atoms adsorbed on melamine powder.

Similarly, the spectra of carbon nitride films are divided into two broad peaks at 288.3-288.7 eV and 285.3-285.5 eV. Primary broad peak at 288.3-288.7 eV is due to the carbon atoms which form triazine likt network in the films. Additionally, the existence of diazine-like rings in the films is obvious from the shoulder around 287.0-287.8 eV. Secondary broad peak at 285.3-285.5 eV consists of both pyridine-like rings and adventitious carbon atoms components. The primary peak becomes sharp (namely, the shoulder decreases) and the secondary peak becomes weak with increasing N/C ratio, in order of (b),(d) and (c) as indicated in Fig. 1. The secondary peak of the film prepared at 200℃ does not include pyridine-like component. After that, as the N/C ratio approaches to 1. 0, pyridine-like and diazine-like components decrease and almost complete triazine-like network is formed. Moreover, the primary peak shifts from 288.3 eV to 288.7 eV with rising substrate temperature, in order of (b), (c) and (d). Higher substrate temperature deposition promotes the formation of triazine -like netwinsted of hydrogen incorporation as amino groups linked with triazine rings in the films.

Figure 4 shows XPSN ls spectra of referential melamine powder and the carbon nitride films prepared at 20 Pa and 50, 200 and 300 ℃. The components due to triazine-, diazine- and pyridine-like structure are not resolved

in N 1s spectra. The spectrum peak of melamine pwoder is lower than those of the films because of +R effect of -NH$_2$ groups. Shake-up peak at 406 eV is caused by $\pi-\pi^*$ transition in the triazine rings. This shake-up structure appears most remarkably for melamine powder. -NH$_2$ group component decreases with rinsing substrate temperature as mentioned above.
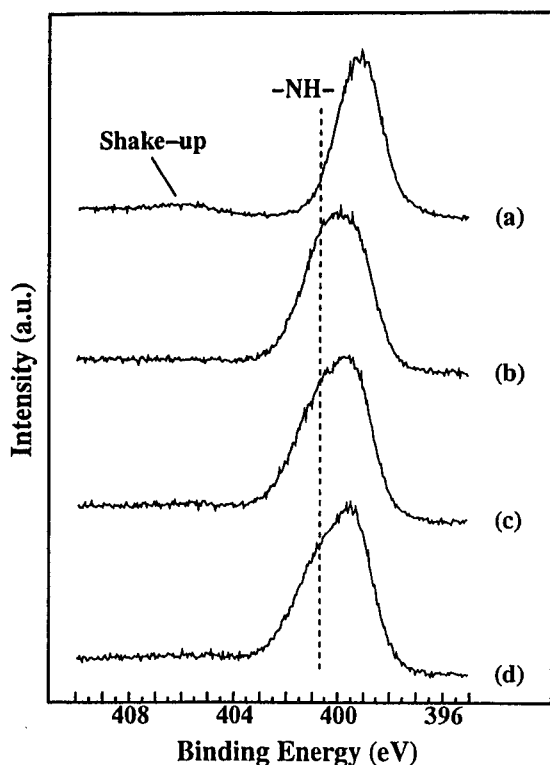

Fig 4. XPS N 1s spectra of (a) referential melamine powder and the amorphous carbon nitride films prepared at the working pressure of 20 Pa and the substrate temperatures of (b) 50℃, (c) 200℃ and (d) 300℃

CONCLUSIONS

In conventional reactive sputter-deposition of carbon nitride films, working pressure is 0. 3-5 Pa The N/C rato in the amorphous carbon nitride films prepared at higher pressure,

20-60 Pa, is twice as high as that in the films synthesized by conventional sputtering Higher pressure deposition leads to the enhancement of chemical reactions among species. Chemical vapor reactions in the space between the target and the substrate are important in order to increase nitrogen concentration in carbon nitride films deposited. All amorphous carbon nitride films prepared in this study mainly consist of aromatic sp^2 plain carbon-nitrogen bonding network like triazine, thus, the films are polymeric and soft. As the N/C ratio approaches to 1.0, pyridine-like and diazine-like components decrease and almost complete triazine-like network is formed.

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