

Carbon nitride thin films prepared by KrF excimer laser ablation in nitrogen gas

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Abstract

Carbon nitride films were deposited by ablation of carbon molecular fragments from a graphite target onto a silicon substrate in nitrogen gas using the KrF excimer laser with and without an application of a bias voltage. In the application of a bias voltage, the ionized carbon clusters were accelerated toward the negatively biased substrate. The deposited films were characterized by SEM, XPS, FT-IR and optical transmission. The effects of nitrogen gas pressure, substrate temperature and biased voltage on the composition and structure of the films were investigated. The maximum value of the atomic ratio N/C for the film deposited at nitrogen pressure of 267 Pa was 0.36. The biased voltage was effective to draw the ionized cluster to the substrate but the internal energy of cluster didn't change greatly, the combining state showing negligible change. Increasing the substrate temperature increased the content of disordered graphite, and decreased the atomic ratio of nitrogen. A detail study of the C1s and N1s XPS spectra of the film showed that the fraction of the sp^2 hybridization C-N bonds was higher than that of sp^3 , suggesting a higher content of the C=N double bond in the films.

Keywords: carbon nitride, KrF excimer laser, laser ablation

I. Introduction

The recent interest in the synthesis of carbon nitride thin films emanates from the theoretical work by Liu and Cohen^[1,2] predicting the existence of a metastable sp^3 covalent-bonded β - C_3N_4 compound, structurally analogous to β - Si_3N_4 and possibly comparable to or greater than diamond. A number of groups have subsequently attempted to deposit β - C_3N_4 using a variety of techniques, including plasma chemical vapor deposition (CVD), sputtering^[3], ion beam assisted deposition (IBAD)^[4] and pulsed laser deposition with^[5-7] and without^[8-12] other energy source. Some of them claimed to have obtained nanocrystalline β - C_3N_4 in the amorphous CN_x matrix. The fraction of nitrogen for almost all films obtained by these techniques were less than C_3N_4 stoichiometry.

An ablation of graphite target in a nitrogen atmosphere is a simple method, where CN radicals are formed in the plasma by the collision of carbon species with the nitrogen molecules during the expansion of the plume. In this study, the KrF excimer laser was used in nitrogen gas with and without an application of a bias voltage. In the application of a bias voltage, the ionized carbon clusters were accelerated toward the negatively biased substrate. The effects of nitrogen gas pressure, substrate temperature and biased voltage on the composition and structure of the films were investigated. The deposited films were characterized by scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared

absorption (FT-IR) and optical transmission.

II. Experimental

Figure 1 shows a schematic representation of the experimental apparatus. It consisted of a KrF excimer laser system (wavelength 248 nm, pulse duration 32 ns) and a reaction chamber for laser ablation. The laser energy was 400 mJ, and the repetition rate was 10 Hz. The laser beam was focussed onto a graphite target at an incidence angle of 40° in nitrogen gas. The distance between the target and the substrate was 1.5 cm. The carbon nitride (CN_x) films were deposited during 30 minutes onto a p-Si (111) and glass substrate. The wafers were cleaned as per standard RCA cleaning procedures. The nitrogen gas pressure was varied in the range from 13.3 to 133 Pa, at the substrate temperature of $30^\circ C$, while the substrate temperature was varied in

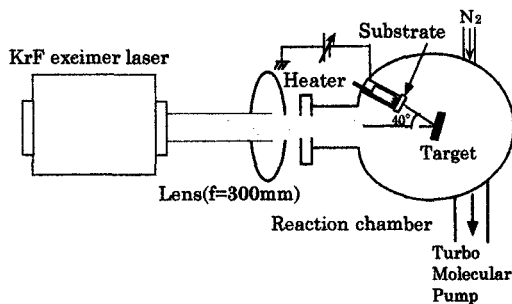


Fig.1 Schematic representation of the experimental apparatus and reactor.

the range from room temperature to 500 °C under constant nitrogen pressure of 66.6 Pa. The DC voltage from 0 to -300 V was applied between the target and the substrate. In this experiment, the distance between the target and the substrate was 4.0 cm, and the incidence angle was 25°. The substrate temperature was 30 °C and the nitrogen pressure was 26.7 Pa.

III. Results and Discussion

The ion flux of ablation plume was measured as ion current into the substrate at nitrogen pressure of 13.3 mPa and 26.7 Pa. Fig.2 shows the waveform of ion current at nitrogen pressure of 13.3 mPa, where the mean free path is longer than the distance between the substrate and the target. The ion current increases with increasing biased voltage, indicating that the ablation plume is ionized and that the biased voltage is effective for drawing ionized cluster to substrate. The result at nitrogen pressure of 26.7 Pa is also shown in this figure. The ion current at 26.7 Pa is much smaller than that at 13.3 mPa, indicating that most of the ionized cluster become neutral by colliding with nitrogen molecules.

The SEM photographs revealed that the surface of the film was smooth. The crystal granule couldn't be found, and few submicron droplets were observed. Very few droplets were identified for the film deposited at nitrogen pressure of 13.3 Pa, and their density increased with increasing nitrogen pressure. The density of droplet decreased with increasing substrate temperature and increased with increasing biased voltage.

The nitrogen content of the film was calculated from the XPS peak areas^[4,6-15]. Fig.3 shows the atomic ratio N/C of the films deposited at various nitrogen pressures and substrate temperatures. As seen in Fig.3 (a), the maximum value of the atomic ratio N/C for the film deposited at nitrogen pressure of 267 Pa was 0.36. The value is lower than that of the stoichiometric β -C₃N₄, i.e., 1.33. Similar lower values, which fall within a range of 0.3-0.5, have been reported by other investigators^[7-12] using pulsed laser deposition in nitrogen gas.

The reason why the atomic ratio N/C increases with increasing nitrogen pressure in the range from 0 to 267 Pa is that the number of the collision of cluster with nitrogen molecule increases with increasing nitrogen pressure. In the range of higher pressure, however, the atomic ratio N/C decreases with increasing nitrogen pressure. A nitrogen atmosphere at too high pressure prevents the deposition of CN_x thin films because the high pressure restricts the expansion speed of the carbon

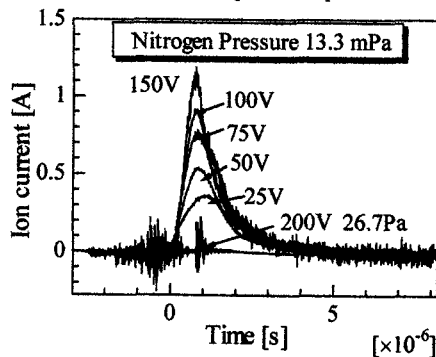


Fig.2 Waveform of the ion current for ablation plume at various biased voltages.

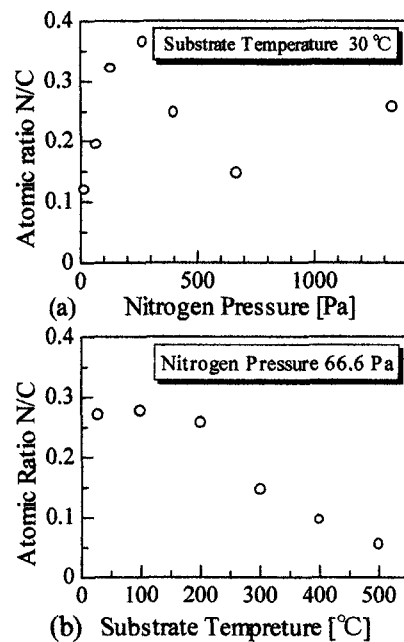


Fig.3 Atomic ratio N/C of film as a function of (a) nitrogen pressure and (b) substrate temperature.

plasma zone and give more chance for collision among carbon species. In addition, CN radicals formed in the plasma are scattered in a series of collisions with the nitrogen molecules^[12]. The atomic ratio at 1333 Pa indicates relatively high value, but the SEM photograph at this condition shows that the surface is coarse.

Fig.3 (b) shows that the value of N/C is almost constant at substrate temperatures lower than 200 °C and decreases with increasing temperature at higher temperatures.

Figs.4 and 5 show the photoelectron spectra of C1s and N1s in the films deposited at various substrate temperatures. The C1s and N1s spectra are deconvoluted into some Gaussian curves associated with different binding energies^[3,4,6,8,9,12-14]. The C1s spectrum mainly consists of four peaks. The peak at 284.6 eV is attributable to the C-C bond while the peak at 288.2 eV is assigned to the CO bond formed at the surface upon air exposure of the sample prior to the measurement. The peaks at 285.8 and 287.0 eV indicate two different bonding states of C-N: i.e., the sp^2 hybridization C-N bond and the sp^3 hybridization C-N bond, respectively. While the sp^2 hybridization C-N bond includes the C=N double bond, the theoretical β -C₃N₄ is composed of the sp^3 hybridization C-N bond. The spectrum shows that the fraction of the C-C bond is largest, followed by the sp^2 hybridization C-N bond and by the sp^3 hybridization C-N bond for most samples. The spectra of the films deposited above 300 °C show that the peak shifts to lower binding energy and the full width at half maximum (FWHM) becomes small, suggesting that the component of the C-C bond becomes large and that the fraction of the C-N bond decreases. This change is consistent with the fact that the atomic ratio N/C decrease with increasing substrate temperature above 200 °C. Thus, the change is explained either by the thermal decomposition of CN bonds or by graphitization

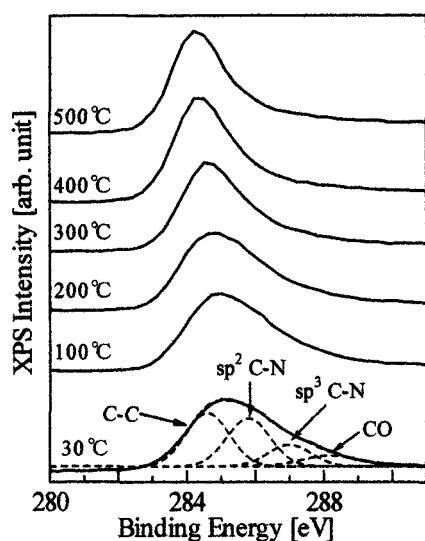


Fig.4 XPS C 1s spectra of the films deposited at nitrogen pressure of 66.6 Pa.

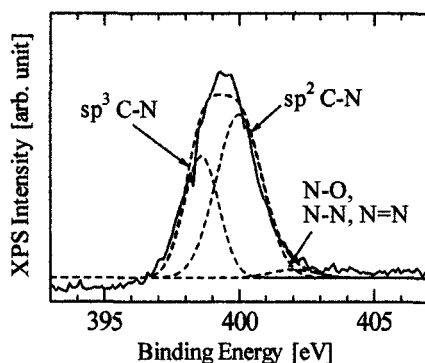


Fig.5 XPS N 1s spectra of the films deposited at nitrogen pressure of 66.6 Pa and substrate temperature of 30 °C.

of the films at higher temperature, as has been observed for pulsed laser deposited diamondlike-carbon^[6]. The shape and peak position of the C1s spectra didn't change by applying biased voltages.

The N1s spectrum in Fig.5 mainly consists of three peaks. The peaks at 398.6, 400.0 and 402.0 eV represent the sp^3 hybridization C-N bond, the sp^2 hybridization C-N bond and the N-O or N-N(N=N) bond, respectively. Fig.5 shows that the fraction of the sp^2 hybridization C-N bond is largest, followed by the sp^3 hybridization C-N bond. However, the difference in the area of the sp^2 hybridization C-N bond and the sp^3 hybridization C-N bond for the N1s spectrum is smaller than that for the C1s spectrum. The peak related to the N-O or N-N bond is considerably low compared with other components. The shape and peak position of the N1s spectra didn't show any peculiar change by changing the deposition conditions.

Fig.6 shows infrared absorption spectra^[3,8-14] of the films deposited at various substrate temperatures. All films present some peaks such as C≡N, C=N, C-N, C=C, C-C and C-H or NH₂. An absorption peak [I] at about 2190 cm⁻¹ represents the C≡N stretching vibration. Absorption peaks [II] corresponding to the graphitelike sp^2 bonded C and the C=N stretching vibration can be

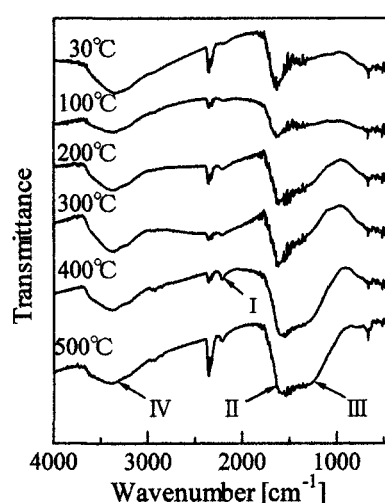


Fig.6 Infrared-absorption spectra of the films deposited at various substrate temperatures.

observed at around 1530-1600 and 1530-1725 cm⁻¹, respectively. Absorption peaks [III] corresponding to the disordered sp^2 bonded C and the C-N stretching vibration can be observed at around 1300-1360 and 1250-1400 cm⁻¹, respectively. An absorption peak [IV] at about 3400 is attributed to the moisture of the films, which is adsorbed after deposition. Fig.6 shows that the shoulder peak at about 1360-1400 cm⁻¹ becomes larger with increasing substrate temperature, indicating an increase in the disordered sp^2 bonded C. The fact is consistent with the results from XPS that the fraction of the C-C bond increases with increasing substrate temperature. Thus, increasing substrate temperature increased the content of disordered graphite, and decreased the atomic ratio of nitrogen. At the same time, increasing substrate temperature makes the absorption peak at 2190cm⁻¹ due to the C≡N bond larger. The shape and peak position of the absorption spectra didn't show any peculiar change by applying biased voltages.

The absorption coefficient α of the films was obtained by measuring the transmission in the range of 330 to 1000 nm; the optical band gap (E_g) was determined by the Tauc's relation^[15],

$$(\alpha h \nu)^{1/2} = B(h\nu - E_g) \quad [1]$$

where B is a constant and $h\nu$ is the photon energy. $(\alpha h \nu)^{1/2}$ of the samples for photon energies $h\nu$ between 1.25 and 3.7 eV is shown in Fig.7. $(\alpha h \nu)^{1/2}$ depends linearly on $h\nu$ in the region of high $h\nu$. The optical band gap was determined by extrapolation of the linear portion of the graph to $(\alpha h \nu)^{1/2} = 0$. The crystalline carbon nitride is theoretically predicted to be semiconductors with a large band gap of about 6 eV^[12]. It is expected that a high quality amorphous-semiconductor film with a low level of disorder will have an E_g close to that of its crystal phase^[12]. Fig.8 shows the E_g as a function of nitrogen pressure, substrate temperature and biased voltage^[10-12,14]. As shown in Fig.8 (a), the maximum value for E_g of the film deposited at nitrogen pressure of 66.6 Pa was 1.75 eV. Fig.8 (b) shows that the value of E_g of the film deposited at 30 and 100 °C are almost equal, and that the value of E_g decreases with increasing substrate temperature in the range of temperature higher than 200 °C. The substrate-

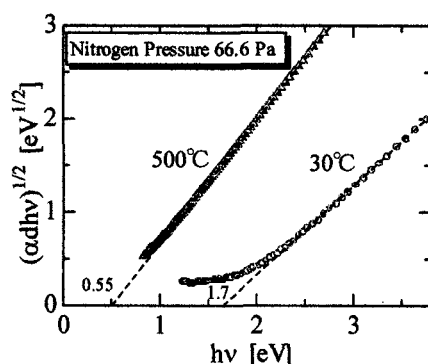


Fig. 7 Tauc plot for the film deposited at substrate temperatures of 30 and 500 °C

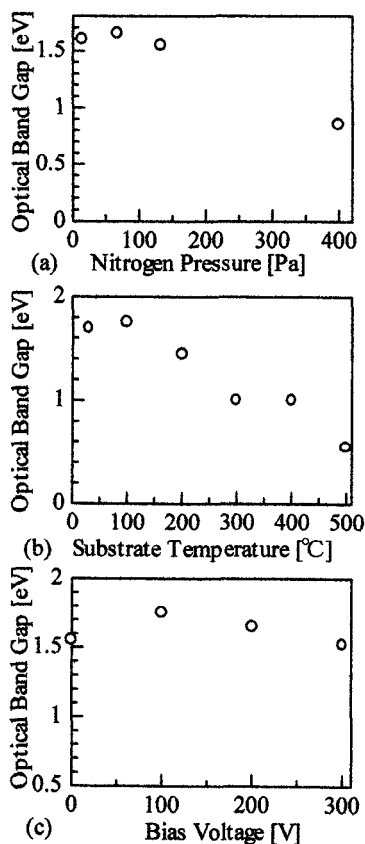


Fig. 8 The optical band gap of the film as a function of (a) nitrogen pressure, (b) substrate temperature and (c) bias voltage.

temperature dependence of the optical band gap is similar to that of the atomic ratio, indicating the graphitization of the film with increasing substrate temperature. On the other hand, the nitrogen-pressure dependence of the optical band gap is different from that of the atomic ratio. At low nitrogen pressures, the atomic ratio decreases with decreasing pressure, while the band gap keeps a high value, suggestion that the increases in atomic ratio does not assure the increase in sp^3 hybridized C-N bond in the film. Fig. 8(c) shows that no drastic change in E_g was brought about by applying biased voltages. The value of E_g increases a little by applying voltage of 100 V, indicating the maximum value of E_g , i.e., 1.75 eV. These results suggest that the

internal energy of the cluster didn't greatly change by applying biased voltage, although the biased voltage is effective to draw the ionized cluster to the substrate as shown in Fig. 2.

IV. Conclusions

Carbon nitride films were deposited by ablation of carbon molecular fragments from a graphite target onto a silicon substrate in nitrogen gas using the KrF excimer laser. The maximum value of the atomic ratio N/C for the film deposited at nitrogen pressure of 267 Pa was 0.36.

The biased voltage is effective to draw the ionized cluster to the substrate but the internal energy of cluster doesn't change greatly, the combining state showing negligible change. Increasing the substrate temperature increased the content of disordered graphite, and decreased the atomic ratio of nitrogen.

A detail study of the C1s and N1s XPS spectra of the film showed that the fraction of the sp^2 hybridization C-N bonds was higher than that of sp^3 , suggesting a higher content of the C=N double bond in the films.

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