Characterization of Amorphous Carbon Nitride Films Formed by Plasma-Enhanced Chemical Vapor Deposition of CN Radicals Using C *K*-edge X-ray Absorption Fine Structure Spectroscopy

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Near-edge X-ray absorption fine structure spectra of the carbon *K*-edge of amorphous carbon nitride (a-CN$_x$) films formed from plasma-enhanced chemical vapor deposition of CN radicals were measured over the excitation energy range 275–320 eV using synchrotron radiation. It was found that a-CN$_x$ films formed from the dissociative excitation of BrCN with microwave-discharge flow of Ar consisted predominantly of a C=N component and several C≡N components. In contrast, a-CN$_x$ films formed from the RF discharge of mixtures of CH$_4$/N$_2$ gas have small amounts of π bonds and large amounts of C-H components.

1.   Introduction

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy is a useful technique for probing the unoccupied electronic structure of molecules and solids. For amorphous carbon materials, which mainly consist of carbon, information on the chemical state is very important for material characterization. Although X-ray photoelectron spectroscopy (XPS) is a well-known technique for state analysis, it is sometimes not sufficient for analysis of amorphous carbon materials because of small chemical shifts or the presence of surface contamination. NEXAFS spectroscopy can be regarded as a complementary technique to

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XPS for chemical state analysis. Carbon K-edge NEXAFS spectroscopy can be used as a probe of the electronic structure of empty valence orbitals of carbon through transitions from specific localized core-level initial states, and it is particularly useful for distinguishing between C-C single and C=C double bond structures.[1–5] Thus, C K-edge NEXAFS spectroscopy has been successfully utilized for the structure determination of amorphous carbon films, but this technique has not been sufficiently applied to amorphous carbon nitride (a-CN_x) films.

Since the mechanical properties of the hypothetical carbon-nitride β-C_3N_4 compound were theoretically predicted to be superior to those of diamond,[6,7] the synthesis of carbon nitride films was attempted using various methods, such as RF-sputtering using N_2 as the reactive gas, chemical vapor deposition (CVD), and nitrogen ion bombardment.[8] However, it has been difficult to promote high nitrogen content in the films. In addition, films formed by CVD contain a certain amount of hydrogen-terminated structures. Saitoh *et al*. have developed a novel CVD method for synthesizing hydrogen-free a-CN_x films using the dissociative excitation reaction of BrCN induced by the microwave discharge flow of Ar.[9] The a-CN_x films formed using this plasma-enhanced CVD method have a high [N]/([N]+[C]) ratio; the N atoms are effectively incorporated into the network structure of the films.

In this study, the characterization of the a-CN_x film produced by plasma-enhanced CVD of CN radicals was carried out by C K-edge NEXAFS spectroscopy. The carbon K-edge data show that NEXAFS spectroscopy is sensitive to the local structure around the absorber carbon atom. The resonance from the $1s$ orbital to unoccupied π orbitals in sp (C≡N) or sp^2 (C=C, C=N) carbon and the resonance from the $1s$ orbital to unoccupied σ orbitals in sp, sp^2 and sp^3 (C-C, C-N, C-H) carbons present a distinguishable difference in energy and a simple identification of each contribution can be made. For reference, NEXAFS spectra of the a-CN_x films formed from the RF discharge of mixed gases of N_2+CH_4 were also observed.

2.   Experimental

The C K-edge NEXAFS measurements were performed using the BL8B1 stage of UVSOR in the Institute for Molecular Science.[10] The experimental apparatus and procedures employed in this study were identical to those in our previous study.[4,5] The synchrotron radiation provided by the 0.75-GeV electron storage ring was dispersed by a constant-deviation constant-length spherical grating monochromator and was perpendicularly irradiated on the sample film surface. Samples were mounted on a copper plate using carbon conductive tape in such a way that the carbon tape was completely covered by the sample and could not be seen from the surface. NEXAFS measurements were performed after evacuating the system overnight. The typical width of the monochromator slits was 20 μm and the resolution of exciting light energy was about 0.5 eV FWHM for this slit width. Absolute photon energy was obtained by aligning the π* (C=C) peak position of graphite to the literature value (285.38 eV).[11] The uncertainty in the calibrated wavelength was estimated to be ±0.2 eV. The C K-edge NEXAFS spectra were measured in the energy range 275–320 eV. The electrons coming from the sample were detected in the total electron yield (TEY) mode. The intensity of the incident photon beams I_0 was measured by monitoring the

photocurrent from a gold film. The absorption signal was given by the ratio between the outgoing electron intensity from the sample, I_s, and the intensity from the gold film, I_0.

The CN_x thin film samples were provided by Professor Ito of Nagaoka University of Technology and were kept in a dry box until the measurements were taken. The a-CN_x films produced from the BrCN/Ar reaction and the CH_4/N_2 reaction were formed using MW-plasma CVD and RF-plasma CVD, respectively. The details of equipment used and methods for forming the a-CN_x films by dissociative excitation have been described in the literature.[12–15] In brief, in the MW-plasma discharge CVD method, Ar gas was introduced into the flow tube through a discharge tube of o.d. ≈15 mm. The discharge was a microwave discharge, and BrCN was introduced just below the exit of the discharge tube. Free CN radicals produced by the dissociative excitation of BrCN with the microwave discharge flow of Ar were deposited on the Si or SiC substrates.[12–15] However, the CN_x films on the Si substrate were easily separated from substrate surface by pumping overnight before the NEXAFS measurement. In the following, a-CN_x film formed by a BrCN/Ar reaction indicates the a-CN_x film on a SiC substrate, because no variation was observed between the NEXAFS spectra of the a-CN_x films on either Si or SiC. The [N]/([N]+[C]) ratio of CN_x thin films produced using this method was reported to be 0.23–0.29 from XPS measurement.[13] In the RF-plasma CVD method, a pair of parallel-plate electrodes 220 mm in diameter, as powered and grounded electrodes, were mounted 20 mm apart. N_2 gas was introduced into the chamber through a needle valve, and a trace amount of CH_4 was introduced into the center of the discharge through a Pyrex glass nozzle of i.d. ≈1 mm. By means of the RF discharge, a-CN_x films were deposited on a Si substrate situated in the center of the grounded electrode.[12] The a-CN_x films formed by the RF discharge of a mixed gas of CH_4 and N_2 are assumed to have a low nitrogen content and to contain hydrogen derived from CH_4.

3.   Results and Discussion

Knowledge of the coordination of carbon atoms is important to discuss the structure of CN_x films. C *K*-edge NEXAFS spectroscopy is sensitive to the local coordination of the CN subunit. In the C *K*-edge NEXAFS spectra, π bonding of carbon atoms produces narrow, intense peaks a few eV below the ionization potential of carbon, called π* resonances, that are due to transitions from the 1*s* core level to the antibonding π* molecular orbitals. Transitions to σ* antibonding orbitals appear at energies above the ionization potential, and the resulting spectral features are broad and asymmetric peaks called σ* resonances. Carbon *K*-edge NEXAFS studies have been reported by several groups for CN_x films prepared by magnetron sputtering,[16–21] nitrogen ion implantation into graphite[22–25] and other methods.[26–28] However, their assignments are not all consistent. Undoubtedly, one reason for the inconsistencies is the lack of uniformity of a-CN_x films, manifested as various concentrations of nitrogen or sometimes hydrogen. It is well known that nitrogen and hydrogen content in a-CN_x films depends on the film formation method and conditions.

Figure 1 depicts the NEXAFS carbon *K*-edge spectrum of the a-CN_x film formed from dissociative excitation of the BrCN/Ar reaction. The spectral features observed in this study agree with of those of a-CN_x films formed from magnetron sputtering reported previously,[16–21] but they do not resemble those of nitrogen-intercorporated carbon materials.[22–25] The
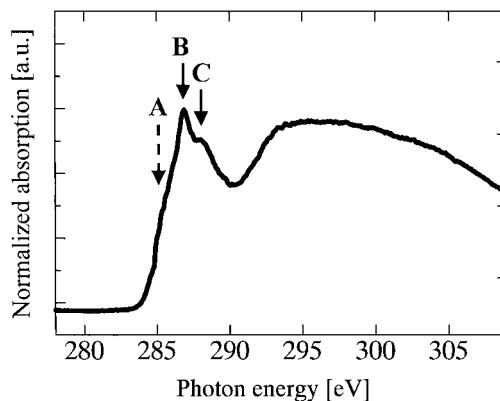
Fig. 1.   The NEXAFS C *K*-edge spectrum of an a-CNx film formed by dissociative excitation of BrCN with Ar discharge flow.

shoulder at ≈285 eV (A) is assignable to transitions from the C 1*s* level to unoccupied π^* orbitals principally originating from sp^2 (C=C) sites. This peak is observed in isolation in the NEXAFS spectrum of an a-CN$_x$ film formed by the RF discharge of CH_4/N_2 mixed gas described in the following. This peak is not present in the diamond spectrum,[29] because diamond consists of only carbon atoms in sp^3 (C-C) sites. The appearance of this peak indicates that some sp^2 C=C bonds are still present in a-CN$_x$ films formed from dissociative excitation of BrCN/Ar. The dominant peak in the low-energy region of the NEXAFS spectrum is observed at 286.6 eV (B). Lopez *et al*. assigned the peak originating from π(C=N) to the shoulder at 286.6 eV and assigned the dominant peak to σ(C=N).[16] However, this sharp peak is not considered to originate from σ(C-N), because σ(C-N) is not expected to build a well-defined molecular structure. Therefore, this sharp dominant peak is interpreted to originate from the transition to a π^* state. Guo *et al*. assigned this peak to the transitions from the C 1*s* level to unoccupied π^* states of the C=N bond.[17] Sánchez-Lopez assigned this peak to transitions to the π^* states of carbon bonded to single nitrogen species and the shoulder at higher energy on top of the dominant peak to the π^* states of carbon bonded to two nitrogen species.[20] Hellegren *et al*. followed the assignment of Sánchez-Lopez for the shoulder and assigned the dominant peak to π(C≡N).[21] In our spectra of CN$_x$ films, at higher energy on top of the dominant peak, a shoulder corresponding to (C) can be observed in isolation at 287.8 eV, and the component giving rise to this peak is estimated to be present in large amounts. It is characteristic of the synthesis in this work that a-CN$_x$ film is directly formed from the deposition of free C≡N radicals; therefore, the content of the C≡N component in the a-CN$_x$ film is expected to be large. We assigned this shoulder to the transition from the C 1*s* level to unoccupied π^* orbitals principally originating from *sp* (C≡N) sites. This assignment is supported because the carbon *K*-edge spectrum of poly(acrylonitrile) was dominated by a sharp π(C≡N) transition at 287.2 eV,[16] and the band due to a C≡N stretching vibration was observed in the FT-IR spectrum of this CN$_x$ film.[9,13] As a result, we assigned the dominant peak B to π(C=N), which is assumed to be the

dominant component of these a-CN$_x$ films, and the peak C to π(C≡N). The broad σ resonance around 295 eV corresponds to C-C, C=C, C-N, C=N and C≡N bonds.

Figure 2 depicts the carbon *K*-edge NEXAFS spectrum of the CN$_x$ film formed from the RF discharge of a gas mixture of CH$_4$/N$_2$. A pre-edge resonance at 285.3 eV (Peak A), which is due to transitions from the C 1*s* level to unoccupied π* orbitals principally originating from *sp*^{2} (C=C) sites, is observed in isolation, as mentioned previously. This indicates that the films formed from the CH$_4$/N$_2$ reaction contain a large amount of carbon not bonded to nitrogen. The dominant peak in this sample was observed at 289.2 eV, which was too high to assign to the unoccupied π* states of carbon. This peak is ascribable to the transition from the C 1*s* level to the σ(C-H) bond by reference to organic polymers; for example, the peak position of σ(C-H) of poly(vinyl alcohol) is observed at 289.3 eV. [30] The CN$_x$ film formed by the CH$_4$/N$_2$ reaction is assumed to contain a large amount of C-H whose hydrogen atoms are provided by CH$_4$. A shoulder around ≈287 eV can be attributed to the transitions to π(C=N) and π(C≡N). The spectral assignments of NEXAFS spectra of CN$_x$ films are summarized in Table 1.

Fig. 2. The NEXAFS C *K*-edge spectrum of an a-CN$_x$ film formed from the RF discharge of mixed N$_2$+CH$_4$ gases.

Table 1
Assignment of peaks in carbon K-edge NEXAFS spectra of a-CN films (eV).

Peak	This study BrCN/Ar	CH$_4$/N$_2$	assignment	Lopez[16]		Guo[17]		Sánchez-López[20]		Hellgren[21]		PAN[16]	PVA[30]
A	285	285.3	π(C=C)	285	π(C=C)	285	π(C=C)	285.5	π(C=C)	285.0	π(C=C)		
				286.6	π(C=N)								
B	286.6		π(C=N)	288	σ(C-N)	285.9	π(C=N)	286.6	π(C-2N)	286.2	π(C≡N)		
C	287.8		π(C≡N)					287.9	π(C-3N)	287.8	π(C-2N)	287.2	
D		289.2	σ(C-H)										289.3

The intensity of the $1s \rightarrow \pi^*(C \equiv N)$ peak in the CN_x film formed by dissociative excitation of BrCN/Ar is larger than that of the same peak in the CN_x films formed by magnetron sputtering. In addition, the relative intensity of the $1s \rightarrow \pi^*(C=C)$ peak to that of the $1s \rightarrow \pi^*(C=N)$ peak in the spectrum of the CN_x film formed by dissociative excitation of BrCN/Ar is smaller than that in the CN_x films formed by magnetron sputtering reported in refs.16–21. These observations are consistent with the high nitrogen content of the CN_x film formed by dissociative excitation of BrCN/Ar. Furthermore, the ratio of the integrated area of the π resonance region to that of the σ resonance region of the CN_x film formed by dissociative excitation of BrCN/Ar was higher than those of CN_x films formed by magnetron sputtering. The prominent intensity of the π^* resonance in the CN_x films, therefore, indicates a high degree of unsaturated carbon bonds. As a result, CVD using the dissociative excitation of the BrCN/Ar reaction can be anticipated to result in the synthesis of hard a-CN_x films with a high nitrogen content and a high π bond content. The integrated area of the π resonance region of CN_x films formed by RF discharge of a mixture of CH_4/N_2 gas is smaller than that films formed by the MW discharge of BrCN with Ar flow. This indicates that the CN_x film formed by the former reaction has a low degree of unsaturated carbon bonds. One reason for the low degree of unsaturated carbon in the CN_x films formed by RF discharge of a mixture of CH_4/N_2 gas is ascribable to the presence of hydrogen atoms derived from CH_4.

4.   Conclusions

The local structures of a-CN_x films formed by plasma-enhanced CVD were investigated using C K-edge NEXAFS spectroscopy. The a-CN_x film formed from dissociative excitation of BrCN with Ar MW-discharge consists of a dominant $\pi(C=N)$ component and contains some $\pi(C \equiv N)$ component. The nitrogen content and the degree of unoccupied carbon sites are larger than those of other reported a-CN_x films. In contrast, a dominant component of a-CN_x films formed from RF-plasma discharge of CH_4/N_2 gas mixtures consisted of carbon that has only σ bonds; the $\sigma(C-H)$ component was found to be present in large amounts.

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