High-Resolution Soft X-Ray Emission Spectra of Crystalline Carbon Nitride Films Deposited by Electron Cyclotron Resonance Sputtering

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The X-ray emission spectra of crystalline carbon nitride films deposited by electron-cyclotron-resonance (ECR) plasma sputtering were observed using a high-resolution soft X-ray spectrometer at the Advanced Light Source to investigate the electronic structure of carbon nitride crystals. The spectral features in C K and N K X-ray emissions from the ECR-deposited carbon nitride films represent the highly degenerated valence orbitals and their highly pure crystalline form. The C K and N K X-ray emission spectra were approximately explained based on the C2p and N2p density of states in the hybridized C-N bonds. The absence of significant peak shifting in selectively excited C K and N K X-ray emission spectra showed that there is a fairly nondispersive structure between valence and conduction bands in ECR-deposited carbon nitride films.

KEYWORDS: X-ray emission spectra, synchrotron radiation, carbon nitride, molecular-orbital calculation, electronic structure

1. Introduction

Carbon nitrides, particularly β-C3N4, have been theoretically predicted by Cohen and coworkers1-3 to be as hard as or even harder than diamond. Synthesizing and characterizing covalent carbon nitride compounds have thus become an important focus in materials science because such superhard materials would have promising technological applications. This has stimulated many material scientists to deposit crystalline carbon nitride films by using various methods. However, most of the deposited films were composed mainly of amorphous carbon nitride or amorphous carbon; little crystalline phase, particularly β-C3N4, was found in any of these films.4-7 Characterization of the carbon nitrides and investigation of their electronic structures have thus become important to understand how atomic bonding affects the calculated hardness. However, most experimental work on characterization has used electron diffraction or transmission electron microscopy to identify carbon nitride crystals; X-ray spectroscopy has not been used much to analyze the electronic structure because of the difficulty in obtaining crystalline films with sufficient purity for X-ray spectroscopy.

Tani et al.8 succeeded in depositing high-purity crystalline carbon nitride films by electron-cyclotron resonance (ECR) plasma sputtering. The crystal structure of these ECR-deposited carbon nitride films was shown by X-ray diffraction (XRD) and chemical stoichiometric analysis to mainly consist of α- and β-C3N4 crystals, which may be spectroscopically high-purity crystalline films. Additionally, it is well known that soft X-ray spectroscopy using highly brilliant synchrotron radiation is a powerful diagnostic tool for characterizing materials and analyzing electronic structures.9,10 We, therefore, measured the high-resolution soft X-ray emission and absorption spectra of such ECR-deposited carbon nitride films to obtain information about their electronic structures. In this paper, we describe the high-resolution C K and N K X-ray emission spectra, including selectively excited and absorption spectra, of ECR-deposited carbon nitride films and discuss the information we derived regarding their electronic structure.

2. Experiment

Carbon nitride films were deposited on Si(100) substrates by ECR sputtering, using a carbon target in a nitrogen atmosphere. The atomic ratio of nitrogen to carbon (N/C) was determined to be approximately 1.35, which agrees well with the stoichiometric composition of C3N4, according to X-ray photoelectron spectroscopy, heavy ion elastic recoil detection, and Rutherford backscattering. The crystal structure was analyzed using XRD. The XRD pattern of the carbon nitride film (Fig. 1) showed distinct peaks, confirming that the film contained sufficient crystalline phases for X-ray spectroscopic measurements. Although an unknown diffraction peak was observed at 19°, the rest of the pattern approximately agrees with the lattice parameter theoretically predicted for α- and/or β-C3N4. Although it is difficult to quantitatively determine the amount of the unknown phase, this pattern suggests that a major portion of the ECR-deposited carbon nitride film was C3N4. The deposition process and chemical analysis of these ECR-deposited carbon nitride films are reported in detail elsewhere.11 An ion-beam-sputtered amorphous carbon film and commercially obtained carbon compounds (graphite powder and diamond powder) were also prepared for reference.

We measured the soft X-ray emission and absorption spectra in the C K and N K regions at the Advanced Light Source (ALS). The X-ray emission spectra were measured using a grating X-ray spectrometer installed in beamline (BL) 8.0.11 The resolving power (E/ΔE) of the spectrometer was estimated to be about 270 in the C K region and 480 in the N K region, using a 100 μm entrance slit. The fluorescence-yield (FY) absorption spectra were also measured using this spectrometer. The total-electron-yield (TEY) absorption spectra were measured by monitoring the sample photocurrent in BL-6.3.2.12 The resolving power of the TEY absorption mea-
measurements was estimated to be 1600 in the C K region and 1000 in the N K region. In the C K absorption measurements, a pop-in photodiode detector, which had negligible carbon contamination, was used as an I₀ monitor to eliminate background carbon contamination.

3. Results and Discussion

Figure 2 shows (a) the C K X-ray emission spectra of the ECR-deposited carbon nitride films and of the reference samples (ion-beam-sputtered amorphous carbon film, graphite powder, and diamond powder) taken at 320 eV excitation and (b) the N K X-ray emission spectrum of the carbon nitride films at 430 eV excitation. In the C K spectra, the spectrum of carbon nitride consisted of a sharp main peak (denoted by A) at 278.5 eV, a low-energy satellite peak (B) at 266.5, and a high-energy-side tail (C) near 282 eV. These spectral features were completely different from those of the reference samples, which essentially had a broad main peak at around 278 eV with a high-energy-side shoulder and a low-energy-side tail.

It is well known that the spectral shapes of graphite and diamond arise from sp² and sp³ carbons, respectively, and that the spectral shape of ion-beam-sputtered amorphous carbon may essentially arise from a mixture of sp² and sp³ carbons. Therefore, the spectral shape of carbon nitride films suggests that the carbon atoms in the films formed C–N bonds rather than sp²- or sp³-structured C–C bonds. Due to the differences in spectral shapes between carbon nitride films and reference carbon compounds, the width of the symmetric main peak in the carbon nitride films (2.8 eV at full-width at half maximum) was narrower than those of reference carbon compounds (8.5 eV for ion-beam-sputtered amorphous carbon and 7.5 eV for graphite and diamond). The valence orbitals in carbon nitride films were apparently more degenerated than those in graphite and diamond. Moreover, the narrow and symmetric features of the main peak suggest that the carbon nitride film contained little amorphous phase. In the N K X-ray emission spectrum of the carbon nitride films, two dominant peaks were observed at 392 and 388 eV (A and B).

To assign the spectral features of the C K and N K X-ray emission spectra of the ECR-deposited carbon nitride films, we calculated the C2p and N2p density of states (DOS) of carbon nitride clusters by using discrete-variational (DV)-Xα molecular-orbital calculation methods. Figure 3 shows the cluster models of carbon nitride used for the calculations: the C₅N₂(H₂) one was used to simulate α-C₃N₄, and the C₁₄N₁₃(H₁₇) one was used to simulate β-C₃N₂. In these models, each carbon atom bonds with four nitrogen atoms, and each nitrogen atom located inside the clusters bonds with three carbon atoms. Nitrogen atoms located outside the clusters terminate with hydrogen atoms (not shown in the figure) or with dangling bonds. The molecular structure of these cluster models was optimized by molecular mechanics using commercially obtained Chem3D Plus software. DV-Xα calculations were carried out using the SCAT program in com-
merically obtained software on a DOS/V computer equipped with a 400 MHz Pentium II processor.

We obtained the DOS of carbon and nitrogen atoms located inside these clusters (denoted by asterisks in Fig. 3). Figure 4 shows the calculated spectra obtained from the occupied C2p and N2p DOS of individual carbon and nitrogen atoms in the (a) hydrogen-terminated and (b) dangling-bond-terminated cluster models. The energy level of the highest occupied molecular orbital (HOMO) was normalized at zero in the molecular-orbital energy. These spectra were obtained by convoluting 0.1- and 1.0-eV-wide Lorentzian functions on the DOS. In the hydrogen-terminated models, the C2p- and N2p-DOS spectra of α-C9N26H42 and of β-C13N33H47 were essentially similar in shape except for the fine structure inside the main peak of C2p DOS. The C2p-DOS spectra of both α-C9N26H42 and β-C13N33H47 consisted of roughly three segments. For C2s and N2s DOS, (A) the main segment in the $-5$ to $-12$ eV region was due to C2p, (B) the low-energy segment from $-16$ to $-21$ eV was due to hybridized C2p–N2s, and (C) the high-energy segment from 0 to $-3$ eV was hybridized C2p–N2p. Their N2p DOS consisted of roughly two segments: (A) the high-energy segment from 0 to $-4$ eV was due to N2p and (B) the low-energy segment from $-5$ to $-15$ eV was due to hybridized N2p–C2p. The spectral shapes of these calculated C2p and N2p DOS approximately agree with those of the experimental X-ray emission spectra of carbon nitride films. Using these calculated C2p-DOS spectral shapes as an analogy, we assigned the spectral features of ECR-deposited carbon nitride films as follows: the main peak (A) was caused by C2p, the low-energy satellite (B) by the hybridized C2p–N2s, and the high-energy tail (C) by the hybridized C2p–N2p in the C K X-ray emission spectrum; the 392 eV peak can be assigned to N2p and the 388 eV peak to hybridized N2p–C2p in N K.

As described above, we found that the chemical bonds in ECR-deposited carbon nitride films were due to the hybridized molecular orbitals between carbon and nitrogen atoms. However, the energy scale and the energy width of the calculated DOS peaks did not agree exactly with those of the experimental spectra. In particular, the main peaks of the C2p DOS in both the hydrogen-terminated α-C9N26H42 and β-C13N33H47 had double-peak fine structures, and the width of these calculated peaks was larger than the observed one. This difference may be due to the effect of dangling bonds in the carbon nitride microcrystalline structure.

The calculated DOS spectra of the dangling-bond-
terminated $\alpha$-C$_2$N$_{36}$ and $\beta$-C$_{13}$N$_{13}$ cluster models (Fig. 4(b)) show the effect of dangling bonds on C2p and N2p DOS. In C2p-DOS spectra of both $\alpha$-C$_2$N$_{36}$ and $\beta$-C$_{13}$N$_{13}$ models, the peak width of the main segment near 10 eV was about half that of the hydrogen-terminated models. Considering the chemical-bonding states at the interface of microcrystalline carbon nitride particles, not only dangling bonds, but also double or triple bonds are likely to exist in the carbon nitride. Therefore, to exactly reproduce the experimental spectra, we plan to calculate the molecular orbitals by using larger model clusters and by considering the effects of dangling or double/triple bonds.

Band dispersion is mainly measured by selectively excited soft X-ray emission spectroscopy and varying the excitation photon energy. Figure 5 shows the selectively excited C K X-ray emission spectra of the ECR-deposited carbon nitride film, along with the TEY and FY absorption spectra, which were essentially similar in shape, except that a 292 eV peak appeared only in the TEY one. This peak may be due to a resonant Auger process. The emission peak intensities of both the 278.5 eV main peak and the 266.5 eV low-energy satellite peak were enhanced for the 288.6 eV excitation. However, no significant spectral-shape changes, such as peak shifting or new-peak appearance, were observed for other energy excita-

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Fig. 5. (a) TEY and FY absorption spectra and (b) selectively excited C K X-ray emission spectra of ECR-deposited carbon nitride films. The excitation energy was tuned from 318.6 to 281.6 eV, as shown by "a" through "m".

Fig. 6. (a) TEY and FY absorption spectra and (b) selectively excited N K X-ray emission spectra of ECR-deposited carbon nitride films. The excitation energy was tuned from 426.5 to 393.5 eV, as shown by "a" through "m".
tions. This suggests that the band structure of C2p in ECR-deposited carbon nitride films is fairly nondispersive.

Figure 6 shows the selectively excited N K X-ray emission and absorption spectra. The high-energy emission peak at 392 eV was enhanced for 407.5 eV excitation tuned at the higher energy absorption peak. In comparison, the low-energy emission peak at 388 eV was enhanced and a small peak appeared at 390 eV for 399.5 eV excitation tuned at the lower energy absorption peak. Aside from these emission-peak intensity enhancements and the appearance of a small peak, no other significant peak shifting was observed. This indicates that the band structure of N2p is also fairly nondispersive.

4. Conclusion

We measured the high-resolution soft X-ray spectra of ECR-deposited carbon nitride films in the C K and N K regions. The narrow spectral shapes observed in the C K X-ray emission showed that carbon nitride films have a highly degenerated electronic structure in the valence orbitals and that the films hardly include any amorphous phase. From DV-Xa molecular-orbital calculations, we approximately assigned the spectral features of C K and N K X-ray emission spectra to C2p and N2p DOS in hybridized C-N bonds. Selectively excited X-ray emission spectral measurements showed that the band structure of carbon nitride film should be fairly nondispersive. Soft X-ray emission spectroscopy is thus a useful method for characterizing carbon nitride crystals.