Atomic arrangement, composition and orientation of hexagonal BCN films synthesized by radiofrequency plasma enhanced CVD

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Oriented hexagonal BCN films were synthesized on Si (1 0 0) substrate by radiofrequency plasma enhanced chemical vapor deposition using tris-(dimethylamino)borane as a precursor. The formation of the crystalline hexagonal BCN hybrids was confirmed by FT-IR and XRD. CH₄ + H₂ carrier gas increased the C content in the films in comparison with N₂ carrier gas. XPS measurement showed that the films were composed of a variety of B-N, B-C, C-N bonds to form the BCN atomic hybrids. The π^* resonance peak in the B K-edge NEXAFS spectra also indicated the presence of the sp^2 hybrid configuration of B-C-N bonds like BN₃ in h-BN. The σ^* resonance peaks suggested the diversity in the σ bonds in the films. Orientation of the h-BCN hybrids was suggested on the basis of the polarization dependence of NEXAFS.

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1. Introduction

Considerable efforts have been given to the synthesis of boron carbonitride (BCN) compounds in the last few years. The cubic phase (c-BCN) is expected to be a superhard compound comparable to diamond.¹⁾ The hexagonal phase (h-BCN) is attractive in the application to electronic and luminescent devices due to its semi-conducting property with variable band-gap energy.²⁾ It might also be applicable to the rechargeable Li-ion battery.³⁾ Syntheses of the ternary BCN compounds with the various compositions using different methods have been reported, though most of the reported BCN compounds are the mixtures of the nano-crystalline hexagonal and cubic phases or the amorphous phase.⁴⁾⁻⁶⁾ Single phase of the h-BCN with large grain size has not been synthesized up to now and efforts were not devoted to clarify the atomic arrangement precisely in the BCN films. Therefore, preparation of the single h-BCN phase is still a challenge.

Previously, we prepared h-BCN hybrid films on Si (1 0 0) by radiofrequency plasma enhanced chemical vapor deposition (RF-PECVD) using tris-(dimethylamino)borane (TDMAB) as the single-source molecular precursor with H₂ carrier gas.⁷⁾ However, the crystalline phase was not detected by XRD, probably due to the short-range order of the atomic arrangement or the amorphous phase. The C content in the films was also low (< 18 at.%) compared with B and N.

In this work, crystalline h-BCN hybrid films with higher C content (22 to 35 at.%) have been prepared by using N₂ or CH₄ + H₂ mixture as the carrier gas. In this paper, we report the atomic arrangement, composition and orientation of the crystalline h-

BCN films prepared by RF-PECVD.

2. Experimental

BCN films were synthesized on Si (1 0 0) substrate by RF-PECVD using TDMAB as the single-source molecular precursor. The detail of the deposition system has been described elsewhere.⁷⁾ N₂ or CH₄ + H₂ mixture was used as the carrier gas. The RF power was varied from 400 to 800 W. Four samples synthesized under the different reaction conditions were considered in this study. Samples (1) and (2) were synthesized at the RF power of 800 and 500 W, respectively by flowing N₂ carrier gas. Samples (3) and (4) were synthesized at the RF power of 700 and 400 W, respectively by flowing CH₄ (10%) + H₂ (90%) mixture.

The chemical bond and the crystalline phase were explored by Fourier transform infrared spectroscopy (FT-IR) and X-ray diffraction (XRD). The chemical composition and the atomic arrangement were studied by X-ray photoelectron spectroscopy (XPS) and Near-edge X-ray absorption fine structure (NEXAFS) measurements. The XPS and NEXAFS measurements were performed at the Beam Line 11A and Beam Line 27A of Photon Factory, KEK, using the linearly polarized synchrotron radiation. The elemental composition (atomic ratio of B, C and N) was determined from the intensity of the B1s, C1s and N1s peaks in the XPS wide scan spectra.⁷⁾ The B1s, C1s and N1s binding energies were calibrated by Au 4f_{7/2} binding energy (84.0 eV). In the NEXAFS analyses, the X-ray incidence angle θ is defined as the angle between the electric field vector of the linearly polarized X-ray and the surface normal of the film.⁸⁾

3. Results

3.1 FT-IR analyses

Figure 1 shows FT-IR transmission spectra of the samples synthesized at different RF powers in the N₂ and CH₄ + H₂ car-

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Fig. 1. FT-IR transmission spectra of the as-deposited samples. The numbers (1)–(4) on the left side of the spectra represent the respective sample: Samples (1) and (2) were synthesized at 800 and 500 W, respectively in N_2 carrier gas. Samples (3) and (4) were synthesized at 700 and 400 W, respectively in $CH_4 + H_2$ carrier gas.

rier gases. The spectra showed two peaks; a broad peak around at 1400 cm^{-1} and a relatively sharp peak at 800 cm^{-1} . These peak positions are almost compatible with the sp^2 -bonded B–N bonds in h-BN.^{4),9)} These samples contain 22 (sample 1), 23 (sample 2), 35 (sample 3) and 35 (sample 4) at.% of C respectively, together with B and N as confirmed by the XPS measurements. Therefore, these peaks suggest the formation of the hexagonal sp^2 -B–C–N atomic hybrid bonds in these films similar to the sp^2 -B–N bonds in h-BN. The broader peaks for samples (3) and (4) {Full Width at Half Maximum (FWHM = $\sim 390\text{ cm}^{-1}$)} than those for samples (1) and (2) (FWHM = $\sim 275\text{ cm}^{-1}$) may be due to the more C incorporation in the films. The observed broadening of the peak from 1000 to 1700 cm^{-1} could be explained as a consequence of the formation of the C = N, C–N, B–C bonds as well as the B–N bond in the films, since these bonds are reported in this region.¹⁰⁾ The increase of C content might result in the increase of the complex combination of B–N, C–N and B–N bonds in the h-BCN hybrids. Formation of a separate phase of binary compound such as $BN/CN_x/BC_x$ was not assumed as the peak splitting was not found in these spectra.

3.2 XRD analyses

XRD patterns of the 4 samples are shown in Fig. 2. Two diffraction peaks observed at 26.3° and 29.2° for these samples seemingly suggest the existence of a crystalline structure in these films. The (0 0 2) diffraction peaks of the h-BN and graphite are reported at $2\theta = 26.8^\circ$ ($d = 3.42\text{ \AA}$) and at $2\theta = 26.6^\circ$ ($d = 3.36\text{ \AA}$), respectively.¹¹⁾ Therefore, the peak at 26.3° ($d = 3.47\text{ \AA}$) could be ascribed to the hexagonal BCN phase as confirmed by FT-IR. The large interplanar distance compared with h-BN and graphite suggests that the h-BCN basal planes are packed a little bit rougher than h-BN and graphite, because of the ternary atomic mixing in the sp^2 basal plane. The peak was stronger for the samples (3) and (4) prepared in $CH_4 + H_2$ than those for sample (1) and (2) prepared in N_2 carrier gas. The more C content might

Fig. 2. XRD patterns of the samples shown in Fig. 1. Samples (1) and (2) were synthesized at 800 and 500 W, respectively in N_2 carrier gas. Samples (3) and (4) were synthesized at 700 and 400 W, respectively in $CH_4 + H_2$ carrier gas.

enhance the formation of the hexagonal phase in these films.

The peak at $2\theta = 29.2^\circ$ ($d = 3.16\text{ \AA}$) has not been reported yet for the BCN compounds. This unknown peak was strong for samples (1) and (3) prepared at the higher RF power than the samples (2) and (4) at the lower RF power. Auxiliary experiments using different substrates such as Ni, Ti and Au were performed in order to confirm this unknown peak. The peak at 29.2° was also revealed on all the substrates. Therefore, the unknown peak must be ascribed to a crystalline BCN phase though more studies are needed to identify the origin of this peak.

3.3 XPS analyses

The B1s, C1s and N1s XPS spectra of the samples are shown in Fig. 3, together with their compositions estimated from the XPS wide scan spectra: $B_{44}C_{22}N_{34}$ (sample 1), $B_{45}C_{23}N_{32}$ (sample 2), $B_{36}C_{35}N_{29}$ (sample 3) and $B_{38}C_{35}N_{27}$ (sample 4), respectively. When the N_2 carrier gas was used, the C content in the films was low compared with B and N (samples 1 and 2). $CH_4 + H_2$ carrier gas increased the C content (samples 3 and 4). This may be due to the higher reactivity of the fragments of CH_4 than that of the N_2 fragments in the plasma.

The B1s, C1s and N1s spectra of the samples prepared in the N_2 and the $CH_4 + H_2$ carrier gases did not change with the RF power. We, therefore, discussed in detail on the samples (1) and (3) prepared in N_2 and $CH_4 + H_2$ carrier gas, respectively. The B1s peak could be fitted almost by a single Gaussian curve as shown in a broken line (Fig. 3(a)). However, the full-width at half maximum (FWHM = $\sim 3.0\text{ eV}$) of the B1s peaks was wide in comparison with that of the h-BN ($\sim 1.7\text{ eV}$).¹²⁾ It suggests that B atoms have various chemical environments. Therefore, the XPS spectra were deconvoluted into component peaks in order to discuss the possible chemical environments in more detail.

The B1s spectra could be well fitted by deconvoluting into two Gaussian peaks centered at 190.8 and 189.6 eV, respectively. These component peaks were assigned to the B–N and the sp^2 -B–C–N atomic hybrid bonds based on their reported binding

Fig. 3. XPS spectra of the samples shown in Fig. 1; (a) B1s, (b) C1s and (c) N1s together with the single Gaussian peak (broken line) and the deconvoluted component peaks (dotted line). The compositions of the samples are also shown.

energies.¹³⁾ However, it is not easy to distinguish between them because the B, C and N atoms are bonded in the chemical environment similar to the sp^2 -B-N-like configurations in h-BN, and the h-BN and the graphite are isoelectronic. As the C content increased and the B content decreased (sample 3), the B1s peak slightly shifted to the higher energy. This may be due to a distortion of the sp^2 -B-C-N chemical environment with the incorporated C.

The C1s spectra were also fitted with a single Gaussian curve (Fig. 3(b)). However, the peaks were broad (FWHM = ~ 3.5 eV) and tailing of the spectra to the higher energy was clearly observed. Therefore, the spectra were also fitted by deconvoluting into three component peaks. The peak centered at 283.1 eV suggests the formation of the C-B bond because the C1s binding energies for $BC_{3.4}$ and B_4C have been reported to be 284.3 and 283.0 eV, respectively.¹⁴⁾ The peak centered at 284.4 eV could be ascribed to the graphite-like C = C bonds.¹⁵⁾ However, no evidence for the separate graphite phase was found. The component peak centered at 286.0 eV is due to C atom bonded to more electronegative N atom.¹⁶⁾ Therefore, the C atoms may also be bonded to B and N to form the B-C-N hybrid bonds while formation of the CN_x phase can not be excluded.

The N1s spectra of the samples could be fitted with a broad single Gaussian curves (Fig. 3(c)) as well as the B1s spectra. The broadening suggests the formation of the BCN atomic hybrids with a variety of configurations. These spectra could also be fitted by deconvoluting two component peaks at least. The deconvoluted peak centered at 398.0 eV could be assigned to the N-B bond.¹⁵⁾ The N-B bond is predominant in accordance with the B-N bond found in the B1s spectra. The component peak centered at the higher binding energy (399.3 eV) is due to the formation of N-C bond. The N-C bond was also suggested from the C1s spectra although the N-C bond in sample (1) was not obvious because of no clear distinction between the h-BN-like configuration and the h-BCN configuration.

It is confirmed from these XPS results that the films are composed of different B-N, B-C, C-N bonds to form the sp^2 -BCN atomic hybrid configurations. No clear evidence of the phase separation such as BN/graphite/ CN_x / BC_x was observed while the tailing of the C1s peaks to the higher binding energy suggested the formation of the small amount of the CN_x phase together with the h-BCN hybrids.

Fig. 4. B K-edge NEXAFS spectra at various incidence angle (θ) of the X-ray for samples (1) and (3). NEXAFS spectrum for h-BN, c-BN and B_4C powders are also shown for comparison.

3.4 Polarization dependence of NEXAFS spectra

The polarization dependence of B K-edge NEXAFS spectra of the typical samples (1) and (3) are shown in Fig. 4, together with the spectra of the h-BN, c-BN and B_4C powders as the references. A broad peak (peak B₂) has been predominantly observed at the photon energy of 191.8 eV at the normal incidence ($\theta = 90^\circ$) of the X-ray.

The predominant peak could be ascribed to the π^* resonance of sp^2 -B-C-N bonds, suggesting the formation of the sp^2 -BCN hybrids with a similar configuration to BN_3 in h-BN. At the grazing incidence angle ($\theta = 15^\circ$), the B₂ peak decreased and some fine structures such as B₁, B₃ and B₄ appeared evidently. It indicates the formation of various atomic configurations around B atoms besides the BN_3 -like configuration. The peak B₁ could be ascribed to the B atoms bonded to B in B_4C -like configuration because of the similar photon energy to B_4C .¹⁷⁾ The peak B₃ could be due to different configuration from the BN_3 like configuration. However, it could not be simply ascribed to the B atoms bonded to N and C atoms such as BN_2C or BNC_2 configuration since the photon energy of B K-edge might decrease by substituting C for more electronegative N atoms around the B atoms. The steric configurations of these different atomic hybrids of BCN have not been identified clearly yet although different

Fig. 5. N K-edge NEXAFS spectra at various incidence angle (θ) of the X-ray for the samples (1) and (3). NEXAFS spectrum for h-BN powder is also shown for comparison.

BCN atomic hybrid configurations with different N vacancies might be formed.¹⁸⁾ The peak B_4 is reported to be the B–O bond which is estimated as the surface contamination.¹⁹⁾ We could not estimate the cubic phase of BCN comparing with the reference spectrum of c-BN. The notable decrease in the B_2 peak height and increase in the σ^* resonance peak (broad feature denoted by B_5) were found as the incidence angle decreased. It suggests that the h-BCN layers with the BN_3 -like configuration may orient in the direction perpendicular to the silicon substrate.²⁰⁾ The B_5 peaks for the both samples are gentle compared with those for the h-BN, indicating that the atomic arrangement around the B atoms are not so well ordered as in h-BN. The decrease of the B_2 peak height for sample (1) was not pronounced and the B_1 and B_3 fine structures were not obvious in comparison with those for sample (3). This implies the predominant existence of the h-BCN configuration like h-BN in sample (1). The predominance of the B_2 configuration for sample (1) also corresponds to the sharp FT–IR peak and the unknown XRD peak at 29.2° .

The polarization dependence of N K-edge NEXAFS spectra of the typical samples (1) and (3) are shown in Fig. 5, together with the spectrum of the h-BN powder as the reference. Similar to the B K-edge spectra, the π^* resonance peak of N K-edge decreased at the grazing incidence of the X-ray. It confirms the orientation of the h-BCN basal planes perpendicular to the silicon substrate surface. However, fine structures are not appearing in the N K-edge spectra and the spectra for sample (1) and sample (3) are very similar to each other. This observation suggests that the atomic arrangement around N atoms in these samples is homogeneous and very similar to each other in comparison with those around the B atoms.

The σ^* resonance peaks are more gentle than those of the h-BN, suggesting the diversity in the σ bonds around N atoms than h-BN. While N atoms in h-BN crystal are regularly surrounded by 3B atoms, the regularity might be reduced in the long range in these samples, probably because of the atomic mixing of B, C and N in the basal planes. However, it is difficult to distinguish the atomic arrangements around N atom because the peak energies corresponding to the N–B and N–C bonds lie very close to each other.²¹⁾

4. Discussion

Based on the results by FT–IR, XRD, XPS and NEXAFS analyses, we discuss on the atomic arrangement, composition and orientation of the h-BCN films prepared by RF-plasma CVD in

different carrier gases.

4.1 Atomic arrangement

All samples prepared in this work exhibited two absorption bands at ~ 1400 and ~ 800 cm^{-1} in their FT–IR spectra (Fig. 1), which are similar to those ascribed to the sp^2 -B–N bonds in h-BN. The samples contained 22–35 at.% C determined by XPS. Therefore, we propose the formation of the ternary mixing of the sp^2 -B–C–N atomic hybrid bonds. The broadening of the FT–IR peaks might be due to the coexistence of a variety of bonds such as B–N, B–C and C–N and their combinations because these bonds exhibit the IR absorption peaks in this reason.¹⁰⁾ The broadening of the spectra with the C concentration suggests the increase in the complexity of the combination of C–N, C–B and B–N bonds. No clear evidence was found for the formation of mixture of the binary compounds such as $BN/CN_x/BC_x$.

The hexagonal structure was also detected for the present samples in terms of the (0 0 2) peak in the XRD patterns (Fig. 2), confirming the formation of the long range order in the atomic arrangement which was not found in the previous work.⁷⁾ The unknown XRD peak at 29.2° which suggested another crystalline phase was remarkable for sample (1), however more studies are needed to clarify the unknown phase. Based on the FT–IR and XRD results we unambiguously propose the hexagonal (h-BCN) atomic arrangement in the present samples.

The XPS spectra (Fig. 3) suggest that the films are composed of different B–N, B–C and C–N bonds to form the sp^2 -BCN atomic hybrid configurations. The wider FWHM of the B_{1s} peaks in comparison with that of h-BN suggests that B atoms have various chemical environments other than the BN_3 configuration similar to h-BN. The little shift of the B_{1s} XPS spectra to the higher binding energy for samples (3) and (4) with higher C content indicates the distortion of the sp^2 -BCN chemical environment with the C concentration. The broader C_{1s} XPS spectra than the graphite implies that the C atoms are not only bonded to C to form the graphite-like configuration but also bonded to B and N to form the sp^2 -B–C–N atomic environments. Tailing of the spectra to the higher binding energy might be ascribed to the binary phase CN_x together with the sp^2 -BCN hybrids. The broad N_{1s} XPS spectra and tailing also suggest the formation of the sp^2 -BCN atomic hybrids with a variety of configurations. However, it is difficult to clearly sort out the different configurations of BCN hybrids by the XPS spectra.

All samples showed broad NEXAFS spectra in comparison with h-BN (Fig. 4). The predominant peak B_2 suggests the formation of the sp^2 -B–C–N configuration like BN_3 in h-BN. The shrinking of the predominant peak B_2 was pronounced and some fine structures became clearer at the grazing incidence of the X-ray for sample (3) with high C content. The incorporated C might reduce the homogeneity in the h-BCN network as suggested from the XPS analyses and hence enhance the formation of the B_4C -like configuration (fine structure B_1) and the different BCN hybrids (fine structure B_3) other than the h-BN-like configuration (fine structure B_2). The π^* resonance of N K-edge decreased without showing fine structures at the grazing incident. This result suggests the atomic arrangements around N atoms are homogeneous in contrast to those around B atoms.

4.2 Composition

The C concentrations in the films (1) and (2) prepared in N_2 carrier gas were lower (22 and 23 at.%, respectively) than those in the films (3) and (4) in $CH_4 + H_2$ carrier gas (35 at.% for both). This may be due to the higher reactivity of the CH_4 fragments

than the N₂ in the plasma. In the XRD patterns, the intensity ratio of the hexagonal (0 0 2) peak at 26.3° to the unknown peak at 29.2° was higher for samples (1) and (2) with lower C content than the samples (3) and (4) with higher C content. The broader NEXAFS spectra and more significant fine structures were found for sample (3) than for sample (1). These results suggest that the composition might influence not only the atomic arrangement but also the crystallinity and/or the crystal structure.

4.3 Orientation

In the NEXAFS spectra (Fig. 4), considerable decrease of the π^* resonance of the sp²-BCN hybrid structure with h-BN-like configuration (B₂ peak) was observed at the grazing incident angle of X-ray in comparison with that at the normal incidence. It is because the direction of the orbital vector **p** of π^* orbital of the sp²-BCN sheets becomes opposite to the electric field vector **E** of the incident beam of X-ray at the grazing incidence.⁸⁾ It hence means that the orientation of the sp²-BCN basal planes with h-BN-like configuration was perpendicular to the Si substrate. The polarization dependence of the fine structures other than B₂ (B₁, B₃ and B₄) were not clear while they clearly appeared at the grazing angle for sample (3). The orientations of the fine structures are so far ambiguous. Similar to the B K-edge, polarization dependence of the π^* resonance peak for N K-edge (Fig. 5) also suggests the orientation of the sp²-BCN sheets perpendicular to the Si substrate.

5. Conclusions

The BCN films were synthesized by RF-PECVD using TDMAB as the precursor. The formation of the crystalline hexagonal BCN phase with h-BN-like configuration was indicated by FT-IR and confirmed by XRD. XPS measurement showed that the films were composed of a variety of B-N, B-C, C-N bonds to form the BCN atomic hybrids. No clear evidence for the phase separation such as BN/graphite/CN_x/BC_x was found though tailing of the C1s XPS peak to the higher binding energy suggested a CN_x phase together with the BCN hybrids. CH₄ + H₂ carrier gas enhanced the C incorporation into the h-BCN. It was also seen from the NEXAFS measurement that the BCN atomic hybrids with sp²-B-C-N bonds consisted mainly of the BN₃-like configuration while small amount of the other local configurations were detected. The polarization dependence of NEXAFS indicated that the h-BCN layers may orient in the direction perpendicular to the Si substrate.

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