Valence band electronic structure of carbon nitride from x-ray photoelectron spectroscopy

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This article reviews the valence band (VB) electronic structure of carbon nitride and reports on results obtained from carbon nitride films prepared by pulsed laser deposition (PLD). In the present work, two series of carbon nitride films have been synthesized by nitrogen-ion-beam-assisted PLD and reactive PLD in nitrogen atmosphere, respectively. X-ray photoelectron spectroscopy (XPS) is applied to determine the VB electronic structures. XPS VB spectra reveal that the electronic structures of the prepared carbon nitride films depend on nitrogen supply manner. In the case of nitrogen-ion-beam-assisted deposition, four bands in the regions ~0–6.2, ~6.2–13.7, ~13.7–20.8, and ~20.8–30 eV are clearly observed in the VB electronic structure, which stem from C 2p electrons associated with π bonds and s p 2 N in a planar graphite structure, C 2p and N 2p electrons associated with σ bonds, a mixture of 2s and 2p electrons, and C 2s and N 2s electrons, respectively. For the films deposited by reactive PLD in a nitrogen atmosphere at room temperature, a new band that results from N lone pairs of β-C 3 N 4 structure appears at ~5 eV in region ~1.0–7.4 eV, instead of the band at ~2.3 eV in region ~0–6.2 eV in the case of nitrogen-ion-beam deposited films. At elevated deposition temperature, the evolution of carbon nitride films towards amorphous carbon structure is observed. Furthermore, both nitrogen content and substrate temperature have a strong influence on the VB electronic structures of carbon nitride films. The evolution of VB electronic structure is also discussed by relating to the XPS core-level spectra of the carbon nitride films. © 2002 American Institute of Physics.

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I. INTRODUCTION

Since Liu and Cohen 1,2 theoretically predicated that the mechanical properties of β-C 3 N 4 might be similar to or superior to those of diamond, numerous experimental efforts were motivated to approach this material. Synthesis of carbon nitride has been attempted by a variety of deposition techniques including atmospheric-pressure chemical process, ion-beam deposition, laser technique, chemical vapor deposition, and reactive sputtering deposition (Refs. 3–5 and references therein). Up to now, in most cases the synthesized carbon nitride has amorphous structure with nitrogen content much lower than 57 at. % corresponding to the β-C 3 N 4 phase. Although the successful synthesis of β-C 3 N 4 was claimed by several groups,6–9 reasonable amounts of crystalline carbon nitride for proper characterization have not yet been obtained.

In nonstoichiometric carbon nitride the structural and electronic modifications introduced by nitrogen are mainly characterized by core-level binding energy based on x-ray photoelectron spectroscopy (XPS) measurements. A common observation in nearly all recent XPS studies on carbon nitride films is that two and three contributions to N 1s and C 1s core-level lines have to be assumed, respectively.10 The binding energies reported for the components of N 1s core-level line are generally located around 398 and 400 eV, and considerable variation in C 1s core-level binding energy is found. On the other hand, only a few results on the valence band (VB) electronic structure of carbon nitride have been reported11–18 although the corresponding studies on diamond, graphite, and amorphous carbon have been extensively conducted. The fingerprint capacity for structural information of VB spectra due to s and p characters in the bonds of carbon nitride materials can be very valuable since this information is sometimes unobtainable from core-level photoelectron spectra. Moreover, mapping the VB electronic structure of carbon nitride films is important for further improvement of their optoelectronic properties.

In this article, we present the VB electronic structure of carbon nitride studied systematically by using XPS. The carbon nitride films have been prepared by nitrogen-ion-beam-assisted pulsed laser deposition (PLD) and reactive PLD in nitrogen atmosphere, respectively. With PLD, the well-known tetrahedrally bonded amorphous carbon (ta-C) can also be produced.19 As a basis for the discussion of our results, recent VB studies on carbon nitride films are reviewed. The aim of this work is twofold: (i) to study the effect of nitrogen supply manner, i.e., nitrogen beam and nitrogen gas, on the VB electronic structure of carbon nitride film; and (ii) to illustrate the influence of nitrogen content and deposition temperature on the VB electronic structure.

II. REVIEW OF RECENT VALENCE BAND STUDIES

The VB spectra of carbon nitride have been recorded using both XPS and UV photoelectron spectroscopy (UPS).

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Chowdhury and coworkers\textsuperscript{11–13} identified three regions in the XPS VB spectra of their carbon nitride films at $\sim 5-14$, $\sim 17.5-22.5$, and $\sim 22.5-27.5$ eV corresponding to pure $2p$ states, $s$-$p$ hybridized states, and $2s$ states, respectively. After annealing at 600°C, the feature at $\sim 22.5-27.5$ eV is gone and the feature at $\sim 5-14$ eV is more refined but the feature at $\sim 17.5-22.5$ eV does not change at all. They concluded that $s$-$p$ hybridized bonding is the most stable and dominating structure of amorphous carbon nitride materials.\textsuperscript{11} At the low binding energy side of the dominant peak ($\sim 17.5-22.5$ eV), Monclus et al.\textsuperscript{13} identified two bands located at $\sim 4-7$ and $\sim 8-12$ eV. The former is due to C 2$p$ and N 2$p$ electrons associated with $\pi$ bonds in aromatic rings and probably N lone-pair electrons,\textsuperscript{14} which are present when a N atom bonds to a C atom in a pyridine-like domain and when $\equiv$N triple bonds are formed. The latter may be due to C–N and C–C $\sigma$ states.\textsuperscript{14,15}

Souto and coworkers\textsuperscript{14} studied the VB structure of carbon nitride by using UPS. They found that on increasing N content three new features emerge at energies near $\sim 9.5$, $\sim 7.1$, and $\sim 4$ to 5 eV, when compared with the spectrum of pure $a$-$C$ that shows two bands located at energies $\sim 7.7$ and $\sim 3.6$ eV, respectively. They identified that: (i) the band, located at $\sim 4$ to 5 eV, is due to lone-pair electrons belonging to N atoms; (ii) the band, located at $\sim 7.1$ eV, is due to C 2$p$ and N 2$p$ electrons associated with $\pi$ bonds in aromatic rings containing at least one substitutional N atom; and (iii) the band, located at $\sim 9.5$ eV, is also due to C 2$p$ and N 2$p$ electrons but shared in $\sigma$ bonds. This explanation was adopted by Hammer et al.\textsuperscript{15,16} to explain their UPS results on CN films, although a little variation in positions and intensities of the peaks existed.

For the electronic structure of hydrogenated carbon nitride films studied by using UPS, Hammer and coworkers\textsuperscript{15,16} found that the intensity associated with the N lone-pair electrons ($\sim 4.2$ eV) is slightly reduced as the N concentration changes from 22 to 16 at. %, which is caused by hydrogen incorporation. Furthermore, the main feature at $\sim 6.5$ eV (C–N $\pi$ bonds) is subsequently replaced by a new component located at 7.6 eV that associates with the increasing number of C–H and N–H bonds.

However, in the study of Bhattacharyya and coworkers, \textsuperscript{17,18} they presented that for their carbon nitride films the positions of $p$-$\pi$, $p$-$\sigma$, $s$-$p$, and $2s$ states were located at 3–4.8, 6.2–7.5, 8.9–10.5, and 13.4–14.3 eV, respectively. This is different from the results of the above research works.\textsuperscript{11–16} They attributed the variation to different N contents in these carbon nitride films. In their carbon nitride films, the highest N content is only 5.5 at. %, while the nitrogen content in the above research works is higher than 10 at. % and around 20–30 at. %. The peak between 4 and 5 eV appeared only for high nitrogen concentration ($\geq 18$ at. %).\textsuperscript{14,15}

\section*{III. EXPERIMENT}

\subsection*{A. Preparation of carbon nitride films}

The carbon nitride films were deposited on Si (100) substrates by pulsed laser deposition (PLD). The base vacuum of the deposition chamber was about $10^{-7}$ Torr. The fourth harmonic from a $Q$-switch Nd:yttrium-aluminum-garnet (YAG) laser with a wavelength of 266 nm and a pulse duration of 10 ns was focused onto a high purity (99.999%) highly oriented-pyrolytic-graphite (HOPG) target. The laser was pulsed at a rate of 10 Hz. The laser fluence was varied from 3.7 to 12.7 J/cm$^2$. Two series of carbon nitride films were prepared under different nitrogen sources. Series 1: a 3-cm ion source was used for providing an active nitrogen beam that was directed toward the substrate surface at an angle of 90°. Through adjusting nitrogen ion energy (100–400 eV) and current (10–40 mA) and laser fluence, carbon nitride films with nitrogen content from 12.4 to 30.0 at. % were synthesized at a substrate temperature of 400°C. Series 2: nitrogen gas of 99.999% purity was applied to react with carbon species. Carbon nitride films with various nitrogen contents of 10.9–45.8 at. % were prepared at different nitrogen gas pressures (0.1–5.0 Torr) and substrate temperatures (RT–600°C). The nitrogen contents of the synthesized carbon nitride films were obtained by x-ray photoelectron spectroscopy (XPS) measurement, i.e., obtained from the ratio of the integrated intensity of N 1$s$ and C 1$s$ peaks corrected by the respective sensitivity factors. Since XPS gives information from the top layers of the films, we assume that the top-layer composition is representative of the film composition. The deposition parameters as well as the nitrogen content for the films synthesized by nitrogen-ion-beam-assisted PLD and reactive PLD are summarized in Tables I and II, respectively. For comparison, pure carbon film was also prepared.

\subsection*{B. Characterization of valence-band structure}

The electronic structure of carbon nitride films was characterized by XPS measurement. XPS was carried out on a
Shimadzu ESCA KI using a Mg Kα 1253.6 eV x-ray source with energy resolution of 0.8 eV. All the VB spectra were calibrated using the signal from a Ag 3d_{3/2} peak at 374.0 eV.

IV. RESULTS

A. Electronic structure of nitrogen-ion-beam-assisted PLD deposited carbon nitride films

1. Low nitrogen content

Figure 1 shows the XPS VB spectra of the carbon nitride films prepared by nitrogen-ion-beam-assisted PLD. The XPS VB spectrum of pure carbon film is also illustrated for comparison. The spectrum of pure a-C shows three bands located at binding energy ∼9.2, ∼16.7, and ∼24.5 eV, respectively. According to the reference spectra of various forms of carbon measured by McFreely et al. using XPS and by Wesner et al. using UPS, the band at ∼9.2 eV is attributed to a mixture of 2s and 2p states, both bands at ∼16.7 and ∼24.5 eV arise from 2s-like states. For the pure carbon film shown in Fig. 1, the predominant VB characteristics are s-p hybridized states and 2s states, while pure 2p states at the region of ∼2–8 eV is hardly distinguished from the slope of the band of s-p hybridized states and the band at 24.5 eV appears as a small shoulder of that at ∼16.7 eV. These features are consistent with the reference spectra in Refs. 20 and 21. However, different features appear after the incorporation of nitrogen. Four regions are found in the VB spectra of carbon nitride films: region I at ∼0–6.2 eV, region II at ∼6.2–13.7 eV, region III at ∼13.7–20.8 eV, and region IV at ∼20.8–30 eV. The band at ∼2.3 eV in region I is associated with C–C π bonds due to C 2p electrons. The sp^2N in a planar graphite structure is also responsible for region I. The origins of regions II–IV are assigned as follows: (1) region II is a contribution of C 2p and N 2p electrons associated with σ bonds; (2) region III is a mixture of 2s and 2p electrons; and (3) region IV is due to C 2s and N 2s electrons. Our assignment is consistent with the investigations described in Sec. II. With increasing nitrogen content from 12.4 to 20.3 at. %, there are no significant changes for these four regions. The spectra show that the s, sp, and p peaks are almost equal in height.

2. High nitrogen concentration

When more nitrogen is introduced into the films, different features appear in the VB spectra, as shown in Fig. 1. The peak intensity of these regions changes with the increase of nitrogen content. When nitrogen content reaches 23.2 at. %, regions I, II, and IV become apparent and the intensities go up, while region III has little change. The bands at regions I, II, and IV are narrower and increase gradually for higher nitrogen content (>25.4 at. %). These bands dominate the spectrum of the carbon nitride film with the highest nitrogen content (30.0 at. %). It implies a structural change in these films induced by the nitrogen incorporation with a high content. Due to a large amount of nitrogen introduced into the films, more carbon–nitrogen bonding forms that could be responsible for the intensity change of these regions. Because the photoemission cross sections of N 2s and N 2p (0.0841, 0.0025, and 0.0049 for 2s_{1/2}, 2p_{1/2}, and 2p_{3/2}, respectively) are much higher than that of C 2s and C 2p (0.047, 0.0006, and 0.0012 for 2s_{1/2}, 2p_{1/2}, and 2p_{3/2}, respectively) when using Mg Kα excitation, the intensity of the VB spectrum changes apparently with the high content nitrogen incorporation. Due to the photoemission the cross section of the s band is 13 times higher than that of the p band for the XPS VB spectrum, region IV has the most obvious change compared with other regions. Moreover, the irradiation of a large amount of energetic nitrogen to the films would induce the graphitization of the films occurring and developing. As a result, C–C π bonds increase and more nitrogen is incorporated into a planar graphite network, which also leads to the intensity of region I increasing. We note that regions I, II, and IV predominate after high content nitrogen is incorporated into the films, which is in contrast to the results by Chowdhury et al. and Monclus et al. In their cases, region III that associated with a mixture of 2s and 2p states is the most striking feature in the VB spectra. By analogy with the VB spectra of carbon films having polymer form, they identified a polymeric-like structure in their carbon nitride films. The results in the present work indicate less polymeric-like features in our carbon nitride films.
B. Electronic structure of nitrogen atmosphere deposited carbon nitride films

1. At room temperature

Figure 2 illustrates the XPS VB spectra of the carbon nitride films prepared under different nitrogen gas pressures at room temperature. Four distinct regions are observed in the valence band spectra: region I' at \( \sim 1.0 - 7.4 \text{ eV} \), region II at \( \sim 7.4 - 13.5 \text{ eV} \), region III at \( \sim 13.5 - 19.7 \text{ eV} \), and region IV at \( \sim 19.7 - 30.8 \text{ eV} \). In this case, region I' (Fig. 1) associated with \( C_2p \) \( \pi \)-bonds and \( sp^2 \) N in a planar graphite structure disappears. Instead, a new band in region I' is clearly shown. According to the reported VB spectra for carbon nitride films and the calculated DOS for the \( b-\text{C}_3\text{N}_4 \) structure, the band located at \( \sim 5 \text{ eV} \) in region I' is associated with N lone pairs, i.e., N and C are assumed to form a structure similar to crystalline silicon nitride where C is \( sp^3 \) hybridized. The assignment of regions II–IV is the same as that in the VB spectra of the carbon nitride films prepared with the nitrogen-ion-beam source, as shown in Fig. 1. With the increase of nitrogen content, the position of these four regions changes whereas the band intensity has no obvious change. That is, for the film with more nitrogen, the valence bands appear at higher binding energy. In addition, the leading edge of the valence band, the intersection of the linear extrapolation of the valence band tail with the energy axis, recedes on increasing N content. This is attributed to a reduction of C–C \( \pi \) states close to the Fermi level. This result is in agreement with that of Souto et al. and with the result of hydrogenated carbon nitride films of Hammer et al.

2. Effect of substrate temperature

Figure 3 shows the VB spectra of the carbon nitride films synthesized in nitrogen gas atmosphere at the substrate temperatures of RT, 200 °C, 400 °C, and 600 °C, respectively. It is clearly seen that the VB structure of these carbon nitride films changes gradually with the substrate temperature. The valence band shifts to a lower binding and the intensities of regions I', II, and IV reduce correspondingly. With increasing of temperature, the band in region I' disappears and a band in region I that was observed in the films prepared by nitrogen-ion-beam-assisted deposition appears, indicating the development of graphitization at high substrate temperature. When the substrate temperature reaches 600 °C, the VB features of the synthesized carbon nitride film are similar to those of pure amorphous carbon without nitrogen, as shown in Fig. 1.

V. DISCUSSION

We know that photoemission is surface sensitive and contaminations may have spectral weight in the valence band region. In order to exclude the influence of contaminations on the VB spectra, we characterized the content of impurities on the surface of the deposited films, especially oxygen and...
fluorine. The latter possibly results from CaF₂ substrate that is used to deposit carbon nitride films for other measurements at the same time as those deposited on Si substrate for XPS measurement. In Fig. 4, the typical core-level spectra of fluorine and oxygen of the deposited films are shown. We can see that no signal of fluorine species is detected in the XPS spectra, which indicates that the fluorine should not contribute to the VB spectra of the films. In the case of oxygen, the measured content is 2 at. % and no systematic variation is observed for all the films. The measured content of oxygen is less than those reported by Lu et al. (~5 at. %) and by Scharf et al. (~3 at. %) in their studies of core-level and VB spectra of diamond-like carbon and amorphous CN films. Moreover, no spectra in Figs. 1–3 show a band around 7.0 eV for O 1s. The binding energy of O 1s is also known to be almost 3.6 and 4.9 eV higher than that of N 2s and C 2s, respectively. Therefore the oxygen is not expected to significantly influence the valence band structure of the films considering its very low content.

The above experimental results indicate that the VB electronic structure of the carbon nitride films strongly depends on the nitrogen supply manner, nitrogen content, and substrate temperature.

In the case of nitrogen-ion-beam-assisted deposition, the band at ~2.3 eV in region I occurs after nitrogen is introduced, as seen in Fig. 1. This could be explained as the graphitization that was caused by hyperthermal nitrogen ions. We know that ta-C film with high sp³ C hybridization could be formed in an optimal energy window of carbon ion. Due to the introduction of hyperthermal nitrogen ions that will lead carbon ion energy beyond this optimized window, sp² C hybridization will increase, which will result in graphitization and part of the nitrogen incorporating into a planar graphite network. Meanwhile, hyperthermal nitrogen ions will improve the crystallization of carbon nitride films. Therefore it is easy to understand that for the films with more nitrogen, the valence bands become narrower and sharper.

The intensity of the band in region II at ~6.2–13.7 eV, which is a contribution of C 2p and N 2p electrons associated with σ bonds, increases obviously for the film with high nitrogen content, indicating that in a carbon–nitrogen bonded phase N–sp³ C bonds became dominant. As a result, the C 2p and N 2p electrons related σ bonds enhance, leading to the increase of the band intensity in region II at high nitrogen content. This can be confirmed by the results of N 1s core-level spectra. Figure 5 shows the evolution of the N 1s core-level spectra of the carbon nitride films deposited by nitrogen-ion-beam-assisted PLD on nitrogen content. The curves show two well-resolved structures at ~398.1 eV (peak A) and ~400.5 eV (peak B) associated with nitrogen atoms in two quite different local configurations. Peak A is assigned to the tetrahedral C–N bonding, i.e., N–sp³ C bonds, while peak B corresponds to the N–sp² C bonding. This assignment is in contrast to the results by Ronning et al., in which they assumed that the N 1s peaks around 400 and 398 eV are attributed to an s electron originating from nitrogen atoms having three and two neighbors, respectively. However, our assignment is consistent with the two-phase system proposed by Marton et al. and the results by Souto et al. We note that peak A becomes dominant in the films containing high nitrogen content. This indicates that the films will have higher N–sp³ C bond fraction at higher nitrogen content (>23.2 at. %). The results are in agreement with those by Sjöström et al. and Suoto et al., in which they suggested that the nitrogen coordination goes from a planar structure to a three-dimensional structure for large nitrogen content. Therefore one can conclude that at low nitrogen content (12.4–20.3 at. %), N–sp³ C bonds and N–sp² C
bonds have a close fraction. Above the nitrogen content of 23.2 at.%, N–sp³C bonds dominate. This could be responsible for the evolution of the VB electronic structure of carbon nitride films on the nitrogen content, as shown in Fig. 1.

In the case of nitrogen atmosphere deposition, because of very low nitrogen energy, the incorporation of nitrogen into films has less influence on the carbon ion energy compared with the hyperthermal nitrogen ion beam. Thus sp³C hybridization is dominant that results in the nitrogen incorporating into an sp³ carbon network. This will be responsible for the band at ~5 eV in region I of the carbon nitride films prepared in nitrogen atmosphere, as shown in Fig. 2. However, due to the low energy and room temperature deposition, the crystallization of the films is low and a broad valence band exhibits.

We note that all the valence bands in regions I', II, III, and IV shift to higher binding energy with increasing nitrogen content. It implies a strong structural change in these samples induced by the high-content nitrogen incorporation. Due to the existence of high-content nitrogen and the formation of carbon–nitrogen bonding, N 2s, N 2p, and the corresponding s-p hybridized bonding states appear in the valence band spectra with positions very close to those of carbon. We know that the binding energies of the valence bands of nitrogen are almost 2 eV (2p states) and 1.3 eV (2s states) higher than those of carbon; therefore it is not difficult to understand the upper shift of the bands with the increase of nitrogen content. In addition, some new bonds would also be formed in the carbon nitride films with high nitrogen content. Figure 6 shows the typical N 1s core-level spectrum of the carbon nitride films prepared in nitrogen atmosphere at room temperature. There is one broad peak in the spectrum. According to the deconvolution of the spectrum in Gaussian, a new subpeak at about 401.5 eV is found besides those at ~398 and ~400 eV. The attribution of the latter two is the same as that of carbon nitride films prepared by nitrogen-ion-beam-assisted deposition. The binding energy at 401.5 eV is associated with the nitrogen in a four-bond configuration by comparison with Siegbahn’s reference spectra. This is consistent with the calculation based on the electronegativity and partial ionic character of the bonds, which suggests that an XPS subpeak from a nitrogen atom participating in four bonds with carbon atoms should reside at 402 eV. The full width at half maximum of ~3 eV of these XPS spectra strongly suggested that multiple bonding configurations should be present in these carbon nitride films with variable relative intensity. The formation of nitrogen in a four-bond configuration could correspond to the shift of the valence band. The nitrogen bound to four carbon atoms is consistent with the structure proposed by Sjöström et al. According to Sjöström et al., for the case of nitrogen bound in a carbon-based graphitic structure, a stable configuration with low energy is for the nitrogen to substitute for a carbon in a five-member ring, which would require forming four bonds.

With the increase of substrate temperature, the valence band at ~5 eV shifts to lower binding energy and finally disappears, then the band at ~2.3 eV appears. This implies that sp³C predominated at high substrate temperature, which will not be favorable to the formation of C₃N₄ structure with high hardness as predicted. It is in agreement with the evolution of N 1s core-level spectra on the substrate temperature, as shown in Fig. 7. For the film prepared at 200 °C, the N 1s peak shifts to low binding energy and splits into two subpeaks (~398 and ~400 eV). It would cause the downward shift of the valence band. At the substrate temperature of 200 °C, the N–sp³C bonds still dominate. When the substrate temperature reaches 400 °C, N–sp²C and N–sp³C bonds have almost the same fraction. This indicates that the N–sp²C bond fraction develops with increasing substrate temperature. Moreover, the graphitization of the film will occur at such a high substrate temperature, resulting in the sp²C–C bonds preferably formed in the film and the VB structure changed correspondingly. When the substrate temperature increases further to 600 °C, the nitrogen content in the film becomes very low and hence only a little of the carbon–nitrogen bonds formed, which will have weak effect on the VB electronic structure of the film. This can be re-

![FIG. 6. Typical XPS N 1s spectrum of the carbon nitride films synthesized by reactive pulsed laser deposition in nitrogen atmosphere at room temperature.](image)

![FIG. 7. XPS N 1s spectra of the carbon nitride films synthesized by reactive pulsed laser deposition in nitrogen atmosphere with the substrate temperatures of 200 and 400 °C, respectively.](image)
sponsible for the VB features of the film similar to those of pure amorphous carbon.

Based on the above discussion, an active nitrogen source with only a few eV energy and a substrate temperature lower than 400 °C will be beneficial to the formation of the crystalline $\beta$-$\text{C}_3\text{N}_4$ structure.

VI. CONCLUSIONS

In summary, the electronic structures of the carbon nitride films synthesized by nitrogen-ion-beam-assisted PLD and reactive PLD in nitrogen atmosphere are determined by XPS VB spectra. The results indicate that the electronic structures of prepared carbon nitride films are correlated to the nitrogen supply manner, nitrogen content, and substrate temperature. In the case of nitrogen-ion-beam-assisted deposition, four bands of the electronic structure in regions I ($\sim 0$–6.1 eV), II ($\sim 6.1$–13.7 eV), III ($\sim 13.7$–20.8 eV), and IV ($\sim 20.8$–30 eV) are clearly observed, which are assigned as $C\, 2p$ electrons associated with $\pi$ bonds and $sp^2$N in a planar graphite structure, $C\, 2p$ and $N\, 2p$ electrons associated with $\sigma$ bonds, a mixture of $2s$ and $2p$ electrons, and $C\, 2s$ and $N\, 2s$ electrons, respectively. For the films with low nitrogen content (12.4–20.3 at.%), these four bands have almost the same intensity. As nitrogen content is higher than 23.2 at.%, the intensities of the bands in regions I, II, and IV increases apparently.

For the films deposited by reactive PLD in nitrogen atmosphere at room temperature, a new band ($\sim 5$ eV) that results from N lone pairs of the $\beta$-$\text{C}_3\text{N}_4$ structure appears in region $I'$ ($\sim 1.0$–7.4 eV), instead of the band ($\sim 2.3$ eV) in region I in the case of nitrogen-ion-beam-deposited films. The bands in regions $I'$, II, and IV predominate and shift to a higher binding energy with increasing nitrogen content. At elevated deposition temperature, the evolution of carbon nitride films towards amorphous carbon structure is observed.

The evolution of the VB electronic structure of the carbon nitride film on the nitrogen supply manner, nitrogen content, and substrate temperature could be attributed to the change of nitrogen–carbon and carbon–carbon bonds at different deposition parameters, as revealed by the XPS core-level spectra of the carbon nitride films.

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