Study on Local Structures of CxN1-x Films by First-Principles 1s Orbital Energy Calculations

Study on Local Structures of C_xN_{1-x} Films by First-Principles 1s Orbital Energy Calculations

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The 1s core level energy is calculated for a few hypothetical structures of C_xN_{1-x} including α-C_3N_4, β-C_3N_4 and graphitic-C_3N_4 by using the all-electron mixed-basis approach. The results are compared with the XPS measurement of a diamond film irradiated with N_2^+ ions. The comparison suggests that the irradiated film is amorphous C_xN_{1-x} whose local structure is similar to β-C_3N_4 or graphitic-C_3N_4.

1. Introduction

A C_xN_{1-x} crystal is a hypothetical material, which was first predicted in an unpublished patent in 1984 by Sung.[1] Since it is expected that the material may be harder than diamond, it has attracted considerable interest.

Combining an empirical model[2] and an ab initio calculation,[3] Cohen *et al.* showed that short covalent bonds between C and N are favorable for achieving low compressibility. They also carried out a local-density-approximation (LDA)-based calculation of the structural and electronic properties of β-C_3N_4, and showed that the bulk modulus of this material would be comparable to that of diamond with an indirect band gap of 3.2 eV and a sound velocity of 10^6 cm/s.[4] In addition, the cohesive energy of β-C_3N_4 was found to be moderately large, suggesting that it might be an energetically favorable phase in the C–N system.[4] This result indicates the possibility of its synthesis under laboratory conditions. Because of this fact, a lot of experimental efforts have been devoted to the synthesis of C_xN_{1-x}.[5-11] In order to identify the C_xN_{1-x}, X-ray photoelectron spectra (XPS) have been measured in many experiments.[5-7,9-11]

Among these experiments, Kusunoki *et al.*[11] carried out the following experiment: Diamond samples grown on Si substrates by CVD were nitrided by irradiating 300–700 eV N_2^+ ion beams, and after this, the samples were heated up to 600°C in ultra-high vacuum (UHV). The C1s and N1s XPS spectra were measured during nitridation and after annealing in UHV. N1s XPS spectra split clearly into two components after annealing, and the width of splitting is 2.2 eV. Then, it is particularly interesting and important to determine if these split XPS spectra can be attributed to a C_xN_{1-x} material.

In this paper, we calculate the 1s level energy of carbon and nitrogen in α-C_3N_4, β-C_3N_4 and graphitic-C_3N_4 structures by a first principles study. The method of calculation which we adopt in this study is the all-electron mixed-basis approach. Let us briefly describe this method.

In order to determine the 1s level energy, it is necessary to calculate the electronic states of not only valence but also core electrons, *i.e.*, one has to use an all-electron formalism. For this purpose, we use a method called the all-electron mixed-basis approach.[12,13] As is usual, it is based on a density-functional framework[14,15] within the local density approximation[16,17] to the exchange and correlation. In the all-electron mixed-basis approach, a wave function is represented by superposing the plane-wave basis functions that are expanded in real space and the numerical-atomic-orbital basis functions that are localized within non-overlapping atomic spheres. Using this method, it is possible to represent localized electronic states like the 1s state by using a relatively small number of basis functions.

In the present work we calculate the 1s level energy of a few hypothetical structures of C_xN_{1-x} using this all-electron mixed-basis approach, and compare the result with the experimental results of XPS. The main purpose of the present study is to make clear the nature of the peaks of the XPS spectra.

2. Calculation

We calculate the 1s level energy of the α-C_3N_4 and β-C_3N_4 structures, which are essentially similar to the α-Si_3N_4 and β-Si_3N_4 structures[18,19] if Si is substituted with C.[4] Both α-Si_3N_4 and β-Si_3N_4 are known to be hard materials. In these structures each C atom has 4 neighbors and each N atom has 3 neighbors. Figure 1 shows these two structures. The β-C_3N_4 structure resembles the phenacite (Be_2SiO_4) structure. It has 14 atoms in the unit cell and has the $P6_3/m$ symmetry. The α-C_3N_4 structure can be described as an ABAB... stacking sequence of the layers of β-C_3N_4 (A) and its mirror image (B). The unit cell contains 28 atoms and has the $P3_1c$ symmetry.[20,21]

At first, each structure is relaxed with the fixed symmetry constants. This stage of calculation is performed by using VASP3.2, that is, a package program using a pseudopotential and a plane-wave basis set. The atomic configurations of both α-C_3N_4 and β-C_3N_4 vary only little, when one compares the relaxed structures with the unrelaxed one.

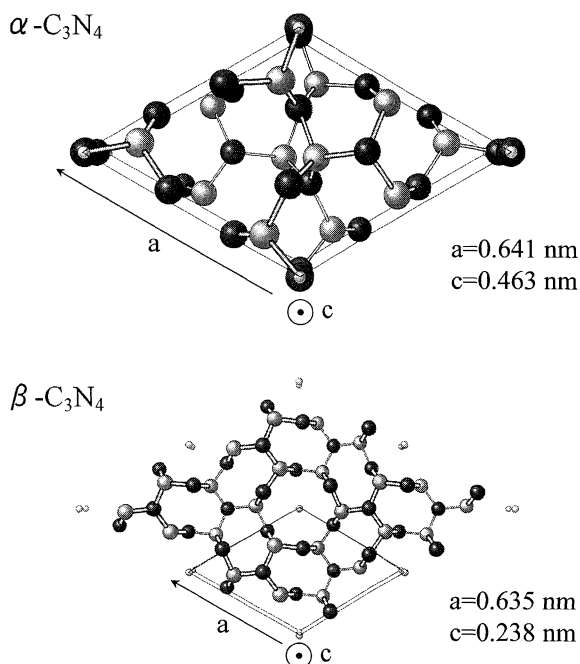---

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α-C_3N_4

a=0.641 nm
c=0.463 nm

$\odot$ c

β -C_3N_4

a=0.635 nm
c=0.238 nm

$\odot$ c

Fig. 1 The α-C_3N_4 and β-C_3N_4 structures after relaxation and their lattice constants ("a" is parallel to the plane and "c" is perpendicular to the plane). White spheres represent carbon atoms and black spheres represent nitrogen atoms.

Next, we calculate C and N1s level energies of the relaxed α-C_3N_4 and β-C_3N_4 structures by the all-electron mixed-basis approach. We also calculate the graphitic-C_3N_4 structure which has been proposed by Liu et al.[22] We take into account only one k-point, i.e., Γ-point, because the 1s level energy does not vary largely by the lattice periodicity. The energy cut-off for the plane waves is chosen to be 37 Ry.

3. Results and Discussion

3.1 Calculated 1s level energy

Figure 2 shows the calculated 1s level energies of C and N. The results for the α-, β- and graphitic-C_3N_4 crystals are shown in left, middle and right graphs. For the α-C_3N_4 structure, all 1s level energies of C or N are located within a width of 1 eV On the other hand, for the β- and graphitic-C_3N_4 structures, although the C1s level lies within 1 eV, there is a large splitting in the N1s level energies. The splitting becomes as large as 2 eV.

3.2 Simulated energy spectrum

Using the above result, we simulate the XPS energy spectrum associated with the 1s level, which can be compared with the experimental XPS spectrum according to Kusunoki et al.[11] Our spectrum is obtained by superposing gaussian functions that are centered at each 1s level energy and normalized such that the integrated area is equal to the number of atoms, which are belong to a same element, per unit volume. The full width at half maximum (FWHM) of each gaussian function is set at 0.67 eV which is the resolution of XPS experimental apparatus according to Kusunoki et al. In the calculation within the LDA only relative values of the level ener-
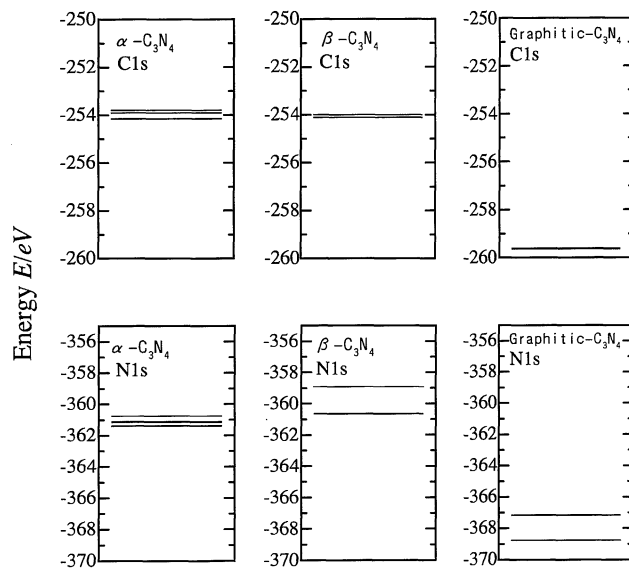
Fig. 2 The C1s level energy (top) and the N1s level energy (bottom) of the α-C_3N_4(left), β-C_3N_4 (middle) and graphitic-C_3N_4 (right) structures.

gies are reliable. Therefore, we adjust the C1s level energy to the experimental C1s binding energy of XPS and then compare the obtained N1s level energy spectrum with the XPS spectrum. Figures 3 and 4 show the C1s and N1s core peaks, respectively. In both figures, the upper graph is the XPS result by Kusunoki et al.,[11] while the lower one is the present result for each structure. The simulated spectrum is shifted so that the C1s peaks are located at 287.4 eV, which is the position of C1s of $C_x N_{1-x}$ (the "C" peak in Fig. 3) from experiment.[11] The reason why we adjust the simulated spectrum to the peak "C" which is the smallest component of C1s XPS spectrum is as follows: Kusunoki et al. show that the peak "C" attributes to the nitrided carbons though "A" and "B" peaks which are located at 284.9 eV and 286.1 eV attribute to the surface side of the diamond and unreacted diamond substrate beneath the ion penetration zone, respectively. In the upper graph of Fig. 4, the dotted and solid lines indicate the XPS spectra before and after annealing, respectively. Kusunoki et al. show that the C1s XPS spectrum changes hardly by annealing except for a little decrease of "B" component.

From Fig. 4 we find that the relative location of the simulated peaks of the N1s level energy spectrum is not far from the experimental N1s peak. This indicates the validity of the present analysis concerning the relative values of the level energies. As shown in the upper graph of Fig. 4, the experimental N1s peak is split into two peaks separated by about 2 eV. The simulated N1s energy spectrum has only a single peak for the α-C_3N_4 structure, while for the β- and graphitic-C_3N_4 structures, it is split into two peaks. The width of this splitting is also about 2 eV. In the calculation the intensity ratio of the two peaks is 3 : 1. This ratio corresponds to the ratio of two inequivalent locations of N atoms (six in the central 12-membered ring and two at the surrounding two C_{3z} centers in the case of the β-C_3N_4 structure, and one two-coordinated and three three-coordinated atoms in the case of the graphitic-C_3N_4 structure) in the unit cell. However, the experimental result shows that the intensity ratio of the two peaks is roughly
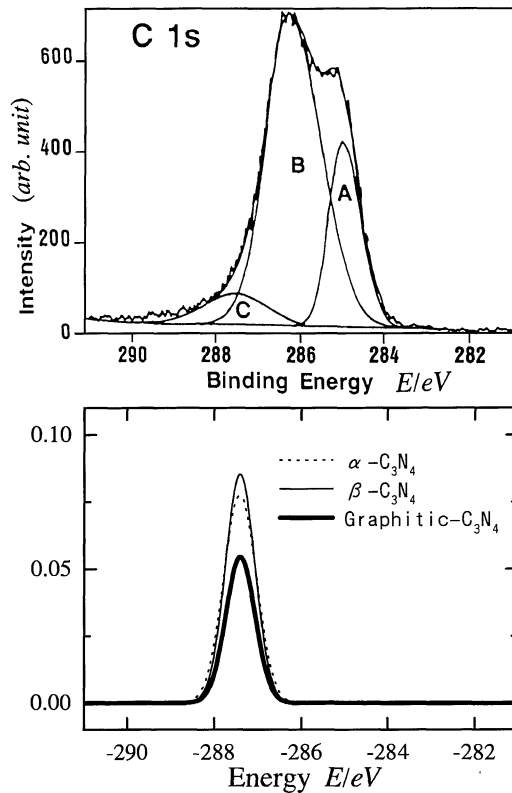
Fig. 3 The experimental XPS spectrum (top) of C1s binding energy by Kusunoki et al.[11] and the simulated 1s level energy spectrum of C (bottom). At the top of the figure, the XPS spectrum is divided into three peaks: A, B and C. At the bottom of the figure, the dotted, thin and heavy lines show the spectra of the α-, β- and graphitic-C_3N_4 structures, respectively.
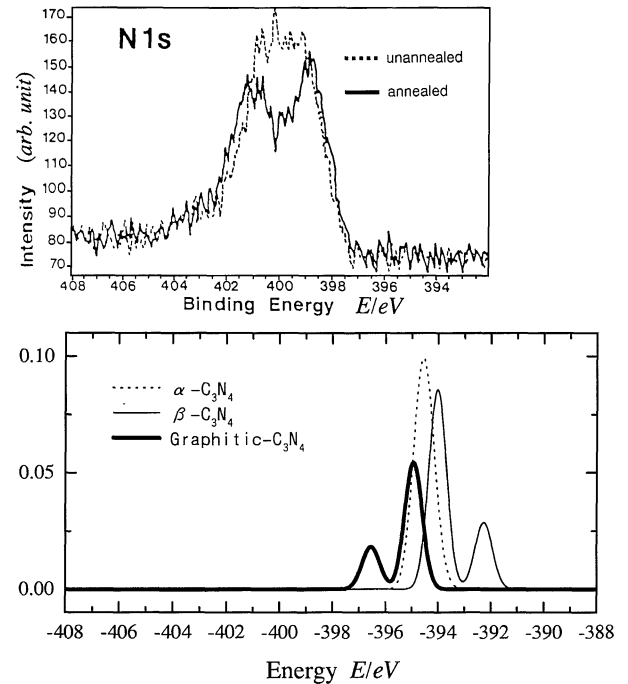

Fig. 4 The experimental XPS spectrum (top) of C1s binding energy by Kusunoki et al.[11] and the simulated 1s level energy spectrum of N (bottom). At the top of the figure, the dotted and solid lines are the XPS spectra before and after annealing. At the bottom of the figure, the dotted, thin and heavy lines show the spectra of the α-, β- and graphitic-C_3N_4 structures, respectively.

1 : 1. This means that the substance of the diamond film exposed to N_2^+ ions may be C_xN_{1-x} whose structure resembles β- or graphitic-C_3N_4 but is not identical. The experimental peak ratio of 1 : 1 suggests that the resulting material is isotropic. From these results, we conclude that the most probable candidate for the material created experimentally would be an amorphous C_xN_{1-x} whose local structure resembles β-C_3N_4 or graphitic-C_3N_4.

4. Conclusion

In summary, by using the all-electron mixed-basis approach, we have calculated the 1s level energy for three hypothetical structures, i.e., α-C_3N_4, β-C_3N_4 and graphitic-C_3N_4. The simulated 1s level energy spectrum was compared with the experimental XPS spectrum. From these results, the following possibility is strongly suggested: the substance created experimentally from a diamond film irradiated by N_2^+ ions is an amorphous C_xN_{1-x} whose local structure is similar to β-C_3N_4 or graphitic-C_3N_4.

5. Acknowledgements

REFERENCES

1) C. M. Sung and M. Sung: Mat. Chem. Phys., 43 (1996), 1–18.
2) M. L. Cohen: Phys. Rev., B 32 (1985), 7988–7991.
3) A. Y. Liu and M. L. Cohen: Science, 245 (1989), 841–842.
4) A. Y. Liu and M. L. Cohen: Phys. Rev., B 41 (1990), 10727–10734.
5) F. Fujimoto and K. Ogata: Jpn. J. Appl. Phys., 32 (1993), L420–L423.
6) J. Q. Zhang, Y. Setsuhara, S. Miyake and B. Kyoh: Jpn. J. Appl. Phys. 36 (1997), 6894–6899.
7) S. Matsumoto, K. K. Chattopadhyay, M. Mieno and T. Ando: J. Mater. Res., 13 (1998), 180–186.
8) A. Leonhardt, H. Gruger, D. Selbmann, B. Arnold and J. Thomas: Thin Solid Films, 332 (1998), 69–73.
9) J.Hong and G. Turban: J. Vac. Sci. Technol.. A 17 (1999). 314–316.
10) K. Yamamoto, Y. Koga, S. Fujiwara, F. Kokai, J. Kleiman and K. K. Kim: Thin Solid Films, 339 (1999), 38–43.
11) I. Kusunoki, M. Sakai, Y. Igari, S. Ishidzuka, T. Takami, T. Takaoka, M. Nishitani-Gamo and T. Ando: Diamond and Related Materials, to be published.
12) K. Ohno, F. Mauri and S. G. Louie: Phys. Rev., B 56 (1997), 1009–1012.
13) K. Shiga, K. Ohno, Y. Maruyama, Y. Kawazoe and T. Ohtsuki: Model. Simul. Mater Sci. Eng., 7 (1999), 621–630.
14) P. Hohenberg and W. Kohn: Phys. Rev., 136 (1964), 864–871.
15) N. D. Mermin: Phys. Rev., 137 (1965), 1441–1443.
16) W. Kohn and L. J. Sham: Phys. Rev., 140 (1965), 1133–1138.
17) O. Gunnarsson and B. I. Lundqvist: Phys. Rev., B 13 (1976), 4274–4298.
18) R. Grün: Acta Cryst., B 35 (1979), 800–804.
19) C. Wang, X. Pan, M. Rühle, F. L. Riley and M. Mitomo: J. Mater. Sci., 31 (1996), 5281–5298.
20) B. Molina and L. E. Sansores: Mod. Phys. Lett., B 13 (1999), 193–201.
21) D. M. Teter and R. J. Hemley: Science, 271 (1996), 53–55.
22) A. Y. Liu and R. M. Wentzcovitch: Phys. Rev., B 50 (1994), 10362–10365.