Spectral Analysis of XPS of Diamond and Graphite by MO Calculations using Model Molecules

K. ENDO,* T. MOROHASHI,ª T. OTSUKA, S. KOIZUMI, M. SUHARA, D. P. CHONG[b]

Deptartment of Chemistry, Faculty of Science, Kanazawa University, Kakuma, Kanazawa 920-1164,
ªAnalytical Laboratory,Ulvac-PHI, 370 Enzo, Chigasaki 253-0084, [b]Department of Chemistry, 2036 Main
Mall, University of British Columbia, Vancouver, BC, Canada V6T 1Z1

It is well-known that diamond is the cubic structure, while the graphite consists of a layer structure of continuous benzene rings. The difference of the structure between diamond and graphite was already reflected in the spectra by several analytical methods: XPS, AES, NMR, IR and so on. In order to clarify the electronic structure of diamond and graphite, we analyzed the valence X-ray photoelectron spectra of diamond and graphite by deMon density-functional theory (DFT) calculation using the model adamantane derivative($C_{10}H_{12}(CH_3)_4$) and pyrene($C_{16}H_{10}$) molecules, respectively. The simulated spectra of valence XPS for diamond and graphite are in considerably good accordance with the experimental ones, respectively. We determined the electronic states and the bond nature of the diamond and graphite.

Introduction

Diamond films are desired for many applications, including wear-resistant coatings, thin film semiconductor devices, X-ray lithographic membranes, and durable infrared windows. These films are usually deposited from gas-phase mixtures containing predominantly hydrogen. On the other hand, graphite is produced especially as very strong fibers by pyrolysis, at 1500°C or above, of oriented organic polymer fibers. When incorporated into plastics the reinforced materials are light and very strong. Other applications of graphite are used as intercalation compounds, since the loose and layered structure of graphite makes it possible for many molecules and ions to penetrate between the layers, forming interstitial or lamellar compounds.

The diamond and graphite differ in their physical and chemical properties because of differences in the arrangement and bonding of the atoms. The difference of the structure between diamond and graphite was already reflected in the spectra by several analytical methods: XPS, AES, NMR, IR and so on. In order to clarify the electronic structure of dia-

mond and graphite, we analyze the valence X-ray photoelectron spectra of diamond and graphite by deMon[1] density-functional theory (DFT) calculations using the model adamantane derivative $(C_{10}H_{12}(CH_3)_4)$ and pyrene $(C_{16}H_{10})$ molecules, respectively.

MO Calculations

The model molecules [adamantane derivative $(C_{10}H_{12}(CH_3)_4)$ and pyrene$(C_{16}H_{10})$] were calculated by deMon DFT programs[1]. For the geometry of the molecules, we used the optimized cartesian coordinates from the semiempirical AM1 (version 6.0) method[2].

The deMon calculations were performed with the exchange-correlation potential labeled as B88/P86, made from Becke's 1988 exchange functional[3] and Perdew's 1986 correlation functional[4]. In the program, we used a nonrandom grid and a polarized valence double-zeta (DZVP) basis of (621/41/1*) for C, and (41) for H with auxiliary fitting functions labeled (4,4;4,4) for C, and (3,1;3,1) for H.

For ionization of an electron from molecular orbital (MO) ϕ_k, for example, we can apply the Janak theorem[5]. For the VIPs of the valence

regions, we use the so-called restricted diffuse ionization (rDI) model which Asbrink et al.[6] proposed in the HAM/3 method. For the rDI model, we already indicated in our previous works [7-11]. In the rDI model, half of an electron is removed evenly from the valence MOs and the negative of the resulting orbital energies correspond to calculated VIPs. This allows us to obtain all the valence VIPs in a single calculation. The C_2H_2 molecule, with 5 valence MOs and 10 valence electrons, can be used as an example. For the rDI model, each valence MO of C_2H_2 has 0.95α and 0.95β electrons.

For the comparison between calculations for a single molecule of the model and experiments on a solid, we must shift each computed vertical ionization potentials (VIPs), I'_k by a quantity WD as $I_k(EF) = I'_k - WD$, to convert to ionization energy $I_k(EF)$ relative to the Fermi level. This quantity WD denotes the sum of the work function of the sample and other energy effects, such as the polarization energy, the width of the interchain band formation and the peak broadening in the solid state, as stated in our previous studies [7-11].

In order to simulate the valence XPS of carbon allotrope theoretically, we constructed from a superposition of peaks centered on the VIPs, I_k. As was done in previous works [7-11], each peak was represented by a Gaussian curve. The intensity was estimated from the relative photoionization cross section for Al $K\alpha$ radiation using the Gelius intensity model [12]. For the relative atomic photoionization cross section, we used the theoretical values from Yeh [13]. In the case of the linewidth (WH(k)), we used $WH(k)= 0.10\ I_k$ for the models, as adopted in previous works[7-11].

Experimental

We used a commercially available diamond crystal, a diamond film as deposited from gas-phase mixture containing hydrogen, and graphite as produced by pyrolysis, respectively.

The experimental photoelectron spectra of the samples were obtained on a PHI 5400 MC ESCA spectrometer, using monochromatized Al $K\alpha$ radiation. The spectrometer was ope-

rated at an X-ray Al $K\alpha$ source power at 400 W, at a constant voltage of 15 kV, and at a constant current of 40 mA. The photon energy was 1486.6 eV. A pass energy of 35.75 eV was employed for high resolution scans in a valence band analysis (50 eV of range). The angle between the X-ray source and the analyzer was fixed at spot 45°. The size in the measurement was 3 X 1 mm.

The use of dispersion compensation yielded an instrumental resolution of 0.5 eV with the full width at half-maximum on the Ag 3d line of silver. Multiple-scan averaging on a multichannel analyzer was used for the valence band region, although a very low photoelectron emission cross section was observed in this range.

Gold of 20 Å thick was deposited on the film(or disc) of the samples using an ion sputter unit(Hitachi E 1030) for scanning electron microscope.

A low-energy electron flood gun was used in order to avoid any charging effect on the surface of the sample. We used the Au 4f core level of the gold decoration membrane(or disc) as a calibration reference. The C1s line positions of diamond and graphite could be fixed at 285.0 eV, respectively.

Results and Discussion

A new feature of the present study is the use of the rDI model using deMon programs which use idea of Slater's transition-state[14] for the simulation of valence spectra of diamond and graphite.

a) Valence XPS of diamond

Diamond is almost found as a hexagonal form with the cubic structure. The hexagonal form is probably unstable toward the cubic, since unlike the cubic, it contains some eclipsed bonds. The hexagonal form in the unit cell is similar to the carbon frame of the adamantane.

Fig. 1 indicates simulated valence spectrum of diamond-like film using adamantane derivative($C_{10}H_{12}(CH_3)_4$) with the experimental spectra. The observed double peaks are in good agreement with results, as obtained in previous works[15,16]. As mentioned earlier, the simu-

Table 1. Observed peaks, main AO photoionization cross-section(PICS), orbital nature, and functional group for valence X-ray photoelectron spectra of diamond

peaks	VIPs[b]	main AO PICS	orbital nature	functional group
17.5 eV (13.0-20.0eV)[a]	{24.36;24.34; 21.92;21.60eV}	C2s	s σ (C2s-C2s)-B	C-C-C
13.0 eV (11.0-14.0eV)[a]	{18.98; 18.96; 18.75 eV}	C2s C2s	s σ (C2s-C2s)-B s σ (C2s-H1s)-B	-C-C-, -C-CH$_3$ -C-H$_2$
shoulder (0.0-11.0eV)[a]	{16.70-15.05 eV} {13.38-13.06 eV} {12.87- 9.00 eV}	C2s C2s C2p	p σ (C2s-C2p)-B p σ (C2p-H1s)-B p π (C2p-C2p)-B	C-C-C, -C-CH$_3$ CH$_3$, C-H C-C-C

[a]Values in parenthesis show the experimental peak range.
[b]Values of VIPs were obtained by rDI methods using DeMon DFT calculations.
We obtained the *WD* (between calculated VIPs of the model and observed ones) as 5.5 eV.

Fig.1 Valence XPS of diamond-like film with simulated spectra of C$_{10}$H$_{12}$(CH$_3$)$_4$ using deMon DFT program
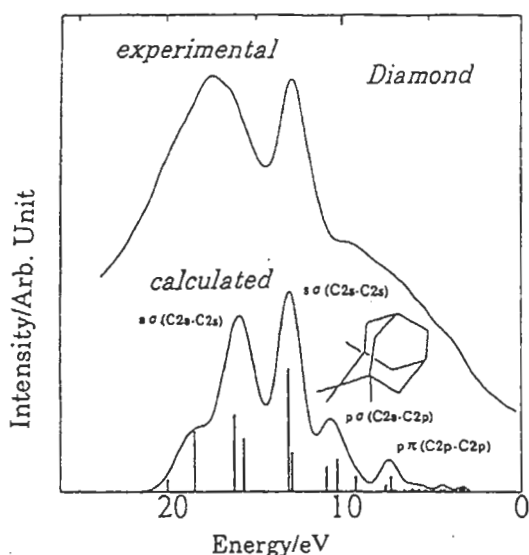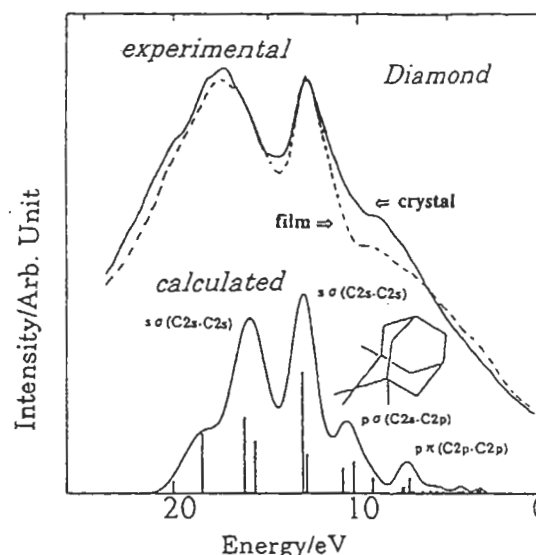
Fig.2 Valence XPS of diamond crystal and diamond-like film with simulated spectra of C$_{10}$H$_{12}$(CH$_3$)$_4$ using deMon DFT program

lation used Gaussian lineshape function for each MO with the linewidth of 0.10 I$_k$ and I$_k$(EF) = I'$_k$ − *WD*. The *WD* was estimated as 5.5 eV. We show the observed peaks, the calculated VIPs, the main atomic orbitals for photoionization cross-section, the orbital characters and the functional group for diamond-like film in Table 1. The outer intense peak at around 13 eV corresponds to the photoionization cross-sections from sσ (C2s-C2s) bonding orbitals which result from C-CH$_3$ and C-C bonds of adamantane frame. In the peak, the contribution of C-CH$_3$ bonds are larger than the C-C ones of the frame. The broader intense peak at around 17.5 eV is due to the sσ (C2s-C2s) bonds of the adamantane frame. These analyses served us the peaks which may result

from methyl groups on the urmost surface of the diamond-like film, as deposited from gas-phase mixtures containing hydrogen.

We are, thus, able to analyze the utmost surface of the diamond(film or crystal) from the ratio of peaks at around 13.0 eV and 17.5 eV, respectively. Fig. 2 shows the difference of the peak ratios between diamond crystal and diamond-like film. The peak ratio for the film approximates as unity, while that of the crystal is less than unity.

(b) Valence X-ray photoelectron spectrum of graphite

The allotrope of carbon, graphite has a layer structure of benzene rings. The separation of the layers is 3.35 A, which is about equal to the sum of van der Waals radii. It is noted that
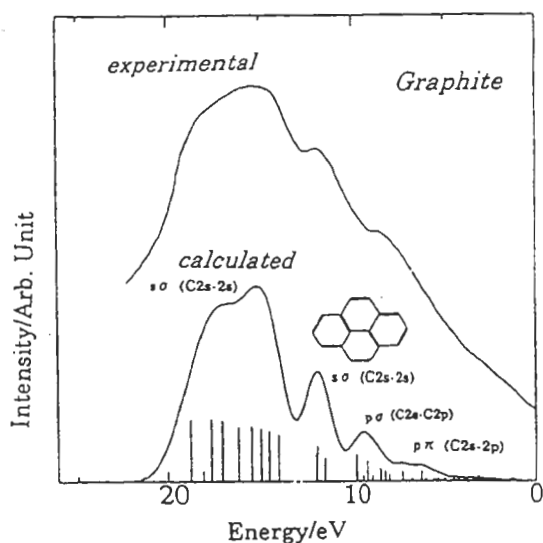
Table 2. Observed peaks, main AO photoionization cross-section(PICS), orbital nature, and functional group for valence X-ray photoelectron spectra of graphite

peaks	VIPs[b]	main AO PICS	orbital nature	functional group
16.0eV (13.0-22.0eV)[a]	{24.67-19.88 eV}	C2s	s σ (C2s-2s)-B	C-C(benzene-ring)
12.0eV (10.0-13.0 eV)[a]	{17.83-17.35 eV}	C2s	s σ (C2s-2s)-B	C-C(benzene-ring)
8.0 eV (3.0-10.0 eV)[a]	{15.64-13.76 eV} many adjacent levels {12.51-7.30 eV}	C2p C2p	p π (C2p-2p)-B p π (C2p-2p)-B	C-C(benzene-ring) C-C(benzene-ring)

[a]Values in parenthesis show the experimental peak range.
[b]Values of VIPs were obtained by rDI methods using DeMon DFT calculations.
We obtained the *WD* (between calculated VIPs of the model and observed ones) as 5.0 eV.

Fig.3 Valence XPS of graphite with simulated spectra of pyrene using deMon DFT program

References

1. St-Amant A., Salahub D. R., Chem. Phys. Lett.(1990) *169*,387; St-Amant A., Ph. D. Thesis, University of Montreal (1991).
2. Dewar M. J. S. and Zoebisch E. G., Theochem.(1988) *180*,1; Dewar M. J. S., Zoebisch E. G., Healy E. F. and Stewart J. J. P., J. Am. Chem.Soc.,(1985) *107*,3902.
3. Becke A. D., Phys. Rev.(1988)*A38*,3098.
4. Perdew J. P., Phys. Rev.(1986)*B33*,8822.
5. Janak J. F., Phys. Rev.,(1978)*A18*,7165.
6. Asbrink L., Fridh C., Lindholm E., Chem. Phys. Lett. (1977) *52*,69.
7. Endo K., Kaneda Y., Aida M., Chong D. P., J. Phys. Chem. Solids,(1995)*56*,1131.
8. Endo K., Inoue C., Kaneda Y., Aida M., Kobayashi N., Chong D. P., Bull. Chem. Soc. Jpn.(1995)*68*,528.
9. Endo K., Kaneda Y., Okada H., Chong D. P., Duffy P., J. Phys. Chem.,(1996) *100*, 19455.
10. Endo K., Chong D. P. , J. Surf. Anal.,(1997)*3*,618; ibid. (1998)*4*,50.
11. Kuroki S., Endo K., Maeda S., Chong D. P., Duffy P., Polym. J.,(1998)*30*,142.
12. Gelius U., Siegbahn K., Faraday Discus. Chem. Soc. (1972)*54*,257: Gelius U., J. Electron. Spectrosc. Relat. Phenom. (1974)*5*,985.
13. Yeh J. -J., "Atomic Calculation of Photoionization Cross Section and Asymmetry Parameters" by Gordon and Breach Science Publishers(1993).
14. Slater J. C., Advan. Quantum Chem.(1972)*6*,1.
15. Cavell R.G., Kowalczyk S.P., Ley L., Pollak R.A., Mills B., Shirley D.A., Perry W., Phys. Rev.,(1973)*B7*,5313.
16. Aleshin V.G., Kucherenko Yu.N., J. Electron Spectrosc. Relat. Phenom.(1976)*8*,411

within each layer each carbon is surrounded by only three others. After forming one σ bond with each neighbor, each carbon would still have one electron and these are paired up into a system of π bonds. We adopted the pyrene as the model molecule of graphite, since it consists of four benzene rings.

In Fig. 3, simulated spectrum using pyrene is in good agreement with observed solid spectrum of graphite. We showed the observed peaks, the calculated VIPs, the main atomic orbitals for photoionization cross-section, the orbital characters and the functional group for graphite in Table 2.

Analysis of C KVV Auger electron spectra for diamond and graphite is now under way.

Referee's comments
:Dr. S. Tanuma (Japan Energy ARC.)

This paper describes the calculations of electronic structures of Diamond and Graphite using deMon DFT program. The result sounds reasonable. However, it is difficult to understand the following points. (I recommend that more explanations should be attached in the section of the discussion with the referee or in Appendix).

1). You calculated valence spectra of diamond and graphite using the models of adamantane derivative and pyrene molecules by deMon program. I would like to know why these models were selected.

2). At first paragraph in page 2, you explains the rDI model. However, we need more information for rDI (and VIP) in order to understand these calculations. I could not understand the meaning of the last sentence " This allows us VIPs in a single calculation". What does " single calculation " mean.

Authors' answers

Thank you very much for referee's comments.

(1) We added 'the reason why these models are used' in the text as follows;
For diamond, "*The hexagonal form in the unit cell is similar to the carbon frame of the adamantane.*"
In the case of graphite, "*We adopted the pyrene as the model molecule of graphite, since it consists of four benzene rings.*"

(2) For the rDI model, we already indicated in our previous papers[7-11] including the papers in JSA.
Please read one of them ; [Endo K., Chong D. P. , J. Surf. Anal.,(1997)3,619-620].
The following sentences were rewritten as;
"*For the rDI model, we already indicated in our previous works [7-11]. In the rDI model, half of an electron is removed evenly from the valence MOs and the negative of the resulting orbital energies correspond to calculated VIPs. This allows us to obtain all the valence VIPs in a single calculation. The C_2H_2 molecule, with 5 valence MOs and 10 valence electrons, can be used as an example. For the rDI model, each*

valence MO of C_2H_2 has 0.95α and 0.95β electrons."