X-Ray Photoelectron Spectral Analysis for Carbon Allotropes,

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We performed DFT calculations using Amsterdam density functional (ADF) program to simulate X-ray photoelectron spectra for carbon allotropes (diamond, graphite, single-wall carbon nanotube (SWCN), and fullerene C_{60}). We firstly described the simulation method for valence electron spectra to distinguish the diamond phase of carbon from the graphite carbon, and secondly evaluated the WD(work function and other energy effects) values from the differences between the calculated core-electron binding energies (CEBE)s of the model molecules (using ΔE_{KS} approach (like ΔSCF method in MO)) and experimental CEBEs of carbon allotropes. The WD values of carbon allotropes correspond to the order of experimental values (CNT < graphite < diamond < C_{60}) for work functions obtained from accurate cylindrical analyzer (CMA) detector by Goto and co-workers.

1. Introduction

Carbon allotropic forms of diamond, (graphite, carbon nanotube) and fullerene differ in their physical and chemical properties because of differences in the arrangement and bonding of tetrahedral sp^3, planer sp^2, and caged sp^2 carbons, respectively.

Diamond films are desired for many applications [1], 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 [2]. For the graphite, it is well-known that the material 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.

Carbon nanotubes [3], which hold a tubular morphology with a tube diameter of several nanometers, have great potential for nano-technological application in various fields such as gas storage [4-6], field emission displays [7], and supercapacitors [8]. In the case of fullerene C_{60}, the material is expected to be applied in lubrication, coating, non-linear optical and electronic device, since the synthesis of the macroscopic quantities [9] and the surface modification have been performed [10].

In the present study, we perform DFT calculations to simulate X-ray photoelectron spectra for carbon allotropes (diamond, graphite, single-wall carbon nanotube (SWCN), and fullerene C_{60}), in order to firstly describe the simulation method for valence X-ray photoelectron spectra to distinguish the diamond phase of carbon from the graphite carbon, and to secondly evaluate the WD values from the differences between the calculated core-electron binding energies (CEBE)s of the model molecules and experimental CEBEs of carbon allotropes.

2. Computational Method

In order to account and somewhat quantify solid-state effects in carbon allotropes under investigations, we defined a quantity WD in our earlier work [11, 12]. The quantity WD denotes the sum of the work function of the sample (W) and other energy effects (D as delta), such as the polarization energy. The WD can be estimated from the difference between experimental or theoretical electron binding energy (I_c, or I_k) of model molecules, and the experimental binding energy of the carbon allotropes. In order to compare the calculated binding energy for the model molecules and the

experimental binding energy of C allotropes, one has to shift each computed value (I_c or I_k) by a quantity WD as $I'_c(= I_c−WD)$ {or $I'_k(= I_k−WD)$}, to convert to I'_c (or I'_k) on a common binding energy axis (relative to the Fermi level).

The MO and DFT calculations of carbon allotropes have been performed within the cluster model approach. The cluster dangling bonds of diamond, graphite, and carbon nanotube except for fullerene have been saturated with H atoms. The model molecules [adamantane derivative ($C_{19}H_{12}(CH_3)_4$), pyrene ($C_{16}H_{10}$), CNT arm-type ($C_{54}H_{12}$), and fullerene C_{60}] in Fig. 1 were calculated by Amsterdam density-functional (ADF) program [13]. For the geometry of the molecules, we used the optimized Cartesian coordinates from the semiempirical AM1 (version 6.0) method [14],

In order to obtain the accurate vertical ionization potentials (VIPs) diamond and graphite in the valence electron region, we used statistical averaging of orbital potentials (SAOP) [15] in ADF program. The SAOP method reproduces a Kohn-Sham exchange-correlation potential which includes the orbital dependent Krieger-Li-Iafrate (KLI) response potential [16] as the orbital relaxation effect. For VIP values, we calculated the ground state of the molecules using the TZP bases [17] for C and H atoms in the SAOP. The intensity of valence XPS was estimated from the relative photoionization cross-section for Mg Kα radiation using the Gelius intensity model [18]. For the relative atomic photoionization cross-section, we used the theoretical values from Yeh [19].

In the CEBE calculation, we employed the ΔE_{KS} method [20] that is based on the total energy difference procedure with the Perdew and Wang exchange [21] and correlation [22] potentials using TZP bases [17].

To simulate the valence XPS, we started with a superposition of peaks centered on each VIP. As described previously, each peak is represented by a Gaussian-shaped curve. In the case of the line width (WH(k)), we used WH(k) = 0.08 I_k (proportional to the ionization energy) for valence XPS.
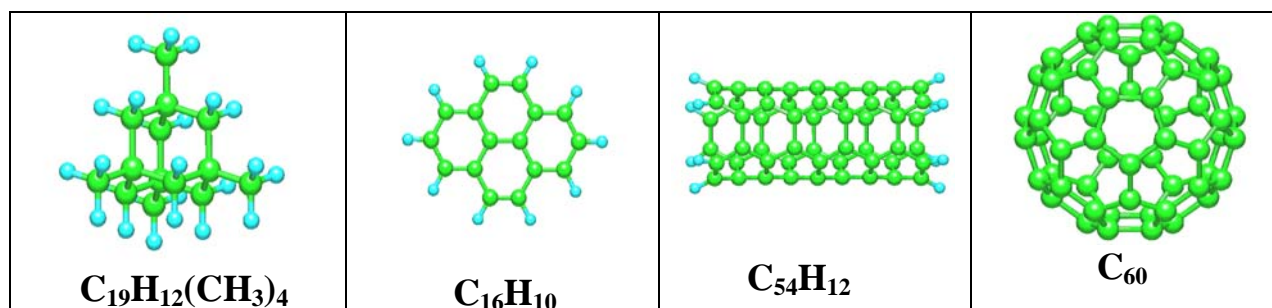

| $C_{19}H_{12}(CH_3)_4$ | $C_{16}H_{10}$ | $C_{54}H_{12}$ | C_{60} |

Fig.1. Carbon allotrope model molecules

3. Results and Discussion

We already performed the detailed analysis for valence XPS, XES, and AES of the diamond, graphite, and fullerene by DFT calculations using similar model molecules [23]. In this section, we aimed to inquire the two following things for carbon allotropes (diamond, graphite, single-wall carbon-nanotube (SWCN), and fullerene C_{60}), to distinguish the diamond phase of carbon from the graphite carbon owing to the simulated valence X-ray electron spectra of the two allotropes, and to secondly evaluate the WD values from the differences between the calculated CEBEs of the model molecules and experimental CEBEs of the carbon allotropes.

(1) Valence XPS to distinguish the diamond phase of carbon from the graphite carbon

In our previous work [24], we indicated that simulated valence spectra of diamond and graphite models are in good accordance with experimental ones in Fig. 2 (A) and (B). On the other hand, we think that some diamond-like films prepared by plasma, or CVD method are not pure diamond films, since the experimental valence spectra of (c) and (d) in Fig. 2(C) [25] are considerably different from our experi-

mental spectrum in Fig. 2 (A). Then, we simulated the valence XPS method to determine the ratio of (diamond/graphite (amorphous carbon)) for such diamond-like films by plasma, or CVD method. Fig. 3 shows simulated valence spectra to determine the ratio

of (diamond/graphite(amorphous carbon)) from each normalization spectrum of diamond or graphite model by ADF calculations. Therefore, the experimental diamond-like films (c) and (d) in Fig. 2 (C) were approximated as 6:4 for the ratio of (diamond/graphite).
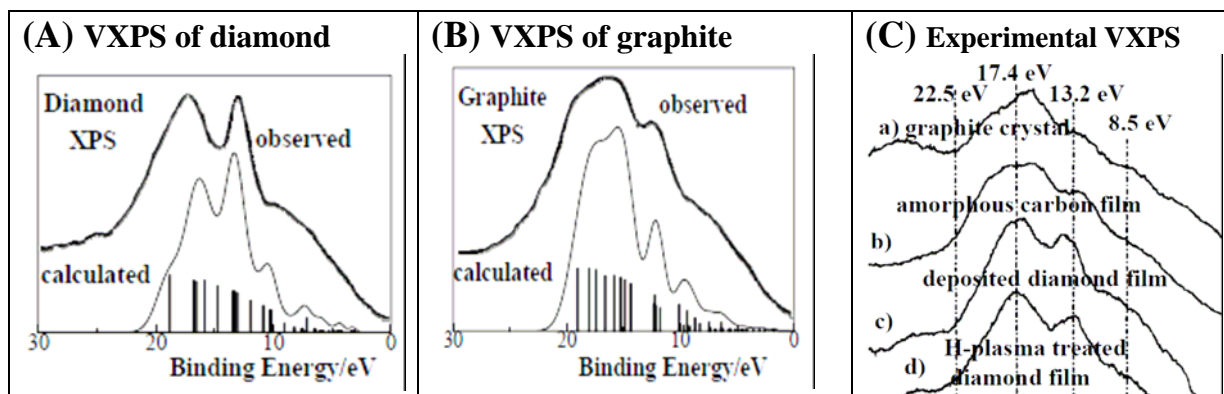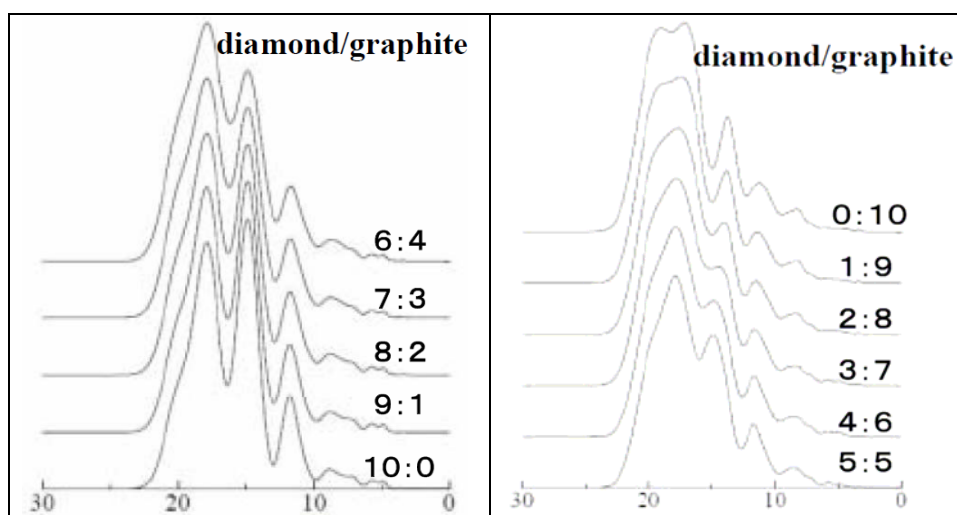

Fig.2. Valence XPS of diamond and graphite

Fig.3. Simulated valence XPS to determine the ratio of (diamond/graphite (amorphous carbon))

Table 1. Calculated core-electron binding energies of carbon allotropes by ADF program using model molecules

Core-electron binding energy (eV) of Carbon Allotropes			
Diamond	**Graphite**	**SWCN**	**C$_{60}$**
C(-C-) 290.014	C1,5,8,14 290.140	C1-C54	C1-C60
C(CH$_2$) 290.137	C2,4,11,13 289.673	289.656-289.854	290.463-290.466
C(CH$_3$) 290.256	C3,12 289.883		
	C6,7 290.091		
	C9,10,15,16 289.916		

Table 2. CEBEs, WD, and work function for carbon allotropes

| Carbon | Core-electron binding energy (eV) | | WD | work function(obsd)* | |
	Calc.(model)	Exp.		as evacuated	after Ar ion sputtering
Diamond	**290.01-290.26**	**284.4**	**5.61-5.86**	**4.83**	**4.38→4.51**
Graphite	**289.67-290.14**	**284.3**	**5.37-5.84**	**4.73**	**4.37→4.63**
CNT	**289.65-289.85**	**284.55**	**5.10-5.30**	**4.35-4.77**	**4.20→4.40**
C_{60}	**290.46**	**284.7**	**5.76**	**6.16**	**5.65→6.12**

(2) WD Values of carbon allotropes

In the CEBE calculation, we used the ΔE_{KS} method obtained ±0.5 eV as the absolute averaged deviation between calculated CEBEs in the model molecules and experimental ones in gas organic molecules [26]. Then, we showed all C1s CEBEs of carbon allotrope model molecules in Table 1. As indicated in previous papers [11, 12], Table 2 showed calculated C1s CEBEs for diamond, graphite, CNT, and C60 model molecules with the experimental C1s CEBEs [25, 27] of the carbon allotropes. In the table, we estimated the *WD* values between 5.10 and 5.86 eV from differences between calculated CEBEs of the carbon allotrope model molecules and the experimental core-electron binding energies. The WD values of carbon allotropes correspond to the tendency of experimental values (CNT < graphite < diamond < C_{60}) for work functions obtained from accurate CMA detector by Goto and co-workers [28].

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