Original Paper

Theoretical analysis of AES of 2nd periodic element containing substances

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We demonstrated to analyze the experimental Auger electron spectra (AES) of 2nd periodic elements and valence X-ray photoelectron spectra (valence XPS) of four solid substances [graphite, GaN, SiO$_2$, LiF] by deMon density functional theory (DFT) calculations using the model molecules. In the deMon program, we will propose a new method to evaluate transition energies of the AES. Simulated AES with the energy calculations of the model molecules by the DFT program are in considerably good accordance with the experimental ones. Experimental AES of the substances can be classified in each range of 1s-2s2s, 1s-2s2p and 1s-2p2p transitions for C, N, O and F *KVV'* spectra, respectively, and seen in individual contributions of the orbitals from the theoretical analysis.

1. Introduction

X-ray photoelectron, and Auger electron spectro- scopies are powerful tools for providing precise information on the electronic states of substances. The experimental electron spectra of solid substances are directly linked to the theoretical results of the electronic states as obtained by density functional theory (DFT) or molecular orbital (MO) calculations using model molecules, because solid substances consist of the repetition units.

A number of studies were already performed on analysis of experimental Auger electron spectra (AES) of many inorganic substances. Since Ramarker and co-workers [1, 2] proposed the one center intensity model for the relative Auger transition intensity, there are almost few studies from the theoretical viewpoints. The reason is due to the difficulty of Auger electron transition energy calculation. Recently, using the deMon DFT program [3], it became possible to calculate accurate core-electron binding energy (CEBE) and vertical ionization potential (VIP). In this study, our aim is to propose a new method to evaluate transition energies of the AES and to demonstrate to simulate the experimental AES of C, N, O and F-containing substances (graphite, GaN, SiO$_2$, LiF) with the method of the energy evaluation by DFT calculations using model molecules.

2. Theoretical Background

(a) Solid-state effect

To explain solid-state effect, we define a quantity *WD* as stated in early works [4-11]. This 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 width of the intermolecular band formation, and the peak broadening in the solid state. The experimental *WD*s can be estimated from differences between theoretical CEBEs of model molecules, and experimental binding energies of the solid substances. Therefore,

for the comparison between the calculated CEBEs for the single molecules of cluster model and experimental CEBEs of the substances, we must shift each computed CEBE (or VIP) I_k' by a quantity *WD* as $I_k (= I_k' - WD)$, to convert to CEBE (or VIP) I_k relative to the Fermi level.

(b) Energy of Auger transition

For the Auger energy, we can express as due to the generalized transition state (GTS) model [12] and ΔE_{KS} - like approach,

$$I_{cjk} \approx I_c - I_j - I_k^* - WD \qquad (1)$$

where, I_c, I_j, I_k^* and *WD* denote the core-electron binding energy, restricted diffusional ionization (rDI, q = +1 (q is charge)), the Auger rDI (A-rDI, q = +2), and solid-state effects, respectively. In the case of I_c calculation, we used the GTS model. For the I_j, and I_k^* calculations of the valence regions, we modified the rDI model which Asbrink et al. [13] proposed in the HAM/3 method. In our rDI model, one, or two of electrons (q = +1 (a hole), or + 2 (two holes)), respectively, are removed evenly from the valence MOs and the negative charge of the resulting orbital energies correspond to calculated VIPs. This allows us to obtain all valence VIPs in a single calculation.

(c) Intensity

The intensity of valence XPS was estimated from the relative photoionization cross-section for Al *K*α radiation using the Gelius intensity model [14]. For the relative atomic photoionization cross-section, we used the theoretical values from Yeh [15].

The Auger transition probability from an initial core hole to the final state with two holes in the valence region and an electron in the continuum was expressed by Wentzel [16] in the following expression involving the two electrons participating in the transition using a single set of orthogonal one-electron orbitals [17],

$$M_{cvv'} = 2\pi \left| \left\langle \Psi(c, \varepsilon) \left| \frac{1}{r_{12}} \right| \Psi(v, v') \right\rangle \right|^2 \quad (2)$$

Here $\Psi(c, \varepsilon)$ is the total wavefunction which denotes the core hole, c, and final-state continuum, ε, orbitals, respectively; the other total wavefunction $\Psi(v, v')$ involves the two final-state hole orbitals in valence levels.

For the relative Auger transition intensity of the simple gas molecules, Siegbahn and co-workers had derived approximate formulae using MO calcula- tions with a liner combination of atomic orbitals [18] under the assumption of intra-atomic transition. On the other hand, Ramarker and coworkers [1, 2] proposed the one-center intensity model for the calculation of Auger electron intensities of solid SiO_2. The relative Auger intensities are given as

$$M_{cjk} = N' \sum_{\mu,v} \left| C_{\mu j} \right|^2 \left| C_{vk} \right|^2 P_{c\mu v} . \quad (3)$$

Here, $|C_{\mu j}|^2$ and $|C_{vk}|^2$ represent the electron density populations of the atomic orbital, Ψ_μ and Ψ_v, respecttively, on the central atom A associated with the MOs, ϕ_j and ϕ_k. N' and $P_{c\mu v}$ denote a statistical factor and the appropriate weighted subshell Auger transition probabilities, we used Eq. (3), and adopted the theoretical values from Chen and co-workers [19].

3. Calculation Details

The geometry optimization of $C_{16}H_{10}$ and $Si_5O_{16}H_{12}$ for graphite and silicon dioxide models were performed by a semiempirical AM1 (version 6.0) method. We considered molecular models from X-ray diffraction data for Ga_6N_6 and Li_4F_4. These model molecules [$C_{16}H_{10}$, Ga_6N_6, $Si_5O_{16}H_{12}$, Li_4F_4] of graphite, gallium nitride(GaN), silicon dioxide(SiO$_2$) and lithium fluoride(LiF), respectively, were calculated by the deMon-KS DFT program [3] to simulate the valence XPS and AES..

The deMon-KS DFT calculations were performed with the exchange-correlation potential labeled B88/P86, made from Becke's 1988 exchange functional [20] and Perdew's 1986 correlation functional [21]. In the deMon-KS DFT program, we used an "fine" and "nonrandom" grid and the correlation-consistent polarized valence triple-ζ (cc-pVTZ) [Li, C, O, F, Si] and polarized valence double-ζ (DZVP) [H, N, Ga] basis set of Dunning and coworkers [22] to calculate CEBEs and VIPs of the model molecules with auxiliary fitting functions labeled (4,4;4,4) for C, N, O and F, (3,1;3,1) for H, (4,3;4,3) for Li, (5,4;5,4) for Si and (5,5;5,5) for Ga.

To simulate the valence XPS and AES of the four substances theoretically, we constructed from a superposition of peaks centered on the VIPs, and on the Auger electron energies, [(CEBE)$_{1s}$ - (VIP) - (VIP')] in the each central atom A on the assumption that Auger process was dominated by Gaussian lineshape functions of an approximate linewidth 0.10 I_k (proportional to the ionization energy) for the valence XPS and a fixed linewidth 3.0 eV for the AES, respectively. The intensity of valence XPS was calculated by the relative photoionization

Table 1. Subshell Auger Transition Proba- bilities of Each Atomic Orbital.

Atom	Subshell Auger Transition Probabilities ($\times 10^{-3}$ a.u.)	
C	P_{1s2s2s}	1.8616
	P_{1s2s2p}	1.8397
	P_{1s2p2p}	2.0030
N	P_{1s2s2s}	1.8001
	P_{1s2s2p}	1.7649
	P_{1s2p2p}	1.9482
O	P_{1s2s2s}	1.7400
	P_{1s2s2p}	1.7000
	P_{1s2p2p}	1.9150
F	P_{1s2s2s}	1.6866
	P_{1s2s2p}	1.6566
	P_{1s2p2p}	1.8831

cross-section for Al $K\alpha$ radiation using the Gelius intensity model [14] combined with the relative atomic photoionization cross-section by Yeh [15]. In the case of AES, we used the theoretical subshell Auger transition values from Chen and co-workers [19] (in Table 1).

4. Experimental

Valence X-ray photoelectron spectra of each pellet sample were obtained on a PHI 5400MC ESCA spectrometer using monochromatized Al $K\alpha$ radiation. The spectrometer was operated at 600W, 15 kV, and 40 mA. Photon energy was 1486.6 eV. A pass energy of 37.75 eV was used for high resolution scans in a valence band analysis (50 eV of range). The angle between the X-ray source and analyzer was fixed at 90°. Spot size was 3×1 mm^2. Dispersion compensation yielded an instrumental resolution of 0.5 eV from full width at half-maximum for the Ag3d line of silver. Multiscan averaging on a multi-channel analyzer was used for the valence band region, although a very low photoelectron emission cross-section was observed in this range. The thickness of the pellet was about 1.0 mm. For the experimental Auger electron spectra of substances (graphite, GaN, SiO$_2$, LiF), we cited the spectra edited by Hedberg [23] .

5. Results and Discussion

Our main purpose in the present work is to clarify the electronic states of Auger electron spectra for four substances by density functional theory (DFT) calculations using the model molecules. In order to simulate the spectra, we proposed a new method to evaluate transition energies of the AES and used deMon-KS DFT calculations for Auger electron energies, and the one-center intensity model by Ramarker and coworkers for Auger electron intensities.

For Auger electron spectra of four substances [graphite, GaN, SiO$_2$, LiF] in Fig. 1a - d, we plotted the intensity versus the energy scale using the Auger electron energies, $[I_c - I_j - I_k - W \mathcal{D}]$ in the each 2nd periodic atom of the
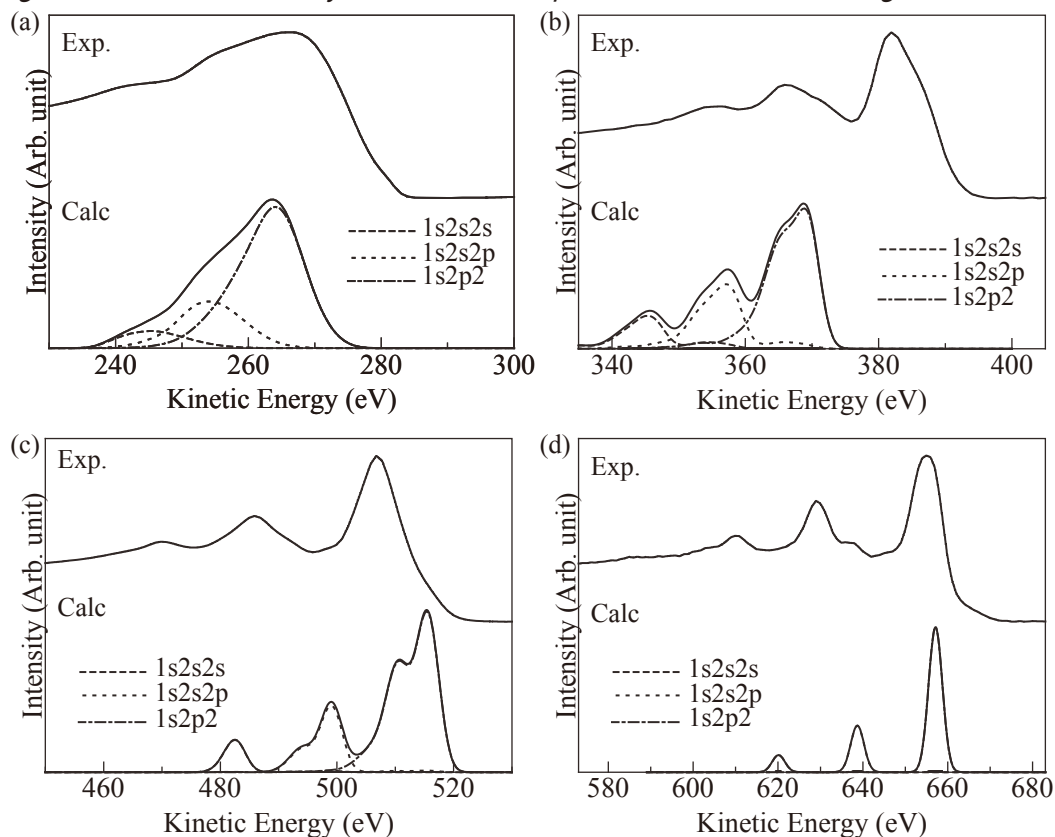
Fig. 1. Simulated KVV' Auger electron spectra of four substances with the experimental ones. (a) graphite (b) GaN (c) SiO_2 (d) LiF
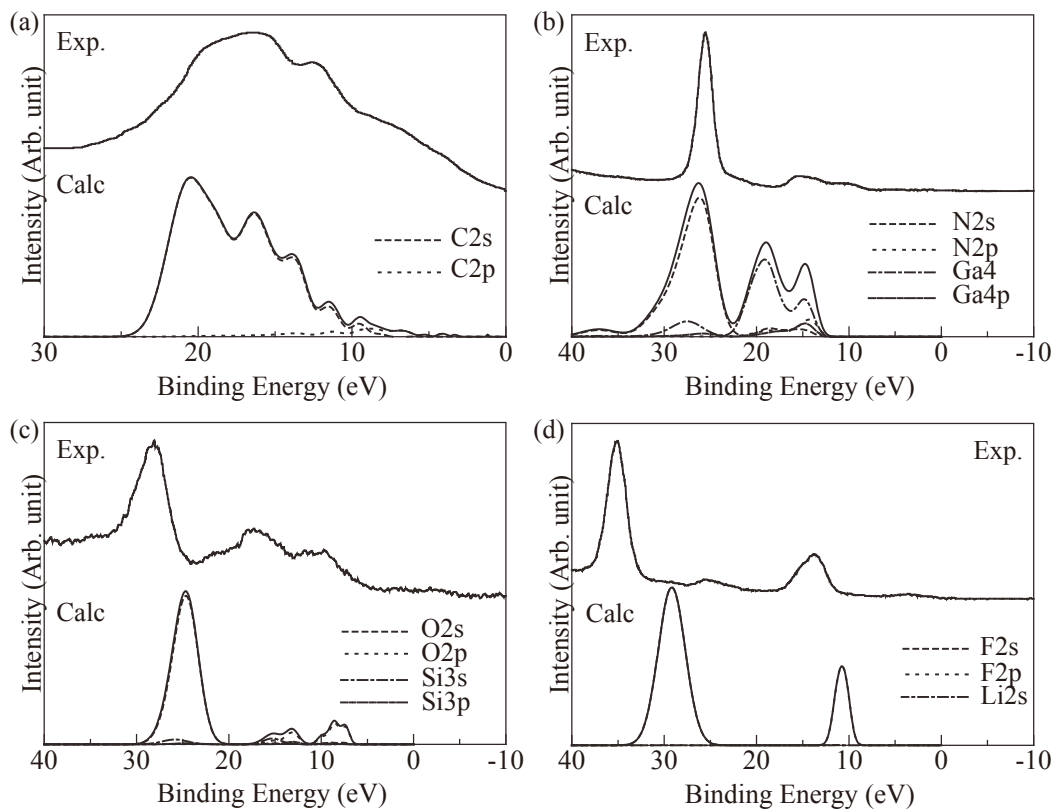

Fig. 2. Simulated Valence X-ray photoelectron spectra of four substances with the experimental ones. (a) graphite (b) GaN (c) SiO_2 (d) LiF

substance.

In the figure, the simulated AES are in considerably good accordance with the experimental spectra except for GaN. In simulated spectra of Fig. 1 a-d, we showed total carbon, nitrogen, oxygen or fluorine *KVV'* AES with solid lines and the individual 1s-2s2s, 1s-2s2p and 1s-2p2p transition spectra with dashed lines, respectively. In the case of graphite, the experimental single peak is seen due to the superposition of the three components that result from the three 1s-2s2s, 1s-2s2p and 1s-2p2p transitions (in Fig. 1(a)). On the other hand, we can see experimental three peaks which can be classified in each range of the three transitions for other substance (in Fig. 1 b-d).

As indicated in the previous work [11], the theoretical error due to the rGDI model is much less than that with the rDI model. Then, we performed the VIP calculations of the model molecules using rGDI method to obtain more accurate theoretical valence XPS. The calcu- lated spectra in Fig. 2 a-d show fairly good accordance with the experimental results.

6. Conclusion

We could analyze the experimental AES of 2ⁿᵈ periodic elements and valence XPS of four solid substances [graphite, GaN, SiO_2, LiF] by deMon DFT calculations using the model molecules. In the deMon program, we proposed a new method to evaluate transition energies of the AES. Thus, simulated AES with the energy calculations of the model molecules by the DFT program are in considerably good accordance with the experimental results.

7. References

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