The Chemical Shift in XPS O_{1s} Spectra of Non-Bridging to Bridging Oxygens in Modified Silicate Glasses

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修飾イオン酸塩ガラス中の非架橋酸素の XPS O_{1s} スペクトルの 架橋酸素に対する化学シフト

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The chemical shift of non-bridging to bridging oxygen in XPS O_{1s} spectra is known to depend on the type of modified cations. Since the chemical shift is closely related to the ionic character of bonds, electronegativity of cations seems to be a useful parameter to interpret this dependence. Our semiquantitative theoretical treatment has confirmed the significant contribution of electronegativity to the chemical shift. The estimated correlation parameter for modified silicate glasses is comparable with that obtained from carbon fluoride polymers.

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Key-words: X-ray photoelectron spectroscopy (XPS), Chemical shift, Electronegativity, Modified silicate glasses, Correlation parameter.

1. Introduction

After the pioneering work carried out by Brückner et al.,¹⁾ X-ray photoelectron spectroscopy (XPS, ESCA) has been extensively applied to oxide glasses, to differentiate non-bridging from bridging oxygens. The powerfulness of XPS to investigate chemical states of non-bridging oxygens has been proved for alkali silicate,^{2),3)} alkali borate,⁴⁾⁻⁶⁾ soda-lime silicate,^{7),8)} soda aluminosilicate,^{7),9)} alkali germanate,²⁾ alkali phosphate,^{8),10)} alkali borosilicate,¹¹⁾ rare earth metal containing silicate¹²⁾ glasses and even for sodium silicate gels.¹³⁾ Further, non-bridging anions in fluorozirconate,^{14),15)} sulfide and selenide glasses¹⁶⁾⁻¹⁸⁾ have been explored.

It is widely accepted that the change in the chemical state of an atom caused by the difference in electron density shifts the photoelectron line, and that is expressed as chemical shift. It has been found that the magnitude of chemical shift is linearly dependent on the convenient parameters such as electronegativity or cationic field strength, although calculation using quantum physics like restricted Hartree-Fock method is necessary to precisely interpret this dependence.¹⁹⁾ Raider et al.²⁰⁾ pointed out the linear dependence of the chemical shift on the summation of electronegativity of bonded species to Si ($\Sigma\chi$). Similar relation has been noted in

XPS B_{1s} spectra for B-doped silicon and related compounds.²⁰⁾⁻²²⁾ On the other hand, Brückner et al.⁸⁾ found the significant influence of cationic field strength for the chemical shift of O_{1s} in alkali silicate glasses. This relationship is proved to be likewise applicable for GeS_2 -based sulfide glasses.¹⁸⁾ In spite of this usefulness of cationic field strength as the parameter, the number of the modified ions next to anions cannot be taken into account. Namely, the chemical shift of $M^+O^{2-}M^+$ (M : cation) and $SiO-M^+$ are not distinguishable, although those have been detected in some alkali silicate glasses.²³⁾ We, therefore, use electronegativity as a parameter to compare the chemical shift of non-bridging oxygens to that of the bridging with the chemical state of oxygens.

2. Theoretical

We will confine ourselves to the discussion on the chemical shift of XPS O_{1s} spectra. For the condition of the constant potential energy of the environment, the change in the potential energy (ΔE) of O_{1s} level resulting from the redistribution of the valence electrons due to the formation of chemical bond can be approximated

$$\Delta E = \Delta q e^2 < \frac{1}{r} > \quad (1)$$

where Δq is the change in charge density of the

nucleus and $\langle \frac{1}{r} \rangle$ is the reciprocal of the mean orbital radius. In the derivation of Eq. (1), we used the approximation that $\langle r \rangle_v \gg \langle r \rangle_{1s}$, where $\langle r \rangle_v$ and $\langle r \rangle_{1s}$ are the mean orbital radius of valence electrons and 1s electron, respectively. The change in the electronic density can be evaluated from the ionic character of bonds and thus from electronegativity,

$$\Delta q = \beta \Delta \chi \quad (2)$$

and

$$\Delta \chi = \chi_A - \chi_B \quad (3)$$

where χ_A and χ_B is the electronegativity of atom A and B, respectively, and β is constant. From Eqs. (1) and (2),

$$\Delta E = K \Delta \chi \quad (4)$$

and

$$K = \beta e^2 \langle \frac{1}{r} \rangle \quad (5)$$

$\langle \frac{1}{r} \rangle$ can be written by using Bohr radius (a_B) as follows,¹⁹⁾

$$\langle \frac{1}{r} \rangle = \frac{z^*}{n^2 a_B} \quad (6)$$

where z^* is the effective electric charge on the nucleus, and n is the principal quantum number. By denoting energy of the electron as ϵ (eV), ϵ relates to n and z^* as

$$\epsilon = \frac{13.6}{n^2} \times z^{*2} \quad (7)$$

thus

$$z^* = n (\epsilon/13.6)^{1/2} \quad (8)$$

and Eq. (6) can be rewritten as

$$\langle \frac{1}{r} \rangle = \frac{(\epsilon/13.6)^{1/2}}{n a_B} \quad (9)$$

Thereby, Eq. (5) comes to

$$K = \frac{\beta e^2}{n a_B} (\epsilon/13.6)^{1/2} \quad (10)$$

and

$$\Delta E = \left\{ \frac{\beta e^2}{n a_B} (\epsilon/13.6)^{1/2} \right\} \times \Delta \chi \quad (11)$$

Consequently, Eq. (11) implies the linear relationship of the chemical shift with $\Delta \chi$ (the difference in the electronegativity of bonded atoms).

3. Discussion

Figure 1 shows the relation between the chemical shift of XPS O_{1s} spectra of non-bridging oxygens to bridging. In this figure, $\Delta \chi$ is estimated from the total difference in electronegativity of modifying cations comparing to Si-O-Si. That is, $\Delta \chi$ for Si-O-Na⁺ is estimated from $\chi(\text{Si}) - \chi(\text{Na})$, and that for Na⁺O²⁻-Na⁺ is from $2[\chi(\text{Si}) - \chi(\text{Na})]$. The electronegativity of each

Fig. 1. Chemical shift of non-bridging oxygens in XPS O_{1s} spectra (ΔE) as a function of the difference in the electronegativity between modified cations and Si ($\Delta \chi$).

Fig. 2. Chemical shift in XPS C_{1s} spectra (ΔE) of fluorocarbon polymers as a function of the difference in the electronegativity between modified species of the carbons in $-(\text{CH}_2-\text{CHF})_n-$ and those of the other carbons or other polymers ($\Delta \chi$).²⁴⁾

atom is based on reference.²⁵⁾ This clear linear dependence of ΔE on $\Delta \chi$ agrees with the theo-

tical approach as Eq. (11). From this figure, K is evaluated as 1.07. According to Harrison,²⁶⁾ ϵ corresponds to 14.13 eV for O_{2p} , and thus β is estimated as 0.077.

On the other hand, the chemical shift of XPS C_{1s} spectra for fluorocarbon polymers is shown in Fig. 2. K in this figure can be estimated as 1.37. ϵ of C_{2c} level is 17.52²⁶⁾ and thus β is 0.089. This similarity of β provides the appropriate region of β in applying this Eq. (11) to other series of modified systems. The small variation of β seems to be caused by the uncertainty of and/or the small change of n for 2p and 2s orbitals.

The advanced theoretical discussion on the dependence of the chemical shift on electronegativity is currently being generalized to other systems and confirmed by the quantitative calculation.

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