A Study of Elastic Scattering Effects on Asymmetrical Distribution of X-ray Photoelectron Emission(II)

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Abstract

Elastic scattering effects give some extent to surface quantification. There are many theoretical discussions based on calculations. However, there are only few experimental discussions reported. This may be caused from the difficulty to perform experiments for wide angles between the directions of X-ray incidence and photoemission detector. Even if the number of angles is not many, experimental results are still very important to check the theoretical calculations for making more accurate quantification.

As some XPS instruments have two aluminum X-ray sources at different polar angles of the sample(one is monochromatized and the other is not), we used such system to compare the intensity ratios of photoelectrons. At present time, we measured 6 elements(V, Mo, Cu, Ag, Au, and poly-Si), and 2 compounds(SiO_2, and V-oxide).

1. Introduction

When the asymmetry parameter β is discussed in studies of angular distribution of X-ray photoelectron emission from the solids, it is common to consider only inelastic scattering. Calculated values of β by Reilman et al. [1], in which elastic scattering was neglected, have been used when spectral data are used for quantification.

Recently, Bashchenko et al. showed that effects of elastic scattering in solids should be taken into account[2]. In the authors' former study, in order to investigate elastic scattering effects on asymmetrical distribution of X-ray photoelectron emission, we measured the ratios of peak area by the s- and p- electrons of six elements, by changing the angle between the incident X-ray and photoemission detection[3]. We compared the intensities calculated from β values by Reilman et al. [1] vs. β^* by Jablonski[4].

In this study for further investigation, the authors also compared the area intensity ratios of photoelectrons from the s-, p-, d- and f- electrons for the six elements described above, and

some other elements and compounds. Intensity ratios are also measured 2s- and 2p- electrons for SiO_2 and poly-Si.

2. The Asymmetry Parameters in XPS Quantification

The XPS spectral peak intensity is given as follows[5];

$$I = I_x \cdot \sigma \cdot y \cdot n \cdot T \cdot A \cdot \Phi \cdot \lambda$$

where I_x is X-ray flux, σ photoelectron cross-section, y the fraction of photoelectrons appeaing in the main peak, T the analyzer transmission and detection efficiency, A the area of the analysis, Φ the angular distribution factor, and λ the photoelectron inelastic mean free path.

The angular distribution factor Φ, is given as

$$\Phi = \frac{1}{4\pi}\left[1 - \frac{\beta}{4}\left(3\cos^2\theta - 1\right)\right]$$

where β is the asymmetry parameter and θ the angle between the directions of X-ray incidence and the detector for emitted photoelectrons.

When the asymmetry parameter β is discussed in studies of quantification, it is still most common to neglect the elastic scattering and to consider inelastic scattering only. Calculated values of β by Reilman et al.[1] have been used for quantification calculation in these situations.

Baschenko et al. [2] demonstrated the effect of elastic scattering by both an experimental and a Monte-Carlo calculation results for Al 2s and 2p photoelectron peaks, which shows that effects of elastic scattering should be taken into account. Jablonski finds that the elastic scattering changes the value β to β^* as follows;

$\beta^*=(0.781-0.00541Z+0.000031Z^2)$

So, we have begun to study the effects of elastic scattering in solids by experiment in order to perform common investigation for a lot of elements and compounds. In this study, we measured the ratios of photoelectron peak areas from the s-, p-, d- and f- orbital electrons for six elements and two compounds(V, Mo, Cu, Ag, Au, poly-Si, SiO_2, and V-oxide), by changing the angle between the directions of X-ray incidence and the photoemission detector. We also compared the obtained data with the calculated values using Reilman's β and Jablonski's β^*.

3. Experiments and Results

The XPS system used was PHI 5600MC, which has 2 aluminum X-ray sources. One is monochromatized source. The sample receives this X-ray from the polar angle of 45 degrees to the sample normal and the azimuth angle of 270 degrees to the tilt axis of the sample which travels the sample at x-direction. The other is a non-monochromatic Al/Mg dual anode source, which is located at 9.7 degrees tilted from the sample normal and 270 degrees azimuth. The analyzer is located at 45 degrees tilt and 90 degrees azimuth.

The measurements were carried out by changing the X-ray sources. The angles of these X-rays were 90deg. and 54.7deg. to the analyzer. These were monochromatic X-ray when the angle was 90 deg., and non-monochromatic X-ray when 54.7 deg.

The peak area ratio of V, Mo, Cu, Ag, Au, poly-Si, SiO_2, and V-oxide were measured.

Table 1. Obtained values for Pure materials

	Raw Data(cps·eV) 90deg	54.7deg	r.90°	r.54.7°	r.90° / r.54.7°	Calc. Value1)	Calc. Value2)
Mo 3p	330,579	356,404					
Mo 3d	406,514	392,974	0.813	0.907	0.896	1.078	1.053
Cu 2p3/2	683,093	650,224					
Cu 3d	97,875	74,830	6.979	8.689	0.803	1.092	1.065
Ag 3p3/2	381,351	289,841					
Ag 3d	1,108,300	767,966	0.344	0.377	0.912	1.078	1.053
Ag 3p3/2	381,351	289,841					
Ag 4d	121,717	98,563	3.133	2.941	1.065	1.067	1.042
Au 4p3/2	199,946	125,958					
Au 4d	987,753	658,092	0.202	0.191	1.058	1.067	1.043
Cu 2p3/2	683,093	650,224					
Cu 3s	199,912	157,788	3.417	4.121	0.829	0.899	0.925
V 2p	242,840	892,576					
V 3s	35,784	114,016	6.786	7.829	0.867	0.908	0.925
Cu 2p3/2	683,093	650,224					
Cu 3p	204,410	147,032	3.342	4.422	0.756	0.982	0.990
Cu 3s	199,912	157,788					
Cu 3d	97,875	74,830	2.043	2.109	0.969	1.214	1.152
Ag 3d	1,108,300	767,966					
Ag 4d	121,717	98,563	9.106	7.791	1.169	0.990	0.990
Au 4p3/2	199,946	125,958					
Au 4f	939,225	587,790	0.213	0.214	0.995	1.121	1.076
Au 4d	987,753	658,092					
Au 4f	939,225	587,790	1.052	1.120	0.939	1.051	1.032

Table 2. Comparison between pure materials and compounds

	Raw Data(cps·eV) 90deg	54.7deg	r.90°	r.54.7°	r.90° / r.54.7°	Calc. Value1)	Calc. Value2)
poly-Si							
Si 2s	42,550	92,988					
Si 2p	36,982	79,062	1.151	1.176	0.979	1.190	1.149
SiO2							
Si 2s	159,239	109,608					
Si 2p	147,392	130,564	1.080	0.839	1.287	1.190	1.149
V							
V 2p	242,840	892,576					
V 3s	35,784	114,016	6.786	7.829	0.867	0.908	0.925
V-Oxide							
V 2p	140,508	456,335					
V 3p	21,138	58,294	6.647	7.828	0.849	0.973	0.980

Tables 1 and 2 are the results of the experiments. Table 1 shows the values for pure elements. Table 2 shows those for comparing pure elements and compounds. In both tables, the first column shows the elements and peaks, and the second column shows the raw data of peak areas for 2 angles (90deg. and 54.7deg.). The third column shows the ratios of peak areas at each angle. The fourth column is the ratio of the two ratios at 54.7deg. and 90deg.. If the elastic scattering gives some effects on photoelectron angle

distribution, these ratios will be closer to 1 than just after generated in the solids. The calculated values 1) are those of the ratios using Reilman's β values. The calculated values 2) are those of the ratios using Jablonski's β* values.

4. Discussion

Calculated ratios of the two ratios on two tables were between 0.89 and 1.21. This fact requires us that the error of the data should be less than 5% or less. This specification is not difficult for sharp peaks but we have to consider much for small and dull peaks. When we perform curve fittings for such small and dull peaks, we often find that the Lorentzian component of the peak is relatively high. This means the tail of the peak tends to overlap with X-ray satellite peaks for non-monochromatic sources. When a X-ray satellite peak is overlapped at a tail part of the major peak, the major peak area may vary more than the intensity ratio of main X-ray and satellite X-ray. In this meaning, we have to take care at s-orbital peaks like Au 4s. We do not show any ratio including Au 4s, Ag 3s and Ag 3p at this reason.

If the elastic scattering simply effects to generated electrons in the solid exactly proportional to the asymmetry equation, experimental ratios can be expected between value 1) and value 2). However, only a few combinations are matched to this expectation. We do not have good explanation of this discrepancy yet.

When we guess the possibility of these discrepancies, several reasons can be considered.

(1) Elastic scattering behavior may be something different from assumptions for calculation. This means that modeling is not suitable enough.

(2) Some other effects may take more important role in peak intensities. Electron diffraction are usually neglected for scattering calculations. In case of poly-Si, two calculated ratios were more than 1, but experimental result was less than 1. Difference was approximately 15 to 18 percents.

However, when looking at the case of SiO_2, which we can expect almost amorphous, the value from experimental results was larger than those of calculated results.

These two data show us that the effects coming from the ample crystalinity is not so small.

5. Conclusion

Simple assumption that experimental values will be an intermediate value between two calculation ratios is not matched to most of the experimental results. We could not obtain good reason of this discrepancy yet.

This discrepancy may not come only from elastic scattering theory, but also from other effects like diffraction. In order to confirm these possibilities, more quantitative discussion will be needed.

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