Journal of Surface Analysis Vol.16, No. 1 (2009) pp. 2−11

Paper

Round Robin Test for the Quantification and Standardization of Sample Damage during XPS Measurements

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(Received: July 13, 2008; Accepted: November 6, 2008)

To evaluate sample degradation during XPS measurement, a round-robin test involving five laboratories was carried out with four kinds of samples such as cellulose nitrate (NC), polyvinyl chloride (PVC), silicon wafer modified with chloropropyltriethoxysilane (CPTES-Si) and gold substrate modified with 1H, 1H, 2H, 2H-perfluorodecanethiol (PFDT-Au) as model samples. In each sample, the degradation behavior followed first-order kinetics with respect to the relative dose provided by the peak intensity of either Ag 3d5/2 or Au 4f derived from Ag or Au substrates, respectively, as an index of X-ray dose. The result shows that the rank order of the damaging factors of samples was almost the same in each apparatus, but the obtained values were different among the apparatuses. On the other hand, from comparison of Au and Ag substrates for calculating relative X-ray dose, it can be seen that the damaging factors using those two metal substrates are almost equivalent. Considering the convenience in handling and the sputtering process, we concluded that Au substrate is more suitable for an index material to estimate relative X-ray dose. Furthermore, the relative damaging factor RDF, i.e. the damaging factor of each material divided by that of PFDT-Au as a reference material, did not depend on the difference of the apparatuses, and indicated close value for each sample, suggesting that the RDF should have universality and provide an useful information for evaluating sample degradation. Thus, the construction of that database would allow the prediction of the sample degradation by measuring degradation behavior of PFDT-Au as a reference material.

1. Introduction

In the field of surface analysis, X-ray photoelectron spectroscopy (XPS) has been recognized as a powerful technique for the determination of both surface chemical composition and depth profile of elements in samples including nanoparticles [1-3], organic / inoragnic hybrid materials [4-6], self-assembled organic monolayers [7-9] and biomolecules [10-14].

On the other hand, the degradation of organic samples during XPS measurements has always been considered as an important issue because the surfaces of many organics are influenced by measurement environments such as X-ray irradiation, heat radiation from filament, photoelectrons generated from the sample itself, bremsstrahlung radiation of the nonmonochromated X-ray, and so on. In addition, the sample degradation also depends on instrument settings such as the X-ray source and its energy, the angle between the X-ray source and the sample surface, and the measuring point viewed by the analyzer and the acceptance solid angle of the analyzer if the degree of sample degradation changes two-dimensionally. Therefore, it is difficult to obtain and compare the information on the quantities of elements derived from the measured photoelectron intensities among different instruments. In order to obtain reliable and quantitative results, it is essential to confirm the

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surface damage behavior for each sample and setting and to measure within a limited time during which the surface damage is negligible. Also, the criterion as a guide for evaluation of sample degradations under various conditions and instruments is desired.

In recent years, we have investigated damages of organic materials in XPS using several kinds of materials such as organic polymers and self-assembled monolayers (SAMs) as an activity of an Organic Materials Group in Surface Analysis Society of JAPAN (SASJ) [15-22]. The previous studies have provided some useful information for our round-robin test in this study as follows:

1) The relation between degradation rate and X-ray source flux suggests that X-ray induced degradation process of a sample can be treated as a first-order kinetics [15-21].
2) Use of relative X-ray dose *D*, which is Ag 3d5/2 area intensity of Ag substrate multiplied by X-ray irradiation time of sample measurement, has been proposed and its availability is confirmed as an index of X-ray dose, because it is difficult to measure absolute X-ray dose actually [15-20].
3) The degradation of SAMs exhibits first-order kinetics and the degradation products from SAMs do not contaminate the vacuum chamber [18-20].
4) Thickness of oxide layer on a silicon wafer affected the degradation rate of SAMs [18].

Based on these results, a round-robin test involving five laboratories was carried out to evaluate the sample degradation by comparing four kinds of samples such as cellulose nitrate (NC), polyvinyl chloride (PVC), silicon wafer modified with chloropropyltriethoxysilane (CPTES-Si) and Au substrate modified with 1H,1H,2H,2H-perfluorodecanethiol (PFDT-Au).

In this round-robin project, we assessed the evaluation method of peak intensity reduction with and without relative X-ray dose calculated from Ag 3d5/2 or Au 4f peak intensity and X-ray irradiation time, and the usefulness of relative damaging factor RDF, i.e. the damaging factor of each material divided by that of reference material.

2. Experimental

2.1 Sample preparation

Cellulose nitrate (NC) was purchased from Advantec. Co., Ltd. and polyvinyl chloride (PVC) was purchased from Morino Chemical Engineering Co., Ltd. NC and PVC were cut into small pieces and cleaned by using compressed air to remove any dust before XPS measurement. 1H,1H,2H,2H-perfluorodecanethiol (PFDT) and chloropropyltriethoxysilane (CPTES) were purchased from Wako Chemicals, and used as surface modification reagents for Au substrate and silicon wafer, respectively.

PFDT on Au substrate (PFDT-Au) was prepared as follows: Au substrates (higher than 99.95%, 0.5 x 10 x 10 mm, some pieces were kindly supplied from Mitsubishi Materials Co. and others were purchased from Nilaco Corp.) were highly polished with alumina sandpaper and cleaned by using an ultrasonic cleaner with isopropyl alcohol. And then PFDT-Au was prepared by immersing the clean substrate into 1mM PFDT in ethanol solution for over a day under nitrogen atmosphere. The substrate was rinsed with excess amounts of ethanol, hexane and acetone. The PFDT-Au was stored in a desiccator until used.

The CPTES-treated silicon wafer (CPTES-Si) was prepared as reported by M. Sato et al. [18, 20]. Before the silane treatment, the silicon wafer substrates were cleaned in detergent and thoroughly rinsed with water several times, then cleaned ultrasonically in water and dried in vacuum. Thereafter the substrates were placed into the mixture (H_2O_2 : NH_4OH : H_2O = 1 : 1: 6) and kept at 80 ºC for 30 minutes to eliminate any organic contaminants on its surface. The clean substrates were again rinsed with water and then dried in vacuum. CPTES-Si was prepared by immersing the clean substrate into 2 %(v/v) CPTES in hexane solution for 6 h, followed by washing with ethanol, hexane and acetone. After drying in a vacuum, the monolayer samples were used for XPS measurements as soon as possible.

For the estimation of relative X-ray dose, Au substrates were the same as those used for the PFDT-Au and Ag substrate was that each laboratory had. These substrates were polished, washed and Ar-ion etched in the XPS chamber as indicated in the recipe.

2.2 XPS measurement

This round-robin test was carried out in five laboratories, and the conditions of each instrument for XPS measurements are summarized in Table 1.

XPS measurements were carried out using a depth

profile mode or other similar acquisition modes without sputtering to obtain the change of peak intensity in each sample. To evaluate the effect of the integrated X-ray flux to the sample surface, i.e. the X-ray dose, the Ag 3d5/2 and/or Au 4f peak intensities were measured using Ag and Au substrates, respectively, just after Ar ion sputtering. The analysis conditions for the sample damaging and X-ray dose measurements were exactly the same.

3. Results and Discussions

Figure 1 shows the profile montage of F 1s, C 1s, and Au 4f of the PFDT-Au. It was found that the F 1s peak intensity originated in PFDT monolayer on the surface of Au substrate decreased with increasing measurement cycle (measurement time). In the C 1s spectra, area intensity corresponding to CH_2 did not decrease, whereas area intensities of the peaks corresponding to CF_3 group (293 eV) and CF_2 group (291 eV) decreased. On the other hand, Au 4f peak intensity, which corresponds to the photoelectrons emitted from the Au substrate, increased with increasing measurement cycle. This increase in photoelectrons leaving the Au substrate is due to the fact that the monolayer, which suppresses the photoelectron generated from Au surface, degraded during XPS measurement.

Figure 2 shows typical results for the change in the particular peaks of CPTES-Si, NC and PVC with time. Upon exposure to X-ray irradiation, a monotonic loss in intensity associated with the Cl 2p of the CPTES-Si and PVC was observed. In a NC sample, N 1s peak corresponding to nitro group also decreased with measurement cycle. In each case, the sample degradation occurred during XPS measurements. Although these degradation behaviors may be affected by the low energy electrons for neutralization and by the evaporation of volatile materials like the stabilizer in polymer materials at high vacuum environment, one of objectives in this work is to evaluate the peak intensity change by the degradation including chemical bond dissociation, evaporation of volatile materials and so on.

To estimate the damage quantitatively, first order reaction kinetics was applied by assuming that the degradation rate of a sample is proportional to both the amount of X-ray dose and the density of an element in a sample. The natural logarithm of the peak area intensity, which was normalized against the initial value of the peak intensity calculated by extrapolation, were plotted as a function of the relative X-ray dose, provided by the peak intensity of either Ag 3d5/2 or Au 4f derived from Ag or Au substrate, respectively, as an index of X-ray dose. Figure 3 shows an example of the semi logarithm plots obtained from Fig. 1 according to the following equation [16, 17, 19, 20]:

$$\ln\left(I_{\mathrm{F1s}}/I^0_{\mathrm{F1s}}\right) = -\beta D_{\mathrm{Au}} = -\beta I_{\mathrm{Au}} t = -kt \qquad (1)$$

where β is the ‘damaging factor’, D_{Au} is relative X-ray dose, I_{Au} is peak intensity of Au 4f, k is the degradation rate constant, and t is the X-ray irradiation time. The relation between $\ln(I_{\mathrm{F1s}}/I^0_{\mathrm{F1s}})$ and D_{Au} is nearly straight up to -0.5 of the former which corresponds to 60 % of the initial peak intensity. The value of damaging factor calculated from the slope was 3.86×10^{-10} $\mathrm{cps^{-1}\cdot eV^{-1}\cdot s^{-1}}$.

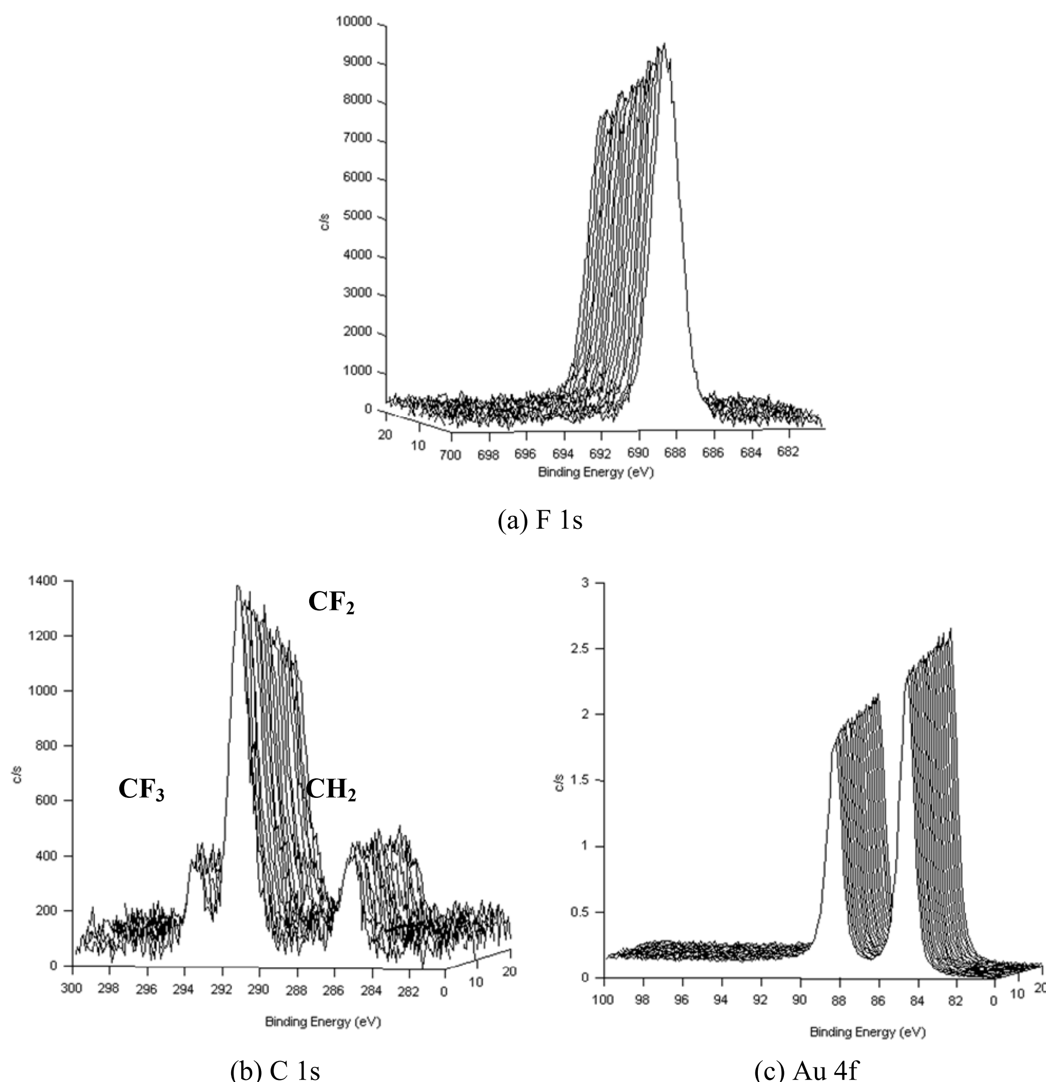
Table 1 Analysis conditions of the participating laboratories and instruments.

	Lab. A	Lab. B	Lab. C	Lab. D1	Lab. D2	Lab. E
Instrument name	PHI Quantera SXM		Thermo Fisher ESCA LAB 250	PHI-5600		
X-ray sourse	mono Al	mono Al	mono Al	mono Al	Mg	Mg
Power of X-ray sourse	25W	25W	150W	300W	200W	350W
Acceleration voltage	15kV	15kV	15kV	14kV	15kV	14kV
X-ray beam diameter	ϕ 0.1mm	ϕ 0.1mm	—	—	—	—
Mode	Spot mode	Raster mode	—	—	—	—
Take-off angle	45°	45°	90°	45°		45°
Aperture size	ϕ 0.1mm	0.4 × 0.2mm	ϕ 1mm	ϕ 0.8mm		ϕ 0.8mm
Pass energy	55eV	55eV	20eV	23.5eV		23.5eV
Step size	0.1eV	0.1eV	0.1eV	0.1eV		0.1eV
Scan range	20eV	20eV	20eV	20eV		20eV

In the same way, the damaging factors of other samples were also estimated by the straight-line portion of the relation between $\ln(I/I^0)$ and D_{Au}.

The damaging factors β obtained by using relative X-ray dose calculated from Ag 3d5/2 of Ag substrate and Au 4f of Au substrate are listed in Tables 2 and 3, respectively. It can be seen that the estimated β factors are different among 5 laboratories because the values of the damaging factor were obtained by using different apparatuses with different analytical conditions. Therefore, the damaging factors obtained by different apparatuses cannot be directly compared. Also, the damaging factors change by selecting substrates to calculate relative X-ray because the peak intensities, i.e. photoionization cross sections, of Ag 3d5/2 and Au 4f are different with each other.

Next, PFDT-Au is regarded as a reference material for damage evaluation, and relative damaging factor RDF, which is defined as the damaging factor of a sample divided by that of PFDT-Au, was calculated for each sample and listed in Tables 4 and 5. The RDF does not depend on the difference of the apparatuses and indicates a close value with each sample. From these results, it was confirmed that the RDF takes a specific value to the material without depending on XPS apparatus. Moreover, from comparisons between Au and Ag substrates for calculating relative X-ray dose, it can be seen as shown in Tables 4 and 5 that the values of each sample obtained by using two kinds of the substrates are almost equivalent. In the use of Ag substrate, a sputtering process is recommended as a pretreatment to eliminate the naturally formed oxide layer and contaminants on the surface. On



(a) F 1s

(b) C 1s

(c) Au 4f

Fig. 1. Profile montage of F 1s, C 1s, and Au 4f spectra of PFDT-Au.

(a) Cl 2p of CPTES-Si

(b) N 1s of NC

(c) Cl 2p of PVC

Fig. 2. Profile montage of (a) Cl 2p of CPTES-Si, (b) N 1s of NC and (c) Cl 2p of PVC.

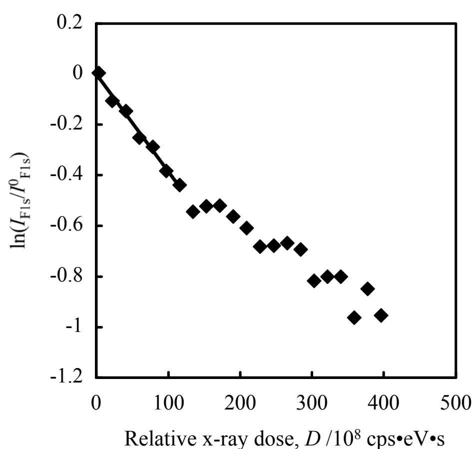


Fig. 3. Plots of $\ln(I_{F1s}/I^0_{F1s})$ versus relative X-ray dose D derived from the Au 4f peak intensity of Au substrate.

Table 2 Comparison of the damaging factors β using the relative X-ray dose value derived from Ag 3d5/2 peak intensity.

	X-ray source	Damaging factor, β x 10^{-10}			
		PFDT-Au (F1s)	CPTES-Si (Cl2p)	PV (Cl2p)	NC (N1s)
Lab. A	mono Al	6.61	13.9	3.43	32.3
Lab. B	mono Al	0.876	1.80	0.433	2.62
Lab. C	mono Al	0.752	2.27	-	2.49
Lab. D1	mono Al	4.06	8.45	3.1	11.7
Lab. D2	Mg	4.41	8.78	3.13	20.9
Lab. E	Mg	2.33	4.87	2.30	8.87

Table 3 Comparison of the damaging factors β using the relative X-ray dose value derived from Au 4f peak intensity.

	X-ray source	Damaging factor, β x 10^{-10}			
		PFDT-Au (F 1s)	CPTES-Si (Cl 2p)	PV (Cl 2p)	NC (N 1s)
Lab. A	mono Al	3.86	8.19	2.03	19.0
Lab. B	mono Al	0.536	1.10	0.263	1.60
Lab. C	mono Al	0.595	1.82	-	2.00
Lab. D1	mono Al	-	-	-	-
Lab. D2	Mg	-	-	-	-
Lab. E	Mg	1.44	2.98	1.38	5.21

Table 4 Comparison of the relative damaging factors R_β normalized by PFDT-Au using the relative X-ray dose value derived from Ag 3d5/2 peak intensity.

	X-ray source	Relative damaging factor, R_β			
		PFDT-Au (F 1s)	CPTES-Si (Cl 2p)	PV (Cl 2p)	NC (N 1s)
Lab. A	mono Al	1 (837)*	2.1	0.519	4.89
Lab. B	mono Al	1 (4490)*	2.05	0.494	2.99
Lab. C	mono Al	1 (2260)*	3.02	-	3.31
Lab. D1	mono Al	1 (6680)*	2.08	0.764	2.88
Lab. D2	Mg	1 (2190)*	1.99	0.71	4.74
Lab. E	Mg	1 (2080)*	2.09	0.987	3.81

*: 10% degradation time(s) of PFDT-Au, $t^{0.1}_{Ref}$, in seconds.

Table 5 Comparison of the relative damaging factors R_β normalized by PFDT-Au using the relative X-ray dose value derived from Au 4f peak intensity.

	X-ray source	Relative damaging factor, R_β			
		PFDT-Au (F 1s)	CPTES-Si (Cl 2p)	PV (Cl 2p)	NC (N 1s)
Lab. A	mono Al	1 (837)*	2.12	0.526	4.92
Lab. B	mono Al	1 (4490)*	2.05	0.491	2.99
Lab. C	mono Al	1 (2260)*	3.06	-	3.36
Lab. D1	mono Al				
Lab. D2	Mg				
Lab. E	Mg	1 (2080)*	2.07	0.958	3.62

*: 10% degradation time of PFDT-Au, $t^{0.1}_{Ref}$, in seconds.

the other hand, because no oxide layer was formed on the surface of Au substrate, the Au surface can be easily cleaned by etching to remove contaminants on the surface. Considering the convenience in handling and the sputtering process, we concluded that Au substrate is more suitable for obtaining the relative X-ray dose. Incidentally, one should note that we could also obtain RDF using degradation rate constants, k, as follows.

$$R_\beta = \beta_{\mathrm{Sample}} / \beta_{\mathrm{Ref}} = k_{\mathrm{Sample}} / k_{\mathrm{Ref}} \tag{2}$$

where the subscript 'Ref' in Eq. (2) means the values for reference material.

The RDF calculated with damaging factors will be more useful than that calculated with degradation rate constants because the process to measure the RDFs gives important information about the differences among each XPS apparatus. The average values and standard deviations of the RDF for each sample shown in Tables 4 and 5 are summarized in Table 6. These results suggest that RDFs are practically useful to predict the characteristics of sample damage in XPS measurement as described below.

As a guide to optimize acquisition time by using RDF, R_β, X-ray irradiation time that gives 10% degradation of a sample, $t^{0.1}$, can be derived as the following procedure.

As 10% degradation means 90% peak intensity of that of initial value, following equations are derived from Eq.(1):

$$\ln\left(\frac{0.9 I^0_{\mathrm{Sample}}}{I^0_{\mathrm{Sample}}}\right) = \ln(0.9) = -\beta_{\mathrm{Sample}} D^{0.1}_{\mathrm{Sample}} = -\beta_{\mathrm{Sample}} I_{\mathrm{Au}} t^{0.1}_{\mathrm{Sample}} \tag{3}$$

$$\ln\left(\frac{0.9 I^0_{\mathrm{Ref}}}{I^0_{\mathrm{Ref}}}\right) = \ln(0.9) = -\beta_{\mathrm{Ref}} D^{0.1}_{\mathrm{Ref}} = -\beta_{\mathrm{Ref}} I_{\mathrm{Au}} t^{0.1}_{\mathrm{Ref}}$$

where I_{Au} is the Au 4f peak intensity of Au substrate for calculating relative X-ray dose. From Eqs. (2) and (3), we can derive

$$t^{0.1}_{\mathrm{Sample}} = \frac{D^{0.1}_{\mathrm{Sample}}}{I_{Au}} = \frac{t^{0.1}_{\mathrm{Ref}}}{R_\beta} = \frac{D^{0.1}_{\mathrm{Ref}}}{I_{Au} \cdot R_\beta} \tag{4}$$

where $D^{0.1}$ is the relative X-ray dose at 10% degradation. From this equation, 10% degradation time, $t^{0.1}_{\mathrm{Sample}}$, is directly determined by that of reference material, $t^{0.1}_{\mathrm{Ref}}$, if R_β is known. Also, the time of other degradation degree can be easily determined in the same way.

Moreover, if $D^{0.1}_{\mathrm{Ref}}$ has been already determined for one condition of X-ray source power, $t^{0.1}_{\mathrm{Sample}}$ is determined from Eq. (4) even if there is a small change in the X-ray power, because $D^{0.1}_{\mathrm{Ref}}$, i.e. β_{Ref}, is almost constant against a small change of X-ray power [16].

In this way, RDF, i.e. R_β, provides a useful information for evaluating sample degradation, and construction of the database of RDFs would allow the prediction of the sample degradation by measuring degradation behavior of a reference material (PFDT-Au).

As a reference material, it is important to verify the reproducibility and the durability. Then the samples after 1, 2 and 3 months preservation were measured with the same conditions. The resulted β values are almost same as that of the sample just after preparation with the mean and standard deviation of $(4.05 \pm 0.03)\times10^{-10}$ $\mathrm{cps^{-1}\cdot eV^{-1}\cdot s^{-1}}$ including the data of sample as prepared with the condition of monochromated Al Kα X-ray source and using Ag substrate for the relative X-ray dose (Lab. D1).

4. Conclusion

We propose a new guide using relative damaging factor and PFDT-Au as a reference material to estimate sample degradation during XPS measurements in round robin investigation. The following conclusions can be drawn:

Table 6 The average value and standard deviation of the relative damaging factor for each sample using Ag 3d5/2 and Au 4f peak intensities to calculate the relative X-ray dose.

Sample	Ag 3d5/2		Au 4f	
	Average value	Standard deviation	Average value	Standard deviation
PFDT-Au	1		1	
CPTES-Si	2.22	0.39	2.33	0.42
PV	0.69	0.20	0.66	0.21
NC	3.77	0.87	3.72	0.73

1) The same rank order of the damaging factors obtained from four kinds of samples in each apparatus was observed.
2) The relative damaging factor, RDF, which is the damaging factor standardized by that of PFDT-Au takes a specific value to the material without depending on XPS apparatus.
3) Au 4f peak of Au substrate is also suitable for obtaining relative X-ray dose as well as Ag 3d5/2 of Ag substrate, because the RDF of each sample was almost same for both substrates.

In conclusion, RDFs using PFDT-Au as a reference material provide useful information for evaluating sample degradation, and construction of the database would allow the prediction of the sample degradation by measuring degradation behavior of PFDT-Au.

5. Acknowledgement

Authors would like to show their sincere thanks to many members of Surface Analysis Society of Japan for their supports and fruitful comments.

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査読コメント

査読者 **1**．阿部芳巳（三菱化学科学技術研究センター）

This paper reporting the quantification and standardization of sample damage caused by X-ray radiation is worth publishing. However, before being recommended for publication some modifications are requested.

［査読者 **1-1**］

Are the other experimental conditions affecting the decrease in peak intensity, such as low energy electrons for neutralization and vacuum environment, taken into consideration? In the case of insulated samples, the flood gun is needed to neutralize. Electron irradiation may cause the sample degradation. In the case of volatile samples, keeping in the UHV chamber will lead to decrease in intensity without any radiations.

［著者］

One of the objectives in this work is to evaluate the

peak intensity change by the degradation including chemical bond dissociation, evaporation of volatile materials and so on. Furthermore, the volatile materials will contain no nitrogen and chlorine atoms. In the document, the following sentences are inserted in the second paragraph in "Results and Discussions".

"Although these degradation behaviors may be affected by the low energy electrons for neutralization and by the evaporation of volatile materials like the stabilizer in polymer materials at high vacuum environment, one of objectives in this work is to evaluate the peak intensity change by the degradation including chemical bond dissociation, evaporation of volatile materials and so on."

［査読者 **1-2**］

In the 4th paragraph of Introduction, useful information 1)-4) provided by the previous studies is cited. Add the references to 1)-4) individually.

［著者］

As commented, references are added to 1)-4) individually.

［査読者 **1-3**］

In Sample preparation, add the details of Au and Ag substrates used in this study. Au or Ag substrates are very important to estimate the relative X-ray dose.

［著者］

Second paragraph in "Sample and preparation" was changed, and last paragraph was inserted for the preparation of Au and Ag substrates.

［査読者 **1-4**］

What is the meaning of "mild etching" to clean the Au substrate? Add the details.

［著者］

For the simple description, we removed the phrase of "mild etching" and the second paragraph of "XPS measurement" was changed.

［査読者 **1-5**］

In Table 1, Labs. A and B use the scanning XPS instruments. How about the conditions of the X-ray beam? Add the details such as beam diameter and probing mode.

［著者］

The information is described in Table 1

［査読者 **1-6**］

In the last paragraph of Results, the reproducibility and durability are discussed. For practical usage, the reproducibility and durability of reference materials are very important, as you described. Are there any advantages of PFDT-Au in the reproducibility and durability?

［著者］

We did not study the advantages of PFDT-Au comparing with other SAMs. However, PFDT is used for the research works in some fields and is easily purchased, and Au is easily modified with thiol derivatives.

［査読者 **1-7**］

For the reader's help, give the specific value of $t^{0.1}_{\mathrm{Ref}}$. In practical surface analysis, the order of $t^{0.1}_{\mathrm{Sample}}$ is very important to prevent from the severe sample degradation.

［著者］

$t^{0.1}_{\mathrm{Ref}}$ values of PFDT-Au are inserted in Tables 4 and 5.

査読者 **2**．高橋和裕（島津製作所）

汎用性のある損傷因子を導き出すための，有意義な研究の一部であり，JSA に掲載すべきであると思います．多くの機関から集まったデータを整理し，これまで SASJ 並びに VAMAS のプロジェクトで得られた手法を用いて解析を進めています．今後のさらなる解析にも期待します．

［査読者 **2-1**］

1. Introduction，段落 2，1 行目．

「On the other hand...」（一方では）で始まっていますが，これに続く文章とその前の段落との関係を考えると，ここには別の接続詞を使用したほうが良いのではないかと思います．前の段落では，XPS がパワフルな表面化学分析テクニックとして認められていることを述べており，この語句の後に続く文章は，試料損傷を考慮することの重要性を述べています. むしろ接続詞は無いほうが良いかも知れません．

［著者］

第 1 段落では，XPS が表面分析において有効かつ強力な手段であると記載しています．つまり，XPS が信頼できる技術であるという意味です．しかし第 2 段落では，場合によっては信頼できないという意味があります．そこで「on the other hand」を使いました．ご理解頂ければ幸いです．

［査読者 **2-2**］

1. Introduction，段落 2，5 行目

「Therefore」（それゆえ）という語は，前後の文章内容を考慮すると，不適切かと思います．前の文章で述べられている「試料損傷を考慮することの重要性」が，なぜ「再現性のある結果を得るには同じ条件で測定する必要がある」につながるのか，明確ではありません．説明を加える必要があると思います．

［著者］

ご指摘を有難うございます．次のコメントを含めて，第 2 段落および第 3 段落をまとめ，かつ全面的に修正しました．

［査読者 **2-3**］

1. Introduction，段落 3

「In addition...」の部分，試料損傷に影響がある装置セッティングが 6 種記されていますが，4 つ目の「the sample area viewed by the analyzer」と 5 つ目の「the acceptance solid angle of the analyzer」がなぜ試料損傷と関係があるのか，明確ではありません．説明を加えるか，もしくは参照文献を指定する必要があると思います．

［著者］

上記のように修正しました．

［査読者 **2-4**］

「profile mode」は，深さ方向分析に使用する測定モードであると思いますが，一般的では無いような気がします．以下のようにしてはいかがでしょうか？

「XPS measurements were carried out by using a depth profile mode or other similar acquisition modes without ... 」

［著者］

ご指摘のように修正しました．

［査読者 **2-5**］

図 1 の上，左カラム

「Also, the damaging factors changed ...」の文章が良くわかりません．‘by utilizing the intensity of ...’は何を意味するのでしょうか？また，‘the change of cross section of those photoelectrons’とありますが，なぜここで光電子の cross section が変化するのか，明確ではありません．説明を追加したほうが良いと思われます．

［著者］

以下のように修正しました．

「Therefore, the damaging factors obtained by different apparatuses cannot be directly compared. Also, the damaging factors change by selecting substrates to calculate relative X-ray because the peak intensities, i.e. photoionization cross sections, of Ag 3d5/2 and Au 4f are different with each other.」

［査読者 **2-6**］

式(2)の直前

「degradation rate constants, *k*,」が突然出てきています．これについての簡単な説明を加えたほうがわかりやすいと思います．

［著者］

ご指摘有難うございます．式(1)に’*k*’’を含む式を加え，かつ’where’の中で説明しておきました．