

# A Method of Evaluating Sample Damage in XPS using Nitrocellulose as a Standard for Organic Materials

T. Maruyama<sup>1</sup>, N.Suzuki<sup>2</sup>, H.Tohma<sup>3</sup>, K.Miura<sup>4</sup> and Organic Materials Group of SASJ

<sup>1</sup>*Fuji Xerox Co.Ltd., Takematsu, Minami-Ashigara, kanagawa 250-0111, Japan*

<sup>2</sup>*Department of Chemistry, Utsunomiya university, Ishii, Utsunomiya, Tochigi 321-8585, Japan*

<sup>3</sup>*Nissan ARC, Ltd., Natsushima, Yokosuka, Kanagawa 237-0061, Japan*

<sup>4</sup>*Tokuyama Corp., Mikage, Tokuyama, Yamaguchi 745-8648, Japan*

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We had proposed methods of evaluating sample damage in XPS measurement, utilizing degradation rates of nitrocellulose. In this paper, applications of the proposed "apparatus damage factor" and "specific damage factor" to some materials are discussed. The "specific damage factor" is an index of the damage rate of materials. Polyacetal and a fluoro-resin were measured with two kinds of XPS equipment, and it was demonstrated that the "specific damage factor" is unique to each material without depending on the XPS equipment. The "apparatus damage factor" is an index to evaluate the damage caused by a XPS equipment under different conditions. The damage rate using a conventional X-ray source was 1.6 times as large as that of using a monochromatized X-ray source. And the damage rate of using a flood gun(4 eV, 0.5  $\mu$ A) was 1.3 times as large as that of the value obtained without flood guns. In addition, the irradiation time of X-ray that gives 10% degradation of materials was indicated by using the "specific damage factor" and the "apparatus damage factor".

## 1. Introduction

It is known that organic materials often suffer damage during XPS measurements [1-8]. The first guide to the damage rates of polymer was performed by G.Beamson and D.Briggs [9]. They indicated relative degradation indices, which give the percentage damage after 500 min at an X-ray source power of 1.4 kW for about 100 polymers. Their degradation indices are useful to estimate the damage rates of polymer. However, one needs to know the damage rates with each apparatus under certain conditions of X-ray to optimize acquisition times for minimum sample damage. And, there is no standard method to evaluate sample damage rate during XPS measurement.

We had investigated damage of organic materials in XPS as an activity of an Organic Materials Group in Surface Analysis Society of JAPAN (SASJ)[10-12]. And consequently, methods of evaluating damage by using nitrocellulose as a standard were proposed. Nitrocellulose is a suitable sample for evaluating the damage of XPS measurement because the intensity of N1s peak originated in the nitrate ester decreases easily by the X-ray

irradiation. An "apparatus damage factor" was introduced to evaluate the damage caused by a XPS equipment, and a "specific damage factor" was introduced as an index of the damage rate of each material [11].

In this paper, the processes of deciding the "apparatus damage factor" and the "specific damage factor" using some materials are discussed. The main purpose is to demonstrate that the proposed "specific damage factor" is unique to each material without depending on the XPS equipment.

## 2. Experimental

As a standard material, a nitrocellulose membrane filter (Advantec Toyo, Poresize=0.1 mm) was used in this work. Polyacetal (Scientific Polymer Products, Inc.) was made a film by hot-pressing at 200°C, 500 kgf/cm<sup>2</sup>. A fluoro-resin that is an industrial material used in a certain company was made a thin film on an aluminum substrate.

The nitrocellulose was analyzed using a VG ESCALAB220i-XL spectrometer with a Mg K $\alpha$  source under several conditions: the power of X-ray source,  $P$ , was 100 W, 200 W

or 300 W; and the distance between the sample surface and the X-ray anode,  $L$ , was 18 mm, 28 mm or 38 mm. A monochromatized Al K  $\alpha$  source of this equipment was applied to only the nitrocellulose to compare the damage rates of the monochromatized X-ray source and the conventional X-ray source. The polyacetal and the fluororesin were measured with the VG ESCALAB220i-XL and a JEOL JPS-9000MX spectrometer using Mg K  $\alpha$  source in the condition shown in Table 1. Pass energies of spectrometers were 27 eV for ESCALAB220i-XL and 20 eV for JEOL JPS-9000MX.

Table 1. X-ray source conditions of VG ESCALAB220i-XL and JEOL JPS-9000MX.

Apparatus	Sample	P(W)	L(mm)
VG	Polyacetal	300	38
	Fluororesin	100	28
JEOL	Polyacetal	100	13
	Fluororesin	100	13

### 3. Results and discussion

#### 3.1. "Apparatus damage factor".

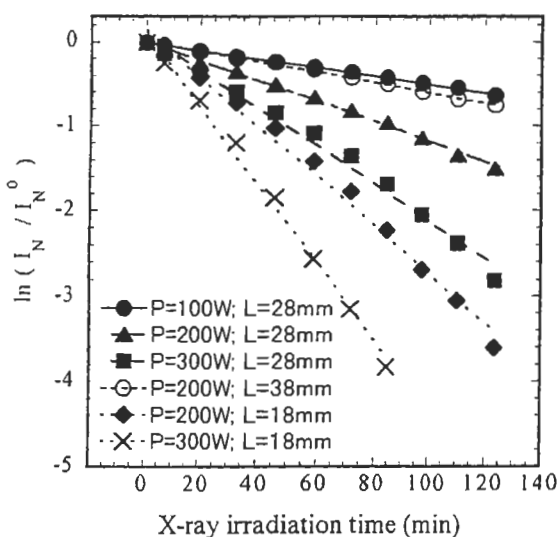


Figure 1. Plots of  $\ln(I_N/I_N^0)$  vs. irradiation time under different X-ray conditions.

$I_N$ : Area intensity of the N1s peak originated in nitrate ester from a nitrocellulose.

$I_N^0$ : Initial value of  $I_N$ .

P: Power of X-ray source, L: Distance between sample surfaces and X-ray anodes.

Figure 1 is a plot of  $\ln(I_N/I_N^0)$  against X-ray irradiation time under six different X-ray conditions, where  $I_N$  is the area intensity of the N1s peak originated in nitrate ester, and  $I_N^0$  is the initial intensity of  $I_N$ . The relation between  $\ln(I_N/I_N^0)$  and  $t$  was almost in a straight line as to each condition.

Next, an introduction of the "apparatus damage factor" is described briefly. The details have been described in another report by Suzuki et al. [11]. Assuming that the decomposition rate of nitrate ester of nitrocellulose is proportional to the product of X-ray dose rate and the density of nitrate ester, the following equation is derived,

$$-\frac{dI_N}{dt} = k D_R I_N \quad (1)$$

where  $D_R$  is a X-ray dose rate and  $k$  is a decomposition rate constant. The Eq.(1) is converted into the next expression.

$$\ln(I_N/I_N^0) = -k D_R t \quad (2)$$

The  $D_R$  is assumed to be a constant, and the " $D_R t$ " means X-ray dose. However it is difficult to measure a X-rays dose of the XPS apparatus actually. Then to evaluate the X-ray dose, a variable "D" was introduced as follows:

$$D = I_{Ag} t \quad (3)$$

where  $I_{Ag}$  is an area intensity of Ag 3d<sub>5/2</sub> spectrum measured under the same condition as the nitrocellulose from a clean silver plate;  $t$  is X-ray irradiation time to the sample.  $I_{Ag}$  is expected to be a constant value during the measurements. This  $D$  will be in proportion to the X-ray dose. Then it will be possible to rewrite Equation (2) as follows:

$$\ln(I_N/I_N^0) = -\beta D \quad (4)$$

where  $\beta$  is a new coefficient constant.

Figure 2 is a plot of  $\ln(I_N/I_N^0)$  as a function of  $D$  under the six different X-ray conditions. The data points were almost on one straight line. The inclination of this straight line:  $\beta$  was defined as "apparatus damage factor" [11]. The value of "apparatus damage factor" obtained from the inclination of the straight line of Figure 2 was  $4.17 \times 10^{-4}$  [Mcps  $\cdot$  eV  $\cdot$  s]<sup>-1</sup>. In Figure 2, the data in the region of less than -1 in ordinate value were omitted, because the accuracy of the data fittingness to

the straight line in this region was not good. It is suggested that the data which the value of  $(I_N/I_N^0)$  is above 0.5, namely  $\ln(I_N/I_N^0)$  is above -0.7 should be used to decide "apparatus damage factors".

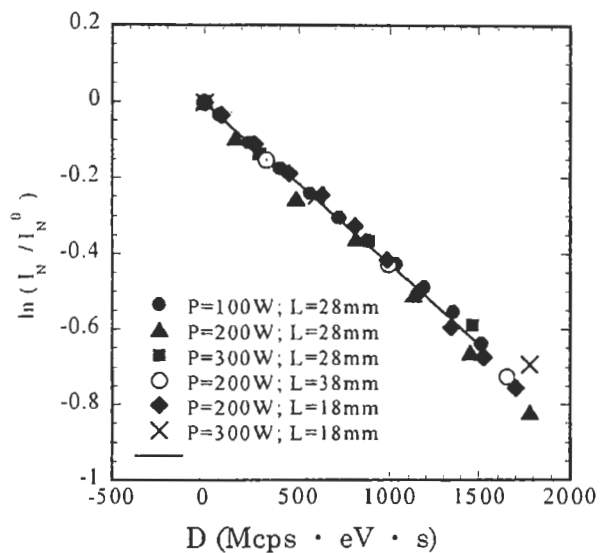


Figure 2. Plots of  $\ln(I_N/I_N^0)$  vs.  $D$  under different X-ray conditions.  
 $D$ : The product of  $Ag3d_{5/2}$  area intensity measured in the same condition as nitrocellulose and X-ray irradiation time.

One also should note that the "apparatus damage factor" depends on the sensitivity of the XPS equipment because the value is obtained by utilizing the intensity of  $Ag 3d_{5/2}$  spectrum. Therefore, the "apparatus damage factor" obtained with different apparatus cannot be directly compared. In the case of using an apparatus, the conditions of spectrometer such as pass energy and analysis area affect the value of "apparatus damage factor". The kind of X-rays also will effect the "apparatus damage factor".

By using the "apparatus damage factor", the damage rates with an apparatus under different conditions were compared. A nitrocellulose was measured using a conventional X-ray source and a monochromatized X-ray source with an ESCALAB220i-XL spectrometer. To equate the analysis area of both cases the diameter of analysis area was set in  $300 \mu m$  with apertures. The X-ray power has been adjusted so that the area intensity of  $Ag3d_{5/2}$  measured with each X-ray source may become equal. And an

electron flood gun (4 eV,  $0.5 \mu A$ ) was used in both cases. Figure 3 is the plots of  $\ln(I_N/I_N^0)$  of the nitrocellulose as a function of  $D$ . The "apparatus damage factors" were derived from the inclinations of two straight lines. The damage rate using a conventional X-ray source was 1.6 times as large as that of using a monochromatized X-ray source. One of the reasons of this result is that a conventional X-ray source emits the Bremsstrahlung continuous X-rays. In addition, the electron from the aluminum window may contribute to the damage. And thermal effects also may contribute to the damage in case of a conventional source because the sample is closer to the X-ray anode.

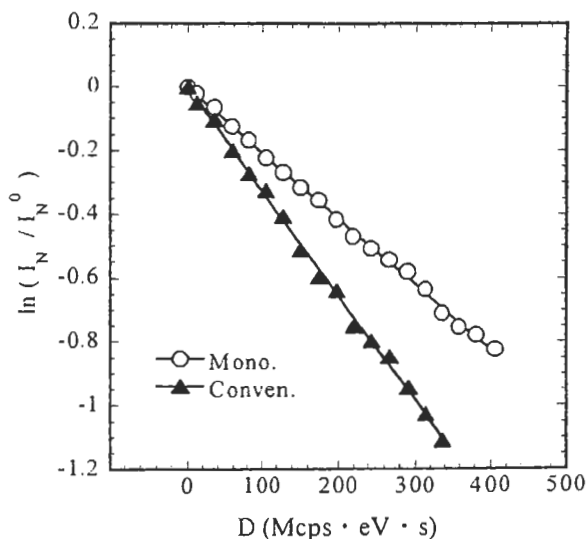


Figure 3. Plots of  $\ln(I_N/I_N^0)$  vs.  $D$  measured with a monochromatized X-ray source and a conventional X-ray source. An electron flood gun (4 eV,  $0.5 \mu A$ ) was used in both cases. To equate the analysis area of both cases the diameter of analysis area was set in  $300 \mu m$  with apertures. The X-ray power has been adjusted so that the  $Ag3d_{5/2}$  peak intensity measured with each X-ray source may become equal.

Similarly, the effect of electron flood gun to the sample damage was examined. Damage with an electron flood gun(4 eV,  $0.5 \mu A$ ) and without flood gun was compared by using a conventional X-ray source at 100W, as shown in Figure4. The value of "apparatus damage factor" with a flood gun was 1.3 times as large as that of without flood guns.

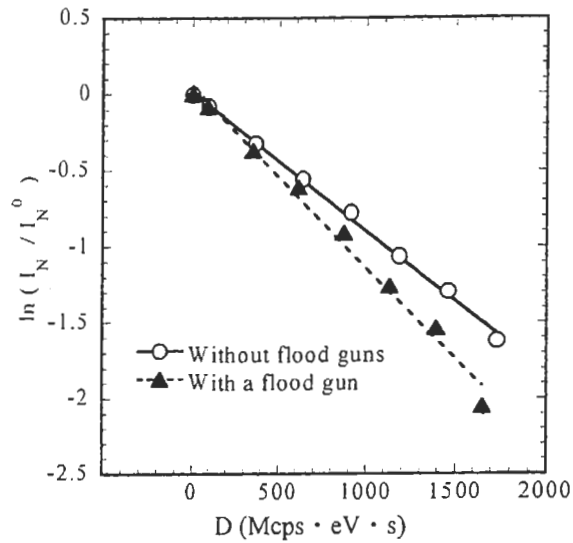


Figure 4. Plots of  $\ln(I_N / I_N^0)$  vs.  $D$  measured by a conventional X-ray source with a flood gun and without flood guns.

### 3.2 "Specific damage factor" of materials

"Apparatus damage factors" for materials other than nitrocellulose can be decided on condition that the damage appears as an attenuation of peak intensities. Considering that the nitrocellulose is a standard material for damage evaluation, "specific damage factor",  $F_x$ , was defined by following formula [11]:

$$F_x = \beta_x / \beta_{NC} \quad (5)$$

where  $\beta_x$  is an "apparatus damage factor" of a material X;  $\beta_{NC}$  is the "apparatus damage factor" of nitrocellulose. The  $\beta_x$  and  $\beta_{NC}$  must be determined with a X-ray source under the same condition of the spectrometer. The  $F_x$  is expected to be independent of the apparatus and measurement conditions.

To demonstrate that the "specific damage factor" is unique to each material without depending on the XPS systems, the "specific damage factors" of polyacetal and the fluoro-resin were measured with two kinds of XPS equipment. The area intensity of O1s spectra,  $I_o$ , of polyacetal was analyzed as well as the case of nitrocellulose. Figure 5 is a plot of  $(I_o / I_o^0)$  as a function of  $D$  measured with the ESCALAB220i-XL spectrometer using a Mg K  $\alpha$  source. The relation between  $\ln(I_o / I_o^0)$  and  $D$  was almost a straight

line. The inclination of this line is the "apparatus damage factor" of polyacetal with ESCALAB220i-XL.

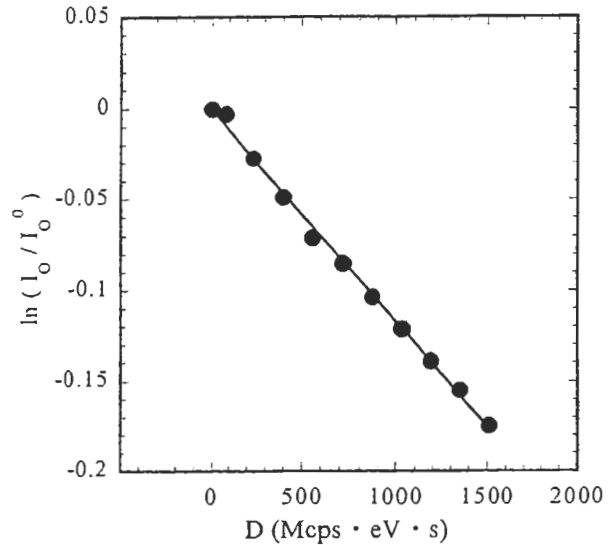


Figure 5. Plot of  $\ln(I_o / I_o^0)$  for polyacetal vs.  $D$ .

$I_o$  : Area intensity of the O1s peak from the polyacetal.

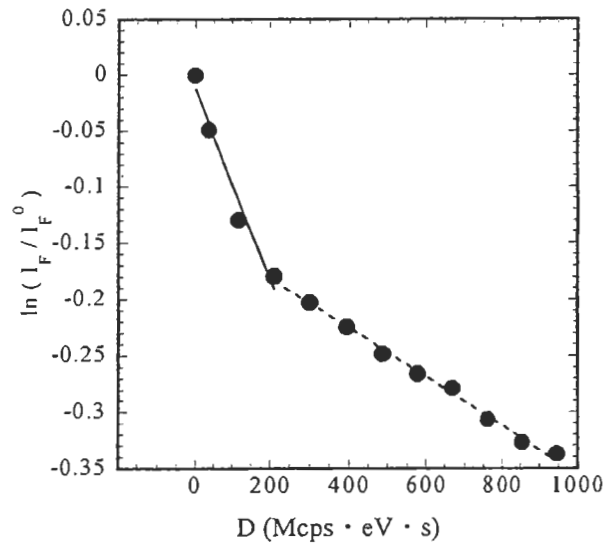


Figure 6. Plot of  $\ln(I_F / I_F^0)$  for a fluoro-resin film vs.  $D$ .

$I_F$  : Area intensity of the F1s peak from the fluoro-resin.

Similar analysis was applied to the F1s peak of the fluoro-resin film that is an industrial material. Figure 6 shows the results of analysis for the fluoro-resin film with a JEOL

JPS-9000MX spectrometer using Mg K  $\alpha$  sources. In this cases, the relations between  $\ln(I_p/I_f^0)$  and  $D$  was not a straight line. However, the data could approximate two straight lines. That is, it is possible to assume that the decomposition rate of fluorine changed on the way. The inclination of the first straight line was regarded as the "apparatus damage factor" of this fluororesin. The result obtained with VG ESCALAB220i-XL for this fluororesin was like Figure 6 that was obtained with JEOL JPS-9000MX.

A set of measurements and analyses were applied to nitrocellulose, polyacetal and the fluororesin with both the ESCALAB220i-XL and the JPS-9000MX spectrometers. The "specific damage factors" obtained by these equipment were tabulated in Table 1. The values obtained by two kinds of XPS equipment were almost equivalent. In consequence, it was demonstrated that the specific damage factor takes a unique value to the material without depending on XPS equipment.

Table.2. "Specific damage factors" obtained by two kinds of XPS equipment.

Apparatus	Polyacetal	Fluororesin
VG	0.15	0.87
JEOL	0.14	0.85

### 3.3 Optimizing of acquisition times

As a guide to optimize acquisition times, X-ray irradiation time that gives 10% degradation of a material "X",  $T_{0.1}$ , can be derived from Equation (3)~(5) as follows:

$$T_{0.1} = \frac{0.105}{I_{Ag}\beta_X} = \frac{0.105}{I_{Ag}(F_X\beta_{NC})} \quad (6)$$

$F_X$  is a unique value to the material and  $\beta_{NC}$  is the constant values decided by the XPS equipment under certain conditions of the spectrometer. Therefore, the  $T_{0.1}$  is calculated from the  $I_{Ag}$  measured under the same condition as the material X;  $T_{0.1}$  for the polyacetal using the ESCALAB220i-XL spectrometer with a Mg K  $\alpha$  source in a condition ( $P=300$  W,  $L=38$  mm) was

calculated as 67 minutes. Similarly, in case of using a JEOL JPS-9000MX with a Mg K  $\alpha$  source ( $P=100$  W,  $L=18$  mm),  $T_{0.1}$  for the polyacetal was calculated as 59 minutes.

### 3. Summary

A method of evaluating sample damage in XPS measurement utilizing degradation rates of nitrocellulose had been proposed as an activity of the Organic Materials Group of SASJ. In this paper, the process of deciding the "apparatus damage factor" and the "specific damage factor" using some materials was discussed. The "specific damage factors" of polyacetal and a fluororesin were determined with two kinds of XPS equipment. The results indicated that the "specific damage factor" take a unique value to each material without depending on XPS equipment. The value of "specific damage factor" for polyacetal was 0.14~0.15. As an example of utilizing the "apparatus damage factor" the damage rates with an apparatus under different conditions were compared. The damage rate using a conventional X-ray source was 1.6 times as large as that of using a monochromatized X-ray source. Similarly, the damage rate of using a flood gun(4 eV, 0.5  $\mu$  A) was 1.3 times as large as that of the value obtained without flood guns. A calculation method of X-ray irradiation time that gives 10% degradation of materials was also described.

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### Comments and Responses

Comments from Dr. M. Yoshitake (NRIM):

The paper nicely shows the validity of 'apparatus damage factor' and 'specific damage factor' as indices for the evaluation of sample damage. However, there are some points to be cleared. Please consider the following points.

1. The result of Fig.3 was obtained with a flood gun. Please add this point in the figure caption.

*Author:* I added this point in the caption of Figure 3.

2. From the text, experimental conditions for Fig.3 and 4 seem equivalent in case of conventional X-ray source. However, data do not coincide when summarized by D. Why is it so?

*Author:* The experimental conditions for Figure 3 and 4 are different. In case of Figure 3, the diameter of analysis area was set in 300  $\mu$  m with apertures to equate the analysis area of the monochromatized X-ray source and the conventional X-ray source. In case of Figure 4, the diameter of analysis area was more than 6 mm. The "D" is dependent on the intensity of Ag 3d<sub>5/2</sub> spectrum under each condition. I added the explanation concerning this in the figure caption of Figure 3. (Similarly, a lens condition of the spectrometer for Figure 2 and 4 were different).

3. The authors write about the relative degradation indices given by G.Beamson and D.Briggs. Can the 'specific damage factors' obtained in this study be compared with their indices in some way?

*Author:* Unfortunately, their database does not include the same kind of cellulose nitrate that we used. It includes cellulose trinitrate. The nitrogen content will effect the decomposition rate. Thus we cannot compare their degradation indices to the "specific damage factors" at the present time. The value of degradation indices for cellulose trinitrate, and polymethylene glycol (polyacetal) are shown for the reference as follows:

Cellulose trinitrate: 65, N/C.

Poly(methylene glycol): 20, O/C;

Their degradation index is derived from  $[100 - (X_t/X_0) \times 100]$  where  $X_t$  is the atomic composition ratio (for example: N/C) at 500 min X-ray exposure time and  $X_0$  is its value at time zero. The ratio of degradation indices of polyacetal to cellulose trinitrate is about 0.3. (The "specific damage factor" of polyacetal utilizing cellulose nitrate is about 0.15).

Comments from Dr. K. Dohmae (TOYOTA CRDL):

This paper reports about evaluating methods for sample damage in XPS measurement. Because there is no standard for evaluating damage rate, the proposition of the universal standard is worth to publish. I have the following suggested revisions.

1. Although this paper proposes two factors "apparatus damage factor" and "specific damage factor" for evaluating damage rate, the reason for introduction of two parameters is not explained. It is expected to explain the background and the purpose for introduction.

*Author:* The "apparatus damage factor" was introduced to evaluate the damage caused by a XPS equipment. On the other hand the "specific damage factor" was introduced as an index of the damage rate of each material. I added this information in the "Introduction".

2. In section 3.1, a factor " $D \cdot t$ " is introduced, and it is explained as a constant. In spite of including a parameter "time", why is that factor to be a constant?

*Author:* That expression was corrected as follows: The " $D$ " is assumed to be a constant.

3. In section 3.1, you express that "apparatus damage factor" depends on only the conditions of spectrometer. I think that "apparatus damage factor" also depends on X-ray source.

*Author:* The "apparatus damage factor" does not depend on the power of X-ray source and the distance between the sample surface and the X-ray anode as shown in Figure 2. But, it also depends on the kind of X-rays. I changed the expression that you pointed out.

4. Although data points in Fig 1 range from 0 to -4 in ordinate, the ordinate scaled from 0 to -1 in Fig 2. It should be indicated that the data less than -1 in ordinate value will be plotted around the line in Fig 2 or not. If it is not, it is expected that the applicable range of "apparatus damage factor" should be shown.

*Author:* Because the accuracy of the data fittingness to the straight line was not good in the region of less than -1 in ordinate value, the data of this region was omitted in Figure 2. It is suggested that the data which the value of  $(I_N/I_N^0)$  is above 0.5, namely  $\ln(I_N/I_N^0)$  is above -0.7 should be used to decide "apparatus damage factors". I added this explanation in the text.

5. The unit of abscissa in Fig 2, 3 and 4 differs from that in Fig 5 and 6. The unit for a parameter should be indicated one unit. And, the  $D$  parameter never takes negative value, then negative value should not be labeled in abscissa.

*Author:* The units of abscissa in Figure 2-6 were unified as  $D$  (Mcps  $\cdot$  eV  $\cdot$  s), and the labels of negative value were deleted in all figures.

6. In Fig 6 the line is bending. How is the result obtained with VG ESCALAB 220i-XL?

*Author:* The result obtained with VG ESCALAB220i-XL was like Figure 6 that was obtained with JEOL JPS-9000MX.