*Paper*

# Effects of Carbon Contaminations on Electron-Induced Damage of $SiO_2$ Film Surface at Different Electron Primary Energies

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Dependence of the electron-induced damage of the clean and carbon-contaminated $SiO_2$ film surfaces during the Auger electron spectroscopy measurement was investigated under irradiation of electrons at different primary energies. The variation in the intensity of the Si-LVV elemental peak with the increase in the electron dose was measured and analyzed within the scheme of the two-step decomposition model [*J. Surf. Sci. Soc. Jpn.* **25**, 212 (2004) (*in Japanese*)]. The results clearly revealed that the rate of the decomposition of $SiO_2$ induced by the electron irradiation is decreased by a small amount of carbon contaminations of ~0.03 nm thickness on the $SiO_2$ surface. The effects of carbon contaminations on the reduction in the electron-induced degradation of $SiO_2$ is significant for the low-primary energy of electrons of 3 keV, and no effects were confirmed at the primary energy of 15 keV. These findings suggest that the primary energy dependence is attributed to the fact that interactions between primary electrons and atoms in the near surface region is much significant when primary electrons with the lower primary energy are irradiated.

## 1. Introduction

The surface chemical analysis using Auger electron spectroscopy (AES) with the high-spatial resolution of the order of 10 nm has recently been practically performed. In such a high-spatial resolution AES analysis, the irradiation of primary electrons with the high-current density is required. The irradiation of primary electrons with the high-current density induces the electron-induced damage of a sample surface, such as the reduction of metal oxides [1-12]. One of possible mechanisms of the electron-induced damage observed for ionic metal oxides is the Auger decay model investigated in detail by Feibelman and Knotek, in which the electron stimulated desorption of oxygen atoms and ions from the metallic oxide is understood as a result of the Auger decay after the ionization of inner-core level of metal and oxygen atoms [13]. The degree of the damage depends on both properties of material to be analyzed and the measurement conditions, and effects of the electron-induced damage on the quantitative analysis are not frequently negligible. One of the most industrially important materials among such materials to be damaged by the electron irradiation is $SiO_2$.

The degradation (reduction) of $SiO_2$ induced by the electron irradiation is considered to consist of two processes, i.e., the primary process of the bond breaking in the Si-O network and the secondary process of the diffusion of oxygen from the electron irradiated region [2]. The electron-induced damage is considered to be correlated with the energy dissipation of primary electrons [1], i.e., the stopping power of primary electrons [9], in the outermost surface region. The primary electron plays important roles in inducing the damage of the $SiO_2$ surface from a point of views of not only the bond breaking in the primary process but also the increase in temperature, which affects the diffusion of oxygen and the re-

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combination of broken bonds in the secondary process. Therefore, the conditions of the electron irradiation, such as the dose rate and primary energy, affect the electron-induced damage. In addition to the condition of the electron irradiation, the carbon contamination on the $SiO_2$ surface affects on the electron-induced damage and is considered to act as a protective layer for the electron-induced damage of the $SiO_2$ surface [1]. However, the correlation between carbon contaminations and the electron-induced damage has not been systematically investigated.

In the regard of the industrial application of $SiO_2$, $SiO_2$ is an important material for the quantitative surface chemical analysis as well as the gate oxide in semiconductor devices. The $SiO_2$ film has been widely used as reference materials for sputter depth profiling in order to align the ion beam [14], to estimate the etching rate, and to calibrate the sputtered depth. From a practical point of view, the determination of the experimental conditions for the AES measurement of $SiO_2$ to avoid or reduce the electron-induced damage as much as possible is required. For this end, understanding of the mechanism of the electron-induced damage and its quantitative evaluation are essential. Furthermore, the investigation of effects of carbon contaminations on the electron-induced degradation is also required for the quantitative evaluation if the carbon contaminations act as a protective layer for the degradation.

In the present study, therefore, effects of carbon contaminations existing on the $SiO_2$ film surface on the electron-induced damage were investigated. The build-up of the elemental Si-LVV peak due to the electron-induced damage observed for the clean and carbon-contaminated $SiO_2$ film surfaces were compared. For the quantitative investigation of the damage, the results were analyzed within the scheme of the two-step decomposition model [9-12], and the critical dose for the electron-induced damage was discussed. This study was carried out as an activity of Japanese committee of VAMAS (The Versailles project on Advanced Materials and Standards)/TWA (Technical Working Area) 2-SCA (Surface Chemical Analysis)-project A7 (evaluation of electron beam damage of $SiO_2$/Si in Auger microprobe analysis) for quantitatively evaluating the electron-induced degradation of the $SiO_2$ surface during the AES measurement.

**2. Experiment**

All measurements were performed using the scanning Auger microscope (PHI-660, ULVAC-PHI). The incident angle of primary electrons for the AES measurement was the surface normal direction, and signal electrons were detected using a coaxial-type cylindrical mirror analyzer (CMA). The base pressure of the analysis chamber was the order of $10^{-9}$ Pa.

The sample used in the present study was the thermally grown $SiO_2$ film of 100 nm thickness on the Si substrate ($SiO_2$/Si), which has been widely used as the reference sample to check the performance of AES and x-ray photoelectron spectroscopy apparatus before sputter depth profiling being performed. In this study, two types of $SiO_2$/Si samples were prepared. One was the as-received sample, in which no pretreatment was performed, and the $SiO_2$ surface was contaminated by carbon. The other was the clean $SiO_2$ surface, which was prepared by heating in air at 400°C for 5 hours [9-12]. Figure 1 shows the typical AES spectra obtained for the (a) as-received and (b) clean $SiO_2$ surfaces. It is clearly confirmed that the heating treatment in air provides the clean $SiO_2$ surface, where no C-KLL peak is observed. In contrast, a small amount of carbon contaminations exist on the as-received $SiO_2$ film surface.

The electron-induced damage of $SiO_2$ was investigated by the AES measurement with irradiating primary electrons at different primary energies of 3, 10, and 15 keV. The primary beam current was approximately 15 nA for all measurements. The total dose of primary electrons was varied within the range of $10^{-2}$ to 10 C/cm$^2$ by changing both the scanned area, i.e., the dose rate, and the irradiation time. The AES spectra were sequentially measured during the irradiation of scanned primary electrons.

The scanned area was measured from the contrast of the damaged $SiO_2$ film surface observed in the scanning electron microscopy image taken at the lower magnification after the measurement of a series of AES spectra. The conditions of the electron irradiation performed for the as-received and clean $SiO_2$ film surfaces are summarized in Tables 1 and 2, respectively.

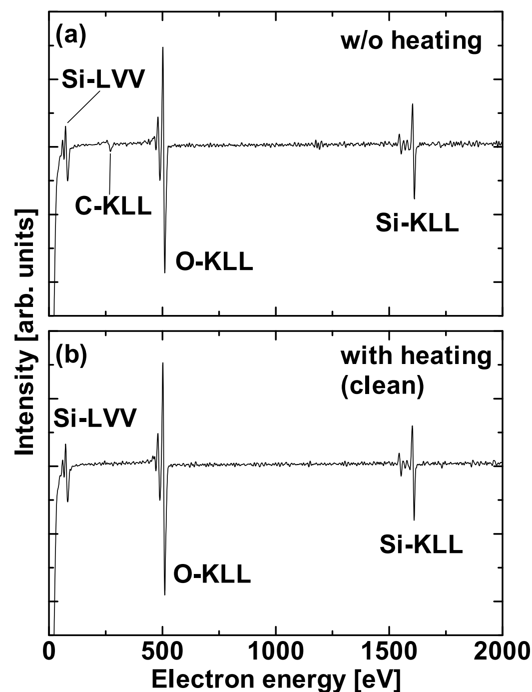


Fig. 1. AES spectra of the (a) as-received and (b) clean $SiO_2$ surfaces. The clean surface was prepared by heating in air at 400°C for 5 hours. The primary energy of electrons used for the AES measurement was 10 keV.

Table 1. Conditions of the electron irradiation performed for the $SiO_2$ film surface with carbon contaminations (as-received sample).

| Primary energy (eV) | Magnification during irradiation | Scanned area ($\mu m^2$) | Dose rate ($C/cm^2s$) |
|---|---|---|---|
| 3 | 500 | 207×254 | $2.9\times10^{-5}$ |
| | 1000 | 103×127 | $1.1\times10^{-4}$ |
| | 2000 | 51.5×63.0 | $4.6\times10^{-4}$ |
| 10 | 1500 | 69.8×84.0 | $2.7\times10^{-4}$ |
| | 3000 | 34.4×42.0 | $1.1\times10^{-4}$ |
| | 6000 | 17.8×23.1 | $3.8\times10^{-3}$ |
| 15 | 2000 | 52.3×63.6 | $4.5\times10^{-4}$ |
| | 4000 | 25.8×32.8 | $1.8\times10^{-3}$ |
| | 8000 | 12.8×15.9 | $7.4\times10^{-3}$ |

Table 2. Conditions of the electron irradiation performed for the clean $SiO_2$ film surface.

| Primary energy (eV) | Magnification during irradiation | Scanned area ($\mu m^2$) | Dose rate ($C/cm^2s$) |
|---|---|---|---|
| 3 | 500 | 207×254 | $2.9\times10^{-5}$ |
| | 1000 | 102×125 | $1.2\times10^{-4}$ |
| | 2000 | 51.5×62.8 | $4.7\times10^{-4}$ |
| 10 | 1500 | 69.8×84.8 | $2.5\times10^{-4}$ |
| | 3000 | 35.9×42.6 | $9.8\times10^{-4}$ |
| | 6000 | 17.3×21.3 | $4.0\times10^{-3}$ |
| 15 | 2000 | 51.5×63.3 | $4.7\times10^{-4}$ |
| | 4000 | 26.0×31.0 | $1.9\times10^{-3}$ |
| | 8000 | 12.9×15.6 | $7.7\times10^{-3}$ |

## 3. Results and Discussion

The amount of carbon contaminations was roughly estimated from Fig. 1 as follows. The relation between the intensities of an Auger peak of element $i$ ($i$ = Si and O) from the clean surface, $I_i$, and that from the as-received surface $I_i'$, is given by

$$I_i' = I_i \exp\left(-\frac{d_C}{\lambda_i \cos\alpha}\right), \quad (1)$$

where $d_C$ is the thickness of carbon contaminations, $\lambda_i$ is the inelastic mean free path of an Auger electron from element $i$ in carbon, and $\alpha$ = 42.3° is the detection angle of the CMA. The typical values of $d_C$ were determined to be 0.034 nm from the peak-to-peak intensities of the Si-LVV and O-KLL peaks with the use of $\lambda_{Si}$ = 0.75 nm and $\lambda_O$ = 1.74 nm [15]. Note that the peak-to-peak intensity of C-KLL normalized by that of Si-LVV corresponding to $d_C$ of 0.034 nm is ~0.2.

Figure 2 shows typical Si-LVV AES spectra obtained during the $SiO_2$ film surface being damaged under the electron irradiation. The peak at approximately 82 eV corresponds to $SiO_2$. With the increase in the electron dose, the intensity of the peak at 94 eV due to elemental Si increases. In the analysis described below, the changes in the elemental Si peak intensities determined as the peak-to-background, where the background intensity was deduced from the intensity at 110 eV, were discussed.

Figure 3 shows the variation in the intensity of the

elemental Si-LVV peak from the as-received $SiO_2$ film surface with the increase in the electron dose. In all primary energies, the decomposition of $SiO_2$ significantly proceeds above a certain dose. The value of this dose is dependent on the primary energy of electrons and clearly larger for the higher primary energy. These tendencies are the same as those reported previously [9-12].

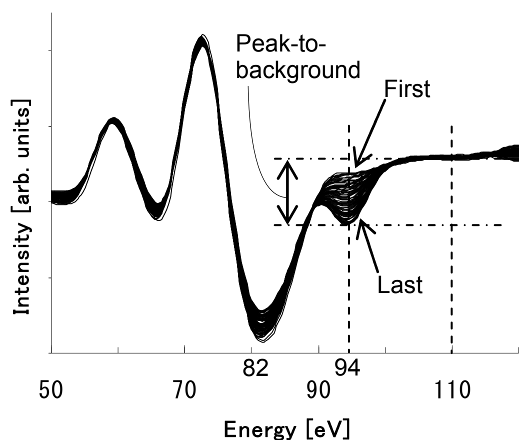


Fig. 2. Changes in the Si-LVV peak from the $SiO_2$ film surface with the increase in the electron dose. The primary energy of electrons was 3 keV. The dose rate was $4.7\times10^{-4}$ C/cm$^2$s. The total dose was 5.7 C/cm$^2$. The electron dose during the measurement of one AES spectrum was $7.1\times10^{-2}$ C/cm$^2$.

The change in the intensity of the elemental Si peak from the clean $SiO_2$ film surface with the increase in the electron dose is shown in Fig. 4. As observed for the as-received $SiO_2$ film surface in Fig. 3, the decomposition of $SiO_2$ slowly proceeds below a certain dose and becomes significant above that dose, which is larger for the higher primary energy. In addition, a comparison between Figs. 3 and 4 revealed that the dose, at which the rate of the decomposition of $SiO_2$ significantly increases, for the as-received $SiO_2$ film surface tends to be larger than that for the clean surface as confirmed from the onset position indicated by thin solid lines in Figs. 3 and 4, except for that at 15 keV, where no significant difference is observed. This result revealed that the electron-induced damage of $SiO_2$ is reduced by carbon contaminations on the $SiO_2$ surface.

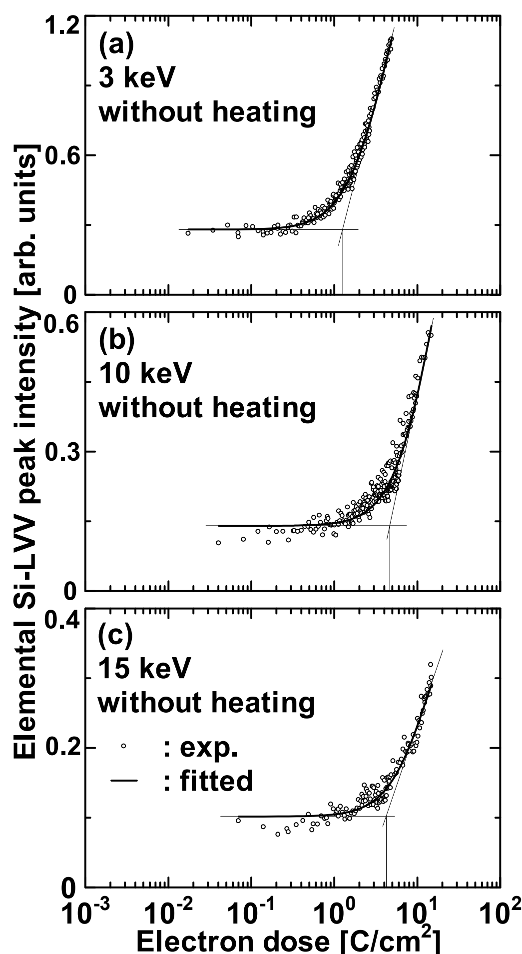


Fig. 3. Changes in the intensity of the elemental Si-LVV peak from the as-received $SiO_2$ film surface, on which carbon contaminations exist. The primary energies of electrons are (a) 3, (b) 10, and (c) 15 keV. Open circles represent the experimental results. Solid lines labeled as “fitted” show the results of the fitting of Eq. (2) describing the two-step decomposition model to the experimental data. Thin solid lines are shown as a guide for eyes to display the onset of the curves.

For more quantitative investigation, the variation in the elemental Si-LVV peak intensity due to the decomposition of $SiO_2$ induced by the electron irradiation was analyzed using the two-step decomposition model, which has been confirmed to reasonably describe the change in the elemental Si-LVV peak intensity from $SiO_2$ films surface due to the reduction induced by the electron irradiation [9-12]. In this model, it is assumed that $SiO_2$ is reduced by the electron irradiation through two-step reaction, i.e., $SiO_2 \rightarrow SiO$ and $SiO \rightarrow Si$. By solving rate equations for these reactions, the surface concentration of elemental Si, i.e., the elemental Si-LVV peak intensity, $N_{Si}$, is given by [12]

$$N_{Si} = k_1\left\{1-\frac{\sigma_2}{\sigma_2-\sigma_1}\exp(-\sigma_1\phi t)+\frac{\sigma_1}{\sigma_2-\sigma_1}\exp(-\sigma_2\phi t)\right\}+k_2 , \quad (2)$$

where $\sigma_1$ and $\sigma_2$ [$cm^2/C$] are the decomposition cross sections for the reactions of $SiO_2 \rightarrow SiO$ and $SiO \rightarrow Si$, respectively. $\phi$ [$C/cm^2s$] is the dose rate and $t$ [s] is the irradiation time. $k1$ and $k2$ are the coefficients to transform the surface composition of elemental Si to the Auger peak intensity. By fitting Eq. (2) to the experimental data shown in Figs. 3 and 4, the decomposition cross sections, $\sigma_1$ and $\sigma_2$ can be determined.

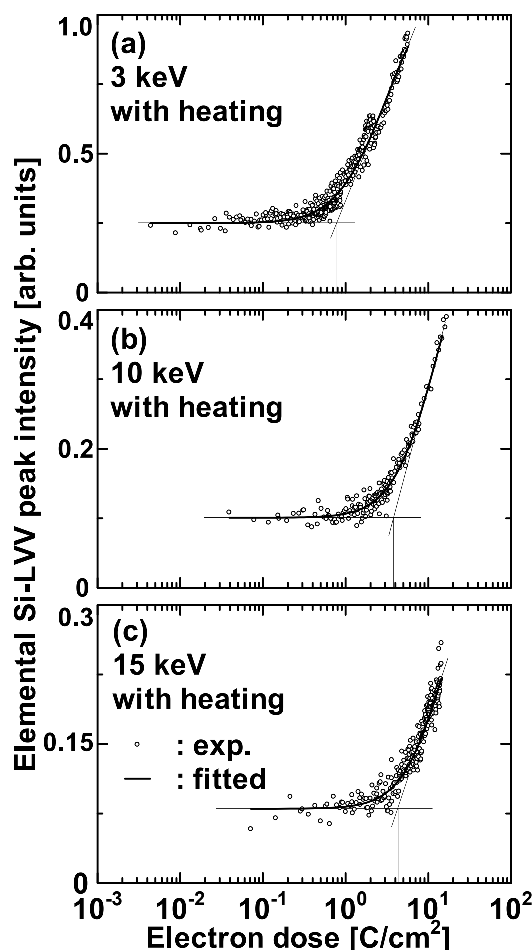


Fig. 4. Changes in the intensity of the elemental Si-LVV peak from the clean $SiO_2$ film surface. The primary energies of electrons are (a) 3, (b) 10, and (c) 15 keV. Open circles represent the experimental results. Solid lines labeled as “fitted” show the results of the fitting of Eq. (2) describing the two-step decomposition model to the experimental data. Thin solid lines are shown as a guide for eyes to display the onset of the curves.

Figure 5 shows the decomposition cross section, $\sigma_1$ and $\sigma_2$, determined by fitting Eq. (2) to the changes in the elemental Si-LVV peak intensity with the increase in the electron dose shown in Figs. 3 and 4. The decomposition cross section is smaller for the higher primary energy of electrons. In addition, the difference in the decomposition cross sections between the clean and as-received (carbon contaminated) $SiO_2$ film surfaces is clearly confirmed, and the cross sections for the clean surface are larger than those for the as-received surface. The difference becomes smaller with the increase in the primary energy of electrons. The present results revealed that a small amount of carbon contaminations of only ~0.03 nm thickness on the $SiO_2$ film surface reduce the electron-induced damage of $SiO_2$ film surface. Note that $\sigma_1$ and $\sigma_2$ are correlated during the fitting procedure within the scheme of the two-step decomposition model, and the evaluation of the damage using the critical dose is more reliable than that using the decomposition cross section.

Since the critical dose $\phi_{CD}$ describing the electron dose giving a certain degree of the decomposition is rather practical than the cross sections, the critical dose corresponding to the decomposition ratio of 5% [9-12] was estimated from the fitted equations, i.e.,

$$\frac{1}{\sigma_1-\sigma_2}[\sigma_2\exp(-\sigma_1\phi_{CD})-\sigma_1\exp(-\sigma_2\phi_{CD})]+1=0.05 \cdot \quad (3)$$

Here, the critical dose at the decomposition ratio of 5% was defined to be a dose, at which the increase in the intensity of the elemental Si-LVV peak is 5% of the total change in the intensity between $\phi = 0$ and $\infty$ estimated from the fitted equation.

Figure 6(a) shows the critical doses $\phi_{CD}$ determined using Eq. (3) and $\sigma_1$ and $\sigma_2$ shown in Fig. 5. The values of the critical dose giving the decomposition rate of 5% for the clean surface are similar to the previously reported values of ~0.6 $C/cm^2$ at 3 keV, ~2.2 $C/cm^2$ at 10 keV, and ~2.5 $C/cm^2$ at 15 keV [9-12], which were determined by the same procedure as those done in the present study. The critical dose for the clean $SiO_2$ film surface linearly depends on the logarithm of the primary energy as that reported previously, suggesting that the critical dose correlate with the stopping power of electrons [9-12].

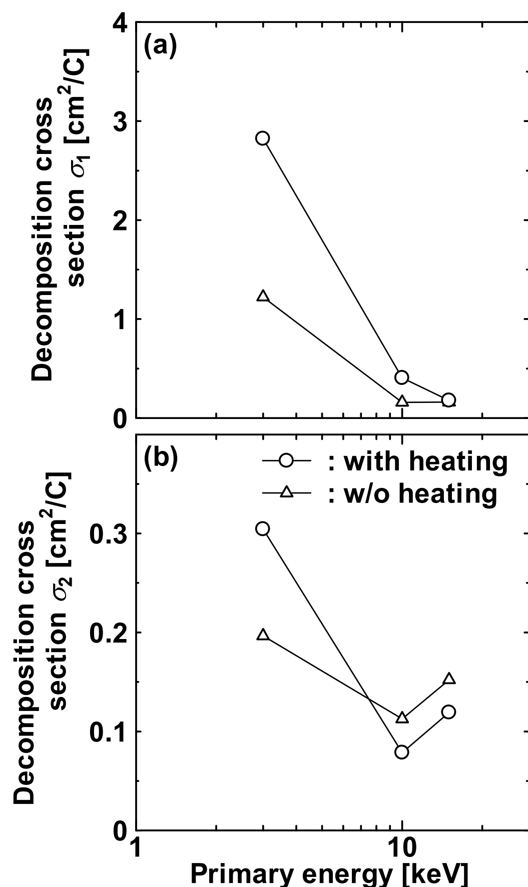


Fig. 5. Decomposition cross sections (a) $\sigma_1$ and (b) $\sigma_2$ for the reactions of $SiO_2 \rightarrow SiO$ and $SiO \rightarrow Si$ described by the two-step decomposition model determined by fitting Eq. (2) to the experimental data shown in Figs. 3 and 4. The fitted equations are shown by solid lines in Figs. 3 and 4. Circles and triangles shows the cross sections determined for the clean and as-received (carbon-contaminated) $SiO_2$ film surfaces, respectively.

From Fig. 6(a), it is clear that the critical dose for the clean surface is tend to be smaller than that for the as-received carbon-contaminated $SiO_2$ film surface. In order to investigate the effects of carbon contaminations on the critical dose, the ratio of the critical dose for the as-received carbon-contaminated surface to that for the clean surface was plotted in Fig. 6(b). When the primary energy is 3 keV, the critical dose for the as-received surface is approximately 1.8 times larger than that for the clean surface. This finding revealed that carbon contaminations of a small amount of only 0.034 nm thickness on the $SiO_2$ surface significantly reduce the electron-induced damage. With the increase in the primary energy of electrons, the ratio of the critical dose for the as-received surface to the clean surface approaches unity, indicating that the effects of carbon contaminations is larger for the lower primary energy of electrons. This is attributed to the fact that the interaction of electrons with surface atoms in the surface region is significant for the lower primary energy of electrons.

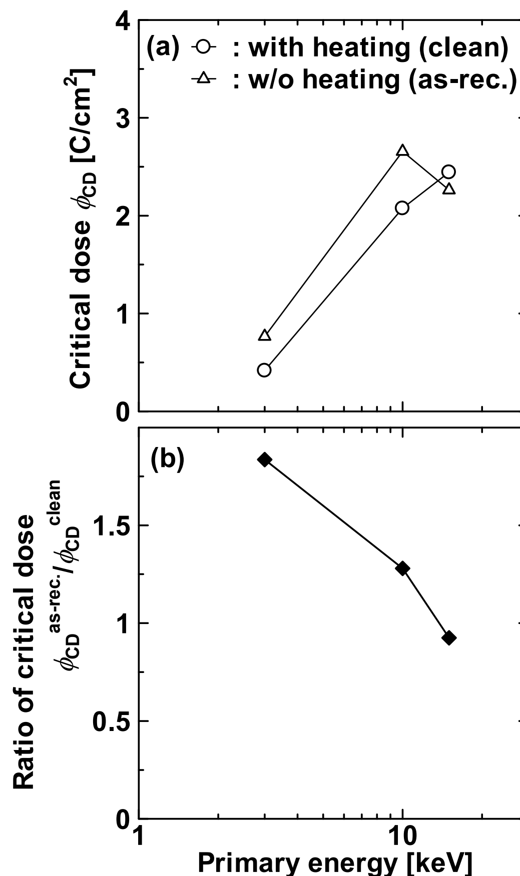


Fig. 6. (a) Critical doses $\phi_{CD}$ for the electron-induced damage of $SiO_2$ film surface determined from the change in the elemental Si-LVV peak intensity. The values are calculated from the decomposition cross sections $\sigma_1$ and $\sigma_2$ shown in Fig. 5 and Eq. (3). Circles and triangles show $\phi_{CD}$ for the clean and as-received carbon-contaminated $SiO_2$ film surfaces. (b) Ratios of the critical doses for the as-received carbon contaminated surface, $\phi_{CD}^{as-rec.}$, to those for the clean surface, $\phi_{CD}^{clean.}$.

## 4. Summary

In the present study, the effects of carbon contaminations on the electron-induced degradation of the $SiO_2$ film surface were investigated. The obtained results are summarized as follows.

(1) A small amount of carbon contaminations of 0.034 nm thickness on the $SiO_2$ film surface act as a protec-

tive layer for the electron-induced damage of $SiO_2$.

(2) The effects of carbon contaminations on the reduction of the electron-induced damage is larger for the lower primary energy of electrons. This is due to the fact that the interactions between primary electrons and surface atoms are more significant for the lower primary energy.

(3) The critical dose giving the decomposition rate of 5% for the carbon-contaminated surface at the primary energy of 3 keV is 1.8 times larger than that for the clean surface. The difference in the critical dose decreases with the increase in the primary energy of electrons and is not observed at 15 keV.

The present results confirmed that carbon contaminations on the $SiO_2$ film surface act as the protective layer for the electron-induced degradation of $SiO_2$, indicating that care is required for the determination of the experimental condition of the AES measurement of $SiO_2$. This behavior of carbon contaminations is probably due to the interaction of carbon atoms with oxygen atoms produced by the decomposition of $SiO_2$, since carbon contaminations are desorbed during the proceed of the degradation. In addition, it is difficult that the small amount of carbon contaminations on the surface affects the primary process of the bond braking in the Si-O network occurring beneath the surface. These findings suggest that the secondary process of the oxygen diffusion plays an important role in the electron-induced damage of the carbon contaminated $SiO_2$ film surface, which may be enhanced by the increase in the local sample temperature induced by the electron irradiation. In order to elucidate this, the systematic investigation of the correlation between the amount of carbon contaminations on the $SiO_2$ film surface and the degree of the decomposition is underway and will be reported shortly.

## 5. Acknowledgement

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## Reviewers' comments

### Reviewer 1. Mineharu Suzuki (Park Systems Japan)

This paper describes the carbon contamination effects on electron induced $SiO_2$ damage depending on the primary energies. This issue has been discussed in the SASJ community for a long time and no one has concluded it. At this point I can recommend to publish this article with discussion on this mysterious issue even this article does not settle it.

**[Reviewer 1-1]**

As to the quantity of contaminated carbon, that may consist of hydro-carbon, oxidized carbon, some organic material, graphite-like carbon, …., it is estimated by eq. (1) as a thickness. Considering the general application of this article, I recommend to describe the peak-to-peak relative intensity to the other main peak suck as Si LVV.

**[Author]**

Thank you for your comments. We added the sentence, "Note that the peak-to-peak intensity of C-KLL normalized by that of Si-LVV corresponding to $d_C$ of 0.034 nm is ~0.2." at the end of the first paragraph of "3. Results and Discussion".

**[Reviewer 1-2]**

The authors report the thickness of 0.034 nm for the contamination using eq. (1) including an IMFP. The number of 0.034 nm is about tenth part of layer distance of graphite. If the authors apply an EAL into eq. (1), I guess the evaluated thickness would be thinner than that you report. Is it right?

**[Author]**

In the present case, the amount of carbon contaminations is very small. Since the difference between IMFP and EAL is attributed to the elastic scattering of signal electrons, there is no difference in the thickness between the use of IMFP and EAL. This corresponds to the fact that values of IMFP and EAL are almost the same at the depth of $z \approx 0$ when IMFP and EAL are plotted as a function of the depth, $z$.

**[Reviewer 1-3]**

In "Results and Discussion" the authors say "In addition, a comparison between Figs. 3 and 4 revealed that the dose, at which the speed of the decomposition of $SiO_2$ significantly increases, for the as-received $SiO_2$ film surface tends to be larger than that for the clean surface as confirmed from the onset position indicated by thin solid lines in Figs. 3 and 4." By my eye sight, it seems to be the case for 3 keV, but difficult to distinguish for 10 keV and 15 keV. Is this my misunderstanding?

**[Author]**

Yes. Your comment is correct. This is why the critical dose plotted in Fig. 6 shows almost the same values for with and without carbon contaminations at the primary energy of 15 keV. This comes from the fact that the electron-induced damage is reduced for the higher primary energy of electrons. To make this point clear, we added the sentence, ", except for that at 15 keV, where no significant difference is observed" after the sentence that the referee pointed out above.

**[Reviewer 1-4]**

In Fig. 5 the composition cross-sections of clean surfaces are greater than those of contaminated surfaces for sigma-1. For sigma-2 they are smaller than those for clean surfaces at 10 keV and 15 keV. Can you comment the error bars for sigma-1 and -2, especially for 10 keV and 15 keV.

**[Author]**

This is a good question. We believe that the error bar in sigma is a little bit large. For this, the most important thing is that $\sigma_1$ and $\sigma_2$ are correlated during the fitting procedure within the scheme of the two-step decomposition model. Therefore, the evaluation of the damage using the critical dose is more reliable than that using the decomposition cross section. To make this point clear, we added the sentence, "Note that $\sigma_1$ and $\sigma_2$ are correlated during the fitting procedure within the scheme of the two-step decomposition model, and the evaluation of the damage using the critical dose is more reliable than that using the decomposition cross section.", at the end of the paragraph starting with the words "Figure 5 shows..."

**[Reviewer 1-5]**

This might be related the comment #4. The thickness of 0.034 nm is less than the bond length of C-C in graphite. Then it is difficult to imagine a layer of contaminants even if it is single atomic layer, leading to island-like contamination phase where some parts of bare silicon oxide surface are directly exposed to atmosphere. Considering this kind of very small amount of contaminants, it is hard to realize a physical picture of interaction between electrons and surface atoms. I guess the authors point out the interaction with Si-O by weakened (less numbered) electrons due to contaminated layer. If the thickness of contaminants was at least one atomic layer, it might be possible. But I am wondering thickness is too small, though it is intuitive. Meanwhile the authors propose the model of oxygen diffusion affecting electron-induced damage in the summary clause. The authors

should discuss or suggest it in the clause of results & discussion on the basis of experimental results.

**[Author]**

As we mentioned in the conclusions as “This behavior of carbon contaminations is probably due to the interaction of carbon atoms with oxygen atoms produced by the decomposition of $SiO_2$, suggesting that the secondary process of the oxygen diffusion plays an important role in the electron-induced damage of the carbon contaminated $SiO_2$ film surface”, the reaction between oxygen and carbon is one of the phenomena playing an important role in this process, which is under detailed investigation. Since it is very difficult to consider that the primary process of the bond braking contributes to the dependence of the degradation on the existence of carbon contamination, it is suggested that the secondary process of the diffusion of oxygen plays an important role. This might be attributed to the increase in the temperature induced by electron irradiation. These discussions are based on the facts those under investigation. Therefore, we described this point in “Conclusions” rather than “Results and Discussion”. We will discuss this point in more detail in further coming papers.

To make these point clear, we modified the sentences pointed out above as “This behavior of carbon contaminations is probably due to the interaction of carbon atoms with oxygen atoms produced by the decomposition of $SiO_2$, since carbon contaminations are desorbed during the proceed of the degradation. In addition, it is difficult that the small amount of carbon contaminations on the surface affects the primary process of the bond braking in the Si-O network occurring beneath the surface. These results and discussion suggest that the secondary process of the oxygen diffusion plays an important role in the electron-induced damage of the carbon contaminated $SiO_2$ film surface, which may be enhanced by the increase in the local sample temperature induced by the electron irradiation.”.

**Reviewer 2. Satoshi Hashimoto (JFE Techno –Rsearch)**

In this paper, new experimental results on the electron induced damage of $SiO_2$ are shown. The results that the damage is affected by the surface contaminated carbon will be very useful for the surface analysis. This manuscript shall be accepted for the publication. My suggestions and comments to this manuscript are shown as follows:

**[Reviewer 2-1]**

Section of Results and discussion: It shall be described whether carbon exists during and after electron irradiation or not. It is all right that the comments is short, because it is described as “In order to elucidate this, the systematic investigation of the correlation between the amount of carbon contaminations on the $SiO_2$ film surface and the degree of the decomposition is underway and will be reported shortly.”

**[Author]**

Carbon contaminations were desorbed during the proceeds of degradation, which will be reported in the next paper in detail. We added the sentence, “carbon contaminations are desorbed during the proceed of the degradation” in the third paragraph of “4. Summary”

**[Reviewer 2-2]**

Section of Summary: It is difficult to understand the reason why the oxygen diffusion plays an important role in the electron-induced damage. A short comment on the role of the diffusion in the electron induced damage for the contaminated material will be helpful to understand.

**[Author]**

We are investigating the effects of carbon contaminations in more detail. As mentioned in Q&A 1, the carbon desorption plays an important role in the degradation. This means that the diffusion of oxygen plays an important role. In addition, it is difficult to consider that the small amount of carbon contaminations on the surface affects the primary process of the bond breaking between Si and oxygen. This is why we speculate as mentioned in “4. Summary”. To make these point clear, we revised the corresponding parts in “4. Summary” as follows. “This behavior of carbon contaminations is probably due to the interaction of carbon atoms with oxygen atoms produced by the decomposition of $SiO_2$, since carbon contaminations are desorbed during the proceed of the degradation. In addition, it is difficult that the small amount of carbon contaminations on the surface affects the primary process of the bond braking in the Si-O network occurring beneath the surface. These results and discussion suggest that the secondary process of the oxygen diffusion plays

an important role in the electron-induced damage of the carbon contaminated $SiO_2$ film surface, which may be enhanced by the increase in the local sample temperature induced by the electron irradiation.”