Approach to Quantitative Evaluation of Electron-Induced Degradation of SiO₂ Film Surface with Different Amounts of Carbon Contaminations

T. Nagatomi,* H. Nakamura, and Y. Takai

*Department of Material and Life Science, Graduate School of Engineering,
Osaka University, Suita, Osaka 565-0871, Japan*

S. Tanuma

*Materials Analysis Station, National Institute for Materials Science,
1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan*

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Effects of carbon contaminations existing on the SiO₂ film surface on the electron-induced damage of SiO₂ were investigated. Carbon contaminations, the amount of which is only ~0.05 nm thickness, are found to act as a protective layer for the degradation. The changes in the elemental and oxide Si-LVV Auger peak intensities due to the electron-induced damage are confirmed to be reasonably described by two- and one-step decomposition models, respectively. The critical dose, at which a certain amount of the damage occurs, is larger for the higher beam current density of primary electrons and the larger initial amount of carbon contaminations. The present results confirmed that the dependences of the degradation on the amount of carbon contaminations and the beam current density are attributed to the diffusion of oxygen and recombination of broken bonds between Si and oxygen, which are enhanced by the increase in the local temperature due to the electron irradiation. Consequently, the small amount of carbon contaminations was found to strongly affect results of the quantitative Auger electron spectroscopy analysis of metal oxides when the electron-induced damage of samples occurs. The present analytical approach, where the critical doses are measured for the SiO₂ surfaces with different amounts of carbon contaminations, is effective to evaluating and estimating the electron-induced damage. [DOI: 10.1380/ejssnt.2011.277]

Keywords: Auger electron spectroscopy; Electron bombardment; Si; SiO₂

I. INTRODUCTION

The spatial resolution of the surface chemical analysis using Auger electron spectroscopy (AES) in practical routine analysis has been improved as high as the order of 10 nm. The high-spatial resolution AES analysis requires the irradiation of primary electrons with the high-current density, resulting in the electron-induced damage of a sample surface, e.g., the reduction of metal oxides [1–12]. The Auger decay model investigated in detail by Feibelman and Knotek is one of possible mechanisms of the electron-induced damage observed for ionic metal oxides, in which the decomposition, i.e., the electron stimulated desorption of oxygen atoms and/or ions from the metallic oxide, is attributed to the Auger decay process occurring after the ionization of inner-core levels of metal and oxygen atoms [13]. The degree of the damage depends on not only properties of samples to be analyzed but also the measurement conditions, and effects of the electron-induced damage on the quantitative AES analysis are not frequently negligible. Among such materials damaged by the electron irradiation, one of the most industrially important materials is SiO₂.

The damage, i.e., the reduction, of SiO₂ induced by the electron irradiation is generally 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 correlated with the dissipation of the kinetic energy of primary electrons [1], i.e., the stopping power of primary electrons [9], in the sur-

face region. The primary electron plays important roles in inducing the damage of the SiO₂ 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 recombination 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 conditions of the electron irradiation, carbon contaminations on the SiO₂ surface affect the electron-induced damage and are considered to act as a protective layer for the electron-induced damage of the SiO₂ surface [1]. However, the correlation between carbon contaminations and the electron-induced damage has not been systematically investigated.

SiO₂ is an industrially important material as not only the gate oxide in semiconductor devices but also the reference material for the quantitative surface chemical analysis. A SiO₂ film on the Si substrate 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. In addition, SiO₂ films can be used as a reference for calibrating the electron-induced damage of samples. From a point of view of the practical AES analysis, the experimental conditions for the AES measurement should be optimized to avoid or reduce the electron-induced damage as much as possible. For this end, understanding of the mechanism of the electron-induced damage and its quantitative evaluation are essential.

In the previous study, effects of carbon contaminations existing on the SiO₂ film surface on the electron-induced damage were investigated [15]. The build-up of the elemental Si-LVV peak due to the electron-induced damage was quantitatively analyzed within the scheme of the two-step decomposition model [9–12]. The results re-

*Corresponding author: nagatomi@mls.eng.osaka-u.ac.jp

vealed that carbon contaminations behave as a protective layer against the electron-induced degradation of SiO_2 , confirming that the secondary process of the oxygen diffusion plays an important role in the electron-induced damage. For more comprehensive understanding of the electron-induced damage of the SiO_2 film surface and obtaining useful information for the practical quantitative AES analysis, the further detailed investigation of how carbon contaminations affect the electron-induced damage is essential, since the adventitious hydrocarbons always exist on the sample surface to be analyzed. Especially, the amount of carbon contaminations is considered to affect the degree of the electron-induced damage of the SiO_2 surface, and the quantitative evaluation of the damage of the SiO_2 surface with the different amount of carbon contaminations is required for the accurate quantitative analysis.

In the present study, therefore, the dependence of the electron-induced damage of the SiO_2 film surface on the initial amount of carbon contaminations was investigated. For this end, the SiO_2 film surfaces having different amounts of carbon contaminations were prepared and uptake curves of the elemental and oxide Si-LVV peaks with the increase in the electron dose were measured. The experimental results were quantitatively analyzed using the two- and one-step decomposition models, and processes occurring in the electron-induced damage were discussed. A novel approach for the quantitative evaluation of the electron-induced damage of the SiO_2 surface with different amounts of carbon contaminations was proposed. 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) for quantitatively evaluating the electron-induced degradation of the SiO_2 surface during the AES measurement.

II. EXPERIMENT

All experiments were performed using Auger microprobe (JAMP-3, JEOL). The apparatus was equipped with an electron gun, a cylindrical mirror analyzer (CMA) and the ultrahigh vacuum floating-type low-energy ion gun (UHV-FLIG). The electron gun of the apparatus had been replaced with that of a JAMP-10 for improving the base pressure of the analysis chamber. The base pressure was $\sim 2 \times 10^{-7}$ Pa. Details of the experimental setup [16–18] and the UHV-FLIG [19] are described elsewhere.

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 order to investigate effects of carbon contaminations existing on the SiO_2 film surface on the electron-induced damage of SiO_2 , the SiO_2 film surfaces with different amounts of carbon contaminations were prepared. For this, 200 eV Ar^+ ions were irradiated onto as-received SiO_2/Si sample surfaces for a short periods of a couple of ten seconds. This low-energy ion irradiation procedure provides SiO_2 surfaces having different amounts of carbon contaminations without the

FIG. 1: AES spectra for the SiO_2 film surfaces with different initial amounts of carbon contaminations. The beam currents of primary electrons were (a) 2, (b) 5, (c) 10, and (d) 50 nA. The values of C/O indicated along with relevant spectra show the ratios of the initial intensity of the C-KLL peak to that of the O-KLL peak. The intensities of the C-KLL and O-KLL peaks were derived as the peak-to-peak intensity.

ion-induced damage of the SiO_2 surface, which was confirmed by the AES measurement.

In order to induce the damage by the electron irradiation, 10 keV electrons were irradiated. The incident angle of electrons was 45° . During the electron irradiation, the damage was monitored by the AES measurement. Primary electrons were irradiated with the spot mode in order to avoid effects introduced by conditions of the electron irradiation, such as the scanned area, and scan speed, on the electron-induced damage. The beam current was varied as 2, 5, 10, and 50 nA and the beam size was measured from the scanning electron microscopy (SEM) image of the Cu mesh used for transmission electron microscopy. For measuring the electron beam size, it was assumed that the broadening of the edge of the bar of the mesh in the SEM image is due to the spread of the electron beam, and the distance, over which the intensity at the edge of the bar is changed from the maximum

FIG. 2: Changes in the Si-LVV peak with the proceed of the electron-induced damage of SiO₂ film. The beam current was 2 nA. The initial amounts of carbon contaminations represented by C/O are (a) 0.003, (b) 0.033, and (c) 0.083.

(100%) to minimum (0%) in the line profile, was measured as the beam radius. The beam size was measured for different beam currents and it was confirmed that the beam size does not depend on the beam current. This means that the beam current density, i.e., the dose rate, is proportional to the beam current. The average value of 6.7 μm was employed as the beam size for all beam current cases.

III. RESULTS AND DISCUSSION

A. Changes in Si-LVV spectra due to electron-induced damage

Figure 1 shows the AES spectra for the SiO₂ surfaces with different initial amounts of carbon contaminations. The spectra were those measured immediately after starting the electron irradiation. The initial intensity of the C-KLL peak normalized by that of the O-KLL peak is shown as C/O. It is found that the SiO₂ surfaces with different initial amounts of carbon contaminations range from nearly 0 to 0.1-0.2. It is also confirmed that there is no damage induced by the 200 eV Ar⁺ irradiation, which would appear as the increase in the elemental Si-LVV peak, for all conditions.

Figures 2 to 5 show the variations in the Si-LVV peak with the proceeds of the electron-induced damage of the SiO₂ film surface for the beam currents of 2, 5, 10, and 50 nA, respectively. Only the Si-LVV peak due to SiO₂ appearing at ~80 eV is observed immediately after starting the electron irradiation. With the proceeds of the electron-induced damage, the elemental Si-LVV peak located at ~91 eV appears and increases. It is clearly confirmed that the electron-induced damage is reduced for

FIG. 3: Variations in the Si-LVV peak with the proceed of the electron-induced damage of SiO₂ film. The electron beam current was 5 nA. The initial amounts of carbon contaminations (C/O) are (a) 0.035, (b) 0.057, and (c) 0.110.

the SiO₂ surface with the larger initial amount of carbon contaminations. This tendency is significant for the lower beam currents and the dependence of the electron-induced damage on the initial amount of carbon contaminations is weak at the beam current of 50 nA.

B. Correction of intensity of Si-LVV peak for attenuation by carbon contamination

From Fig. 1, it is clear that the intensities of the SiO₂ peak obtained at the same beam current are lower for the SiO₂ surface with the larger initial amount of carbon contaminations. This indicates that the intensity of the Si-LVV peak, the kinetic energy of which is very low, is attenuated by the carbon contaminations. In contrast, the energy of the O-KLL peak is high so that the O-KLL peak does not show the attenuation of its intensity due to the carbon contamination. Therefore, in the present study, the Si-LVV peak intensity should be corrected for the attenuation due to the existence of carbon contaminations on the surface.

Figure 6 shows an example of AES spectra before and after the irradiation of the electron beam. In addition to the appearance of the elemental Si peak due to the electron-induced damage of SiO₂, the C-KLL peak disappears after the electron irradiation. Since the C-KLL peak intensity changes during the electron irradiation, the Si-LVV peak intensity during the proceeds of the damage of SiO₂ should be corrected according to the C-KLL peak intensity. Note that the disappearance of the C-KLL peak during the proceeds of the damage of SiO₂ is considered to be promoted by the desorption of carbon contaminations, which might be oxidized by oxygen decomposed from SiO₂ under the electron irradiation. The desorption of carbon

FIG. 4: Changes in the Si-LVV peak with the proceed of the electron-induced damage of SiO₂ film. The beam current was 10 nA. The initial amounts of carbon contaminations represented by C/O are (a) 0.014, (b) 0.036, (c) 0.136, and (d) 0.217.

contaminations due to oxidation is under investigation in detail and will be reported shortly.

Figure 7 shows the variations in the C-KLL peak intensity with the increase in the electron dose. It is found that the C-KLL peak intensity decreases with the increase in the electron dose, revealing that carbon contaminations are desorbed from SiO₂ surface by the electron irradiation. As described below, the Si-LVV peak intensity given as a function of the electron dose is corrected according to the C-KLL peak intensity shown in Fig. 7.

For correcting precisely the attenuation of the Si-LVV peak intensity by carbon contaminations on the surface, information, such as the attenuation length, the inelastic mean free path (IMFP) and the thickness of the carbon contamination layer, is required. However, we need only the correction for the attenuation of the Si-LVV peak intensity due to the carbon contamination layer. In addition, since the amount of carbon contaminations is very small, the C-KLL peak intensity can be assumed to be proportional to the amount, i.e., the thickness, of the carbon contamination layer. Under such an assumption, the Si-LVV peak intensity with carbon contaminations on the surface, $I_{\text{Si-LVV}}$, is given by

$$I_{\text{Si-LVV}} = I'_{\text{Si-LVV}} \exp(-\alpha I_{\text{C-KLL}}), \quad (1)$$

where $I'_{\text{Si-LVV}}$ is the Si-LVV peak intensity without carbon contaminations on the surface and $I_{\text{C-KLL}}$ is the C-KLL peak intensity. α is a coefficient describing the decay of the Si-LVV peak intensity by the existence of the carbon contamination layer. Therefore, after obtaining α , the Si-LVV peak intensity at each step of the electron dose can be corrected using the relevant C-KLL peak intensity shown in Fig. 7 by the following equation,

$$I'_{\text{Si-LVV}} = I_{\text{Si-LVV}} \exp(\alpha I_{\text{C-KLL}}). \quad (2)$$

FIG. 5: Variations in the Si-LVV peak with the proceed of the electron-induced damage of SiO₂ film. The electron beam current was 50 nA. The initial amounts of carbon contaminations (C/O) are (a) 0.011, (b) 0.073, (c) 0.124, and (d) 0.189.

FIG. 6: Comparison of AES spectra of the SiO₂ surface before and after the electron irradiation. The beam current of electrons was 50 nA and the initial amount of carbon contaminations was C/O = 0.189, corresponding to the experiment shown in Fig. 4(d). Si_{el} indicates the elemental Si peak appeared by the electron-induced damage of SiO₂.

Figure 8 shows the relation between the initial oxide Si-LVV and C-KLL peak intensities. As shown by a curve in Fig. 8, Eq. (1) was fitted to the experimental data and α was obtained to be ~ 0.47 . Figure 9 shows an example of the correction of the Si-LVV peak intensity. At the beginning of the electron irradiation, the effect of the correction for the attenuation of the Si-LVV peak intensity is significant, resulting in the increase in the Si-LVV peak intensity of approximately 10%. With the increase in the electron dose, the correction becomes small since carbon contaminations are desorbed. In the present study, both the elemental and oxide Si-LVV peak intensities were cor-

FIG. 7: Changes in the C-KLL peak-to-peak intensity with the increase in the electron dose. The electron beam currents were (a) 2, (b) 5, (c) 10, and (d) 50 nA, respectively. The intensities are normalized by the initial O-KLL peak intensity in the relevant series of the measurement. The value shown along with each data represents the initial amount of carbon contaminations, C/O.

rected using Eq. (2), and the dependence of the variation in the Si-LVV peak intensity with the increase in the electron dose on the initial amount of carbon contaminations was investigated.

With respect to the correction of the Si-LVV peak intensity for the attenuation in the carbon contamination layer, using Eq. (2) with α is sufficient. For more detailed investigation to understand how the small amount of carbon contaminations on the SiO₂ surface affects the electron-induced damage, the thickness of the carbon contamination layer was roughly estimated. In our experimental system, the tilted CMA, where the axis of the CMA is not in the sample surface normal direction, was employed. Therefore, the effective information depth should be taken into account. In the present experimental setup, the detection angle of the CMA, $\Theta(\theta, \varphi)$, measured from the sample surface normal direction is given by

$$\Theta(\theta, \varphi) = \cos^{-1} (\sin 42.3^\circ \sin \theta \sin \varphi + \cos 42.3^\circ \cos \theta), \quad (3)$$

where θ is the tilted angle of the axis of the CMA measured from the sample surface normal and φ is the azimuthal angle of the entrance of the CMA measured from the line parallel to the sample surface. Equation (3) means that the detection angle depends on the azimuthal angle of the entrance position of the CMA. Details of the derivation of the detection angle for the tilted CMA is described elsewhere (see Fig. 1 of ref. [18]).

Now, let us consider the detection of the oxide Si-LVV peak beneath the carbon contamination layer. Providing the IMFP of Si-LVV Auger electrons in carbon as $\lambda_{\text{Si}} = 0.74$ nm [20], the thickness of the carbon contamination

FIG. 8: Relation between the initial intensities of the oxide Si-LVV and C-KLL peaks. The oxide Si-LVV peak intensity was derived as the peak-to-background intensity, where the peak intensity was the intensity of the oxide Si-LVV peak located at ~ 80 eV and the background intensity was determined as the average intensity from 120 to 150 eV. Both the C-KLL and oxide Si-LVV peak intensities are normalized by the initial O-KLL peak-to-peak intensity. Solid line represents the exponential curve given by Eq. (1) fitted to experimental values. α was obtained to be 0.47.

FIG. 9: Oxide Si-LVV peak intensities before (circles) and after (reverse triangles) the correction for the attenuation within the carbon contamination layer using Eq. (2). The peak intensity is normalized by the initial O-KLL peak intensity. The experimental Si-LVV spectra correspond to those shown in Fig. 5(d).

layer, d_C , may be written by,

$$d_C = -\lambda_{\text{Si}} \langle \cos \Theta(\theta, \varphi) \rangle \ln \frac{I_{\text{Si-LVV}}}{I'_{\text{Si-LVV}}}. \quad (4)$$

where $\langle \cos \Theta(\theta, \varphi) \rangle$ represents $\cos \Theta(\theta, \varphi)$ averaged over the azimuthal angle, φ . In the present experimental system, $\theta = 81^\circ$ and $30^\circ \leq \varphi \leq 150^\circ$ [18], and $\langle \cos \Theta(\theta, \varphi) \rangle$ is given as 0.66 corresponding to the effective detection angle of 48° . Furthermore, $I'_{\text{Si-LVV}}$ was obtained to be 0.35 by fitting Eq. (1) in Fig. 8. Using these values, the thickness of the initial carbon contamination layer, d_C , for the thickest case, i.e., $I_{\text{Si-LVV}} = 0.32$ at C/O = 0.217 in Fig. 8, is estimated to be 0.05 nm. The present results revealed that only a small amount of carbon contaminations on the SiO₂ film surface has strong influences on the

FIG. 10: Changes in the elemental Si-LVV peak intensity with the increase in the electron dose. The beam currents of primary electrons are (a) 2, (b) 5, (c) 10, and (d) 50 nA. C/O given as the ratio of the initial C-KLL peak intensity to that of the O-KLL peak represents the initial amount of carbon contaminations on the SiO₂ film surface. The elemental Si-LVV peak intensity was derived as the peak-to-background intensity, where the peak intensity was the intensity of the elemental Si-LVV peak located at ~ 91 eV and the background intensity was determined as the average intensity from 120 to 150 eV. The elemental Si-LVV peak intensity is normalized by the initial O-KLL peak-to-peak intensity. Curves indicate the results of the fitting of Eq. (5) describing the two-step decomposition model to the experimental data. $\delta N_{\text{Si}}^{5\%}$ is the amount of the change in the elemental Si-LVV peak intensity giving the critical dose, $\phi_{\text{CD}}^{\text{Si}}$ (see text at Eqs. (8) and (9)).

electron-induced damage of the SiO₂ film [15].

C. Analysis of change in Si-LVV peak intensity

Figures 10 and 11 show the variations in the elemental and oxide Si-LVV peak intensities, respectively, with the increase in the electron dose at the beam currents of (a) 2, (b) 5, (c) 10, and (d) 50 nA. It is clear that the electron-induced damage, i.e., the increase and decrease in the elemental and oxide Si-LVV peak intensities, respectively, is much reduced for the SiO₂ film surface with the larger amount of initial carbon contaminations. The dependence of the damage on the beam current, i.e., the dose rate, is also clearly observed. When primary electrons with the lower beam current are irradiated, the electron dose, at which the damage is observable in the Si-LVV peak, becomes smaller. In the present study, the primary electron beam is irradiated with the spot mode and the beam size was confirmed to be the same for all beam currents. Therefore, the apparent dependence of the electron-induced damage on the beam current, i.e., the dose rate, revealed that secondary processes in the electron-induced damage of SiO₂, such as the diffusion of oxygen and/or SiO decomposed from SiO₂, recombination of broken bonds between Si and oxygen, and the increase in the local temperature, play important roles in the electron-induced damage phenomena.

For the more quantitative investigation, the variation in the elemental Si-LVV peak intensity due to the decomposition of SiO₂ 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 the SiO₂ films surface due to the reduction induced by the electron irradiation [9–12]. In this model, it is assumed that SiO₂ is reduced by the electron irradiation through two-step reaction, i.e., SiO₂ $\rightarrow$ 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]

$$N_{\text{Si}}(\phi t) = k_1 \left\{ 1 - \frac{\sigma_2}{\sigma_2 - \sigma_1} \exp(-\sigma_1 \phi t) + 1 - \frac{\sigma_1}{\sigma_2 - \sigma_1} \exp(-\sigma_2 \phi t) \right\} + k_2, \quad (5)$$

where σ_1 and σ_2 [cm²/C] are the decomposition cross sections for the reactions of SiO₂ $\rightarrow$ SiO and SiO $\rightarrow$ Si, respectively. ϕ [C/cm²s] is the dose rate and t [s] is the irradiation time. k_1 and k_2 are the coefficients to transform the surface composition of elemental Si to the Auger peak intensity.

With respect to the decrease in the oxide Si-LVV peak intensity with the increase in the electron dose, we assumed that the decomposition of SiO₂ into suboxide state, SiO_x, may result in the decrease in the oxide Si-LVV peak intensity. Under such an assumption, the rate equation describing the one-step decomposition model may give the following equation for the oxide Si-LVV peak intensity, N_{SiO_2} ,

$$N_{\text{SiO}_2}(\phi t) = k_3 \exp(-\sigma_3 \phi t) + k_4, \quad (6)$$

where σ_3 [cm²/C] is the decomposition cross section for the reaction of SiO₂ $\rightarrow$ SiO_x. k_3 and k_4 are the coefficients to convert the surface composition of SiO₂ to the Auger peak intensity.

From the change in the elemental Si-LVV peak intensity, the decomposition cross sections, σ_1 and σ_2 , were determined by fitting Eq. (5) to the experimental data shown in Fig. 10. The change in the oxide Si-LVV peak intensity with the increase in the electron dose shown in Fig. 11 was analyzed using Eq. (6) and the decomposition cross section, σ_3 , was determined. It should be noted that the peak intensities of both elemental Si and SiO₂ normalized by the relevant initial O-KLL peak intensity should not depend on the beam current at the limit of $t = 0$. Therefore, in the fitting process of Eq. (5) to the

FIG. 11: Variations in the oxide Si-LVV peak intensity with the increase in the electron dose. The beam currents of primary electrons are (a) 2, (b) 5, (c) 10, and (d) 50 nA. C/O given as the ratio of the initial C-KLL peak intensity to that of the O-KLL peak represents the initial amount of carbon contaminations on the SiO₂ film surface. The oxide Si-LVV peak intensity was determined as the peak-to-background intensity as mentioned in the caption of Fig. 8 and normalized by the initial O-KLL peak-to-peak intensity. Curves indicate the results of the fitting of Eq. (6) describing the one-step decomposition model to the experimental data. $\delta N_{\text{SiO}_2}^{5\%}$ is the amount of the change in the oxide Si-LVV peak intensity giving the critical dose, $\phi_{\text{CD}}^{\text{SiO}_2}$ (see text at Eqs. (8) and (9)).

experimental data shown in Fig. 10, the boundary condition that $N_{\text{Si}}(t=0) = k_2$ should be the same for all sets of experimental data is used. In the similar way, for the fitting of Eq. (6) in Fig. 11, it is assumed that $N_{\text{SiO}_2}(t=0) = k_3 + k_4$ should be the same for all series of experimental data.

The fitted curves are shown in relevant Figs. 10 and 11. It is found that the experimental variations in the elemental and oxide Si-LVV peak intensities due to the electron-induced damage are reasonably reproduced by Eqs. (5) and (6), respectively. Note that the saturation of the decrease in the oxide Si-LVV peak tends to occur at the smaller electron dose than that of the increase in the elemental Si-LVV peak. This might be attributed to the existence of suboxide states during the decomposition process. The saturation in the change in the Si-LVV peak intensity might occur after a certain amount of SiO₂ within the volume probed by Si-LVV Auger electrons is decomposed. The decrease in the oxide Si-LVV peak must saturates after the disappearance of a certain amount of SiO₂ within the volume. In contrast, the increase in the elemental Si-LVV peak continues after the saturation of the decomposition of SiO₂ in the probed volume as well because suboxide states might decompose into elemental Si.

Figure 12 shows the decomposition cross sections, (a) σ_1 and (b) σ_2 , for the reactions of SiO₂ → SiO and SiO → Si, respectively, in the two-step decomposition model

FIG. 12: Decomposition cross sections, (a) σ_1 and (b) σ_2 , for the reactions of SiO₂ → SiO and SiO → Si, respectively, in the two-step decomposition model describing the increase in the elemental Si-LVV peak intensity due to the electron-induced damage of the SiO₂ film. σ_1 and σ_2 determined for the different beam currents of primary electrons are plotted as a function of the initial C-KLL peak intensity (C/O). These parameters were determined by fitting Eq. (5) to the experimental data shown in Fig. 10.

describing the increase in the elemental Si-LVV peak intensity due to the electron-induced damage of the SiO₂ film. Figure 13 shows the decomposition cross section for the reaction of SiO₂ → SiO_x, σ_3 , in the one-step decomposition model describing the decrease in the oxide Si-LVV peak intensity. From these figures, it is confirmed that the decomposition cross sections tend to be smaller for the SiO₂ film surface with a larger amount of carbon contaminations under the irradiation of primary electrons. Note that the order of magnitude of σ_1 and σ_2 is similar to those reported previously [9–12, 15].

D. Dependence of critical dose on amount of carbon contaminations

In order to evaluate more quantitatively the degree of the electron-induced damage, the critical dose is rather practical as reported previously [9–12]. In the case of the analysis of the elemental Si-LVV peak, the critical dose was defined as the dose, at which the elemental Si-LVV peak increases by a certain amount, such as 5%, of the total change in the intensity between $t=0$ and ∞ estimated from the fitted Eq. (5). However, it is clearly confirmed

FIG. 13: Decomposition cross section for the reaction of $\text{SiO}_2 \rightarrow \text{SiO}_x$, σ_3 , in the one-step decomposition model describing the decrease in the oxide Si-LVV peak intensity due to the electron-induced damage of the SiO_2 film. σ_3 determined for the different beam currents of primary electrons are plotted as a function of the initial C-KLL peak intensity (C/O). These parameters were determined by fitting Eq. (6) to the experimental data shown in Fig. 11.

from Fig. 10 that the elemental Si-LVV peak intensity, i.e., the degree of the decomposition, at the larger electron dose tends to saturate and strongly depends on the beam current, i.e., the dose rate. Therefore, in the present

study, the critical dose was defined as follows.

Since, among the present experimental conditions, the irradiation of the electron beam at the highest beam current of 50 nA onto the SiO_2 film surface with the smallest amount of carbon contaminations of $\text{C/O} = 0.011$ gave the most significant damage, the results obtained under this condition was used as the reference. From the fitted Eqs. (5) and (6) to the experimental results obtained for 50 nA with $\text{C/O} = 0.011$ (black curves in Figs. 10(d) and 11(d)), the amounts of the change in the elemental and oxide Si-LVV peak intensities corresponding to 5% of the total change between $t = 0$ and ∞ , $\delta N_{\text{Si}}^{5\%}$ and $\delta N_{\text{SiO}_2}^{5\%}$, were determined as

$$\begin{aligned}\delta N_{\text{Si}}^{5\%} &= 0.05[N_{\text{Si}}(\infty) - N_{\text{Si}}(0)]_{50\text{nA}, \text{C/O}=0.011} \\ &= 0.05k_1|_{50\text{nA}, \text{C/O}=0.011} = 0.05k'_1, \\ \delta N_{\text{SiO}_2}^{5\%} &= 0.05[N_{\text{SiO}_2}(\infty) - N_{\text{SiO}_2}(0)]_{50\text{nA}, \text{C/O}=0.011} \\ &= 0.05k_3|_{50\text{nA}, \text{C/O}=0.011} = 0.05k'_3.\end{aligned}\quad (7)$$

$\delta N_{\text{Si}}^{5\%}$ and $\delta N_{\text{SiO}_2}^{5\%}$ are shown in Figs. 10(d) and 11(d), respectively. Then, $\delta N_{\text{Si}}^{5\%}$ and $\delta N_{\text{SiO}_2}^{5\%}$ are used as the amounts of the change in the intensities giving the critical doses for the elemental and oxide Si-LVV peaks, $\phi_{\text{CD}}^{\text{Si}}$ and $\phi_{\text{CD}}^{\text{SiO}_2}$, obtained under all other experimental conditions, and $\phi_{\text{CD}}^{\text{Si}}$ and $\phi_{\text{CD}}^{\text{SiO}_2}$ are determined by solving following equations for each of fitted Eqs. (5) and (6),

$$\begin{aligned}N_{\text{Si}}(\phi_{\text{CD}}^{\text{Si}}) - N_{\text{Si}}(0) &= k_1 \left\{ 1 - \frac{\sigma_2}{\sigma_2 - \sigma_1} \exp(-\sigma_1 \phi_{\text{CD}}^{\text{Si}}) + \frac{\sigma_1}{\sigma_2 - \sigma_1} \exp(-\sigma_2 \phi_{\text{CD}}^{\text{Si}}) \right\} = 0.05k'_1 \\ N_{\text{SiO}_2}(\phi_{\text{CD}}^{\text{SiO}_2}) - N_{\text{SiO}_2}(0) &= k_3 \left\{ \exp(-\sigma_1 \phi_{\text{CD}}^{\text{SiO}_2}) - 1 \right\} = 0.05k'_3.\end{aligned}\quad (8)$$

Figures 14(a) and (b) show the critical doses determined for the elemental and oxide Si-LVV peaks, $\phi_{\text{CD}}^{\text{Si}}$ and $\phi_{\text{CD}}^{\text{SiO}_2}$, respectively, as a function of the initial amount of carbon contaminations. It is found that the critical dose depends on the beam current, i.e., the beam current density, and the critical dose is larger for the higher beam current density. In addition, the SiO_2 film surface with the larger amount of initial carbon contaminations provides the larger critical dose, indicating the reduction in the electron-induced damage.

In Fig. 14, it is found that the dependence of the critical doses, $\phi_{\text{CD}}^{\text{Si}}$ and $\phi_{\text{CD}}^{\text{SiO}_2}$, on the initial amounts of carbon contaminations, IC-KLL, might be approximated by the linear function on the semi-log plot, i.e.,

$$\begin{aligned}\log \phi_{\text{CD}}^{\text{Si}} &= a_{\text{Si}} I_{\text{C-KLL}} + b_{\text{Si}}, \\ \log \phi_{\text{CD}}^{\text{SiO}_2} &= a_{\text{SiO}_2} I_{\text{C-KLL}} + b_{\text{SiO}_2}.\end{aligned}\quad (9)$$

Then, by fitting Eq. (9) to the experimental data shown in Fig. 14, the critical dose, at which the initial amount of carbon contaminations is zero, can be estimated. The critical dose estimated for $I_{\text{C-KLL}} = 0$, $\phi_{\text{CD}}^{\text{Si}}$ and $\phi_{\text{CD}}^{\text{SiO}_2}$, i.e., $\exp(b_{\text{Si}})$ and $\exp(b_{\text{SiO}_2})$, are shown in Figs. 15(a) and 15(b), respectively. In Figs. 16(a) and 16(b), the fitting

parameters a_{Si} and a_{SiO_2} are also shown. Note that the fitting of Eq. (9) can basically separate effects of carbon contaminations and the beam current density on the electron-induced damage. $\exp(b_{\text{Si}})$ and $\exp(b_{\text{SiO}_2})$ shown in Fig. 15 provide information on how much the beam current has effects on the electron-induced damage. a_{Si} and a_{SiO_2} shown in Fig. 16 provide information on how much carbon contaminations affect the electron-induced damage for different beam currents, i.e., the dose rate.

E. Electron-induced damage of SiO_2 film surface

From Fig. 15, it is found that the higher beam current density provides the higher critical dose in both cases of the elemental and oxide Si-LVV peaks. This might be attributed to the secondary processes in the electron-induced damage of SiO_2 as mentioned in the text at Figs. 10 and 11. In the present experiments, the beam sizes for different beam currents were confirmed to be the same. Under such conditions, the volumes, in which the kinetic energy of a primary electron is dissipated, can be regarded to be the same for the different beam currents. The dose rates are different for the different beam cur-

FIG. 14: Critical doses for the electron-induced damage of the SiO₂ film surface determined for the (a) elemental, ϕ_{CD}^{Si} , and (b) oxide Si-KLL peaks, $\phi_{CD}^{SiO_2}$, as a function of the initial amount of carbon contaminations (C/O). The critical dose was defined as the dose, at which the changes in the peak intensity with the increase in the electron dose reach 5% of the total change estimated from the fitted Eqs. (5) and (6) for the experimental data obtained under the beam current of 50 nA and C/O = 0.011 (black curves in Figs. 10(d) and 11(d)), i.e., $\delta N_{Si}^{5\%}$ and $\delta N_{SiO_2}^{5\%}$. Lines correspond to the results of the fitting of Eq. (9) to the dependence of ϕ_{CD}^{Si} and $\phi_{CD}^{SiO_2}$ on I_{C-KLL} .

rents, resulting in the amounts of the kinetic energy dissipated near the surface region per unit time are different. The higher beam current results in the higher temperature at around the incident point of primary electrons. The increase in the temperature at the surrounding region also depends on the beam current. Taking into account the increase in the local temperature near the incident point of primary electrons, the secondary processes, such as the diffusion of oxygen and/or SiO decomposed from SiO₂, recombination of broken bonds between Si and oxygen, are considered to play important roles in the dependence of the electron-induced damage on the beam current rather than the primary process of the bond breaking between Si and oxygen induced by the impact of the primary electron. Since the higher electron beam current density provides the higher critical dose, it is speculated that the recombination of broken bonds between Si and oxygen is particularly enhanced by the increase in the local temperature for the higher beam current density.

The fact that the critical dose is smaller for the lower

FIG. 15: Critical doses for the (a) elemental, $\phi_{CD}^{Si'} (= \exp(b_{Si}))$, and (b) oxide Si-LVV peak intensities, $\phi_{CD}^{SiO_2'} (= \exp(b_{SiO_2}))$, at which the initial amounts of carbon contaminations is zero, i.e., $I_{C-KLL} = 0$, estimated by fitting Eq. (9) to the experimental results shown in Fig. 14. Top axis represents the dose rate calculated from the beam current and the beam size.

beam current density indicates that the electron dose to be irradiated before the certain degree of the degradation of SiO₂ being introduced is smaller for the lower beam current density. However, as confirmed for the elemental Si-LVV peak shown in Fig. 10, the final amount of the damage at the larger total dose depends on the beam current density and tends to be smaller for the lower beam current density. These findings revealed that the enhancement of the diffusion of oxygen and/or SiO decomposed from SiO₂, which is enhanced by the increase in the local temperature at the high beam current, plays important roles as well as the recombination of broken bonds between Si and oxygen. The recombined bonds between Si and oxygen may be broken again and oxygen may diffuse. Some oxygen atoms may be recombined and others may escape from the surface. This is the competitive process among the bond breaking, recombination, and diffusion, and the higher beam current tends to result in the larger damage at the final state. Therefore, when we determine the experimental condition to perform the analysis with reducing the electron-induced damage, both the critical dose and the final amount of the damage, which depend

FIG. 16: Fitting parameters (a) a_{Si} and (b) a_{SiO_2} determined by fitting Eq. (9) to the experimental results of the dependence of the critical doses, $\phi_{\text{CD}}^{\text{Si}}$ and $\phi_{\text{CD}}^{\text{SiO}_2}$, on the initial amount of carbon contaminations, $I_{\text{C-KLL}}$, shown in Fig. 14. Top axis represents the dose rate calculated from the beam current and the beam size.

on the beam current density, should be taken into account.

Another point to be enhanced is that the critical dose strongly depends on the beam current density. The difference in the critical doses between the beam currents of 2 and 50 nA is one order of magnitude for the elemental Si-LVV peak and two order of magnitude for oxide Si-LVV peak, respectively. The electron-induced damage is generally investigated by changing the scanned area of primary electrons to vary the dose rate over wide range of the order of magnitude. However, taking into account the present results, the condition of scanning primary electrons, such as an area, the number of scan lines, and scan speed, affects the speed of the proceed of the electron-induced damage. In addition, no care has been generally paid for the size of the primary electron beam. The present results confirmed that cares for these electron irradiation conditions should be paid for precisely evaluating the electron-induced damage for not only the self-estimation of the damage in daily practical analysis but also the interlaboratory investigations such as RRT (round robin test).

From Fig. 16, it is found that the dependence of the electron-induced damage on the initial amount of carbon contaminations is significant for the lower beam current. Although the role played by carbon contaminations in the reduction of the electron-induced damage of SiO₂ is not clear at present, the carbon contamination layer is considered to behave as the protective capped layer for the decomposition of SiO₂ [1, 15]. The carbon contaminations are desorbed with the increase in the electron dose probably by the oxidation by oxygen decomposed from SiO₂. Since the secondary processes of oxygen diffusion and recombination of broken bonds are significant for the higher beam current density, the effects of carbon contaminations are not significant for the higher beam current density. In contrast, the oxygen diffusion is not significant for the lower beam current density, and the carbon contamination layer more remarkably tends to act as the protective layer against the desorption of oxygen and/or SiO decomposed from SiO₂.

Note that the amounts of carbon contaminations on the SiO₂ film surface in the present experiments are the typical values as the adventitious hydrocarbons on the sample surface. This means that the amount of carbon contaminations may affect the results of the quantitative AES analysis of metal oxide samples when the electron-induced damage occurs, since the degradation depends on both the amount of carbon contaminations and the beam current density (electron irradiation conditions). For further elucidating effects of carbon contaminations on the electron-induced damage, more detailed investigation is required and underway.

IV. SUMMARY

In the present study, the electron-induced damage of SiO₂ film surfaces having different amounts of carbon contaminations was investigated. For this end, the dependence of the electron-induced damage on the beam current density of primary electrons was also investigated. For the quantitative evaluation of the electron-induced damage, the changes in the Si-LVV peak intensity due to the proceed of the damage with the increase in the electron dose were analyzed using the two- and one-step decomposition models. The obtained results are summarized as follows.

- (1) Carbon contaminations on the SiO₂ film surface, the amount of which is roughly only 0.05 nm thickness and typical as the adventitious hydrocarbons on the sample, acts as the protective layer against the electron-induced degradation of SiO₂. The degree of the damage strongly depends on the amount of carbon contaminations ranging from ~0 to 0.05 nm thickness.
- (2) The electron-induced damage strongly depends on the beam current of primary electrons, i.e., the dose rate. This finding indicates that the secondary processes in the electron-induced damage of SiO₂, such as the diffusion of oxygen and/or SiO decomposed from SiO₂, and recombination of broken bonds between Si and oxygen, play an important role. The

enhancement of such secondary processes might be attributed to the increase in the local temperature induced by the electron irradiation at the higher dose rate.

- (3) The increase in the elemental Si-LVV peak intensity and the decrease in the oxide Si-LVV peak intensity with the increase in the electron dose were analyzed by the two- and one-step decomposition models. The results revealed that the change in the elemental and oxide Si-LVV peak intensities are reasonably described by the relevant models. The saturation of the change in the oxide Si-LVV peak tends to occur at the lower electron dose than that in the elemental Si-LVV peak. This might be due to the existence of suboxide states during the decomposition of SiO₂ to elemental Si.
- (4) The critical electron doses, at which the change in the Si-LVV peak due to the electron-induced degradation arrives a certain amount of total changes, were determined for different beam current densities. The critical dose depends on both the beam current density of primary electrons and the initial amount of carbon contaminations. The higher beam current density and larger initial amount of carbon contaminations give the larger critical dose.
- (5) By measuring the critical dose for the SiO₂ surface with different amounts of carbon contaminations, effects of carbon contaminations and beam current density on the electron-induced damage can be separately discussed. The critical dose for the SiO₂ surface without carbon contaminations can be estimated.
- (6) The increase in the critical dose for the higher beam current, i.e., the dose rate, might be attributed to the enhancement of the recombination of broken bonds between Si and oxygen induced by the increase in the local temperature.
- (7) Although the higher beam current density provides the larger critical dose, it results in the higher degree of the degradation at the larger electron dose, indicating that the diffusion of oxygen and/or SiO decomposed from SiO₂ plays an important role in the degradation. For the optimization of the measurement conditions for metal oxides, both the crit-

ical dose and the final amount of the damage, both of which depend on the beam current, should be taken into account.

- (8) For evaluating the electron-induced damage, the beam diameter was confirmed to be a basic and important factor in addition to other electron irradiation conditions, such as the scanned area, and scan speed. Furthermore, since the level of the saturation of the damage depends on the beam current density, the care should be paid for the definition of a certain amount of the degradation used for determining the critical dose.
- (9) Carbon contaminations are desorbed with the increase in the electron dose. This might be attributed to the oxidation of carbon contaminations by oxygen decomposed from SiO₂. One of the reasons of the reduction in the electron-induced damage due to carbon contaminations might be that the carbon contamination layer acts as the protective layer against the desorption of oxygen and/or SiO from the SiO₂.

The present results revealed that carbon contaminations, the amount of which is only ~0.05 nm thickness, strongly affect the results of the quantitative AES analysis of metal oxides when the electron-induced damage occurs. By measuring the degrees of the degradation for the sample with different amounts of carbon contaminations, the electron-induced damage can be quantitatively evaluated using the present approach, resulting in the more precise evaluation of results of the quantitative analysis, optimization of measurement conditions to reduce the degradation, and the estimation of the damage before performing AES measurements. For more detailed understanding of the electron-induced degradation of the SiO₂ surface, the investigation of effects of the oxygen desorption is underway and will be reported shortly.

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