Study of Electron Beam Irradiation Damage Factor for SiO_2 Films

Makoto Nakamura and Electronic Materials Group of SASJ
Advanced Process Integration Dep. ULSI Development Div., FUJITSU Ltd.
Kamikodanaka 4-1-1, Nakahara-ku Kawasaki 211-8588, JAPAN
(marumakan@kawa.to.ed.fujitsu.co.jp)

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The damage of silicon oxide by electron beam irradiation is a well known phenomenon [1][2][3]. We already reported about the factors that determine the damage by electron beam irradiation on thin silicon dioxide films in earlier works [4][5][6]. Our finding can be summarized as follows : 1) beams with low incident energy cause heavier damage than beams with high incident energy, 2) a low incident angle (which would be a high angle relative to the surface normal) causes heavier damage than a high incident angle. In this paper we discuss various calculations for explaining the factors determining electron beam irradiation damage. We reached the following conclusions : 1) The results of Monte Carlo (MC) simulations with respect to the energy distribution of back scattered electrons are useful for studying the factors involved in electron beam irradiation damage, 2) the results of inelastic mean free path (IMFP) calculation are also useful for studying these factor. We propose a new algorithm for estimating electron irradiation damage which uses the energy distribution as derived by both MC simulation and IMFP calculation.

1. INTRODUCTION

We have examined various materials that are used in electronics by electron spectroscopy (Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS)) so as to provide base for discussing proper analysis conditions, sample treatment, cleaning methods and related topics. As part of our activities, we examined the factor determining electron beam irradiation damage on thin silicon dioxide films. The damage of thin silicon dioxide films by electron beam irradiation is a well known phenomenon [1][2][3] and we believe that it is common knowledge for all AES operators. We tried to identify the decisive parameters that determine the electron beam irradiation damage that occurs during AES measurement. We studied in our experiments the dependence of the damage on incident beam acceleration energy and on the irradiation angle. A detailed description of the experiments was already reported earlier [4][5][6]. Our findings can be summarized as follows : 1) a reduced rate of change in the *Si-LMM* spectra can be achieved by using electrons with low acceleration energy than by using electrons with high energy, 2) a reduced rate of change in the *Si-LMM* spectra can be achieved by using a low incident angle than by using a high incident angle. We tried to explain these finding by employing various calculation methods for clarifying the process of damage by electron beam irradiation.

2. EXPERIMENTS

We will first briefly describe the conditions of our earlier experiments in order to give better understanding of the background for this paper. The detailed experimental conditions are reported in our previous work [4][5][6].

2-1 Examined Sample

We used in all of our experiments thermal silicon dioxide films that were grown on *p-Si (100)* substrates in dry oxygen. The thickness of the silicon oxide layer was *50nm*.

2-2 Dependence on Electron Energy

We used a Auger spectrometer by *Physical Electronics Inc. model 670xi* for the experiments on acceleration energy dependence. We used *3, 5* and *10 kV* as the incident energy of electrons, a constant electron current density of *11.5 mA/cm*^{2}, and an electron incident angle of *30 degrees* with respect to the surface normal.

2-3 Electron Incident Angle Dependence

We used *VG Scientific Microlab 310F* Auger spectrometer for the experiments on incident angle dependence. We used *0, 30* and *60 degrees* as incident angles with respect to the surface normal, a constant electron current density of *142mA/cm*^{2} and electron energies of *5* and *10kV*.

3. MONTE CARLO (MC) SIMULATION

In the first step, we employed MC simulation to analyze the results of our previous experiments. MC simulation is a popular method for estimating the behavior of electrons and ions in solid substances. We obtained the simulator from a NIFTY Serve (the most popular network service in Japan) freeware library. The program had been produced by Dr. K. Kanda from Instrument Division of Hitachi, Ltd.. This program was developed mainly to analyze scanning electron microscope (SEM) images. Figure 1 shows typical simulation results for our experiments. The simulator provides the following

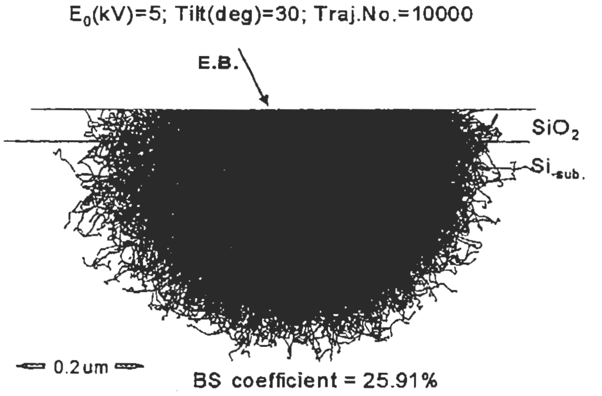

Figure 1 One of the typical result of Monte Carlo simulation.

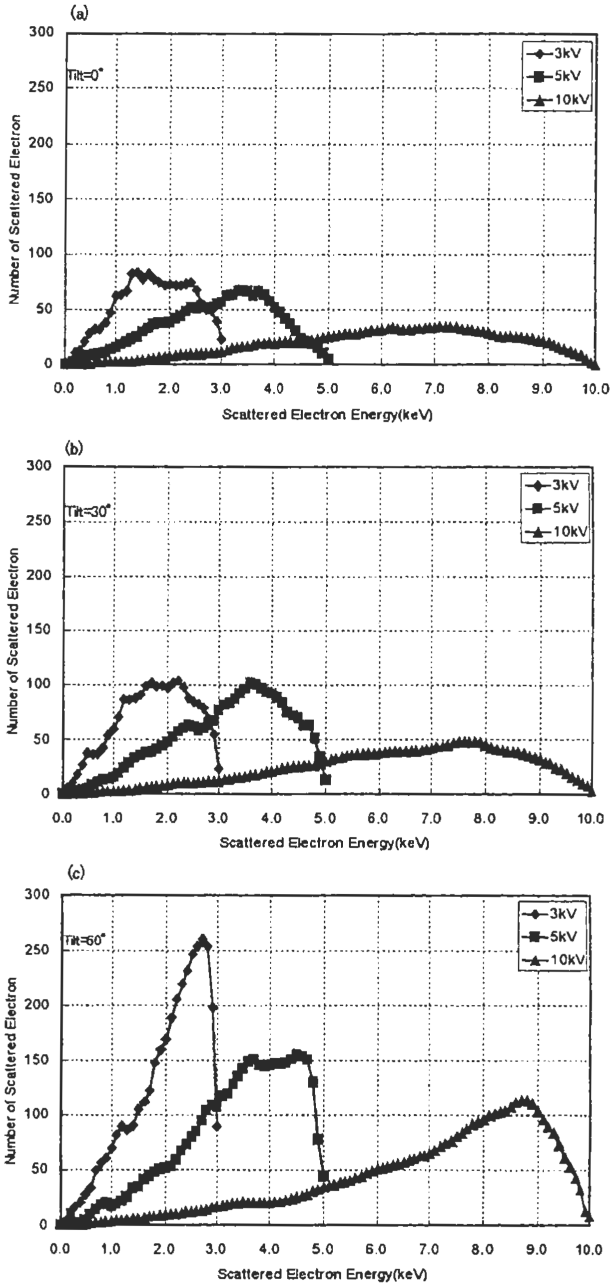

Figure 2 The results of the number of back scattered coefficient of electron using Monte Carlo simulation.

Table1 The results of the number of back scattered coefficient(%) of electron using Monte Carlo(MC) simulation.

	3kV	5kV	10kV
Tilt=0°	16.2	17.7	18.7
Tilt=30°	20.4	25.9	23.8
Tilt=60°	36.6	40.0	41.6

information : ① the distribution of incident electrons in a solid sample (shown in figure 1), ② the back scatter coefficient (BSC), ③ the actual beam diameter near the surface region of the sample and ④ the energy distribution of scattered electrons near the surface region of the sample.

We decide to consider mainly the energy distribution of the scattered electrons for analyzing our results. We performed calculations for *10,000* electrons within our experiment. We spend a few minutes to calculate the respective conditions on a low-end DOS/V PC (*Pentium 90MHz*). Figure 2 shows the energy distribution of scattered electrons near the surface region depending on the incident energy according to MC simulation. Figure 2(a) shows the results with respect to the dependence of the energy dissipation on incident energy for incidence from normal direction, figure 2(b) shows the results for an incidence from *30 degrees* and figure 2(c) shows the results for an incidence from *60 degrees* with respect to the surface normal, respectively. A summary of MC simulation results for the BSC of electrons is shown in table 1. It is easily understandable intuitively and in the light of the experimental results that the BSC obtained for an incident from the surface normal is smaller than that for oblique incidence. This result of the MC simulation with respect to the angle dependence of the BSC well explains our earlier findings. On the other hand, the predicted energy dependence of the BSC is not sufficient for explaining our earlier findings. Another algorithm is needed for explaining the energy dependence that was observed in our earlier findings.

Table 2 The resultant value of Everhart and Hoff's algorithm applied to our experiments.

	3kV	5kV	10kV
Tilt=0°	4.23	2.28	1.00
Tilt=30°	4.96	2.75	1.19
Tilt=60°	7.71	5.55	2.33

4. EVERHART & HOFF'S ALGORITHM [7]

S. Ichimura et al. and K. Min et al. used the following algorithm which was proposed by P. E. Everhart and P. H. Hoff, to examine the energy and incident angle dependence of the quantity of damage by electron beam irradiation [8][5]. This algorithm determines the value of energy dissipation in its correlation to the dissociation of the *Si-O* bond. Employing this algorithm, we tried to calculate the energy dissipation value E_d in thin silicon dioxide film by

$$E_d = fE_p\int_0^t \lambda(y)dy \qquad (1)$$

where

$$\lambda(y) = 0.60 + 6.21y - 12.40y^2 + 5.69y^3 \qquad (1.a)$$

and f denotes the effective energy incidence with respect to the back scattering effect, E_p (in *keV*) is the incident energy of electrons, and t is the thickness of the silicon dioxide film normalized for the electron range R_g. In the case of silicon dioxide, R_g is given by the following equation :

$$R_g(\mu m) = 0.018E_p^{1.75}(keV) \qquad (1\text{-}b)$$

Based on these equations, it is possible to calculate the dissipation value of the incident energy of the electron in a thin silicon dioxide layer. Table 2 shows the resulting values for the parameters used in our experiments. The value in table 2 is normalized for the case of a *10kV* incident from normal direction.

The results provided by this algorithm seem suitable for explaining our findings, but we think that there are the following problems in connection with this : first, the algorithm estimates the total amount of energy consumption in thin film. The algorithm naturally predicts that thick samples consume more energy than thin samples because of this approach. However, in our experience, the first phase of reduction takes place only in the surface region. Second, the difference of incident angles matched the difference in thickness : For example, the case of the low incident angle matched the case of the thick sample. The thickness of the samples is assumed to change in proportion to $1/\sin\theta$. Finally, this algorithm neglects the effect of electron that are back scattered from the substrate by using a constant value for *f*. We conclude therefore that this algorithm is not suitable for our experiments. The usability of this algorithm is probably limited to samples of bulk type such as in connection with the electron beam evaporation process.

5. IMFP CALCULATION

Most data on of Inelastic Mean Free Path (IMFP), as obtained both by experimental methods and numerically, show that the IMFP increases monotonic in dependence on the increase of electron energy except for the low energy region (electron energy less than *<50eV*) [9][10][11][12][13]. These results suggest that low energy electrons easily interact with the sample and easily lose their energy in excitation. In the meantime the sample easily receives energy from low energy electrons which leads to some damage in the sample, and finally the energy from the electron breaks up the *Si-O* bond and leads to a reduction of the silicon dioxide film. We adopted an algorithm TPP-2M [9], which is one of the most popular algorithm for estimating IMFP values for analyzing our experiments. The formula for TPP-2M is as follow :

$$\lambda = \frac{E}{E_p^2 \left(\beta \ln(\gamma E) - C/E + D/E^2 \right)} \qquad (2)$$

here λ is the IMFP value (in Å), E is the electron energy (in *eV*), $E_p = 28.8\ (N_v \rho / M)^{1/2}$ is the free-electron plasmon energy (in *eV*), ρ is the density of the substance (in g/cm^3), N_v is the number of valence electrons per atom (for elements) or molecule (for compounds), and M is the atomic or molecular weight. The terms β, γ, C and D are parameters given by

$$\beta = -0.10 + 0.944 (E_p^2 + E_g^2)^{-1/2} + 0.069 \rho^{0.1} \qquad (2\text{-a})$$

$$\gamma = 0.191 \rho^{-0.5.} \qquad (2\text{-b})$$

$$C = 1.97 - 0.91U \qquad (2\text{-c})$$

$$D = 53.4 - 20.8U \qquad (2\text{-d})$$

$$U = N_{Np}/M = E_p^2/829.4 \qquad (2\text{-e})$$

and E_g is the band gap energy (in *eV*) for the insulator.

A plot of the results from TPP-2M is shown in figure 3. We used TPP-2M up to an energy range of *10,000 eV* even the applicable range for TPP-2M is reportedly limited from *10 eV* to *2000 eV*, as we had found no other suitable tool for calculating the IMFP value.

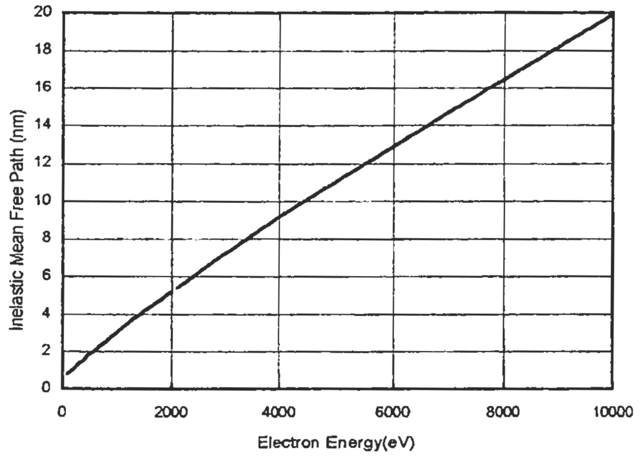

Figure 3 The result of IMFP calculation applied to SiO_2 using TPP-2M for our experiments.

Table 3 The results of calculation to estimate relative value (F_d) of electron beam irradiation damage.

	3kV	5kV	10kV
Tilt=0°	41.35	29.19	16.59
Tilt=30°	50.89	38.87	20.16
Tilt=60°	78.33	56.33	31.64

The plot in figure 3 shows that the IMFP value for electrons with an energy of *10 keV* is about three times larger than for electrons with an energy of *3 keV*. Overall, the probability of inelastic scattering for an electron energy of *10 keV* electron energy is only about *1/3* of that for electrons with an energy of *3 keV*.

6. CONSIDERATION

The amount of back scattered electrons, the amount of incident electrons and the energy dependence of the respective IMFP value seems to be the significant factors with respect to electron beam induced damage. We propose the following equation for estimating the degree of electron beam damage (factor of damage (F_d)) :

$$F_d = \frac{N}{\lambda(E_0)\cos\theta} + \int_0^{E_0} \frac{I(E)}{\lambda(E)} dE \qquad (3)$$

here N is the number of incident electrons, E_0 is the energy of the incident electrons, $\lambda(E_0)$ is the IMFP value of incident electrons as calculated with any suitable algorithm (such as TPP-2M), $I(E)$ is the amount of back scattered electrons in dependence on the energy and $\lambda(E)$ is the IMFP value of back scattered electrons depending on the energy. A summary of the relative values of electron beam damage according to above equation is shown in table 3. The applicable range for our equation is limited by the condition that the irradiation area has to be sufficiently lager than the actual beam diameter.

In this study we used TPP-2M for calculating the value for $\lambda(E)$. However, if there is any other suitable algorithm to calculate the IMFP value, it could be used as well.

There is a close correlation between the results of our experiments and the numerical results for the above equation. We think therefore that our equation is suitable for estimating the damage by electron beams.

7. CONCLUSION

We analyzed the factor that determine the damage by electron beam irradiation so as to clarify the results of our earlier work. We found that MC simulation and IMFP calculation are useful for a practical estimation of damage by electron beams.

We propose a new equation that is based on the results of the energy distribution for electrons near the surface region. The equation uses MC simulation and employs IMFP values that were provided by TPP-2M calculations. We confirmed the suitability using our previous work. Then we are certain our new equation is useful for providing a practical estimation of the relative value of damage by electron irradiation on silicon oxide films.

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Discussion with reviewer

Author ; M. Nakamura et al.
Reviewer ; Dr. S. Ichimura (ETL),
Dr. Joong-Whan Lee (K-MAC)

[Dr. S. Ichimura]
In this paper the author describes damage caused by an electron beam irradiation to a SiO_2/Si sample, and tries to discuss it quantitatively by proposing a new approach. The paper is acceptable for publication. In order to improve the quality of the paper, the following points have to be considered.

It may be reasonable to assume that the damage caused by e-beam irradiation to a SiO_2/Si sample relates to the number of inelastic scattering events which occurs within a certain amount of depth. Probably it is the reason why the author used eq. 3, it is necessary to calculate the energy distribution of back scattered electrons and consequently it takes longer time than to estimate the damage using eq. 1. Since the calculated results are not directly compared with the experimental results, it is not clear why we had better use eq. 3 instead of eq. 1. It is necessary, therefore, to estimate the observed damage quantitatively, and compare them with the calculated results by eq. 1 and eq. 3.

[M. Nakamura]
I am grateful for your kindness about correcting my unskilled English.
The eq. 1 is very simple but eq. 1 is not so good equation to estimate the damage of thin films on substrate. In my understanding eq. 1 is applicable to estimate total energy dissipation in bulk and thin films (for example TEM samples) but we should not use eq. 1 for thin films on substrate. Because electron beam damage layer is only few *nm* but the diffusion depth of incident electron is *um* order. Most of the energy dissipation is caused under damage layer. Therefore the rate of energy dissipation in surface region is very small compared with total energy dissipation.
I think we need only short time to calculate energy distribution of back scattered electrons because the performance of today's PC is enough high. The calculation time is only few minutes using eq. 3 if we establish the program of calculation procedure completely. Therefore I propose eq. 3 is practically suitable to estimate electron beam induced damage れ relatively.

[Dr. Joong-Whan Lee]
<Minor Corrections>
1. The table 1 in page 2 and table 2 in page 3 are better to have the same format as table 3 in page 4.
2. The "*10,000Kv*" in the last sentence on left column of page 4 seems to be mistype of "*10,000eV*".
3. The "MC" in the 5th sentence on left column of page 3 is better to be "Monte Carlo (MC)" and The "IMFP" in the 3rd sentence on left column of page 4 is better to be "Inelastic Mean Free Path (IMFP)".
[M. Nakamura]
Thanks for your kind comment. I correct tables and mistipe following your advice except "MC" in the 5th sentence on left column of page 3 because I have already written full character of MC in page 2.

<Major Considerations>
[Dr. Joong-Whan Lee]
1. This paper proposed the electron beam irradiation damage factor. However the "damage" only observed by surface analysis techniques such as AES and/or XPS. Therefore the title of this paper would like to be "The surface damage".
[M. Nakamura]
In this paper we describe only surface damage but electron beam make damage not only surface region but also bulk region. Surface damage is only first step of electron irradiation damage. This is the reason why I don't revise the title.

[Dr. Joong-Whan Lee]
2. Think about the surface damage - like as the sentence "the first phase of reduction takes place only in the surface region" in the right

column on page 3 - the reduction will occur only when the oxygen atoms could removed from matrix (i.e. surface), otherwise the bond will regenerate by recombination.

[M. Nakamura]

I don't know about recombination probability but there is any possibility to make recombine the dangling-bond by incident electron because the energy of incident electron is enough high to recombine the bonds. I think XPS is one of the most powerful tool If we want to investigate about recombination process. To research reduction process is one of the subject to future.

[Dr. Joong-Whan Lee]

3. Therefore, It seems to correlate between the number of electrons scattered at the surface region and the degree of damage (i.e. reduction). It also be considered that the effective cross sections for breaking *Si-O* bonds according to electron energy.

[M. Nakamura]

You are correct, we need to think effective cross section for breaking *Si-O* bonds according to electron energy but we don't have good calculation methods. Please teach me if you know any algorithm. So we assumed an inverse number of inelastic scattering coefficient correlate with effective cross section for reduced sample. This is the reason why we used TPP-2M in my paper.

[Dr. Joong-Whan Lee]

4. The eq. 3 in the last sentence on the right column of page 4 "$F_d=N/(\lambda(E_0)*\cos(\theta))+$ " has several meaning. $1/\lambda(E_0)$: the IMFP value of incident electrons could correlate with the effective cross sections for breaking *Si-O* bonds according to electron energy.

- $1/\cos(\theta)$: it will correlate with the number of scattered electrons near the surface.
- the second term $(I(E)/\lambda(E))$: it will correlate with backscattered electrons from under levels to surface region.
- therefore, this equation can be used after minor considerations for the meaning.

[M. Nakamura]

First term of equation means increase of actual inelastic scattering probability caused by slant incident. We used inelastic scattering probability to calculate easily of course we knew to use effective cross section for breaking *Si-O* bonds according to electron energy is right procedure essentially. We are going to replace λ with effective cross section immediately in the eq. 3 if we can easily calculate effective cross section.