Dose Dependent Etching Selectivity in SiO₂ by Focused Ion Beam

Taizoh Sadoh, Hiromi Eguchi, Atsushi Kenjo, and Masanobu Miyao
Department of Electronics, Kyushu University, 6-10-1 Hakozaki, Fukuoka 812-8581, Japan
Phone: +81-92-642-3952, FAX: +81-92-642-3974, E-mail: sadoh@ed.kyushu-u.ac.jp

1. Introduction
Nano-patterning of SiO₂ is becoming more essential with shrinking feature sizes of devices in ULSI. It is expected that maskless patterning with 10nm-precision becomes possible by irradiation with focused ion-beams (FIB) and subsequent selective etching. To establish this influence of irradiation parameters of FIB on etching characteristics of SiO₂ was comprehensively investigated.

2. Experimental Procedure
In the experiment, SiO₂ films (thickness: 140nm) were grown by thermal oxidation. The samples were irradiated with 40keV Si⁺ FIB (dose: 8x10¹⁵-1x10¹⁶cm⁻², temperature: 25-400°C, irradiation-area: 200x40 𝜇m²) and etched with a buffered HF at 25°C. The etching steps were measured by using a contact surface profiler.

3. Results and Discussion
(a) Etching Characteristics and Modeling
Figure 1(a) shows depth profiles of the etching rate for samples irradiated with various doses at 25°C. The dose dependence of the etching rate in the shallow region (<25nm) is different from that in the deep region (40-80nm), which is summarized in Fig. 1(b). The features are as follows: (1) for both shallow and deep regions, the etching rate increases with increasing dose, however it decreases for doses exceeding a critical value (1x10¹⁵cm⁻²), (2) the maximum etching rate is larger in the shallow region than in the deep region. The TRIM simulation indicated that irradiation with this critical value resulted in fully knocked-on of Si atoms in SiO₂.

Dose dependence of the etching rate was precisely investigated as a function of irradiation temperature. Figures 2(a) and (b) show the etching characteristics in the shallow region. The etching rate decreases with increasing irradiation temperature for all doses. The temperature dependence becomes remarkable with increasing dose up to the critical dose, however it then becomes weak with dose. Figures 2(c) and (d) show the characteristics in the deep region. The temperature dependence of the etching rate is very weak.

These complicated results cannot be understood only by considering that the introduced damage enhances etching. Consequently, we introduce an assumption that implanted excess Si retards etching, and propose an etching model as shown in Table I.

Figure 3(a) shows depth profiles of vacancy at the Si site and implanted Si in SiO₂, calculated by TRIM for various low doses (<1x10¹⁵cm⁻²). The peak position is shallower for vacancy than for implanted Si. Therefore, in the shallow region, the etching characteristics are mainly governed by the behavior of vacancy, which shows large temperature dependence, as shown in (A) of Table I. On the other hand, in the deep region, the concentration of implanted Si is not negligible. Since implanted excess Si scarcely annihilates comparing to vacancy, the temperature dependence of the etching rate becomes weak ((B) of Table I).

Figure 3(b) shows the profiles for high doses (>1x10¹⁵cm⁻²). The concentration of vacancy saturates at 1.7x10²⁵cm⁻³ due to fully knocked-on, however that of implanted excess Si increases with dose. Thus, the contribution of excess Si becomes significant ((C) of Table I). With increasing dose, the etching rate decreases for the high dose condition.

(b) Quantitative Analysis
In order to examine our assumption, i.e., retarded etching by implanted excess Si atoms, samples irradiated with 1x10¹⁵cm⁻² were annealed at 800°C for 2h to remove damage without changing excess Si. The change of etching rate due to this process is shown in Fig. 4 as a function of the depth. Significant retardation effect is observed in the deep region, which clearly confirms our assumption.

In order to analyze the etching characteristics quantitatively, the depth profiles of the etching rate ER(d) for various doses (Fig. 1(a)) were analyzed by using the following equation:

\[ E_R(d) = aV(d) - bI(d), \]

where V(d) and I(d) are concentration of vacancy and implanted Si, respectively, at depth d, and a and b constants. The values of ER(d) and I(d) for all doses are plotted as a function of V(d) and I(d) in Fig. 5. The solid line shows the fitted curve with a=1.8x10²⁵ and b=2.0x10²⁵cm⁻²/s. All experimental data can be represented by the identical equation, which shows the validity of our model. These results suggest that etching rate can be precisely controlled by choosing both profiles of vacancy and excess Si. Optimization of irradiation and annealing parameters is now under way.

4. Summary
The etching characteristics of SiO₂ irradiated with FIB were comprehensively studied. The complicated features were quantitatively understood, and the equation to predict the etching rate was firstly presented. This quantitative relation enables the precise control of etching selectivity by optimizing both irradiation and annealing parameters.

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Fig. 1 Depth profile of etching rate (a) and dose dependence of etching rate in shallow (<25nm) and deep (40-80nm) regions (b).

Fig. 2 Dose dependence (a) and irradiation temperature dependence (b) of etching rate in shallow region, and those in deep region ((c), (d)).

Fig. 3 Concentration profile of vacancy at Si site (V) and implanted Si (I) in SiO2 for low (<1x10^{10}cm^{-2}) (a) and high (>1x10^{13}cm^{-2}) (b) doses.

Fig. 4 Change of etching rate of SiO2 by irradiation (1x10^{16}cm^{-2}) and subsequent annealing (800°C, 2h).

Table I Etching model for dose dependent characteristics. Critical dose (1x10^{15}cm^{-2}) corresponds to dose for fully knocked-on of Si in SiO2. V: vacancy, I: implanted Si.

<table>
<thead>
<tr>
<th>Shallow region (0&lt;d&lt;25nm)</th>
<th>Deep region (40&lt;d&lt;80nm)</th>
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<tbody>
<tr>
<td>Low dose (&lt;1x10^{10}cm^{-2})</td>
<td>(A) V dominant</td>
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<tr>
<td></td>
<td>E_{V} increase with dose</td>
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<td>large T dependence</td>
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<tr>
<td>High dose (&gt;1x10^{13}cm^{-2})</td>
<td>(C) I dominant</td>
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<tr>
<td></td>
<td>E_{I} decrease with increasing dose</td>
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<td>small T dependence</td>
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Fig. 5 Dependence of E_{V}(d)/E_{I}(d) on V/I(d). The data E_{V}(d) were obtained for various doses (8x10^{12}-1x10^{15}cm^{-2}) at depth d (0-150nm). The solid line is the fitted curve.