Atomic layer etching (ALET) can be an indispensable method for the fabrication of future devices such as nanoscale devices, quantum devices, etc., because current etch technology utilizing reactive ion etching does not have precise etch rate controllability and tends to damage the surface of the devices physically and electrically due to the use of energetic reactive ions to achieve vertical etch profiles.

ALET technology has been investigated since the early 1990s for GaAs and Si devices. To achieve ALET, many cycles of sequential steps consisting of the adsorption of halogen gas such as chlorine or fluorine and the desorption of the formed halide by heat, laser, or Ar\textsuperscript{+} ions are required. For the Si(100) ALET, precise Si etch rates per cycle were obtained by many researchers, however, among the researchers the reported etch rates were different. 1.5-3.0 Å/cycle was reported for the silicon (100) etching by fluorine gas and 0.68 ~ 1.36 Å/cycle\textsuperscript{4,5} and 0.52 Å/cycle\textsuperscript{6} were reported for the silicon (100) and (111) etchings by Cl\textsubscript{2} gas, respectively. In addition, for the anisotropic etching of the silicon during the ALET, directional Ar\textsuperscript{+} ions were used in general for the desorption, and which could cause electrical charging damage to the devices similar to that of the conventional reactive ion etching.

In fact, the decrease of damage to the semiconductor which occurred during the plasma etching can be obtained by using neutral beam etching instead of conventional reactive ion etching. Figure 1a shows the photorefractance spectroscopy (PRS) data of GaAs etched using Cl\textsubscript{2} neutral beam and Cl\textsubscript{2} inductively coupled plasma (ICP) etching. For comparison, not only the etch depth but also the energy of the neutral beam and the bias voltage of the ICP etching were maintained the same. As shown in the figure, the GaAs etched using the Cl\textsubscript{2} ICP showed the change of the PRS curve compared to non-etched reference GaAs while the GaAs etched using the Cl\textsubscript{2} neutral beam showed a similar PRS curve as the reference. The change of the PRS curve indicates the existence of surface defects, therefore, the surface damage could be decreased significantly by using a neutral beam instead of conventional reactive ion etching.

The charging damage to the gate oxide of the MOS device during the exposure to the O\textsubscript{2} ICP was shifted compared to the reference sample indicating the charging damage to the gate oxide of the MOS device during the exposure to the O\textsubscript{2} ICP. However, in the case of the MOS device exposed to the neutral beam, the C-V curve was similar to the reference indicating insignificant damage to the device.

Therefore, in this letter, the ALET of Si was carried out for the first time using an Ar neutral beam instead of the Ar\textsuperscript{+} ion beam to avoid charge-related damage during the desorption of the halide and its ALET characteristics of Si by Cl\textsubscript{2} were investigated. Especially, the ALET of Si having different orientations of (100) and (111) were investigated to understand the silicon etch rate per cycle.

A low energy Ar neutral beam was generated by a low-angle (5°) forward reflected neutral beam technique. The neutral beam source was composed of a 2 MHz radio frequency (rf) ion source for the generation of a parallel Ar\textsuperscript{+} ion beam and a low angle planar-reflector for the neutralization of the Ar\textsuperscript{+} ion beam and the formation of a parallel Ar neutral beam. A two-grid commercial ICP-type ion gun, which was made by Commonwealth Scientific (CS), Inc., was used as the rf ion source. In order to control the Ar neutral beam energy, the voltage applied to the first grid located close to the source (accelerator grid) was fixed at 50 V while the second grid was grounded. With the energy of the Ar neutrals obtained with the ions accelerated by 50 V, the silicon sputter rate was negligible and only silicon chlorides formed on the silicon surface were removed.

Also, the contamination of the silicon surface by the sputtering of the reflector plate during the ALET was negligible due to the low Ar\textsuperscript{+} ion energy and the low reflection angle. The measured neutralization efficiency of the Ar\textsuperscript{+} ions extracted from the ion gun followed by the reflection on the low angle planar-reflector was above 99%. Between the neutral beam source and the substrate, an automatic shutter was installed to control the Ar neutral beam irradiation time during the Si etching cycle. Chlorine gas was supplied during the adsorption period and was controlled simultaneously with the shutter motion. The Cl\textsubscript{2} feed time, the Cl\textsubscript{2} purge time, the Ar neutral beam irradiation time, and the etch product purge for the ALET process were 20, 30, 60 ~ 840, and 20 s, respectively, and the detailed experimental parameters are shown in Table I. The details of the neutral beam source used in the experiment are described elsewhere.

In this experiment, p-type Si(100) and (111) wafers patterned with a photoreist were used as the samples. The samples were B-doped Si with the resistivity of 1-10 Ω cm. The samples were dipped in a buffered HF solution to remove the remaining native oxide on the Si wafers followed by rinsing with deionized water and blow drying using N\textsubscript{2} just before loading into the chamber. The etch step height was measured using a step profilometer (Tencor Instrument, Alpha Step 500) and the measured step height was divided by the total number of ALET cycles to yield the etch rate.

Figure 2 shows the Si etch rate (Å/cycle) measured as a function of the Ar neutral beam irradiation time for silicon (100) and (111)
The Cl₂ pressure was maintained at 0.46 mTorr and the Ar irradiation time could be divided into three regions. Region 1 is the region where the etch rates of silicon 111 is still increased with increasing Ar irradiation time. Region 2 is the region where the etch rates of both silicon 100 and silicon 111 increase linearly with increasing Ar irradiation time. Region 3 is the region where the etch rates of silicon 100 and silicon 111 are saturated. The differences in the etch rates with the Ar neutral beam irradiation time are related to the removal of silicon chloride from the silicon surface. The linear increase of the silicon etch rate with increasing Ar irradiation time in region 1 is related to the continuous removal of silicon chloride from the both the (100) and (111) surface with the Ar neutrals supplied during the irradiation time. The saturation of the silicon etch rate with increasing the irradiation time in the region 3 is related to the removal of all of the silicon chloride on the (100) and (111) surfaces by supplying enough Ar neutrals during the irradiation time. The saturation of the silicon (100) etch rate and the incomplete saturation of the silicon (111) etch rate in region 2 are related to the differences in the silicon surface atomic density of silicon (100) and (111) surfaces which are 6.78 × 10²⁹/cm² and 7.83 × 10²⁹/cm², respectively. Therefore, more silicon chloride bonds are formed on the silicon (111) surface compared to those on the (100) silicon surface. It follows that more Ar neutrals have to be provided by increasing the irradiation time compared to the (100) surface to remove all silicon chloride bonds formed on the silicon (111) surface. The effect of Ar neutral irradiation time on the silicon etch rate can be represented from the following equations

\[ E_{SiCl} = k_f N_{Ar} \quad \text{when } f_{Ar} < f_{Ar_{crit}} \]  

\[ E_{SiCl} = k_f N_{Ar} \quad \text{when } f_{Ar} > f_{Ar_{crit}} \]

where \( k_f \) is the desorption rate constant, \( E_{SiCl} \) is the silicon etch rate (Å/cycle), \( f_{Ar} \) is the Ar neutral beam dose related to the Ar neutral beam irradiation time, and \( f_{Ar_{crit}} \) is the critical Ar neutral beam dose required to remove one monolayer of SiCl on the silicon surface. From Eq. 1, the desorption constant for the (100) surface, \( k_{1(100)} \), is higher than that for the (111) surface, \( k_{1(111)} \), and \( f_{Ar_{crit}(100)} \) for the (100) surface is lower than \( f_{Ar_{crit}(111)} \) for the (111) surface. The higher \( k_{1(100)} \) compared to \( k_{1(111)} \) appears related to the stability of the (111) surface compared to the (100) surface. However, the higher \( f_{Ar_{crit}(111)} \) compared to \( f_{Ar_{crit}(100)} \) is related to the higher atomic density of the (111) surface compared to the (100) surface. When the Ar neutral beam irradiation time was enough, as shown in the Fig. 2, the etch rates of (100) and (111) silicon wafers were 1.36 and 1.57 Å/cycle, respectively, which correspond to one atomic layer of the respective silicon surfaces.

To obtain one atomic layer etching, the silicon surface should be covered with one monolayer of silicon chloride before the Ar neutral beam irradiation. Figure 3 shows the effect of Cl₂ pressure on the silicon etch rate (Å/cycle) for two different Ar neutral beam irradiation times.
The Cl₂ pressure was varied from 0.24 mTorr to 0.67 mTorr. As shown in the figure, the increase of Cl₂ pressure increased the silicon etch rate. However, when the Cl₂ pressure was higher than 0.24 mTorr, the etch rates of both the silicon (100) and the silicon (111) were saturated independent of Cl₂ pressure. It is known that Cl₂ is chemisorbed on the silicon surface by the Langmuir isotherm and the coverage of chemisorbed silicon chloride (θ_{SiCl₂}) on the silicon surface is represented by the following equation

\[ \theta_{SiCl₂} = \frac{k_2 P_{Cl₂}}{1 + k_2 P_{Cl₂}} \]

where \( k_2 \) is the adsorption rate constant and \( P_{Cl₂} \) is the Cl₂ pressure. \( k_2 \) is known to depend on the temperature of the substrate and the adsorption enthalpy. In this experiment, the substrate temperature was maintained at room temperature as shown in Table I, therefore, \( k_2 \) remained the same and, thus, the coverage of silicon chloride \( \theta_{SiCl₂} \) was dependent on the pressure of the Cl₂ \( P_{Cl₂} \). Therefore, when \( P_{Cl₂} \) is lower than a critical value (that is, 0.24 mTorr of Cl₂ pressure in Fig. 2), \( \sqrt{k_2 P_{Cl₂}} \) is less than 1, and the coverage is approximately represented as \( \theta_{SiCl₂} \approx \sqrt{k_2 P_{Cl₂}} \). When \( P_{Cl₂} \) is higher than the certain value, \( \sqrt{k_2 P_{Cl₂}} \) is higher than 1, and the coverage is represented approximately as \( \theta_{SiCl₂} \approx 1 \).

If the effects of the Ar neutral beam irradiation time and the coverage of silicon chloride on the silicon surface on the silicon etch rate are combined, the following equation on the self-limited silicon etch rate can be obtained

\[ E_{SiCl₂} \times k_1 \theta_{SiCl₂} f_{Ar neu} \quad \text{when} \quad f_{Ar neu} < f_{Ar crit} \]

\[ E_{SiCl₂} \times k_1 \theta_{SiCl₂} f_{Ar neu} \quad \text{when} \quad f_{Ar neu} \geq f_{Ar crit} \]

Therefore, the initial increase of the silicon etch rate with increasing Cl₂ pressure in Fig. 3 was related to the increase of coverage of silicon chloride on the silicon surface and the saturation of the silicon etch rate at high Cl₂ pressures was related to the saturation of silicon chloride on the silicon surface, that is, \( \theta_{SiCl₂} \approx 1 \). The saturated silicon (100) etch rates for both 480 and 780 s of Ar irradiation time were the same as one atomic layer per cycle due to the Ar neutral beam irradiation higher than \( f_{Ar neu} \) at \( \theta_{SiCl₂} = 1 \) for both conditions as shown in Fig. 2. However, in the case of the silicon (111) etch rates, the saturated silicon etch rate with 480 s of Ar neutral beam irradiation time was 1.22 Å/cycle, which is less than one atomic layer per cycle, while the saturated silicon etch rate with 780 s of the Ar neutral beam irradiation time was 1.57 Å/cycle, which is one atomic layer per cycle. The lower (111) silicon etch rate than one atomic layer per cycle at 480 s of Ar irradiation time was related to the unsaturated Ar neutral beam dose \( f_{Ar neu} \) at \( \theta_{SiCl₂} = 1 \) as represented by the Eq. 5 and as shown for the region 1 and 2 in Fig. 2.

Using the self-limited atomic layer etching conditions, the etch depth and etch rate of silicon (100) and (111) were measured for different etch cycles. The results are shown in Fig. 4. Cl₂ pressure was maintained at 0.46 mTorr which is higher than 0.24 mTorr \( (\theta_{SiCl₂} \approx 1) \) and the Ar neutral beam irradiation time was kept at 780 s \[ f_{Ar neu} > f_{Ar crit} \] for both silicon (100) and (111). As shown in the figure, with the etching conditions, the etch depth per cycle remained exactly same as 1.36 and 1.57 Å/cycle and for (100) and (111) silicon wafers, respectively, and therefore, the etch depth could be controlled exactly with the number of etch cycles.

In conclusion, the ALET of silicon (100) and (111) was conducted by Cl₂ adsorption followed by the desorption of silicon chloride using an Ar neutral beam irradiation instead of Ar⁺ ion beam irradiation to etch silicon without charging damage. The result showed that, the etch rates of silicon were dependent on the Cl₂ pressure and Ar neutral beam irradiation time, and by maintaining enough Cl₂ pressure \( (\theta_{SiCl₂} \approx 1) \) and enough Ar neutral beam irradiation dose \( (f_{Ar neu} \gg f_{Ar crit}) \), one atomic layer etching per cycle of 1.36 Å/cycle for silicon (100) and 1.57 Å/cycle for silicon (111) could be obtained, therefore, the exact etch depth control without charging damage was possible.

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