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# Surface Roughness Variation during Si Atomic Layer Etching by Chlorine Adsorption Followed by an Ar Neutral Beam Irradiation

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In this study, the etch rate and surface roughness during the Si atomic layer etching using $Cl_2$ and Ar neutral beam were investigated for Si(100) and Si(111). When the $Cl_2$ pressure (flux) and the Ar neutral beam irradiation time (dose/cycle) were lower than the critical values, the etch rate (Å/cycle) and the surface roughness were varied with $Cl_2$ pressure and Ar neutral beam irradiation time. When both $Cl_2$ pressure and Ar neutral beam irradiation time were higher than the critical values, the saturated etch rates of a monolayer per cycle of 1.36 and 1.57 Å/cycle for Si(100) and Si(111), respectively, and the lowest surface roughness of 1.45Å close to the reference sample could be obtained. From these results, it is believed that the silicon etching is controlled by the coverage of silicon chloride during the $Cl_2$ adsorption by the Langmuir isotherm and the removal of the silicon chlorides by the Ar neutral beam dose/cycle (atom/$cm^2$ cycle).
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According to Moore's rule, the critical dimensions of devices for the silicon integrated circuit have decreased continuously, and it has reached to near tens of nanometer in the devices for research and development. However, to obtain working nanometer-scale devices, various practical issues have to be resolved and some of them are etch-related issues such as precise controllability of etch depth and the removal of damage during the etching.[1-4] 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. Therefore, to achieve atomic scale etch controllability without physically damaging the surface for nanoscale devices, atomic layer etching (ALET) has been investigated by many researchers.[5-10]

Generally, the ALET of silicon using halogen gases such as $Cl_2$ is a cyclic process consisting of four sequential steps: (*i*) adsorption of $Cl_2$ on the Si surface, (*ii*) evacuation, (*iii*) $Ar^+$ ion beam irradiation to the $Cl_2$ adsorbed surface for the desorption of Si-$Cl_x$ chemisorbed species, (*iv*) evacuation of the Si-$Cl_x$ etch products. But, during the desorption step with $Ar^+$ ion beam irradiation, the device may be damaged electrically due to the charged particles such as positive ions generated in the plasma. In addition, the reported etch rates are different among the researchers because the ALET mechanism is not understood exactly.

In this letter, the ALET of Si was carried out using an Ar neutral beam irradiation instead of an $Ar^+$ ion beam irradiation to avoid possible charge-related damage during the cyclic process. To study the Si ALET mechanism by $Cl_2$ adsorption and an Ar neutral beam irradiation, the Si etch rates and the variation of surface roughness as functions of $Cl_2$ pressure (flux) and Ar neutral beam irradiation time (dose/cycle) for different substrate orientations have been investigated.

The low energy Ar neutral beam was generated by a low-angle forward reflected neutral beam technique. A low-angle forward reflected neutral beam source was composed of a 2 MHz radio frequency (rf) ion gun and a low angle planar reflector. A two-grid inductively coupled plasma (ICP) type ion gun, which is made by Commomwealth Scientific (CS), Inc., was used as the ion source. The Ar neutral beam was formed by reflecting the $Ar^+$ ion beam from the parallel polished stainless steel plates at low angles. The neutralization efficiency of this neutral beam source was higher than 99%. In order to supply adequate energy to the Ar neutral beam, the voltage applied to the first grid located close to the ion source (accelerator grid) was maintained at 50 V, while the second grid was grounded. With the energy of the Ar neutral beams 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.[11] Between the neutral beam source and the substrate, an automatic shutter was installed to control 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. Details of the neutral beam source and the ALET system used in experiment are described elsewhere.[12-14] Typical experimental parameters are shown in Table I.

A typical sequence for the ALET process is shown in Fig. 1. One cycle of etching consists of four steps. During the first step, $Cl_2$ is introduced into the chamber for the duration of $t_{Cl_2}$. The $Cl_2$ does not spontaneously etch the silicon because Cl adsorbed on the silicon surface cannot desorb spontaneously at room temperature. During the second step, excess $Cl_2$ is exhausted, so that only the adsorbed chlorine remains on the silicon surface. During the third step, the Ar neutral beam irradiates the silicon surface and surface atoms bonded with chlorine are etched off by the Ar neutral-beam-induced chemical etching. During the fourth step, the chamber is evacuated, so that the etch products are purged after one cycle of ALET is completed. These steps are repeated.

The samples used in this experiment were p-type Si(100) and Si(111) wafers patterned with a photoresist. 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 DI water and blow drying with $N_2$ just before loading into the chamber. The etched step height was measured using a step profilometer (Tencor Instrument, Alpha Step 500). The measured step height was divided by the total number of ALET cycles to yield the etch rate (Å/cycle). An atomic force microscope (AFM, Thero-microscopes, CP Research) was used to measure the surface roughness.

Figure 2 shows the effect of $Cl_2$ pressure on the etch rate of Si ALET and the root-mean-square (rms) roughness of the silicon surface measured after the etching for 100 cycles. The Ar neutral beam irradiation time was maintained at 780 s while $Cl_2$ pressure was varied from 0 to 0.67 mTorr, which corresponds to the flux of chlorine molecules incident on the silicon surface from 0 to 1.73 $\times 10^{17}$ molecules/$cm^2$ s. As shown in the figure, when the Ar neutral beam was irradiated without $Cl_2$ adsorption, extremely small silicon etch rates of about 0.15 Å/cycle were obtained for both Si(100) and Si(111), and the rms roughness was also small for both Si(100) and Si(111) as 1.691 and 1.352 Å, respectively. The extremely small etch rate by the Ar neutral beam without $Cl_2$ is be-

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**Table I. Typical experimental parameters of Si ALET.**

| | |
|---|---|
| Base pressure | $2.0 \times 10^{-6}$ Torr |
| Chamber pressure | $2.5 \times 10^{-4}$ Torr |
| Inductive power | 800 W |
| Acceleration grid voltage | 50 V |
| Ar flow rate | 10 sccm |
| Ar neutral beam irradiation time ($t_{open}$) | 60 ~ 840 s |
| $Cl_2$ pressure | 0 ~ 0.67 mTorr |
| $Cl_2$ supply time ($t_{Cl_2}$) | 20 s |
| Substrate temperature | Room temperature |

lieved to be from the low sputter etch yield of silicon at the low neutral beam energy less than 50 eV. However, with the increase of $Cl_2$ pressure during the $Cl_2$ adsorption stage, as shown in Fig. 2, the etch rates for Si(100) and Si(111) were increased and were finally saturated near the $Cl_2$ pressure of 0.24 mTorr. The saturated silicon etch rates were 1.36 Å/cycle for Si(100) and 1.57 Å/cycle for Si(111), which corresponds to one monolayer/cycle. With the increase of $Cl_2$ pressure up to 0.14 mTorr, the etched silicon surface roughness was increased to 4.719 and 4.179 Å for Si(100) and Si(111), respectively. However, the further increase of $Cl_2$ pressure to 0.24 mTorr decreased the etched silicon surface roughness for both Si(100) and Si(111) to 1.45 Å. The further increase of $Cl_2$ pressure did not change the surface roughness significantly.

The variation of silicon etch rate and surface roughness shown in Fig. 2 is related to the formation of silicon chlorides on the silicon surface with the addition of $Cl_2$ and the change of silicon chloride coverage ($\theta_{SiCl_x}$) with $Cl_2$ pressure. When the silicon surface is exposed to $Cl_2$, chlorine is adsorbed on the silicon surface by the Langmuir isotherm, therefore, the silicon chloride formed on the silicon surface is limited by a single layer and also the coverage ($\theta_{SiCl_x}$) of the silicon chloride is represented by $\theta_{SiCl_x} = \sqrt{k_1 P_{Cl}}/1 + \sqrt{k_1 P_{Cl}}$.[15] Here, $k_1$ is the adsorption rate constant and $P_{Cl}$ is the $Cl_2$ gas pressure. $k_1$ is dependent on the adsorption enthalpy and system temperature. However, in this experiment, the substrate was kept at room temperature, therefore, $k_1$ can be regarded as a constant, and the coverage ($\theta_{SiCl_x}$) is only dependent on the $Cl_2$ pressure ($P_{Cl}$).[15] When silicon chloride is formed on the silicon surface by the Langmuir isotherm, due to the electron transfer from Si-Si to Si-Cl, the Si-Si bonding is easily broken compared to Si-Cl bonding during the bombardment by energetic particles,[16]

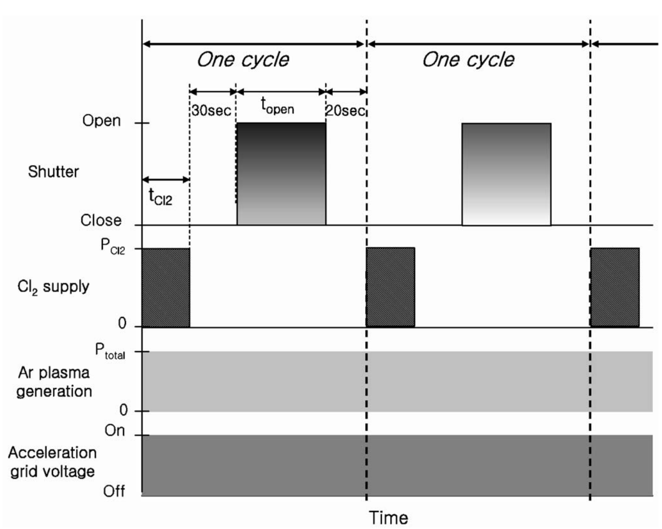


**Figure 1.** The sequence of the atomic layer etching process used in this experiment.

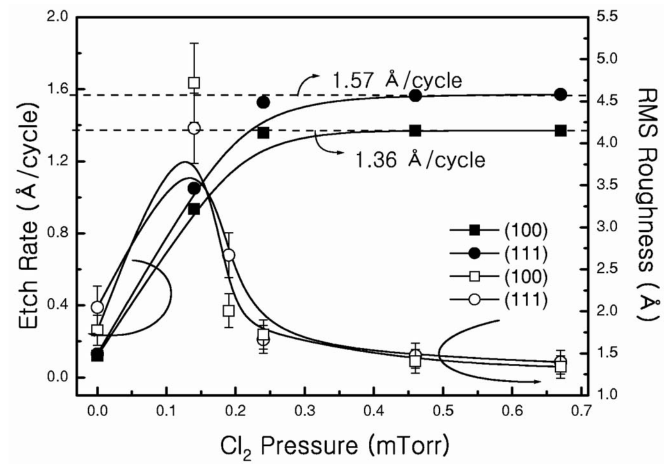


**Figure 2.** Silicon etch rate (Å/cycle) by the ALET and the surface roughness variation as a function of $Cl_2$ pressure from 0 to 0.67 mTorr which corresponds to the flux of chlorine molecules incident on the silicon surface from 0 to $1.73 \times 10^{17}$ molecules/$cm^2$ s. (Process conditions were inductive power, 800 W; acceleration grid voltage, 50 V; Ar neutral beam irradiation time, 780 s; and $Cl_2$ gas supply time, 20 s).

therefore, Si surface atoms bonded to Cl atoms are removed during the Ar neutral beam irradiation. Especially, when the Ar neutral beam dose/cycle is higher than the surface atomic density of Si(100) and Si(111), that is $6.78 \times 10^{14}/cm^2$ for Si(100) and $7.83 \times 10^{14}/cm^2$ for Si(111), the silicon etch rate is changed with the coverage of Cl adsorption which is dependent on the $Cl_2$ pressure (flux). The dependence of silicon etching on the removal of Si-Cl bonds formed on the silicon surface can be understood by the Si surface roughness measured by atomic force microscopy. The initial increase of surface roughness with $Cl_2$ pressure up to 0.14 mTorr ($3.6 \times 10^{16}$ molecules/$cm^2$ s) is related to the removal of silicon only from the area covered by the chlorine ($\theta_{SiCl_x}$) during the each cycle, where $\theta_{SiCl_x}$ is less than 0.5. However, with the increase of $\theta_{SiCl_x}$ higher than 0.5 with increasing $Cl_2$ pressure, the roughness is decreased and, when the $\theta_{SiCl_x}$ is 1.0, the minimum surface roughness is obtained due to the removal of a silicon monolayer per cycle. Due to the monolayer adsorption of chlorine on the silicon surface by the Langmuir isotherm, it is believed that most of the etch product by the ALET is silicon monochloride (SiCl).

If the Ar neutral beam dose/cycle (atom/$cm^2$ × cycle) is lower than a critical value, even though the $Cl_2$ coverage is 1.0, the silicon etching by a monolayer per cycle cannot be obtained. Figure 3 shows the effect of the Ar neutral beam dose/cycle on the silicon etch rate and silicon rms roughness measured by AFM for both Si(100) and Si(111) at the $Cl_2$ pressure of 0.46 mTorr ($1.19 \times 10^{17}$ molecules/$cm^2$ s) which is pressure higher than the critical pressure for $\theta_{SiCl_x} = 1$. To change the Ar neutral beam dose/cycle, Ar neutral beam irradiation time was varied while keeping the acceleration voltage for the $Ar^+$ ion gun at 50 V. The $Ar^+$ ion flux measured by a Faraday cup before the reflection at 50 V of the acceleration voltage was $3.08 \times 10^{12}$ ions/$cm^2$ s. However, due to the difficulty in measuring the neutral flux after the reflection, the exact Ar neutral beam flux could not be estimated. As shown in Fig. 3, the silicon etch rate was increased with the increase of the Ar neutral beam irradiation time up to 480 s for Si(100) and 780 s for Si(111) and the further increase of Ar neutral beam irradiation time saturated the etch rate to one monolayer per cycle. In the case of Si rms roughness, the increase of Ar neutral beam irradiation time decreased the roughness continuously until the saturation of the etch rate was reached and the further increase of the Ar neutral beam irradiation time did not change the roughness significantly for both Si(100) and Si(111). The increase of the silicon etch rates with the increase of Ar

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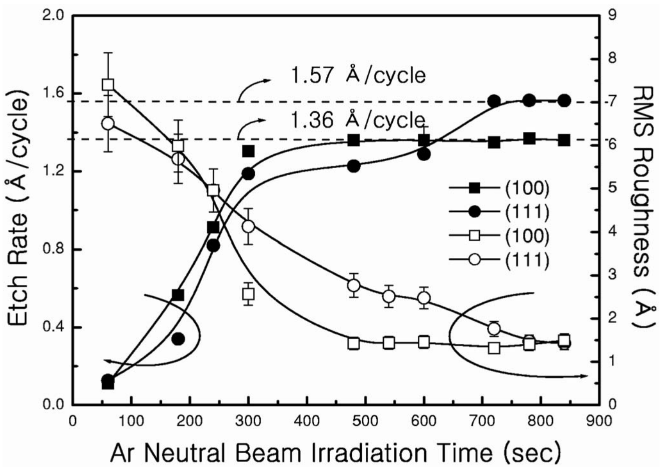


**Figure 3.** Silicon etch rate (Å/cycle) by Si ALET and the surface roughness variation as a function of Ar neutral beam irradiation time. (Process conditions were inductive power, 800 W; acceleration grid voltage, 50 V; $Cl_2$ gas supply time, 20 s; and $Cl_2$ gas pressure, 0.46 mTorr.) The $Ar^+$ ion flux measured by a Faraday cup before the reflection at 50 V of the acceleration voltage was $3.08 \times 10^{12}$ ion/$cm^2$ s. However, due to the difficulty in measuring the neutral flux after the reflection, the exact Ar neutral beam flux could not be estimated.

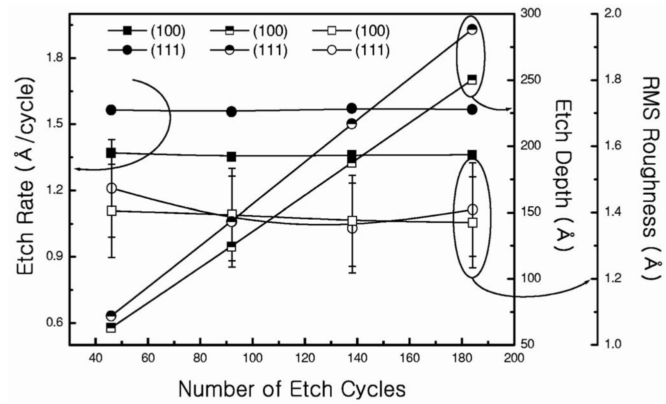


**Figure 4.** Silicon etch depth and etch rate (Å/cycle) by Si ALET and the surface roughness variation as a function of the number of etch cycles. (Process conditions were inductive power, 800 W; acceleration grid voltage, 50 V; Ar neutral beam irradiation time, 780 s; $Cl_2$ gas supply time, 20 s, and $Cl_2$ pressure, 0.46 mTorr.)

neutral beam irradiation time is from the increased silicon chlorides removed from the surface by the increased energetic particle dose/cycle (atom/$cm^2$ cycle) and the saturation of the silicon etch rates is related to the removal of one monolayer of silicon by the sufficient flux of Ar energetic particles. The longer Ar neutral beam irradiation time for Si(111) compared to Si(100) is partially related to the higher surface atomic density. The silicon etching characteristics with Ar neutral beam irradiation time can be also understood by the measured surface roughness. The decrease of Si rms roughness with increasing Ar neutral beam irradiation time is related to the removal of more silicon chlorides which are formed on the surface, therefore, it is related to the suppression of silicon rms roughness caused by the partial removal of silicon chlorides on the surface during each cycle. The roughness is finally minimized at about 1.45 Å for both Si(100) and Si(111) by the complete removal of the silicon chloride, during each cycle. This roughness is similar to that measured for the nonetched reference; therefore, it is believed that the etching is controlled by the removal of silicon chlorides formed on the surface through the Ar neutral particle bombardment, not by sputter etching of silicon or the spontaneous vaporization of silicon chlorides.

Figure 4 shows the silicon etch rate, etch depth, and rms roughness measured as a function of etch cycles for the etch conditions of a monolayer etching per cycle. The $Cl_2$ pressure was 0.46 mTorr, and the Ar neutral beam irradiation time was 780 s for both Si(100) and Si(111). As shown in the figure, with the increasing number of etch cycles, the etch depth was increased linearly while the etch rate remained at 1.36 and 1.57 Å/cycle for Si(100) and Si(111), respectively. Also, the Si rms roughness remained similar at close to 1.45 Å for both Si(100) and Si(111) regardless of the number of etch cycles. These results show that the Si etch depth can be precisely controlled by adjusting the etch cycles while keeping the monolayer etching conditions.

In this study, the etch characteristics of ALET using $Cl_2$ and Ar neutral beams were investigated for Si(100) and Si(111) and their etch mechanisms were studied. When the $Cl_2$ pressure (flux) and the Ar neutral beam irradiation time (dose/cycle) were lower than the critical values {$Cl_2$ pressure, $>0.24$ mTorr; Ar neutral beam irradiation time, $>480$ s for Si(100) and $>780$ s for Si(111)}; the silicon etch rate (Å/cycle) and the silicon surface roughness were varied with $Cl_2$ pressure and Ar neutral beam irradiation time. However, by using a $Cl_2$ pressure higher than the critical pressure followed by supplying more than the critical Ar neutral beam irradiation time, the constant etch rate of a monolayer per cycle (1.36 and 1.57 Å/cycle for Si(100) and Si(111), respectively) and the lowest surface roughness of 1.45 Å close to the reference sample could be obtained regardless of $Cl_2$ pressure and Ar neutral beam irradiation time. From the dependence of etch rate and surface roughness on the $Cl_2$ pressure and Ar neutral beam irradiation time, it can be concluded that the silicon etching by ALET is controlled by the coverage ($\theta_{SiCl_x}$) of silicon chloride on the silicon surface by the Langmuir isotherm and the removal of the silicon chlorides by the Ar neutral beam flux (atom/$cm^2$ cycle).

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