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Atomic Layer Etching of Cl-Adsorbed Silicon by Using a Low-Angle Forward Reflected Ar Neutral Beam

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Atomic layer etching (ALET) of Si has been carried out using Cl_2 adsorption followed by irradiation with an Ar neutral beam generated by using low angle forward reflection of an Ar^+ ion beam. The etch rate of (100) Si was saturated exactly at one monolayer per cycle (1.36 Å/cycle) and was independent of the Cl_2 pressure and the irradiation time of the Ar neutral beam. These results indicate that Si etching by using ALET is determined by a self-limited mechanism which is composed of chemisorption of Cl_2 by the dissociative Langmuir isotherm and of preferential etching of the silicon chloride formed during the adsorption period of Cl_2 by the Ar neutral beam due to the differences in the binding energies between silicon-to-silicon and silicon-to-silicon chloride.

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I. INTRODUCTION

Atomic layer etching (ALET) is expected to be one of the important processes for the fabrication of future devices, such as nano-scale devices, quantum devices, *etc.* [1, 2] 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. For Si devices, ALET of Si has been carried out using sequential steps composed of the adsorption of a reactant gas, such as chlorine [3–8] or fluorine [9], to the silicon surface and the desorption of silicon halides on the silicon surface by using a low-energy Ar^+-ion beam irradiation. If ALET is to be achieved, a self-limited mechanism determined by the thermodynamical saturation condition is essential [10], and the adsorption of Cl_2 on Si is well described by the dissociative Langmuir isotherm chemisorption [3]. In addition, the reactant gas and the Ar^+ ions should not induce spontaneous etching of Si and damage the exposed layer [11]. However, due to the use of Ar^+ ions for the desorption of silicon halides and, in some cases, due to the exposure to photons generated in the plasma, the previously investigated ALET methods may induce charging damage to nano-scale devices.

In fact, a decrease in the damage to the semiconductor occurring during plasma etching can be obtained by using neutral beam etching instead of conventional reactive ion etching. The damage to the gate oxide of the metal oxide semiconductor (MOS) device during the etching can be decreased by using a neutral beam. Lee *et al.* [12] showed that, for the capacitance-voltage (C-V) data of MOS devices exposed to an O_2 neutral beam and an O_2 inductively coupled plasma (ICP), the C-V of the MOS device exposed to the O_2 ICP was shifted compared to the reference sample, indicating charging damage to the gate oxide of the MOS device during the exposure to the O_2 ICP. However, in the case of MOS device exposed to the neutral beam, the C-V curve was similar to the reference, indicating insignificant damage to the device.

In this study, ALET of Si was carried out using Cl_2 adsorption followed by an Ar neutral beam irradiation, instead of an Ar^+ ion beam irradiation to avoid charge-related damage and exposure to the plasma that could cause other damage, such as ultra-violet (UV) ray damage, to next generation devices. The ALET etch characteristics of Si by Cl_2 were also investigated.

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II. EXPERIMENT

A low-energy Ar neutral beam was generated by using a low-angle forward reflected neutral beam technique. The low-angle forward reflected neutral beam source was composed of a 2-MHz radio-frequency (rf) ion source for the generation of a parallel Ar^+ ion beam and a low angle planar-reflector for the neutralization of the Ar^+ ion beam and the formation of a parallel Ar neutral beam. The details of the neutral beam source used in the experiment are described elsewhere [13, 14]. A two-grid commercial ICP-type ion gun, Commomwealth Scientific (CS) Inc, was used as the ion beam source. The neutralization efficiency by 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 with the shutter motion. Typical experimental parameters are shown in Table 1, and a typical sequence and time for the ALET process are shown in Fig. 1.

Table 1. Typical experimental parameters for ALET used in the experiment.

Base pressure	2.0×10^{-6} Torr
Chamber pressure	2.5×10^{-4} Torr
Inductive power	800 Watts
Acceleration grid voltage	50 Volts
Ar flow rate	10 sccm
Ar neutral beam irradiation time (t_{open})	60 $\sim$ 600 sec
Cl_2 pressure	0 $\sim$ 0.67 mTorr
Cl_2 supply time (t_{Cl_2})	20 sec
Substrate temperature	RT

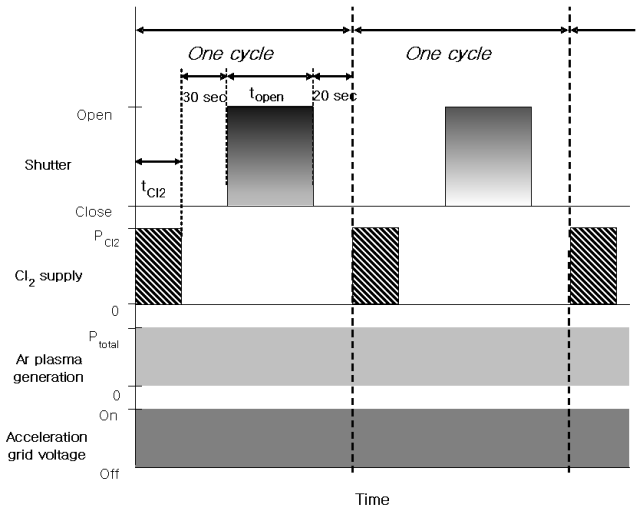

Fig. 1. Sequence of the ALET process used in this experiment.

The samples used in this experiment were p-type (100) Si wafers patterned with a photoresist. The samples were dipped in a buffered HF solution to remove remaining native oxide on the Si wafers, rinsed with DI water, and blow dried with N_2 just before being loaded into the chamber. To remove the remaining native oxide further, in addition to the HF solution, we sputtered the samples by using an Ar neutral beam from an ICP ion gun at an acceleration grid voltage of 200 V for 3 min just before the ALET experiment. 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 per cycle.

III. RESULTS AND DISCUSSION

Fig. 2 shows the (100) Si etch rate measured as a function of the Cl_2 pressure. The process conditions are summarized in Table 1, and the Ar neutral beam irradiation time per cycle was varied from 180 to 480 s. The acceleration voltage of the ion gun was maintained at 50 V to minimize the damage to the silicon surface and to minimize the sputtering effect during the ALET. When the Ar neutral beam was irradiated on the (100) silicon surface without the Cl_2 adsorption with an acceleration voltage of 50 V, a very low Si sputter rate of less than 0.15 Å/cycle was obtained, similar to the simulation data obtained by Kubota *et al.* [15]. In fact, the Ar neutral beam irradiated the Cl_2 adsorbed silicon surface rather than the bare silicon surface during the etch cycle; therefore, the silicon sputter etch rate is believed to be negligible for the conditions used in this experiment.

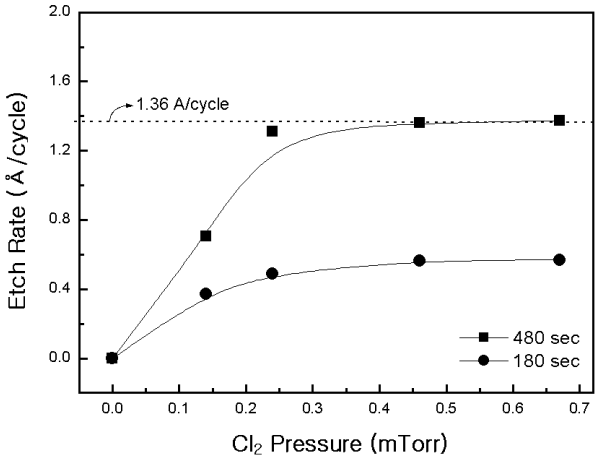

Fig. 2. Silicon etch rate per cycle by using ALET as a function of Cl_2 pressure (mTorr). The inductive power was 800 Watts, the acceleration grid voltage was 50 Volts, the Ar neutral beam irradiation time was 180 and 480 sec, and the Cl_2 gas supply time was 20 sec.

As Fig. 2 shows, when the Cl_2 pressure is lower than 0.24 mTorr, the silicon etch rate increased with increasing Cl_2 pressure; however, when the Cl_2 pressure was higher than 0.24 mTorr, the silicon etch rate was saturated. The saturated silicon etch rate for the Ar neutral beam irradiation time with 180 s per cycle was 0.57 Å/cycle. When the Ar neutral beam irradiation time per cycle was increased to 480 s, the silicon etch rate was increased to 1.36 Å/cycle, which is one atomic layer per cycle for (100) Si, and was independent of the Cl_2 pressure. The initial increase and the saturation of the silicon etch rate with Cl_2 pressure can be explained by the coverage area of the Si-Cl bonds on the silicon surface with increasing Cl_2 pressure. In general, silicon atoms on the (100) Si surface are reconstructed and form buckled silicon dimers to sustain thermodynamically stable states, so, when the (100) silicon surface is exposed to Cl_2, Cl_2 is dissociatively chemisorbed onto the dangling bonds of the buckled dimmers to form SiCl [16,17], as shown by [18]:

$$Cl_{2(g)} + 2Si_{(ad)} \xrightarrow{k_1} 2SiCl_{(ad)} \quad (1)$$

where k_1 is the Cl_2 adsorption rate constant. As the Cl_2 is chemically adsorbed on the silicon surface, the coverage of Si-Cl bonds on the silicon surface is increased, and the coverage of Si-Cl bonds on the (100) silicon surface can be expressed by Eq. (2), which corresponds to the Langmuir isotherem [19]:

$$\theta_{SiCl} = \frac{\sqrt{k_1 P_{Cl}}}{1 + \sqrt{k_1 P_{Cl}}} \quad (2)$$

where k_1 is the adsorption rate constant shown in Eq. (1) and P_{Cl} is the Cl_2 pressure. k_1 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 1; therefore, k_1 remained the same. Thus, the coverage of Si-Cl bonds (θ_{SiCl}) depended on the pressure of the Cl_2 (P_{Cl}) [19], and when P_{Cl} was lower than a critical value (that is, 0.24 mTorr of Cl_2 pressure in Fig. 2), $\sqrt{k_1 P_{Cl}}$ was less than 1, and the coverage could be approximately represented as $\theta_{SiCl} \approx \sqrt{k_1 P_{Cl}}$. On the other hand, when P_{Cl} was higher than the critical value, $\sqrt{k_1 P_{Cl}}$ was higher than 1, and the coverage could be approximately represented as $\theta_{SiCl} \approx 1$. Therefore, the coverage of the Si-Cl bonds on the (100) silicon surface increased initially with increasing of Cl_2 pressure initially; however, the coverage of Si-Cl bonds eventually saturated when the Cl_2 pressure was high enough. A further increase in the Cl_2 pressure after the formation of one Si-Cl monolayer will induce excessive Cl_2 on the silicon surface, and these excessive Cl_2 molecules could be physisorbed on the silicon surface. However, due to the low binding energy between Cl_2 molecules and Si-Cl bonds caused by the van der Waals force, the physisorbed Cl_2 molecules are easily removed by an extremely low external energy

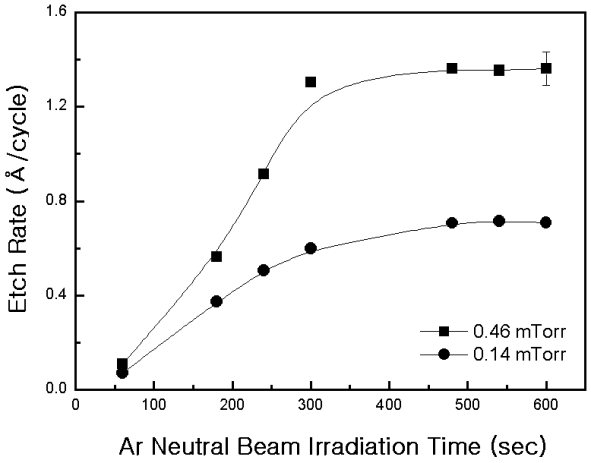

Fig. 3. Silicon etch rate per cycle by ALET as a function of Ar neutral beam irradiation time. The inductive power was 800 Watts, the acceleration grid voltage was 50 Volts, the Cl_2 gas supply time was 20 sec, and the Cl_2 pressure was 0.14 and 0.46 mTorr.

[20]. The bond strengths of Si-Cl and Si-Si are 3.393 eV and 4.215 eV, respectively [21]; therefore, the removal of SiCl from the silicon surface is easier than the removal of Si atoms from the silicon surface. By the application of energetic particles having energies between the threshold energy required to remove SiCl and that required to remove silicon atoms from the (100) silicon surface, a preferential removal of SiCl can be achieved. Therefore, the coverage of Si-Cl bonds is proportional to the silicon etch rate shown in Fig. 2 when particles are bombarded of sufficient energy to the surface. In this experiment, an Ar neutral beam formed by the reflection of an ion beam extracted from an ion gun having an energy of 50 eV was used, and, by the application of a Cl_2 pressure of more than 0.24 mTorr to form one-monolayer of Si-Cl bonds, a self-limited one monolayer silicon etching per cycle was obtained.

Even though one monolayer of Si-Cl bonds is formed on the silicon surface and energetic particles having energies above the threshold energy bombarded the surface, one monolayer of silicon can not be etched away per cycle if the flux of energetic particles is not high enough. Fig. 3 shows the effect of the Ar neutral beam irradiation time on the silicon etch rate; the Cl_2 pressure was varied from 0.14 to 0.46 mTorr. As Fig. 3 show, when the pressure of Cl_2 was 0.46 mTorr, θ_{SiCl}, the coverage of Si-Cl bonds, was close to 1, and when the pressure of Cl_2 was 0.14 mTorr, θ_{SiCl} was less than 1. As Fig. 3 shows, when the Ar neutral beam irradiation time per cycle was lower than 300 s, the silicon etch rate increased with the Ar neutral beam irradiation time; however, when the irradiation time per cycle was higher than 300 s, the silicon etch rate was saturated at 1.36 Å/cycle for 0.46 mTorr of Cl_2 pressure and at 0.71 Å/cycle for 0.14 mTorr of Cl_2, regardless of the irradiation time. The etching of SiCl

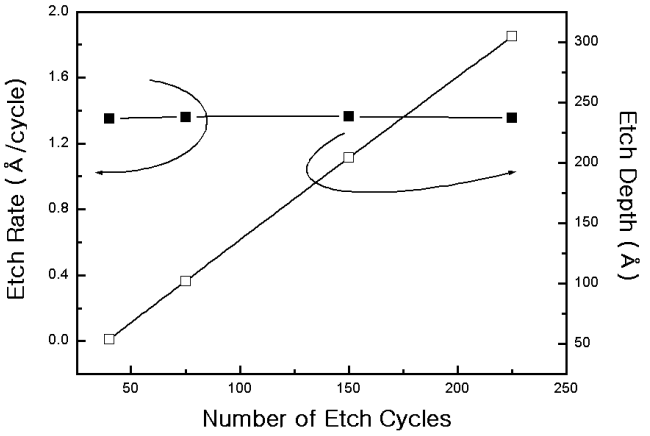

Fig. 4. Silicon etch depth and etch rate per cycle by ALET as a function of the number of etch cycles. The inductive power was 800 Watts, the acceleration grid voltage was 50 Volts, the Ar neutral beam irradiation time was 480 sec, the Cl_2 gas supply time was 20 sec, and the Cl_2 pressure was 0.46 mTorr.

from the silicon surface can be expressed as.

$$SiCl_{(ad)} \xrightarrow{k_2, Ar_{neu}} SiCl_{(g)} \quad (3)$$

If the Cl_2 adsorption process shown in Eq. (1) is included, the silicon etching during the Cl_2 atomic layer etching can be expressed as [18].

$$f_{SiCl} \propto k_2 \theta_{SiCl} f_{Ar_{neu}} \text{ when } f_{Ar_{neu}} \leq f_{Ar_{crit}} \quad (4a)$$

and

$$f_{SiCl} \propto k_2 \theta_{SiCl} \text{ when } f_{Ar_{neu}} > f_{Ar_{crit}} \quad (4b)$$

where f_{SiCl} is the removed SiCl from the Cl_2 adsorbed silicon surface, k_2 is the desorption rate constant, $f_{Ar_{neu}}$ is the Ar energetic neutral beam dose related to the Ar neutral beam irradiation time, and $f_{Ar_{crit}}$ is the critical Ar energetic neutral beam dose required to remove one monolayer of SiCl from the (100) silicon surface. Therefore, the ALET of silicon depends on θ_{SiCl} and $f_{Ar_{neu}}$ until the critical values of θ_{SiCl} and $f_{Ar_{neu}}$ are reached, and when $\theta_{SiCl} = 1$ and $f_{Ar_{neu}} > f_{Ar_{crit}}$, the ALET of silicon no longer depends on θ_{SiCl} and $f_{Ar_{neu}}$ and shows a constant silicon etch rate of one monolayer of (100) silicon per cycle.

Fig. 4 shows the silicon etch rate (Å/cycle) and the etch depth of silicon measured as functions of the number of etch cycles for the etch condition of a self-limited one-monolayer silicon etching. 0.46 mTorr of Cl_2 and a 480 s Ar neutral beam irradiation time were used to obtain a one-monolayer (100) silicon etching per cycle. As the figure shows, even though the number of etch cycles increased from 50 to 225 cycles, the silicon etch rate remained the same, 1.36 Å/cycle. Also, the etch depth increased linearly with the number of etch cycles; therefore, precise etch depth control can be obtained by varying of the number of etch cycles.

IV. CONCLUSIONS

In this study, by forming Si-Cl bonds on the (100) silicon surface and by bombarding the surface with a low energy neutral beam for the desorption of SiCl, we could obtain a precise self-limited etching of (100) silicon corresponding to one monolayer (1.36 Å/cycle). Obtaining that the precise etch rate required that the Cl_2 pressure be higher than a certain critical value (> 0.24 mTorr). Also, a neutral beam energy between the threshold energy required to remove SiCl and that required to remove silicon atoms from the (100) silicon surface and a neutral beam dose high enough to remove all of the Si-Cl bonds were required to obtain precisely one monolayer of silicon etching per cycle. We believe that, by using a neutral beam, instead of an ion beam, for the desorption of Si-Cl bonds, the precise ALET without charging damage required for next-generation silicon-device etching can be obtained.

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