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Atomic Layer Etching of Si(100) and Si(111) Using Cl_2 and Ar Neutral Beam

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Atomic layer etching of Si(100) and Si(111) was carried out using Cl_2 adsorption followed by the Ar neutral beam irradiation for the removal of charging damage during the etching. By supplying Cl_2 and Ar neutrals higher than the critical doses, the exact same depth per cycle corresponding to one atomic layer per cycle of 1.36 Å/cycle for silicon (100) and 1.57 Å/cycle for silicon (111) could be obtained by a self-limited etching mechanism. The critical Cl_2 pressure and Ar neutral beam irradiation time corresponded to one monolayer chemisorption of chlorine by the dissociative Langmuir isotherm and the irradiation of Ar neutral beam was enough to remove one layer of silicon chloride formed on the silicon surfaces, respectively.
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Atomic layer etching (ALET) can be an indispensable method for the fabrication of future devices such as nanoscale 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.

ALET technology has been investigated since the early 1990s for GaAs and Si devices.[3-9] To achieve ALET, many cycles of sequential steps consisting of the adsorption of halogen gas such as chlorine[3-8] or fluorine[9] and the desorption of the formed halide by heat, laser, or Ar^+ 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[9] and 0.68 ~ 1.36 Å/cycle[6-8] and 0.52 Å/cycle[8] were reported for the silicon (100) and (111) etchings by Cl_2 gas, respectively. In addition, for the anisotropic etching of the silicon during the ALET, directional Ar^+ 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 photoreflectance spectroscopy (PRS) data of GaAs etched using Cl_2 neutral beam and Cl_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_2 ICP showed the change of the PRS curve compared to nonetched reference GaAs while the GaAs etched using the Cl_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 damage to the gate oxide of metal oxide semiconductor (MOS) device during the etching can also be decreased by using a neutral beam. Figure 1b shows the capacitance-voltage (C-V) data of the metal oxide semiconductor (MOS) devices exposed to an O_2 neutral beam and an O_2 ICP. The dielectric material of the MOS device was composed of Si_3N_4(50 nm)/SiO_2(2 nm) and the size of the MOS device was 200 × 200 μm. For comparison, the exposure time was maintained until a 1.5 μm thick photoresist was removed, which corresponds to 30 min for the O_2 neutral beam and 2 min for the O_2 ICP. As shown in the figure, the C-V of the MOS device exposed to the O_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_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^+ ion beam to avoid charge-related damage during the desorption of the halide and its ALET characteristics of Si by Cl_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^+ 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. A two-grid commercial ICP-type ion gun, which was made by Commomwealth 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.[10] Also, the contamination of the silicon surface by the sputtering of the reflector plate during the ALET was negligible due to the low Ar^+ ion energy and the low reflection angle. The measured neutralization efficiency of the Ar^+ 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_2 feed time, the Cl_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.[11,12]

In this experiment, p-type Si(100) and (111) wafers patterned with a photoresist 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_2 just before loading into the chamber. The etched 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)

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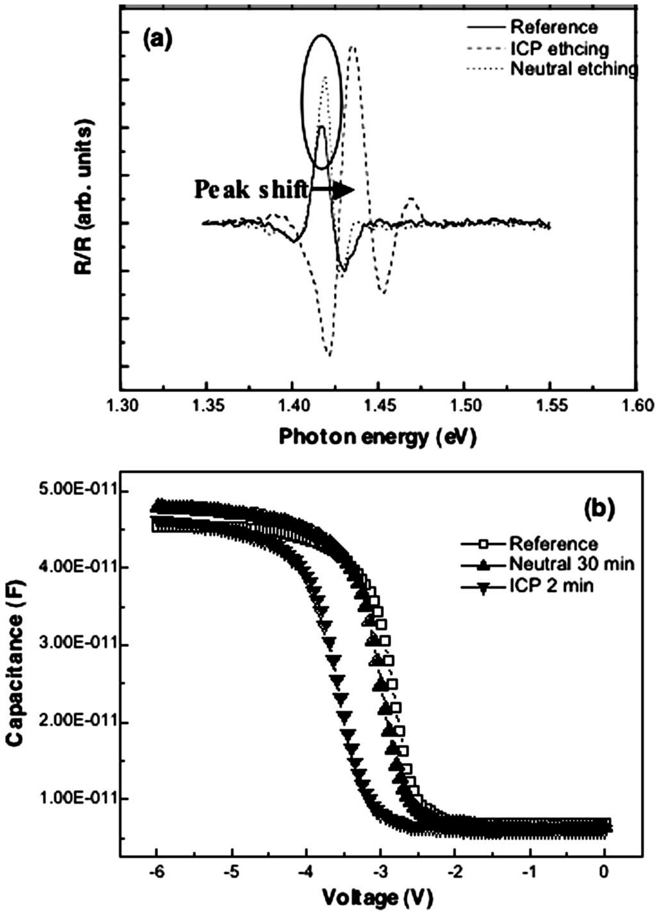

Figure 1. (a) Photoreflectance spectroscopy data of GaAs etched by a Cl_2 neutral beam and a Cl_2 ICP. For the comparison, not only the etch depth but also the energy of the neutral beam and the bias voltage of the ICP etching were maintained the same at 70 nm and 400 V, respectively. (b) C-V characteristics of a MOS device exposed to an O_2 ICP and an O_2 neutral beam. The MOS devices were exposed to both conditions until a 1.5 μm thick photoresist was removed.

wafers. The Cl_2 pressure was maintained at 0.46 mTorr and the Ar neutral beam irradiation time was varied from 60 to 840 s. As shown in the figure, the silicon etch rate measured as a function of the Ar irradiation time could be divided into three regions. Region 1 is the region where the etch rates of both silicon (100) and silicon (111) increase linearly with increasing Ar irradiation time. Region 2 is the region where the etch rate of silicon (100) is saturated, however, the etch rate of silicon (111) is still increased with increasing Ar irradiation time. Region 3 is the region where the etch rates of both silicon (100) and silicon (111) are saturated. The differences in

Table I. Typical experimental parameters of the neutral beam ALET used in this experiment.

Base pressure	2.0×10^{-6} Torr
Chamber pressure	2.5×10^{-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

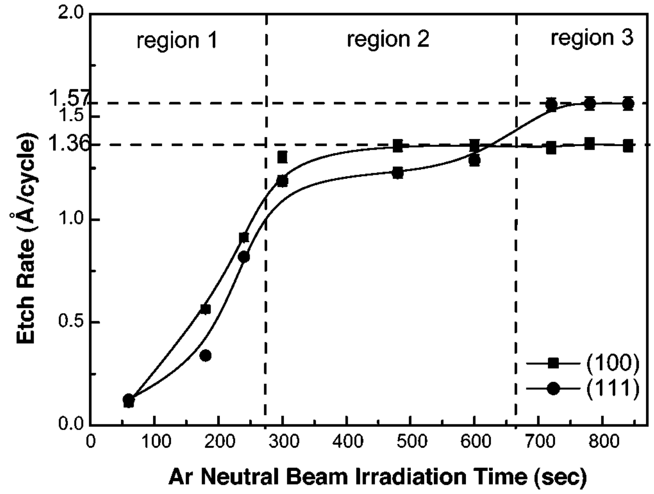

Figure 2. Silicon etch rate by neutral beam ALET as a function of Ar neutral beam irradiation time. (Process condition: acceleration grid voltage, 50 V, and Cl_2 gas pressure, 0.46 mTorr.)

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 $6.78 \times 10^{14}/cm^2$ and $7.83 \times 10^{14}/cm^2$, 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

$$E_{SiCl_x} \propto k_1 f_{Ar_{neu}} \text{ when } f_{Ar_{neu}} < f_{Ar_{crit}} \quad [1]$$

$$E_{SiCl_x} \propto k_1 f_{Ar_{crit}} \text{ when } f_{Ar_{neu}} \geqslant f_{Ar_{crit}} \quad [2]$$

where k_1 is the desorption rate constant, E_{SiCl_x} is the silicon etch rate (Å/cycle), $f_{Ar_{neu}}$ 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 $SiCl_x$ on the silicon surface. From Fig. 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 $f_{Ar_{crit}(100)}$ 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 Cl_2 pressure on the silicon etch rate (Å/cycle) for two different Ar neutral beam irradia-

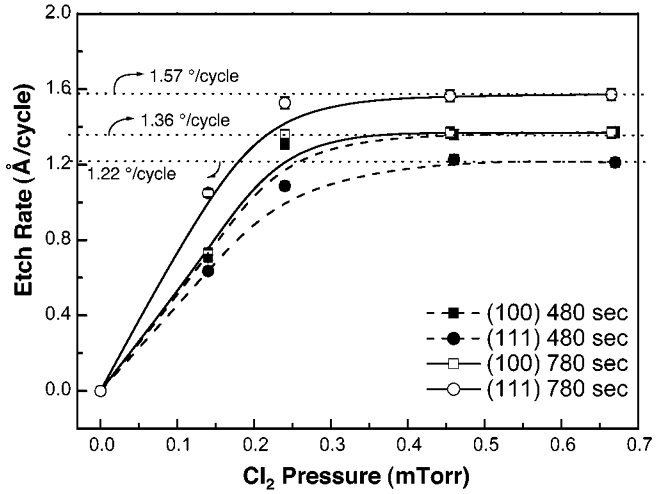

Figure 3. Silicon etch rate by neutral beam ALET as a function of Cl2 pressure. (Process condition: acceleration grid voltage, 50 V, Ar neutral beam irradiation time, 480 s, 780 s.)

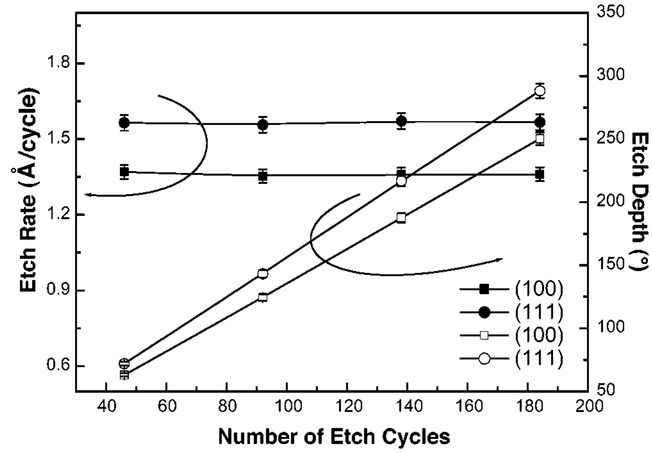

Figure 4. Silicon etch depth and etch rate by neutral beam ALET as a function of number of etch cycles. (Process condition: acceleration grid voltage, 50 V, Ar neutral beam irradiation time, 780 s, and Cl_2 gas pressure, 0.46 mTorr.)

tion time of 480 and 780 s. The Cl_2 pressure was varied from 0 to 0.67 mTorr. As shown in the figure, the increase of Cl_2 pressure increased the silicon etch rate. However, when the Cl_2 pressure was higher than 0.24 mTorr, the etch rates of both the silicon (100) and the silicon (111) were saturated independent of Cl_2 pressure. It is known that Cl_2 is chemisorbed on the silicon surface by the Langmuir isotherm[13] and the coverage of chemisorbed silicon chloride (θ_{SiCl_x}) on the silicon surface is represented by the following equation

$$\theta_{SiCl_x} = \frac{\sqrt{k_2 P_{Cl}}}{1 + \sqrt{k_2 P_{Cl}}} \qquad [3]$$

where k_2 is the adsorption rate constant and P_{Cl} is the Cl_2 pressure. k_2 is known to be dependent on the temperature of the substrate and the adsorption enthalpy.[13] 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 (θ_{SiCl_x}) was dependent on the pressure of the Cl_2 (P_{Cl}). Therefore, when P_{Cl} is lower than a critical value (that is, 0.24 mTorr of Cl_2 pressure in Fig. 2), $\sqrt{k_2 P_{Cl}}$ is less than 1, and the coverage is approximately represented as $\theta_{SiCl_x} \approx \sqrt{k_2 P_{Cl}}$. When P_{Cl} is higher than the certain value, $\sqrt{k_2 P_{Cl}}$ is higher than 1, and the coverage is represented approximately as $\theta_{SiCl_x} \approx 1$.

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

$$E_{SiCl_x} \propto k_1 \theta_{SiCl_x} f_{Ar_{neu}} \text{ when } f_{Ar_{neu}} < f_{Ar_{crit}} \qquad [4]$$

$$E_{SiCl_x} \propto k_1 \theta_{SiCl_x} f_{Ar_{crit}} \text{ when } f_{Ar_{neu}} \geqslant f_{Ar_{crit}} \qquad [5]$$

Therefore, the initial increase of the silicon etch rate with increasing Cl_2 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 Cl_2 pressures was related to the saturation of silicon chloride on the silicon surface, that is, $\theta_{SiCl_x} \approx 1$. The saturated silicon (100) etch rates for both 480 and 780 s of the Ar irradiation time were the same as one atomic layer per cycle due to the Ar neutral beam irradiation higher than $f_{Ar_{crit(100)}}$ at $\theta_{SiCl_x} \approx 1$ 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 insufficient Ar neutral beam dose ($f_{Ar_{neu}} < f_{Ar_{crit}}$) at $\theta_{SiCl_x} \approx 1$ 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 silicons (100) and (111) were measured for different etch cycles. The results are shown in Fig. 4. Cl_2 pressure was maintained at 0.46 mTorr which is higher than 0.24 mTorr ($\theta_{SiCl_x} \approx 1$) and the Ar neutral beam irradiation time was kept at 780 s [$f_{Ar_{neu}} \geqslant f_{Ar_{crit}}$ for both silicons (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 silicons (100) and (111) was conducted by Cl_2 adsoprtion followed by the depsortion 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 Cl_2 pressure and Ar neutral beam irradiation time, and by maintaning enough Cl_2 pressure ($\theta_{SiCl_x} \approx 1$) and enough Ar neutral beam irradiation dose ($f_{Ar_{neu}} \geqslant f_{Ar_{crit}}$), 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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References

1. *Atomic Layer Growth and Processing*, T. F. Kuech, P. D. Dapkus, and Y. Aoyagi, Editors, *Mater. Res. Soc. Symp. Proc.*, **222** 115 (1991).
2. P. D. Agnello, *IBM J. Res. Dev.*, **46** 317 (2002).
3. Y. Aoyagi, K. Shinmura, K. Kawasski, T. Tanaka, K. Gamo, S. Namba, and I. Nakamoto, *Appl. Phys. Lett.*, **60**, 968 (1992).
4. T. Meguro, M. Ishii, K. Kodama, Y. Yamamoto, K. Gamo, and Y. Aoyagi, *Thin Solid Films*, **225**, 136 (1993).
5. K. K. Ko and S. W. Pang, *J. Vac. Sci. Technol. B*, **11**, 2275 (1993).
6. B. J. Kim, S. H. Chung, and S. M. Cho, *Appl. Surf. Sci.*, **187**, 124 (2002).

7. T. Matsuura, J. Murota, and Y. Sawada, *Appl. Phys. Lett.*, **63**, 2803 (1993).
8. S. D. Athavale and D. J. Economu, *J. Vac. Sci. Technol. B*, **14**, 3702 (1996).
9. Y. Horiike, T. Tanaka, M. Nakano, S. Iseda, H. Sakaue, A. Nagata, H. Shindo, S. Miyazaki, and M. Hirose, *J. Vac. Sci. Technol. A*, **8**, 1844 (1990).
10. S. D. Park, K. S. Min, B. Y. Yoon, D. H. Lee, and G. Y. Yeom, *Jpn. J. Appl. Phys., Part 1*, **44**, 389 (2005).
11. D. H. Lee, J. W. Bae, S. D. Park, and G. Y. Teom, *Thin Solid Films*, **398-399**, 647 (2001).
12. D. H. Lee, S. J. Jung, S. D. Park, and G. Y. Yeom, *Surf. Coat. Technol.*, **177-178**, 420 (2004).
13. J. B. Hudson, *Surface Science*, John Wiley & Sons Inc, New York, (1998).