# Surface Analysis of Atomic-Layer-Etched Silicon by Chlorine

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Silicon atomic-layer etching (ALET) was carried out by the adsorption of $Cl_2$ to form silicon chlorides followed by the desorption of the silicon chlorides formed on the surface by irradiating an Ar neutral beam of a low energy. The silicon surface during the silicon ALET was investigated by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy, and its etch mechanism was studied. XPS data showed that during the $Cl_2$ adsorption stage, silicon chloride bonding peaks related to SiCl and $SiCl_3$ were formed. The peak intensity related to SiCl bonding is slowly decreased during the desorption of silicon chlorides, and when the SiCl bondings are removed completely by irradiating enough Ar neutral-beam dose to the surface, the saturated silicon etch rate of 1.36 Å/cycle which is related to one Si monolayer per cycle could be obtained. Also, at this condition, the surface roughness is close to the roughness of the silicon substrate itself. The SiCl bondings formed on the silicon surface during the adsorption stage are related to the desorption species during the ALET, while the $SiCl_3$ bondings are related to the species formed with the surface silicon damaged during the desorption stage.
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As the critical dimension of the semiconductor devices is decreased to nanoscale, etching techniques that can etch and control semiconductor materials with the atomic scale have become increasingly important.[1] Conventional dry-etching techniques such as reactive ion etching can etch nanoscale devices vertically and fast; however, they cannot control the etch depth with the atomic scale and tend to cause surface damage due to the irradiation of high-energy ions during the etching.[2,3]

To resolve the above problems related to conventional etching techniques and to etch the semiconductor materials with the atomic scale, atomic-scale etching techniques named as molecular-layer etching, layer-by-layer etching, digital etching, etc. have been investigated by various researchers.[4-9] The atomic-scale etching is carried out using a process cycle composed of (step 1) adsorption of reactant molecules on the surface, (step 2) evacuation of the excess reactant, (step 3) energetic particles irradiation to the reactant-adsorbed surface for the desorption of surface-reactant chemisorbed species, and (step 4) evacuation of the etch products. Many publications related to the surface reaction of silicon and $Cl_2$ (step 1) can be found, even though some of them are not related to the atomic-scale etching, and its adsorption mechanism has been well investigated.[10] However, possibly due to various differences in the experimental setup and parameters, conflicted results are found on the removal of the adsorbed species, which is related to the etch rates for the atomic scale etching.[7-9]

In this study, based on the our previous experiments related to the silicon atomic-layer etching (ALET) carried out using $Cl_2$ gas and an Ar neutral beam of a low energy,[11] the adsorbed $Cl_2$ bonding states during the $Cl_2$ adsorption and the desorption mechanism of silicon chlorides formed on the silicon surface by the Ar neutral beam were investigated.

Figure 1 shows the schematic diagram of the ALET system used in the experiment. The system consisted of a two-grid inductively coupled plasma source-type ion gun, a low-angle planar reflector for the neutralization of the ions extracted from the ion gun, a loadlock system, a process chamber for etch processing, and a pumping system. Radio frequency (rf) power (800 W 13.56 MHz) was applied to the plasma source, and to the first grid (acceleration grid) of the ion gun, 35–225 V dc was applied while the second grid was grounded. The Ar+ ion beam extracted from the ion gun was neutralized by the reflection at the low-angle reflector installed below the ion gun. More details on the low-angle-reflected neutralization technique can be found elsewhere.[12,13] The substrate was maintained at room temperature by a water-chilling system and, to distribute $Cl_2$ gas during the adsorption stage, a gas shower ring was installed. Also, between the substrate and the Ar neutral-beam source, an automatic shutter was installed to control the Ar-beam irradiation time.

$Cl_2$ gas was supplied from the shower ring for 20 s, and the $Cl_2$ pressure was maintained at 0.46 mTorr, which is a pressure higher than required for one monolayer adsorption of $Cl_2$. The flow rate of Ar to the ion gun for the desorption stage was maintained at 10 sccm and the Ar neutral-beam irradiation time was varied from 0 to 600 s. The detailed process conditions and steps for the ALET used in the experiment are shown in Table I.

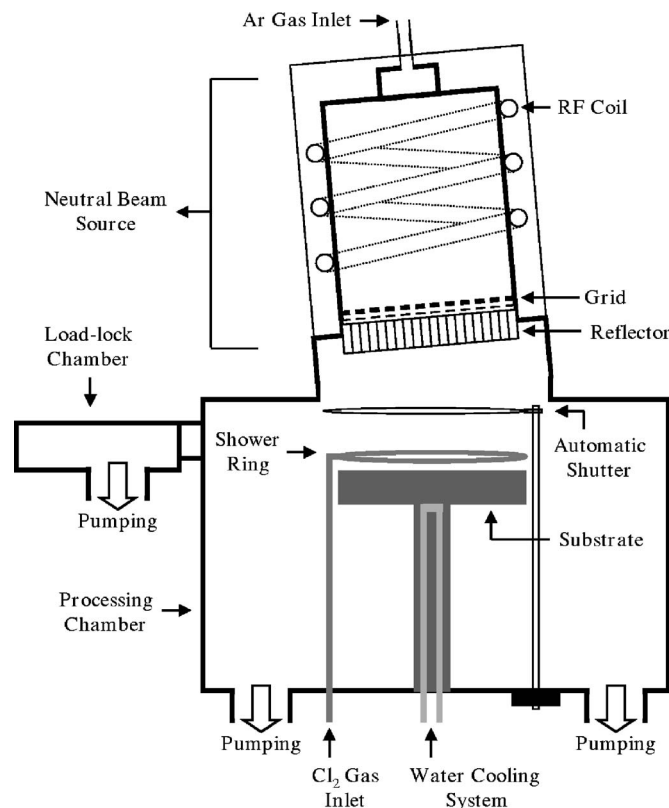The sample used in the experiment was p-type (100) Si. The



**Figure 1.** Schematic diagram of the ALET system used in the experiment.

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**Table I. Typical experimental parameters of ALET used in this experiment.**

| | |
|---|---|
| Base pressure | $2.0 \times 10^{-6}$ Torr |
| Working pressure | $2.5 \times 10^{-4}$ Torr |
| Inductive power | 800 W |
| Acceleration grid voltage | 35–225 V |
| Ar gas-flow rate | 10 sccm |
| Ar neutral-beam irradiation time | 0–600 s |
| $Cl_2$ pressure | 0.46 mTorr |
| $Cl_2$ supply time | 20 s |
| Substrate temperature | Room temperature |

sample was B-doped Si with the resistivity of 1–10 $\Omega$ cm. Before loading the sample into the processing chamber, the native oxide on the sample was removed by treating with buffered oxide etch (BOE) followed by deionized (DI) water rinse and $N_2$ blow drying. Stylus profilometry (Tencor Instrument, Alpha Step 500) was used to measure the etch depth and the etch rate (etch depth/cycle) was estimated by dividing the total etch depth by total etch cycles. X-ray photoelectron spectroscopy (XPS, Thermo VG, MultiLab 2000, Al Ka source) was used to investigate the binding states of $Cl_2$ on silicon surface during the ALET. An atomic force microscope (AFM, Thero-microscopes, CP Research) was used to measure the surface roughness of the sample after the ALET.

Figure 2 shows the effect of Ar neutral-beam irradiation time per cycle on the etch rate of Si (taken from the previous experiment[14]) and the total Si etch depth when total Ar irradiation time was maintained at 10 h. The Ar neutral-beam irradiation time was varied from 60 s per cycle to 840 s per cycle and, to obtain 10 h of irradiation time, the number of processing cycles was varied from 600 to 43, respectively. The acceleration grid voltage to the $Ar^+$ ion gun was maintained at 50 V to avoid the sputtering of silicon surface atoms. As shown in the figure, when the Ar neutral-beam irradiation time per cycle is shorter than 300 s, due to the insufficient beam dose per cycle, all of the silicon chlorides formed on the surface formed during the adsorption stage are not completely removed during the desorption stage and, therefore, the etch rate (Å/cycle) is increased by increasing the Ar neutral-beam irradiation time. However, when the Ar neutral-beam irradiation time per cycle is longer than 300 s, the etch rate becomes close to one monolayer [1.36 Å for (100) Si]/cycle, and when the irradiation time is longer than 480 s, the
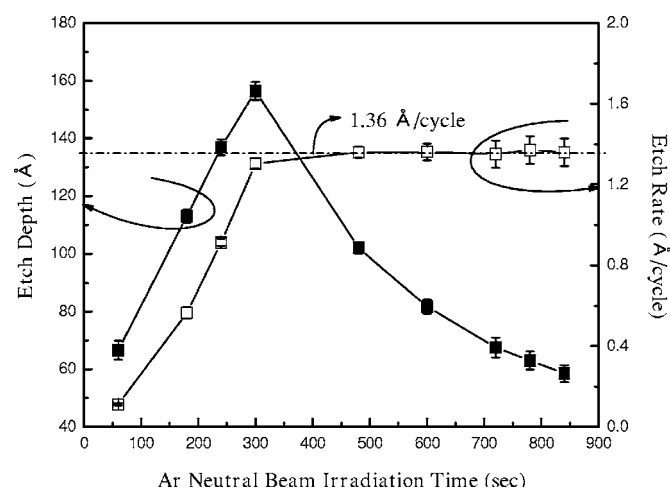


**Figure 2.** Silicon etch rate (Å/cycle) and total silicon etch depth as a function of Ar neutral-beam irradiation time per cycle. (Process condition: inductive power 800 W, acceleration grid voltage 50 V, Ar gas-flow rate 10 sccm, total Ar neutral-beam irradiation time 10 h, Ar neutral-beam irradiation time per cycle 60–840 s, $Cl_2$ pressure 0.46 mTorr, and $Cl_2$ supply time (20 s)).

etch rate is saturated at 1.36 Å/cycle because the beam dose is higher than that required to remove all the silicon chlorides formed on the silicon surface.

In the case of the total etch depth, when the etch rate is lower than 1.36 Å/cycle, the total etch depth is increased by increasing the Ar neutral-beam irradiation time, and after the etch rate is saturated at 1.36 Å/cycle, the total etch depth is decreased by further increasing the irradiation time. The decrease of total etch depth with increasing Ar neutral-beam irradiation time ($>300$ s) is believed to be related to the supply of Ar neutral-beam dose per cycle more than enough to remove the silicon chlorides formed on the silicon surface; therefore, after the removal of the monolayer, the rest of the Ar neutral beam just bombards the surface without removal of silicon atoms from the silicon surface due to the low Ar neutral-beam energy. When silicon chloride is formed on the silicon surface, due to the charge transition from Si–Si bonding to Si–Cl bonding, the bonding strength between underlayer Si and surface Si in the form of $SiCl_x$ is decreased.[14] Therefore, when the Ar neutral beam having adequate energy ($\sim 50$ eV) is supplied, only the silicon chlorides formed on the silicon surface are adsorbed without sputtering of underlayer Si, and when all of the silicon surface is covered with silicon chlorides ($>0.46$ mTorr) and enough Ar neutral-beam dose ($>480$ s) is supplied, only one monolayer of 1.36 Å is removed per each cycle.

The initial increase of total etch depth with increasing Ar neutral-beam irradiation time is not clearly understood currently, but it may be related to the surface roughness formed by the insufficient removal of silicon chlorides during each desorption stage, similar to the phenomenon observed by other researchers.[15-19] Figure 3 shows the surface roughness of the silicon measured by AFM after the etch for 50 cycles for the Ar neutral-beam irradiation time of 60 s/cycle and 600 s/cycle. Other etch conditions were the same as the conditions for Fig. 2. The surface roughness of the silicon measured before the etching (reference) is also shown. As shown in the figure, the root–mean–square (rms) surface roughness of the reference and the silicon etched by 600 s of Ar neutral-beam irradiation time shows similar values of 1.69 and 1.46 Å, respectively, due to the complete removal of monolayer silicon chlorides formed on the silicon surface by the sufficient Ar neutral-beam irradiation. However, when the Ar neutral-beam irradiation time is not enough to remove all the silicon chlorides on the silicon surface at each etch cycle, the surface roughness is higher than the reference and is increased with decreasing the Ar neutral-beam irradiation time due to the partial removal of silicon chlorides on the surface. As shown in the figure, when the Ar neutral-beam irradiation time is 60 s/cycle, the surface roughness is 7.5 Å. Silicon chlorides formed on the rough silicon surface are believed not to be easily removed by the low-energy Ar neutral beam compared to the silicon chlorides on the flat surface due to the increased possibility of redeposition of etch products on the silicon surface through the bombardment of energetic Ar with slant angles. Therefore, the decrease of total etch depth with decreasing Ar neutral-beam irradiation time for the condition less than one monolayer etching (1.36 Å/cycle) is probably related to the increase of surface roughness with decreasing Ar neutral-beam irradiation time even though the exact reason is not currently understood.[14]

The binding states of silicon with chlorine during the adsorption stage and the removal of those silicon chlorides during the desorption stage by the Ar neutral beam with the energy of $\sim 50$ eV were observed using XPS and the results are shown in Fig. 4. As a reference, silicon surface observed after the Ar neutral-beam irradiation without the formation of silicon chlorides is included. For XPS, to observe the silicon binding states near the surface, a low take-off angle of 20° was used. As shown in the figure, the silicon surface irradiated only by the Ar neutral beam shows the binding peaks related to bulk Si, $Si^+$, $Si^{3+}$, and $SiO_2$ at 99.27, 100.04, 102.09, and 103.51 eV, respectively. The $SiO_2$ peak is related to the air exposure during the transportation from the etch chamber to the XPS while
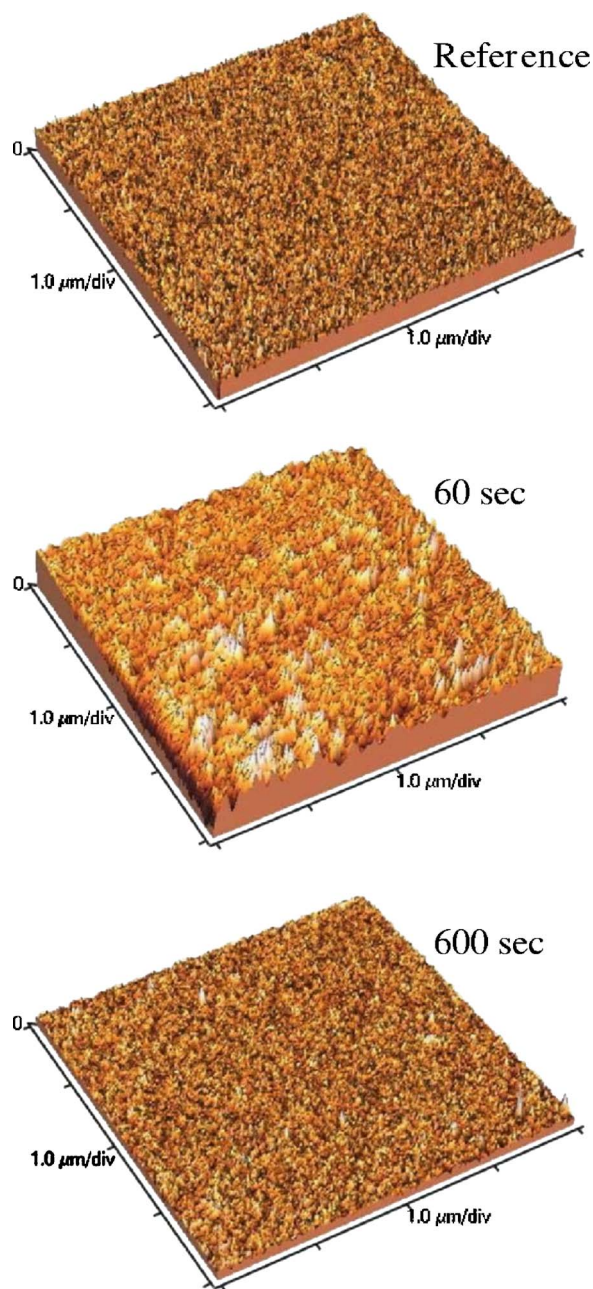
**Figure 3.** (Color online) AFM image of silicon surface as a function of Ar neutral-beam irradiation time per cycle. (Process condition: inductive power 800 W, acceleration grid voltage 50 V, Ar gas-flow rate 10 sccm, Ar neutral-beam irradiation time 60 and 600 s, $Cl_2$ pressure 0.46 mTorr, and $Cl_2$ supply time 20 s). AFM image of the silicon surface before the etching was included as a reference.



**Figure 4.** Binding states of silicon [Si, $SiO_2$, $Si^+$ (SiCl), and $Si^{3+}$ ($SiCl_3$)] during the adsorption stage and the removal of the silicon chlorides during the desorption stage observed by XPS. (Process condition: inductive power 800 W, acceleration grid voltage 50 V, Ar gas-flow rate 10 sccm, Ar neutral-beam irradiation time 0–600 s, $Cl_2$ pressure 0.46 mTorr, $Cl_2$ supply time 20 s, and take-off angle of XPS 20°.

the peaks related $Si^+$ and $Si^{3+}$ are believed to be from the dangling bonds of Si formed during the Ar neutral-beam irradiation.[16] The variation of chlorine itself on the silicon surface with the Ar neutral-beam irradiation could not be evaluated because the chlorine binding peak, $Cl_{2p}$, was observed like a noise peak with 20° of XPS take-off angle (not shown). When $Cl_2$ is adsorbed on the silicon surface irradiated by the Ar neutral beam, as shown in the figure, the peaks related to $Si^+$ and $Si^{3+}$ shift to higher binding energies of 100.55 and 102.35 eV, respectively, possibly due to the binding of silicon with chlorine as SiCl and $SiCl_3$, respectively. However, as soon as the Ar neutral-beam irradiation is started, the peak related to $SiCl_3$ moves back to 102.09 eV of $Si^{3+}$, indicating vaporization of
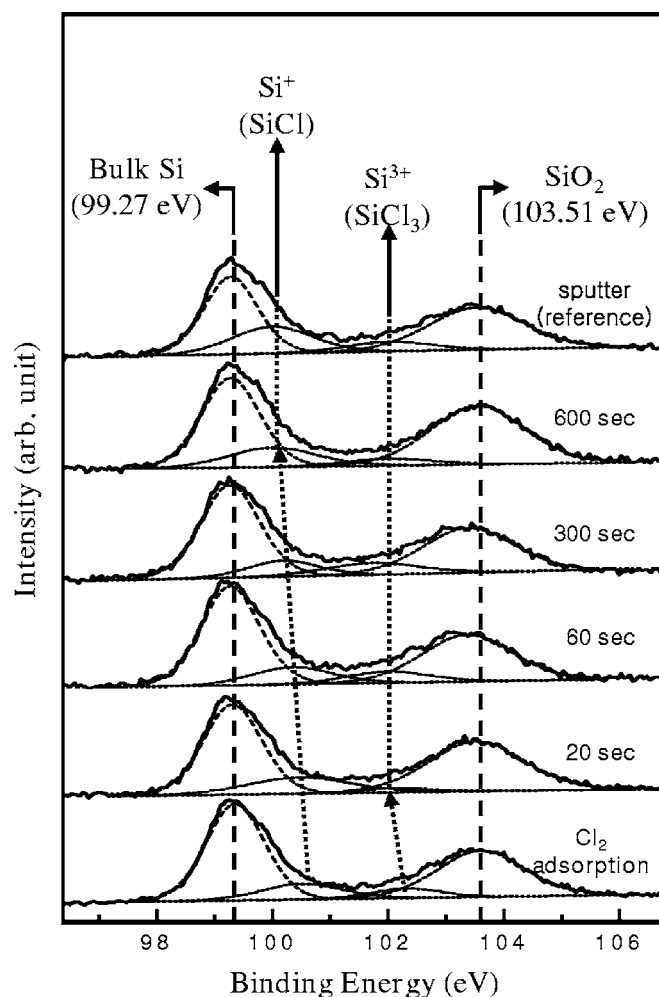
$SiCl_3$, and the peak position remains throughout the desorption stage. In the case of the peak related to SiCl, the peak position is slowly shifted to the lower binding energy throughout the desorption stage, and after the Ar neutral beam is irradiated for more than 300 s, the peak position is returned to 100.04 eV of $Si^+$. (No significant intensity variations of $Si^+$ and $Si^{3+}$ are observed during the Ar neutral-beam irradiation. By the Ar neutral-beam irradiation, SiCl and $SiCl_3$ are desorbed from the surface, and on the silicon surface, unbound silicon atoms such as $Si^+$ and $Si^{3+}$ are exposed after the desorption of SiCl and $SiCl_3$. Therefore, the peak intensities related to $SiCl_x$ are decreasing while the peak intensities related to $Si^{x+}$ are increasing by the replacement of chlorine-bound $Si^+$ to silicon-bound $Si^+$ and chlorine-bound $Si^{3+}$ to silicon-bound $Si^{3+}$ with the increase of Ar neutral-beam irradiation time.) The comparison of XPS results with the results shown in Fig. 2 shows that the silicon chlorides on the silicon surface are not completely removed for 300 s of the Ar neutral-beam irradiation with the energy of ~50 eV; however, when the Ar neutral beam is irradiated more than 300 s, all of the silicon chlorides on the silicon surface are removed and the Si etch rate of one monolayer per cycle (1.36 Å/cycle) is obtained. Therefore, the removal of SiCl on the silicon surface is believed to be the main etch mechanism of the ALET in our experiment.
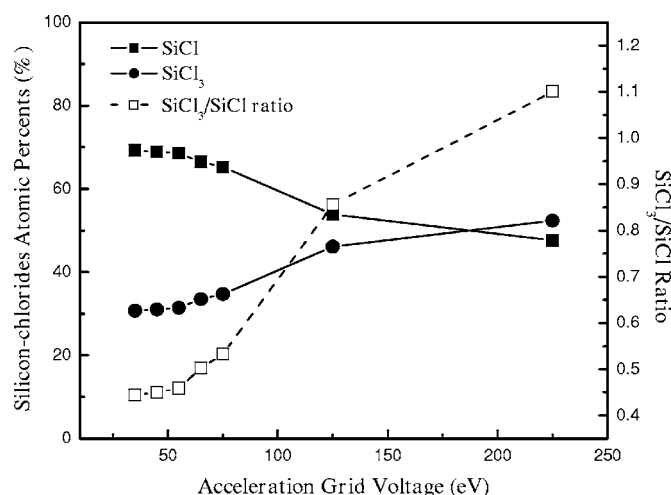
**Figure 5.** Relative atomic percents of SiCl and SiCl$_3$ on the silicon surface during the adsorption stage and the SiCl$_3$/SiCl ratio as a function of acceleration grid voltage. (Process condition: inductive power 800 W, acceleration grid voltage 35–225 V, Ar gas-flow rate 10 sccm, Ar neutral-beam irradiation time 600 s, Cl$_2$ pressure 0.46 mTorr, Cl$_2$ supply time 20 s, and take-off angle of XPS 20°.

To investigate the source of SiCl$_3$ formed on the silicon surface during the etch cycle, the ALET was carried out with different Ar neutral-beam energies. The energy of the Ar neutral beam was varied by controlling the acceleration grid voltage ($\sim$Ar neutral-beam energy) of the source from 35 to 225 V while the Ar neutral-beam irradiation time was fixed at 600 s/cycle. Other process conditions were the same as shown in Table I. After 50 cycles of etch processing, the silicon wafers were exposed to Cl$_2$ for 20 s and their surface silicon binding states were observed using XPS with the take-off angle of 20° to observe the near-surface characteristics. The relative atomic percentages of the silicon chlorides as a function of acceleration-grid voltage are shown in Fig. 5. Similar to the results shown in Fig. 4, as the silicon chlorides, the peaks related to SiCl and SiCl$_3$ are observed. No peak related to SiCl$_2$ is observed possibly due to the relatively higher instability of the molecule compared to SiCl and SiCl$_3$.[10,20] As shown in the figure, when the neutral-beam energy is in the range of 35–55 eV, the atomic percentages of SiCl and SiCl$_3$ are not significantly changed with increasing energy of the Ar neutral beam. However, when the beam energy is higher than 55 eV, the atomic percentage of SiCl is decreased and that of SiCl$_3$ is increased with increasing the beam energy. When the ratio of SiCl$_3$ to SiCl is taken, the ratio remains at minimum until 55 eV and the further increase of the beam energy increases the ratio significantly from about 0.4 to 1.1. When the beam energy is higher than 55 eV, the sputtering of surface silicon is observed and the increase of the Ar neutral-beam energy increases the damage to the silicon surface. Therefore, it is believed that SiCl$_3$ formed on the silicon surface is related to the silicon chloride formed with the

damaged silicon atom, and when the beam energy lower than 55 eV is used, the ALET can be carried out with negligible physical damage to the surface.

In this study, the etch mechanism of the ALET of silicon carried out using Cl$_2$ and an Ar neutral beam was investigated using surface analysis such as XPS and AFM. By supplying high-enough Cl$_2$ pressure and an Ar neutral-beam dose of a low energy corresponding to $\sim$50 eV during the adsorption stage and desorption stage, respectively, 1.36 Å/cycle which is one monolayer etch depth of silicon per cycle could be obtained. For the etch condition of one monolayer per cycle, the surface roughness is the lowest and is similar to that before the etching. During the adsorption stage of the ALET, the silicon chlorides formed on the silicon surface are SiCl and SiCl$_3$. When the Ar neutral-beam energy is lower than the energy for silicon sputtering, the ratio of SiCl$_3$/SiCl remains similar, but when the Ar neutral-beam energy is increased further, the ratio is increased significantly, Therefore, SiCl bonding formed on the silicon surface during the adsorption stage is believed to be related to the desorption species during the ALET; however, SiCl$_3$ bonding is believed to be related to the species formed with the surface silicon damaged during the desorption stage.

## Acknowledgment

## References

1. *International Technology Roadmap for Semiconductors* (ITRS), International Sematech, Austin, TX.
2. T. Kinoshita, M. Hane, and J. P. McVittee, *J. Vac. Sci. Technol. B*, **B14**, 560 (1996).
3. K. Nishikawa, H. Ootera, S. Tomohisa, and T. Oomori, *Thin Solid Films*, **374**, 190 (2000).
4. Y. Aoyagi, K. Shinmura, K. Kawasaki, T. Tanaka, K. Gamo, S. Namba, and I. Nakamoto, *Appl. Phys. Lett.*, **60**, 968 (1992).
5. T. Meguro, M. Ishii, K. Kodama, Y. Yamamoto, K. Gamo, and Y. Aoyagi, *Thin Solid Films*, **225**, 136 (1993).
6. K. K. Ko and S. W. Pang, *J. Vac. Sci. Technol. B*, **B11**, 2275 (1993).
7. Y. Horiike, T. Tanaka, M. Nakano, S. Iseda, H. Sakaue, A. Nagata, H. Shindo, S. Miyzaki, and M. Hirose, *J. Vac. Sci. Technol. A*, **A8**, 1844 (1990).
8. T. Matsuura, J. Murota, and Y. Sawada, *Appl. Phys. Lett.*, **63**, 2803 (1993).
9. S. D. Athavale and D. J. Economu, *J. Vac. Sci. Technol. B*, **B14**, 3702 (1996).
10. H. Okada, K. Inagaki, H. Goto, K. Endo, K. Hirose, and Y. Mori, *Surf. Sci.*, **515**, 287 (2002).
11. S. D. Park, D. H. Lee, and G. Y. Yeom, *J. Korean Phys. Soc.*, **47**, 469 (2005).
12. M. J. Chung, D. H. Lee, and G. Y. Yeom, *Thin Solid Films*, **420**, 579 (2002).
13. D. H. Lee, S. J. Jung, S. D. Park, and G. Y. Yeom, *Surf. Coat. Technol.*, **177**, 420 (2004).
14. S. D. Park, C. K. Oh, D. H. Lee, and G. Y. Yeom, *Electrochem. Solid-State Lett.*, **8**, C117 (2005).
15. Y. Ayagi, K. Shinmaura, K. Kawasaki, K. Gamo, and S. Namba, *Thin Solid Films*, **225**, 120 (1993).
16. A. Benninghoven, *Z. Phys.*, **230**, 403 (1970).
17. S. Hofmann, *Appl. Phys.*, **9**, 59 (1976).
18. S. Hofmann, *Appl. Phys.*, **13**, 205 (1977).
19. J. M. Sanz and S. Hofmann, *Surf. Interface Anal.*, **8**, 147 (1986).
20. K. J. Kim, K. T. Park, and J. W. Lee, *Thin Solid Films*, **500**, 356 (2006).