

Precise Depth Control of Silicon Etching Using Chlorine Atomic Layer Etching

Sang-Duk PARK, Kyung-Suk MIN, Byoung-Young YOON, Do-Haing LEE and Geun-Young YEOM*

Department of Materials Science & Engineering, Sungkyunkwan University, Suwon, Kyunggi-do 440-746, Korea

(Received June 28, 2004; revised September 8, 2004; accepted October 21, 2004; published January 11, 2005)

In this study, the atomic layer etching (ALE) of Si was carried out using Cl_2 adsorption followed by Ar^+ ion beam irradiation with a low energy Ar^+ ion beam generated by an inductively coupled plasma ion gun. A saturated silicon etch rate due to chlorine ALE could be obtained when the Ar^+ ion acceleration voltage of the ion gun was in the range of 70 to 90 V, as a result of the preferential etching of silicon chloride formed during the chlorine adsorption period by the Ar^+ ions while the silicon sputter etch rate remains insignificant. This was attributed to the differences in the silicon-to-silicon and silicon-to-silicon chloride binding energies. The saturated silicon etch rate by ALE was dependent on the chlorine flow rate, i.e. the surface coverage of chlorine and the Ar^+ ion irradiation time. In this experiment, a silicon etch rate of $1.36 \text{ \AA}/\text{cycle}$, which is a (100) silicon monolayer per cycle, could be obtained by flowing more than 10 sccm chlorine gas followed by bombarding the surface by Ar^+ ions with an acceleration voltage of 70 V for more than 40 seconds. Under this condition, when a 30 nm scale silicon etch profile was examined after 200 cycles, a silicon etch profile with no undercut could be obtained.

[DOI: 10.1143/JJAP.44.389]

KEYWORDS: atomic layer etching, precise depth control, silicon, chlorine, Ar^+ ion beam

1. Introduction

According to the Moore's rule, the critical dimensions for silicon integrated circuits have decreased continuously, and have reached near the tens of nanometer in the research and development area. In order to achieve nanometer scale working devices, various practical issues need to be resolved and some of them are etch related issues such as the controllability of the etch depth and damage.^{1–4)} However, current etch technology utilizing reactive ion etching does not have a precise control of the etch rate, which tends to damage the surface of the device both physically and electrically due to the use of energetic reactive ions to achieve the vertical etch profiles. Atomic layer etching (ALE) has been investigated by many researchers with the aim of atomic scale etch controllability without physical damage to the surface for nano-scale devices.^{5–10)}

ALE technology has been investigated from the early 1990s for GaAs and silicon devices.^{5–10)} For silicon devices, ALE of (100) silicon by fluorine gas has investigated by Horiike *et al.*⁸⁾ by the adsorption of fluorine gas followed by irradiation of approximately 20 eV Ar^+ ions generated by electron cyclotron resonance (ECR) plasma for the desorption of the SiF_x reaction product. They obtained approximately $1.5 \text{ \AA}/\text{cycle}$, which is close to one monolayer (1.36 \AA). However, the substrate has to be cooled down to -160°C in order to prevent spontaneous etching of the silicon by fluorine gas during the adsorption stage, Matsuura *et al.*⁹⁾ reported that ALE of silicon could be achieved at room temperature using chlorine gas with about 10 eV Ar^+ ions generated by ECR plasma. For (100) silicon, they obtained $0.68 \text{ \AA}/\text{cycle}$, which is half a monolayer of the (100) direction. ALE of (100) silicon by chlorine gas was also examined by Athavale *et al.*¹⁰⁾ using a helicon plasma for the Ar^+ ion source. However, they obtained approximately one monolayer of $1.36 \text{ \AA}/\text{cycle}$.

The exact etch rate of the silicon per etch cycle for ALE using chlorine gas is not consistent among the researchers and requires more investigation. In addition, the above ion

sources are easy to scale to the large area substrates that are required for the next generation substrates due to the difficult physics involved in those plasma sources such as the resonance.¹¹⁾ Therefore, in this study, an inductively coupled plasma (ICP) ion gun ion source, which could easily be scaled to the wafers of next generation, was used as the Ar^+ ion source for desorption, and the ALE etch characteristics of silicon by chlorine were investigated. It is believed that the present investigation will provide valuable insights into semiconductor fabrication requiring atomic-order accuracy and for the fabrication processing of nanotechnology in the next generation.

2. Experimental

Figure 1 shows the ALE system used in this experiment. The ALE of silicon was performed using chlorine with a two-grid ICP type ion gun made by Commonwealth Scientific (CS) Inc. The RF power applied to the ICP source

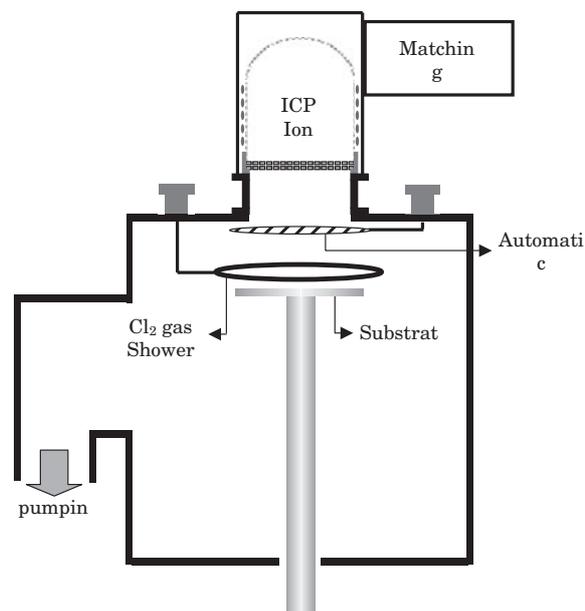


Fig. 1. Schematic diagram of the ALE system used in the experiment.

*Corresponding author. E-mail address: gyyeom@skku.edu

Table I. Typical experimental parameters used for atomic layer etching.

Base pressure	2.0×10^{-6} Torr
Operating pressure	2.5×10^{-4} Torr
Inductive power	800 W
Acceleration grid voltage	40–150 V
Ar flow rate	10 sccm
Ar ⁺ ion irradiation time (topen)	10–50 s
Cl ₂ flow rate	0–30 sccm
Cl ₂ supply time (t _{Cl₂})	20 s
Distances between the ion gun and the substrate	30 cm
Substrate Temperature	RT

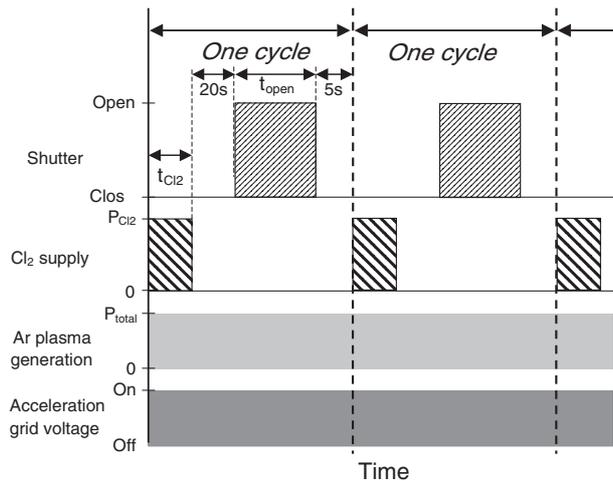
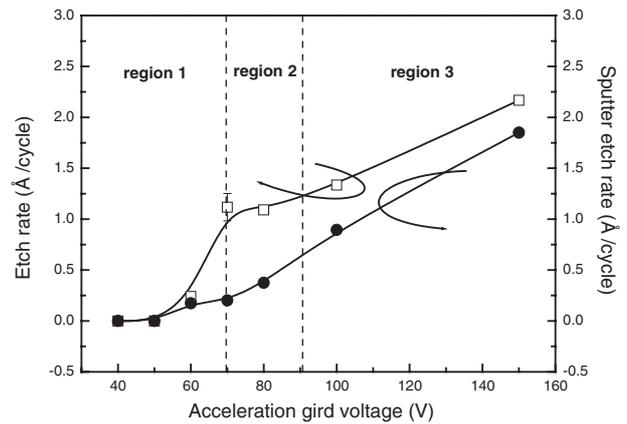


Fig. 2. The sequence of the atomic layer etching process used in these experiments.

was 800 W with a frequency of 2 MHz. In order to control the Ar⁺ ion acceleration energy, the voltage applied to the first grid located close to the source (accelerator grid) was varied from 40 to 150 V while the second grid was grounded. The energy width of the Ar⁺ ions extracted from the ion gun was approximately $\pm 20\%$ of the ion acceleration voltage. An automatic shutter was installed between the plasma source and the substrate to control the Ar⁺ ion irradiation time during the silicon etching cycle. Chlorine gas was supplied during the adsorption period and was controlled simultaneously with the shutter motion. Table I shows the typical experimental parameters used in the system and Fig. 2 shows the typical sequence and time for the ALE process.

The samples used in this experiment were p-type (100) silicon wafers patterned with a 20 nm thick and 30 to 100 nm wide Cr/Ni alloy. The samples were dipped in a buffered HF solution to remove the remaining native oxide on the silicon wafers followed by rinsing them with DI water and blow-drying them with N₂ immediately before loading the wafers into the chamber. In order to remove the remaining native oxide further, in addition to dipping the wafer in a HF solution, the sample was sputtered by Ar⁺ ions with the ICP ion gun at 200 V of an acceleration grid voltage for 3 minutes immediately before the ALE experiment. After the experiment, the Ni/Cr mask was removed using a solution consisting of a 1 : 1 : 3 mixture of HCl : NH₃ : H₂O. The etched step height was measured using a step profilometer

Fig. 3. Silicon etch rate by ALE and the silicon sputter rate by Ar⁺ ion per each cycle as a function of the acceleration grid voltage of the ICP ion gun. [process condition: inductive power (800 W), Cl₂ gas supply time (20 s), Cl₂ gas flow rate (20 sccm), and Ar⁺ ion irradiation time (30 s)]

(Tencor Instrument, Alpha Step 500) and atomic force microscopy (AFM, Thermo-microscopes, CP research). AFM was also used to measure the surface roughness. The measured step height was divided by the total number of ALE cycles to yield an etch rate per cycle. Scanning electron microscopy (SEM, Hitachi S-4700) was used to observe the silicon etch profile.

3. Results and Discussion

Figure 3 shows the p-type (100) silicon etch rates (Å/cycle) as a function of the Ar⁺ ion acceleration voltage from 40 to 150 V during ALE. The chlorine gas flow rate was 20 sccm and the gas flow time per cycle for adsorption was 20 seconds. The Ar⁺ ion irradiation time per cycle for desorption was 30 s. Figure 3 shows the Ar⁺ ion sputter etch rate (Å/cycle) of silicon measured at the same condition without supplying chlorine gas, which was included as a reference. As shown in the figure, the silicon etch rate by ALE as a function of acceleration voltage could be divided into three regions. Region 1 is the region of the acceleration voltage <70 V, where the silicon etch rate was initially <0.2 Å/cycle and rapidly increased from 60 to 70 V. Region 2 is the region of the voltage between 70 to 90 V, where the silicon etch rate is remaining constant near 1.12 Å/cycle. Region 3 is the region of the voltage >90 V, where the silicon etch rate is increasing again linearly with the acceleration voltage. In the case of the silicon sputter etching by Ar⁺ ions, the increase in the acceleration voltage up to 80 V slowly increased the silicon sputter etch rate and a further increase in the acceleration voltage increased the sputter etch rate linearly. Among the regions, region 2 showed the largest differences between the silicon etch rates by ALE and the silicon sputter etch rates.

The low silicon etch rate in region 1 appears to be related to the insufficient energy transfer of Ar⁺ ions to silicon chloride formed on the surface as a result of the adsorption of chlorine while the high silicon etch rate in region 3 appears to be related to the energy transfer of Ar⁺ ions not only to the silicon chloride but also to the silicon wafer itself. The rapidly increased and stabilized silicon etch rate in region 2 appears to be related to the Ar⁺ ion enhanced the effective removal of silicon chloride. At this region, the

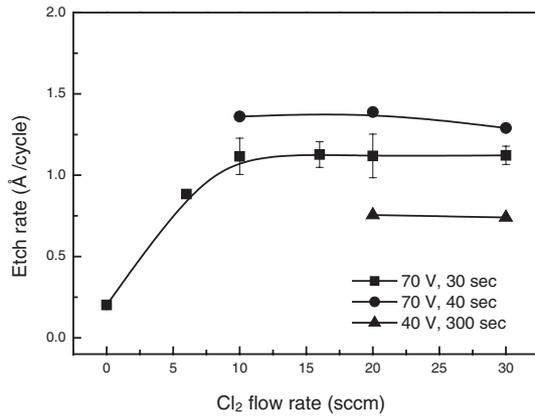


Fig. 4. Silicon etch rate per cycle by ALE as a function of the chlorine gas flow rate (sccm) [process condition: inductive power (800 W), acceleration grid voltage (40, 70 V), Ar⁺ ion irradiation time (30, 40, 300 s) and the Cl₂ gas supply time (20 s)]

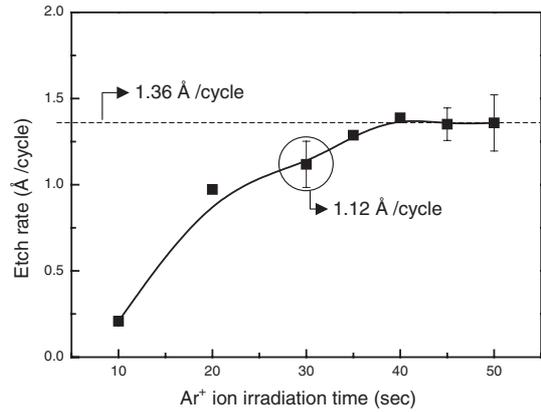


Fig. 5. Silicon etch rate per cycle by ALE as a function of the Ar⁺ ion irradiation time. [process condition: inductive power (800 W), acceleration grid voltage (70 V), Cl₂ gas supply time (20 s) and Cl₂ gas flow rate (20 sccm)]

silicon sputter rate was much lower than the etch rate of silicon chloride formed on the silicon surface possibly due to the higher silicon-to-silicon binding energy between the silicon wafer than that between the silicon-to-silicon binding energy of silicon chloride due to electron transfer to chlorine for silicon-silicon chloride.¹²⁾ The rapidly increasing silicon chloride etch rate by ion bombardment >75 eV ions and the low sputter yield of silicon approximately 0.07 atoms/ion by the bombardment of 100 eV Ar⁺ ions were also reported by other researchers, which is similar to our results in region 2.^{13,14)}

Because the acceleration voltage of 70 V showed the largest etch rate differences between the silicon etch rate by the chlorine ALE and the pure silicon sputter etching by Ar⁺ ions, the most of the following experiments were carried out at acceleration voltage of 70 V. Figure 4 shows the effect of the chlorine flow rate on the p-type (100) silicon etch rate by the ALE with 20 seconds of chlorine flow time per cycle and Ar⁺ ion acceleration voltage of 70 V. The Ar⁺ ion irradiation time per cycle was varied from 30 to 40 seconds, and as a reference, the silicon etch data obtained at an Ar⁺ ion acceleration voltage of 40 V with 300 s of chlorine gas supply time per cycle was included. As shown in the figure, when the chlorine gas flow rate was >10 sccm, the silicon etch rate by ALE was saturated. The saturated (100) silicon etch rate for the Ar⁺ ion acceleration voltage of 70 V with 30 seconds of irradiation time per cycle was 1.12 Å/cycle. When the Ar⁺ ion irradiation time per cycle was increased to 40 s, the silicon etch rate was increased to 1.36 Å/cycle, and was not dependent on the chlorine flow rate when the chlorine flow rate was varied from 10 to 30 sccm.

Indeed, a monolayer of (100) silicon is 1.36 Å. Therefore, the etch rate obtained at an Ar⁺ acceleration voltage of 70 V with 30 s of irradiation time per cycle was less than the monolayer per cycle. It is believed that the silicon etch rates of less than the monolayer per cycle for region 2 in Fig. 3 and for the condition of an Ar⁺ acceleration voltage of 70 V with 30 s of irradiation time per cycle in Fig. 4 are related to the insufficient Ar⁺ ion flux for etching the silicon chlorides formed on the silicon surface even though the silicon chloride coverage on the silicon surface was close to 100%. The silicon etch rate, which is not dependent on the chlorine

gas flow rate when the gas flow rate is >10 sccm, appears to support the saturation of the chlorine adsorption coverage on the silicon surface by the Langmuir isotherm.¹⁵⁾ Athavale *et al.* reported using a simulation technique that 1.16×10^{16} ions/cm², which is approximately ten times larger than the surface atomic density, is required to remove a monolayer of silicon adsorbed by chlorine.¹⁶⁾ The total ions to the substrate at 70 eV for 30 s in these experiments appears to be insufficient to desorb all the silicon chloride formed on the surface per cycle. By increasing the Ar⁺ ion irradiation time to 40 s, the silicon etch rate close to the monolayer per cycle could be obtained, which suggests there is sufficient ion flux for the monolayer etching. The Ar⁺ ion flux measured by a Faraday cup was 2.12×10^{13} ions/cm²sec in the case of an Ar⁺ acceleration voltage of 40 V. Therefore, in this case, the Ar⁺ ion irradiation time of approximately 530 s per cycle may be required. In addition, at this condition, as shown in Fig. 3, the sputter etch rate of silicon is negligible compared with that at 70 V. As shown in Fig. 3, 0.755 Å/cycle could be obtained when silicon was etched by an Ar⁺ acceleration voltage of 40 V for 300 s per cycle, suggesting a silicon etch rate of approximately one monolayer per cycle for 530 s per cycle.

Figure 5 shows the effect of the Ar⁺ ion irradiation time on the silicon etch rate (Å/cycle) for an Ar⁺ acceleration voltage of 70 V, 20 sccm of chlorine flow rate, and 20 s of chlorine gas flow per cycle. As mentioned above, as the Ar⁺ ion irradiation time was increased to more than 40 seconds, the silicon etch rate was increased to one monolayer per cycle and was saturated possibly due to the sufficient number incident Ar⁺ ions per cycle for the desorption of all of the silicon chlorides formed on the silicon surface. The increased deviation above 40 s appears to be partly related to the increased sputter etch rate per cycle even though the sputter etch rate of silicon at the condition is still much smaller than the silicon etch rate by ALE. Therefore, the silicon etch rate by chlorine ALE is dependent not only on the chlorine gas flow rate, which is the chlorine working pressure, but also on the total Ar⁺ ions per cycle with sufficient energy to remove all the silicon chlorides formed on the surface. In these experimental conditions, one monolayer of (100) silicon could be etched per cycle by chlorine ALE using chlorine

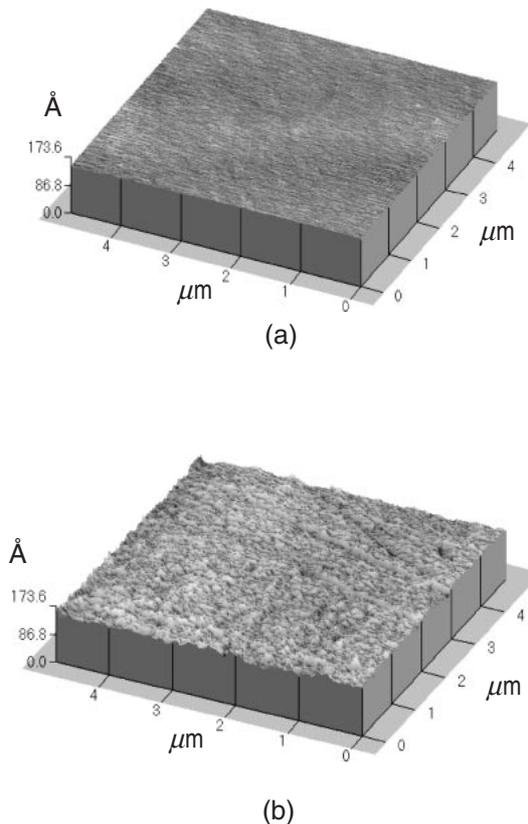


Fig. 6. AFM images of the silicon surfaces (a) before and (b) after the ALE for 100 cycles. [process condition: inductive power (800 W), acceleration grid voltage (70 V), Ar^+ ion irradiation time (40 s), Cl_2 gas supply time (20 s), and Cl_2 gas flow rate (20 sccm)]

flow rate higher than 10 sccm and an Ar^+ ion irradiation time longer than 40 seconds with an Ar^+ acceleration voltage of 70 V. Therefore, a precise silicon etching of one monolayer per cycle was obtained through the full coverage of chlorine on the silicon surface during the chlorine gas flow period and the etching all of the silicon chlorides formed on the silicon surface with sufficient Ar^+ in ion flux without the etching of silicon due to the differences in the binding energy during the Ar^+ ion bombardment period.

Figure 6 shows the surface root-mean-square (RMS) roughness of the silicon as-received and etched by ALE measured using AFM. The silicon etch condition was a chlorine flow rate of 20 sccm for 20 seconds and 40 s Ar^+ ion irradiation time with an Ar^+ acceleration voltage of 70 V. In order to measure the RMS roughness, the silicon was etched for 100 cycles. Therefore, the ALE etched 136 Å. As shown in the figure, the roughness of the as-received silicon was approximately 1.68 Å and that of etched silicon was 4.28 Å, which is approximately two atomic diameters. It is believed that the roughness after the ALE will be similar to that before the ALE due to the characteristics of a self-limited process of the ALE. However, as described by Ikeda *et al.*¹⁷⁾ for germanium ALE, the roughness appears to have increased as a result of surface contamination and defects. Indeed, the roughness obtained after the ALE in these experiment is similar to the roughness (4.94 Å) obtained by Athavale *et al.*,¹⁰⁾ even though roughness of their as-received silicon was 4.13 Å, which is similar to the roughness of the etched silicon. Therefore, the etch roughness obtained by the

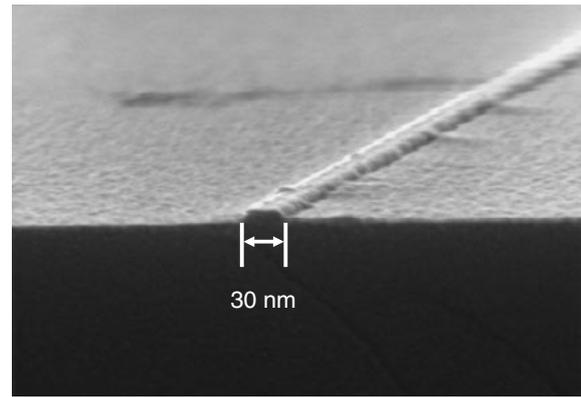


Fig. 7. Silicon etch profile of the 30 nm pattern measured using SEM after ALE for 200 cycles. [process condition: inductive power (800 W), acceleration grid voltage (70 V), Ar^+ ion irradiation time (30 s), Cl_2 gas supply time (20 s), and Cl_2 gas flow rate (20 sccm)]

ALE in the present experiments does not appear to be a significant problem.

SEM was used to observe the nanometer scale profile of silicon etched by ALE after removing the Ni/Cr mask layer, and the result is shown in the Fig. 7. The chlorine gas flow time was 20 s at a flow rate of 20 sccm and the Ar^+ ion irradiation time was 30 s at a 70 V of Ar^+ ion acceleration voltage. The etch cycle was 200 cycles. As shown in the figure, the obtained silicon etch profile with a 30 nm pattern showed no undercut by the chlorine ALE, because the ALE was performed mainly by the desorption of silicon chloride through the directional Ar^+ ion bombardment and not by the spontaneous etching of silicon through the thermal vaporization of silicon chloride.

4. Conclusions

In this study, the etch characteristics of silicon through ALE were investigated using chlorine and ICP as etch gas and Ar^+ ion source, respectively, as a function of the chlorine flow rate, the Ar^+ ion bombardment energy, and the Ar^+ irradiation time.

Due to the differences in the binding energies between the silicon-to-silicon and the silicon-to-silicon chloride, there were significant differences between the silicon sputter etch rate by Ar^+ ion and the silicon etch rate by the chlorine ALE at Ar^+ ion acceleration voltages ranging from 70 to 90 V. In this Ar^+ ion acceleration voltage range, the silicon etch rate by the chlorine ALE was almost saturated due to the preferential etching of silicon chloride formed during the adsorption period of chlorine by the Ar^+ ions while the silicon sputter etch rate remains insignificant. However, the silicon etch rate by the ALE was also related to the chlorine flow rate, i.e. the coverage of chlorine on the silicon surface and the amount of the Ar^+ ions. When the coverage of chlorine was less than 100% due to the insufficient supply of chlorine and when the total Ar^+ ions bombarding the surface were too low to etch all the silicon chloride formed on the surface, the silicon etch rate by ALE was less than one monolayer per cycle even though saturation of the silicon etch rate could be also obtained. In this experiment, a silicon etch rate of 1.36 Å/cycle, which is the (100) silicon monolayer per cycle, could be obtained by flowing >10 sccm chlorine gas followed by bombarding the surface

by Ar⁺ ions with an acceleration voltage of 70 V for more than 40 s. Under these conditions, the surface roughness was increased slightly after 100 cycles. In addition, when a 30 nm scale silicon etch profile was examined after 200 cycles, a silicon etch profile with no undercut could be obtained.

Acknowledgments

This work was supported by the National Program for Tera-Level Nanodevices of the Korea Ministry of Science and Technology as a 21st Century Frontier Program.

- 1) International Technology Roadmap for Semiconductor (ITRS), International Sematech, Austin, TX.
- 2) T. Nozawa and T. Kinoshita: *Jpn. J. Appl. Phys.* **34** (1995) 2107.
- 3) T. Kinoshita, M. Hane and J. P. McVitte: *J. Vac. Sci. Technol. B* **14** (1996) 560.
- 4) K. Hashimoto: *Jpn. J. Appl. Phys.* **32** (1993) 6109.
- 5) Y. Aoyagi, K. Shinmura, K. Kawasski, T. Tanaka, K. Gamo, S. Namba and I. Nakamoto: *Appl. Phys. Lett.* **60** (1992) 968.
- 6) T. Meguro, M. Ishii, K. Kodama, Y. Yamamoto, K. Gamo and Y. Aoyagi: *Thin Solid Films* **225** (1993) 136.
- 7) K. K. Ko and S. W. Pang: *J. Vac. Sci. Technol. B* **11** (1993) 2275.
- 8) Y. Horiike, T. Tanaka, M. Nakano, S. Iseda, H. Sakaue, A. Nagata, H. Shindo, S. Miyzaki and M. Hirose: *J. Vac. Sci. Technol. A* **8** (1990) 1844.
- 9) T. Matsuura, J. Murota and Y. Sawada: *Appl. Phys. Lett.* **63** (1993) 2803.
- 10) S. D. Athavale and D. J. Economou: *J. Vac. Sci. Technol. B* **14** (1996) 3702.
- 11) O. A. Popov: *High Density Plasma Sources — Design, Physics and Performance* (Noyes Publications, United States, 1995) p. 109.
- 12) Y. Ayagi, K. Shinmura, K. Kawasaki, K. Gamo and S. Namba: *Thin Solid Films* **225** (1993) 120.
- 13) N. A. Kubota, D. J. Economou and S. J. Plimpton: *J. Appl. Phys.* **83** (1998) 4055.
- 14) B. Chapman: *Glow Discharge Processes* (John Wiley & Sons, 1980) p. 395.
- 15) K. Suzue, T. Matsuura, J. Murota, Y. Sawada and T. Ohmi: *Appl. Surf. Sci.* **82/83** (1994) 422.
- 16) D. Athavale and D. J. Economou: *J. Vac. Sci. Technol. A* **13** (1995) 966.
- 17) K. Ikeda, S. Imai and M. Matsumura: *Appl. Surf. Sci.* **112** (1997) 87.