

Atomic-order layer-by-layer role-share etching of silicon nitride using an electron cyclotron resonance plasma

Takashi Matsuura,^{a)} Yasuhiko Honda, and Junichi Murota

Laboratory for Electronic Intelligent Systems, Research Institute of Electrical Communication, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

(Received 15 December 1998; accepted for publication 15 April 1999)

Atomic-order layer-by-layer etching of silicon nitride has been investigated using an ultraclean electron-cyclotron-resonance plasma. The surface nitrogen atoms in silicon nitride within only about one atomic layer from the surface were found to be removed selectively by excited hydrogen gas under well-controlled conditions. The remaining outermost silicon atoms were removed selectively by irradiation of a low-energy Ar⁺ and H⁺ ion mixture. By repeating these role-share cycles alternately, the resultant etching amount per cycle corresponded to one mean atomic layer of silicon nitride. © 1999 American Institute of Physics. [S0003-6951(99)04323-5]

With the decreasing dimensions of Si semiconductor devices, atomically precise fabrication techniques are becoming increasingly important. At the same time, it is becoming necessary to fully utilize the advantages of various available materials. Self-limited atomic-layer etching of Si and Ge was realized by ultraclean chlorine adsorption with alternating irradiation of low-energy Ar⁺ ions.¹⁻⁴ However, the bond strength between silicon and nitrogen (3.5 eV) in silicon nitride is stronger than that in Si (2.4 eV) and Ge (2.0 eV),⁵ and it is difficult for surface nitrogen atoms to react with chlorine; thus, atomic-order layer-by-layer etching of silicon nitride has been unsuccessful using the above method and is still open to investigation. In the present study, selective removal of the surface nitrogen atoms in silicon nitride has been achieved by excited hydrogen gas exposure, and by using this as the first half of the cycle, the role-share etching method is proposed, in which the remaining outermost silicon atoms are removed in the second half of the cycle by irradiation of a low-energy Ar⁺ and H⁺ ion mixture. By repeating these cycles alternately, silicon nitride is etched layer-by-layer by one mean atomic layer per cycle.

An ultraclean electron cyclotron resonance (ECR) plasma apparatus, the details of which have been described previously,^{1,6} was used to suppress contamination which might disturb the intrinsic reaction. Ar⁺ ions generated in the ECR plasma-generating chamber are transported by the divergent magnetic field, and ion irradiation onto the wafer in the reaction chamber is controlled by opening and closing the shutter in front of the wafer. The energy of ions at the wafer position as measured by an electrostatic method⁷ was less than 20 eV in the present study. Hydrogen gas was supplied into the reaction chamber, and the plasma was generated continuously for exciting the hydrogen gas. The partial pressure of Ar (P_{Ar}) was 0.27 and 0.80 Pa, that of H₂ (P_{H_2}), 0.02–0.44 Pa, and the microwave power, 165–700 W. In the first half of the role-share etching cycle, the shutter was closed so that the surface nitrogen atoms were removed by diffused excited hydrogen gas. In the second half of the

cycle, the shutter was opened and the Ar⁺ and H⁺ ion mixture irradiated the wafer so that the remaining outermost silicon atoms were removed.

The silicon nitride films used were deposited on Si(100) by ultraclean low-pressure chemical vapor deposition at 650 °C using NH₃, SiH₄, and H₂. The thickness was about 12 Å. The etched surface was analyzed by x-ray photoelectron spectroscopy (XPS), and the expected intensity ratio change with the layer-by-layer etching was calculated by setting the escape depth of photoelectrons for silicon nitride as 18.1 Å in our measurement conditions.^{8,9}

Selective removal of the surface nitrogen atoms: Figure 1 shows the typical XPS Si 2*p* (a) and N 1*s* (b) spectra of the initial silicon nitride film and those after exposure of the film to excited hydrogen gas. In the initial Si 2*p* spectrum (A), two peaks are identified: one is from the Si substrate [denoted by Si_{2*p*}(sub)] and the other is from Si in silicon nitride [denoted by Si_{2*p*}(Si–N)]. After exposure to excited hydrogen gas (B), although the Si_{2*p*}(sub) peak does not change (i.e., the apparent thickness of silicon nitride is maintained), the Si_{2*p*}(Si–N) peak intensity decreases and the additional Si peak resulting from Si bonding with O [denoted by Si_{2*p*}(Si–O)] appears. The intensity of the N 1*s* peak decreases after the exposure to the excited hydrogen gas. These results indicate that only the surface nitrogen atoms are removed selectively by the excited hydrogen gas, and almost all the surface silicon atoms remain, although they are oxidized. It should be noted that one main origin of oxygen is the quartz window used for the introduction of microwaves into the plasma-generating chamber during the process, because the silicon nitride coating on the window partly suppressed the oxidation. Another origin is oxidation during transport of the wafer to the XPS apparatus, because chlorine adsorption on the entire surface immediately after exposure to the excited hydrogen gas suppressed the oxidation further. Therefore, it is considered that the selective removal of only the surface nitrogen atoms in silicon nitride is not significantly affected by the present oxygen contamination.

Figure 2 shows the dependence of the N 1*s* XPS intensity ratio [$N_{1s}/Si_{2p}(\text{total})$] on the excited hydrogen gas exposure time under various plasma conditions (Table I). The

^{a)}Electronic mail: matsu@riec.tohoku.ac.jp

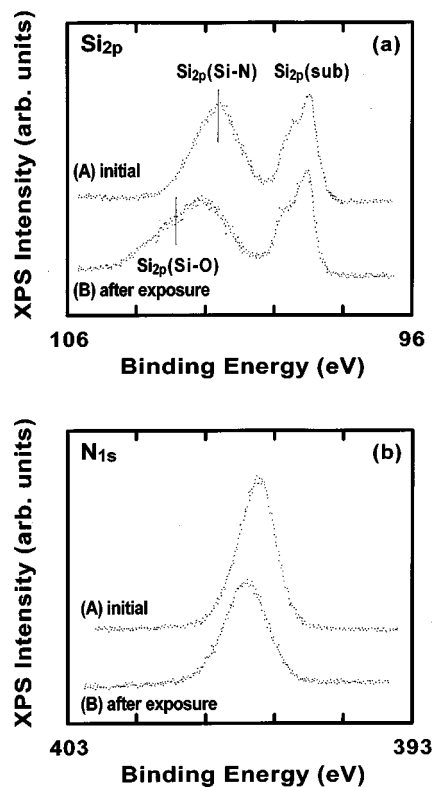


FIG. 1. Typical XPS Si 2p (a) and N 1s (b) spectra of the initial silicon nitride film and that after exposure to excited hydrogen gas. $P_{Ar}=0.27$ Pa, $P_{H_2}=0.12$ Pa, microwave power=165 W, and exposure time=45 min.

mean atomic-layer thickness of silicon nitride (1.87 Å) was calculated by the mean volume of one Si–N bond, which was calculated by the mean density of silicon nitride (2.95 g/cm³). “1AL,” “2AL,” and “3AL” denote the expected N 1s XPS intensity ratio when nitrogen atoms within one, two, and three mean atomic layers, respectively, are desorbed from the surface. In Fig. 2, two groups are identified. In group 1, the entire amount of removed nitrogen atoms is from within about one mean atomic layer from the surface and tends to saturate, while in group 2, it is from within about three mean atomic layers from the surface.

From the electrostatic ion energy distribution measurements for each plasma condition of group 1 and group 2, it was found that the total existent ion amount was different by about one order of magnitude between group 1 and group 2.

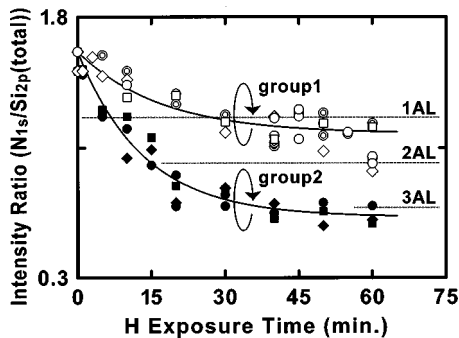


FIG. 2. Dependence of the N 1s XPS intensity ratio $[N_{1s}/Si_{2p}(\text{total})]$ on the excited hydrogen gas exposure time under various plasma conditions (Table I). “1AL,” “2AL,” and “3AL” denote the expected N 1s XPS intensity ratio when nitrogen atoms within one, two and three mean atomic layers, respectively, are desorbed from the surface.

TABLE I. Plasma conditions in Fig. 2.

Symbol	P_{Ar} (Pa)	Microwave power (W)	P_{H_2} (Pa)
○	0.27	165	0.12
⊙	0.27	220	0.12
◇	0.27	350	0.12
□	0.27	700	0.44
●	0.80	700	0.12
◆	0.80	700	0.04
■	0.27	700	0.08

More hydrogen ions are present in group 2 which may remove nitrogen atoms from the surface even if the shutter is closed. On the other hand, less hydrogen ions are present in group 1, and the radical reaction may become dominant so that nitrogen atoms only within about one mean atomic layer from the surface may be removed selectively. From group 1, we chose a typical condition for the first half of the role-share etching cycle (Ar partial pressure; 0.27 Pa, H₂ partial pressure; 0.12 Pa, microwave power; 165 W, shutter; closed, reaction time; 45 min), by means of which the nitrogen atoms within one mean atomic layer from the surface are desorbed from the silicon nitride surface.

Etching of the remaining silicon atoms: After the first half of the cycle, the wafer was irradiated continuously by an Ar⁺ and H⁺ ion mixture for etching the remaining Si atoms. In the XPS Si 2p spectra taken after the irradiation, the Si_{2p}(Si–O) disappeared and the Si_{2p}(sub) peak intensity increased. This means that the remaining outermost silicon atoms were removed and the surface became similar to the initial surface by the ion irradiation, where the additional oxidation was suppressed. From the various conditions examined, we chose a condition with the highest selectivity as the second half of the role-share etching cycle so that further desorption of the second-layer nitrogen atoms could be suppressed, where the Ar partial pressure was 0.27 Pa, the H₂ partial pressure 0.02 Pa, the microwave power 165 W, the shutter open, and the ion irradiation time was 1 min.

The role-share etching process constitutes alternate repetition of these two half-cycles under the optimum conditions as determined above. Figure 3 shows the change of the XPS intensity ratio versus etching cycle. “–1AL,” “–2AL,” and “–3AL” denote the expected Si_{2p}(sub) in-

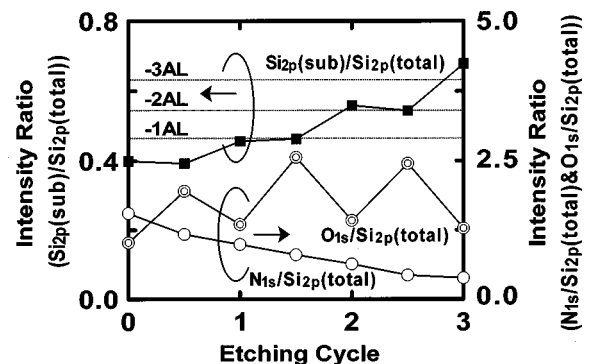


FIG. 3. Plot of the XPS intensity ratio vs the role-share etching cycle. “–1AL,” “–2AL,” and “–3AL” denote the expected Si (substrate) intensity ratio when the silicon nitride was etched by one, two, and three mean atomic layers, respectively.

tensity ratio when the silicon nitride was etched by one, two, and three mean atomic layers, respectively. After the first half-cycles (at 0.5, 1.5, and 2.5 cycles), the intensity ratio of $\text{Si}_{2p}(\text{sub})/\text{Si}_{2p}(\text{total})$ does not change much, and that of $\text{N}_{1s}/\text{Si}_{2p}(\text{total})$ decreases significantly. Additional oxidation is also clear in the intensity ratio of $\text{O}_{1s}/\text{Si}_{2p}(\text{total})$. After the second half-cycles (at 1, 2, and 3 cycles), the intensity ratio of $\text{Si}_{2p}(\text{sub})/\text{Si}_{2p}(\text{total})$ increases, that of $\text{N}_{1s}/\text{Si}_{2p}(\text{total})$ decreases slightly, and the additional oxygen is removed. From the stepwise increase of the intensity ratio of $\text{Si}_{2p}(\text{sub})/\text{Si}_{2p}(\text{total})$, the etching amount per cycle corresponds to one mean atomic layer of silicon nitride.

In conclusion, the surface nitrogen atoms in silicon nitride within only about one atomic layer from the surface are removed selectively by excited hydrogen gas under well-controlled conditions, and the remaining surface silicon atoms are removed by irradiation of the low-energy Ar^+ and H^+ ion mixture. As a result, the atomic-order layer-by-layer role-share etching of silicon nitride with one mean atomic layer per cycle has been realized using an ECR plasma.

The authors would like to acknowledge Dr. M. Sakuraba and Dr. T. Watanabe for preparing silicon nitride films and for valuable discussions. This study was carried out at the

Superclean Room of Laboratory for Electronic Intelligent Systems, Research Institute of Electrical Communication, Tohoku University, and was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture, Japan, the Research for the Future Program from the Japan Society for Promotion of Science, the Corning Research Grant, and the Mitsubishi Foundation.

¹T. Matsuura, J. Murota, Y. Sawada, and T. Ohmi, *Appl. Phys. Lett.* **63**, 2803 (1993).

²K. Suzue, T. Matsuura, J. Murota, Y. Sawada, and T. Ohmi, *Appl. Surf. Sci.* **82-83**, 422 (1994).

³T. Sugiyama, T. Matsuura, and J. Murota, *Appl. Surf. Sci.* **112**, 187 (1997).

⁴T. Matsuura, T. Sugiyama, and J. Murota, *Surf. Sci.* **402-404**, 202 (1998).

⁵Calculated using the data in *CRC Handbook of Chemistry and Physics*, 79th ed., edited by D. R. Lide (CRC, Boca Raton, 1998), pp. 5-21.

⁶T. Matsuura, H. Uetake, T. Ohmi, J. Murota, K. Fukuda, N. Mikoshiba, T. Kawashima, and Y. Yamashita, *Appl. Phys. Lett.* **56**, 1339 (1990).

⁷K. Suzuki, S. Okudaira, and I. Kanomata, *J. Electrochem. Soc.* **126**, 1024 (1979).

⁸T. Watanabe, M. Sakuraba, T. Matsuura, and J. Murota, in *Chemical Vapor Deposition XIII* (Electrochemical Society, Pennington, NJ, 1996), p. 504.

⁹T. Watanabe, A. Ichikawa, M. Sakuraba, T. Matsuura, and J. Murota, *J. Electrochem. Soc.* **145**, 4252 (1998).