Selective etching of silicon nitride over silicon oxide using ClF$_3$/H$_2$ remote plasma

Won Oh Lee$^{1,5}$, Ki Hyun Kim$^{1,5}$, Doo San Kim$^2$, You Jin Ji$^3$, Ji Eun Kang$^4$, Hyun Woo Tak$^1$, Jin Woo Park$^1$, Han Dock Song$^4$, Ki Seok Kim$^3$, Byeong Ok Cho$^2$, Young Lae Kim$^2$ & Geun Young Yeom$^{1,4,*}$

Precise and selective removal of silicon nitride (Si$_3$N$_4$) over silicon oxide (SiO$_x$) in a oxide/nitride stack is crucial for a current three dimensional NOT-AND type flash memory fabrication process. In this study, fast and selective isotropic etching of Si$_3$N$_4$ over SiO$_x$ has been investigated using a ClF$_3$/H$_2$ remote plasma in an inductively coupled plasma system. The Si$_3$N$_4$ etch rate over 80 nm/min with the etch selectivity (Si$_3$N$_4$ over SiO$_x$) of ~130 was observed under a ClF$_3$ remote plasma at a room temperature. Furthermore, the addition of H$_2$ to the ClF$_3$ resulted in an increase of etching selectivity over 200 while lowering the etch rate of both oxide and nitride due to the reduction of F radicals in the plasma. The time dependent-etch characteristics of ClF$_3$, ClF$_3$ & H$_2$ remote plasma showed little loading effect during the etching of silicon nitride on oxide/nitride stack wafer with similar etch rate with that of blank nitride wafer.

As the semiconductor device size is decreased to sub-nanoscale and the device integration is changed from two dimensional to three dimensional structure, more precise and selective etch technology is required for the semiconductor device fabrication$^1$. In the various semiconductor devices, silicon nitride has been widely used as a barrier layer for dopant diffusion, a gate sidewall spacer layer, a buffer layer, etc. due to high insulating characteristics, high thermal and mechanical stability, etc. and selective etching of silicon nitride over silicon and/or silicon oxide is important for various microelectronic applications$^2$.

These days, in the three dimensional NOT-AND type flash memory fabrication, the number of silicon nitride/silicon oxide (Si$_3$N$_4$/SiO$_x$) stack is increasing and the thickness of repeating Si$_3$N$_4$/SiO$_x$ layer is decreasing continuously for higher memory density in the vertical direction. Therefore, the etching of Si$_3$N$_4$ layers uniformly and ultra-high selectively to SiO$_x$ layers in the Si$_3$N$_4$/SiO$_x$ stack is becoming more challenging process. Until now, the selective etching of Si$_3$N$_4$ in Si$_3$N$_4$/SiO$_x$ stacks is achieved by wet etching using a hot phosphoric acid (H$_3$PO$_4$)$^3$-$^6$. In case of the wet etching, however, the penetration of an etch solution into holes is getting more challenging as the thickness of the Si$_3$N$_4$/SiO$_x$ layer is decreased and the remaining SiO$_x$ layers can be collapsed due to the surface tension. Moreover, several additives for increasing the etch selectivity of Si$_3$N$_4$/SiO$_x$ are found to cause oxide regrowth problems after etching unless its process condition is not carefully controlled$^7$. To solve these problems, a dry process for isotropic and selective etching of Si$_3$N$_4$ needs to be developed as an alternative technology for three dimensional NOT-AND type flash memory fabrication.

Various studies have been reported for selective etching of Si$_3$N$_4$ over SiO$_x$ using dry etch processes. For example, an ultra-high selective etching of Si$_3$N$_4$ over SiO$_x$ was reported using CF$_4$-based (CF$_4$/O$_2$/N$_2$, CF$_4$/CH$_4$/Ar) gases with a microwave chemical downstream etcher and an inductively coupled plasma (ICP) etcher$^7$-$^9$. In addition, NF$_3$-based (NF$_3$/O$_2$/NH$_3$, NF$_3$/O$_2$/N$_2$) gases were also used to ultra-high selective etching of silicon nitride over silicon oxide with downstream etchers based on ICP or capacitively coupled plasma (CCP)$^{10}$-$^{13}$. However, the etch selectivity of nitride over oxide still needs to be increased further for the application of current semiconductor process due to the thin thickness of oxide. Moreover, the use of fluorocarbon (CF$_x$) etch gases has contamination issues by carbon or deposition of CF$_x$(CH$_y$) polymers on the surface of the film, and which is a detrimental factor for a device fabrication. Even though these limits for engineering aspects are excluded,

1 School of Advanced Materials Science and Engineering, Sungkyunkwan University, 2066 Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do 16419, Republic of Korea. 2 Research and Development Group, Wonik Materials Co. Ltd., Cheongju 28125, Republic of Korea. 3 Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA, USA. 4 SKKU Advanced Institute of Nano Technology (SAIN), Sungkyunkwan University, 2066 Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do 16419, Republic of Korea. 5 These authors contributed equally: Won Oh Lee and Ki Hyun Kim. *email: gyyeom@skku.edu
the high global warming potentials (GWPs) of CF₄- and NF₃-based etch gases [GWP values; CF₄ (7,390), NF₃ (17,200)] arouse the needs for the alternative etch gases for environmental aspects in the near future¹⁴. ClF₃ with the GWP of ~ 0 has been used primarily as an in-situ cleaning gas for chemical vapor deposition (CVD) chambers in replacement of perfluorocarbon compounds (PFC), which have high GWP values or as an etch gas for silicon etching by heating, neutral cluster beam etching, reactive ion beam etching, etc.¹⁵–¹⁹. In addition, the ClF₃ have been investigated for etching of SiGe in an ICP system²⁰, SiC etching with ultra-high etch rate over 10 µm/min²¹, selective etching of transition metals and metal nitrides such as tantalum (tantalum nitride) over metal oxide (Ta₂O₅) with low pressure gaseous etching method²². In this study, ClF₃ remote plasma was applied for a fast and ultra-high selective etching of silicon nitride (SiNx) over silicon oxide (SiOₓ) applicable for current and next-generation semiconductor device fabrication including three dimensional NOT-AND type flash memory. The etching of SiNx using ClF₃ showed high etch rate over 80 nm/min and the etch selectivity of SiNx over SiOₓ of ~ 130. The etch selectivity of SiNx was further increased with H₂ addition in the ClF₃ plasma. The effect of Cl, F, and H radicals on the selective etching of SiNx was investigated using plasma and surface analysis tools, and its etch mechanism was suggested.

**Experimental section**

**Etching of silicon nitride.** Figure 1 is a schematic drawing of a remote type inductively coupled plasma (ICP) etching system used in this study. The inside of process chamber was coated with an aluminum oxide layer by anodizing. The base pressure of the process chamber measured with a convection gauge was maintained at 3 × 10⁻³ Torr and the operating pressure monitored by capacitance manometer (Baratron gauge) was maintained at 200 mTorr. 13.56 MHz RF power was applied to the planar type ICP coil at upper side of a chamber. For the isotropic etching of SiNx, double grids with multiple holes with 1.5 mm radius were arranged at the center of ICP reactor to prevent an ion bombardment effect and deliver radicals on the substrate. The substrate temperature was measured at the sample stage below the sample, which was monitored by a thermocouple and adjusted from 25 to 500 °C by a silicon carbide (SiC) heater located below the substrate.

**Sample preparation.** Blank 1.5 µm thick SiNx thin films, blank 300 nm thick SiOₓ thin films, and multilayer stacks composed of repeating SiOₓ (27 nm) and SiNx (27 nm) thin films were deposited by a plasma enhanced chemical vapor deposition (PECVD) process ( supplied by WONIK IPS Inc.).

**Characterization.** The etch rate of SiNx and SiOₓ were measured by a step profilometer (Tencor, Alpha-step 500) and with Scanning Emission Microscopy (SEM, Hitachi S-4700) after patterning with photoresist (PR, AZ 5214E) as an etch mask. Also, the etch profiles of the multilayer thin films composed of SiNx/SiOₓ stacks were observed by the SEM. The surface roughness of films after the etching was measured by atomic force microscope (AFM, XE-100, Park System) with a non-contact measurement mode. The characteristics of ClF₃/H₂ plasma were analyzed with Optical Emission Spectrometry (OES, Avaspec-3648). Byproduct gases during etching process were monitored with Fourier-Transform Infrared Spectroscopy (FT-IR, MIDAC 12,000). The binding state and atomic composition of SiNx and SiOₓ (thin films of initial thickness of 500, 300 nm, respectively) before and after the etching were analyzed by X-ray Photoelectron Spectroscopy (XPS, MXP10, ThermoFisher Scientific) with a monochromated Al Kα source (1,486.6 eV) with spot size of 400 µm. The expected energy resolution of XPS is below 0.5 eV FWHM. The Avantage 5.0 software was used for curve fittings and the areas of each peak.
were calculated with shirley background. The incident angle of X-ray to the sample was 50° and a hemispherical sector energy analyzer was positioned perpendicular to the sample stage.

Results and discussion

Figure 2 shows etch characteristics of SiNx and SiOy with ClF3 gas only and ClF3 remote plasmas. For ClF3 remote plasmas, 200 sccm of Ar was added to 200 sccm of ClF3 for the plasma stability. As shown in Fig. 2a, the etch rates of SiNx and SiOy were increased gradually with increasing rf power due to the enhanced dissociation of ClF3 reaching the maximum etch rates of SiNx and SiOy at ~ 90 and ~ 0.8 nm/min, respectively. Note that, the etch selectivity of SiNx over SiOy didn't vary significantly (~ 120) over rf powers of 100 ~ 400 W. As shown in Fig. 2b, the SiNx and SiOy could be also etched just by flowing ClF3 gas only without dissociating ClF3 by rf plasmas and the increase of substrate temperature increased the etch rates of both films. However, the overall SiNx etch rates by ClF3 gas flow only were much lower compared to etching with ClF3 remote plasmas, and which demonstrates that ClF3 remote plasma etching is much more effective method for SiNx etching compared with that by thermal etching without plasma. Meanwhile, even though etch rates of both materials were increased with increasing the substrate temperature, the etch selectivity of SiNx over SiOy was decreased. Same trend was observed for remote plasma etching. As shown in Fig. 2c, the increase of substrate temperature to ~ 500 °C at a fixed rf power of 300 W showed a gradual decreases of etch selectivity below 40 while showing increased SiNx etch rates over 600 nm/min. The effect of process temperature on the etching of SiNx and SiOy can be understood by plotting the etch rates of SiNx and SiOy logarithmically as a function of inverse temperature (1/T) for ClF3 remote plasma etching as shown in Fig. 2d. For the chemically activated etching, the etch rates can be described as a following Arrhenius equation.

\[
\ln k = -\frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

where \( k \) is a rate constant, \( R \) is the gas constant (1.987 cal K⁻¹ mol⁻¹), \( T \) is the process temperature (K), and \( E_a \) is the activation energy. The calculated activation energies \( (E_a) \) of SiNx and SiOy were 1.93 and 3.18 kcal/mol, respectively. The higher activation energy of SiOy means that the etch rate of SiOy rises faster than that of SiNx with the increase of temperature, and which leads to the decreases in etch selectivity of SiNx over SiOy even
though the etch rates of both materials are increased exponentially with increasing substrate temperature. The root mean square (RMS) surface roughness of SiNx and SiOy after the etching with each process condition (remote plasma- and thermally-etching) showed no significant differences in the RMS surface roughness among the samples for different etch methods (Figure S1, supplementary information).

To improve the etch selectivity of SiNx over SiOy, H2 was added to ClF3 in addition to Ar (Ar was also added to ClIF3/H2 for plasma stability) and the effect of H2 addition to ClF3 on the etch characteristics of SiNx and SiOy was investigated as a function of H2 percentage in ClF3/H2 (ClF3/H2/Ar plasma) and the results are shown in Fig. 3a. To increase the H2 percentage in ClF3/H2, H2 flow rate was increased while keeping the substrate temperature at 25 °C, operating pressure at 200 mTorr, the ClF3 flow rate at 200 sccm, Ar flow rate at 200 sccm, and the rf power at 300 W. The etch rates of both SiNx and SiOy were decreased with the increase of H2 percentage, however, the etch selectivity of SiNx over SiOy was increased with the increase of H2 percentage in ClF3/H2. To study the mechanism of selectivity SiNx etching over SiOy, the dissociated species in the plasmas was investigated by OES at the center of chamber and the byproducts during the process was monitored using FTIR at the pumping site.

Figure 3b,c shows optical emission spectra and the relative emission peak intensities of Cl, F, and H normalized by the intensity of Ar as a function of H2 percentage in ClF3/H2, respectively. In Fig. 3b, the optical emission intensities of Cl, F, and H were normalized by the optical emission intensity of Ar (750 nm) to minimize the effect of electron density on the estimation of radical density from the emission intensity. As shown in Fig. 3c, the increase of H2 percentage did not change the intensity of Cl, however, it decreased F intensity while increasing H intensity. Figure 3 shows the FTIR data of the byproduct gases such as SiF4 and HF measured at the pumping site for different H2 percentage in ClF3/H2. As the flow rate of H2 is increased, the concentration of SiF4 was decreased, and which means that the etching of SiNx was suppressed while increasing HF concentration due to the reaction of hydrogen (H) with fluorine (F) radical in the plasma. Usually, the addition of hydrogen to fluorine based plasma leads to scavenging of F radicals by forming gaseous HF molecules which have negligible effects on the etching of SiNx (and SiOy) unlike their aqueous (ionized) state.

The Si binding states and surface composition of SiNx and SiOy after the ClF3/H2 plasma etching were analyzed using X-ray Photoelectron Spectroscopy (XPS) and the results are shown in Fig. 4 and Table 1. The Si Nx and SiOy
were etched at the substrate temperature of 25 °C, operating pressure at 200 mTorr, the ClF3/H2/Ar flow rates at 200/(0 and 40)/200 sccm, and the rf power at 300 W. As shown in Fig. 4a,d, the reference SiNx and SiOy showed only Si–N at 101.7 eV, Si–O at 103.4 eV, respectively. After the etching with ClF3 plasma, however, significant Si–F bonding (103.6 eV) was formed on the SiNx surface, presumably due to the bonding of Si with F (Fig. 4b). The Si–F bonding ratio decreases with addition of H2 (20%) because of the reduction of F in the plasma (Fig. 4c and Table 1). However, no chlorine or Si-Cl bonding (~103.3 eV) was observed on the surface of SiNx even though there were enough Cl radicals in the ClF3/H2 plasma as confirmed through OES data in Fig. 3b, presumably, due to the immediate reaction of Si-Cl with F radicals. Meanwhile, as shown in Fig. 4e,f), there was no significant change in F concentration on the SiOy surface during etching with ClF3 and ClF3/H2 plasma. Also, no noticeable

Figure 4. XPS narrow scan (Si 2p) data of SiNx (a-c), SiOy (d-f), and Cl 2p (g, h) after etching with a remote ClF3/H2 plasma.

| Sample               | Binding state | B.E. (eV) | FWHM (eV) | % Area | Gaussian % |
|----------------------|---------------|-----------|-----------|--------|------------|
| SiNx (ClF3 only)     | Si 2p         | 99.7      | 1.3       | 1.6    | 88.8       |
|                      | Si–N          | 101.7     | 1.7       | 84.5   | 87.5       |
|                      | Si–F          | 103.6     | 1.55 (±0.05) | 13.9   | 85.7       |
| SiNx (ClF3 & H2 (20%))| Si 2p         | 99.7      | 1.3       | 1.6    | 88.8       |
|                      | Si–N          | 101.7     | 1.7       | 88     | 87.5       |
|                      | Si–F          | 103.6     | 1.55 (±0.05) | 10.4   | 85.7       |
Si–F bonding formation on the SiO₂ surface during the etching with ClF₃ and ClF₃/H₂ plasma was observed from the deconvolution of Si narrow scan data (Si 2p) indicating that most of F is adsorbed on the SiO₂ surface after the etching. Furthermore, the amount of F on the SiO₂ surface is much lower than that of SiNx because Si–O bonding is less reactive with F radical compared with SiNx. As shown in Fig. 4g,h, no chlorine was observed on the surface of both SiNx and SiO₂ even though the chlorine was observed in OES (Fig. 3b). The parameters used for curve fitting of SiNx is described in Table 1 and the normalized chi-square value for curve fitting was below 0.01. The compositional information of each element can be found in Table S1, supplementary information.

Figure 5 shows the etch mechanism of SiNx and SiO₂ under Cl, F radicals. As the bonding energy of Si–F (565 kJ/mol) is higher than those of Si–N (355 kJ/mol) and Si–O (452 kJ/mol)²², the SiNx and SiO₂ can be etched spontaneously under sufficient F radicals in the plasma although the etching is much active for SiNx than SiO₂. However, the bonding energy of Si-Cl (381 kJ/mol) is slightly higher than that of Si–N but lower than that of Si–O, and which means the Cl radical can react only with SiNx and forms Si-Cl bonding. Once the Si–N changes to Si-Cl, Si-Cl can be more easily converted to Si–F by F radicals in the plasma (due to the quick conversion of Si-Cl to Si–F as shown in Fig. 5), no chlorine could be observed on the surfaces of SiNx and SiO₂ during the etching with ClF₃/H₂ plasma, then Si–F on SiNx is removed as a volatile SiF₄ compound. Meanwhile, the addition of H₂ in the ClF₃ plasma reduces the density of F radicals by forming HF in the plasma causing the decreases of
Si–F formation on the surfaces of SiNx and SiOy, and which results in the decrease of etch rates of SiNx and SiOy. However, because the concentration of chlorine in the plasma is not significantly affected by the addition of H2 as confirmed through OES data in Fig. 3c), the etching of SiNx is decreased more slowly compared to that of SiOy with increasing H2 percentage through the conversion of Si-Cl on the surface of SiNx to Si–F, and which appears to increases the etch selectivity of SiNx over SiOy.

Using the etch conditions of ClF3 and ClF3/H2 (20%), stacked layers of SiNx/SiOy were etched and the results are shown in Fig. 6. Figure 6a is the reference stack of SiNx/SiOy before the etching. Figure 6b,c are the stacked layer of SiNx/SiOy after the etching using ClF3 and ClF3/H2 (20%) plasmas for 5 min and 10 min, respectively. As shown in Fig. 6b,c, highly selective etching of SiNx over SiOy could be observed for both ClF3 and ClF3/H2 (20%) by showing no noticeable differences in SiOy thickness along the etch depth. Therefore, it appears that the etch selectivity for the real SiNx/SiOy could be higher than that measured with blank wafers. The etch depth with increasing the etch time was also measured and the results are shown in d) for both ClF3 and ClF3/H2 (20%). The measured etch rates of SiNx with ClF3 and ClF3/H2 remote plasma were 80 and 26 nm/min, respectively, which have similar values with blank samples at the same plasma conditions (Fig. 2a, 3a) because of isotropic etch characteristics of reactive radicals. Furthermore, the etch depth with etch time was linear for both conditions, therefore, no aspect ratio dependent etching was observed. (The process time-dependent etch profiles of SiNx/SiOy stacks are shown in figure S2 and S3, supplementary information).

**Conclusion**

The isotropic and selective etching of SiNx over SiOy was studied using ClF3/H2 remote plasma with an ICP source. The SiNx etching using plasma assisted thermal processes showed the highest etch rate as well as the smoothest surface morphology compared with that etched only with thermal etching or plasma etching. The temperature dependent etch characteristics of SiN and SiO demonstrated a higher activation energy of SiO compared that of SiNx in the ClF3 remote plasma. Furthermore, the addition of H2 (20%) to the ClF3 plasma improved the etch selectivity of SiNx over SiOy from 130 to 200 even though the etch rate of SiNx was decreased from ~ 83 to ~ 23 nm/min. We believe the fast and ultra-high selective SiNx etching technology can be applied not only to next generation three dimensional NOT-AND type flash memory fabrication process but also to various semiconductor processes where precise etching of SiNx is required.

**Figure 6.** Etch characteristics of ClF3 only and ClF3/H2 (20%) plasma in stacked SiNx/SiOy. (a) SEM images of reference stacked SiNx/SiOy. Etch profile of stacked SiNx/SiOy after the etching with (b) ClF3 plasma and (c) ClF3/H2 (20%) for 5 min and 10 min, respectively. (d) Etch depth of SiNx in the stacked SiNx/SiOy with etch time for ClF3 and ClF3/H2 (20%) plasmas.
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Author contributions

G.Y.Y initiated the project. W.O.L., K.H.K. and G.Y.Y contributed to the experimental design. W.O.L., K.H.K. wrote the main manuscript text. D.S.K., J.W.P. contributed to the experimental setup. H.W.T. carried out OES measurement. Y.J.Y, J.E.K. performed plasma processing. All authors reviewed the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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Correspondence and requests for materials should be addressed to G.Y.
