Recent Development of Si Chemical Dry Etching Technologies
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Abstract
Chemical dry etching in wafer processing was innovated and developed in 1976 using CF$_4$/O$_2$ downflow plasma for poly-Si etching. Thereafter, many researchers developed and reported various chemical dry etching methods.

Advanced Si chemical dry etching technology was developed in 2010, using N$_2$ downflow plasma and NF$_3$ flowing to the downflow plasma area. The etchant production mechanism for this technology was explained by us.

In these technologies, the plasma source is necessary to produce the etchants (F for Si etching and HF+NH$_3$ for SiO$_2$ etching).

Recently, a novel Si chemical dry etching technology was innovated and developed by us without plasma source, in which F atoms generated in F$_2$+NO$\rightarrow$F+FNO reaction are used for Si etching in the pressure range of 100 to 1000 Pa. The etch rate at room temperature is more than 5000 nm/min, and is dependent on the flow rate and on the distance between the gas mixing point and the wafer position. Increasing the substrate temperature, the minimum etch rate was obtained at 60ºC. Over this temperature, the etch rate increased again with increase of the substrate temperature. In the lower temperature region, the chemisorbed layer may be formed and the chemical reaction may be enhanced in this condensed layer. Increasing the temperature, this chemisorbed layer disappears around 60ºC. Over this temperature, the surface reaction mainly takes place according to Arrhenius equation.

Keywords: Wafer processing; Dry etching

Introduction
Chemical dry etching (CDE) in wafer processing was first developed by Horiike and Shibagaki [1], using CF$_4$/O$_2$ downflow plasma for poly-Si etching, to prevent the degradation of the electrical properties of integrated circuits (IC's) due to the bombardment of charged particles. Thereafter, many researchers developed and reported various chemical dry etching methods [2-11]. Mogab et al. [2] reported the O$_2$ addition effect in CF$_4$/O$_2$ radial flow reactive plasma, in which the maximum Si etch rate was obtained at an O$_2$ mixing ratio of 15%. A similar phenomenon was observed in a planar capacitive coupled plasma reactor [12]. Flamm et al. [4] derived the regression equation of the Si etch rate observing the chemiluminescence from SiF$_3$ on the Si wafer and the etch rate as a function of the wafer temperature, and also showed that the reaction probability of Si with F was 0.00168 at room temperature. Ninomiya et al. [13] reported that the reaction probability of Si with F was 0.1 at 300 K by gas-phase titration method under careful treatment, avoiding surface oxidation by the ambient. Energetic beam induced XeF$_2$, etching of Si was investigated by Coburn and Winters [14]. In this report, it was also suggested that the etch rate of Si by XeF$_2$ gas without beam irradiation was 0.5-0.7 nm/min (at flow rate of XeF$_2$=2x10$^{15}$ mol/s). The O$_2$ addition effect in the planar capacitive coupled plasma reactor was clearly explained observing the negative ions emerged from etched Si surface [15]. In this study, it was confirmed that the etch rate decrease above the 15% O$_2$ mixing ratio was mainly due to surface oxidation, because the CF$_3$ negative ion current observed by a mass spectrometer was approximately constant. CF$_3$ molecules are generally formed on the wall surface and released from the surface, because CF$_3$ molecule is very stable and CF$_3$ ion is formed by thermal electron attachment with the energy of 0.5 eV in the sheath region. In the O$_2$ mixing ratio lower than 15%, the etched surface was covered with CF$_3$ film. At around the maximum etching rate region, CF$_3$ film was removed effectively by O atoms and ions, and therefore, F atoms might be consumed by reaction with Si. Further increasing O$_2$ concentration, the etched surface was partially covered with SiO$_2$ and F consumption decreased. This mechanism leads to the distinct maximum of Si etch rate and F concentration. Therefore, it is supposed that the similar phenomenon takes place on the Si etched surface in the CF$_4$/O$_2$ radial flow reactive plasma.

Thus, chemical dry etching technologies have been studied and developed, but have not been used in wafer fabrication as one of the major etching technologies, because the etch rate cannot be readily controlled, and/or no anisotropic etching profile is obtained. However, this technology turns into a very important one because the removal of damaged Si layer around the gate electrode and residual oxide layer after gate oxide are strongly required in the ultrafine pattern fabrication with a half pitch lower than 45 nm. In these process, slow etch rate is required in order to control the etched depth of around 10 nm, which is damaged by a prior reactive ion etching [16-18], or remains in a prior oxide etching.

CDE Technologies with Long Life Time Plasma Source
The plasma source is constituted by quartz or aluminum oxide tube for these remote plasma sources. Quartz tube is preferably used because recombination of produced hydrogen atoms [19] and fluorine atoms on the quartz tube inner wall is relatively lower. However, when fluorine-containing compound is fed and decomposed in the discharge area, the quartz tube itself is eroded by fluorine containing plasma and has to be replaced with a new one after several hundred batches. If the fluorine containing etchants are produced outside the remote plasma source, the erosion of the plasma source is considerably reduced and the lifetime of the source material becomes longer owing to the reduction in the extent of fluorine erosion.

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Received August 27, 2012; Accepted October 10, 2012; Published October 20, 2012

Citation: Hayashi T (2012) Recent Development of Si Chemical Dry Etching Technologies. J Nanomed Nanotechol 515:001. doi: 10.4172/2157-7439.515-001

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Chemical dry etching technology for native oxide removal by flowing NF3 to H2+H2O down flow plasma was first developed by Kikuchi et al. [20,21], to avoid damage to the quartz tube by plasma irradiation. In this process, NF3 is not decomposed in the plasma source. However, it is thought that the oxide layer is also removed through a similar etching mechanism in the NF3/ NH3 down flow plasma on the wafer [8]. Oxide layer removal can also be carried out using H2, N2+H2, or NH3, down flow plasma and NF3, flow without decomposition [22]. In these down flow plasmas, hot H atoms initiate the reaction with NF3 in the down flow area, and then successive reactions take place between H atoms and NF3 (x=1-2) [23]. Finally, HF and NH3 are produced and adsorbed on the wafer surface, proceeding to condensed phase on the wafer surface. In this condensed phase, a sort of ammonium fluoride etching in the liquid phase takes place. It was reported that the etch rate wafer surface. In this condensed phase, a sort of ammonium fluoride adsorbed on the wafer surface, proceeding to condensed phase on the wafer surface. In this condensed phase, a sort of ammonium fluoride etching in the liquid phase takes place. Therefore, experimentally, by decreasing wafer temperature, etch rate increases, depending on temperature. Figure 2 shows the calculated molecular structure of (NH4)2SiF6 formed on the SiO2 surface through the reaction

\[ \text{SiO}_2 + 2\text{NH}_3 + 6\text{HF} \rightarrow (\text{NH}_4)_2\text{SiF}_6 + 2\text{H}_2\text{O} \]

This complex molecule with two NH4 groups on the same side is more stable than that with two NH4 groups on opposite sides to each other, because the coulomb interaction in NH4–F–NH4 takes place and stabilizes the molecule. This complex molecule decomposes with an increase in the wafer temperature up to 373 K to release SiF6 and the white powder remains on the wafer surface, which was deduced as FH–NH4–HF (coordinate bonded H of HF with N of NH4) [8]. However, the total cohesive energy (hydrogen bond energy) between two HF and NH3 molecules is -0.606 eV, which is lower than -0.663 eV of the hydrogen bond energy between HF and NH3 molecules in B3LYP/6-31+G(d,p) level. This implies that the white powder is not composed of only FH–NH4–HF and should rather be a huge molecule composed of (NH4F)4. It was found from the molecular orbital calculation that the white powder was mainly composed of stratified n(NH4F)n with a C3 symmetry axis [23].

A Si etching technology using NF3, flow into N2 down flow plasma was found by Tajima and Takahashi [25], at the distance of 20-40 cm apart from the edge of the N2 plasma source. They reported that the etch rate strongly depended on the etching conditions of the NF3, and N2 flow rates at the pressure of 100 to 500 Pa, by applying 2.45 GHz microwave power of 1-2 kW. In their report, the etch rate was especially dependent on the N2 flow rate ratio at the distance of 40 cm Si was not etched under a condition of the N2 and NF3 flow rates of 0.5 and 1 SLM, and increasing the N2 flow rate to 1 SLM Si was etched. This means that backward flow of NF3, does not take place (owing to viscous flow). This etch rate dependence on the N2 flow rate ratio is very useful to remove the damaged Si layer of approximately 10 nm around gate electrode [16-18], where clean removing the damaged layer without any etched residues is required, and is also to be controllable within 1 to 2 minutes by changing the N2 flow rate ratio.

Figure 3 shows a schematic diagram of the reaction chamber, in which NF3 is fed 20-40 cm from the edge of the discharge area at pressures of 100-500 Pa [26]. Under this condition, NF3 is fed into the downflow area without decomposition and reacts with activated N atoms, and/or activated N2 molecules, and three-body reactions partially take place because of the short mean free path (order of μm) of molecules in viscous flow. The total flow rate is several liters/min under standard conditions and the flow rate ratio of N2 to NF3 is 0.5 to 1.0, which is deduced from the overall reaction scheme of

\[ \text{N}_2 + 2\text{NF}_3 \rightarrow 2\text{N}_2 + 6\text{F} \]

In the experimental aspects, the absolute density of N2(A2Σu+)

Figure 1: Deduced chemical reaction schemes of NF3 in H2 afterglow plasma.

Figure 2: Stable molecular structure of etched product. The numerical values denote the charge density on the atoms.
the density of N(4\text{So}) decreased as the pressure increased. In the theoretical aspect, the rate constant for the NF$_3$ + N(4\text{So}) → NF$_2$ + NF gas phase reaction was calculated using the transition state theory based on MP2/6-31G(d) of the Gaussian 03 program by Barreto et al. [28], to explain the growth kinetic mechanism of boron nitride films. No other theoretical investigations are found. Therefore, we calculated the N+NF$_3$ (x=1 to 3) reactions using a molecular orbital method to clarify the F production mechanism in N$_2$ downflow plasma and flowing NF$_3$.

Figure 4 shows the potential curves of NF$_3$ for the ground state, the negative ion state and the ionized state with C$_{3v}$ structure, calculated using the B3LYP/6-311G(d). The lowest triplet state was calculated using B3LYP/6-31+G(d) and superimposed on this figure, because the lowest triplet state is a Rydberg state. The calculated energies for these states are good agreements with the experimental ones [29,30]. The calculated vertical transition energy to the lowest triplet state is 6.58 eV. This energy is very close to the N$_2$(A$_{3\Sigma^+u}$) energy (approximately 7 eV) [31]. This means that the following energy transfer reaction takes place resonantly:

$$\text{N}_2(\text{A}_{3\Sigma^+u}) + \text{NF}_3(1\text{A}_1) \rightarrow \text{N}_2(\text{X}_{1\Sigma^+g}) + \text{NF}_3(3\text{E}_1) \rightarrow \text{N}_2(\text{X}_{1\Sigma^+g}) + \text{NF}_2 + \text{F}$$

Figure 5 shows N+NF$_3$ reaction potentials as a function of reaction coordinate. The following three reaction schemes are possible:

$$\text{N}^+(\text{S}_1) + \text{NF}_3 \rightarrow \text{NF}_2 + \text{NF} \Delta E_a=0.72 \text{ eV} \Delta E_H=-1.16 \text{ eV} \ \ (2)$$

$$\text{N}^+(\text{S}_1) + \text{NF}_3 \rightarrow \text{N}^=\text{NF}_2 + \text{NF} \Delta E_a=1.2 \text{ eV} \Delta E_H=+0.28 \text{ eV} \ \ (3)$$

$$\text{N}^+(\text{D}) + \text{NF}_3 \rightarrow \text{N}^=\text{NF}_2 + \text{F} \Delta E_a=0 \text{ eV} \Delta E_H=-3.6 \text{ eV} \ \ (4)$$

Where $\Delta E_a$ is activation energy (reaction barrier) and $\Delta E_H$ is reaction enthalpy. The calculated result for the reaction scheme (2) is almost the same with that obtained by Barreto et al. [28]. The temperature of atomic nitrogen estimated from the spectra taken at 14 cm from the DC discharge area at 100 Pa was estimated as 0.2580 eV for pure N$_2$ plasma [32]. Therefore, it is considered that the reaction (4) is only possible for N+NF$_3$ reaction. The calculated state energy of N$^+(\text{D})$ was approximately 2.75 eV above the ground state energy of N$^+(\text{S}_1)$ in B3LYP/6-31+G(d) level, slightly larger than the experimental energy difference of 2.38 eV [31].

The total reaction scheme is summarized and illustrated in Figure 6. The solid line shows the main reaction routes and the dashed line shows the minor reaction routes. Surveying Figure 6 and the aforementioned reaction schemes, it is thought that the electron attachment dissociation can be neglected because the electrons produced in the plasma cannot survive at the NF$_3$ flowing point (20-40 cm apart from the discharge

![Figure 3: Schematic diagram of Si chemical dry etching system.](image-url)

![Figure 4: The calculated potential curves of NF$_3$ for the ground state, the negative ion state, the lowest triplet state, and the ionized state, obtained by using B3LYP/6-311G(d) and 6-31+G(d).](image-url)

![Figure 5: N+NF$_3$ reaction potentials as a function of reaction coordinate.](image-url)

![Figure 6: The total reaction schemes obtained by B3LYP/6-31+G(d).](image-url)
area in the pressure range of 100 to 500 Pa). Similarly, it is deduced that the contribution of \( \text{N}_2(\text{A}^3\Sigma_u^+) \) is not so high, because the density of \( \text{N}_2(\text{A}^3\Sigma_u^+) \) decreases as the pressure increases, whereas the density of \( \text{N}(\text{D}) \) was not dependent on the pressure (20–100 mTorr), according to the results shown by Horikawa et al. [27]. Therefore, the main reactions should be initiated by \( \text{N}(\text{D}) \). Then, \( \text{NF}(\text{3Σ}) \) and/or \( \text{NF}_2 \) radicals are produced in the downstream area. \( \text{NF} \) and \( \text{NF}_2 \) radicals are very unstable, so these radicals easily react with ground state nitrogen atoms \( \text{N}(\text{S}) \), proceeding to \( \text{N}_2 \) molecule and \( \text{F} \) atom(s). Decreasing the distance between the discharge region and the \( \text{NF}_2 \) flowing position, Si etch rate increases [25] because the densities of \( \text{N}(\text{A}^3\Sigma_u^+) \), and electrons also increase.

**CDE Technology without Plasma Source**

Chemical dry etching in view of gas-surface chemistry was first studied by Coburn and Winters [14]. In this work, they found that ion irradiation plays a very important role to enhance surface chemical reaction of \( \text{XeF}_2 \) with Si. This means that bond breaking of Si-Si and dangling bond formation enhances the surface chemical reaction. They also suggested that the purely chemical etch rate by \( \text{XeF}_2 \) was 0.5–0.7 nm/min at room temperature at the flow rate of \( \text{XeF}_2 = 2 \times 10^{15} \text{ mol/s} \) (corresponding to approximately 600 nm/min at 2.7 sccm), without ion irradiation. The surface chemistry of \( \text{F} \) atoms with Si was further investigated by Flamm et al. [4], using \( \text{F}_2 \) downflow plasma. They observed the relation between the etch rate and chemiluminescence, emitted from \( \text{SiF}_2^+ \) produced by \( \text{SiF}_2^+ \text{F} \) reaction near the Si surface and proposed the surface chemical reaction model that a layer of \( \text{SiF}_2 \) groups was chemically bound to the Si surface and the rate determinant reaction of impinging \( \text{F} \) atoms with \( \text{Si} \) bonds of the chemisorbed layer controlled the etching rate of Si with a chemiluminescent layer. Coburn et al. [5] studied surface chemical reactions of \( \text{XeF}_2 \) and \( \text{F} \) atoms with Si, in pressure range of 0.05 to 2 Torr. They clarified that the chemical reaction of \( \text{XeF}_2 \) with Si was different from that of \( \text{F} \) atom with Si. In the case of \( \text{F} \) atom, the etch rate was fit to a general form of the Arrhenius equation, as a function of substrate temperature, whereas an Arrhenius plot of the \( \text{XeF}_2 \) etch rate data exhibited a complex behavior. Below 450 K, the etch rate decreased with increasing temperature, between 360 and 450 K, it reached a minimum, and finally at higher temperatures it increased. They concluded that physisorbed and condensed \( \text{XeF}_2 \) layers contributed to the reaction rate below 450 K temperature region. Similar phenomena were observed for inter-halogen compounds, such as \( \text{ClIF}_2 \), \( \text{BrF}_2 \), and \( \text{IF}_2 \) with Si [6].

The common properties of these compounds may be having relatively weak bond energy and heavy weight mass. The bond energy of \( \text{F}_2 \) is also very low (1.8 eV [33]). The low bond energy means very reactive with Si, because Si-F bond energy is very high (approximately 6 eV [34]). The molecules with heavy mass have an inter-molecular force (Van der Waals forces), so the adsorption readily takes place on Si and then bond distortion may take place due to strong Si-F bond energy, resultantly leading to Si etching.

These gases, therefore, are very interesting to etch Si without any plasma source. However, the running cost is too high to respond to requirement of mass production lines.

**New CDE System without Plasma Source**

A new silicon etching process was innovated by us, using \( \text{F}^2 + \text{NO} \rightarrow \text{F} + \text{FNO} \) reaction [35], in the pressure region of 100 to 1000 Pa. This technology receives much attention for etching process engineers, in view of the initial and the running costs. The etch rate was comparable with that obtained using \( \text{XeF}_2 \) chemical dry etching. Arrhenius plot of the etch rate data obtained in the \( \text{F}_2 \) + NO mixing gas exhibited a complex behavior [36], similar to \( \text{XeF}_2 \) etching. Below 430 K, the etch rate decreased with increasing temperature, it reached a minimum between 430 and 450 K, and finally at higher temperatures it increased. The etch rate as a function of the substrate temperature is shown in Figure 7.

In the feasibility experiments [35,36], A 6 mm (width)×15 mm (length)×0.53 mm (thickness) Si sample was placed on the ceramic heater, which was covered by the Al foil inserted in the Pyrex® tube with the inner diameter of 25 mm and the length of 150 mm. The Si sample was exposed to the gas mixture of NO at a flow rate of 5 sccm (8.5×10^1 Pa-m/s) diluted with Ar at a flow rate of 49.5 sccm (8.4×10^2 Pa-m/s), and \( \text{Ar}/5\%\text{-F}_2 \) at a flow rate of 54.5 sccm (9.2×10^2 Pa-m/s). The corresponding \( \text{F}_2 \) flow rate was 2.7 sccm (4.6×10^2 Pa-m/s). In this study, the temperature on the ceramic heater was adjusted between 27°C and 300°C by the variable autotransformer, while measuring the temperature by the K-type thermocouple placed on top of the ceramic heater under the Si substrate. Pressure in the Pyrex® tube was maintained at 600 Pa throughout the process time of 0.5 ~ 5 min. Base pressure of this chamber was maintained at ~ 10^−6 Pa by the dry pump, so the small amount of \( \text{H}_2\text{O} \) was considered to be remained in the chamber.

Two Si samples were prepared. One was p-type Si (100) sample with the resistivity of ~1000 Ω-cm with a 1 µm-thick SiO₂ mask layer that had 8 µm×8 µm square patterns. This sample was exposed in NO and \( \text{F}_2 \) gases for 0.5 min in the aforementioned process chamber. The other was the non-doped Si (100) sample with the resistivity of >3000 Ω-cm for the surface morphology and the surface chemical bonding structure analysis. This sample was cleaned with acetone, ethanol, deionized (DI) water, 13% hydrochloric acid and 49% hydrofluoric (HF) acid for 5 min, followed by rinsing in DI water for <5 s to terminate the Si surface with H. This H-terminated Si sample was exposed to NO and \( \text{F}_2 \) gases for 0.5 min in the aforementioned process chamber.

Figure 8 shows the representative cross-sectional SEM images of the patterned p-type Si (100) samples placed in NO and \( \text{F}_2 \) gases, when the Si was heated at 27°C ~ 300°C. We found that the etched Si surface was very rough when the substrate temperature was 27°C, and increasing the temperature up to 70°C, the etch rate decreased and the roughness also decreased. Nanoporous features were observed in the microscopically rough etched profile at this temperature range. When
the Si sample was heated at 60°C ~ 230°C, the etched bottom surface became smooth with the absence of nanoporous features. The etch rate decreased with increase of the temperature up to ~ 70°C and increased again at above 70°C. When the substrate temperature was adjusted at above 230°C, the sidewall of the etched profile became vertical. The crystallographic orientation was evolved and the etch rate increased with the temperature by the increase of the rate constant of F, F₂, and NO and the large coordinated compound could be ignored. The multiple chemical reactions between the molecules in the gas phase and the Si surface occurred at different rates, leading to produce complex nanoporous features in microscopically rough etched profiles. The reduction of F, F₂, NO and large molecules in the chemisorbed layer decelerated the etch rate at an intermediate temperature. When the substrate temperature was ramped at above 230°C, the Si etching was mainly performed by F, F₂, and NO at the Si surface, and contribution of NO and the large coordinated compound could be ignored. The crystallographic orientation was evolved and the etch rate increased with the temperature by the increase of the rate constant of F, F₂, and NO and the Si surface.

Summary

The development of the chemical dry etching technologies is reviewed historically in this literature. The downflow chemical dry etching technology using CF₄/O₂ is now available to fabricate LSI and power devices. The chemical dry etching technology using XeF₂ without plasma is widely used in the field of micro electro-mechanical system (MEMS) fabrication process. The N₂ downflow plasma and NF₃ flow system is considered to be a new damage less process after the poly-Si gate etching, to remove ion damaged layer of 10 nm. The chemical dry etching using CIF₂ gas is considered as a candidate to reduce reflectance of solar cell devices. Thus, the chemical dry etching technologies are selectively used according to adaptable application area.

The chemical dry etching technology in F₂+NO gas mixture is considered as a most promising candidate to be applicable to a wide variety of devices, because of its low initial and running costs and the changeable surface morphology depending on the substrate temperature. The sacrificial layer removal for MEMS devices and the surface texturing for solar cell devices can be carried out at room temperature with the rate of several 1000 nm/min. The damanged layer removal after wafer thinning by the chemical-mechanical polishing (CMP) method for 3 dimensional devices is also capable and anticipated as the most promising technology. This process can be carried out using the ramp technology of the substrate temperature. High rate etching is used in the initial stage and low rate etching with smooth surface is used in the final stage.

References


