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 60°C. 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 60°C. 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 Horike 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 (ICs) 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 for the etch rate observing the chemiluminescence from SiF$^+$ 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. Energetic beam induced XeF$_2$ etching of Si was investigated by Coburn and Winters [14]. In this report, it was also 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 ultraline pattern fabrication with a half pitch lower than 45 nm. In these processes, 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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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 of the chemical dry etching method by flowing to the H₂, N₂+H₂, or NH₃ down flow plasma was 1 to 10 nm/min at the room temperature, not depending on the distance between the NF₃ flow position and the wafer stage [22]. These processes are very useful to remove thin oxide layer (10 to 20 nm) for the etching around the gate electrode without the plasma damage.

The reaction mechanism for the thin oxide layer removal using H₂ downflow plasma and flowing NF₃ into this downflow plasma at around 500 Pa was clarified by us [23], in which backward flow of NF₃ does not take place owing to viscous flow and F atom is not generated in the plasma source. The total reaction scheme is summarized and illustrated in Figure 1. The solid line shows the main reaction routes and the dashed line shows the minor reaction routes. Some of the reactions depicted in this figure also take place at the surface, because a strong hydrogen bond is formed between the HF and NH₃ produced and the boiling point of this complex molecule exceeds 500 K [24]. Finally, HF and NH₃ are formed and adsorbed on the wafer surface, on which a condensed phase is formed, so that a type 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 \((\text{NH}_4)_2\text{SiF}_6\) 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 SiF₄ and the white powder remains on the wafer surface, which was deduced as FH−NH₃−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−NH₃−HF and should rather be a huge molecule composed of \((\text{NH}_4)_2\text{SiF}_6\). It was found from the molecular orbital calculation that the white powder was mainly composed of stratified \(\text{n(NH}_4\text{F)}\), with a C₃ symmetry axis [23].

A Si etching technology using NF₃ flow into N₂ downflow 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 \(N_i(A^2\Sigma^+u^+)\),
the density of N(\(4^3\Sigma^+\)) decreased as the pressure increased. In the theoretical aspect, the rate constant for the NF\(_2\)+N(\(4^3\Sigma^+\))→NF\(_3\)+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\(_3\)v structure, calculated using the B3LYP/6-311G(d). The lowest triplet state was calculated using B3LYP/6-31G(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}\(_2\)(A\(_3\)\Sigma^u\(^+\)) + NF \rightarrow N(\text{F}) + \text{NF}_3 + \text{F} \]

Figure 4 shows N+NF\(_3\) reaction potentials as a function of reaction coordinate. The following three reaction schemes are possible:

\[ \text{N}\(_3\)(\text{F}) + NF \rightarrow \text{NF}_2 + \text{F} \quad \Delta \text{E}_a = 0.72 \text{ eV} \quad \Delta \text{E}_H = -1.16 \text{ eV} \quad (2) \]

\[ \text{N}\(_3\)(\text{F}) + NF \rightarrow \text{NF}_2 + \text{F} \quad \Delta \text{E}_a = 1.2 \text{ eV} \quad \Delta \text{E}_H = 0.28 \text{ eV} \quad (3) \]

\[ \text{N}\(_3\)(\text{F}) + NF \rightarrow \text{NF}_2 + \text{F} \quad \Delta \text{E}_a = 0 \text{ eV} \quad \Delta \text{E}_H = -3.6 \text{ eV} \quad (4) \]

Where \(\Delta \text{E}_a\) is activation energy (reaction barrier) and \(\Delta \text{E}_H\) is reaction enthalpy, obtained by B3LYP/6-31+G(d). Negative value means exothermic energy. 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\(_3\)(\text{F}) was approximately 2.75 eV above the ground state energy of N\(_3\)(\text{F}) 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

\[ \text{N}\(_3\)(\text{F}) + NF \rightarrow \text{NF}_2 + \text{F} \quad \Delta \text{E}_a = 0 \text{ eV} \quad \Delta \text{E}_H = -3.6 \text{ eV} \quad (4) \]

Figure 6: The total reaction schemes obtained by B3LYP/6-31+G(d).
area in the pressure range of 100 to 500 Pa). Similarly, it is deduced that the contribution of N(2Δg) is not so high, because the density of N(2Δg) decreases as the pressure increases, whereas the density of N(2Δg) 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 N(2Δg). Then, NF(3Σ−) and/or NF2 radicals are produced in the down flow area. NF and NF2 radicals are very unstable, so these radicals easily react with ground state nitrogen atoms N(4S0), proceeding to N2 molecule and F atom(s). Decreasing the distance between the discharge region and the NF3 flowing position, Si etch rate increases [25] because the densities of N(4S0), 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 XeF2 with Si. This means that bond breaking of Si-Si and irradiation plays a very important role to enhance surface chemical reaction. They also suggested that the purely chemical etch rate by XeF2 was 0.5–0.7 nm/min at room temperature at the flow rate of XeF2=2×1013 mol/s (corresponding to approximately 600 nm/min at 2.7 sccm), without ion irradiation. The surface reaction of F atoms with Si was further investigated by Flamm et al. [4], using F2 downflow plasma. They observed the relation between the etch rate and chemiluminescence, emitted from SiF* , produced by SiF+F reaction near the Si surface, and proposed the surface chemical reaction model that a layer of SiF2 was formed. Decreasing the distance between the discharge region and the NF3 flowing position, Si etch rate increases [25] because the densities of N(4S0), and electrons also increase.

**New CDE System without Plasma Source**

A new silicon etching process was innovated by us, using F2 + NO→F + 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 XeF2 chemical dry etching. Arrhenius plot of the etch rate data obtained in the F2+NO mixing gas exhibited a complex behavior [36], similar to XeF2 etching. Below 430 K, the etch rate decreased with increasing temperature, it reached a minimum between 430 and 450 K, and the etch rate finally 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 (8.5×10−3 Pa·m3/s) diluted with Ar at a flow rate of 49.5 sccm (8.4×10−2 Pa·m3/s), and Ar/5%F2 at a flow rate of 54.5 sccm (9.2×10−2 Pa·m3/s). The corresponding F2 flow rate was 2.7 sccm (4.6×10−3 Pa·m3/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 ~10−4 Pa by the dry pump, so the small amount of H2O 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 F2 gases for 5 min for the etch rate and the etched profile analysis. 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 F2 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 F2 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 observed from these SEM images where the bottom surface was (100) and the sidewall was (110). Corner undercutting with the exposure of {211} and {411} were also observed at the corner of the etched profile [36].

Thus, morphology of the etched bottom surface and the sidewall surface of the p-doped Si was dramatically changed when the Si was heated at different temperatures. Figure 9 shows the top view of the Si (100) placed in the NO and F2 gases for 0.5 min. The microscopically rough etched profile were observed, similarly when the Si was chemically dry etched in XeF2 or ClF3 gases [5,6]. Previous studies stated that the evolution of the rough surface was due to the chemisorption of not only F but also XeF2, XeFCl2, Cl2, Cl that would etch Si differently. The residence time of those molecules on the Si surface was long when the substrate temperature was low. The high Si etch rate at the low temperature in NO and F2 gases observed in Figure 8 and 9 can be explained by the presence of the chemisorbed F2, F and others that would promote the etching. In addition to F2 and F, NO would inhibit the etching by capping the dangling bonds. FNO would act as both a chemisorbed F, F2 and FNO 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 FNO 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 CIF4 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 damaged 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.

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