Etch-Induced Physical Damage and Contamination during Highly Selective Oxide Etching Using \( \text{C}_4\text{F}_8/\text{H}_2 \) Helicon Wave Plasmas

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Physical damage and residue remaining on the silicon wafer during the oxide overetching using helicon wave plasmas, and the effects of various cleaning and annealing methods on the removal of the remaining damage and residue, were investigated. The remaining residue was composed of carbon, fluorine, and oxygen, and the addition of 30\% \( \text{H}_2 \) to the \( \text{C}_4\text{F}_8 \) plasma changed the C/F ratio, the carbon bonding states, and the thickness of the residue on the etched silicon surface. Hydrogen was also present in the residue. The fluorine component in the residue was easily removed by \( \text{O}_2 \) plasma cleaning, while the carbon component still remained, regardless of gas chemistry. Most of the residues on the etched surfaces could be removed by oxygen-plasma cleaning followed by thermal annealing over 450\°C. Physical defects were observed on the silicon wafers overetched by both \( \text{C}_4\text{F}_8 \) plasma and 70\% \( \text{C}_4\text{F}_8/30\% \text{H}_2 \) plasma. Compared to the silicon wafer overetched by \( \text{C}_4\text{F}_8 \) plasma, the observed defects were located deeper after the overetching by 70\% \( \text{C}_4\text{F}_8/50\% \text{H}_2 \) plasma. Annealing at 1000\°C for 30 min was required to completely remove these defects for \( \text{C}_4\text{F}_8 \) plasma overetched silicon, and higher temperatures were required for 70\% \( \text{C}_4\text{F}_8/30\% \text{H}_2 \) plasma overetched silicon. The residue appears to reduce the formation of Co silicides more compared to the physical defects remaining on the silicon surface.

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Highly selective oxide etching is a key process for successful fabrication of next-generation semiconductor devices. 1 To achieve this goal, high-density plasma sources are generally studied using a combination of high C/F ratio gases (e.g., \( \text{C}_4\text{F}_8 \) and \( \text{C}_2\text{F}_6 \)) and hydrogen-containing gases (e.g., \( \text{H}_2 \) and \( \text{CHF}_3 \)). The use of high C/F ratio gases with hydrogen-containing gases generates higher C/F ratio plasmas, according to the scaling rule, the minimization and effective removal of physical damage on the exposed silicon during the overetch period. 2-7 As the depth of the contact junction becomes shallower according to the scale rule, the minimization and effective removal of the damage and contamination remaining on the overetched silicon surface becomes more necessary. This can only be done through optimization of both the specific etch processes and the following postetch treatment processes, such as cleaning and annealing. 9,13,14,16

Previously, the damage and residue remaining on silicon surfaces overetched using magnetically inductively coupled \( \text{C}_4\text{F}_8 \) plasmas during oxide etching and the effects of various cleanings and annealing on the removal of the damage and residue have been reported. 8,9 Currently, not only various types of inductively coupled plasma sources but also various types of helicon plasma sources are actively studied as promising next-generation oxide-etching plasma sources which can provide highly selective and vertical oxide etch processes with high oxide etch rates. However, not many studies on the damage and contamination during the oxide etching using helicon wave plasmas have been reported. 7,17

Therefore, in this study, the damage and contamination remaining on the etched silicon surface after the oxide overetching by \( \text{C}_4\text{F}_8/ \text{H}_2 \) helicon wave plasmas and the cleaning and annealing methods on the removal of the damage and contamination were studied. Also, Co silicides were formed on the etched and postetch treated silicon surfaces, and the effects of remaining damage and residue on the formation of stable Co silicides were investigated.

Experimental

In this study, a helicon wave plasma etcher with a Nagoya-type antenna was used for the highly selective contact oxide etching. \( \text{C}_4\text{F}_8 \) and 70\% \( \text{C}_4\text{F}_8/30\% \text{H}_2 \) helicon plasmas with other process parameters fixed as described previously, the etch rates were 670 and 450 nm/min, and the etch selectivities over silicon were 10 and 115.145.196.103 address. Redistribution subject to ECS license or copyright; see ecsdl.org/site/terms_use
22, respectively. The etch profiles were nearly vertical for both cases. These wafers were 50% overetched to expose silicon surfaces, and the remaining damage and residues on the exposed silicon surfaces were investigated. The residues consisted of carbon, fluorine, and oxygen for both gases when measured using XPS; however, the thickness of the residue was thicker for 70% C₄F₈/30% H₂ compared to that for C₄F₈. The thickness of the residue was 68 Å for 70% C₄F₈/30% H₂ and 45 Å for C₄F₈ when measured using a spectroscopic ellipsometer.

The distribution of residue composition and carbon bonding states in the residue were measured using angle-resolved XPS. Figure 1a shows the C/F ratio of the residues from C₄F₈ and 70% C₄F₈/30% H₂. Fig. 1b for carbon (1s) bonds of the residue from C₄F₈, and Fig. 1c for carbon (1s) bonds from 70% C₄F₈/30% H₂. In the figures the lower angle represents the surface side of the residue. As shown in Fig. 1a, the surface side of the residue was more fluorine-rich than inside the residue for both gas conditions, but the residue from 70% C₄F₈/30% H₂ was more carbon-rich throughout the residue thickness compared to that from C₄F₈. Also, in the case of carbon bonding states as shown in Fig. 1b and c, the C–CFₓ bonding state was the most abundant state throughout the residue, and slightly more C–CFₓ and C–C/H bondings were found inside the residue compared to the surface side of the residue, while C–Fₓ (x = 1,2,3) bondings remain similar.

The overetched wafers were postetch treated by piranha cleaning, oxygen-plasma cleaning, and oxygen-plasma cleaning followed by furnace annealing in N₂ at 450 and 600°C. Figure 2 shows some of the XPS data on the compositions of the residues remaining on the etched and the postetch treated silicon wafers for C₄F₈ (a) and 70% C₄F₈/30% H₂ (b). The oxygen-plasma cleaning alone removed most of the fluorine component of the residue, and the annealing up to 600°C after the oxygen-plasma cleaning recovered the relative atomic percent of silicon (66% for 70% C₄F₈/30% H₂ and 60% for C₄F₈) close to 69% of the control (clean silicon) wafer. These data were taken without final HF dipping to remove the oxide formed during the postetch treatment. When the surfaces of the etched wafers annealed at 600°C after the oxygen-plasma cleaning were examined again using XPS after 100:1 HF dipping, the ratio of Si:C:O was 74:16:11 for C₄F₈ and 82:11:7 for 70% C₄F₈/30% H₂, while that of control wafer after the HF dipping was 85:8:7. Therefore, after the annealing at 600°C, the residue on the silicon wafer overetched with 70% C₄F₈/30% H₂ was almost removed, similar to that of the control wafer. This result was also supported from the thickness data of the remaining residue measured during the oxygen-plasma cleaning.

![Figure 1](image_url). Angle-resolved XPS data of the residues on the silicon etched using C₄F₈ and 70% C₄F₈/30% H₂: (a, above) C/F ratio of the residue for C₄F₈ and 70% C₄F₈/30% H₂; relative intensities of each carbon bonding states for the (b, top right) C₄F₈ and (c, right) 70% C₄F₈/30% H₂.
using the spectroscopic ellipsometer. Even though the remaining residue from 70% C₄F₈/30% H₂ was thicker than the residue from C₄F₈ after the etching, the residue from 70% C₄F₈/30% H₂ was removed faster (1 Å/min) than the residue from C₄F₈ (0.5 Å/min).

The carbon 1s bonding states of the residues remaining after etching and after postetch treatments were investigated and are shown in Fig. 3a for C₄F₈ and 3b for 70% C₄F₈/30% H₂. Oxygen-plasma cleaning generally reduced most of the C–Fₓ (x = 1, 2, 3) bondings and many of the C–CFₓ bondings, however, other bondings, such as C–C/H, C–O, and C–Si, remained similar for both gas conditions. Therefore, the residue changed to carbon-rich after the oxygen-plasma cleaning. Annealing after the oxygen-plasma cleaning for both gas conditions removed the carbon-rich residue, and more residue was removed by increasing the annealing temperature to 600°C. The amount of residue remaining after the annealing at 600°C was small for both gas conditions; however, more residue containing Si–C bondings (20%), known to be difficult to remove, remained on the C₄F₈-etched surface compared to the 70% C₄F₈/30% H₂ etched surface.

Some energetic species from the plasmas can be implanted into silicon surface during the overetching and can diffuse into silicon.

Figure 2. Composition of the residues formed on the silicon surface etched using (a, top) C₄F₈ and (b, bottom) 70% C₄F₈/30% H₂ plasmas as a function of postetch treatments. Composition measured using XPS with 90° take-off angle.

Figure 3. Carbon 1s narrow scan data of the silicon surfaces etched using (a, top) C₄F₈ and (b, bottom) 70% C₄F₈/30% H₂ plasmas as a function of postetch treatments.
during postetch treatment processes. Because hydrogen, which could be one of the most abundant species on the silicon surface overetched using the 70% C4F8/30% H2 plasma, cannot be measured using XPS, SIMS was used to investigate the degree of implantation of hydrogen, in addition to the other residue components such as carbon and fluorine, into silicon. In Fig. 4, SIMS depth profiles of carbon, fluorine, and hydrogen for 70% C4F8/30% H2 plasma-etched and postetch treated silicon surfaces are shown. For comparison, the depth profile of a control wafer was included. In the figures, the estimated implanted depths of carbon, fluorine, and hydrogen in the etched silicon surface appeared to be as deep as 500 Å, even though the exact implanted depths of the species could not be easily meas-

**Figure 4.** SIMS depth profile data of (a, above) carbon, (b, top right) fluorine, and (c, right) hydrogen on the etched silicon as a function of postetch treatments.
sured. Also, from the data on the hydrogen depth profile, it appeared that a considerable amount of hydrogen was included in the residue in addition to carbon and fluorine, and also inside the silicon surface. However, after the annealing at 450°C, the depth profiles of carbon; fluorine, and hydrogen became close to those of control; therefore, most of the implanted species appeared to be removed by outdiffusion or by forming volatile products, even though the exact mechanism cannot be given at this time.

The faster removal rate of the residue from 70% \( \text{C}_4\text{F}_8/30\% \text{H}_2 \) compared to that from \( \text{C}_4\text{F}_8 \) which was observed in Fig. 2 and 3, might be related to the hydrogen contained in the residue from 70% \( \text{C}_4\text{F}_8/30\% \text{H}_2 \), shown in Fig. 4c. Rather than C–C bondings, the residue might have many C–H bondings in C–C/H bondings (C–C bondings and C–H bondings cannot be separated in the XPS analysis due to the very close energies of those emitted photoelectrons), and C–H bonds are more easily broken compared to the C–C bonds. Therefore, during the oxygen-plasma cleaning and the annealings, this residue with C–H bonds can be effectively removed by forming volatile products and by thermal decomposition, compared to the residue only with C–C bondings such as the residue from \( \text{C}_4\text{F}_8 \).\(^\text{10}\)

The energetic ion bombardment, implantation, and diffusion of the species described can produce physical and electrical defects on the overetched silicon surface. The physical and electrical damage received on the exposed silicon wafer during the 50% overetching of 1 \( \mu \text{m} \) phosphosilicate glass with \( \text{C}_4\text{F}_8 \) and 70% \( \text{C}_4\text{F}_8/30\% \text{H}_2 \), and the recovery of the physical and electrical defects after the postetch treatment processes, were investigated using HRTEM for physical defects and using a SPV technique for electrical defects.\(^\text{18}\) On both the silicon surfaces overetched with \( \text{C}_4\text{F}_8 \) and 70% \( \text{C}_4\text{F}_8/30\% \text{H}_2 \), physical defects were observed, and the depth of the defects in wafers overetched with 70% \( \text{C}_4\text{F}_8/30\% \text{H}_2 \) were greater (550 Å) than those with \( \text{C}_4\text{F}_8 \) (250 Å), possibly due to energetic hydrogen ion implantation and diffusion. Figure 5 shows HRTEM of the defects observed on the silicon surface overetched with \( \text{C}_4\text{F}_8 \) (a) and with 70% \( \text{C}_4\text{F}_8/30\% \text{H}_2 \) (b). As shown in the figures, defects were made of [111] and [311] stacking faults and point defect clusters. When the lifetime of those etched wafers was measured to estimate electrical damage using the SPV technique, more electrical damage was also measured for the silicon wafer overetched with 70% \( \text{C}_4\text{F}_8/30\% \text{H}_2 \) and annealed at 600°C appeared to show the lowest resistivity of 765 mΩ, close to...
780 mΩ of the silicide made with the control wafer, because almost all the remaining residue was removed as shown in Fig. 3b. The change of the residue to carbon-rich by the oxygen-plasma cleaning also appeared to affect the formation of the stable silicide. After the piranha cleaning, even though the thickness of the residue remaining on the silicon surface after overetching with 70% C₄F₈/30% H₂ was thicker than the residue with C₄F₈, the resistivity was lower for the silicide formed on the silicon etched with 70% C₄F₈/30% H₂, possibly due to the carbon-rich residue for 70% C₄F₈/30% H₂, as shown in Fig. 3b. More physical defects were found on the silicon surface etched with 70% C₄F₈/30% H₂, as shown in Fig. 5, however, the resistivity was lower. Therefore, the physical defects remaining on the silicon surface appear to affect the electrical properties of Co silicides formed on the etched silicon surface significantly compared to the residue remaining on the etched silicon surface, possibly due to the easier consumption of the physical damage during the Co silicidation.

Conclusions

Damage and residue remaining on the silicon wafer overetched using C₄F₈ and C₄F₈/H₂ helicon wave plasmas and postetch treated by various cleaning and annealing methods were investigated using SE, XPS, SIMS, HRTEM, a SPV technique, etc. Piranha cleaning, oxygen-plasma cleaning, and annealing after the oxygen-plasma cleaning were used to remove the residue and/or damage. Co silicides were fabricated on the etched and postetch treated silicon surfaces to investigate the effects of the remaining residue and damage on the formation of stable Co silicides.

Remaining residue on the silicon surface overetched with C₄F₈ residue was composed of carbon, fluorine, and oxygen, and the addition of 30% H₂ to the C₄F₈ plasma increased the C/F ratio and the thickness of the residue and changed the carbon bonding states of the residue on the etched silicon surface. Also, hydrogen was included in the residue. Fluorine component in the residue was easily removed by the O₂-plasma cleaning, while the carbon component remained, regardless of the gas chemistry. The residue formed by 70% C₄F₈/30% H₂ helicon wave plasma was removed by postetch treatments faster than the residue formed by C₄F₈, and the cleanest surface close to the control surface could be obtained on the silicon overetched with 70% C₄F₈/30% H₂ by 600°C annealing after the oxygen-plasma cleaning. However, the physical and electrical defects remained on the silicon surface overetched with both C₄F₈ and 70% C₄F₈/30% H₂. Thermal annealing at 1000°C for 30 min appeared to be required to completely remove physical damages for C₄F₈-plasma-overetched silicon and at a higher temperature for 70% C₄F₈/30% H₂-plasma-overetched silicon. After the postetch treatment using the oxygen cleaning followed by thermal annealing at 600°C, the sheet resistance of Co silicides showed the lowest value close to the control sample. The remaining physical defects did not obstruct the formation of Co silicide compared to the remaining residue, possibly due to the easier consumption of the physical damage during the Co silicidation.

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References