

Etch-Induced Physical Damage and Contamination during Highly Selective Oxide Etching Using C₄F₈/H₂ 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% H₂ to the C₄F₈ 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 O₂ 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 C₄F₈ plasma and 70% C₄F₈/30% H₂ plasma. Compared to the silicon wafer overetched by C₄F₈ plasma, the observed defects were located deeper after the overetching by 70% C₄F₈/30% H₂ plasma. Annealing at 1000°C for 30 min was required to completely remove these defects for C₄F₈ plasma overetched silicon, and higher temperatures were required for 70% C₄F₈/30% H₂ plasma overetched silicon. The residue appears to reduce the formation of Co silicides more compared to the physical defects remaining on the silicon surface. © 1999 The Electrochemical Society. S0013-4651(98)04-044-0. All rights reserved.

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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., C₄F₈ and C₂F₆) and hydrogen-containing gases (e.g., H₂ and CHF₃). The use of high C/F ratio gases with hydrogen-containing gases generates higher C/F ratio plasmas, and results in highly selective oxide etching under high ion bombardment of high-density plasmas, such as helicon wave plasmas and inductively coupled plasmas.²⁻⁷

However, the use of high-density plasma sources with very high C/F ratio gas compositions often generates a thick residue layer and physical damage on the exposed silicon during the overetch period.⁸⁻¹² As the depth of the contact junction becomes shallower according to the scaling 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 magnetized inductively coupled C₄F₈ 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 C₄F₈/H₂ 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. C₄F₈

and 70% C₄F₈/30% H₂ gases were used to etch 1 μm thick phosphorus-silicate-glass (PSG) deposited on an n-type silicon wafer. A radio frequency (rf) power of 13.56 MHz was applied to the antenna, and a separate 13.56 MHz was varied to achieve -80 V of dc self-bias on the substrates while the operating pressure was kept at 1.5 mTorr and the total flow rate at 30 sccm. The oxide etch time was set by achievement of a 50% overetch period of 1 μm thick PSG, resulting in exposed silicon surfaces. The overetched silicon wafers were cleaned using a piranha cleaning solution (H₂SO₄:H₂O₂ = 4:1, 90°C) for 10 min. Oxygen-plasma cleaning was also performed using a microwave plasma asher (Astex Company) at 200 W, 500 mTorr, and 120°C of substrate temperature for 40 min. In addition to these cleaning methods, the overetched silicon wafers were annealed from 200 to 1000°C for 30 min in N₂ after O₂-plasma cleaning to remove remaining residue and physical/electrical damage.

To observe the thickness and chemical composition of the remaining residue layer on the etched silicon surfaces before and after the postetch treatments, spectro-ellipsometry (SE, Gaertner L104N) and X-ray photoelectron spectroscopy (XPS, Fison's system Escalab 220i) were employed. Also, to investigate the degree of implantation and diffusion of the residue component into silicon, secondary ion mass spectrometry (SIMS, PHI-7200 TOF SIMS) was used. To estimate electrical damage remaining on the etched and annealed silicon surfaces, carrier lifetime and diffusion length were measured using an SPV technique (surface photovoltage, Semiconductor Diagnostics, Incorporated, CMS III-A), and high-resolution transmission electron microscopy (HRTEM, JEOL JEM 2000EX) was used to observe the remaining physical defects before and after thermal annealing. Cobalt silicides were fabricated on the silicon surfaces before and after post-treatments by the electron-beam evaporation of 700 Å thick Co followed by rapid thermal annealing at 700°C for 1 min in 500 mTorr Ar. These silicon wafers were dipped in a diluted HF solution before the evaporation of Co to remove native oxide. X-ray diffraction (XRD, Rigaku D/max-B system) and a sheet resistance measurement were used to evaluate the degree of silicidation, where the sheet resistance was measured using a four-point probe (CMT SR-1000).

Results and Discussion

When 1 μm thick PSG-deposited silicon wafers were etched in C₄F₈ and 70% C₄F₈/30% H₂ 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

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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% $C_4F_8/30\% H_2$ compared to that for C_4F_8 . The thickness of the residue was 68 Å for 70% $C_4F_8/30\% H_2$ and 45 Å for C_4F_8 when measured using a spectroscopic ellipsometer.

The distribution of residue composition and carbon bonding states in the residue were measured using angle-resolved XPS.^{10,15} Figure 1a shows the C/F ratio of the residues from C_4F_8 and 70% $C_4F_8/30\% H_2$, Fig. 1b for carbon (1s) bonds of the residue from C_4F_8 , and Fig. 1c for carbon (1s) bonds from 70% $C_4F_8/30\% H_2$. 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% $C_4F_8/30\% H_2$ was more carbon-rich throughout the residue thickness compared to that from C_4F_8 . Also, in the case of carbon bonding states as shown in Fig. 1b and c, the C-CF_x bonding state was the most abundant state throughout the residue, and slightly more C-CF_x and C-C/H bondings were found inside the

residue compared to the surface side of the residue, while C-F_x (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 C_4F_8 (a) and 70% $C_4F_8/30\% H_2$ (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% $C_4F_8/30\% H_2$ and 60% for C_4F_8) 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 C_4F_8 and 82:11:7 for 70% $C_4F_8/30\% H_2$, 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% $C_4F_8/30\% H_2$ 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

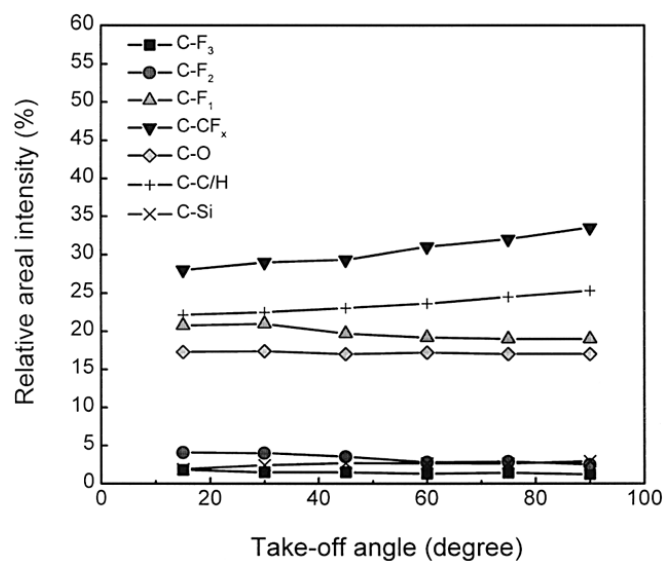
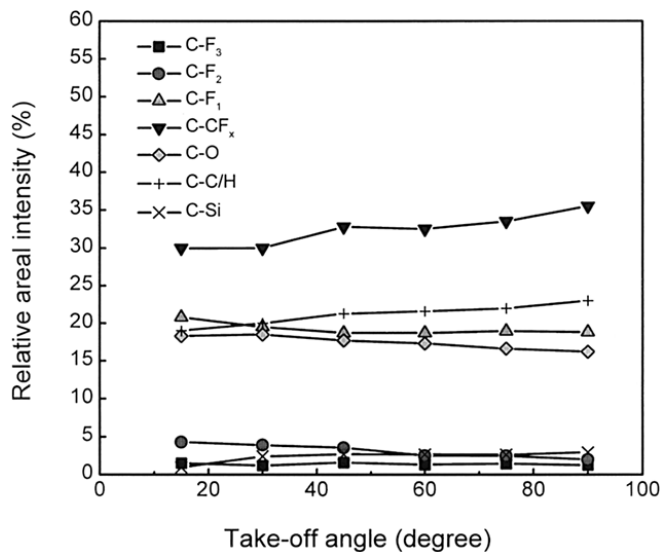
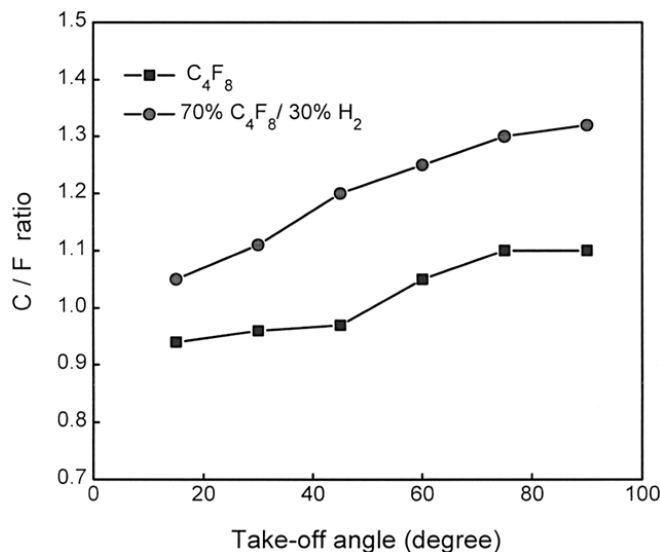


Figure 1. Angle-resolved XPS data of the residues on the silicon etched using C_4F_8 and 70% $C_4F_8/30\% H_2$: (a, above) C/F ratio of the residue for C_4F_8 and 70% $C_4F_8/30\% H_2$; relative intensities of each carbon bonding states for the (b, top right) C_4F_8 and (c, right) 70% $C_4F_8/30\% H_2$.

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-F_x (x = 1, 2, 3) bondings and many of the C-CF_x 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

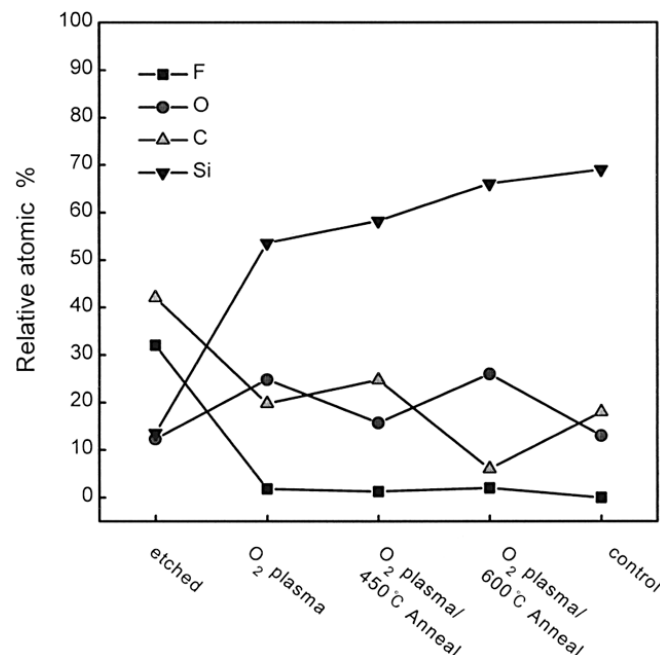
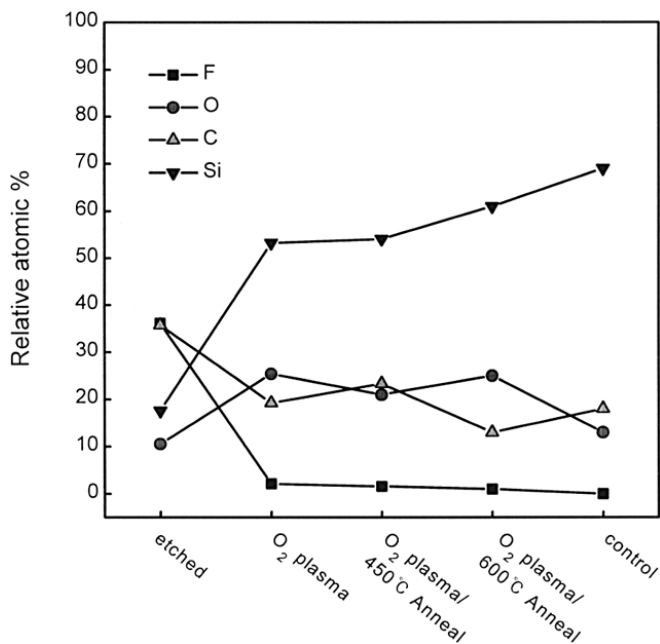


Figure 2. composition of the residues formed on the silicon surface etched using (a, top) C₄F₈ and (b, bottom) 70% C₄F₈/30% H₂ plasmas as a function of postetch treatments. Composition measured using XPS with 90° take-off angle.

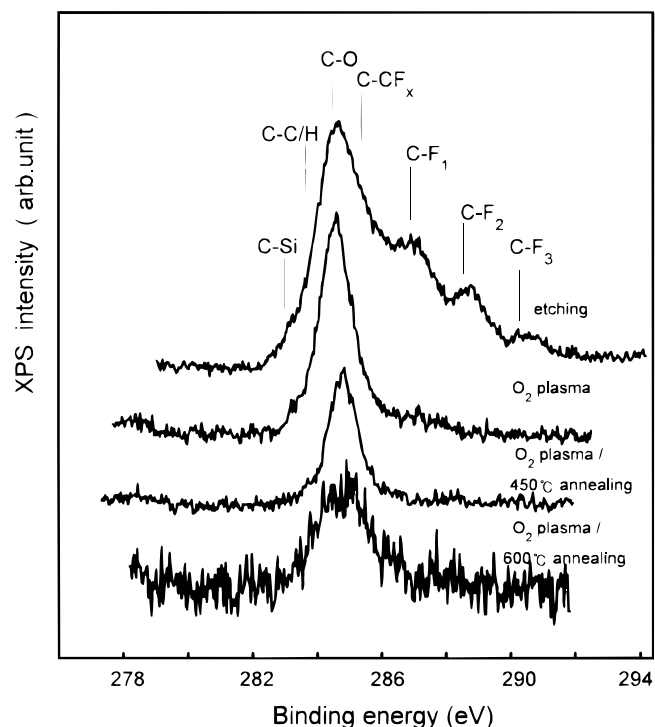
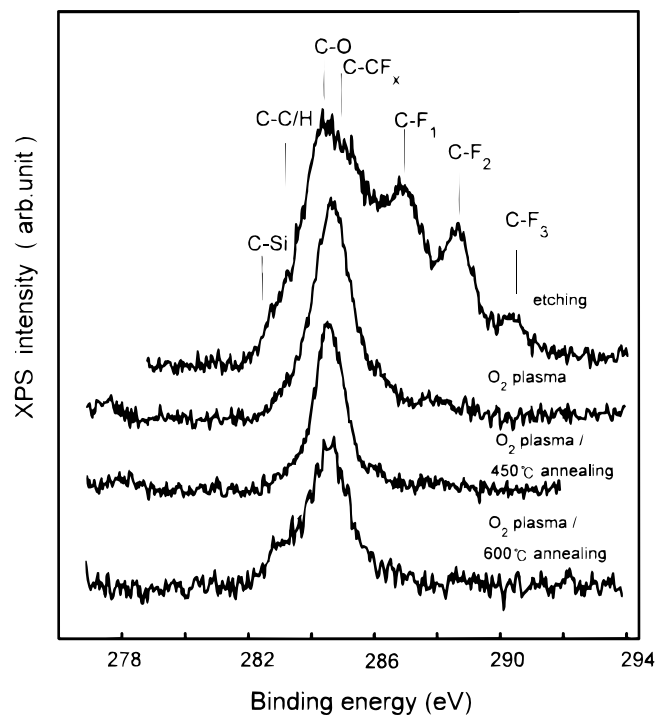


Figure 3. Carbon 1s narrow scan data of the silicon surfaces etched using (a, top) C₄F₈ and (b, bottom) 70% C₄F₈/30% H₂ plasmas as a function of postetch treatments.

during postetch treatment processes. Because hydrogen, which could be one of the most abundant species on the silicon surface overetched using the 70% $C_4F_8/30\%$ H_2 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 car-

bon, fluorine, and hydrogen for 70% $C_4F_8/30\%$ H_2 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 mea-

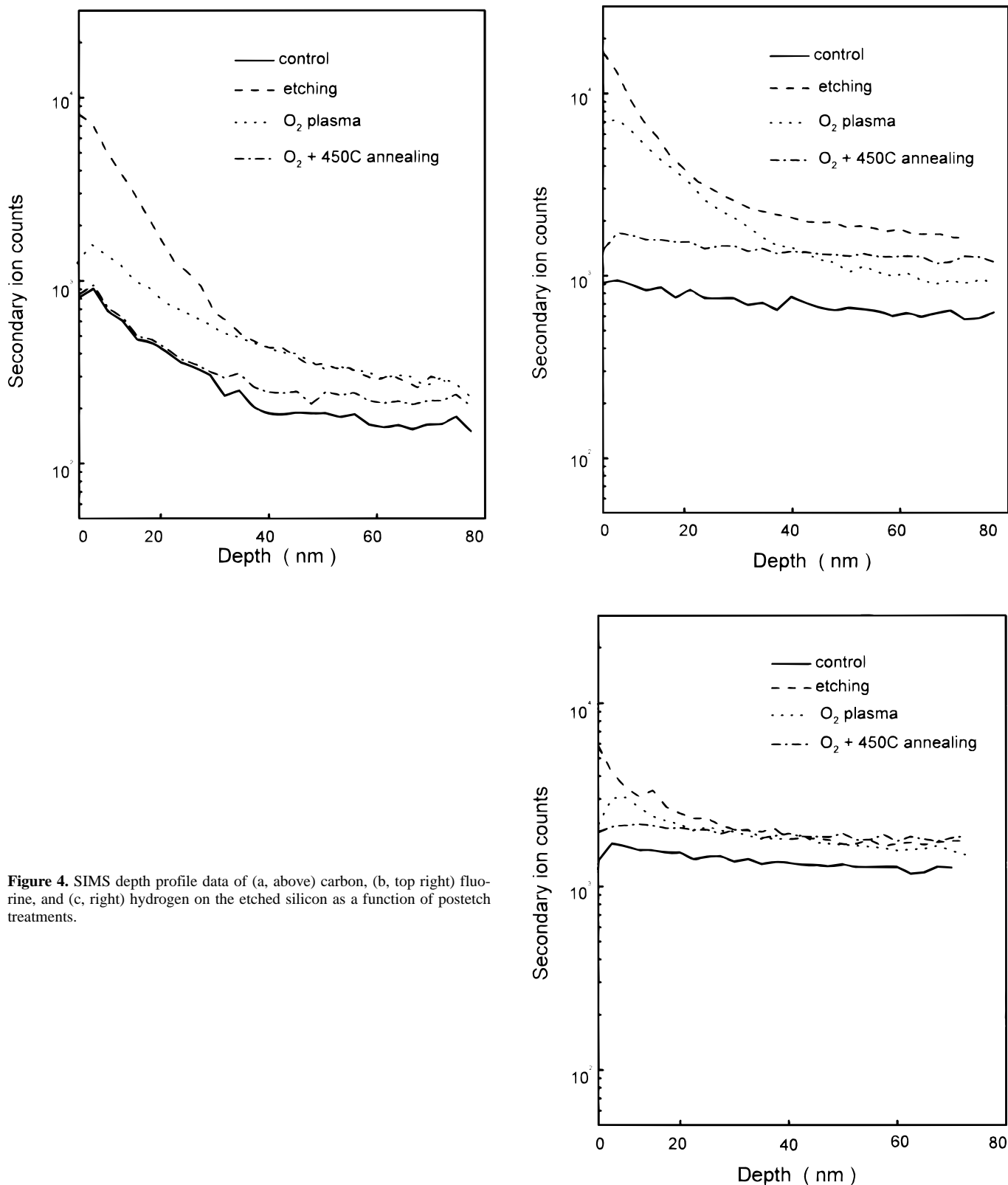


Figure 4. SIMS depth profile data of (a, above) carbon, (b, top right) fluorine, and (c, right) hydrogen on the etched silicon as a function of postetch treatments.

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% C₄F₈/30% H₂ compared to that from C₄F₈ which was observed in Fig. 2 and 3, might be related to the hydrogen contained in the residue from 70% C₄F₈/30% H₂, 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 C₄F₈.¹⁰

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 μm phosphosilicate glass with C₄F₈ and 70% C₄F₈/30% H₂, 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.¹⁸ On both the silicon surfaces overetched with C₄F₈ and 70% C₄F₈/30% H₂, physical defects were observed, and the depth of the defects in wafers overetched with 70% C₄F₈/30% H₂ was greater (550 Å) than those with C₄F₈ (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 C₄F₈ (a) and with 70% C₄F₈/30% H₂ (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% C₄F₈/30% H₂ (173 235 μs) compared to that with C₄F₈ (286-348 μs). More detailed analysis on the electrical damage is currently under investigation.

When these overetched silicon wafers were annealed at 1000°C in N₂ for 30 min after the oxygen-plasma cleaning, all the physical defects observed in the transmission electron microscope (TEM) appeared to be removed in the case of the silicon overetched with C₄F₈. However, in the case of the silicon overetched with 70% C₄F₈/30% H₂, one or two short {111} stacking faults located at depths less than 100 Å were still observed on the annealed silicon surface, even though most of the surface area observed in the TEM was defect-free. To completely remove the physical defects generated from the overetching with 70% C₄F₈/30% H₂, higher annealing temperature or longer annealing time appears to be required.

Often after the contact oxide etching, contact silicide is formed to reduce contact resistivity. The formation of titanium silicide on reactive-ion-etched silicon surfaces has been reported by other researchers, and the results show that the formation of the stable silicide is largely dependent on the remaining residue and the formation of Si–C bondings on the etched silicon surface before the silicidation increases the sheet resistance of titanium silicide.¹⁶ The formation of cobalt silicide on the magnetized inductively coupled plasma etched silicon surface is also reported and shows the importance of the composition of the residue on the formation of stable cobalt silicide, where fluorine-rich residue obstructed the formation of the stable cobalt silicide compared to carbon-rich residue.⁹ In this study, to investigate the effects of the remaining residue and damage during the oxide overetching with C₄F₈ and 70% C₄F₈/30% H₂ helicon plasmas on the formation of stable contact silicide, 2000 Å Co thin film was deposited on the etched and postetch treated silicon surfaces and was annealed to form cobalt silicides. Before the deposi-

tion of cobalt, the silicon wafers were cleaned in a HF solution. Figure 6 shows the sheet resistances of cobalt silicides formed on the etched and variously postetch treated silicon wafers after C₄F₈ and 70% C₄F₈/30% H₂ helicon plasma overetching. As shown in the figure, the resistivities of the silicides reduced in the order of postetch cleaning processes, that is, in the order of just etched, piranha cleaned, oxygen-plasma cleaned, and 600°C annealing after oxygen-plasma cleaning. When the resistivities of silicides were compared between the process gases after a same postetch treatment, the resistivity of silicide formed on the silicon surface overetched with C₄F₈ was higher than that with 70% C₄F₈/30% H₂. The lower resistivity for the oxygen-plasma-cleaned silicon wafers and the lowest resistivity for the 600°C annealed silicon wafers are believed to be from the reduction of the residue thickness through the postetch processes. In addition, as shown in Fig. 2 and 3, hydrogen-containing residue was removed more effectively. Therefore, the silicide formed on the silicon wafer overetched with 70% C₄F₈/30% H₂ and annealed at 600°C appeared to show the lowest resistivity of 765 mΩ, close to

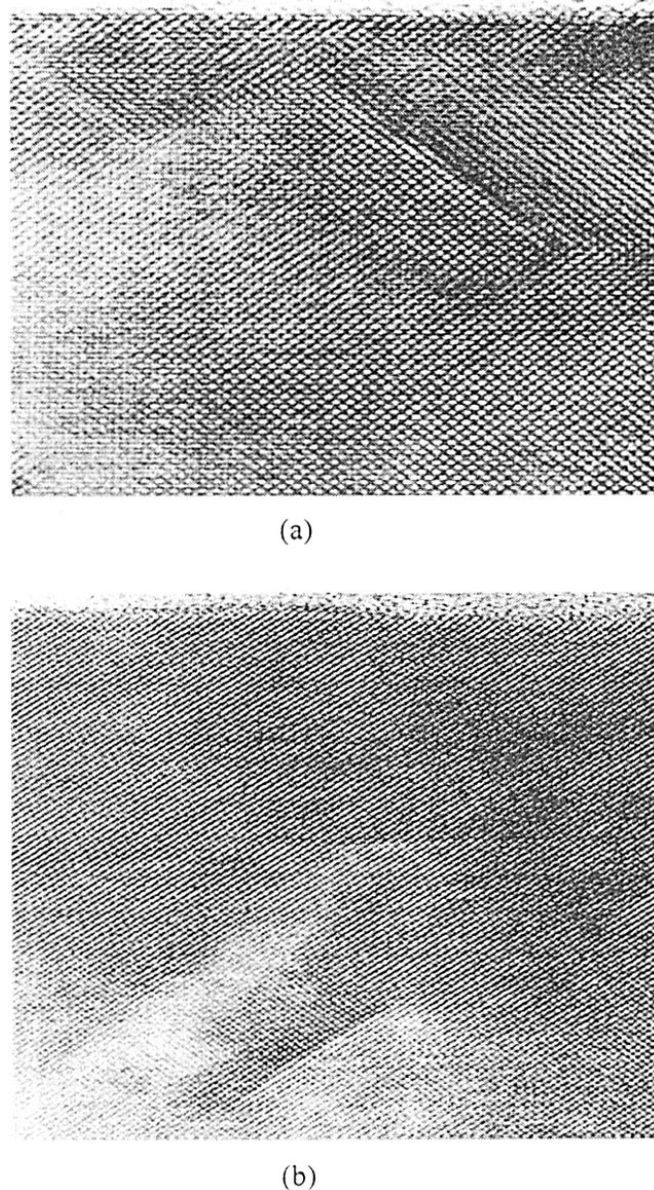


Figure 5. HRTEM micrographs of the silicon surfaces etched using (a) C₄F₈ and (b) 70% C₄F₈/30% H₂ plasmas.

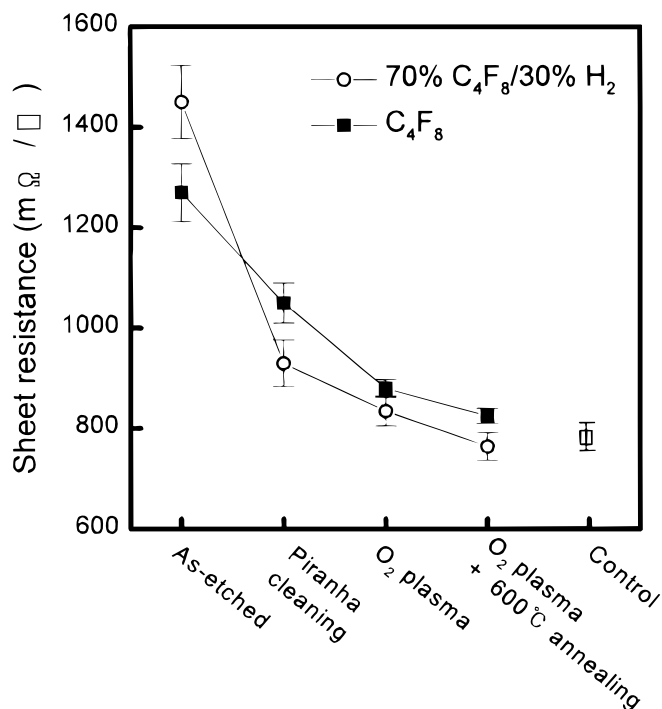


Figure 6. Sheet resistances of the Co silicides measured by a four-point probe.

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.^{9,16} 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. 1. 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 etched silicon surface appears not 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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