A Study on Modified Silicon Surface after CHF_3/C_2F_6 Reactive Ion Etching

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ABSTRACT

The effects of reactive ion etching (RIE) of SiO_2 layer in CHF_3 / C_2F_6 on the underlying Si surface have been studied by X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometer, Rutherford backscattering spectroscopy, and high resolution transmission electron microscopy. We found that two distinguishable modified layers are formed by RIE : (i) a uniform residue surface layer of 4 nm thickness composed entirely of carbon, fluorine, oxygen, and hydrogen with 9 different kinds of chemical bonds and (ii) a contaminated silicon layer of about 50 nm thickness with carbon and fluorine atoms without any observable crystalline defects. To search the removal condition of the silicon surface residue, we monitored the changes of surface compositions for the etched silicon after various post treatments as rapid thermal anneal, O_2, NF_3, SF_6, and Cl_2 plasma treatments. XPS analysis revealed that NF_3 treatment is most effective. With 10 seconds exposure to NF_3 plasma, the fluorocarbon residue film decomposes. The remained fluorine completely disappears after the following wet cleaning.

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I. INTRODUCTION

Reactive ion etching (RIE) of SiO_2 on Si in a fluorocarbon plasma is a standard process in the production of very large scale integrated devices. But it can cause damage and contamination effects in exposed materials [1,2].

In fact, plasma species can be trapped in the silicon matrix, and residue layers can be made up of reactant species and reaction products.

Various fluorocarbon plasma treatments and their interaction with the Si or SiO_2 surfaces have been analyzed in recent years [3-5].

For removal of silicon surface residue resulting from the RIE, oxygen plasma ashing or downstream soft etching treatments have been studied [6,7]. Although oxidizing process is used for removing the surface residue at present, this approach presents a problem of consuming the silicon substrate due to oxidation and changing in the physical dimension for a cell.

In this study, a modified silicon surface after RIE in CHF_3 / C_2F_6 plasma has been interpreted in detail using X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometer (SIMS), Rutherford backscattering spectroscopy (RBS), and high resolution transmission electron microscopy (HRTEM).

And as post etch treatments to remove silicon surface residue resulting from the RIE, the effects of O_2, NF_3, SF_6, and Cl_2 plasma treatments have been studied. Rapid thermal anneal treatment has been also carried out.

II. EXPERIMENTAL

A layer of 600 nm thick oxide was deposited on a chemically cleaned 0.85-1.15 ohm-cm, B doped (100) silicon wafer by low pressure chemical vapor deposition method. RIE process were performed in QUAD 484 Dryteck system using a CHF_3 / C_2F_6 gas mixture. RF power density was 1.203 W/cm^2. The gas flow was 100 sccm and the chamber pressure was 700 mTorr. In this experiment, 80 seconds of silicon overetching was performed after reaching the SiO_2/Si interface. The etch end point was detected by laser interferometry. O_2 plasma treatment was effectuated with PR stripper of Barrel type. NF_3, SF_6, and Cl_2 plasma treatments were carried out after RIE using Applied Materials Precision 5000 system without applying a magnetic field. The gas pressure was 100 mTorr and RF power was 150 watts. Post etch treated samples were immersed in H_2SO_4 / H_2O_2 (4 / 1) and in 1 / 20 buffered HF successively to investigate the wet cleaning effect. Rapid thermal anneal (RTA) treatments were carried out at nitrogen atmosphere for 1 minute. Prior to RTA treatments, the wafers were given a wet cleaning.

The XPS experiments were performed on a V. G. Scientific ESCALAB 200R spectrometer using Mg kα (1253.6 eV) operating at 300 W radiation. Narrow scan spectra of all regions of interest were recorded with 20 eV pass energy in order to quantify the surface composition and identify the elemental bonding states. The

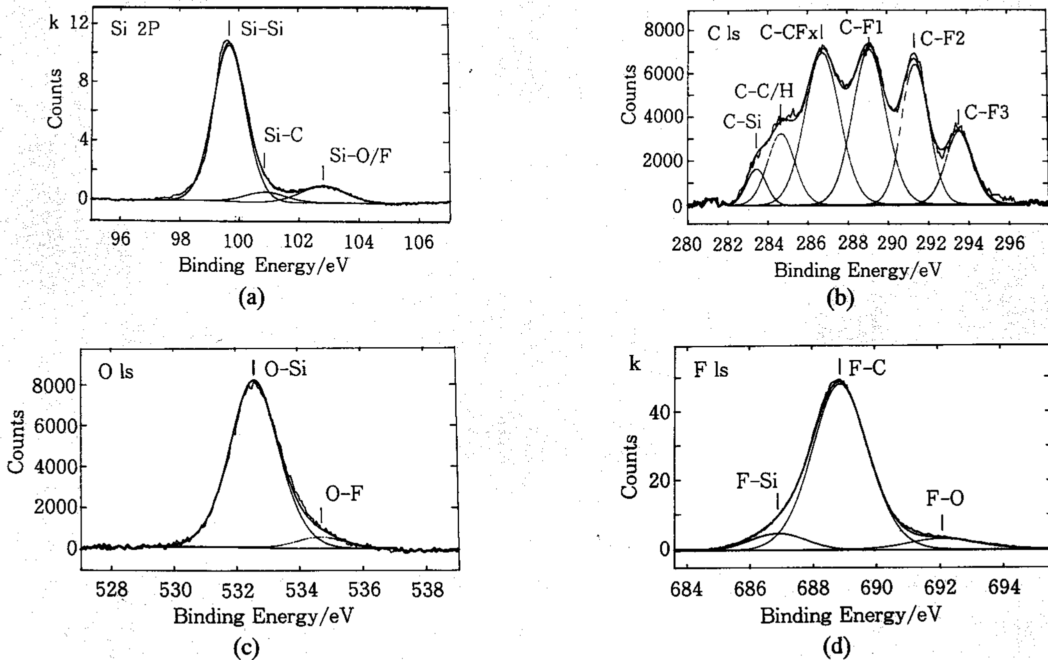


Fig. 1. Deconvolutions of narrow scan spectra with pass energy of 20 eV for reactive ion etched sample; (a) Si 2p, (b) C ls, (c) O ls, and (d) F ls.

SIMS results were obtained with CAMECA IMS-4F by monitoring the negatively charged secondary ions using oxygen ions bombardment. The oxygen primary beam current was 30 nA with net bombarding energy of 8 keV. For ion channeling experiments, He^+ ions of 1 MeV were used and backscattered ions were collected at the detection angle of 110 degrees with NEC 3SDH. The cross-sectional HRTEM analysis was carried out with Philips CM20T / STEM and operating voltage was 200 kV.

III. RESULTS AND DISCUSSION

The XPS analysis shows that the residue film due to exposure of silicon surface to CHF_3 / C_2F_6 reactive ion plasma consists mainly of carbon and fluorine.

Fig. 1 represents narrow scan spectra of Si, C, O, and F. No considerable peak shape change due to X-ray irradiation has been observed during the measurement. Their peak attributions, binding energy, full width at half maximum (FWHM), and percent of total area (contributions of several bonds to the integrated peak) are listed in Table 1. The Si 2p spectrum

Table 1. Decompositions of the Si 2p, C ls, O ls, and F ls core level distributions.

	Peak attribution	Peak binding energy (eV)	FWHM (eV)	% of area
Si 2p	Si-Si	99.7	1.34	82
	Si-C	100.8	1.65	6
	Si-O/F	102.8	1.81	12
C ls	C-Si	283.4	1.21	4
	C-C/H	284.7	1.64	10
	C-CF_X	286.7	2.10	28
	C-F_1	289.1	2.01	27
	C-F_2	291.4	1.61	20
	C-F_3	293.5	1.66	11
O ls	O-Si	532.6	1.90	94
	O-F	534.8	1.80	6
F ls	F-Si	686.9	2.10	9
	F-C	688.9	2.16	85
	F-O	692.1	2.60	6

can be resolved into Si-Si, Si-C, and Si-O/F. The binding energy of Si as 102.8 eV for Si-O bond means that incomplete oxidation of silicon occurs [8] because 103.4 eV binding energy is observed for normal Si-O bond in SiO_2. And the Si-O bond contains a small quantity of Si-F bond because a few fluorine is revealed to bind to silicon in F 1s spectrum. The C 1s spectrum can be resolved into 6 chemical components which can be attributed to C-Si, C-C or H, C-CF_x ($x \leq 3$), C-F_1, C-F_2, and C-F_3, respectively. The majority of O atoms bind to Si with a binding energy of 532.6 eV. The O 1s binding energy of 534.8 eV seems to be resulted from the bond with a high electronegative element as fluorine. In the F 1s spectrum, we also find the presence of the bond with oxygen at 692.1 eV.

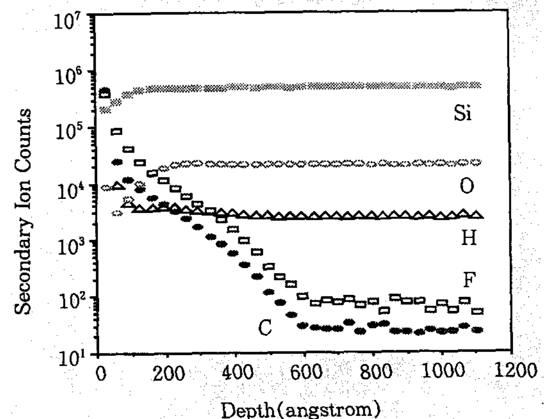


Fig. 2. SIMS depth profile after reactive ion etching.

Fig. 2 represents the depth profile of various elements measured by SIMS. It is shown that the impurities in the ~50 nm thick silicon substrate mainly consists of carbon and fluorine. RBS / channeling spectra are given in Fig. 3 for reactive ion etched silicon and control samples. The control sample has been cleaned with a buffered HF solution before RBS measurement. At 183, 236, and 273 channels, peaks due to C, O, and F contaminants are shown for the reactive ion etched silicon. Increase in the silicon surface peak intensity for the reactive ion etched sample may result from the existence of the fluorocarbon residue

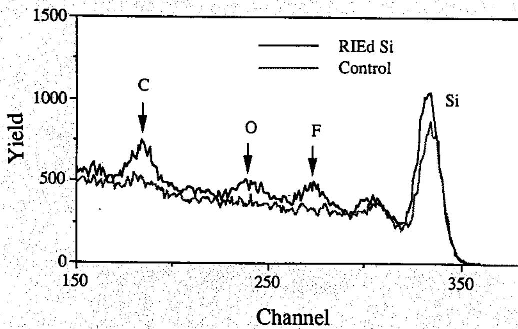


Fig. 3. Ion channeling spectra of control sample and reactive ion etched sample.

film on the reactive ion etched silicon surface or from silicon crystalline defects which can be produced by carbon and fluorine contaminants. The position of the silicon surface peak for the reactive ion etched sample has been shifted by about 2.4 keV relative to the control sample due to the energy loss of He^+ beam during the passage through the residue layer. To check any possible crystalline damage in the silicon substrate containing the impurities, cross-sectional HRTEM images have been taken for the reactive ion etched silicon. About 40 nm thick gold is deposited to distinguish the fluorocarbon residue layer from epoxy which is used for cross-sectional TEM specimen preparation.

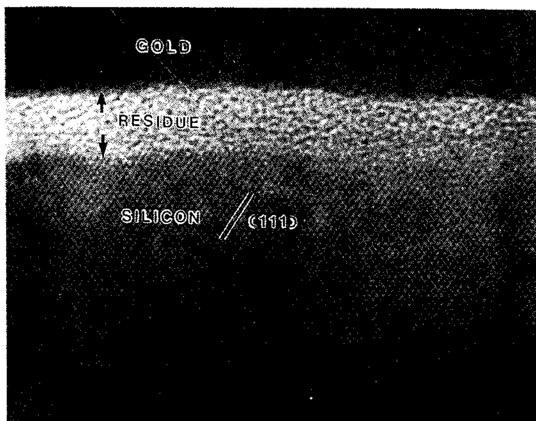


Fig. 4. Cross-sectional HRTEM image of reactive ion etched silicon.

Fig. 4 represents the image. The residue layer is continuous and uniform. The thickness of the residue layer is measured as $\sim$ 4 nm using a spacing of Si (111) planes of 0.313 nm as an internal magnification standard. The interface between the residue layer and silicon substrate is sharply defined and smooth. In the substrate silicon lattice image, we can find neither point defect cluster nor distinct planar defect. From these results, the relatively high intensity of silicon surface peak for the reactive ion etched sample compared to the control sample in ion channeling spectra (Fig. 3) can be attributed to the residue layer. Therefore we can conclude that under our experimental conditions the major modifications by RIE are the formation of a 4 nm thick fluorocarbon residue layer on the silicon surface and a $\sim$ 50 nm thick contaminated silicon layer which contains carbon and fluorine atoms but no crystalline defect.

Angle resolved XPS has been carried out for analyzing the distribution of chemical bonds in the residue film. The angle between sample surface and detector (take-off angle) varies from 15 to 75 degree. For the deconvolution of the spectra, the binding energies and the FWHMs in Table 1 are used.

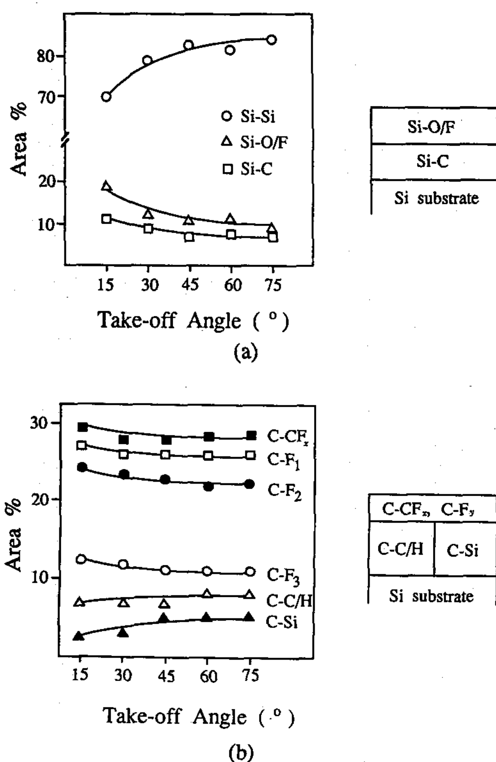


Fig. 5. Take-off angle dependencies of observed bonding species; (a) Si and (b) C.

Fig. 5 represents the variations of chemical contributions to silicon and carbon with take-off angle. As the angle decreases, the contribu tion of the surface bonding state to the observed peak intensity increases. From the comparison of slope changes of bonding contributions with take-off angle, the distribution of bondings can be defined. For silicon (Fig. 5(a)), Si-C bonding is found to be under the Si-O bond, but above the silicon substrate. In Fig. 5(b), area % of C-CF$_x$ and C-F$_y$ (y=1, 2, 3) slightly decrease and those of C-Si and C-C/H increase.

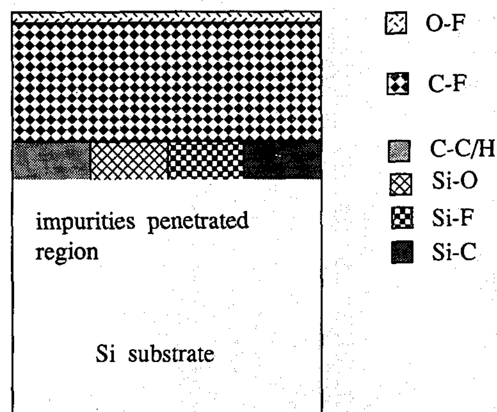


Fig. 6. Schematic diagram of reactive ion etched silicon surface.

This implies that C-Si and C-C/H bonds exist under the C-F polymer layer. Since the sample is exposed to air for transfer to analyze, we have to always consider the physisorbed 1~2 mono-layer (ML) of carbon on the top of the sample. This physisorbed carbon causes a decrease in slope with take-off angle. Then although the slope change of C-Si is larger than C-C/H, we cannot say that the C-Si bond exists under the C-C/H bonds. With oxygen and fluorine, from the comparison of the slope changes for the area % of each bond constituents, it can be said that O-F bond exists on the O-Si one and F-C bond exists between F-O and F-Si ones.

From these results, the schematic descript ion of silicon surface after RIE can be given in Fig. 6. The physisorbed 1-2 ML of extra

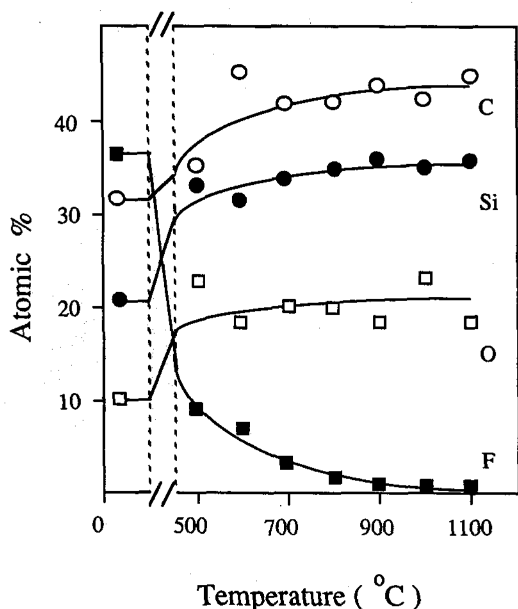


Fig. 7. Composition change of the reactive ion etched silicon surface after rapid thermal anneal.

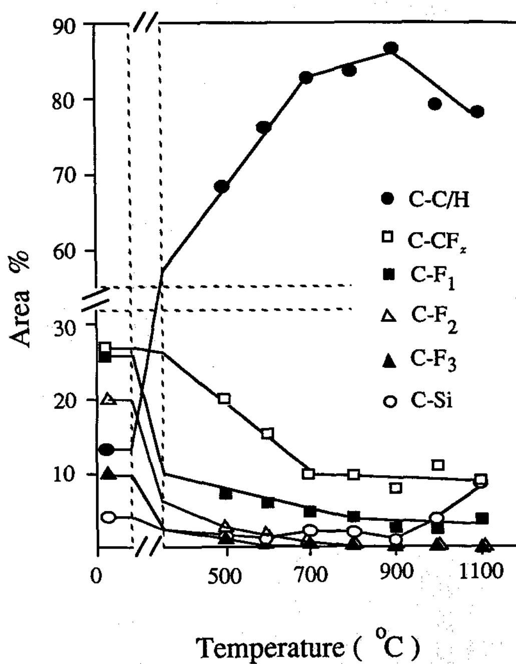


Fig. 8. The variation of chemical contributions for C ls with anneal temperature.

carb on has not been considered. At the surface, O-F bond over C-F polymer which mainly compo ses residue layer is found. Between the C-F polymer layer and the Si substrate, C-C/H, Si-C, Si-O, and Si-F bonds exist.

Fig. 7 shows a composition change of the reactive ion etched silicon surface using XPS after RTA treatment under nitrogen atmosphere for 1 minute. After anneal above 800°C, fluorine remains under 1 atomic percent. This means that above 800°C, thermal decomposition of residue layer is completed.

Fig. 8 shows the variation of chemical contributions for C 1s with annealing temperature. As shown in Fig. 7, area percents of C-CF$_x$ and C-F$_y$ bonds remain constant after anneal above 800°C. Decrease of C-C/H bond is found due to the formation of Si-C bond between carbon and substrate silicon above 900°C.

Depth profile results using SIMS for the annealed samples at 600°C and 800°C are presented in Fig. 9. In Fig. 2, we have found that the thickness of contaminated silicon layer is ~ 50 nm. RTA treatment at 600°C is revealed to induce in-diffusion of C and F species to ~ 100 nm depth, but no in-diffusion phenomenon is observed for the 800°C treated specimen. This seems due to the fast decomposition of the C-F residue film which remains on the surface till 600°C and plays an important role of diffusion source. With 800°C annealed sample, the

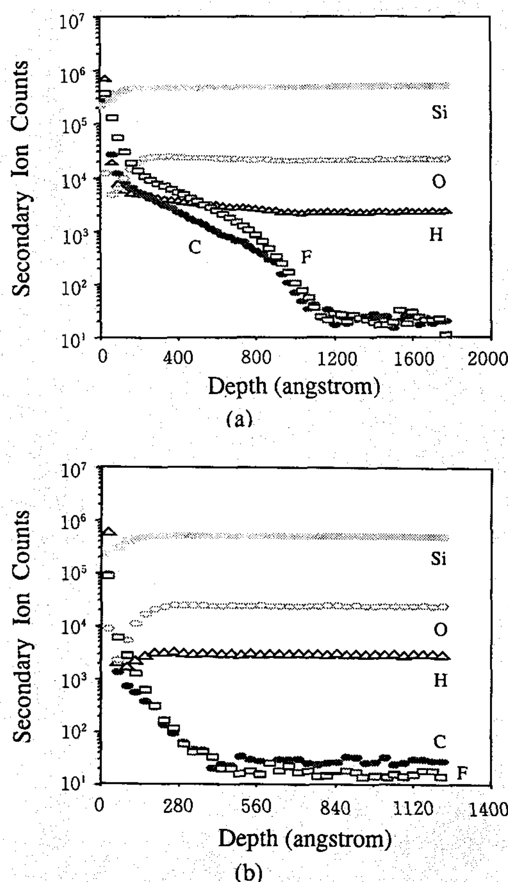


Fig. 9. Depth profile analysis using SIMS for annealed samples at (a) 600°C and (b) 800°C, for 1 minute, respectively.

secondary ion counts profile of carbon remains higher than that of fluorine. This may result from the almost remained carbon with C-C/H or Si-C bonds after anneal above 800°C.

O_2, NF_3, SF_6, and Cl_2 plasma treatments have been carried out to remove the residue layer as post etch treatments. Fig. 10 shows a composition changes of the reactive ion etched silicon surface by XPS analysis after the treatments. And wet cleaning process has been applied to all of the post etch treated samples. The remained fluorocarbon residue after every post etch treatments can be estimated from the changes of the fluorine and silicon compositions.

Fig. 11 shows C 1s (a) and F 1s (b) peaks obtained after the O_2 treatment. With the first 1 minute exposure, the liberation of fluorine from fluorocarbon residue layer proceeds. For the C 1s spectrum, the peaks corresponding to the C-F_y bondings continuously decrease and almost disappear after 10 minutes exposure. The C- CF_x contribution also decreases but after 2 minutes exposure, it becomes constant. It seems to be due to the appearance of C-O bond which has nearly the same binding energy as C-CF_x. With fluorine, according to the exposure, the contribution of the F-O slightly increases and that of F-Si severely increases. The F-C bond is almost completely converted into F-Si bond above 20 minutes exposure to the O_2 plasma. Above 10 minutes of exposure to the O_2 plasma, the atomic % remains almost constant and the formation of SiO_2 is almost saturated with 3-4 nm thickness. These bonding states of the polymer film as F-Si, C-O, and Si-O after the O_2 treatment are found to be easily eliminated by successive cleaning process. Through NF_3, SF_6, and Cl_2 treatments, no additional elements such as nitrogen, sulfur, and chlorine are detected. Surface compositions drastically change after

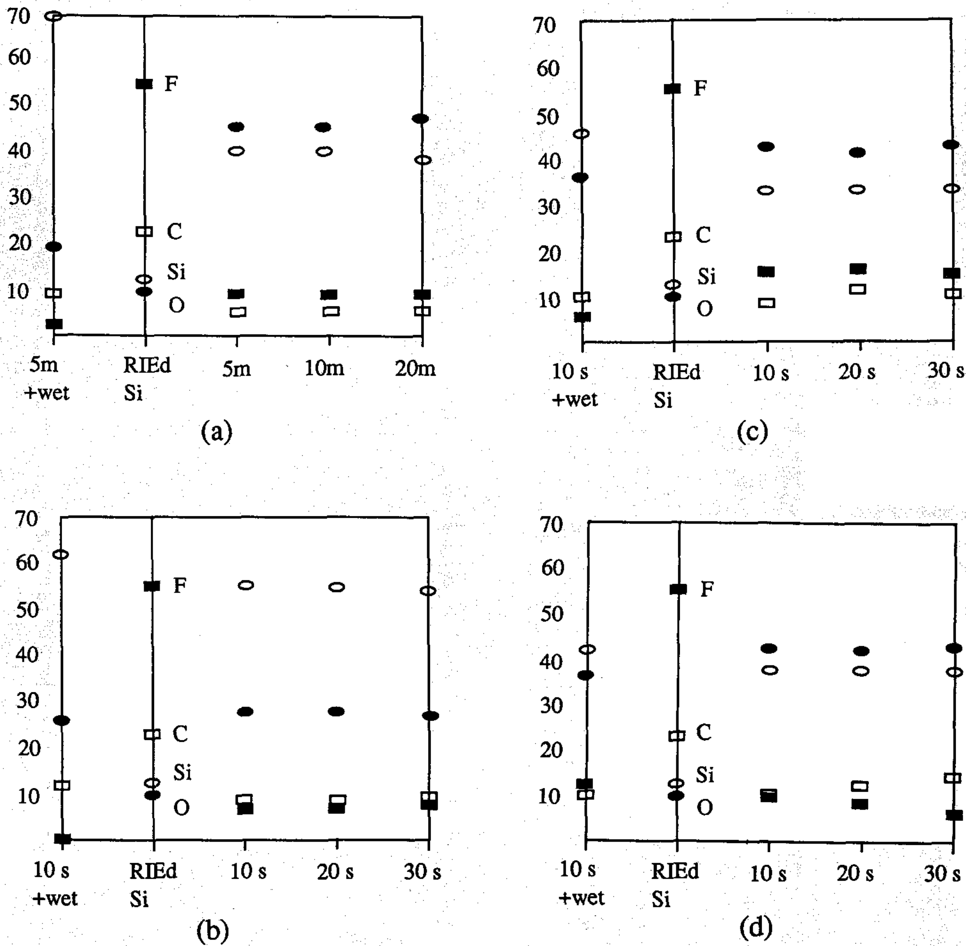
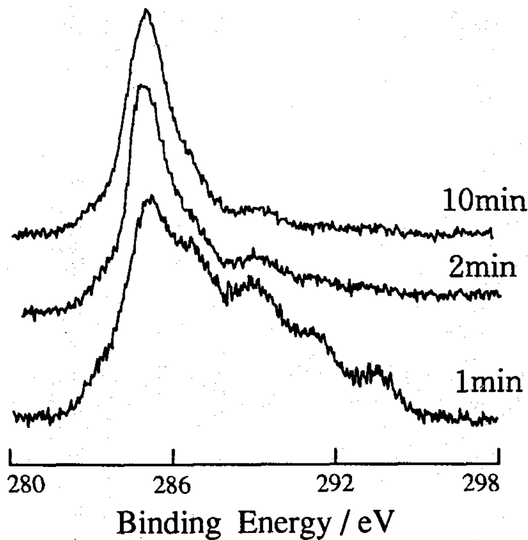


Fig. 10. Composition changes of the reactive ion etched silicon surface after (a) O_2, (b) NF_3, (c) Cl_2, and (d) SF_6 treatments.

the treatments for 10 seconds, but maintain almost constant with exposure times of 10 to 30 seconds. The effects of post etch treatments seem to be saturated within 10 seconds exposure. Among the above three treatments, NF_3 treatment (Fig. 10(b)) results in the smallest fluorine atomic %. And after successive wet treatment, no fluorine is detected in the sample treated using NF_3 plasma. With SF_6 plasma, the atomic % of fluorine decreases to an half value after the wet treatment, but with Cl_2 plasma it does not change.

Fig. 12 represents the photoelectron spectra of fluorine after NF_3, SF_6, and Cl_2 plasma



20min
10min
2min
1min
681
685
689
693
697
Binding Energy / eV

Fig. 11. Influence of O_2 plasma treatment on (a) C ls and (b) F ls.

exposures for 10 seconds, respectively. The shape and bonds distribution of the fluorine peak for Cl_2 plasma exposure is almost the

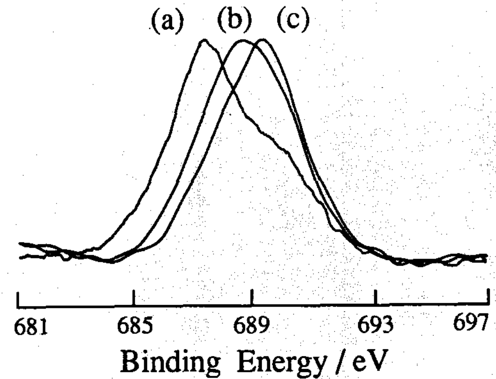


Fig. 12. Photoelectron spectra of fluorine after (a) NF_3, (b) SF_6 and (c) Cl_2 plasma exposures for 10 seconds, respectively.

same with that of just reactive ion etched sample. Fluorine mainly binds to carbon with a binding energy of ~ 689 eV. With SF_6 plasma treatment, fluorine peak enlarges and peak position moves to a low binding energy value comparing to that of Cl_2 plasma treated sample. This is due to the increase of F-Si bond contribution with a binding energy of 686.9 eV. Increase of F-Si bond is clearly seen with NF_3 plasma treated sample. Area of F-Si bond is nearly two times larger than that of F-C bond. This chemical state change means the decomposition of the residue layer and induces the easy removal of residue by successive wet cleaning. These results show that NF_3 plasma treatment is most effective to remove the residue layer on the reactive ion etched sil-

icon surface.

IV. CONCLUSIONS

By cross-sectional HRTEM analysis, about 4 nm thick residue layer is observed on the reactive ion etched silicon surface in the CHF_3 / C_2F_6 plasma. It is found that carbon in the residue layer consists of 6 chemical components as C-Si, C-C/H, C-CF_x ($x \leq 3$), C-F_1, C-F_2, and C-F_3 using XPS, SIMS, RBS / channeling, and HRTEM works show that $\sim$ 50 nm thick contaminated silicon layer which contains mainly carbon and fluorine, has no observable amount of defect. With rapid thermal anneal, in-diffusion phenomenon of C and F into the silicon lattice is found under 800°C. NF_3 treatment is revealed to be the most effective post-etch treatment for removing the surface residue. Fluorocarbon residue layer decomposes with 10 seconds exposure to NF_3 plasma and completely disappears with successive wet cleaning.

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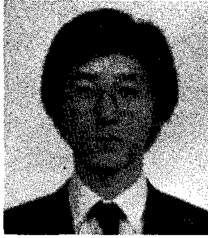

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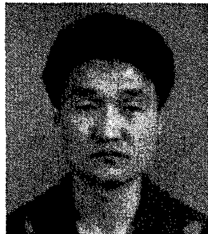

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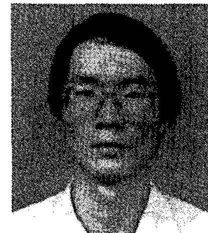

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