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

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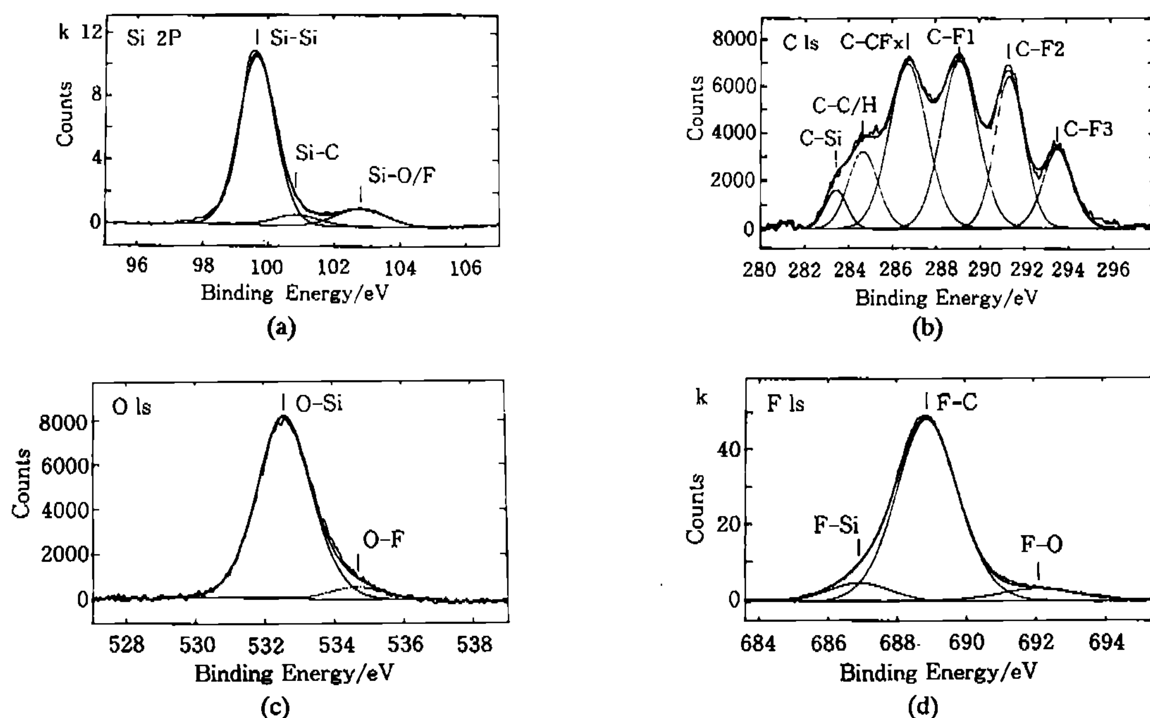

Fig. 1. Deconvolutions of narrow scan spectra with pass energy of 20 eV for reactive ion etched sample; (a) Si 2p, (b) C ls, (c) O ls, and (d) F ls.

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.

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

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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
	$C\text{-}CF_X$	286.7	2.10	28
	$C\text{-}F_1$	289.1	2.01	27
	$C\text{-}F_2$	291.4	1.61	20
	$C\text{-}F_3$	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, $C\text{-}CF_x$ ($x \leq 3$), $C\text{-}F_1$, $C\text{-}F_2$, and $C\text{-}F_3$, 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.

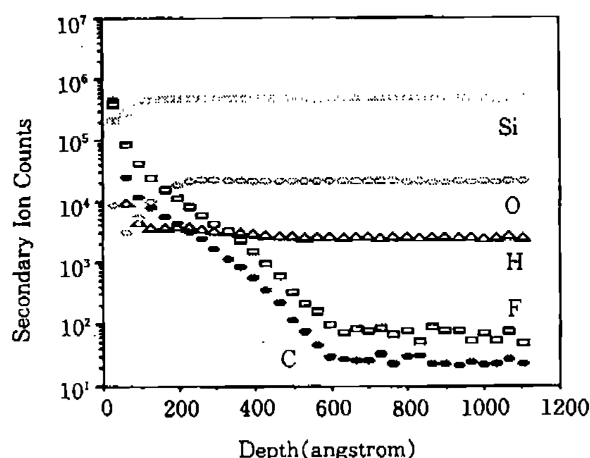

Fig. 2. SIMS depth profile after reactive ion etching.

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

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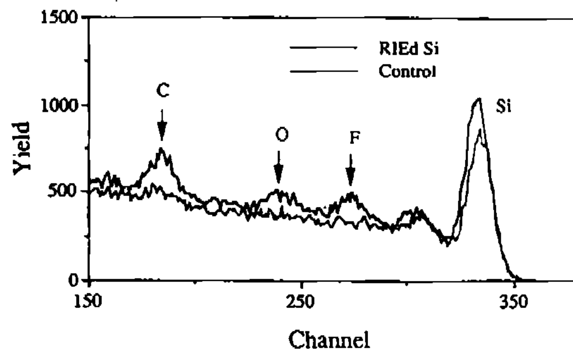

Fig. 3. Ion channeling spectra of control sample and reactive ion etched sample.

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

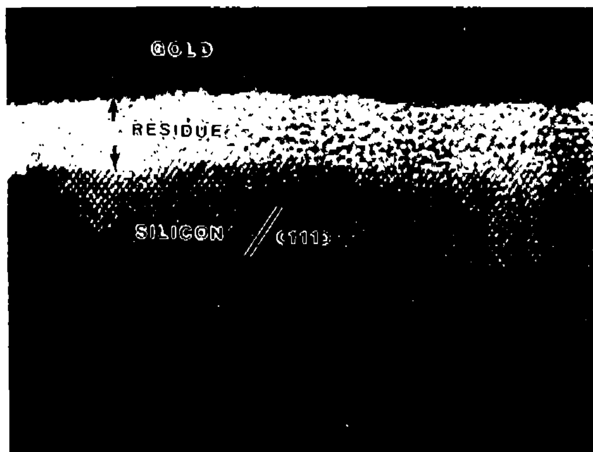

Fig. 4. Cross-sectional HRTEM image of reactive ion etched silicon.

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 represents the image. The residue layer is continuous and uniform. The thickness of the residue layer is measured as ~ 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 ~ 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.

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