XPS STUDY ON OXIDE ETCH RESIDUE AND CLEANING

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Abstract — A layer structure, chemical composition and cleaning process of oxide dry etch residue on silicon substrate were studied. It was observed that the structure of the etch residue consisted of CF_x-polymer/SiO_yC_z. The ratio of y and z in SiO_yC_z layer is monotonously changing with depth: y/z is maximum at the interface of CF_x-polymer and SiO_yC_z, and minimum at the interface of SiO_yC_z and silicon substrate. Two step cleaning was proposed: dry and wet cleaning. The most effective process was silicon light etch (CF_4/O_2 REMOTE PLASMA), followed by NH_4OH-H_2O_2 mixture and HF dip. From X-Ray Photoelectron Spectroscopy (XPS) data, it was found that oxide etch residue was completely removed by dry and wet cleaning.

INTRODUCTION

In a dynamic random access memory (DRAM) fabrication process, oxide etching is employed to expose a silicon substrate for electrical contact. Normally an oxide etch is followed by an overetching step to make it sure that oxide is completely removed for good contact. The oxide etch chemistry and etch mechanism, fluorocarbon-based reactive ion etch (RIE) or magnetic enhanced reactive ion etch (MERIE), inevitably lead to the deposition of fluorocarbon polymer layer on the contact area and cause Si-substrate damage.

Works have been done to identify the residue chemistry [1-7]. The deposition of a thin C, F containing film was found, when a clean silicon surface was exposed to CF_4/H_2 plasma [1, 2]. The structure of the film is reported to be affected by H_2 concentration in the feed and by the discharge voltage and current values and the polymerization rate decreases with temperature after a threshold [3]. A silicon-carbide layer was discovered to be localized near the fluorocarbon-film /Si interface. The existence of the carbide layer was found to be independent of gas composition from 0-40% H_2 for 1 min plasma exposure [4]. Near surface region (30-50Å), the silicon substrate was heavily disordered and the damage consisted of atomic defects (e.g., Si self-defects and impurities of the plasma cons-

tituents) [5, 6]. Various post-RIE treatments such as O_2 RIE, O_2 ashing and O_2 annealing were proposed for the recovery of device quality surface [7].

Up to now, what is revealed in an oxide etch residue is that it consists of C, F containing film and silicon carbide. There has been no report on the influence of oxide etch residue on device and process. Little study has been done on how to get rid of oxide etch residue. Since the structure and composition of oxide residue practically depend on etching gas chemistry and composition, work to identify the oxide etch residue for each etching gas should be done.

In a DRAM fabrication process, when a silicon substrate was exposed by an oxide etching and overetching process, following an ion implantation step, it was observed that no oxide was grown on the silicon substrate in subsequent thermal oxidation step (850°C, 30 min), while a thin thermal oxide of 60Å was deposited on the wafer which did not undergo the etch process. This paper deals with an oxide etch residue composition when $CHF_3/CF_4/Ar$ plasma was used as an etching gas and subsequent cleaning processes to remove the residue.

EXPERIMENT

Bare p-type Si(100) wafers with a resistivity of 9-12 Ω-cm was precleaned by aqueous HF solution and then CVD oxide of 2000Å thickness was deposited

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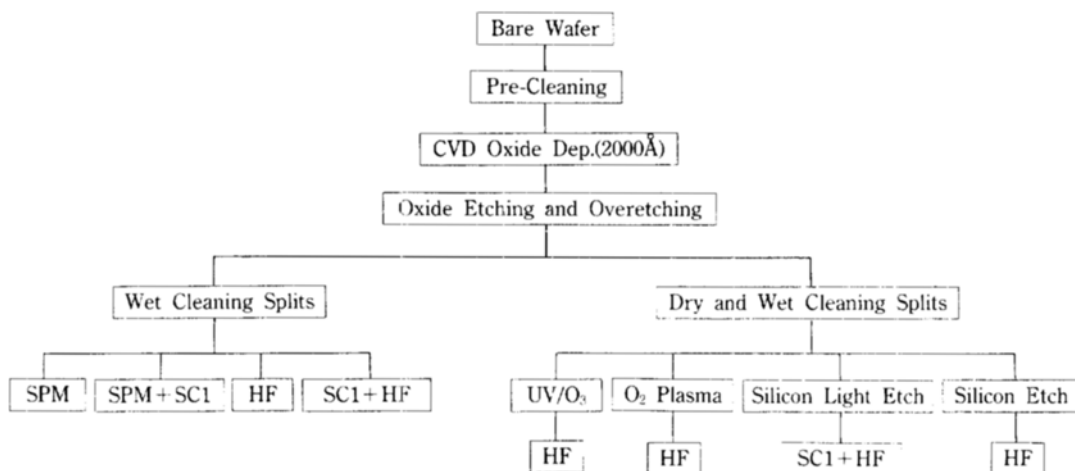**To whom all correspondences should be addressed.

Fig. 1. Experimental procedure.

by silane based-reacting gas at 800℃. Wafer with the CVD oxide was etched with $CHF_3/CF_4/Ar$ (=3:1:8) MERIE chamber under 10 Pa and 500 Watt, followed by 10% overetch: CHF_3 were added to the main etching gas of CF_4 for improving the selectivity of CVD oxide to silicon while the addition of Ar made the plasma drift effect and ion temperature reduced. Cleaning steps, either wet or dry-wet cleaning, were performed. The wet cleaning splits included 50:1 HF acid dip for 30 sec at room temperature, $NH_4OH-H_2O_2-H_2O$ mixture (=1:1:5, SC1, Standard Cleaning 1) dip for 10 min at 80℃, $H_2SO_4-H_2O_2$ mixture (=4:1, SPM, Sulfuric Acid Hydrogen Peroxide Mixture) for 10 min at 130℃. and their combinations. Dry cleaning methods consisted of O_2 plasma under 50 Pa and 900 Watt, ultraviolet/ozone ashing at 300℃, silicon light etch (CF_4/O_2=1: 13 remote plasma) under 20 Pa and 250 Watt, and silicon etch (HBr/Cl_2=1:4 plasma) under 35 Pa and 150 Watt. The experimental split is shown in Fig. 1. Wafers after cleaning were examined by XPS (PERKIN ELMER PHI 5400).

RESULTS

1. Residue Structure

The XPS results of as-overetched wafer are shown in Fig. 2. Main residual elements were F, O, C, and Si. Three bonding states were observed in Si_{2p} peak: Si-Si (99.5 eV), Si-C (100.2 eV), and Si-O (102.5 eV). Si-Si came from silicon substrate while Si-C and Si-O bonds states were originated from the oxide etch residue. Si-O bond state of oxide etch residue was different from that of thermal oxide of which typical binding energy is 103.5 eV. In C_{1s} peaks, C-Si (283.4
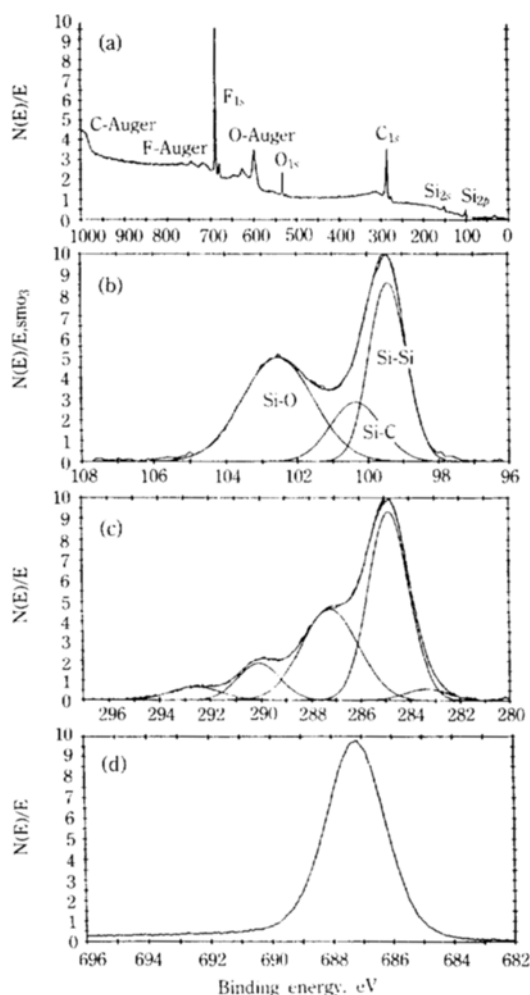

Fig. 2. XPS spectra of oxide overetched wafer: (a) wide spectrum (b) Si_{2p} peak (c) C_{1s} peak (d) F_{1s} peak.

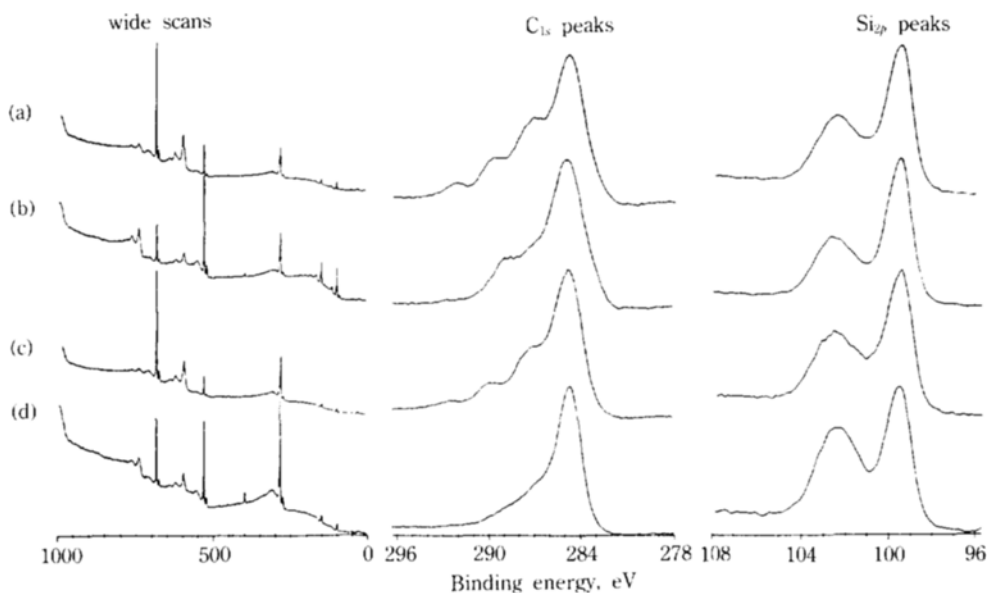**Table 1. Area changes of Si-C and Si-O with photoelectron take-off angle**

Take-off angle	Chem. bond	Si-C (100.2 eV) (cps)	Si-O (102.5 eV) (cps)	Ratio$\left(\dfrac{\text{Si-C}}{\text{Si-O}}\right)$
20°		30	73	0.411
30°		80	150	0.533
45°		140	250	0.560
60°		306	347	0.882

eV) was positioned at the lowest energy state among C_{1s} peaks. C=O and C-H bonds at 284.9 eV from organic carbon were observed, which is always detected for a wafer once exposed to the air. CF_x-polymer showed three bonding states of C-F (287.4 eV), $C-F_2$ (290.0 eV), and $C-F_3$ (292.5 eV). O_{1s} peak mainly attributes to the oxygen content in residual layer and adsorbed molecular oxygen from air. F_{1s} (686 eV) was hard to identify the fluorine bond state in detail due to the highest electronegativity of fluorine. The $C-F_x$ bond states were disappeared by 3 KeV Ar^+ sputtering for 25 sec and then Si-O and Si-C bonds were gone by additional 220 sec sputtering, which reveals that the top surface was covered with CF_x-polymer and a layer of Si-O and Si-C bonds formed the underneath layer. The reason Si-O and Si-C bonds are not interpreted as SiO_2 and SiC, respectively, is that the Si-O bond of etch residue was chemically inert in HF acid, oxide wet etching chemical, and the oxygen and carbon con-

tents were detected throughout the residual layer depth. Table 1 shows the change of Si-O and Si-C area ratio with the photoelectron take-off angle.

As the take-off angle increased, the areas of both Si-C and Si-O decreased, compared to Si-Si bond area and also the area ratio of Si-C to Si-O increased, which gives the relative concentration of oxygen and carbon in-depth. Carbon content was increased with depth, while oxygen content was decreased. Considering the observation that Si-O bond was chemically stable against HF solution, and Si-O and Si-C bonds were detected throughout the residual layer, the residue could not be separated into SiO_2 and SiC layers. Instead, it should be thought as one layer of SiO_yC_z in which relative amounts of O and C contents are changing in depth. Therefore, the residual layer structure was found to be CF_x-polymer/SiO_yC_z. SiO_yC_z layer is chemically stable in HF solution and retards the further thermal oxidation.

In case of underetched wafer with 300Å thick remaining oxide, no Si-C bond was detected and the residue was simply CF_x-polymer/SiO_2. It was thought that the Si-C bond in SiO_yC_z residue was originated from the chemical reaction of carbon plasma with damaged silicon substrate during oxide overetching process. Si-O bond seemed to form at the vacancy of Si-C by the diffusion of oxygen in the ambient which penetrated through the CF_x-polymer. The carbon plasma, which were the source of Si-C bonds, had the higher kinetic energy than ambient oxygen and pene-

Fig. 3. XPS spectra of wet cleaned wafers: (a) SPM (b) SPM+SC1 (c) HF (d) SC1+HF.

trated into silicon substrate with the deeper depth than oxygen to show the monotonous decrease of the ratio of y/z in the SiO_yC_z with depth toward the silicon substrate.

WET CLEANING SPLITS

The narrow-scans of C_{1s} and Si_{2p} peaks, and wide scans when various wet chemical was used for cleaning the residual layer appear in Fig. 3. H_2SO_4-H_2O_2 mixture, wet chemical aimed to remove heavy organic material like photoresist, was ineffective to remove the residue. This was true of HF acid and NH_4OH-H_2O_2 solution.

It was observed that H_2SO_4-H_2O_2 mixture reduced the C-F and C-F_2, and C-F_3 bond population in CF_x-polymer peaks, that is, this wet chemical removed the carbon polymer but the major peaks of carbon residue were still distinctively observed and there was no change in Si_{2p} peak after H_2SO_4-H_2O_2 mixture cleaning.

NH_4OH-H_2O_2 solution, of which NH_4OH is wet etching chemical of silicon and silicon carbide, and light organic material, was a little effective to get rid of some CF_x-polymer and SiO_yC_z residues. When the SPM and SC1 cleaning solutions were used in series, the major portion of the residue still remained on the wafer.

In case of 50:1 HF solution, extension of dipping time to 500 sec did not have any effect on the cleaning ability, which revealed that the SiO_yC_z was not etched by HF solution at all so the removal of CF_x-polymer

through lift-off could not be expected. When the SC1 and HF solutions were applied for removing the etch residue sequentially, only the SC1 cleaning effect was observed.

Among the wet chemicals, the most effective one in removing the CF_x-polymer and SiO_yC_z, was NH_4OH-H_2O_2 mixture but SC1 cleaning still left the major portion of the oxide etch residue. H_2SO_4-H_2O_2 mixture could get rid of CF_x-polymer, even though small amount. SiO_yC_z was not etched by the aqueous HF solution. Therefore, it was observed that any wet cleaning was ineffective for removing the CF_x-polymer/ SiO_yC_z residue.

DRY AND WET CLEANING SPLITS

Since only wet cleaning was insufficient to remove the oxide etch residue, serial treatment of dry and wet cleaning was tried. Four dry cleaning methods were applied: O_2 remote plasma, ultraviolet/ozone ashing, silicon light etch (CF_4/O_2 plasma), and silicon etch (HBr/Cl_2 plasma). The XPS results are shown in Figs. 4 and 5.

O_2 remote plasma and UV/ozone ashing, which are typical dry photoresist strip methods, had the nearly same efficiency for removing the residue. CF_x-polymer was removed through CO, CO_2, COF_2, etc. but small amount of CF_x-polymer still remained. Due to the excessive O_2 and ozone, the population of Si-O bond increased. Sequential H_2SO_4-H_2O_2 mixture cleaning was ineffective but HF cleaning could remove the oxide

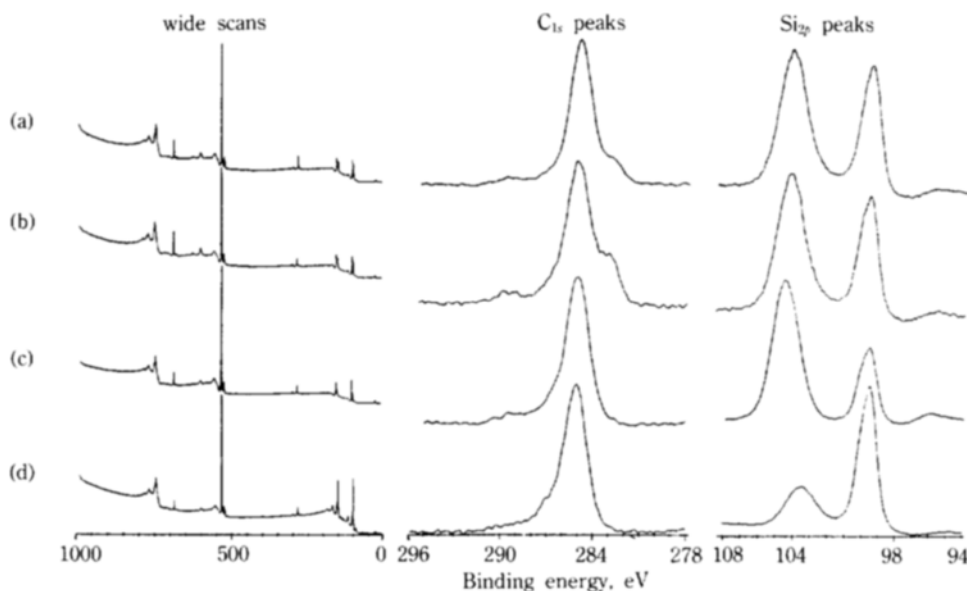Fig. 4. XPS spectra of dry cleaned wafers: (a) O_2 plasma (b) UV/O_3 (c) silicon light etch (d) silicon etch.

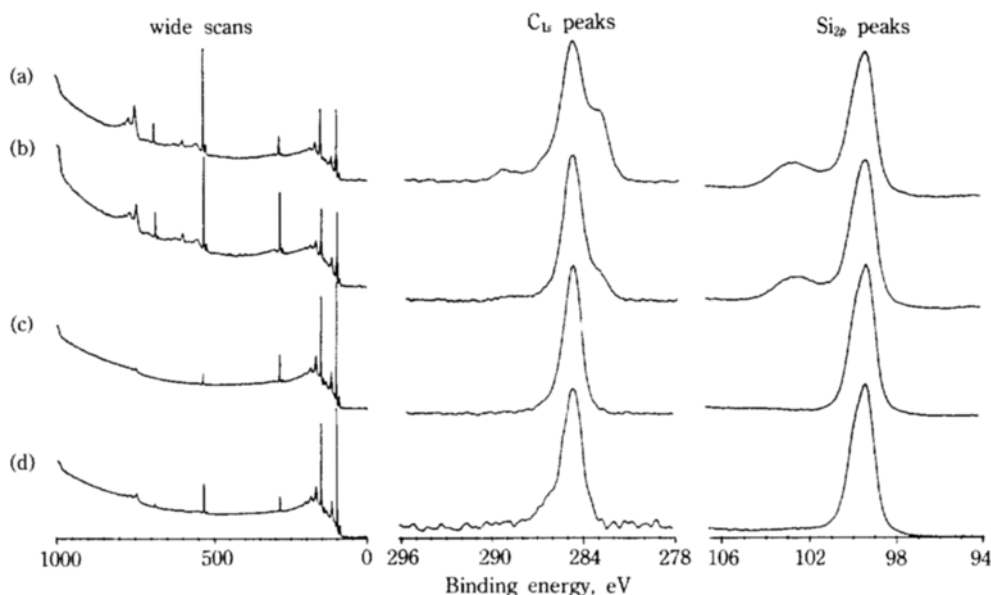wide scans   C$_{1s}$ peaks   Si$_{2p}$ peaks

Fig. 5. XPS spectra of dry and wet cleaned wafers: (a) O$_2$ plasma + HF (b) UV/O$_3$ + HF (c) silicon light etch + SC1 + HF (d) silicon etch + HF.

layer grown by O$_2$ plasma or ozone. But this cleaning process could not remove the SiO$_x$C$_z$ layer satisfactorily.

After the silicon light etch with CF$_4$/O$_2$ remote plasma, the residual layer was changed to CF$_x$-polymer /SiO$_2$, that is, Si-C bond was completely removed. In narrow scanning of C$_{1s}$ peak (286-294 eV), only the small amount of CF$_x$-polymer was observed. Si-O bond was detected in Si$_{2p}$ peak uniquely and the thickness of the oxide was above 30Å as shown in Fig. 5. The silicon light etch residue, CF$_x$-polymer and SiO$_2$, was completely cleaned by NH$_4$OH-H$_2$O$_2$ and subsequent HF dip. CF$_x$-polymer is removed by the same mechanism as the O$_2$ plasma, SiO$_x$C$_z$ layer by forming SiF$_4$, CO, and CO$_2$, and silicon substrate by way of SiO$_2$ and subsequently CO$_2$ and SiF$_4$. The XPS spectrum of wafer at this stage was exactly the same as the initial wafer which was dipped into HF acid.

Silicon etch with HBr and Cl$_2$ plasma left small quantity of CF$_x$-polymer, Cl and Br. HBr/Cl$_2$ plasma removes the oxide etch residue by lift-off of the silicon substrate through forming highly volatile SiBr$_4$ and SiCl$_4$. The removal of oxide residue by physical lift-off causes the silicon substrate damaged and hard to control the thin etching depth (silicon etch rate = 90 Å/sec). The native oxide to be thought was removed by HF acid dip.

Among the two step cleanings, silicon light etch and subsequent NH$_4$OH-H$_2$O$_2$ mixture and HF acid dip was found to be most effective in removing the oxide

etch-overetch residue on the silicon substrate.

CONCLUSION

The oxide dry etch residue consists of CF$_x$-polymer/SiO$_y$C$_z$. Wet cleaning only was not effective in removing the oxide etch residue. Among two step cleanings of dry and wet, the most effective method to clean up the oxide etch residue was silicon light etch using CF$_4$/O$_2$ plasma and subsequent wet cleaning: NH$_4$OH-H$_2$O$_2$ mixture and then HF acid.

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