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Surface Residue Island Nucleation in Anhydrous HF/Alcohol Vapor Processing of Si Surfaces

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Anhydrous HF/methanol vapor-phase chemistries were employed to etch SiO₂/Si surfaces at low pressure (5-50 Torr) and ambient temperature. The oxides on Si were formed from the following: (*i*) RCA chemical cleaning and (*ii*) UV-ozone treatment. Atomic force microscopy (AFM) and lateral force microscopy (LFM) were used to analyze the HF vapor-cleaned Si surfaces. AFM/LFM displayed residue islands distributed randomly upon the Si surface as a result of vapor-phase cleaning. As a result of etching RCA chemical oxides, the average lateral dimension of the residue islands is 40 nm and the average height of the islands is 6 nm. As a result of etching UV-ozone oxides, the average lateral dimension of the residue islands is 30 nm, and the average height of the islands is 3.5 nm. A decrease in residue island density is observed after the removal of a UV-ozone oxide compared to RCA chemical oxide removal. Secondary ion mass spectroscopy was used to characterize chemical impurities (O, C, F, and N) in the SiO₂ films and and the Si surface after HF vapor-phase cleaning. The constituents of the residue islands have been attributed to nitrogen impurities and silicon atoms imbedded in the passivating oxides. Results indicate that condensation of methanol vapor onto the bare Si surface, after oxide removal, is necessary for residue island formation. We suggest a model in which residue island nucleation occurs from nonvolatile N-Si complexes that form hydrogen bonds with methanol molecules and diffuse into the adsorbed alcohol layer. The molecular impurities then interact and form residue islands.

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Wafer cleaning processes are the most frequently repeated steps in the manufacturing of an integrated circuit (IC). There is risk of surface contamination any time the Si surface is exposed to ambient conditions. Wet chemical cleaning is most commonly utilized to remove contamination from the Si surface. Wet cleaning steps predominantly consist of variations of the RCA clean developed by Kern and Puotinen.¹ The RCA clean is used for the removal of particles, surface organics, and metals contamination.²⁻⁴ Due to the nature of the RCA clean, the Si surface is passivated with a chemical oxide layer (~1 nm thick) that protects the Si surface from recontamination. Dry cleaning techniques are also employed to clean and oxidize the Si surface during IC manufacturing. A UV-ozone treatment is a dry cleaning technique typically used to remove organic contamination from the Si surface.⁴⁻⁶ This technique leaves the Si surface passivated with a "dry" oxide (~ 1 nm thick). In both cases, the presence of the oxide may detrimentally effect next step processing.

In many processes, aqueous HF-last etching has been appended to cleaning techniques to remove the protective oxide layer and replace it with an H-terminated Si surface. However, as device geometries get smaller, cleaning needs become more stringent.^{2,7} The trend toward integrated systems (*e.g.*, cluster tools), makes aqueous HF as the final surface preparation step more difficult.⁸ The realization of cluster-tool processing provides an opportunity for the integration of vapor- and gas-phase cleaning technologies into critical device fabrication sequences such as gate dielectric formation and raised source/drain structures involving Si selective epitaxy.⁸

Exposure of a Si surface to HF vapor and a solvent results in three different regimes: (*i*) the condensed phase regime where a thin liquid layer forms on the surface, (*ii*) the enhanced adsorption regime characterized by monolayer-type adsorption, and (*iii*) the gas-phase regime characterized by submonolayer adsorption. These regimes have been defined experimentally and theoretically for HF and water.⁹⁻¹² Several studies have demonstrated that HF vapor-phase cleaning requires the formation of an adsorbed layer of HF and solvent (H₂O or methanol) in order for oxide etching to occur at a reasonable rate.⁹⁻¹²

HF vapor-phase cleaning has shown distinct advantages over conventional HF aqueous cleaning. The advantages include (*i*) cluster-tool integrated cleaning processes; (*ii*) cleaning high aspect ratio regions; (*iii*) lack of rinsing or drying steps; (*iv*) reduced chemical contamination and degradation; (*v*) improved process uniformity; and (*vi*) reduced chemical consumption and waste.^{10,12} However, as with any novel cleaning technique there are always limitations. The major limitation of vapor-phase cleaning compared to aqueous cleaning is that the process is isolated to the surface. In an aqueous cleaning process the etched species can diffuse into the liquid bath, but in gas vapor-phase cleaning the only way for the reactants and products to leave the surface is by evaporation or desorption. Therefore, it is necessary to suppress the formation of nonvolatile species on the surface. Water is a product of the HF/SiO₂ etching reaction, Eq. 1, and it is the least volatile specie of the reaction

$$4HF + SiO_2 \rightarrow SiF_4 \text{ and } 2H_2O$$
[1]

An extended residence time of H_2O , condensed on the surface, may lead to reactions with SiF₄ to form particles and nonvolatile liquids on the surface.¹³⁻¹⁵ It has been shown that vapor etching SiO₂ with HF/H₂O chemistry results in surfaces with high particle counts.^{13,15} Ma *et al.*¹⁴ have shown that the critical step for particle reduction is the continuous desorption of SiF₄ during oxide removal. Izumi *et al.*¹⁵ explain that if SiF₄ is not readily desorbed from the surface it may dissolve in H₂O and precipitate SiO₂ particles, or SiF₄ may bond with HF to form nonvolatile liquids in the form of H₂SiF₆. An aqueous rinse is one approach for removing particles and liquids from the surface after vapor-phase cleaning.¹⁶ Although a rinse may suffice, this approach negates an advantage that an all-vapor-phase cleaning process has over aqueous approaches.

A drying agent, such as the aliphatic alcohols (isopropyl alcohol, methanol, or ethanol), may be employed to increase desorption rates of the etch products.^{14,15,17} The aliphatic alcohols have higher vapor pressures than water and will desorb from the surface at a much faster rate than water.^{17,18} The aliphatic alcohols also increase the desorption rate of water. This occurs by the formation of hydrogen bonds between the alcohol and water molecules.¹⁹ The use of alcohols in vapor-phase cleaning has resulted in reduced particle contamination, increased wafer uniformity, and increased device yield.²⁰ However, it has been found that employing alcohol in the vapor-phase process results in the nucleation of surface residue during the etching of chemical oxides.²¹ Although the suppression of particle generation is achieved with HF/alcohol chemistries, a new surface defect is observed in the form of small residue islands distributed randomly upon

the oxide-free Si surface. The constituents of the residue have been attributed to nonvolatile impurities imbedded in the chemical oxide.²¹ During the oxide etching process, the nonvolatile impurities that remain on the surface nucleate into residue islands.

The proposal that oxide impurities result in surface residue formation was developed from a previous study in which thermal, RCA chemical, and aged RCA chemical oxides were vapor etched using an HF/isopropyl alcohol (IPA) vapor chemistry.²¹ It was observed that the removal of thermal oxides did not result in identifiable surface residue, but the removal of chemical oxides did result in a high density of small residue islands which were observed using atomic force microscopy (AFM). It was proposed that the residue island formation is dependent upon the purity of the oxide being etched. This was based on the assumption that a thermal oxide is extremely pure SiO₂ compared to the chemical oxides. This assumption explained why residue islands were not observed for the removal of thermal oxides. The role of the alcohol was further clarified in that residues were not observed with HF/H₂O vapor chemistry.

It is therefore suggested that either a chemical or physical property of the alcohol molecules, which differs from water molecules, assists in the residue island nucleation. It is not necessarily a chemical difference since both alcohols and water have the ability to form hydrogen bonds with electronegative elements.²² However, it should be noted that the formation of hydrogen bonds is viewed as a critical element for residue island nucleation. There is a physical difference between alcohol and H₂O in terms of how the molecules react when in contact with a hydrogen-terminated Si surface. Water molecules will not form an adsorbed layer on H-terminated Si, because the surface is hydrophobic. That is, the surface tension of H₂O is greater than that of the passivated Si surface, so water molecules will not wet the surface.²³ In contrast, alcohol molecules will form an adsorbed layer on H-terminated Si because the surface tension of alcohol is less than that of Si allowing the alcohol to wet the surface.²³ This property has an effect in terms of vapor-phase cleaning with either H₂O or alcohol as the etch solvent. For HF/alcohol vapor chemistries there is no transition from a hydrophilic to a hydrophobic state as the SiO_2 is removed from the surface.²⁴ The alcohol molecules will continue to wet the Si surface after the SiO₂ is removed. The formation of residue islands using HF/alcohol vapor chemistries is derived from the physical property that alcohol molecules may continue to form an adsorbed layer on the Si surface. This is not the case for HF/H₂O chemistries. McIntosh et al.²⁵ have described how the condensed layer of HF and H2O breaks down as the last monolayer of the oxide is removed. This is attributed to a surface transition from a hydrophilic state to a hydrophobic state, where the hydrophobic state will no longer support a condensed phase.

In this study we investigate vapor-phase cleaning employing anhydrous HF/methanol vapor chemistries for removal of RCA chemical and UV-ozone oxides at low pressures and ambient temperature. Scanning force microscopy [AFM/lateral force microscopy (LFM)] is used to observe and characterize surface residue formation. Etching at low pressures is performed to reduce the condensed phase of methanol vapor on the Si surface. Secondary ion mass spectroscopy (SIMS) is employed to characterize chemical differences between RCA oxides and UV-ozone oxides. In addition, SIMS is used to chemically characterize a Si surface with residue islands. The results lead us to propose a possible mechanism for surface residue island nucleation by considering molecular interactions between nonvolatile oxide impurities and methanol molecules.

Experimental

In this study 4 in. diam n- and p-type Si(100) wafers were used. Prior to vapor phase etching, passivating oxides were grown on the Si substrates via RCA chemical cleaning or UV-ozone exposure. The native oxide was initially removed with a 2% HF dip followed by a 2 min DI (deionized water) rinse. The RCA chemical treatment was performed using the two standard steps: (*i*) SC-1 (5:1:1 $H_2O:NH_4OH:H_2O_2$ at 70°C) and (*ii*) SC-2 (5:1:1 $H_2O:HCI:H_2O_2$ at 70°C). Each step consisted of a 5 min dip in each chemical followed by a 5 min DI rinse. The UV-ozone treatment consisted of a 5 min exposure of the Si surface to UV light and ozone gas in a Samco UV and ozone dry stripper, model UV-1. The UV system is dedicated to this application and does not suffer from contaminants often transmitted in photoresist stripping. The RCA chemical cleaning and UV-ozone treatment grew ~1.5 nm thick oxides, as determined by ellipsometry measurements. The control surfaces in this study were an RCA cleaned/HF dipped surface and a UV-ozone treated/HF dipped surface. Wet chemical treatments were performed in a laminar flow wet chemical hood. Immediately after the passivating oxides were grown, the wafers were loaded into a loadlock connected to a sixport single-wafer processing cluster tool. The loadlock was evacuated to ~5 × 10⁻⁶ Torr prior to transfer into the wafer handler. The wafer handler base pressure measured ~6 × 10⁻⁸ Torr, and wafer transfer between chambers occurred at ~1 × 10⁻⁶ Torr.

Vapor-phase cleaning was accomplished in a modified Advantage 2000 system that was donated by Genus Corporation. The system was retrofitted to be high vacuum compatible. It is a single-wafer stainless steel chamber with a SiC dome. The system base pressure is $\sim 2 \times$ 10^{-7} Torr. The system employees anhydrous hydrogen fluoride (AHF) gas delivered from a gas cylinder and methanol vapor that is vacuum evaporated from a Teflon-coated stainless steel sampling cylinder. The AHF gas flow rate is from 0 to 500 sccm and is controlled by a mass flow controller (MFC). The methanol gas flow range is from 0 to 67 sccm at room temperature and is controlled by an N_2 calibrated MFC. Nitrogen is used to establish the desired process pressure, and after the cleaning process is complete, N_2 is used to purge the system prior to wafer transfer. The nitrogen flow range is from 0 to 1000 sccm controlled by an MFC. Process gases are delivered via a Teflon injector into the process chamber. Process pressure is measured by a baratron gauge and is regulated using a downstream throttle valve. The wafer is held horizontally in the process chamber and etching occurs at ambient temperature (~20°C) with process pressures ranging from 0.5 to 75 Torr. In this study, wafers were processed at 0.5, 5, 25, and 50 Torr for process times of 1-5 min.

After the wafers were processed they were transferred out of the cluster-integrated vapor cleaning system and examined with atomic force microscopy (AFM). A Park Scientific M5 atomic force microscope, in contact mode, was employed to measure surface roughness and characterize the surface morphology. Signals for AFM and LFM were collected and observed simultaneously. Typical scan sizes used to characterize the cleaning and surfaces were $2 \times 2 \mu m$ with 256×256 data points. Scans were performed in the center and 0.5 in. from the edge of each wafer. The lateral resolution of the AFM is ~1-2 nm. The vertical resolution of the AFM is subnanometer. Silicon nitride tips with a 4.1 N force constant were used for surface scanning. Long range surface variations were removed from the images using a second order polynomial fit. The root mean square (rms) roughness values were then calculated for each of the scanned surfaces. Accuracy of the rms roughness values is estimated to be ± 0.05 nm.

SIMS analysis was performed to analyze contaminants in RCA chemical oxides and in UV-ozone oxides. SIMS was also employed to study contamination concentrations on the Si surface after HF vapor cleaning or HF dipping RCA chemically oxidized surfaces. Oxidized and cleaning surfaces were capped with \sim 50 nm of poly-Si at 650°C. Capping was achieved in a rapid thermal processing (RTP) chamber, which is part of the integrated cluster environment. After capping, wafers were sent to Evans East for SIMS analysis. The samples were analyzed with a PHI model 6600 secondary ion mass spectrometer using 3 keV casium primary ion bombardment and negative ion detection. Ions were detected in a quadrupole mass spectrometer. Interfacial concentration of O, C, F, and N were measured. Data was obtained in terms of atom/cm³ and atom/cm². The overall accuracy of the concentration scales is estimated to be 15-20%, and the accuracy of the total depth scales is estimated to be 5-10%.

Results

HF vapor cleaning of oxidized Si surfaces using AHF/methanol was performed at 0.5, 5, 25, and 50 Torr for process times of 1-5 min.

Process parameters	Residue density (island no./4 μ m ²)	Residue dimensions (lateral/height) ave. (nm/nm)	Range of island height (nm)	rms roughness (nm)
50 Torr, 5 min	100	40/6.9	3.5-8.5	0.89
50 Torr, 3 min	118	40/6.5	4.0-9.0	0.93
50 Torr, 1 min	92	40/6.1	4.5-8.5	0.84
25 Torr, 5 min	90	45/7.2	4.0-12.0	1.1
25 Torr, 3 min	99	40/6.3	4.0-9.5	0.99
25 Torr, 1 min	126	35/5.9	2.5-8.2	0.69
5 Torr, 5 min	78	40/6	2.5-8.0	0.47
5 Torr, 3 min	75	40/4.6	2.0-6.5	0.58
5 Torr, 1 min	76	40/4	2.0-6.5	0.57

Table I. Process parameters, residue island density, average residue dimensions, and rms values for HF vapor-etched RCA chemical oxides.

Table II. Process parameters, residue island density, average residue dimensions, and rms values for HF vapor-etched UV-ozone oxides.

Process parameters	Residue density (island no./4 µm ²)	Residue dimensions (lateral/height) ave. (nm/nm)	Range of island height (nm)	rms roughness (nm)
50 Torr, 5 min	13	30/3.0	2.5-4.2	0.14
50 Torr, 3 min	12	30/3.0	2.4-4.0	0.18
50 Torr, 2 min	15	30/3.3	2.0-5.0	0.17
25 Torr, 5 min	13	30/3.9	2.5-5.0	1.21
25 Torr, 3 min	18	30/3.1	2.3-4.2	0.15
25 Torr, 2 min	14	25/3.7	1.6-6.4	0.21

Surfaces were examined with AFM to identify the presence of residue islands identified in our previous study.²⁴ The results are summarized in Tables I and II. Etching of RCA chemical oxides for 1, 3, and 5 min for process pressures of 5, 25, 50 Torr resulted in residue formation (Fig. 1). Etching of UV-ozone oxides for 2, 3, and 5 min for process pressures of 25 and 50 Torr also resulted in residue formation (Fig. 2). The residue islands were observed after etching Si wafers passivated with either an RCA chemical oxide or a UV-ozone oxide. There was a significantly larger amount of surface residue after etching of the RCA chemical oxide surface as compared to the UV-ozone surface (Fig. 3).

Both n- and p-type wafers were oxidized and vapor etched, to determine if there is any dependence on residue formation with substrate doping. Vapor cleaned n- and p-type wafers resulted in surface residue. There appeared to be no difference in residue formation as a result of differences in substrate doping. Residue island height and lateral dimension were measured for all identifiable peaks in an AFM image. As a result of RCA chemical oxide removal at 50 and 25 Torr, average island height and lateral dimension measure to be \sim 6-7 nm and 40 nm, respectively (Fig. 4a). A slight decrease in island density and vertical dimension was observed for vapor etching chemical oxides at 5 Torr. Processing at 5 Torr resulted in an average island height of 4.8 nm. As a result of UV-ozone oxide removal, the average island height and lateral dimension measure to be \sim 3-4 nm and 30 nm, respectively (Fig. 4b).

Processing chemical oxides at 0.5 Torr and UV-ozone oxides at 0.5 and 5 Torr did not result in surface residue formation. An RCA chemical oxide was processed for 15 min at 0.5 Torr and then dipped in H_2O to observe if it would wet or dewet. The surface displayed hydrophilic characteristics to H_2O , indicating that the oxide was not completely etched. Similar tests and the same results were observed for etching of UV-ozone oxides at 0.5 and 5 Torr for extended process times. The lack of observable residue for processing at the lower pressures is attributed to the fact that complete etching of the oxide did not occur.

A 100 nm thermal oxide was also processed for 10 min at 0.5 and 5 Torr and measured by ellipsometry pre- and postetch to determine



Figure 1. AFM images of HF vapor-etched RCA chemical oxides at (a) 5, (b) 25, and (c) 50 Torr.



Figure 2. AFM images of HF vapor-etched UV-ozone oxides at (a) 25 and (b) 50 Torr.

if etching occurred. No measurable difference in oxide thickness could be obtained by ellipsometry. Thermal oxide etch rates were obtained for vapor processing at 50 and 25 Torr. Etch rates were obtained by measuring five points on the thermal oxide before and after etching. Thermal oxide etch rates ranged from approximately 1.0 to 1.5 nm/min. There did not appear to be significant variations in etch rate due to process pressure change between 25 and 50 Torr. It should be noted that thermal oxides typically etch more slowly than other oxides (*e.g.*, wet chemical or deposited).^{9,10,23}

RCA chemical oxide removal resulted in a high residue density with roughness values ranging from 0.5 to 1.0 nm rms. UV-ozone oxide removal resulted in a lower residue density with roughness values ~ 0.2 nm rms. An estimation of the actual Si surface roughness may be measured by excluding the surface residue from the AFM images. Roughness values of ~ 0.2 to 0.3 nm were measured for all vapor-etched SiO₂ surfaces by excluding the residue islands. The rms values for the control surfaces are ~ 0.15 nm (Fig. 5c). The estimated rms values for HF vapor-cleaned surfaces are comparable to the control surfaces. In contrast, surfaces with a higher density of residue result in larger rms roughness values. The increase in rms roughness values, compared to the control wafers, is due to the surface residue, which was also observed in an earlier study.²²

Lateral force microscopy (LFM) was used to measure variations in surface friction on the HF-vapor-cleaned surfaces. A very small (or negligible) difference in frictional forces between the Si surface and the residue islands is observed (Fig. 5a and b). This suggests that the Si surface and residue islands consist of predominantly the same material (*i.e.*, Si). An HF vapor cleaned surface (with residue islands) was oxidized by a UV-ozone treatment and imaged with LFM. A difference in frictional forces is observed between the SiO₂ surface and the residue islands (Fig. 5c and d). This suggests that the oxide surface and residue islands consist of different materials.

SIMS spectra were obtained to measure oxide concentrations of O, C, F, and N. Interfacial concentrations for an RCA chemical

oxide are 4.25×10^{15} , 2.81×10^{12} , 2.64×10^{11} , and 1.79×10^{12} 10¹³ atom/cm² for O, C, F, and N, respectively (Fig. 6). Interfacial concentrations for a UV-ozone oxide are 4.59×10^{15} , 4.60×10^{12} , 2.53×10^{12} , and 2.50×10^{11} atom/cm² for O, C, F, and N, respectively (Fig. 6). One monolayer (ML) on a Si surface is equivalent to \sim 6.8 × 10¹⁴ atom/cm². Also, 0.1 nm of SiO₂ contains 4.64 × 10¹⁴ O/cm². Using these values, the RCA chemical oxide and the UVozone oxide concentrations of oxygen are equivalent to 6.2 ML and 6.7 ML, respectively; which corresponds to oxide thicknesses of \sim 0.92 and \sim 0.99 nm for the UV-ozone and RCA oxides, respectively. Carbon concentrations in both oxide films are comparable, but there is about an order of magnitude more fluorine in the UVozone oxide compared to the RCA chemical oxide. The RCA chemical oxide has significantly more nitrogen in the film than the UVozone oxide. There is almost a two order of magnitude difference in nitrogen concentration between the two oxides.

SIMS spectra were obtained to measure residual species of O, C, F, and N as a result of vapor etching an RCA chemical oxide and HF dipping an RCA chemical oxide. This was done to investigate differences in the surface chemistry between a surface with a high density of residue islands and a residue-free surface. Interfacial concentrations for an HF vapor-cleaned surface are 8.84×10^{13} , 7.62×10^{13} , 5.07×10^{11} , and 1.46×10^{12} atom/cm² for O, C, F, and N, respectively (Fig. 6). Interfacial concentrations for an HF-dipped surface are 2.01 \times 10¹⁴, 8.69 \times 10¹³, 9.14 \times 10¹¹, and 4.15 \times 10¹¹ atom/cm² for O, C, F, and N, respectively (Fig. 6). Residual oxygen on the vapor-cleaned surface is <1/8 ML. Residual oxygen on the HF-dipped surface is $\sim 1/4$ ML. Residual O, C, and F as a result of HF vapor cleaning are less than an HF dipped surface. Residual N as a result of HF vapor cleaning is greater than for an HFdipped surface. It is likely that the additional N contamination after the RCA process is due to the SC1 etch which includes NH₃OH.

Discussion

We first consider the effectiveness of the HF vapor process to etch oxide films. RCA chemical oxides can be removed in process times of 1 min or less at process pressures of 5, 25, 50 Torr. Complete removal of UV-ozone oxides was achieved in process times of 2 min or less at process pressures of 25 and 50 Torr. The difference in the etch time for complete removal of the UV-ozone oxides as compared to the RCA chemical oxides may be attributed to differences in the etch delay time.^{10,12,17,24} An RCA chemical oxide is a hydrous oxide (contains moisture), whereas a UV-ozone oxide is a dry oxide. We suggest that the difference in moisture content between the two types of oxide leads to the different etch times necessary for oxide removal. Differences in the moisture content may also explain why UV-ozone oxides and thermal oxides did not etch at 5 Torr. The moisture content in the chemical oxides may induce an adsorbed layer for vapor etching at lower pressures, which is not observed for dry oxides.



Figure 3. AFM images of (a) vapor-etched RCA chemical oxide, (b) vapor etched UV-ozone oxide, and (c) HF dipped RCA chemical oxide.

3516

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Figure 4. Schematic of residue islands displaying relative lateral dimension and height as a result of vapor etching (a) RCA chemical oxide and (b) UVozone oxide.

For all cases, except for processing at 5 Torr, residue island size and surface density are independent of the process time or the process pressure. This implies that the residue islands are not etched by the HF vapor cleaning process. These results further suggest that complete oxide removal is necessary before residue formation occurs. The results also indicate that residue formation occurs soon after oxide removal and before desorption of the condensed methanol layer. Vapor etching chemical oxides at 5 Torr displayed a slight variation in residue density and an overall smaller dimension compared to vapor etching chemical oxides at 25 and 50 Torr. It is suggested that vapor etching at this pressure, resulted in a reduced overall thickness of the condensed phase. This implies that a reduction in the condensed layer yields smaller residue islands. Therefore complete suppression of a condensed phase on the exposed Si surface could significantly reduce residue island nucleation.

We next consider the dependence of residue island size and density on the differences in oxide purity.²³ A wet chemically grown oxide is more likely to incorporate elemental defects in the oxide than a UV-ozone oxide grown in a "dry" environment. These contaminants can be divided into major constituents and minor constituents. The major constituents typical in a passivating oxide are C,



Figure 5. (a) AFM of vapor-etched RCA chemical oxide and (b) corresponding LFM image of the vapor etched surface. (c) AFM image of oxidized vapor etched surface and (d) corresponding LFM image of oxidized vapor-etched surface.



Figure 6. Graph displaying the areal concentrations of O, C, F, and N concentrations for an RCA chemical oxide, a UV-ozone oxide, an HF-vapor cleaning surface and an HF-dipped surface, as measured by SIMS.

F, H, and N. These typically range from 10^{13} - 10^{14} atom/cm².²⁶ The following minor constituents are typical in a passivating oxide: B, Mg, Al, P, S, Cl, Ca, and Br (range 10^{6} - 10^{12} atom/cm²) and Fe, Ni, Cu, and Zn (10^{10} atom/cm²).²⁶

It is appropriate to consider the size of the residue islands in order to determine their chemical composition. Since the residue islands are on the order of several monolayers in size, it is considered that the minor constituents do not significantly contribute to the residue composition. However, the minor constituents may very well con-



Figure 7. (a) illustration of impurity complex diffusion. (b) Illustration of initial residue island nucleation and growth. (c) Lateral growth of residue island. (d) Stable residue island.

tribute to the nucleation process. We now consider the major constituents and their role in the residue formation. Since Si and O are present in thermal oxides it is not likely that Si and O alone are responsible for the residue islands, although they may contribute to the residue composition. Hydrogen incorporation into SiO₂ has been observed as Si-F, mostly observed at the Si-SiO₂ interface.²⁷ Vapor etching oxide films with H or F incorporation would likely yield Si- H_r , Si- F_r , OH_r species. Such species are volatile and will not remain on the surface. Therefore H or F are not considered to be the constituents which cause the formation of the residue islands. This leaves carbon and nitrogen as the more likely constitutes responsible for island nucleation and residue formation in the HF/methanol vapor process. Many thermal oxide processes employ a 5 min N₂ anneal prior to oxidation. The N2 anneal is effective in preventing carbon contamination from being incorporated into the oxide during growth.²⁸ Nitrogen incorporation into thermal SiO₂ usually requires gases other than N_2 .²⁹ An extended N_2 exposure of an SiO₂ film at temperatures greater than 1000°C is necessary for nitrogen incorporation into a thermal oxide.³⁰ Most thermal oxide processes employ an N₂ annealing step prior to growth and occur at temperatures less than 1000°C. Therefore, significant carbon or nitrogen contamination is not likely in a thermal oxide. However, carbon and nitrogen contamination can be prevalent in a chemical oxide.

Therefore, we consider carbon or nitrogen species, as the possible contaminants responsible for surface residue formation. Again given the size of the surface residue, it could be assumed that the residue consists of complexes of N or C with Si and/or O and not N or C alone. HF vapor chemistries are not likely to attack and break Si-N, N-O, Si-C, or C-O bonds as readily as Si-O bonds.³¹ In order to determine the chemical composition of the impurity complex, it is appropriate to consider the acquired LFM images. It is observed, using LFM, that the frictional forces of the Si surface and a residue island are comparable. It is also observed that the frictional forces of an SiO₂ surface and a residue island differ. This implies that the islands mainly consist of Si and less N or C, but not O or SiO₂.

At this point it is important to consider the SIMS spectra for the two types of oxides (Fig. 6), which result in different residue island size and surface densities. Carbon concentrations in the two types of oxides measured 2.81×10^{12} and 4.60×10^{12} atom/cm², for the RCA and UV-ozone oxides, respectively. It is observed that the carbon contamination in both types of oxides is comparable. Nitrogen concentrations in the two types of oxides measured 1.79×10^{13} and 2.50×10^{11} atom/cm², for the RCA and UV-ozone oxides, respectively. A significant difference in nitrogen contamination is observed between the two oxides. Vapor etching an RCA chemical oxide results in larger residue islands and a higher density of the surface residue compared to vapor etching a UV-ozone oxide. Correlating the AFM results with the SIMS results, we suggest that nitrogen contamination in the oxide is the component responsible for residue island formation.

SIMS spectra of the vapor-cleaned surface and the HF-dipped surface also displayed a difference in the amount of nitrogen contamination on the Si surface (Fig. 6). The measured concentration of nitrogen for the HF-vapor cleaned surface is 1.46×10^{12} atom/cm² compared to 4.15×10^{11} atom/cm² for an HF-dipped surface. With this model that the residue islands consist of nitrogen, the HF-vaporcleaned surface should and did exhibit a larger surface concentration of nitrogen.

From LFM and SIMS data, we propose that the chemical composition of the residue islands consists of nitrogen and silicon. Given the above considerations, the following suggests a possible mechanism to explain the residue island formation. First, we assume that a condensed layer of alcohol remains on the Si surface after the SiO₂ film is etched. We then assume that the hydrogen bonding provides a means for the impurity complex to diffuse in the condensed alcohol layer. Diffusion in the condensed film allows impurities to interact with one another (Fig. 7a). This initiates a nucleation process, and complexing with other N-Si impurities, which leads to island growth (Fig. 7b). If the impurity-impurity bonding were not favorable, then impurities would simply diffuse, but not combine to nucleate larger surface residue. As the impurity complex continues to grow it reaches a size such that growth in the vertical directions slows. At the same time, growth in the lateral direction may continue (Fig. 7c). This would explain the dimensions of the residue islands being larger diameter flat features on the surface. Considering the difference in island size for vapor etching at 5 Torr compared to etching at higher pressure (25 and 50 Torr), it may be suggested that the vertical size of a residue island is dependent upon the thickness of the condensed layer of alcohol. The growth rate of the impurity complex is reduced as the number of available N-Si impurities decreases (Fig. 7d). It is probable that some methanol molecules remain as a part of the residue island after the condensed film desorbs.

Since the residue islands are not observed for partial removal of SiO_2 , it may be assumed that the impurities cannot diffuse and nucleate. In this case, it is suggested that one or more of the Si atoms, bonded to the N atom, is still covalently bonded in the SiO_2 microstructure. Therefore the N-Si impurity will not diffuse until all covalent bonds to the surface are broken.

Conclusions

Surface residue islands were observed and characterized using AFM, LFM, and SIMS. Residue island nucleation is attributed to adsorbed alcohol layers on the Si surface and molecular interactions between alcohol molecules and nonvolatile impurity complexes. Nitrogen contamination in the oxide is suggested to be the impurity, which leads to the formation of surface residue islands. It is suggested that the size of the residue islands is dependent upon the impurity concentration that is available and possibly dependent upon the thickness of the adsorbed alcohol layer. It appears that residue island density is mostly dependent upon the N impurity concentration in the oxide. We suggest that the residue islands are largely composed of nitrogen-silicon complexes. Our proposed mechanism for residue island nucleation is made up of four steps: (i) formation of an adsorbed layer of alcohol on the Si surface, (ii) hydrogen bonding between N-Si impurity complexes and alcohol molecules, (iii) diffusion and interaction of impurity complexes, (iv) nucleation and growth of residue islands.

Nucleation on partially etched SiO_2 is not observed. It is suggested the residue formation cannot occur on the SiO_2 surface, because impurity diffusion is restricted. The results described here suggest two approaches for minimizing the formation of residue islands: (*i*) minimize nitrogen contamination in oxides to be etched using the AHF/methanol process or (*ii*) manipulate the vapor cleaning process such that an adsorbed layer of alcohol does not form on the Si surface after oxide removal. Both these techniques are currently being explored in our lab.

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