TOFSIMS Characterization of Molecular Contamination Induced Resist Scumming

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Abstract. In conventional semiconductor processes, gross photoresist scum has been detected with inspections using optical microscope or secondary electron microscope; trace molecular contamination or photoresist residue could be removed during wafer processes employing vigorous thermal, chemical, plasma or ion beam steps and thus had negligible effects on semiconductor manufacture. However, advanced semiconductor technology has become increasingly sensitive to molecular contamination that might be difficult to detect with traditional inspection and analysis techniques.

Direct surface analysis by TOFSIMS provides sensitive detection of both elemental and molecular contamination that may be originated from environmental sources or from wafer fabrication processes. Monolayer level molecular contamination and very thin photoresist scum that were not detectable with conventional inspection techniques have been characterized with TOFSIMS in this paper. Detrimental effects of the very thin photoresist scum have been demonstrated with a 130 nm technology process. Cleaning process to remove molecular contamination was validated with TOFSIMS analysis. Detection of very thin photoresist scum can be accomplished with TOFSIMS imaging analysis.

Keywords: Photoresist scum, molecular contamination, time-of-flight secondary ion mass spectrometry (TOFSIMS), DUV photolithography, surface analysis techniques, etch residual

INTRODUCTION

As the drive for ever-shrinking dimensions and ever-improving device performance continues, more stringent requirements for surface contamination control and monitoring have been imposed on semiconductor fabrication processes. While the effects of elemental contamination are understood and metrology techniques are continuously improved to meet the monitor requirements, the effects and monitoring requirements for molecular contamination are not as mature.

X-ray photoelectron spectroscopy and infrared spectroscopy are commonly useful for surface chemical analyses but lack the sensitivity in detecting trace level contaminants. Electron beam based analysis techniques such as Auger spectroscopy induce carbon build up and typically do not provide molecular bonding or structure information for chemical identification. Thermal desorption with gas chromatography-mass spectrometry provides adequately sensitive detection and library spectra for chemical identification of volatile or semi-volatile molecular contamination; while contaminants need to be effectively sampled with thermal desorption, typically from full wafers.

Time-of-flight secondary ion mass spectrometry (TOFSIMS) provides direct surface analysis sensitive to outermost monolayers on wafers and is useful in detecting both elemental and molecular contaminants demonstrated by this and other groups. Surface contamination analyses by TOFSIMS are
comprehensive for contaminants of different chemical nature such as acids, bases, condensables, and dopants, as well as from different sources such as environmental sources or wafer fabrication processes.

Photoresist and etch residues are two common molecular contaminants originated from wafer fabrication processes. For example, gross photoresist scum, or development residue, have caused severe process or performance issues by blocking subsequent etch or implant processes. Fluorocarbon etch residual has been correlated with delamination of polymeric low K dielectric thin film. Although oxygen plasma based de-scum process has been used in mitigating gross resist scum, very thin resist scum layers at 10 nm or thinner can be difficult to detect but still cause process issues in the most advanced semiconductor fabrication processes.

In this paper, we demonstrated the first reported TOFSIMS detection of very thin resist scum, not detectable by optical or electron beam based wafer inspections yet detrimental to ultra low energy implantation for 130 nm technology and beyond. While nitrogen-containing molecular base has been demonstrated to cause photo-resist poisoning and T-topping, this paper provides the first experimental data that a non-base molecular contamination at monolayer level can interact with DUV photoresist to cause scum that is difficult to remove. TOFSIMS chemical analysis provides further insight for the resist scum formation and is critical to eliminate such thin residue layers.

EXPERIMENTAL

Clean Si wafers were used for experiments involving dry etch, photolithography and cleaning processes in semiconductor manufacture. Photolithography processes were performed with DUV photoresist and equipment suitable for 130 nm technology node. Wafers subjected to dry etch were processed with fluorocarbon-containing etch chemistry. Cleaning processes include piranha-based wet clean and dry ash process using oxygen plasma. Photolithography steps were processed with a test pattern and large exposed areas were used for TOFSIMS surface spectra analyses.

TOF-SIMS experiments were conducted with an ION-TOF TOFSIMS IV Instrument using a pulsed 25 keV Ga⁺ ion beam rastered over 60μm X 60μm area for surface spectra. Depth profiles were acquired with the 25 keV Ga⁺ analytical beam over 50μm X 50μm area, interleaved with a 3keV Cs⁺ sputter beam over 300μm X 300μm area. Ion image analyses were performed with the 25 keV Ga⁺ ion beam rastered over 500μm X 500μm area. Low energy electron flood was employed for charge compensation during the analyses.

RESULTS AND DISCUSSION

Detection of Fluorocarbon at Monolayer Level after Dry Etch Process

Residual fluorocarbon polymer formation from dry etch processes has been detected with TOFSIMS and correlated with process issues such as adhesion of low K dielectrics. However, systematic characterization of such etch residual to correlate with process integration and device performance have not been reported. Sensitive detection of fluorocarbons by TOFSIMS provides an effective technique for such analysis.

Figure 1 presents the TOFSIMS surface spectra from a clean Si wafer surface and a wafer exposed to the fluorocarbon based dry etch process. Only prominent Si* and SiOH⁺ ion peaks are detected in Figure 1A, which is characteristic of a clean Si wafer surface; fluorocarbon ion peaks (QF⁺) are detected in the dry etched wafer spectrum of Figure 1B. The Si⁺ ion intensity in Figure 1B is approximately 10X lower than that in Figure 1A. Since TOFSIMS surface spectra detection is most sensitive to the outermost monolayer on the wafer surface, the 10X reduction of the Si⁺ ion intensity in the spectrum and an additional depth profile analysis with low energy sputter beam indicate that the fluorocarbon contamination is at approximately one monolayer level on the dry etched wafer.

Interaction of fluorocarbon etch residual with photolithography

Molecular contamination at monolayer level such as the fluorocarbon residual detected in Figure 1B could be effectively removed or irrelevant to many semiconductor fabrication steps that involve rigorous chemical, thermal, plasma or ion beam processes. However, an interaction between the fluorocarbon residual and a DUV photolithography process is detected in the TOFSIMS spectra of Figure 2. A clean wafer and a wafer exposed to dry etch, identical to those in Figure 1, were processed through a DUV
photolithography process, including photoresist coating, light exposure, and development steps using a test pattern mask.

FIGURE 1. TOFSIMS positive ion surface spectra of (A) a clean Si wafer, and (B) a Si wafer surface after a dry etch process.

Surface spectra in Figure 2 were acquired from a light-exposed area on both photo processed wafers. Clean Si substrate is detected in Figure 2A with prominent Si$^+$ and SiOH$^+$ ion peaks; hydrocarbon (C$_x$H$_y^+$) ion peaks, consistent with photoresist polymer, and tetramethyl ammonium hydroxide ion (TMAH, C$_4$H$_9$N$^+$) from development chemistry are detected on the wafer exposed to dry etch prior to the photo process. Depth profiling analysis of the residue layer detected on the dry etched wafer is shown in Figure 3. Elements including C, S, N, and F are detected in the residue layer and are characteristic of the photoresist composition. Based on the sputtering rate of similar polymer materials, the photoresist scum layer is estimated at a thickness of 10 nm.

Electrical impact of fluorocarbon-induced photoresist scum

The physical and electrical effects of the 10 nm photoresist scum layer were further examined. Wafers were processed with a 130 nm technology process flow with and without the dry etch step before photoresist processing to define a low energy (sub 5keV) PMOS extension implant region.

FIGURE 2. Positive ion surface spectra from wafers after photolithography process. Hydrocarbon ion peaks indicative of residual photoresist are (A) not detected on clean Si wafer, and (B) clearly detected on wafer exposed to the dry etch process prior to lithography process.

FIGURE 3. Negative ion depth profile indicates that a thin photoresist scum layer of 10 nm is present on wafer detected with photoresist in Figure 2B.
SIMS analyses demonstrated that the boron extension dopant suffered a 26% dose loss due to the resist scum layer present on the wafer with dry etch.

Electrical characterization with the transistor test structures, Id-Vg and Gm-Vg plots in Figure 4, indicated loss of PMOS drive current from the transistor fabricated with the dry etch step, which was consistent with the substantial extension implant blockage by the photoresist scum layer.

![Id-Vg:PMos](A)

![Gm-Vg:PMos](B)

**FIGURE 4.** (A) PMOS Id-Vg (drain current vs. gate voltage), and (B) Gm-Vg (transconductance vs. gate voltage) plots of devices fabricated with (square) and without (diamond) dry etch step prior to photo process.

### Removal of fluorocarbon etch residual

Cleaning processes prior to the photoresist step were evaluated to effectively remove the fluorocarbon residuals and thus to prevent resist scum layer formation. Dry etched wafers were cleaned with a piranha based wet clean process and an oxygen plasma dry ash process. TOFSIMS results in Figure 5 indicated effective removal of the fluorocarbons with the dry ash but not with the wet clean. Experiments with the following photoresist step demonstrated no resist scum with the dry ash clean versus remaining thin scum with the wet clean.

![Fluorocarbon etch residual](A)

**FIGURE 5.** Fluorocarbon etch residual (A) is not effectively cleaned with wet clean, and (B) is removed with dry ash, as detected in the positive ion surface spectra.

### TOFSIMS Imaging Analysis of Photoresist Scum

Photoresist scum or residue layer as thin as 10 nm is demonstrated to be detrimental for 130 nm technology in the experiments discussed above. Optical and electron beam based inspection metrology tools are inadequate to detect such thin resist residues. Further experiments were conducted to detect very thin resist scum layer with TOFSIMS imaging analysis.

**FIGURE 6.** Optical microscope images from two wafers processed with different photolithography processes. While very subtle features are noticeable along the edges of some of the test structures in image 6A, such observation does not completely reveal the photoresist residue layer on the patterned regions.

**FIGURE 7.** TOFSIMS images in Figure 7 were acquired from the same wafers in Figure 6. It is clear in Figure 7B that all the exposed/developed regions in the test
pattern are clear of photoresist residues, indicated by bright Si$^+$ ion signal from the substrate and lack of C$_4$H$_9^+$ ion intensity from the photoresist in the developed regions.

Figure 7A shows that some of the same exposed/developed regions as those in Figure 7B, are still covered with a thin layer of photoresist layer, indicated by lack of Si$^+$ ion intensity and prominent C$_4$H$_9^+$ ion signal in these regions.

While the optical microscope images in Figure 6A does present some abnormality on the developed patterns, TOFSIMS imaging data in Figure 7 clearly detects the properly developed regions from those covered with photoresist residues. Other TOFSIMS analyses have detected photoresist residues that were completely indiscernible with either optical microscope or scanning electron microscope.

FIGURE 6. Optical microscope pictures of two photo processes: images were acquired with approximately 500µm X 500µm area of the same test pattern on each wafer. Only subtle features were observed in image A suggesting photoresist abnormality on the wafer.

FIGURE 7. TOFSIMS ion images of two photo processes in Figure 6: (A) resist scum is clearly detected (arrow pointed areas); (B) resist was effectively developed in the exposed areas. The ion images were acquired with 500µm X 500µm analytical area and ion intensity is presented with brightness in the images.

CONCLUSION

TOFSIMS provides direct surface analysis of trace molecular contamination and very thin photoresist scum at 100Å or less. Such chemical contamination and very thin resist scum are not detectable with other wafer inspection and analysis techniques.

Formation of a very thin photoresist scum was related to chemical interaction of the DUV photoresist with trace fluorocarbon etch residual on wafer surface from previous process step. Severe effects of such thin resist scum to transistor properties were demonstrated with SIMS dopant analysis and electrical characterization of wafers fabricated with a 130 nm technology process flow. Effective cleaning process was evaluated with TOFSIMS analysis, resulting in elimination of the resist scum.

Effective detection of very thin photoresist scum layer was further demonstrated with TOFSIMS imaging analysis. Resist scum that was not detectable or was only subtle abnormality in optical microscope image can be clearly detected by TOFSIMS due to its sensitivity to the outermost surface layer.

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