

## Characterization of Plasma-Etched RuO<sub>2</sub> Substrates

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A blanket film of 1000 Å of RuO<sub>2</sub> deposited on top of 50 Å HfO<sub>2</sub> was etched with a variety of gases. Experiments were designed primarily to determine the optimal etch recipe, to characterize emissions, especially process conditions conducive to RuO<sub>4</sub> formation, to obtain data on chamber clean procedures and emissions, and to determine the best Ru surface analysis method. The goal in the etching process is to form volatile Ru-containing byproducts without using oxidizing gases such as CO, O<sub>2</sub>, or NO that would form the highly toxic RuO<sub>4</sub>. Significant center-to-edge variation was observed (~20%) on the wafers because the Ru target used was only 4 in. diameter. Each etch step was anticipated to remove approximately 200 Å so that multiple passes were possible, maximizing process variation capability.

Ruthenium is an extremely hard material, and is impervious to all acids including HF. Ruthenium tetraoxide is highly injurious to eyes and mucous membranes, and as an extremely strong oxidizer, is flammable upon reaction with reducing agents such as H<sub>2</sub>, NH<sub>3</sub> and cellulose.

Film thickness measurements were attempted before and after etching to determine etch rates, but due to the center-to-edge variation, reliable thickness measurements were difficult to obtain. The etch recipes were first attempted on bare silicon wafers to test the analytical equipment and to verify that the recipes would run successfully. Etch recipes used in the first round of testing (Table 1) included SF<sub>6</sub>/Ar, BCl<sub>3</sub>/Cl<sub>2</sub>, and SF<sub>6</sub>/BCl<sub>3</sub>/Ar. Boron is a potent oxygen scavenger, which would reduce the likelihood of RuO<sub>4</sub> formation. At this time, analytical evaluation of the abatement device was also performed.

The process was monitored at the chamber level using optical emission spectroscopy (OES) and residual gas analysis (RGA). Downstream emissions were characterized using Fourier transform infrared (FTIR) spectroscopy using a 10 m pathlength heated cell, and Fourier transform ion cyclotron resonance (FTICR) spectroscopy, a type of ion trap using both magnetic and electrostatic fields to trap ions. The device is equipped with a pulse valve to admit sample effluent and a getter ion pump to allow mass analysis in the 10<sup>-9</sup> Torr range. Unknown species detected by FTIR were characterized with the aid of FTICR spectra.

At the conclusion of the first series of etch experiments, the wafers were visually inspected. Due to the absence of any changes in film appearance, more aggressive etch recipes were used in the second round of testing. Chamber pressure and bias power were increased, and the duration of the etch recipes was increased. Also included for the first time was a recipe using O<sub>2</sub> and Ar. No Ru-containing species were detected in the RGA or FTICR mass spectra (e.g. Figure 1) for any etch recipes used, however, because Ru possesses six stable isotopes above 5 % natural abundance, significant isotope dilution

occurs. OES spectra indicated several possible Ru emission lines, but FTIR detected a RuO<sub>4</sub> spectral feature at 922 cm<sup>-1</sup> (Figure 2), which was only detected using the O<sub>2</sub>/Ar etch recipe. The impact on manufacturability using an oxygen plasma to etch RuO<sub>2</sub> is its poor selectivity with photoresist.

Chamber contamination analysis was conducted following the etch experiments. Wafers were passed through the chamber, and the top and bottom sides of the wafers analyzed using TOF-SIMS and TXRF (Ag anode). VPD/ICPMS is not effective for the analysis of Ru due to its insolubility in HF. TOF-SIMS analysis indicated higher Ru ion signal on the top side of the wafers, suggesting that volatilization of Ru had occurred as a result of the etch process.

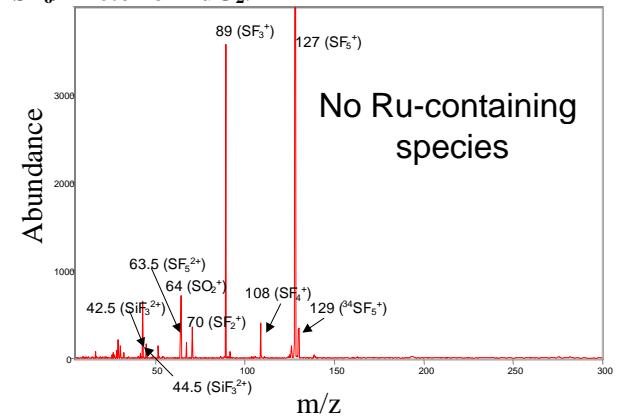
Prior to wet clean, a long-duration O<sub>2</sub>/Ar plasma process was applied to the chamber to volatilize any remaining Ru-containing species while monitoring emissions by FTIR.

Data indicate that etch rates of RuO<sub>2</sub> are very low for all process chemistries attempted, and that only O<sub>2</sub>/Ar plasmas produced an analytically-detectable RuO<sub>4</sub> signal. A longer pathlength FTIR cell may be better suited for detection of volatile Ru specie. Patterned wafers would also be advantageous for etch rate analysis.

**Table 1: Process parameters for RuO<sub>2</sub> etching**

Experiment Seq.	Recipe	Pressure	Bias Power	Source Power	Duration
1	125 sccm SF <sub>6</sub> 75 sccm Ar	4 mTorr	75 W	500 W	20 sec
2	50 sccm BCl <sub>3</sub> 75 sccm Cl <sub>2</sub>	3 mTorr	75 W	500 W	20 sec
3	75 sccm BCl <sub>3</sub> 50 sccm Cl <sub>2</sub>	3 mTorr	75 W	500 W	20 sec
4	125 sccm SF <sub>6</sub> 75 sccm Ar	4 mTorr	75 W	500 W	20 sec
5	125 sccm SF <sub>6</sub> 25 sccm BCl <sub>3</sub> 75 sccm Ar	4 mTorr	75 W	500 W	20 sec

**Figure 1: FTICR mass spectrum obtained during SF<sub>6</sub>/Ar etch of RuO<sub>2</sub>.**



**Figure 2: FTIR spectrum indicating presence of RuO<sub>4</sub> emitted from O<sub>2</sub>/Ar recipe.**

