Rapid Monitoring of FOUP Outgassing with the Vocus CI-TOF

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FOUP Outgassing

Semiconductor manufacturing often involves hundreds of processes that do not occur in a continuous sequence. Between steps, wafers are transported and stored in specialized plastic enclosures called Front Opening Unified Pods (FOUPs). Certain defects in wafers have been related to increases in the time between processes ("queue times") and to the interaction of wafers with compounds that outgas from the surfaces inside the FOUPs [1]. Precise and sensitive measurement of the outgassing compounds could guide process adjustments to decrease defects related to queue time and optimize the cleaning process of individual FOUPs prior to loading with new batches of wafers. More importantly, such measurements could inform development of next generation of FOUPs using novel polymeric materials and new surface treatment procedures [2]. This work presents use of a TOFWERK Vocus chemical ionization mass spectrometer for continuous monitoring of FOUP outgassing after a process that simulated standard cleaning procedures.

Experimental Procedure

Outgassing from a FOUP (~50 liters) was monitored using a Vocus CI-TOF mass spectrometer with an Aim Reactor using iodide and protonated ethanol dimers as reagent ions (Figure 1). The Vocus CI-TOF directly samples air and instantaneously reports the concentrations of trace organic and inorganic compounds in the air.

Experiments were conducted by spraying two solutions into the FOUP, one containing molecular acids (MA) and volatile organic compounds (VOCs), and the other containing molecular bases (MB). After spraying the solution, the FOUP was flushed with nitrogen to simulate the cleaning process. The equivalent mass deposited into the FOUP from the solution ranged between 0.15 µg to 1 µg. Hydrofluoric acid (HF) was introduced into the FOUP using a permeation tube with an emission rate of 125 ng/min. The internal volume of the FOUP was

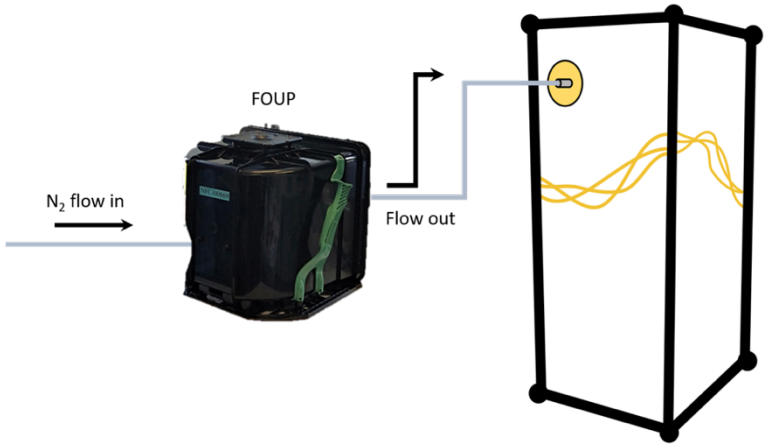

Figure 1. *Schematic diagram of the experimental procedure*

flushed with a constant flow of N_2 (2 L/min) to ensure the FOUP interior was well mixed and to simulate the cleaning of the FOUP container. This resulted in a FOUP ventilation rate of < 60 minutes was well mixed and to simulate the cleaning of the FOUP container. This resulted in a FOUP ventilation rate of < 60 minutes.

The measurement protocol had three steps: 1) measure the background of the FOUP for 5 minutes to establish the clean FOUP background 2) place the HF permeation tube inside the FOUP for two minutes and then immediately inject the acid solution 3) continuously measure the mixing and subsequent decay of the introduced compounds until concentrations return to background values.

Results

After injection of the acid and basic solutions, the mixing inside the FOUP took approximately 3-4 minutes (including evaporation of the injected solution) before the flushing initiated a decay of analyte concentrations within it. Figures 2 and 3 show the decay of molecular acids (MA) and VOCs (MC), and molecular bases (MB) respectively. As shown in Figures 2 and 3, some molecular contaminants persist at trace concentrations (10-30 pptv) for many hours. Formic, acetic, hydrofluoric and hydrobromic acids all reached near background concentrations (90% decrease) in the first 60 minutes, implying no severe attenuation or memory on the inner FOUP surfaces. Cleaning of such substances inside an otherwise empty FOUP is likely straightforward. However, the much slower decay of nitric, hydrochloric acids and bases (Figure 3) suggests that cleaning processes which are not optimized for the slow outgassing of these compounds or that cannot detect them at sufficiently low concentrations could result in their outgassing and at levels capable of causing air molecular

contamination (AMC) problems and reducing wafer yield. Separate experiments were run with acids and bases to simulate gas partitioning processes, as concomitant presence of acids and bases can lead to the formation of nm-sized particles that must either be removed mechanically or evaporated from the FOUP surfaces during the flushing cycle. The formation of such acid-base salts in FABs significantly increases the persistence of contamination on FOUP surfaces. Because these particles evaporate slowly, trace-level gas-phase detection is required to ensure cleanliness.

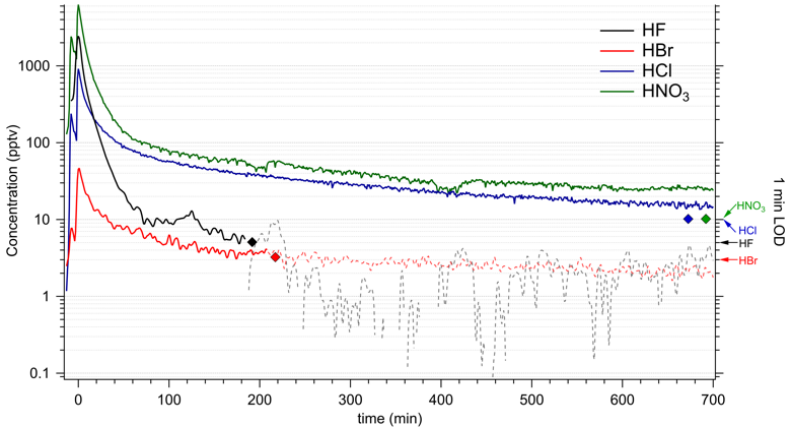

Figure 2. *Concentration decay of common inorganic acids in FAB environment. The markers show the quantification limit of each compound. Arrows on the right axis show the 1-minute LOD of the Vocus CI-TOF. Diamonds show the point in the 11-hour long flushing experiment where the measured signal falls below the LOD of the instrument. For HCl and HNO3 , measurable signal persists even after 11 hours*

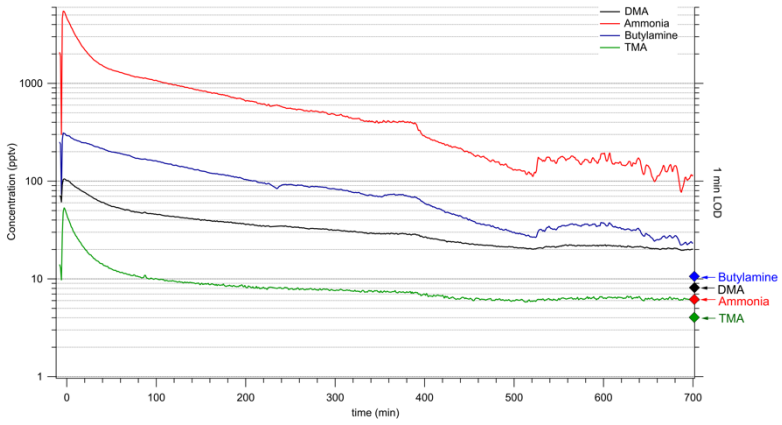

Figure 3. *Concentration decay of common bases in a FAB environment. The markers show the quantification limit of each compound. Arrows on the right axis show the 1-minute LOD of the Vocus CI-TOF. Diamonds show the point in the 16-hour flushing experiment where the measured signal falls below the LOD of the instrument, which is not reached during the experiment time for dimethylamine (DMA) and trimethylamine (TMA).*

Compound	Molecule	1 s LOD *(pptv)*	1 min LOD *(pptv)*	T90 *(s)*
Hydrochloric acid	HCl	230	10	2.4
Hydrobromic acid	HBr	128	3	1.5
Hydrofluoric acid	HF	24	5	4.0
Nitric acid	HNO_3	41	5	11.1
Formic acid	HCOOH	90	11	1.9
Acetic acid	CH_3COOH	314	40	1.9
Ammonia	NH_3	55	7	3.0
Dimethylamine	$(CH_3)_2NH$	65	8	2.0
Trimethylamine	$(CH_3CH2)_3N$	20	4	3.0
Butylamine	$CH_3(CH2)_3NH_2$	75	10	2.0

***Table 1**. Detection limits and response times* for target acids and bases.*
**Sulfuric acid and phosphoric acid can be measured by Vocus CI-TOF but neither was included due to their low volatilities.*

Table 1 summarizes the performance of the Vocus CI-TOF for the detection of organic and inorganic acids, as well as bases relevant in the FAB environment. The fast time response of the instrument (a few seconds for most compounds, T90) allows one instrument to screen many different measurement points or to be deployed on a mobile platform to measure at different points in the FAB. The ultra-low detection limits and simple autonomous operation present a paradigm shift in FAB operators' ability to quantify airborne and surface-bound AMC at ever lower concentrations as line widths are pushed to ever smaller dimensions. Note that the list of targeted molecules can be extended or customized and data can be revisited because TOF mass analyzers always acquire full mass spectra containing signals of all detectable compounds.

Conclusion

With the Vocus CI-TOF integrated in FABs, new insights into FOUP cleanliness can be attained in real time and at pptv concentrations. Through the introduction of a novel on-line AMC detection technology, improvements in FAB operators' ability to control the FOUP - and more generally the FAB environment - will minimize wafer

defects due to surface contaminations or mask degradation. While these data highlight use in FOUP cleaning, there are numerous other use cases in the FAB for which the Vocus CI-TOF is well suited, such as: detection of trace molecules in FAB AMC monitoring, quality control of gases fed into deposition and etch reactors and in lithography equipment, and estimation and control of scrubber efficiency. All of these can be addressed with unprecedented speed and accuracy by Vocus CI-TOF.

References

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2. Gonzalez-Aguirre et al. Control of HF Volatile Contamination in FOUP Environment by Advanced Polymers and Clean Gas Purge. 2015
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