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 CI-TOF 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 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 a solution with hydrochloric acid (HCl), hydrobromic acid (HBr), formic acid (CH_2O_2), acetic acid (CH_3COOH) and nitric acid (HNO_3) into the FOUP and then flushing the FOUP 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 flushed with a constant flow of N_2 (2 L/min) to ensure the FOUP interior

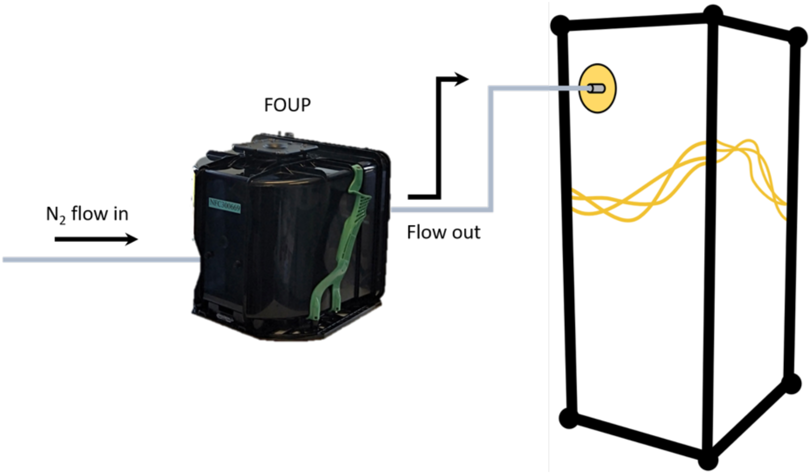

Figure 1. *Schematic diagram of the experimental procedure*

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 solution, 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 inside the FOUP. Figure 2a shows as example of the decay of nitric acid and the reproducibility of acetic acid decay between repeat experiments (Figure 2b). All compounds showed a double exponential decay, with some sticky compounds persisting at trace concentrations (10-100 pptv) even 100 minutes after injection. The double exponential fit (Equation 1) was used to retrieve the compound dependent time constants, which represent the flushing timescales of each compound from the FOUP. $\tau1$ in equation 1 represents the e-folding time for the fast decay (gas volumetric exchange in the FOUP) and the second time constant ($\tau2$) represents the slower outgassing from FOUP surfaces. The latter is significantly longer and depends on the interactions of the acid with the FOUP inner surfaces. Figure 2a shows an example of the double exponential fit for HNO_3 which has significant interaction with the walls of the FOUP and therefore persists for much longer than other acids tested.

Equation 1 $C(t) = C_1 e^{-t/\tau_1} + C_2 e^{-t/\tau_2} + C_b$

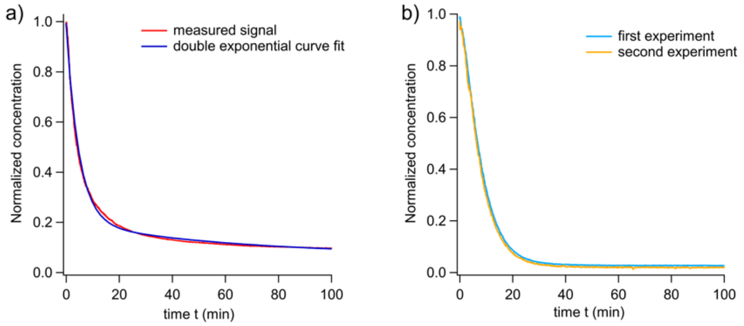

Figure 2. a) Normalized concentration C(t) of nitric acid (red) and its double exponential fit (blue). B) Normalized concentration of acetic acid after deposition of 1 µg (first experiment) and 0.15 µg (second experiment), showing the reproducibility of the system.

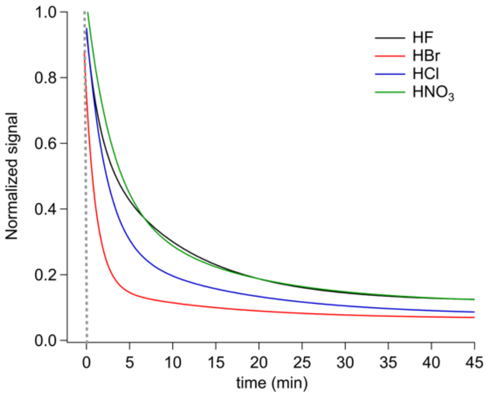

Figure 3. Exponential decay of different inorganic acids during the first 45 minutes of FOUP flushing. The response of the acids to flushing is related to their vapor pressure and surface interactions with the inner FOUP surfaces.

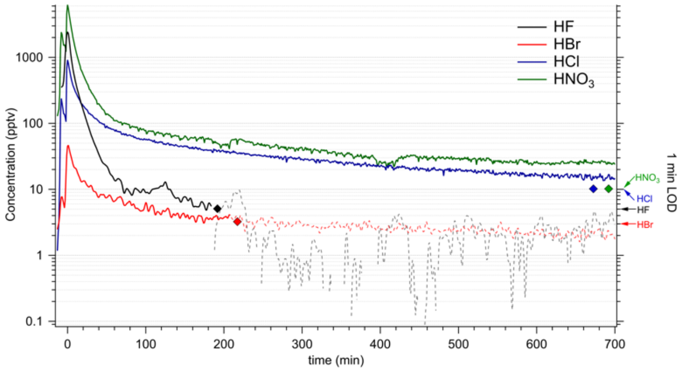

Figure 4. Concentration decay of common inorganic acids in FAB environment. The markers show the quantification limit of each compound. Arrows on the right axis show the 1-minute LOD of the Vocus CI-TOF. Diamonds show the point in the 11-hour long flushing experiment where the measured signal falls below the LOD of the instrument. For HCl and HNO3 , measurable signal persists even after 11 hours.

Figure 3 shows the response of HF, HBr, HCl and HNO_3 to nitrogen flushing over the first 45 minutes after reaching stable concentrations in the FOUP. Table 1 summarizes the time constants (τ_i) from the double exponential fits in figure 3. Most of the acids have similar response in the first few minutes in the FOUP when volumetric flushing dominates, however, as shown in figure 4 on longer timescales some acids 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 (Table 2). In other words, cleaning of such substances inside an otherwise empty FOUP is likely straightforward, and therefore easy to estimate the optimal ending point of a FOUP cleaning process. However, the much slower decay of nitric and hydrochloric acids suggests that cleaning processes which are not optimized for the slow outgassing of these acids or that cannot detect them at sufficiently low concentrations could suffer from later outgassing of acids from the inner FOUP surfaces, which could present an Airborne Molecular Contamination (AMC) problem inside the FOUP atmosphere – reducing wafer yield.

Compound	τ_1 (min)	τ_2 (min)
HCl	2.3	15
HF	1.9	12
HBr	1.3	29
HNO_3	4.2	35

***Table 1**. Decay time constants (τ) for each acid shown in Figure 3. The values of τ2 are calculated according to the fit when the concentration starts to stabilize.*

Table 2 summarizes the performance of Vocus CI-TOF for the detection of organic and inorganic acids relevant in the semiconductor fabrication plant (FAB) environment. The fast time response of the instrument (few seconds for most compounds, T90) allows one instrument to screen many different measurement points or be deployed on mobile platform to measure at different points in the FAB. The outstanding 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.

With the Vocus CI-TOF integrated in the FAB, new insights into FOUP cleanliness can be attained in real time and at pptv concentrations. Through the introduction of a novel on-line acid detection technology, improvements in FAB operator's ability to control the FOUP - and more generally the FAB environment - will minimize wafer defects due to surface contaminations or mask degradation. While here we highlight the use in FOUP cleaning, there are numerous other use cases in the FAB where Vocus CI-TOF would be well suited, such as: detection of trace acids in FAB AMC monitoring, quality control of gases fed into deposition and etch reactors as well as in lithography equipment, and estimation and control of scrubber efficiency. All of these can be addressed with unprecedented speed and accuracy by the Vocus CI-TOF.

Name	Formula	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

Table 2. *Detection limits and response time*

References

1. Jeong et al. Control of Wafer Slot-Dependent Outgassing Defects during Semiconductor Manufacture Processes. 2019 DOI: 10.1109/ASMC.2019.8791794
2. Gonzalez-Aguirre et al. Control of HF Volatile Contamination in FOUP Environment by Advanced Polymers and Clean Gas Purge. 2015 DOI:10.4028/www.scientific.net/SSP.219.247

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