Real-time monitoring of critical AMC compounds in the photolithography cell using a novel laser-based, multi-species detection system

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ABSTRACT

There is widespread recognition in the industry that as the design rule decreases, the number of airborne molecular compounds that can drive defect formation is increasing at an exponential rate [citation: IRDS 2020]. The vast majority of these new critically important AMCs are volatile organic compounds. These VOCs are difficult to measure in the gas phase at the parts-per-billion and parts-per-trillion levels that are needed for the tight process control requirements of advanced design rules. In this paper, we report on a novel AMC chemical metrology solution for measuring critical VOCs that are relevant to the photolithography cell. The heart of the system is a real-time laser-based analyzer (SI9110, Picarro, Inc) based on a new analytical technique called Broad Band Cavity Ring Down Spectroscopy (BB-CRDS). The SI9110 has several features which make it ideally suited to AMC measurements in the production environment: ultra-trace measurements at ppb levels without the need for calibration, 24/7 operation without user intervention, and negligible consumables. The analyzer was integrated into a state-of-the-art multiplexer to monitor ten VOC species in the photolithography cell in a modern semiconductor fab. We report on multiple observations made, including transient solvent leak events, multifunction chemical filter performance, and baseline characterization of AMCs inside track tools.

Keywords: AMC, lithography, CRDS, VOC, haze, real-time, cleanroom.

1. INTRODUCTION

The role of Airborne Molecular Compounds (AMCs) in increasing wafer-level defects and thereby negatively affecting wafer yields is becoming increasing critical. The 2020 IRDS document lists a classification of a variety of contaminants that can affect various process equipment, processes, and devices (Fig 1)[1]. While strong acids and bases such as hydrofluoric acid, hydrochloric acid, and ammonia were traditionally considered the most impactful AMCs, the vast majority of the new contaminants are Volatile Organic Compounds (VOCs)[2].

	Impact				
AMC Class	Process	Equipment	Device		
			FEOL	MOL	BEOL
Roadmap terminology	POU	POE	POP	POP	POP
Inorganic Acids	Yes	Yes	No	Yes	Yes
Organic Acids	Yes	Yes	Unknown	Unknown	Yes
Inorganic Bases	Yes	No	Yes	Yes	Yes
Organic Bases	Yes	Yes	Yes	Yes	Yes
Esters	Unknown	Yes	Unknown	Unknown	Unknown
Aldehydes/Ketones	Unknown	Yes	Unknown	Unknown	Unknown
Alcohols/Phenolic	Yes	Unknown	Unknown	Unknown	Unknown
Aromatics	Unknown	Yes	No	No	No
Plasticizers	Yes	No	Yes	No	No
Aliphatics	No	Yes	No	No	No
Heterocyclic	Unknown	Yes	Unknown	Unknown	Unknown
Siloxanes	Unknown	Yes	Unknown	Unknown	Unknown
Fluorinated	Unknown	Yes	No	No	No
Sulfurous	Yes	Unknown	Unknown	Unknown	Unknown
Halocarbons	Unknown	Unknown	Unknown	Unknown	Unknown

Figure YE-5 Proposed New Classification of AMC Contaminants

Figure 1: Classification of AMC compounds per IRDS.

There is a growing recognition that fabs need to monitor not just classes of compounds for potential impact wafer yield, but also individual species need to be monitored so that targeted control strategies may be implemented. The IRDS 2021 working group is working on specifying individual species and the concentrations at which specific AMCs impact equipment, processes, and device. The concentration of the various inorganic and organic species that need to be monitored and controlled are in the parts-per-billion and parts-per-trillion range. Unfortunately, measuring at these low levels, especially for VOCs in the gaseous phase, is extremely challenging in the fab environment. Most low-level detection techniques, such PTR-MS are slow, expensive, and cumbersome to use. Other techniques such as gas chromatography require involved sample preparation and suffer from slow times to detection.

In this work, we demonstrate the capabilities of Picarro's novel chemical metrology system to measure ten organic gas phase contaminants down to ppb levels. The specific compounds measured include Acetic acid, acetone, isopropyl alcohol, propylene glycol methyl ether (PGME), propylene glycol methyl ether acetate (PGMEA), D3 siloxane, D6 siloxane, hexamethyldisiloxane (HMDSO), trimethyl silanol (TMS), and n-methyl pyrrolidone (NMP). These compounds were specifically chosen due to their relevance in the photolithography cell.

It is well known that haze, salt formation caused by the reaction of ammonia with acids, causes defects on reticles and coats scanner optics leading to loss in pattern fidelity and even wafer defects[4,5]. Strong bases such as NMP can cause T-topping defects by poisoning the resist[6]. Figures 2 and 3 further illustrate the chemistry of AMC's and the problems caused in photolithography.

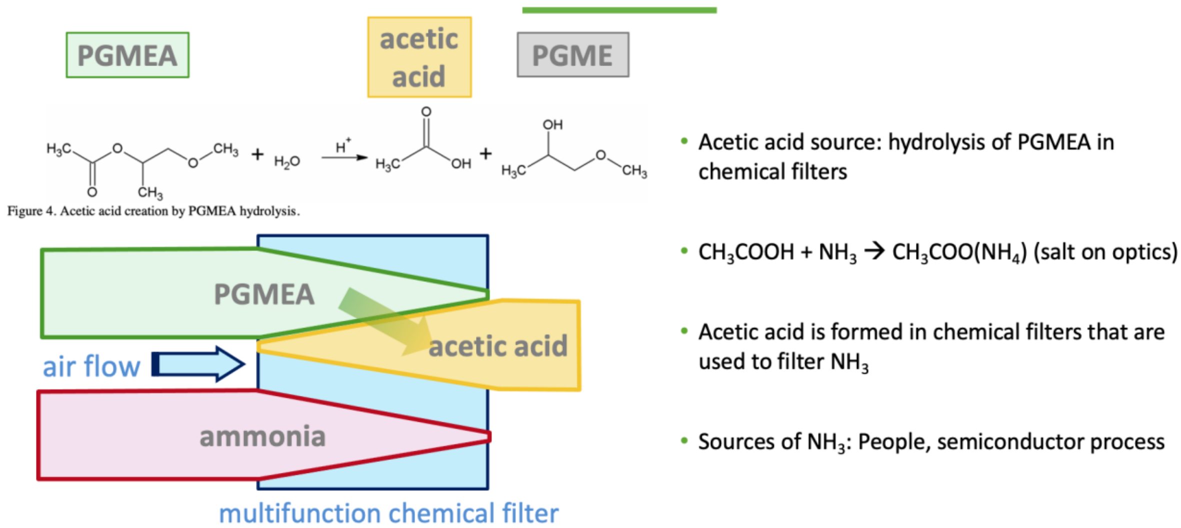

Figure 2: Hydrolysis of PGMEA, a common thinner solvent used in photolithography, within ammonia chemical filters on track tools releases acetic acid. Acetic acid is released from the chemical filter and can react with ammonia to form haze on scanner optics[7].

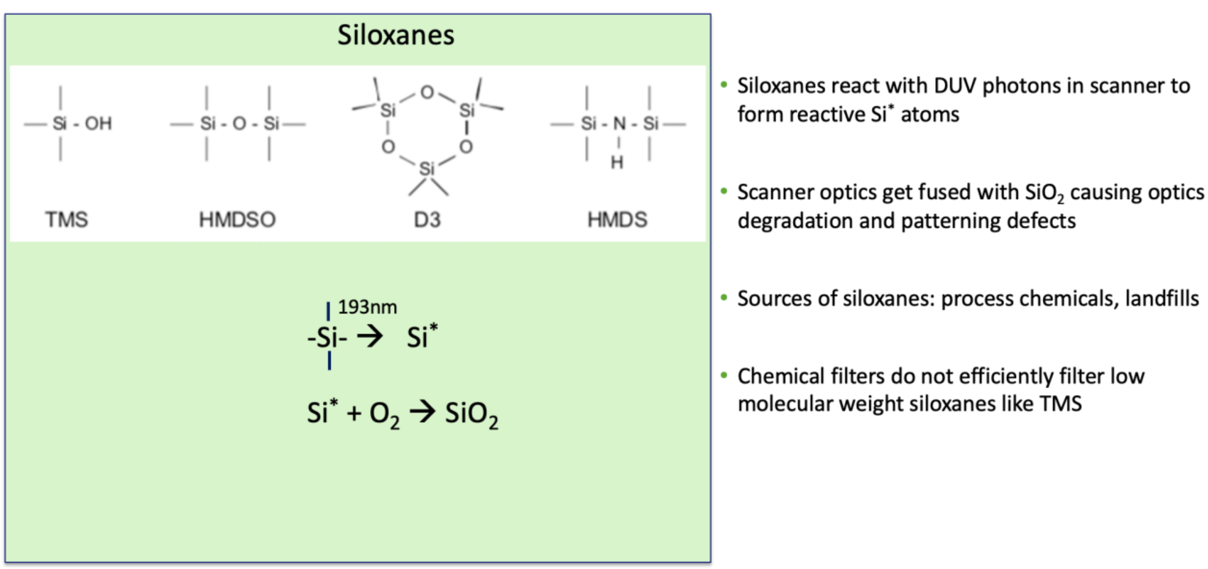

Figure 3: Chemistry of siloxanes in the presence of DUV to form silicon dioxide leads to irreparable damage of expensive scanner optics[8].

In the current study, a number of applications in the semiconductor fab environment were targeted:

- Scanner chemical filter monitoring
- Coater/Developer tool environment monitor
- AMC monitoring in the lithography bay for transient solvent leaks

2. INSTRUMENT DESCRIPTION

Picarro's new Chemical Metrology system to detect airborne molecular contamination in real-time is shown in Figure 4 below.

Figure 4: Picarro's Chemical Metrology system for real-time monitoring of air-borne molecular contamination.

The metrology system consists of 19" rack-mounted CRDS (Cavity Ring-Down Spectroscopy) analyzers that accurately measure the concentration of AMC's integrated into a state-of-the-art multiplexing system, or the Picarro SAM (Sample Analyze, Monitor.) The SAM provides up to 32 sample ports for sampling specific regions in the litho cluster. The complete AMC solution for the application consists of a system integrated with three CRDS analyzers: SI3401 to measure to measure NH3, HF, HCl; the SI5450 analyzer to measure SO2, and the SI9110 to measure the 10 volatile organic compounds. This study focuses on the measurement of the 10 VOC species that has become possible for the first time with cavity ringdown spectroscopy.

2.1 Broadband Cavity Ringdown Spectroscopy

Detailed descriptions of Picarro's patented Broadband Cavity Ringdown Spectroscopy (BB-CRDS) technology can be found elsewhere[3]. Briefly, laser is injected into a high-finesse cavity, which is temperature controlled to <1 mK and pressure controlled to < 0.1 torr. The cavity consists of 3 high reflective mirrors that bounce the light inside the cavity thousands of times, resulting in an effective path length of 20 km. This large effective pathlength lowers the detection limits from ppm to ppb concentration levels. With the assistance of a wavelength monitor to precisely target the laser frequency resonant with the cavity, it only takes a few seconds to scan over the entire tuning range. A multivariable regression is used to extract the VOC concentrations using each molecule's unique absorption spectra. In addition to lower limits of detection, selectivity is optimized through the selection of frequencies to be scanned. This new and patented Broadband Cavity Ring-Down Spectroscopy technology brings exciting capabilities to quantify the VOCs at very low limits of detection with good chemical selectivity.

2.2 Picarro SAM (Sample Analyze Monitor)

The Picarro SAM is a modular, multi-port sampling system that is available in two basic configurations: SAM-S and SAM-C. The smaller SAM-S is a mobile unit that supports up to 16 independent sampling ports and 2 Picarro analyzers. The SAM-S can also be equipped with an uninterrupted power supply enabling 50 minutes of continuous use when disconnected from house power. The larger SAM-C is a stationary unit that accommodates up to 32 independent ports and 4 Picarro analyzers.

The SAM platform is designed to optimize AMC time-to-detection within semiconductor manufacturing environments. SAM achieves this by 1) ensuring all wetted paths are non-reactive, 2) inactive ports are continually flushed with sample gas, and 3) system flow restrictions are minimized. The latter allows sample delivery rates to be maximized, lowering the overall system response-time to nearly that of a bare Picarro analyzer. This performance level can be maintained even when sample tubes are of moderate length (i.e., ~ 50 – 60 meters). Additionally, the mechanical layout of the pneumatic system optimizes sample stream isolation which reduces cross-channel contamination. The pneumatic system is designed to be cleaned in bulk, allowing users to quickly distinguish between real signals and system fouling. SAM also offers an isolated delivery path for reference gases. This reference path bypasses upstream sample handling and directly accesses the analyzer inlets to verify instrument performance.

The SAM control software provides a platform to define and execute a customized sequence of measurements based on users' situational needs. These measurements can be performed either manually or looped indefinitely by user-created plans. All resulting analyzer data are streamed over a private network and stored in a time-series database on the SAM computer. Users are presented customizable data visualizations based on either chemical species or measurement location. The software provides an export feature that allows users to download all relevant data into a common .CSV format if offline analysis is desired. Additionally, REST API calls are available to integrate SAM systems into preexisting, facility-wide monitoring platforms.

2.3 Intrinsic performance of Picarro SI9110 VOC analyzer

The lower detection limit (LDL) for the SI9110 is in the low ppb range.

In the factory, the instrument was challenged with elevated levels of key VOCs to ensure that the measurements of the other VOCs are not compromised. Starting from compressed air cylinders containing ~ 10 ppm of a single VOC (Airgas, Radnor, PA, USA), a gas sample with varying concentration of the challenge VOC is prepared by diluting the source gas with synthetic air using mass flow controllers (Alicat Scientific, Tucson, AZ, USA). The results of this step challenge experiment are shown in Figure 5 for acetone and isopropyl alcohol, two common solvents that are often found at elevated levels in a fab setting. The results show that despite challenges of several thousand ppb of these two compounds, the reported concentration of the other key species are not significantly affected.

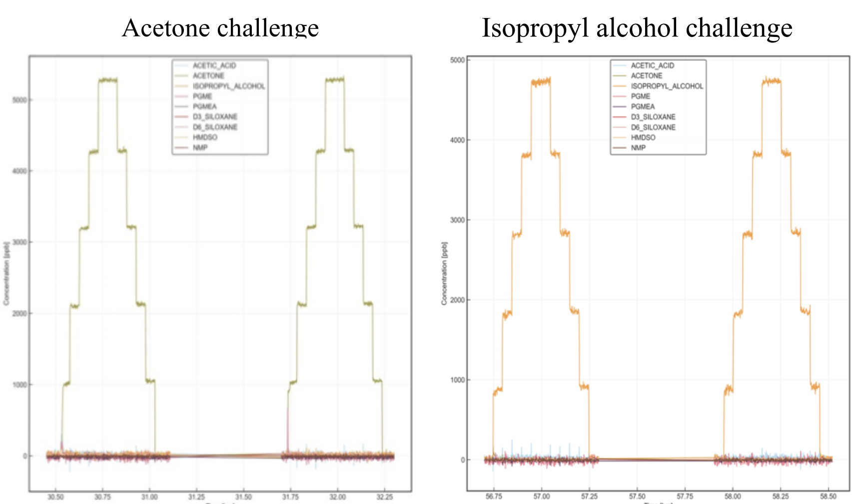

Figure 5: VOC – VOC cross talk study with varying amounts of acetone and isopropyl alcohol.

3 RESULTS

The chemical metrology system was installed in the sub-fab and connected to various sampling locations in the lithography cell. PFA tubes of varying lengths up to 50m were used to sample air from specific locations as shown in Figure 5. The system operates by sequentially sampling each location for 10 minutes at each sample port and reports the concentration of all the above molecules at each location as a function of time. The data rate is 3-5s per point.

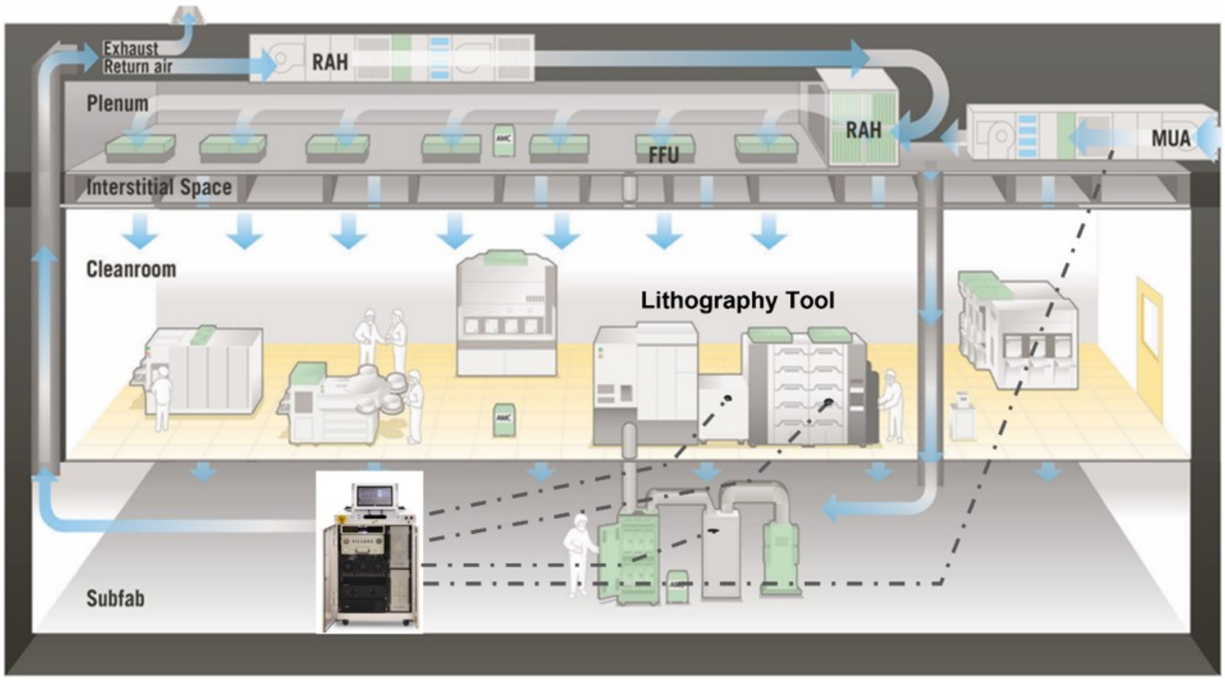

Figure 6: High level AMC sampling scheme in the lithography cluster in relation to the fab.

3.1 Baseline AMC levels in the cleanroom

The cleanroom is a well-controlled environment. Fabs use sophisticated air circulation and contamination control methods to minimize particulate contamination. More recently, with increasing recognition that gas phase airborne molecular contamination can also significantly impact overall wafer yield as well as equipment performance and process control, chemical filtering strategies to minimize the impact of these AMC's have grown in importance. The baseline levels of AMCs in a cleanroom are generally stable and well controlled because of increased AMC filtering and mitigation strategies. However, there can be circumstances that can cause the cleanroom condition to change resulting in the release and transport of AMCs, such as a chemical leak or spill.

The air close to four reticle stockers was sampled inside the cleanroom to get an idea of the baseline levels of various AMCs. These points were sampled for a few days continuously and the baseline level of the 10 AMCs were determined. Figure 7 shows the baseline levels of all 10 VOC's at one sampling location. The baseline levels are all within 10ppb and close to the LDL of each species for this instrument. The average baseline level for each species measured over the duration of the sampling time is shown in Table 1.

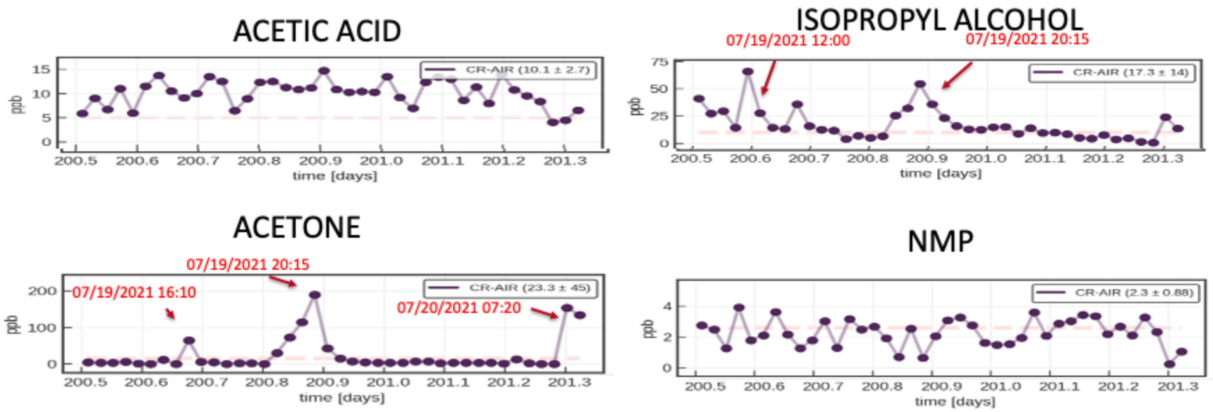

Figure 7: Time series of 4 VOC species, acetic acid, isopropyl alcohol, acetone, and n-methyl pyrrolidone (NMP). Several transient events for isopropyl alcohol and acetone are observed indicating the dynamic nature of the cleanroom air.

Figure 8 shows snapshots in time when the concentration of two VOCs measured, isopropyl alcohol and acetone, increase well above the baseline. The Picarro tool was able to capture these events in real time.

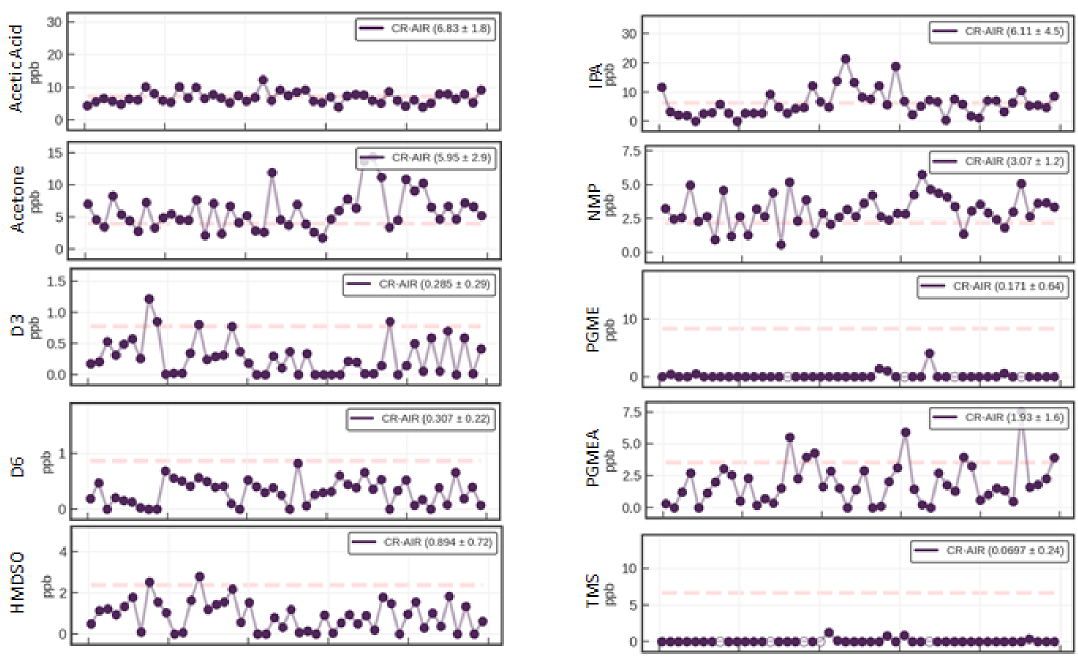

Figure 8: Baseline levels (event free) of the 10 VOC species inside the cleanroom. Sampling time is 10 minutes at each port. Each data point represents the average concentration of acetone over the sampling duration.

	CR Location 1	CR Location 2	CR Location 3	CR Location 4
Acetic Acid (ppb)	10.10	6.91	12.2	6.78
Acetone (ppb)	1.07	0.52	5.3	7.89
D6 (ppb)	0.50	0.40	0.44	0.21

Isopropyl Alcohol (ppb)	2.00	0.03	17.1	4.13
NMP (ppb)	2.24	1.13	1.89	3.22
HMDSO (ppb)	0.79	0.80	1.29	1.03
D3 (ppb)	0.10	0.14	0.36	0.43
Formic Acid (ppb)	0.46	1.73	1.78	2.01
PGME (ppb)	0.79	1.12	0.00	0.38
PGMEA (ppb)	0.30	0.31	1.01	2.15
TMS (ppb)	0.01	0.06	0.03	0.11

Table 1: Baseline levels of 10 VOCs measured at four different locations inside the cleanroom. These locations are near reticle stockers and were sampled for 10 minutes each. We have excluded "events" defined as levels of AMC's above twice the LDL of the instrument when determining these baseline levels.

3.2 Scanner chemical filter monitoring

Chemical filters in lithography tools play a vital role in filtering airborne molecular contamination that negatively impact the performance of the scanner. The chemical filters in litho tools are multistage chemical filters with three access sampling ports: filter inlet, filter middle stage, and filter outlet. In this fab, a filter monitoring campaign was planned to monitor and analyze the performance and efficiency of three different chemical filters, Filter A, Filter B, and Filter C of the same model and made by the same manufacturer but with different operational times and maintenance schedules. The sampling port in each filter is sampled for a duration of 10 minutes. Figure 9 shows the chemical filter sampling setup.

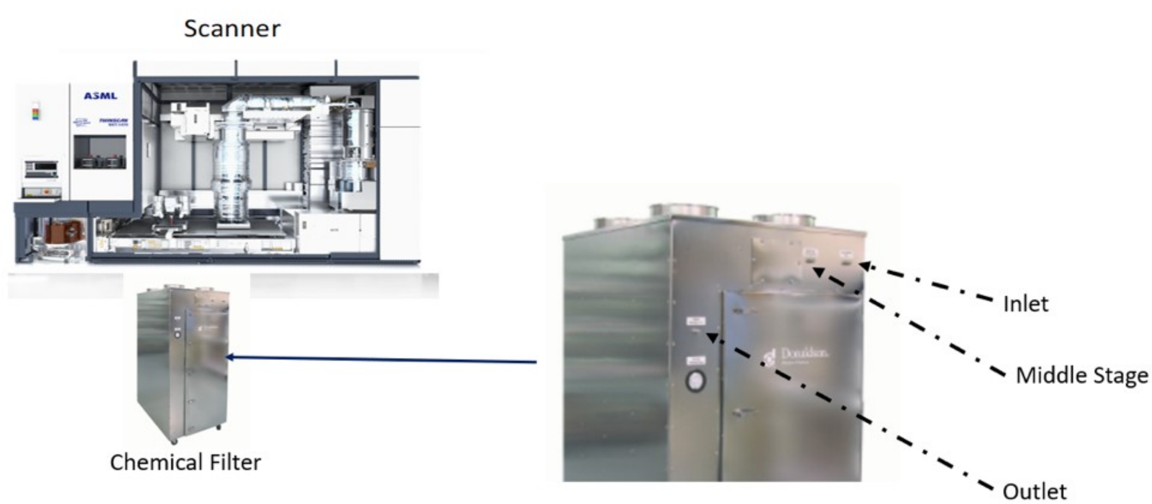

Figure 9: AMC sampling ports for multi-function chemical filters that filter the air going into a scanner.

Figure 10 shows the time series plot of acetone measured at the inlet port, middle port, and outlet port of the three different chemical filters on three different scanners in the fab.

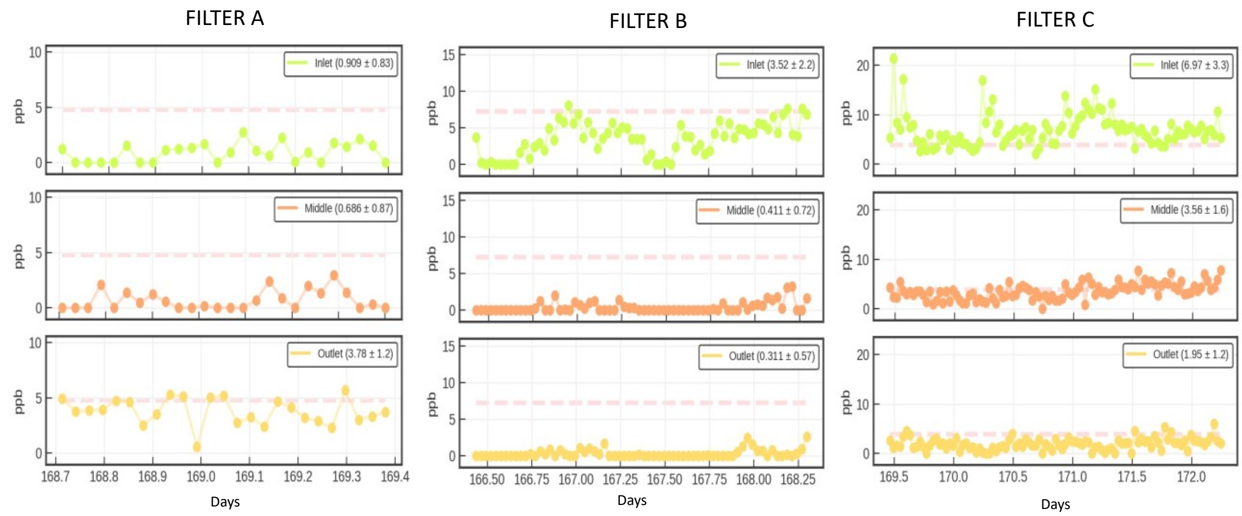

Figure 10: Time series plot of acetone measured at the sampling ports of chemical filters on three different scanner tools. Sampling time is 10 minutes at each port. Each data point represents the average concentration of acetone over the sampling duration.

Ambient air from the cleanroom flows through the inlet and is expected to undergo filtration across the two stages of the filter. It is expected that the air at the outlet of the filter is the cleanest as it undergoes the most filtration.

A study of Figure 7 shows that for filters B and C, the reported acetone levels indicate that it is filtered out by the filters – the concentration of acetone after the outlet is less than the inlet. However, for the filter A on stepper 1, the acetone concentration at the inlet is lower than the outlet! This indicated that the filter on stepper 1 had not been installed correctly; it had been installed backwards and was swiftly corrected based on this observation. A comparison of the plots for Filter B and C at the middle and outlet shows that they have different filtering performance with Filter B being more efficient.

3.3 Track tool monitoring

The Track tool consists of several modules for different processes. In the AMC monitoring study in this fab, the following modules were sampled to determine baseline AMC levels: process robot arm, interface junction, developer plate, and hot plate. Figure 11 shows the sampling setup. The Track monitoring campaign was conducted to monitor the baseline levels of the 10 AMCs and detect excursion events in two litho-clusters. Each sample port is sampled for a duration of 10 minutes.

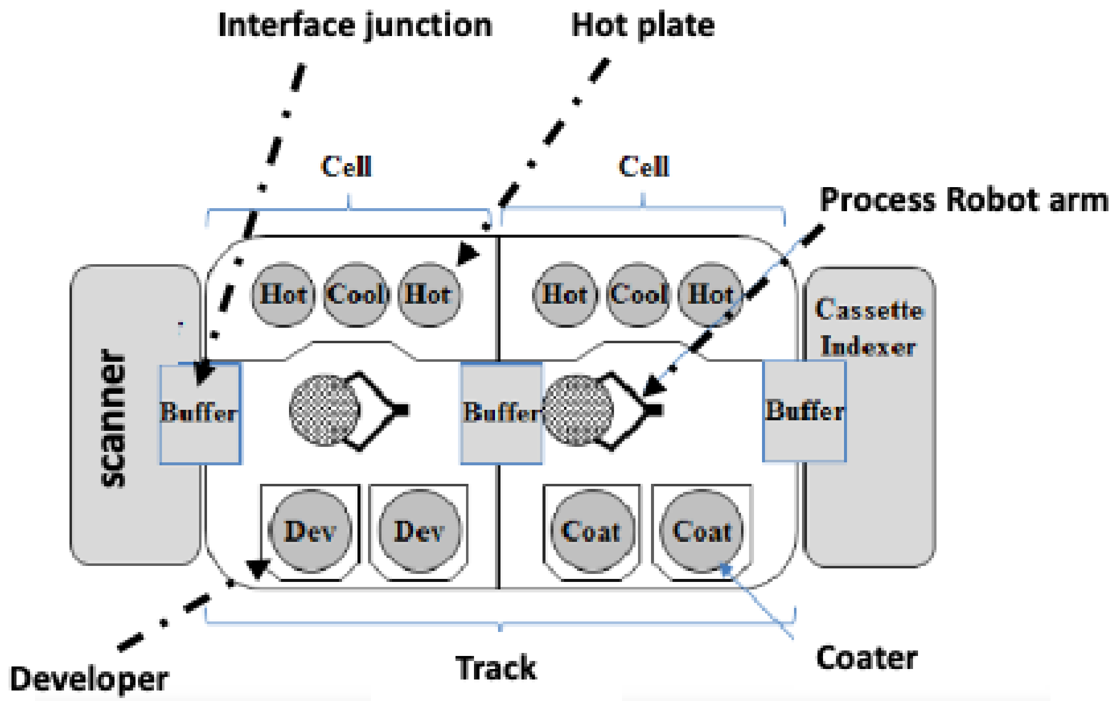

Figure 11: AMC sampling ports for a Track tool in litho-cluster.

Figure 9 shows the real-time snapshot of acetone at various points measured on the track tool.

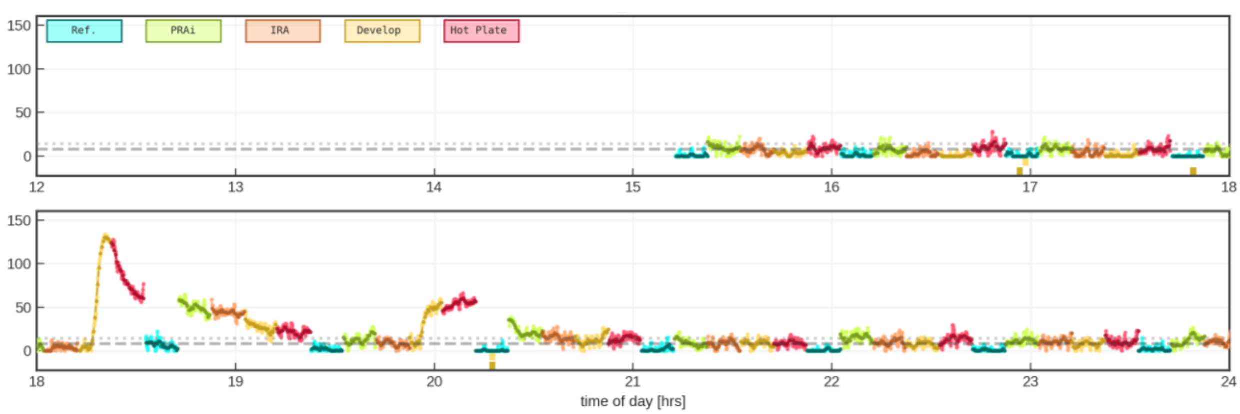

Figure 11: Real-time snapshot of acetone measured at various points in a Track tool. Locations monitored are PRAi (Process Robot Arm Interface), IRA (Interface Junction), developer module, and hot plate. X-axis shows the 12-hour period when measurements were made.

An acetone event is clearly observed that peaks to 300ppb in the developer module and gradually decreases in the hot plate, PRAi, and IRA sometime on hour 18. The event lasts for about one hour before returning to baseline level followed by another minor event on hour 20 that peaks at about 50ppb.

The ability to track AMCs in real-time can be powerful to track the source and spread of AMCs through critical process tools. This type of real time data on AMC measurements can also be compared with in-line data on events that happened on the tool (such as preventive maintenance, repair, process change) to perform faster corrective actions and thereby saving time and cost.

3.4 Reticle stocker monitoring

Since reticle defects impact wafer yield, it is important to ensure cleanliness of reticle stockers where reticles are stored. In this fab, some reticle stockers were equipped with filters to filter some AMCs. The cleanroom bay and reticle stockers were monitored for the 10 VOCs to study the transport of any transient AMC events that occurred in the bay into the stocker. The sampling setup is shown in Figure 12.

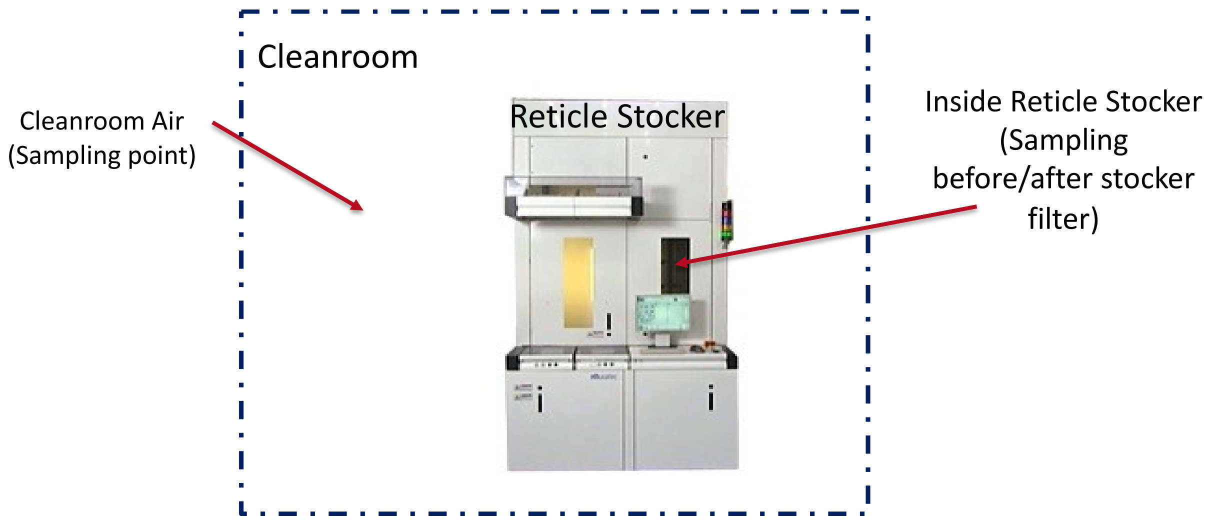

Figure 12: AMC sampling setup in the reticle stocker area. The surrounding cleanroom air as well as the air before and after the filter on the reticle stocker were sampled for 10 minutes.

Figure 13 shows the time series of isopropyl alcohol measured at various points in and around the reticle stocker.

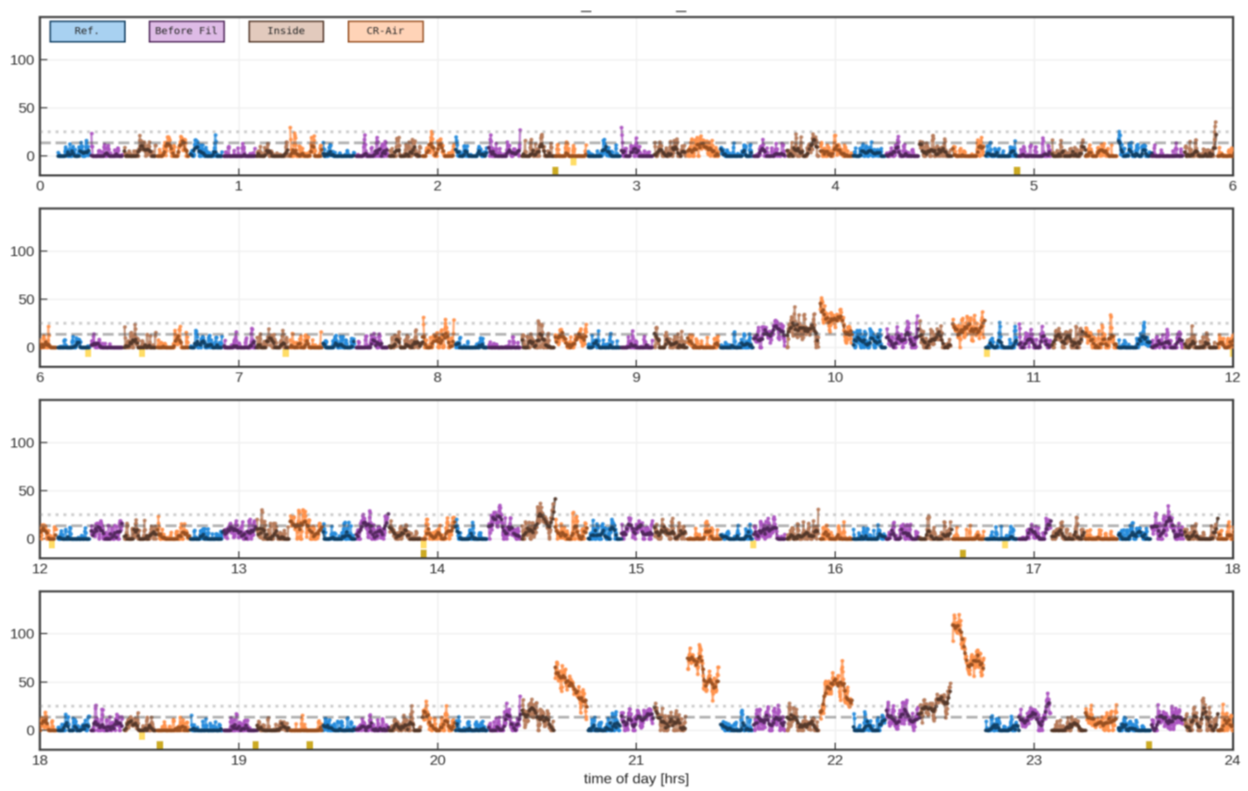

Figure 13: Time series of isopropyl alcohol over a period of a few hours measured in the cleanroom and before and after the filter on the reticle stocker.

We notice an event between hours 20 and 21 and three more thereafter that peak in the cleanroom to a level of 50-100ppb. The first three events seem to die down before the air inside the stocker is sampled. However, the fourth event is seen to rise outside the filter, continues to rise inside the stocker and peaks in the cleanroom before dying down. This shows that there are several transient events that happen in the cleanroom and that the filter on the stocker does not filter out isopropyl alcohol as shown by the peaks at the filter outlet inside the stocker. It is well known chemical filters do not remove all components with the same efficiency. However, it is important for the fabs to be alerted of any changes in air contamination or filtering efficiency. These can only be detected by real-time measuring capabilities.

4 CONCLUSIONS

The impact of AMCs on critical equipment, processes and wafers has been recognized for several years. However, one of the roadblocks to establishing the correlation between AMC levels in the fab and overall wafer yield has been the lack of production worthy, real-time technologies that can provide fabs accurate and reliable measurements at the ppb and ppt levels, especially for VOCs. In this paper, we have presented one of the first studies of VOC monitoring within a photolithography cell at a major logic fab using Picarro's real-time chemical metrology system for VOC monitoring based on broadband cavity ringdown spectroscopy. The types of studies that have been described in this paper can be further optimized to enable fabs to understand

a) How dynamic is the environment in the cleanroom and in and around critical process tools and reticle stockers. This knowledge can guide a systematic study of AMC impact and enable the setting of actionable control limits to minimize yield loss.

b) The lifetime and performance of chemical filters on critical process tools. When these filters break down and pass through AMCs, significant problems can ensue such as lens hazing. A robust filter monitoring strategy can help fabs save time and money by providing early warning of impending filter breakdown.

c) The transport of contaminants from track tools into the scanner. Track tools are a source of several VOCs due to photoresist chemistry. It is vital to ensure that these VOCs do not get inside the scanner and cause issues in patterning. A real-time track tool monitoring strategy will enable fabs to understand and control the transport of VOCs and assess the impact inside the scanner.

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