A METHOD FOR THE COMBINED MEASUREMENT OF VOLATILE AND CONDENSABLE ORGANIC AMC IN SEMICONDUCTOR APPLICATIONS

*Authors: Charles M. Miller,
Emily C. Zaloga and Jürgen M. Lobert*

Abstract

Monitoring airborne molecular contamination (AMC) at the parts-per-trillion (ppt) level in cleanroom environments, scanner applications and compressed gas lines is essential for processes, equipment and yield-control. For the operation of EUV tools, in particular, volatile organic contamination is known to have as much impact as condensable organic compounds, which requires a suitable sampling and measurement methodology.

Some of the current industry standards use sample traps comprised of porous 2,6-diphenylene-oxide polymer resin, such as Tenax®, for measuring volatile organic (<6 C-atoms, approximately IPA/acetone to toluene) and condensable organic (>6 C-atoms, about toluene and higher) AMC. Inherent problems associated with these traps are a number of artifacts and chemical reactions that reduce accuracy of reported organic AMC concentrations. The break-down of the polymeric material forms false positive artifacts when used in the presence of reactive gases, such as nitrous acid and ozone, which attack and degrade the polymer to form detectable AMC. Most importantly, these traps have poor capture efficiency for volatile organic compounds (VOC).

To address the disadvantages of polymer-based sample traps, we developed a method based on carbonaceous, multilayered adsorbent traps to replace the 2,6-diphenylene-oxide polymer resin sample trap type. Along with the new trap's ability to retain volatile organics, the trap was found to provide artifact-free results. With industry trends towards detecting more contaminants while continuously reducing required reporting limits for those compounds, artifact-free and accurate detection of AMC is needed at the parts-per-quadrillion (ppq) level. The proposed, multilayered trap substantially increases laboratory productivity and reduces cost by eliminating the need to analyze condensable and volatile organic compounds in two separate methods.

In our studies, even some organic compounds with 6 C-atoms, that are part of exposure tool OEM requirements, were not effectively retained by polymeric traps, but were fully retained on the multilayered adsorbent trap. This demonstrates that the standard trap used in the industry will result in significantly underreporting actual AMC concentrations for volatile organic compounds, including some siloxanes (TMS, HMDSO, D3).

Performance of the proposed trap was excellent at both zero and 50% relative humidity, an important metric, as the trap is used for AMC detection in dry supply gases and humidified environments. Retention of all organic compounds was quantitative for more than 30 liters of air, sufficient for ppq-level detection limits. Desorption efficiency was 94% for C26 compounds.

Pressure drop through the new trap was comparable to that of polymer-based traps and much lower than other, commercially available carbonaceous traps. Precision of repeated analyses was 5%, a very good result. Resolution of IPA and acetone was complete and that of a mix of halogenated refrigerants was much improved over existing methods.

We propose to adopt this methodology as a new industry standard to overcome widespread inaccuracy in the reporting of volatile organic AMC and false positive condensable AMC.

Introduction

Similar to deep-ultraviolet (DUV) semiconductor processes, extreme-ultraviolet (EUV) lithography systems are affected by optics surface degradation. The primary cause for degradation of the EUV systems is from carbon deposition on reflective mirror surfaces. Carbon deposition, or carbonization, is caused when organic components are adsorbed onto surfaces and fractured by the energy of the EUV light (13.5 nm wavelength, energetic enough to split any molecule). Carbonization has

been observed on titanium dioxide (TiO2)[1] and ruthenium (Ru)[2] capped mirrors and gold surfaces.[3] Deposition commonly occurs as a result of resist outgassing, but evidence has shown that volatile compounds, such as acetone,[4] play a key role in carbonization of surfaces. As acetone concentrations increased, the thickness of carbon deposits increased, leading to decreased reflection of the coated multilayered mirrors.[1] In contrast to DUV lithography, where volatile organic AMC is not considered to cause significant equipment problems, this may become a major issue with EUV, both in ambient air introduction to load-lock chambers as well as supply gases, because the carbonization happens with any form of carbon, regardless of source molecule. Considering the cost of replacing critical reflective surfaces and the associated production downtime, the need for accurate volatile organic AMC measurements is critical.[3] In addition, for technology nodes below 32 nm, it is suspected that volatile organic compounds can form surface films on wafers and weaken or delaminate subsequent coatings of critical structures. This may become more important with increasing process sensitivity.

Current industry standards for AMC measurement, such as cleanroom, scanner, track and tool OEM requirements, as well as the ITRS[9] guidelines recommend the use of polymer-based sample traps to capture organic AMC. In applications to study condensable organic AMC, these are adequate, albeit hampered by artifacts, but in applications requiring analysis of volatile compounds, the lack of retention on these traps provides inaccurate results. This is widely accepted as a method limitation and so far had little ramification on DUV processes or on equipment down to the 65 nm technology node. Starting with technology nodes at 32 nm or less, and based on their increasing sensitivity to surface contamination, we have observed increased awareness and concerns about volatile organic AMC, both for their measurement as well as their removal through AMC filtration. The onset of EUV processes has identified all carbon-containing compounds as potential contaminants for reflective surfaces.

Applications and sample traps to quantitatively capture volatile organic AMC exist, but have other drawbacks, such as high pressure drop through those sample traps, requiring special pumps, and the fact that results for the overall range of compounds requires two separate analytical methods, increasing overall cost and overhead.

To address the disadvantages of polymer-based and high pressure drop carbonaceous sampling traps used to measure organic AMC in microlithography processes and to minimize analytical cost, we developed a method based on carbonaceous, multilayered adsorbent traps to replace the 2,6-diphenylene-oxide polymer resin sample and cryogenic focusing trap types, selected a suitable separation column and developed a gas chromatography method for short runtime with maximized peak-to-peak resolution for the retention, release and separation of compounds in the range of IPA to ~C26.

We propose to adopt that methodology as a new industry standard to overcome widespread inaccuracy in the reporting of volatile organic AMC and false positive artifacts for condensable AMC.

Methodology

Development Approach

Development of the analytical method was divided into four parts, (a) finding the most suitable sample trap, (b) developing a similar cold trap for pre-concentration, (c) finding the most suitable analytical column and (d) developing a suitable separation method with optimized resolution for all compounds in a reasonable time.

Stage one consisted of identifying a sample trap with strong adsorbent beds capable of capturing volatile organic AMC and a weak bed capable of capturing and releasing condensable organics up to hexacosane (C26). Form factor of the trap needed to match that of currently used traps (8.9 cm × 6.4 mm diameter) for use in common thermal desorption systems. To find the most suitable, commercially available sample trap, we compared six trap types using standard LeanSigma® tools and slowly narrowed the selection until we concluded that there is only one good solution that is commercially available. Commercial availability was important, as we set out with a new industry standard in mind. There are methods and sample traps available to capture volatile and very volatile organic AMC, such as Carbotrap® 300 traps, which are often used in semiconductor applications. However, this approach requires the use of a separate sampling and analytical method, making cost undesired and prohibitive particularly in DUV applications where volatile organic AMC is mostly studied only for academic reasons, not because

they are causing actual process problems. For EUV, this approach will change, as all organic AMC is known to cause equipment problems.

The second stage focused on identifying adsorbents to create a cryogenic focusing trap (cold trap) capable of analyzing both volatile and condensable organics. The same polymer-based adsorbent that is used in current sample traps for collecting AMC in DUV processes is also commonly used in cold traps in thermal desorption systems that feed the concentrated gas sample to the analytical gas chromatography system. This adsorbent is used because it is inexpensive, widely available and has the ability to capture and release a wide range of organic compounds when cooled. However, that trap type breaks down over time, particularly during the frequent heating to 300°C or more in the desorption system, causing the formation of artifacts after repeated heating cycles, including some silicon-containing compounds such as octamethylcyclotetrasiloxane (D4). Another disadvantage is the retention of water on these traps. Even though the porous polymer is hydrophobic, there is still a significant amount of moisture retained on the adsorbent and then released onto the analytical column during the desorption step, resulting in premature column breakdown.

Stage three was to identify a low-bleed separation column capable of separating isopropyl alcohol and acetone as well as other low boiling "refractory" compounds (such as volatile, halogenated refrigerants) commonly measured in semiconductor fabs. Typical gas chromatograph/mass spectrometer (GCMS) applications for high molecular weight organic AMC analysis utilize a 5% Phenyl, 95% dimethyl arylene siloxane based polymer as coating of a fused silica capillary column. Columns are designed to operate at temperatures exceeding 300°C to minimize column bleed during the final stages of desorption and separation. Column bleed happens when the base polymer chain breaks down over time and releases compounds that appear as a rising baseline in chromatograms. Excessive column bleed also results in poor chromatography (peak tailing) and poor recovery of higher molecular weight organics such as hexacosane (C26), the high end of lithography tool AMC specifications. If bleed is excessive, the mass spectrometer's components are also clouded, resulting in considerable sensitivity loss. Even though the phenyl based columns exhibit low bleed at high temperatures, they are

unable to adequately separate low boiling compounds such as acetone and isopropyl alcohol (IPA), which are often reported as a merged signal. Columns designed for the separation of low molecular weight organics, on the other hand, are often proprietary phases that usually have an upper temperature limit of 240°C, which is insufficient for semiconductor applications measuring up to C26.

This study concentrated on developing a sample and analytical method for volatile and condensable organic AMC, starting with IPA at the most volatile end. We did purposely not include any "very volatile organic" (VVOC) AMC with compounds more volatile than IPA (for example, ethanol, methanol, low molecular weight alkanes), because these compounds presumably will be pumped out of EUV vacuum systems more efficiently than those with higher boiling points and because they are not as prone to adsorb on surfaces as much as their higher boiling point counterparts. Our method is, however, fundamentally suitable to be used for many of those VVOC compounds as well, but sampling, preconcentration and separation parameters would need to be optimized for that application. This paper does not consider VVOC determination.

Finally, stage four optimized method parameters both for performance and speed and determining method detection limits was part of this. Thermal desorption systems use inert gases, such as helium or nitrogen as purge and carrier gases for each thermal desorption stage (sample trap purge, primary desorption and secondary desorption). Each stage was optimized using LeanSigma tools to decrease operational time and gas consumption by nearly 15%. Instrument detection limits were targeted at the upper parts-per-quadrillion (ppq) level by adjusting concentration range and also by increasing the amount of sample reaching the separation column without overloading the mass spectrometer's sensor.

Creating Challenge Gases

Challenge gases for the main lab tests were created in the concentration range of 8 to 420 ppbV using permeation and diffusion devices. Vials with individual or mixed chemicals were placed in a heated chamber held at a constant 35°C. Extra clean dry air (XCDA®) was created using Entegris GateKeeper® purifiers and flowed through the chamber to create a primary dilution. Concentrations were adjusted by varying the flow rate

of the XCDA source. A secondary dilution XCDA supply was used to create a humidified gas stream by passing the XCDA through DI water. Flows were monitored using calibrated digital flow meters.

Adsorbent Cleanliness and Artifacts

To prepare test beds for the sample and preconcentration traps, each adsorbent was added to custom 6.4 mm OD glass traps with a 3 cm high, packed beds. Each trap was purged with an inert gas and heated to 300°C for twenty minutes to remove residual organic compounds from the material or introduced through handling. Following conditioning, each adsorbent bed was purged with forty liters of XCDA. Traps were then analyzed by GCMS to determine the amount of AMC outgassed by the adsorbent. Following the background tests, challenge testing was performed using aggressive inorganic acids and organic compounds commonly known to cause artifacts in Tenax, such and trifluoroacetic acid, nitrous acid, acetic acid and limonene.[6]

Break-through Volume

Several volatile and condensable compounds commonly found in semiconductor fabs were selected for testing. Break-through volumes (BTV) were determined by creating a challenge gas from permeation or diffusion sources and diluting it with XCDA, then introducing that gas stream through two sample traps configured in series at a constant flow rate, established with critical orifices. Samples were collected for each compound with sample volumes ranging from four to 62 liters. Analyte responses were measured for each sample trap by GCMS and break-through volumes were compared to those of the porous 2,6-diphenylene-oxide polymer resin sample traps. BTV was defined with AMC retention at 95% or better capture efficiency (Equation 1).

The maximum sample time for the proposed sample trap was determined by sampling 53 ppb of acetone at 130 mL/min, slightly less than our standard flow rate for organic AMC sampling (150 mL/min). Flows were verified using a calibrated flow meter. Sample volume was increased by extending the sampling time until capture efficiency dropped below 90%.

Break-through volume on Tenax style traps also heavily depends on the amount of adsorbent packing. The polymer granulate varies in density from batch to batch and we found packing of these traps to vary between 150 and 300 mg of material, making for very substantial variability in maximum retention volumes, yet another disadvantage of these traps.

Precision and Accuracy

Method precision was estimated by performing replicate measurements of gas challenges described in section 2.2 and calculating the standard deviations.

For determination of accuracy, known concentrations of volatile and condensable compounds were collected onto the multi-bed carbonaceous sample traps and analyzed by GCMS. Concentrations of the challenge streams were determined using gravimetric analysis. Traps were tested with acetone, benzene and hexadecane, spanning the range of interest. Concentration of each analyte was varied by increasing the secondary dilution flow. Upper and lower control limits were set to ±10% of the absolute value. Twenty five samples with varying concentrations were collected and analyzed to determine the probability that a measured result will fall outside the control limits.

Desorption Efficiency/Recovery

The upper end of the range of captured organic compounds is typically limited by sufficient recovery or desorption efficiency, i.e. the ability to quantitatively release a compound when undergoing thermal desorption with standard parameters. To study recovery, a solution of hexacosane (C26 hydrocarbon, a solid at-room temperature) was prepared in hexane. Complete transfer of C26 from the sampling trap to the analytical column was confirmed using three steps. Step 1 was to determine the response of a one micro-liter injection of the same compound onto the analytical column through a 2 mm glass injection port liner packed with glass wool, 1 cm high, to promote mixing and complete vaporization of the solution. The on-column injection represents the benchmark response. For step 2, a sorbent trap was spiked with one micro-liter of the same solution and thermally desorbed, thus

$$\text{Capture efficiency} = {}^{\text{Trap 1 Response}}\!\big/\!{}_{(\text{Response of Trap 1 + Trap 2})} * 100 \ (\%) \quad \textbf{Eq. 1}$$

$$\text{Desorption efficiency} = {}^{\text{Des 1 Response}}\!\big/\!{}_{(\text{Response of Des 1 + Des 2})} * 100 \ (\%) \quad \textbf{Eq. 2}$$

determining potential loss due to the analyte binding to the cold trap. In step 3, one micro-liter of the same solution was injected onto sorbent sample traps and each trap was then purged in injection direction with 40 liters of XCDA to simulate the distribution and broadening during a standard air sample, followed by standard desorption in reverse direction. Efficiency was determined by comparing responses from each injection. Desorption efficiency is defined in Equation 2.

Influence of Humidity on Capture Efficiency

Three analytes were selected to determine the effect of sample moisture on capture efficiency. A gas stream as described in section 2.2 was established at 50% RH. An inline hygrometer was used to confirm humidity levels in the air stream. Capture efficiency of each analyte was compared to that found at 0% RH.

AMC Capacity

As AMC concentrations increase and capacity of one adsorbent bed is exhausted, AMC will migrate from the weaker to the more retentive beds. If that migration occurs, condensable AMC may no longer desorb from the stronger adsorbent beds and the capacity of the trap will be used up over time, rendering it useless. Capacity of the carbon based traps (in ppb-h) was determined using a benzene challenge of varying concentrations. The use of the unit ppb-h for trap capacity results from the product of sampling time (h) and challenge concentration (ppb) and allows for the calculation of each sub-unit when the other is known. This is a common approach in specifying AMC filter lifetimes as well (sample traps can be considered to be miniature AMC filters).

Challenge concentrations were set between 180 and 420 ppb. Fifteen samples were collected and analyzed by GCMS. Response for each trap was plotted versus capacity to determine maximum sample concentration and time.

Separation Column

A number of GC separation columns were selected for testing based on stationary phase, upper temperature limit and configuration (inside diameter, phase thickness and length). The resolution of acetone and IPA was used as one deciding factor for the quality of separation, as these two compounds are often merged and reported as one signal. Other low boiling refractory compounds, such as halogenated refrigerants, were considered, too, as well as the column bleed at temperatures exceeding 300°C, which is necessary for separation of high boiling constituents.

Method Optimization and Detection Limits

The last step in the method development process was to optimize the thermal desorption unit settings and GC temperature program. Statistical software was used to determine optimized settings to analyze samples taken in actual semiconductor environments. Performance parameters were speed of analysis (maximum sample throughput) and maintaining method robustness. Method robustness can be described as the ability to reproduce the analytical measurement under different circumstances, such as varying relative humidity or concentration, without experiencing differences to the expected results. Instrument detection limits (IDL) and method detection limits (MDL) were calculated using a modified Hubaux-Vos[7,8] method with a weighted least squares (WLS) response at 99% confidence.

Results

Preconcentration Trap

To replace the commonly used Tenax-style cold/preconcentration trap in GCMS systems, we looked at available solutions and were not able to find a commercially available trap. However, we developed an easy way to manufacture these traps in small lab settings, using empty cold trap tubes as supplied by GCMS vendors for the desorption system and filling them with several layers of different carbons to mimic the sample trap behavior and capabilities. The multi-layered, carbon-based cold trap that we developed eliminates the formation of organic artifacts and also reduces moisture retention. Other parameters studied are included in their respective sections below. Design and manufacturing details are available from the authors.

Adsorbent Cleanliness and Artifacts

In contrast to polymer-based traps, adsorbents used for the carbonaceous traps did not exhibit any organic outgassing (Table 1). Minor amounts of carbon dioxide were detected in the cold trap and some sulfur dioxide was found in the sample trap, neither affects organic AMC analysis.

TABLE 1. ADSORBENT TRAP OUTGASSING RESULTS.

Trap Identification	AMC	Outgassing (µg/g)
2,6-diphenylene-oxide polymer resin	D3, D4	0.2, 0.3
Carbonaceous sample trap	SO_2	0.1
Carbonaceous cold trap	CO_2	0.2

Each adsorbent trap was sampled with a mixed challenge of acetic acid, nitrous acid, trifluoro-acetic acid and limonene. Artifact concentrations (Table 2) were determined by subtracting the results from challenge testing from the outgassing values. No such artifacts were found in the carbonaceous sample or cold traps.

TABLE 2. ARTIFACTS PRODUCED ON POLYMER–BASED SAMPLE TRAP

Artifact Identification	Artifact (µg/g)
Benzene	2.0
D3	0.6
Benzaldehyde	1.8
D4	2.2
D5	1.0
2,5-diphenyl-2,5-cyclohexadiene-1,4-dione	97

Break-through Volume

All organic AMC considered condensable is usually fully retained by polymer traps, but as volatility of compounds increases, retention on the Tenax trap decreases. Toluene, a compound near the volatile end of the condensable organics range, is retained by Tenax sample traps for up to 6 hours at 0.15 L/min. However, benzene, a compound near toluene, already showed major break-through after 32 liters of air and acetone, the compound that defines the low end of the volatiles range, showed significant breakthrough after collecting as little as four liters of air. In addition, as stated, break-through on Tenax style traps also heavily depends on the amount of packing and may vary from batch to batch. Capture efficiency results are shown in Figure 1.

From these results, it is clear that polymer-based sample traps are not capable of collecting sufficient amounts of air to achieve ppt-level detection limits. The most common application of these traps uses sample times of 2−4 hours or 18−36 liters of air to achieve low-ppt-level detection limits. At this point, we observed substantial break-through, especially at the most volatile end of the compound range, which would dramatically underestimate actual AMC concentrations. This has been a known limitation and is widely ignored for DUV applications. However, for EUV applications, accurate results are important to estimate the total carbon loading, including volatile organics.
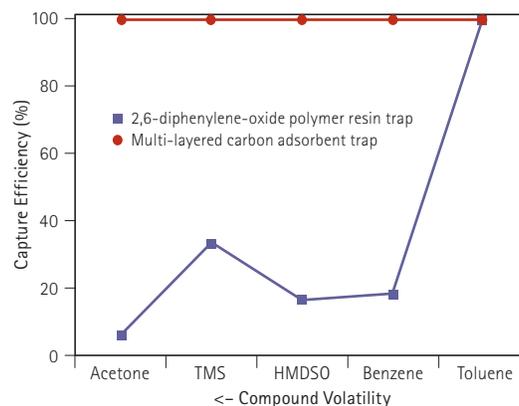

Figure 1. Capture efficiency as a function of compound volatility for 32 liters of air at 40% RH.

Sample Trap Pressure Drop

Sample trap pressure drop is important to ensure that standard, low-cost pump equipment such as Pocket (SKC) can be used for AMC sampling. Pressure drop of Tenax TA traps is low, on the order of 1.5 kPa, whereas Carbotrap 300 traps typically have a 3−4x higher pressure drop, requiring more powerful pumps. Tenax GR, the style that is commonly used to quantify volatile organics along with condensable organics, showed a pressure drop twice as high as Tenax TA and the new carbonaceous trap, but can still be operated with most low cost pumps.
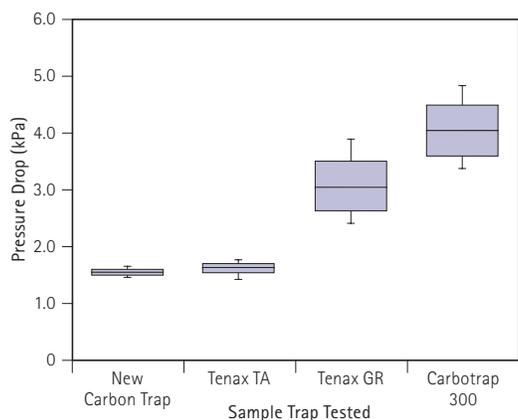
Figure 2. Sample trap pressure drop distribution.

The trap we propose has a pressure drop very similar to that of the polymer traps, allowing for the use of all types of and including legacy pumps. Distribution of pressure drop measurements is listed in Figure 2. Box "whiskers" indicate high and low reading, the box itself represents plus/minus one standard deviation. Ten traps of each trap type were tested.

Precision and Accuracy

Our method development targeted an accuracy within 10% of actual concentration. When sampled on Tenax, 95% of the acetone was lost and retention and recovery were less than 5% of the actual amount. When sampled using the carbonaceous sample trap, capture efficiency and release were within 97% of challenge concentration.

When using statistical software to analyze accuracy data, the probability of measuring acetone outside ±10% of known value on our carbonaceous trap was only 0.8%, the equivalent of one measurement outside the control limits in 125 at 99.97% confidence. Precision and accuracy measurements for acetone are depicted in Figure 3.
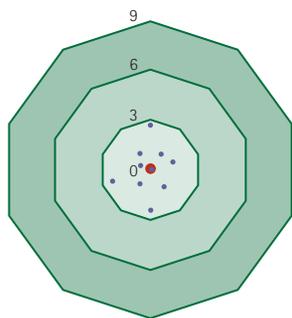

Figure 3. Precision and accuracy measurements for acetone: deviation (in ppbV) from actual 53 ppbV challenge.

Even though trimethylsilanol (TMS), a volatile compound, was fully retained after collecting 32 liters of air, recovery of TMS varied dramatically and cannot be considered accurate,[5] see next section. Capture efficiency and recovery was tested with additional compounds and results were consistent and similar to acetone.

Desorption Efficiency/Recovery

Desorption efficiency of each carbon trap was determined by comparing the response of an absolute concentration (µg) from an on-column injection to two manually spiked sorbent traps (one purged with 40 liters of XCDA). Desorption efficiency for C26 was greater than 94% for each trap (Table 3). This was confirmed by analyzing four additional traps spiked with the same solution and purged with 40 liters of XCDA. Desorption efficiency for each trap was compared and averaged 99.7 ±0.32% (Table 4). Desorption efficiency of octacosane (C28) was also studied using similar techniques, but recovery of the compound was less than 85%.

TABLE 3. C26 DESORPTION EFFICIENCY – COMPARISON TO ON–COLUMN INJECTION.

Trap Type	Desorption Efficiency
Cold trap	95%
Sample trap	94%

As mentioned, we found TMS recovery to vary substantially with the age of the trap, we consistently find TMS being retained and not released in the gas phase on aging carbonaceous sample traps, which was the reason for developing a stand-alone analytical method for TMS.[5] With each thermal desorption cycle of the trap, recovery of TMS appears to diminish further.

TABLE 4. C26 DESORPTION EFFICIENCY MEASURED BY MULTIPLE DESORPTION CYCLES.

Desorb Cycle	Trap 1	Trap 2	Trap 3	Trap 4
1	100.0%	100.0%	99.4%	99.5%
2	0.0%	0.0%	0.6%	0.5%
3	0.0%	0.0%	0.0%	0.0%

Performance Under Humidified Conditions

Hydrophobic adsorbents were used for both the new sampling and cold traps. Performance of the proposed traps was excellent at zero and 50% relative humidity (Table 5). This is an important result, as the traps are used for AMC detection in both dry supply gases (CDA, N_2, CO_2) and humidified environments (air handlers, clean-rooms, subfabs, AMC filter cabinets).

TABLE 5. ANALYSIS RESULTS FOR VOLATILE AND CONDENSABLE ORGANIC AMC ON THE PROPOSED MULTI–LAYERED SAMPLE TRAP.

Compound	RH	Challenge (ppbV)	Measured (ppbV)	Capture Efficiency
Acetone	0%	53	53	101%
Acetone	50%	26	26	101%
Benzene	0%	41	43	104%
Benzene	50%	57	56	98%
Hexadecane	0%	7.9	8.1	103%
Hexadecane	50%	17	17	100%

Maximum Sample Time/Break-through volume

Maximum sample time and associated BTV was determined by measuring the break-through curve for acetone, the compound that defines the low end of the volatiles range. Our break-through tests targeted a capture efficiency greater than 95% as a cutoff for sample time.

The polymer based trap showed significant break-through after collecting 4 liters of air (45 minutes at 0.15 L/min) and never reached our target (Figure 4). The carbon based trap showed 100% capture efficiency up to 32 liters of air (213 minutes at 0.15 L/min) and supported a sample size greater than 55 liters with capture efficiency more than 90%, the equivalent of 366 minutes when sampled with a flow rate of 0.15 L/min.
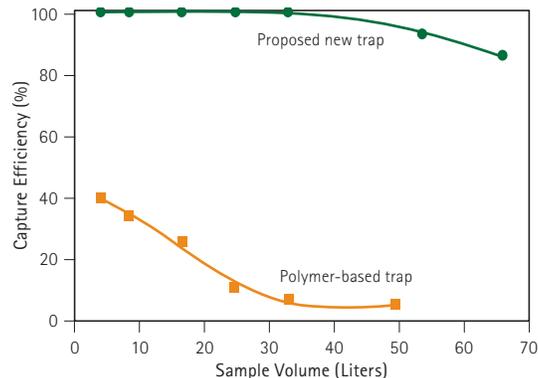

Figure 4. Break-through curve for 53 ppbV acetone

AMC Capacity and Migration

Capacity in this analytical sampling method has two different aspects. There is absolute capacity of volatile organic AMC before it breaks through the trap and gets lost. For high boiling point compounds, however, that capacity is irrelevant and we need to consider capacity on the respective adsorbent bed that the compound is captured, before it breaks through to the next higher retentive bed and, even though fully retained, does not get recovered.

The capacity for retention on the designated adsorbent bed of the multi-layered carbon sampling trap, as well as the capacity on the cold trap were determined using benzene. More volatile compounds were not investigated for this because they will quantitatively desorb from any of the retention beds of the trap. Their absolute capacity results directly from data in the *Maximum Sample Time/Breakthrough Volume* section. Benzene is the best compound to monitor migration, as it is readily adsorbed onto the weaker absorbent bed, yet volatile enough to migrate onto the stronger adsorbent bed downstream.
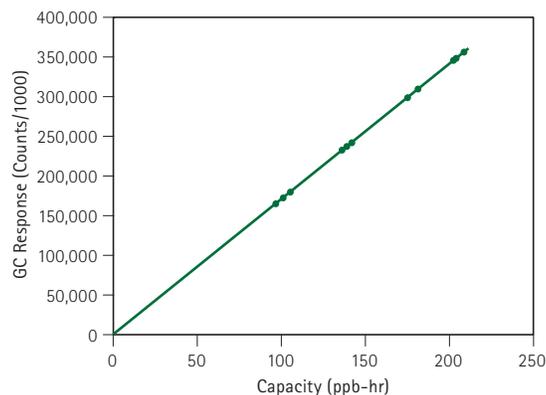

Figure 5. AMC capacity for the sample trap.

For the sample trap, migration of benzene to the next weak adsorbent bed was not observed after 210 ppb-h. This is sufficient for semiconductor environments that typically do not exceed 20 ppb of total hydrocarbon concentrations and much less for any one compound.

For the cold trap, migration of benzene from the weak to the stronger adsorbent bed was not observed with sample concentration exceeding 420 ppb (time is not considered, as it is short when preconcentrating a sample on the cold trap).

Separation Column

Selection of the GC separation column was based on good resolution of IPA and acetone and low column bleed. The DB5 separation column commonly used for the analysis of condensable organics is unable to resolve IPA and acetone when included into the overall range scope, and also exhibits measurable column bleed when operating at temperatures above 320°C.
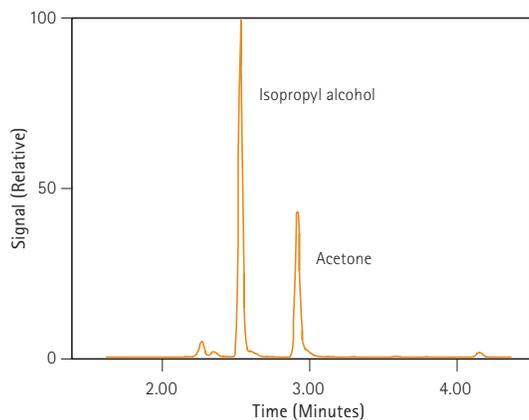
Figure 6. Resolution of isopropyl alcohol and acetone.

The separation column we selected found for our new method, IPA and acetone were completely resolved while maintaining low column bleed at the upper temperature limit (Figure 6). Resolution for low boiling point, halogenated ("refractory") compounds was substantially improved, allowing for increased accuracy of their measured concentrations and reporting of individual compounds rather than that of a merged signal (Figure 7).
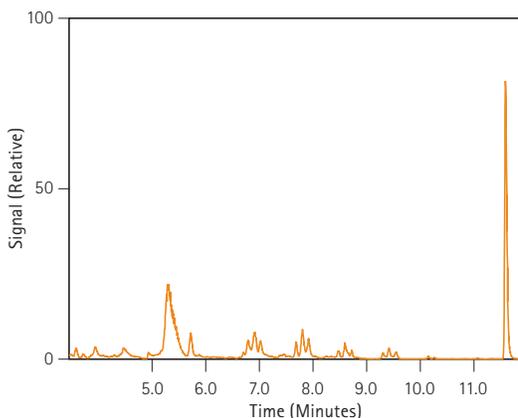
Figure 7. Resolution of low boiling point, halogenated refrigerants commonly found in semiconductor environments.

Method Detection Limits

Method detection limit (MDL) at 99% confidence interval was determined using statistical software and the approach described by Hubaux-Vos[7] and practically implemented by Coleman and Vanatta.[8] We used known concentrations of gas-phase toluene-D8 for this study, as we use it for all standard calibrations, an approach superior to and less variable than the use of liquid standards.

TABLE 6. GAS–PHASE METHOD DETECTION LIMITS.

MDL @ 99% Confidence		MDL @ 95% Confidence		MDL @ 90% Confidence	
ng	pptV	ng	pptV	ng	pptV
0.2	1.7	0.2	1.2	0.1	1.0

Detection limits for organic AMC in this study, expressed "as toluene," were between one and two ppt (Table 6), with instrument detection limits (IDL) in the upper ppq range (typically about half of the MDL).

The linearity range of mass spectrometers (typically 3–3.5 orders of magnitude) does not allow measurement of high ppq to high ppb level with linear calibration and the low end of these detection limits is governed by the upper measurement range. To achieve MDLs at the ppq level, real-world samples need to be analyzed using two separate thermal desorption methods, individually calibrated. We determine method application by anticipated sample cleanliness (for example CDA vs. ambient) and analytical needs.

When adjusting concentration range accordingly (with a lower concentration limit at the upper-end), it is straight-forward to push detection limits further into the mid- or even low parts-per-quadrillion (ppq) range, as needed. A more challenging part of that goal, however, remains the in-field sampling of organic AMC, which is ultimately limited by the cleanliness of sample operation, trap handling, storage and transport.

Disadvantages of Multi-layer, Carbon-based Traps

From an operational perspective, the proposed method is a substantial improvement over existing methods in all technical respects. One disadvantage of using the carbon-based sampling trap is the initial start-up cost, as the purchase cost of these traps is roughly 30% higher than that of polymer-based and Carbotrap 300. However, this added cost is easily offset because the number of methods required to accurately measure both volatile and condensable organics is cut in half and reduced to one.

In addition, there is currently no commercial availability for the cold trap we designed and cold trap preparation needs to be considered. Cold trap preparation is done with well established techniques for packed columns, but it represents an added manual step. Cold trap lifetime is expected to be one year, about the same as for polymer-based traps.

Even though an advantage from a scientific aspect, increased accuracy may not always be received as a welcome change. Current industry standard measurements for some exposure tool systems are based on results from Tenax GR, a carbon-coated version of the pure polymeric adsorbent. Results of volatile organic compounds as demonstrated in this study, are inaccurate and the more so, the more volatile a compound is. The method proposed here will result in higher volatile AMC concentrations reported for the studied environments when compared to Tenax results. Whereas higher concentrations of hydrocarbons have little or no operational impact on DUV systems, some halogenated and silicon-based compounds can cause scanner system environments to be out of warranty, if the found concentrations are too high. Accurate collection and higher reporting of these compounds may suddenly put environments or tools out of specifications. Whereas higher accuracy of results is always desirable from a technical standpoint, its acceptance by tool operators may be reluctant based on commercial aspects.

Conclusions

As lithography processes move from DUV to EUV, the need for accurate measurements of particularly volatile organic AMC is critical to gauge EUV system exposure to total carbon load and evaluate where AMC mitigation is necessary.

The current industry standard uses a polymer-based sample trap type that is not suitable for measuring volatile compounds. It also produces substantial artifacts when heated or exposed to inorganic acids in fab environments.

This study shows results from a new type of carbon-based sample trap, which offers superior performance across the entire range of organic compounds. Accurate and artifact-free results lead to a better understanding of total organic AMC load for process control and can help reduce costly carbon deposition on EUV exposure system mirrors.

By using the proposed carbon-based sample and cold traps, improvements to AMC measurements can be made in these areas:

- Adsorbent cleanliness – carbon-based sample and cold traps do not exhibit any organic-based artifacts and produced only minor inorganic AMC.

- Accuracy and capture efficiency for volatile organic AMC – carbon-based sample and cold traps fully retain all organic compounds, including IPA, for four or more hours of sampling at 0.15 L/min (36 liters of volume).

- Desorption of high molecular weight organics – the desorption efficiency of hexacosane, the upper end of the combined organics range, was about 95%.

- Cost reduction – combining the sampling and measurement of both volatile and condensable organic AMC into one analytical method saves cost and makes adoption of this method as an industry standard more likely.

We propose to establish this analytical method as a new industry-wide standard for the combined measurement of volatile and condensable organic AMC. Please contact the authors for technical details.

References

1. S. B. Hill et al, *Measuring the EUV-induced contamination rates of TiO₂-capped multilayer optics by anticipated production-environment hydrocarbons,* Proc. SPIE, 7271-39 (2009).

2. R. Wasielewski et al, *Surface chemistry of Ru: relevance to optics lifetime in EUVL,* Proc. SPIE, Vol 6533, 653316 (2007).

3. Al-Montaser et al, *Carbon contamination and oxidation of Au surfaces under extreme ultraviolet radiation: An x-ray photoelectron spectroscopy study,* J. Vac. Sci. Technol., B 30 (4), Jul/Aug 2012.

4. S. B. Hill et al, *Accelerated lifetime metrology of EUV multilayer mirrors in hydrocarbon environments,* Proc of SPIE, 6921-42 (2008).

5. Lobert et al., *Measurement of low molecular weight silicon AMC*, Proc. SPIE, 7272-81 (2009).

6. Kleno et al, *Degradation of adsorbent Tenax TA by nitrogen oxides, ozone, hydrogen peroxide, OH radicals and limonene oxidation products,* Environ Sci. Technol., 2002,36, 4121-4126.

7. Hubaux, A., Vos, G., *Decision and detection limits for linear calibration curves,* Anal. Chem., 42, 8 (1970) 849-855.

8. Coleman, D. and Vanatta L., *"Statistics in analytical chemistry: A new American Laboratory column,"* Analytical Laboratory, Sep-2002 and the following 19 issues.

9. ITRS: International Technology Roadmap for Semiconductors (ITRS), *"Yield Enhancement for Wafer Environment Contamination Control (YE-WECC),"* (2012 Update). http://www.itrs.net

ENTEGRIS, INC.
Corporate Headquarters | 129 Concord Road | Billerica, MA 01821 USA
Customer Service Tel. +1 952 556 4181 | Customer Service Fax +1 952 556 8022
In North America 800 394 4083 | *www.entegris.com*

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