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Characterization and Control of Organic Airborne Contamination in Lithographic Processing

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AUTHORS
ANDREW J. DALLAS & KRISTINE GRAHAM OF DONALDSON COMPANY, INC. (USA)
MARC CLARYSSE & VIC FONDERIE, OF IMEC (BELGIUM)

ABSTRACT

Airborne gas-phase contaminants, such as ammonia (NH_3) and 1-methyl-2-pyrrolidinone (NMP), are known to present several processing problems in DUV lithography. These contaminants can be controlled using either acid-base or ion-exchange chemistry. However, as lithographic processing moves towards smaller features, condensable organic contamination presents an ever-increasing concern. The range of the chemical and physical properties of organic contamination does not easily lend itself to control using the chemisorptive techniques currently applied.

In conjunction with efforts to improve adsorbtive filters used to control organic contamination, we have attempted to characterize such contamination found in the lithographic processing environment. In this report, we will present our current findings and reveal some of the benefits and concerns associated with the use of activated carbon-based filters for this application.

Keywords: Airborne molecular contamination, organic contamination, condensable organics, chemical filtration, contamination control, hexamethyldisiloxane (HMDSO), amines, ammonia

INTRODUCTION

Airborne molecular contamination (AMC) found in semiconductor processing can be divided into four groups: (1) basic gases [molecular bases] (2) acidic gases [molecular acids] (3) volatile organic vapors and (4) condensable organic vapors. In lithographic processing, much of the focus in the past decade has been on molecular bases. This was primarily due to their deleterious interactions with chemically amplified resists. The need to address organic contamination in semiconductor processing arises from recent reports indicating organic contaminants as leading to: (1) physical or masking and (2) electrical processing effects. This necessitates the application of filtration methods directed at their control and removal.

Several papers have attempted to characterize the volatile and condensable organic contamination found in cleanrooms, lithographic processing areas and tools, controlled enclosures, optics, and purge gases. These studies do not adequately address chemical filter performance within an application. Therefore, this study attempts to characterize the volatile and condensable organics in the lithographic environment and their effective removal using activated carbon filters.

This study has two primary objectives (1) characterization of the organic fractions of the contamination in a lithographic environment and (2) evaluation of the ability of chemical filters to protect the lithographic process against specific organics. We have chosen to study the performance of activated carbon filters in detail. Specifically, we have chosen to evaluate the performance of citric acid impregnated activated carbon (CAIC) filters since they are currently the only single layer chemical filter that effectively deals with both the basic and organic fractions. In this study, we have evaluated the performance of two sets of CAIC filters (1) a set that was used in a field application for more than 3 years and (2) a set that was installed in the same field application for 1 day.

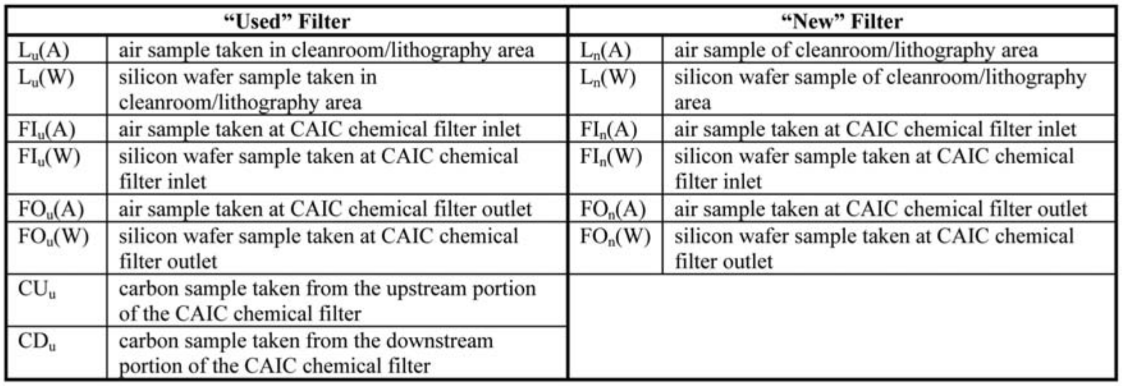
For brevity we will only address the former set of results on this website. Please see contact information above for a full transcript.

EXPERIMENTAL

We have characterized the volatile and condensable organics present within (1) a lithographic processing area (2) the airstream to the inlet of a chemical filtration unit [Donaldson LITHOGUARD model] and (3) the airstream exiting the chemical filtration unit and directed into a DUV lithography cluster. Air samples on adsorbent tubes and silicon wafer samples were taken in all three locations. This complete series of samples has been duplicated for two different sets of CAIC filters (1) “Used” [installed for more than 3 years] and (2) “New” [installed for 1 day]. In addition, we have sampled the upstream and downstream portions of the “Used” filters in order to evaluate filtration performance against specific organic contaminants.

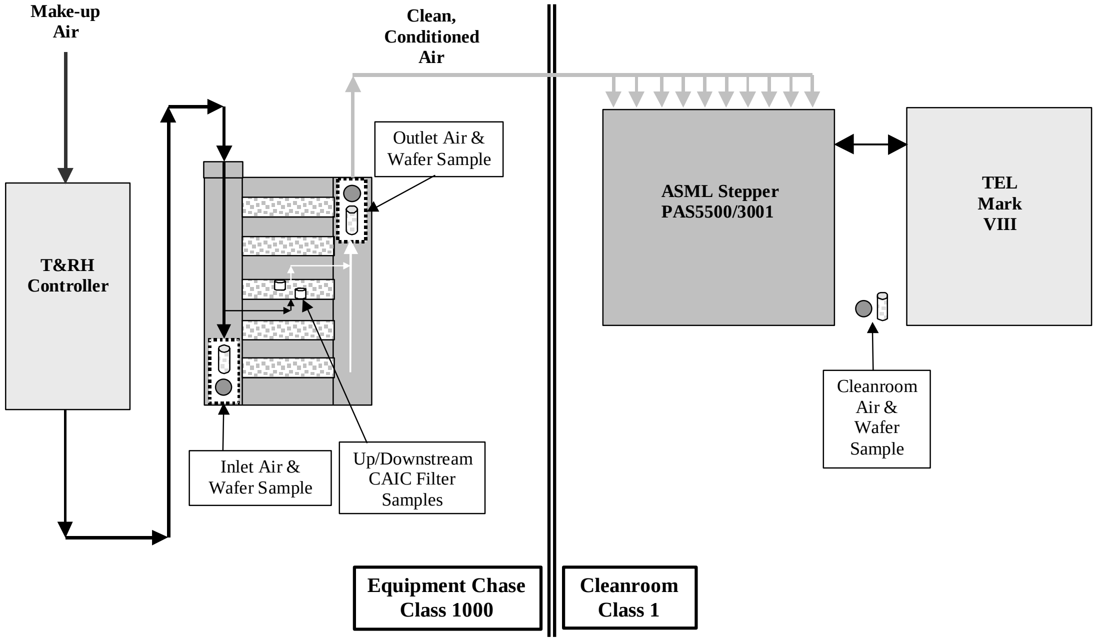
In Figure 1, the facility and sampling diagrams for the “chase” (Class 1000) and the cleanroom (Class 1) areas are given. The DUV cluster involved is located at IMEC Leuven, Belgium. It includes an ASML PAS 5500/300 stepper interfaced with a TEL Mark-8 coat and develop track. This cluster is generally used for pilot plant production of 0.18 µm and smaller CMOS technologies using positive environmentally stable chemically amplified photoresist (ESCAP). Sampling protocol and the analytical methodology used to evaluate the samples taken at each designated location is given in Table 1.

Table 1: Samples considered in this study.



“Used” Filter		“New” Filter	
L_u(A)	air sample taken in cleanroom/lithography area	L_n(A)	air sample of cleanroom/lithography area
L_u(W)	silicon wafer sample taken in cleanroom/lithography area	L_n(W)	silicon wafer sample of cleanroom/lithography area
FI_u(A)	air sample taken at CAIC chemical filter inlet	FI_n(A)	air sample taken at CAIC chemical filter inlet
FI_u(W)	silicon wafer sample taken at CAIC chemical filter inlet	FI_n(W)	silicon wafer sample taken at CAIC chemical filter inlet
FO_u(A)	air sample taken at CAIC chemical filter outlet	FO_n(A)	air sample taken at CAIC chemical filter outlet
FO_u(W)	silicon wafer sample taken at CAIC chemical filter outlet	FO_n(W)	silicon wafer sample taken at CAIC chemical filter outlet
CU_u	carbon sample taken from the upstream portion of the CAIC chemical filter		
CD_u	carbon sample taken from the downstream portion of the CAIC chemical filter		

Figure 1



2.1 Organic Airborne Molecular Contamination:

Balazs Analytical Laboratory (BAL; Fremont, CA) performed these analyses using thermal-desorption, gas-chromatography, mass-spectrometry (TD-GC-MS). Sample and control (shipping blank) adsorbent tubes were obtained from BAL. The air at each one of these locations was sampled for 6 hours at a flow rate of 100 ml/min. This method is primarily designed for evaluating volatile and semi-volatile organics in the range of C_7-C_{28}. The typical reporting limit is 1 ng/liter. In addition to these samples, we present results from a similar study at another site to support our observations with CAIC filters for controlling organic contaminants.

2.2 Condensable Organic Airborne Molecular Contamination:

BAL performed these analyses using TD-GC-MS methods. Organic-free sample and control (shipping blank) 200 mm silicon wafers were obtained from BAL. The air at each of these locations was sampled for 24 hours. In the case of the lithographic area the wafers were placed in a pre-cleaned holder on the surface of a table. The wafers at the inlet and outlet of the chemical filtration unit, were exposed to an airflow rate of $750 m^3/hr$.

2.3 Organics Adsorbed on a Citric Acid Impregnated Carbon (CAIC) Chemical Filter:

Donaldson Chemical Services Laboratory performed these analyses using TD-GC-MS methods. Samples of carbon were taken from the upstream and downstream portions of the “Used” CAIC filter. Thermal desorption methods using pre-cleaned glass tubes and a purge of ultra-high purity helium at 50 ml/min. Desorbed organics were trapped on a series of adsorbent tubes. Several desorption temperature steps were used, 25°C, 100°C, 150°C, and 250°C, thereby desorbing organics by the relative “strength” of their interaction with the carbon surface. Due to the poor recovery of strongly adsorbed, higher boiling, organics from the CAIC filter, only semi-quantitative results are presented. Our intention in providing these data is to give some indication of the filter’s performance against a specific organic species.

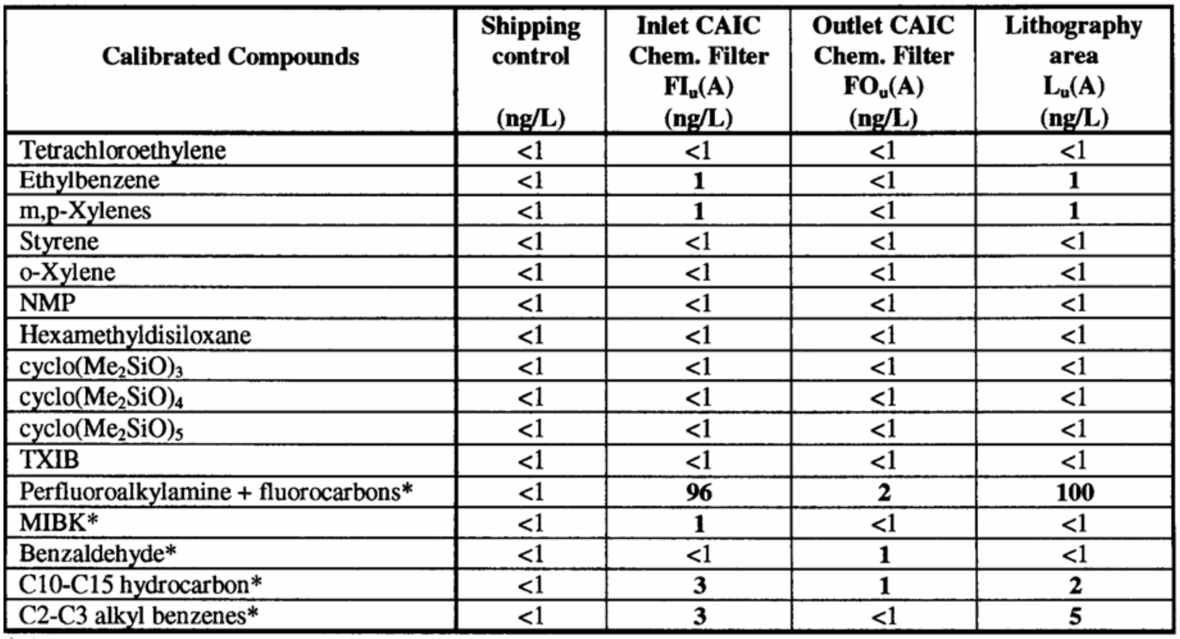
RESULTS

3.1 "Used" CAIC Chemical Filters

3.1.1 Air Sampling:

Semi-quantitative results are provided in Table 2.

Table 2: Semi-quantitative levels of airborne organic compounds with the "Used" filters installed.



Calibrated Compounds	Shipping control (ng/L)	Inlet CAIC Chem. Filter FI_u(A) (ng/L)	Outlet CAIC Chem. Filter FO_u(A) (ng/L)	Lithography area L_u(A) (ng/L)
Tetrachloroethylene	<1	<1	<1	<1
Ethylbenzene	<1	**1**	<1	**1**
m,p-Xylenes	<1	**1**	<1	**1**
Styrene	<1	<1	<1	<1
o-Xylene	<1	<1	<1	<1
NMP	<1	<1	<1	<1
Hexamethyldisiloxane	<1	<1	<1	<1
cyclo($Me_2SiO)_3$	<1	<1	<1	<1
cyclo($Me_2SiO)_4$	<1	<1	<1	<1
cyclo($Me_2SiO)_5$	<1	<1	<1	<1
TXIB	<1	<1	<1	<1
Perfluoroalkylamine + fluorocarbons*	<1	**96**	**2**	**100**
MIBK*	<1	**1**	<1	<1
Benzaldehyde*	<1	<1	**1**	<1
C10-C15 hydrocarbon*	<1	**3**	**1**	**2**
C2-C3 alkyl benzenes*	<1	**3**	<1	**5**

* Amounts are estimated using integrated total ion chromatogram area relative to response factor of n-decane external standard.
NMP = 1-methyl-2-pyrrolidinone; TXIB = texanol isobutyrate; MIBK = methyl isobutyl ketone

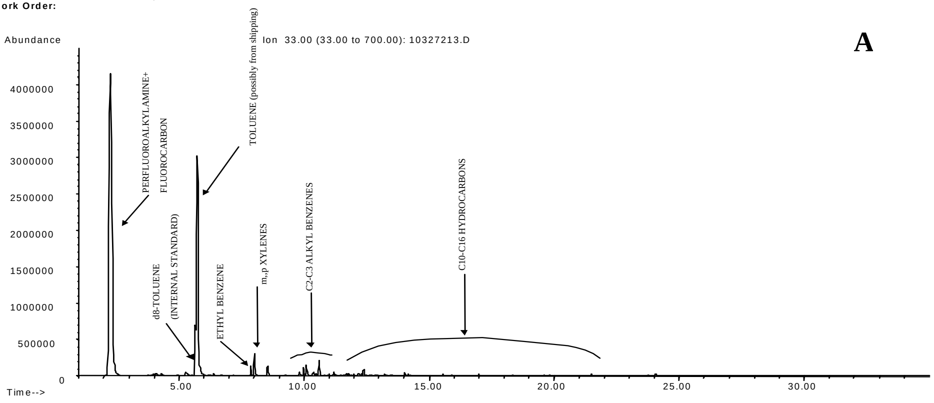
The only contaminant found in the shipping control is toluene. The total ion chromatograms for the air samples are given in Figure 2.

Figure 2: Total ion chromatograms for air samples with the "Used" filters installed: A) cleanroom / lithography area; B) chemical filter inlet; and C) chemical filter outlet (TD-GC-MS analysis performed by Balazs Analytical Laboratory).

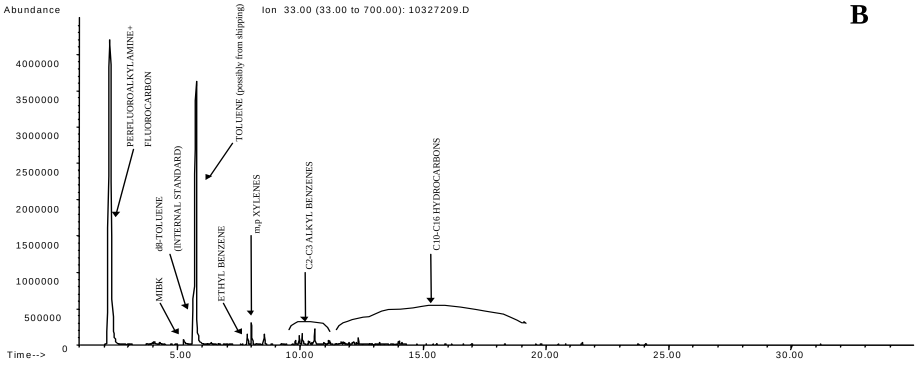
[See next page]

Figure 2

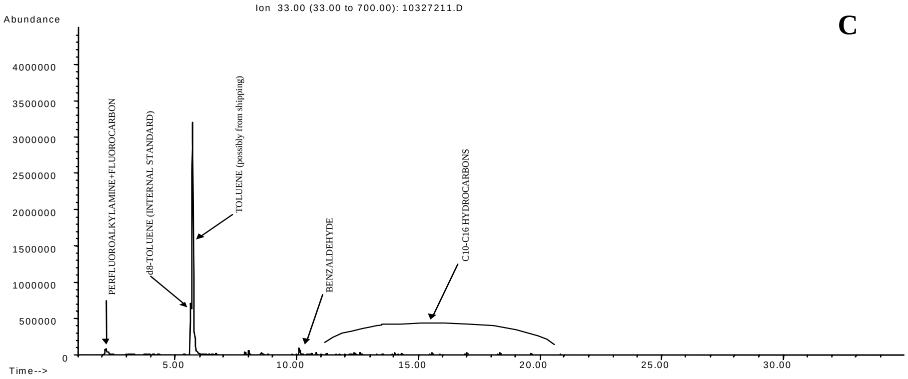
Sample ID: LITHOGRAPHY AREA
Method of Analysis: Dynamic Headspace TD-GC-MS (Thermal Desorption-Gas Chromatography-Mass Spectrometry)
Objective: Analysis of Organic Airborne Molecular Contaminants trapped onto sampling tubes packed with proprietary adsorbents
Sampling Conditions: Air sampled for ~6 hours at 100 mL/minute using calibrated air sampling pumps
Internal Standard: Toluene-d_8
Balazs Work Order:



Sample ID: INLET DONALDSON EQUIPMENT
Method of Analysis: Dynamic Headspace TD-GC-MS (Thermal Desorption-Gas Chromatography-Mass Spectrometry)
Objective: Analysis of Organic Airborne Molecular Contaminants trapped onto sampling tubes packed with proprietary adsorbents
Sampling Conditions: Air sampled for ~6 hours at 100 mL/minute using calibrated air sampling pumps
Internal Standard: Toluene-d_8
Balazs Work Order:

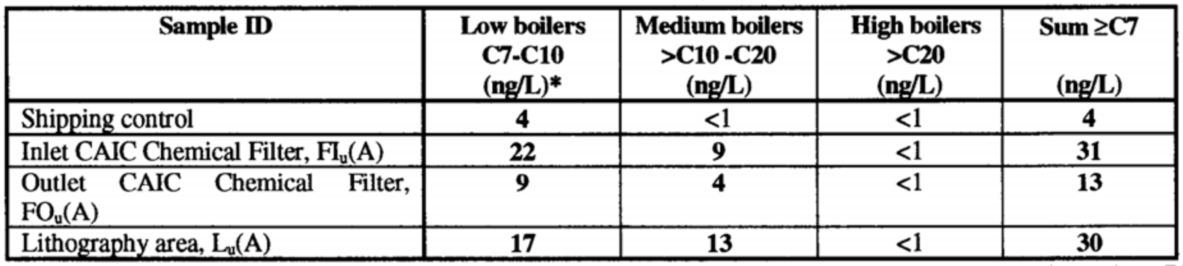


Sample ID: OUTLET DONALDSON EQUIPMENT
Method of Analysis: Dynamic Headspace TD-GC-MS (Thermal Desorption-Gas Chromatography-Mass Spectrometry)
Objective: Analysis of Organic Airborne Molecular Contaminants trapped onto sampling tubes packed with proprietary adsorbents
Sampling Conditions: Air sampled for ~6 hours at 100 mL/minute using calibrated air sampling pumps
Internal Standard: Toluene-d_8
Balazs Work Order:



It is possible to group the organics into three boiling ranges, low-boiling (C_7-C_{10}), medium-boiling (>C_{10}-C_{20}), and high-boiling (>C_{20}). The results for these groupings are provided in Table 3.

Table 3: Total airborne organics with the "Used" chemical filters installed.



Sample ID	Low boilers C7-C10 (ng/L)*	Medium boilers >C10 -C20 (ng/L)	High boilers >C20 (ng/L)	Sum ≥C7 (ng/L)
Shipping control	**4**	<1	<1	**4**
Inlet CAIC Chemical Filter, FI_u(A)	**22**	**9**	<1	**31**
Outlet CAIC Chemical Filter, FO_u(A)	**9**	**4**	<1	**13**
Lithography area, L_u(A)	**17**	**13**	<1	**30**

*Perfluoroalkylamines and fluorocarbons are not included in this range because they are lower boiling than C_7 n-alkanes. Toluene is also not included in this range.

From the total ion chromatograms in Figure 2 and the results in Table 2, we see the level of organic contamination in this location is relatively low. Although after 3 years the “Used” filter is near the end of life condition for medium boilers, it still has capacity for low-boilers such as perfluoroalkylamines, fluorocarbons, and solvents such as methyl isobutyl ketone.

If we compare similar results from an alternative semiconductor processing site. *For the sake of brevity, we have omitted these results in this synopsis.* We see the level of organic contamination the CAIC filters were exposed to was significantly higher. High levels of trimethylsilanol (TMS), hexamethyldisiloxane (HMDSO), methoxypropanol, 1-methoxy-2-propanol acetate (PGMEA), ethyl ethoxypropionate, and siloxanes were observed at the inlet. After 1.5 years in the field, the CAIC filters still reduced the level of these organics and other organic contamination to levels below the reporting limits. It is shown that CAIC chemical filters have excellent capacity for TMS and HMDSO.

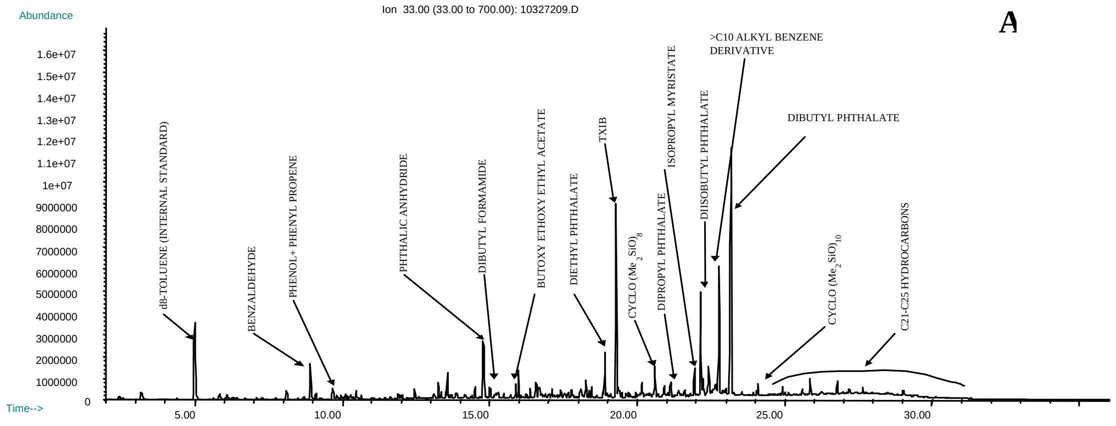
3.1.2 Wafer Sampling:

The shipping control wafers were found to be very clean. The total ion chromatograms for the wafer samples are given in Figure 3.

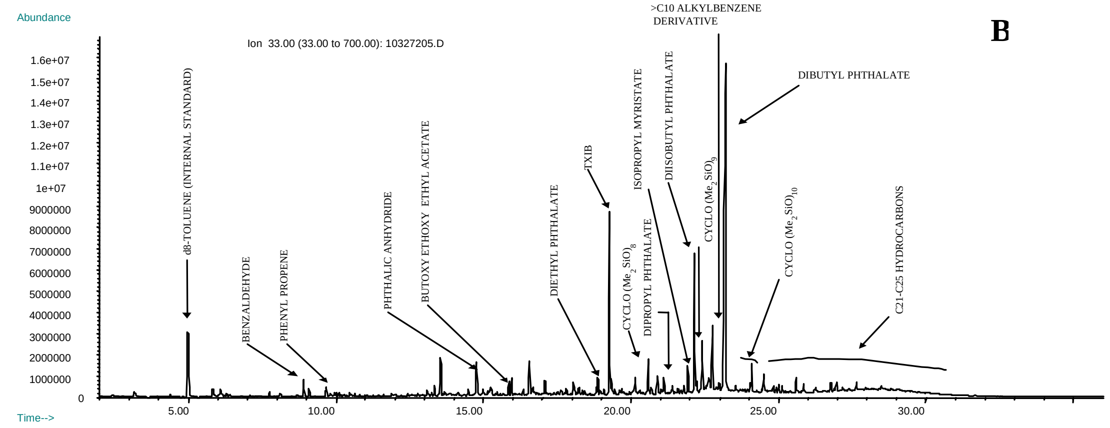
Figure 3: Total ion chromatograms for condensable organics (wafer samples) with the “Used” filters installed: A) cleanroom / lithography area L_u(W); B) chemical filter inlet, FI_u(W); and C) chemical filter outlet, FO_u(W) (TD-GC-MS analysis performed by Balazs Analytical Laboratory).

The semi-quantitative results for these data are provided in Table 4 and grouped by boiling point in Table 5.

Sample ID: Lithography area
Method of Analysis: Dynamic Headspace TD-GC-MS (Thermal Desorption-Gas Chromatography-Mass Spectrometry)
Objective: Analysis of organic compounds desorbed from witness wafer at 400 °C for 30 minutes
Sampling Conditions: Witness wafer exposed to the fab environment for 24 hours
Internal Standard: Toluene-d_8
Balazs Work Order:



Sample ID: Inlet Donaldson equipment
Method of Analysis: Dynamic Headspace TD-GC-MS (Thermal Desorption-Gas Chromatography-Mass Spectrometry)
Objective: Analysis of organic compounds desorbed from witness wafer at 400 °C for 30 minutes
Sampling Conditions: Witness wafer exposed to the fab environment for 24 hours
Internal Standard: Toluene-d_8
Balazs Work Order:



Sample ID: Outlet Donaldson equipment
Method of Analysis: Dynamic Headspace TD-GC-MS (Thermal Desorption-Gas Chromatography-Mass Spectrometry)
Objective: Analysis of organic compounds desorbed from witness wafer at 400 °C for 30 minutes
Sampling Conditions: Witness wafer exposed to the fab environment for 24 hours
Internal Standard: Toluene-d_8
Balazs Work Order:

Table 4: Semi-quantitative results for condensable organics (wafer samples) with “Used” filters.

Identified Compounds*	Shipping control wafer (ng /cm^2)	Inlet CAIC Chem. Filter $FI_u(W)$ (ng /cm^2)	Outlet CAIC Chem. Filter $FO_u(W)$ (ng /cm^2)	Lithography area $L_u(W)$ (ng /cm^2)
Benzaldehyde	<0.1	**0.1**	<0.1	**0.2**
Phenol + phenyl propene	<0.1	**0.1**	<0.1	**0.1**
Phthalic anhydride	<0.1	**0.3**	<0.1	**0.4**
Dibutyl formamide	<0.1	<0.1	<0.1	**0.1**
Butoxy ethoxy ethyl acetate	<0.1	**0.1**	<0.1	**0.1**
Alkyl phthalates (diethyl-, di-isopropyl-, di-isobutyl- and dibutyl phthalates)	<0.1	**4.5**	<0.1	**2.8**
Cyclo($Me_2SiO)_5$	**0.1**	<0.1	<0.1	<0.1
TXIB	<0.1	**1.0**	<0.1	**0.9**
Cyclo($Me_2SiO)_8$	<0.1	**0.2**	<0.1	**0.2**
Isopropyl myristate	<0.1	**0.2**	<0.1	**0.1**
Cyclo ($Me_2SiO)_9$	<0.1	**0.3**	<0.1	**0.2**
>C10 alkyl benzene derivative	<0.1	**0.5**	<0.1	**0.7**
Cyclo($Me_2SiO)_{10}$	<0.1	**0.2**	<0.1	**0.1**
C21-C25 hydrocarbons	<0.1	**2.9**	<0.1	**3.1**

* The amounts for each compound are estimated using a response factor for an n-hexadecane external standard.

Table 5: Total condensable organics with the "Used" chemical filters installed.

Wafer ID	Low boilers C7-C10 (ng/cm^2)	Medium boilers >C10-C20 (ng/cm^2)	High boilers >C20 (ng/cm^2)	Sum ≥C7 (ng/cm^2)
Control wafer	0.2	0.5	0.4	1.1
Inlet CAIC chemical filter, $FI_u(W)$	1.0	12.6	5.8	19.4
Outlet CAIC chemical filter, $FO_u(W)$	0.3	0.6	0.2	1.1
Lithography area, $L_u(W)$	1.1	11.3	4.5	16.9

There appears to be significantly more condensable organics in the airstream than volatile organics; however, the volume of air sampled is dramatically different. The wafers were exposed to 1.8×10^7 liters of air, whereas the adsorbent tubes sampled only 36 liters of air. Even after 3 years in the field, the “Used” CAIC filter still has a high capacity for condensable organics. It is clear from the results given in Table 5, that the level of condensable organics at the outlet of the CAIC filter is the same as the control (shipping) wafer.

3.1.3 Evaluation of Organics Adsorbed on the “Used” CAIC Filter:

The difficulties associated with the evaluation of volatile and condensable organics adsorbed on carbon filters are discussed above and in detail in this study. Difficulty in the analysis can be attributed to decomposition of the impregnant at desorption temperatures higher than 150°C and poor recovery of the strongly adsorbed condensable organics, even at temperatures as high as 250°C.

The total ion chromatograms for the TD-GC-MS analysis of the upstream portion of the “Used” CAIC filter are given in Figures 4 and 5 below for tubes 1 and 2 respectively. For brevity, we have not presented the total ion chromatograms for the 250°C run and the downstream sample.

Figure 4: Total ion chromatograms for volatile and condensable organics desorbed from the upstream side of the "Used" CAIC chemical filters, CUu, and trapped on adsorbent Tube 1. The following desorption temperatures are shown: A) 25°C; B) 100°C; and C) 150°C (TD-GC-MS analysis performed at Donaldson Co., Inc.).

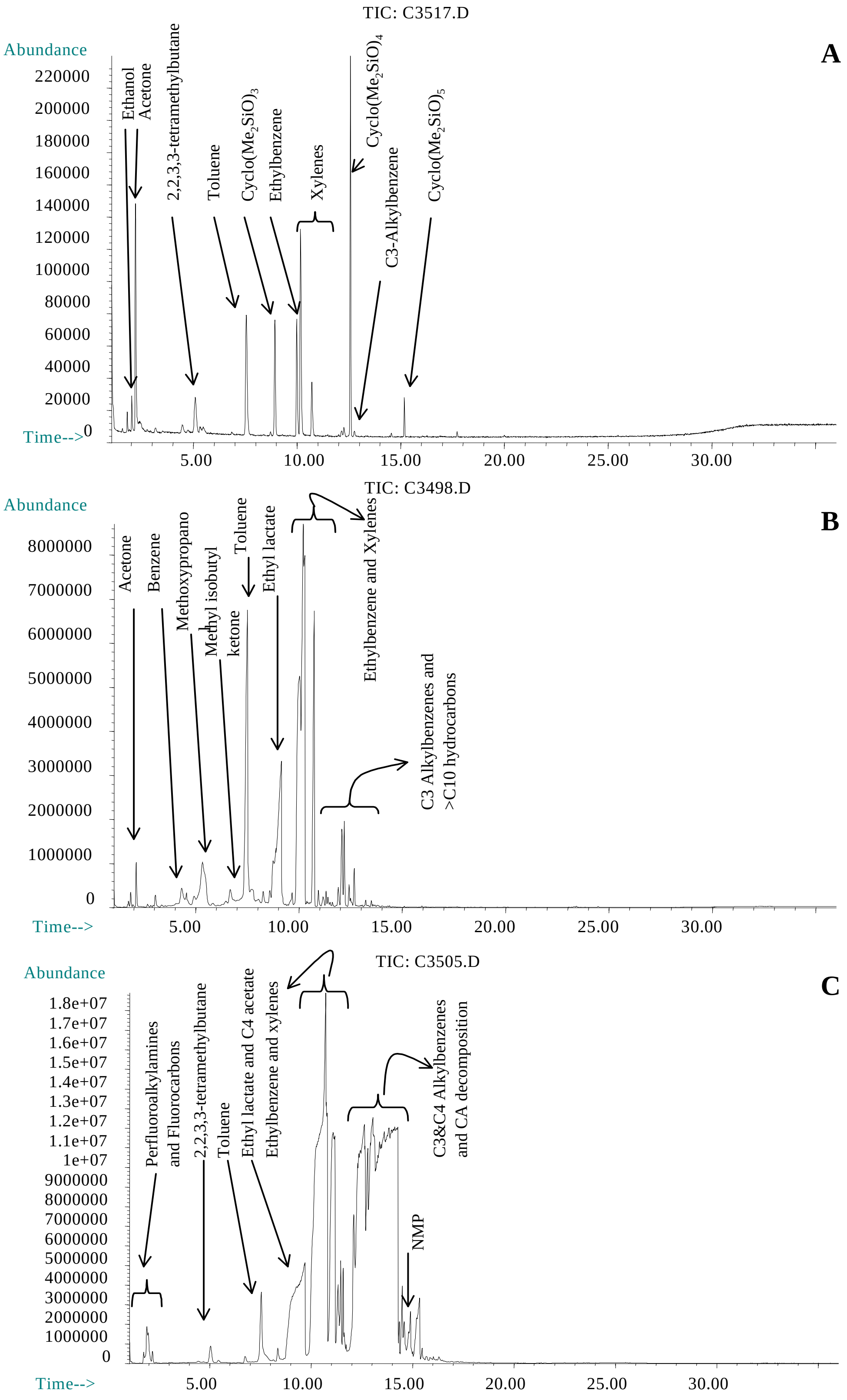
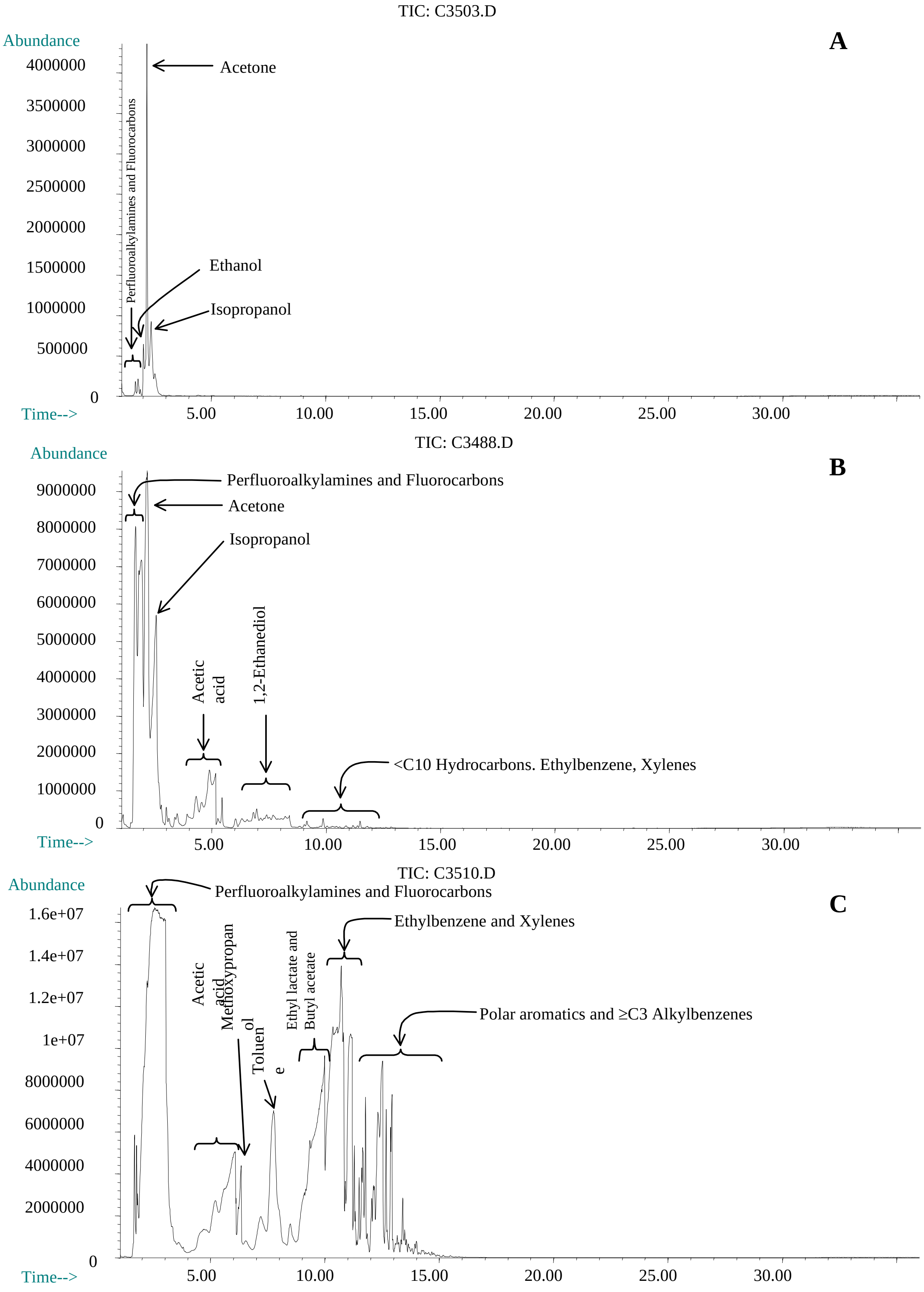


Figure 5: **Total ion chromatograms for volatile and condensable organics desorbed from the upstream side of the "Used" CAIC chemical filters, CUu, and trapped on adsorbent Tube 2. The following desorption temperatures are shown: A) 25°C B) 100°C and C) 150°C (TD-GC-MS analysis performed at Donaldson Company, Inc.)**



In both Figures 4 and 5, peaks appear to be “cut-off” at 17 minutes. This is evidence of the inefficient desorption of strongly adsorbed condensable organics from the carbon surface. For analytical purposes, this inefficiency is problematic. However, when considering the performance of the filter it is critical that organics are not released from the adsorbent surface. It is also apparent from Figures 4 and 5 that desorption at elevated temperatures releases large amounts of volatile organics. In our study we present the semi-quantitative results for the top 25 organics found on the CAIC filter. As might be expected (1) the amount of organics on the upstream portion of the filter is higher than on the downstream portion (2) many of the organics used in the lithography process are found in significant amounts on the CAIC filter.

DISCUSSION

Should the organic contamination level be constant over the 3 years of operation, the CAIC filters evaluated in this work were exposed to approximately 1,600 grams of organics in each year of operation. Over 3 years this corresponds to a carbon adsorption capacity of 14% by weight. At the low concentration level of the reported organics, this level of adsorption capacity is good when we consider a typical adsorption isotherm for activated carbon. This capacity for organics is even better given that the impregnant reduces the available surface area of the carbon.

Although a majority of the organics used at the IMEC site was found in the inlet airstream and the process areas, HMDSO and TMS were not. However, by considering data from an additional site, it was shown that CAIC filters are effective at removing these compounds. All of the organics found in the airstream were also found on the CAIC filter. These filters controlled the level of volatile and condensable organics to a level similar to that of the air sampling and wafer control samples

Additional processing benefits may be realized by the indicated performance of the CAIC filters. From the data for condensable organics, it is possible to estimate the potential extent of wafer masking that may result. If the condensed organic fraction is modeled on the molecular area of dodecane (C_{12}), it is possible to estimate the fraction of a monolayer that results from this level of organic contamination. The amount of condensable organic contamination at the CAIC filter inlet is enough to create 50% of a monolayer of a C_{12} hydrocarbon on a wafer surface. This corresponds to approximately 10^{14} molecules/cm^2. This exceeds the suggested levels for preventing electrical breakdown effects by at least an order of magnitude. However, downstream of the CAIC filter this level is reduced by more than a factor of 100, significantly below the suggested levels to prevent electrical breakdown.

SUMMARY

It is clear that organic contamination can have a detrimental impact on semiconductor processing. These contaminants evolve from a wide variety of sources, such as

(1) solvents used in the cleanroom
(2) photoresists
(3) make-up and return air
(4) construction materials
(5) cleaning solutions
(6) people
(7) wafer storage materials and
(8) shipping materials.

Their adsorption on wafer surfaces usually results in physical, masking and electrical effects. They can impair the lithographic process by reducing light transmission and damaging optical surfaces.

In this study, we have characterized volatile and condensable organic contamination in a lithography processing environment, and at the inlet and outlet of an activated carbon filtration system. In addition, we have evaluated the ability of this filtration system to effectively control and remove these organic contaminants. We have considered the performance of these filters under two extreme filter conditions: a set of filters that have been in the field for 3 years and a new set of filters.

Significant levels of volatile and condensable organic contaminants were found in the processing environment and at the chemical filter inlet. These organic contaminants are representative of those typically found in the lithography areas. However, hexamethyldisiloxane (HMDSO), trimethylsilanol (TMS), ethyl lactate, and 1-methoxy-2-propanol acetate (PGMEA) were not observed at the test.

The CAIC filters exhibited excellent performance against all of the volatile and condensable organic contaminants found in both extreme cases considered. By considering results from an additional study, we have been able to dismiss previous misconceptions regarding the performance of these types of filters for HMDSO and TMS. In fact, for all of the organic contaminants observed in this work, CAIC filters were capable of reducing their concentration to minimum detectable levels.

ACKNOWLEDGMENTS

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