# Improved airborne molecular contaminant filter performance for photolithography

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# ABSTRACT

Airborne molecular contaminants continue to pose cost of ownership challenges in photolithography. Recent advances in understanding siloxane removal have led to the development of an innovative filtration configuration utilizing new media that works in concert to increase overall filter life for acids, bases and silicon containing organic contaminants. This paper examines accelerated testing results, for these state-of-the-art filtration assemblies versus legacy products, to demonstrate improved system performance. The state-of-the-art filtration assemblies have been evaluated in production semiconductor fabs and have shown favorable performance.

Keywords: chemical filtration, airborne molecular contamination, AMC, contamination control, lens protection, lens hazing, Photolithography, hexamethyldisilazane, HMDS, hexamethyldisiloxane, HMDSO, trimethylsilanol, TMS, activated carbon, ion exchange resin, T-topping, surface contamination.

## **1. INTRODUCTION:**

Recent semiconductor manufacturing trends and forecasts have shown increasing investment in semiconductor equipment and, anticipate record equipment spending in 2017.<sup>[1]</sup> A major driver of this investment is increasing semiconductor device demand around the world. In addition to capital investment, semiconductor fabs are increasingly concerned with improving their existing tool and process uptime. As it pertains to airborne molecular contamination (AMC) control, filtration is a primary contributor to tool, material, and process yield protection.

Molecular base contamination, such as ammonia, has been linked to poor feature definition and defects in photolithography, such as T-topping. This first became a problem with the introduction of chemically amplified photosensitive resists nearly 30 years ago. More recently, acid gases have been observed to react with airborne water forming salts, in the presence of high intensity light sources. These salts can then deposit, on optical components, altering light transmission and creating aberrations in the intended pattern. Further, organic contaminants can lead to lens hazing which decreases optical transmittance, thereby decreasing feature definition. This is an increasing problem with decreasing feature size. Finally, refractories and specifically silicon containing refractories such as hexamethyldisilazane (HMDS), hexamethyldisiloxane (HMDSO), and trimethylsilanol (TMS) have shown to be especially problematic. Contamination from these sources can lead to irreversible damage to the optics.

Findings indicate that silicon containing refractories can be effectively removed through the deliberate use of specific adsorbents and chemistries.<sup>[2]</sup> For example, use of acidic surfaces within an AMC filter will facilitate the conversion of TMS into HMDSO which can be more easily removed. Utilizing this mechanism, the lifetime of an AMC filter against total siloxanes can be increased. Further, with proper balancing of additional adsorbents within a filter, the overall lifetime of an AMC filter can also be increased against multiple contaminants.<sup>[3]</sup> The value of a filter providing this performance is observed through the minimization of cleaning and rework, increasing yield, and elongating service intervals. Each of these impacts total cost-of-ownership for AMC filtration.

Leveraging these learnings, this paper will investigate the performance differences between Donaldson Company Inc., BSMmax technology and Donaldson Company Inc. Lens Protection System (LPS) technology. The developmental and experimental process for the creation of this technology will be discussed hereafter, including a comparison to prior generation technology. Finally, results from customer field trials will be presented and discussed.

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# 2. EXPERIMENTAL

#### 2.1 Breakthrough testing

The Donaldson Lithoguard® 12 and Entegris E2600 cabinets are filtration cabinets designed for removing AMC from the air, for lithography tools. The cabinets are designed for a flow of 2600 m<sup>3</sup>/hr. The various filters investigated here use proprietary media. A brief description of the media and nomenclature follows.

Abbreviation	Description
AGR	Basic impregnated activated carbon
ITM <sup>1</sup>	Class of citric acid impregnated activated carbons
OBX <sup>1</sup>	Class of strong acid impregnated activated carbons
SRT	Surface modified activated carbon

The Lithoguard® 12 system contains twelve filters organized such that there are two in series and six in parallel. Each filter contains two beds of adsorbent media. In the Lithoguard® 12 cabinet the air passes through four layers of media total. The BSMmax and LPS versions use the same construction but differ in media used as shown in the following table.

	Filter 1 Layer 1	Filter 1 Layer 2	Filter 2 Layer 1	Filter 2 Layer 2
Lithoguard® 12 BSMmax	AGR	ITM	AGR	ITM
Lithoguard® 12 LPS	AGR	OBX	SRT	OBX

The E2600 cabinet contains twelve filters organized such there are three in series and four in parallel. Donaldson BSMmax and LPS technologies have been packaged in filters to fit in the E2600 cabinet. Each filter contains one adsorbent media layer. Thus, in the E2600 cabinet the air passes through three media layers. The BSMmax and LPS versions use the same construction but differ in media used as shown in the following table.

	Filter 1	Filter 2	Filter 3
E2600 BSMmax	ITM	AGR	ITM
E2600 LPS	OBX	AGR	OBX

Accelerated breakthrough testing was carried out to determine performance for removal of AMC's from an air stream. Testing was performed using various breakthrough test benches set up to evaluate the contaminant of interest. A representative block diagram is given in reference [4]. Testing was carried out on representative media samples scaled to match the face velocity and residence time the media would see in actual application (2600 m<sup>3</sup>/hr). The air streams were conditioned to 25°C and 50% Rh. Testing was carried out at high concentrations, relative to actual application, to accelerate the testing. Concentrations were chosen so a test lasts on the order of days, whereas at application concentrations the filters could last years.

Ammonia was tested at 10ppm, as a surrogate basic gas, using an ion mobility spectrometer type analyzer (PMS AirSentry II). Sulfur dioxide was tested at 10ppm, as a surrogate acid gas, using a phosphorescent type analyzer (Thermoelectron 43C SO<sub>2</sub> analyzer). Hexamethyldisiloxane was tested at 10ppm, as a surrogate organic vapor, using a FTIR type analyzer (MKS MultiGas 2030). Trimethylsilanol was tested at 20ppm, as another surrogate organic vapor, using a FTIR type analyzer (MKS MultiGas 2030). The challenge gas, for ammonia and sulfur dioxide, were prepared using dynamic dilution of a certified gas mixture. To generate the hexamethyldisiloxane, a small flow of clean dry air was bubbled though liquid HMDSO at 10°C. This stream of saturated vapor was then diluted to obtain the desired concentration and flow rate. Trimethylsilanol was generated using the method described in [2]. This method involves the gas phase hydration reaction of hexamethyldisilozane to trimethylsilanol and ammonia with a small side conversion to hexamethyldisiloxane. Due to the multiple reactions taking place, the results were presented as total silicon efficiency. This accounts for all the silicon containing components present.

<sup>&</sup>lt;sup>1</sup> This media can have varied surface area, impregnation level and mesh size for the various implementations.

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#### 2.2 Field trials

Several end customers installed LPS filters in cabinets on production tooling for trials. On regular intervals a set of filters in series were removed from the cabinet and returned to Donaldson for analysis. Since the Lithoguard® 12 cabinet has six sets of filters in parallel, this allowed the changeout of only one set at a time. The remaining sets would stay in place and be removed later to obtain additional data sets.

When filters were returned to Donaldson, the media was extracted, homogenized, and breakthrough tests were performed on the used media, as described in section 2.1. This breakthrough test data was then compared to the same test on fresh media to determine the percent remaining capacity at the 99% efficiency breakthrough point.

## **3. RESULTS AND DISCUSSION**

#### 3.1 Lithoguard® 12: BSMmax vs LPS

#### 3.1.1 Ammonia

Ammonia was used as a surrogate compound for gas phase basic contaminants. Acid impregnated activated carbons have excellent removal efficiency, and life, for certain basic gases. Figure 5.1 shows the NH<sub>3</sub> efficiency curves and resultant performance of Lithoguard® 12 BSMmax and Lithoguard® 12 LPS. As noted in section 2.1, ITM is used in Lithoguard® 12 BSMmax filters, while OBX is used in Lithoguard® 12 LPS filters. The acid impregnated adsorbents, ITM and OBX, in each Lithoguard® 12 system was designed for the removal of basic and organic contaminants. Both Lithoguard® 12 BSMmax and Lithoguard® 12 LPS have excellent removal efficiency; >99.5% at the inlet concentration of 10 ppm ammonia, as tested per section 2.1 above.

The NH<sub>3</sub> capacity with Lithoguard<sup>®</sup> 12 LPS was about 30% better than the Lithoguard<sup>®</sup> 12 BSMmax. The increase in NH<sub>3</sub> life is attributed to the stronger acid impregnation and a higher surface area in OBX as compared to ITM.

## 3.1.2 TMS

Trimethylsilanol (TMS) was selected for gas phase silicon containing contaminants, because removal of TMS from fab environments is critical to avoid damaging crucial surfaces, e.g. lenses and other optical components.<sup>[2]</sup> Figure 5.2 shows total Si efficiency curves for the Lithoguard® 12 BSMmax and Lithoguard® 12 LPS. Note that the total Si contaminants are the sum of reaction components according to the hydrolysis reaction of HMDS to TMS and HMDSO.<sup>[2]</sup>

Remarkably, even though TMS is very difficult to remove, both Lithoguard® 12 BSMmax and Lithoguard® 12 LPS have excellent removal efficiency, >99% at the inlet concentration of 20 ppm TMS. Since TMS is lower molecular weight and more volatile than other organosilanes, such as HMDS or HMDSO, it tends to be very difficult to control with only activated carbon or acid impregnated carbon. Previous work has shown acid impregnated carbon can be used to convert TMS to HMDSO, and HMDSO can be removed by physisorption with acid gas removing carbon.<sup>[2]</sup> As expected, the total Si removal efficiency curve with BSMmax shows effective TMS removal; because ITM converts TMS to HMDSO which can be adsorbed by the downstream filter media layers. The TMS capacity, at 99% removal efficiency, of Lithoguard® 12 LPS, was about 45% better than Lithoguard® 12 BSMmax. The increase in the LPS configuration is attributed to the addition of the SRT adsorbent in the LPS configuration with its modified surface area, and chemistry, from treatment with a strong acid. The addition of the AGR & OBX combination in Lithoguard® 12 LPS was incorporated for removing total silicon containing compounds and basic gas. OBX is not only impregnated with a stronger acid than ITM, but also possesses a greater amount of acid sites, thus affecting the TMS conversion to HMDSO. These results confirm the combination of AGR-OBX-SRT-OBX in Lithoguard® 12 LPS significantly increases TMS removal versus the combination of AGR-ITM-AGR-ITM in Lithoguard® 12 BSMmax, because of an improved acid catalyzed reaction for TMS. These Lithoguard® 12 LPS results are very encouraging for extending protection against lens hazing in the lithography tools.

## 3.1.3 HMDSO

Hexamethyldisiloxane (HMDSO) was used as a surrogate compound for gas phase silicon containing condensable organic contaminants. HMDSO is a bulky, condensable organic compound so it is primarily adsorbed through physisorption.

Figure 5.3 shows both Lithoguard® 12 BSMmax and Lithoguard® 12 LPS have excellent removal efficiency, >99% at the test concentration of 10 ppm HMDSO as tested and referenced previously. At 99% removal efficiency, the Lithoguard® 12 LPS efficiency curve shows a minimum of 9% increased performance over Lithoguard® 12 BSMmax. While the HMDSO removal by LPS was improved over BSMMax, it was not increased to the same extent as TMS. As discussed in the TMS section 3.1.2, the stronger and greater amount of acid impregnated carbon is beneficial for the TMS conversion to HMDSO. However, this suggests that the greater amount of acid impregnation on the OBX versus ITM reduces the available OBX surface area for HMDSO removal. It is then suggested the additional removal of HMDSO with Lithoguard® 12 LPS is due to the use of SRT adsorbent. The SRT in the Lithoguard® LPS system has a greater HMDSO removal capacity as compared to other AGR, OBX, and ITM adsorbents, due to the modification of chemistry and surface area.

## 3.1.4 SO<sub>2</sub>

 $SO_2$  was used as a surrogate compound for acid gas contaminants. Non-impregnated and impregnated activated carbons have removal efficiency and life for certain acid gases. AGR is used in both Lithoguard® 12 systems and is an acid gas removal carbon. Historically, the Lithoguard® 12 BSMmax significantly exceeds the  $SO_2$  lifetime requirement in semiconductor fabs and lithography tools. Figure 5.4 shows the excellent removal efficiency and long filter life for  $SO_2$  on both Lithoguard® 12 BSMmax and LPS systems.

We have noticed that the SO<sub>2</sub> efficiency curve, with Lithoguard® 12 BSMmax, is better than that of Lithoguard® 12 LPS; because there are two AGR beds in the Lithoguard® 12 BSMmax, versus only one AGR bed is used in the Lithoguard® 12 LPS. The replacement of the AGR bed was to enhance the removal capacity of TMS, refractories, and condensable organic contaminants, while still having SO<sub>2</sub> removal capacity in excess of other AMC contaminants, and tool manufacture requirements.

## 3.2 E2600: BSMmax vs LPS

The combination of OBX-AGR-OBX is used in E2600 LPS while ITM-AGR-ITM is used in E2600 BSMmax. We noted that the OBX and ITM carbons in E2600 systems are different from OBX and ITM in Lithoguard® 12 systems regarding activation, granular size, and acid impregnation level. These differences were needed to balance performance for the various contaminants while fitting the different form factor and flow path of the cabinets.

## 3.2.1 Ammonia

Ammonia was used as a surrogate compound for basic gas contaminants. The  $NH_3$  efficiency curves for E2600 BSMmax and LPS are shown in Figure 5.5. Both E2600 BSMmax and LPS have excellent removal efficiency, >99.5% at the test concentration of 10 ppm ammonia, as tested per section 2.1 above. The acid impregnated carbon in each E2600 system was designed for the removal of basic contaminants, ITM for E2600 BSMmax, and OBX for E2600 LPS. The  $NH_3$  capacity with E2600 LPS was about 30% better than that with E2600 BSMmax. The increase in  $NH_3$  life is attributed to the stronger acid impregnation in OBX as compared to ITM.

# 3.2.2 TMS

Trimethylsilanol (TMS) was used as a surrogate compound for gas phase silicon containing contaminants. Figure 5.6 shows total silicon efficiency curves for E2600 BSMmax and LPS. Note that the total silicon contaminants is the sum of TMS and HMDSO according to the hydrolysis reaction of HMDS to TMS and HMDSO. Both E2600 BSMmax and LPS have excellent removal efficiency, >99% at the test concentration of 20 ppm TMS. Based on what was previously discussed regarding TMS removal, for Lithoguard® 12 systems above, the results shown in Figure 5.6 for E2600 BSMmax and LPS were expected. The TMS capacity at 99% removal efficiency of E2600 LPS is slightly better than that of E2600 BSMmax, due to the lower impregnation level of OBX carbon versus ITM. These results confirm the acid catalyzed reaction to convert TMS to HMDSO and the combination of OBX-AGR-OBX and ITM-AGR-ITM have excellent removal capacity and efficiency for TMS.

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#### 3.2.3 HMDSO

Hexamethyldisiloxane (HMDSO) was used as a surrogate compound for silicon containing and condensable organic contaminants. HMDSO is a bulky and condensable organic compound. This compound is primarily adsorbed through physisorption. Figure 5.7 shows both E2600 BSMmax and LPS have >99% removal efficiency, at the test concentration of 10 ppm HMDSO as referenced above. The efficiency curve of E2600 LPS shows 90% improvement as compared to that of E2600 BSMmax. This is understood to be because OBX has more available surface area versus ITM.

## 3.2.4 SO<sub>2</sub>

 $SO_2$  was used as a surrogate compound for acid gas contaminants. Note that non-impregnated and impregnated activated carbons can have removal efficiency and life for certain acid gases. Figure 5.8 shows the excellent removal efficiency and long filter life for  $SO_2$  on both E2600 BSMmax and E2600 LPS systems. The  $SO_2$  efficiency curve of E2600 LPS is 10% better than that of E2600 BSMmax, because OBX has more surface area than ITM. It suggests that  $SO_2$  was reacting with  $H_2O$  to form  $H_2SO_3$  and/or  $H_2SO_4$  which can be chemisorbed, as well as physiosorbed, on the surface of activated carbon.

## 3.3 Field trial discussion

Field trials are the only reasonable way to confirm full filter performance at the low concentrations seen in actual application. Air monitoring and remaining life tests typically are used in conjunction to evaluate performance and qualify new systems. Unfortunately air monitoring data will not be discussed here.

The remaining life test performed by Donaldson is a reasonable test to confirm that the filters still have remaining capacity after a given service time. The remaining life tests do have some limitations that should be noted. Remaining life tests are a destructive test. Ideally a core sample would be used but this is not practical, so a sample is extracted and homogenized. The test is also accelerated by running at high concentrations.

Donaldson evaluated returned Lithoguard® 12 LPS filters from four end customer trials and E2600 LPS filters from one end customer trial. Figure 5.9 is a scatter plot of remaining capacity via a remaining life test as a function of time installed for all customers. All returned filters thus far have shown significant remaining capacity in their trials. For some unexplained reason, many of the trials show a larger reduction in capacity in the first 6 months. Subsequent testing at one year or longer do not reflect this. This demonstrates the importance of taking multiple data points over a longer period of time and do not rely so much on a single point in time.

## 4. Conclusion

This paper investigated the performance differences between Donaldson Company Inc. BSMmax technology and LPS technology. It was observed that using specifically selected and arranged adsorbents, the effective service life of LPS filters has increased over equivalent BSMmax filters. In Lithoguard® 12 systems, the increased service life for amines (NH3), organics (HMDSO), and refractories (TMS) was 30%, 9%, and 45%, respectively. In E2600 systems, increases of 30%, 90%, 3%, and 10% are observed for amines (NH3), organics (HMDSO), refractories (TMS), and acids (SO<sub>2</sub>), respectively. The service life against acid gas contamination for Lithoguard® 12 systems continues to be higher than industry requirements and significantly longer than other sources of contamination.

This increased service life provides semiconductor tool owners the opportunity to extend their filter service intervals without sacrificing the critical protection their equipment requires. The field trials, conducted over the previous three years in production fab conditions, demonstrate increased lifetime and protection of valuable materials and equipment. This benefit immediately impacts the total cost-of-ownership for AMC filtration products while also providing the opportunity to increase tool and process uptime. As semiconductor product demand continues to increase, the importance of total cost-of-ownership will also increase.

## 5. Figures and data

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5.1 Basic (NH<sub>3</sub>) AMC control for Lithoguard® 12: BSMmax vs LPS







#### 5.4 Acidic (SO<sub>2</sub>) AMC control for Lithoguard® 12: BSMmax vs LPS





#### 5.5 Basic (NH<sub>3</sub>) AMC control for E2600: BSMmax vs LPS







5.7 Organic (HMDSO) AMC control for E2600: BSMmax vs LPS









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#### **Full citation**

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