

# Prevention of Airborne Molecular Contamination

MIKAEL FORSLAND & SEAN O'REILLY, *Camfil AB, Sweden*

## ABSTRACT

**C**leanroom environments have classically been constructed to protect persons or processes against particulate contamination in the air. Today, the amount of airborne gaseous species arriving at a surface is much larger than that of particulate species. This fact is already well known under the name "airborne molecular contamination" (AMC). AMC is far more difficult to control than particles. Nevertheless, there are solutions available that concentrate on either eliminating the source or purifying the contaminated air. Some such solutions are described here.

## INTRODUCTION

Cleanroom environments have classically been constructed to protect persons or processes against particulate contamination in the air and to maintain a very well controlled environment in general. Besides particle contamination, demands on other controlled environmental parameters must be met, including temperature, humidity, vibrations and electromagnetic radiation. In particular, an expanding area of concern is the presence of chemical gases in the air. Today, the amount of airborne gaseous species arriving at a given surface is much larger than the amount of particulate species. This fact is already well known and discussed within the microelectronics industry under the name "airborne molecular contamination" (AMC). Wafer hazing, corrosion and uncontrolled doping are some examples of AMC-induced defects resulting in reduced yield. This article will discuss definitions of AMC, its occurrence and the problems caused by it, as well as describing solutions for particle filtration and chemical filtration with low chemical outgassing suitable for the most advanced applications in the microelectronics industry. However, AMC may be of equal importance in any other cleanroom-based production situation, depending on the processes used.

Semiconductor Equipment and Materials International (SEMI), in the SEMI F21-951 standard, has given a classification system for AMC gases [1]. This standard divides AMC into four classes: acids (MA), bases (MB), condensables (MC) and dopants (MD). In order to show kinship with the classification system for particles used in FS 209E, the classes also use a 1, 10, 100, ... notation but refer to a concentration in pptM instead of a number of particles per unit volume (pptM denotes

TABLE 1.  
THE SEMI AMC CLASSIFICATION SYSTEM

Material Category	Classification				
	1	10	100	1000	10 000
Acids	MA-1	MA-10	MA-100	MA-1000	MA-10 000
Bases	MB-1	MB-10	MB-100	MB-1000	MB-10 000
Condensables	MC-1	MC-10	MC-100	MC-1000	MC-10 000
Dopants	MD-1	MD-10	MD-100	MD-1000	MD-10 000

parts per trillion,  $10^{-12}$ , by number of moles of substance; a mole is  $6.022 \times 10^{23}$  molecules of any substance). The SEMI classification system is shown in Table 1.

In order to assess potential problems the sources of AMC must first be identified. If AMC at trace levels is a matter of concern then AMC candidates from numerous sources need to be considered. The four most important source groups are:

- actual chemicals used in microelectronics production
- personnel – the human body releases many substances, including ammonia
- outgassing from construction materials used in filters, ceilings, floors, furniture and production equipment
- make-up air contaminated by urban pollutants, e.g. sulfur and nitrogen oxides and ozone.

Measurement techniques, source minimisation and appropriate filtration solutions will be discussed below.

After obtaining a system to classify AMC by nature and level, and identifying the sources, the next step is to estimate at what level AMC may actually impair production yields. In order to succeed with this the chemical behaviour of an AMC class must be correlated to the actual production steps.

A classic AMC paper is the 1995 SEMATECH forecast for permissible AMC concentrations in the 250 nm process [2]. Data on AMC-related process defects were collected from the industry by interviews and by literature search and were ranked according to reliability using a confidence level. From these data four production steps, deemed as most sensitive to AMC, were selected: pre-gate oxidation, salicidation, contact formation and DUV photolithography. The findings are summarised in Table 2, which shows the four process

steps versus AMC class and the maximum permissible concentration together with a maximum sit time.

From Table 2 it is evident that pre-gate oxidation is extremely sensitive to dopants, that salicidation and contact formation are most sensitive to acids and that DUV photolithography is most sensitive to bases. However, in the case of dopants the forecast has not been met since the problem can be assessed by adjusting process parameters.

Today, AMC limitation requirements are forecasted by the 1999 issue of the International Technology Roadmap for Semiconductors (ITRS-99) [3]. According to ITRS-99, the "percentage of process steps affected by non-particulate or molecular contamination is expected to increase". Important areas of AMC reduc-

tion are, for lithography, the control of airborne ammonia/amine concentrations and ionic/metal contaminants and, for defect reduction, the control of organic AMC, which is a cause of lens clouding.

Furthermore, the use of wafer isolation technology such as enhanced clean devices (ECDs) or minienvironments is emphasised as one of the important needs for future processes. These small, confined spaces will put special demands on AMC filtration in terms of low pressure drop, cleanliness and minimum form factor in order to avoid costly redesign of existing constructions.

A comparison of the demands on the 250 nm process and the present forecast of ITRS-99, discussed above, is shown in Table 3.

Comparing the forecast of 1995 with present (2000) levels, Table 3 shows that the requirements on bases for lithography are still at the same level (1000 pptM). For the gate (pre-gate oxidation) metals are important (0.3 pptM) and the dopants stressed earlier are less critical (>10 pptM). Organics (condensables) are more important, with the present levels at 200 pptM. Also, for salicidation and contact formation the levels are much lower for both acids and bases.

**TABLE 2: SEMATECH FORECAST OF AMC LIMITS FOR SELECTED PROCESS STEPS IN THE 0.25  $\mu$ m PROCESS**

Process Step	PROJECTED AMC LIMITS IN (pptM)				
	Max sit time (h)	MA	MB	MC	MD
Pre-Gate oxidation	4	13 000-50	13 000-50	1 000-75	0.1-90
Salicidation	1	180-50	13 000-25	35 000-75	1 000-75
Contact Formation	24	5-50	13 000-25	2 000-75	100 000-75
DUV Photolithography	2	10 000-75	1 000-90	100 000-50	10 000-50

The figure after the actual concentration shows the percentage confidence level of the data.

### PREVENTION OF AMC

If AMC may be of concern one must devise a strategy to control the problem and choose the most suitable prevention techniques. It is of the utmost importance to make AMC prevention a general responsibility within a fab and to involve all specialist groups in order to find the best solution. A suggested strategy includes the following steps:

1. Perform measurements.
2. Identify if any of the AMC substances present will affect the processes.

**TABLE 3. A COMPARISON OF THE LIMITS FOR THE 250 nm PROCESS AND THE PRESENT FORECAST OF ITRS-99**

#### Airborne Molecular Contaminants (pptM)

Year	1995	1999	2000	2001	2002	2003	2004	2005	2008	2011	2014
Tehnology Node	250 nm	180 nm			130 nm			100 nm	70 nm	50nm	35 nm
Lithography-Bases (as amine, amide, or NH <sub>3</sub> )	1000	1000	1000	1000	750	750	750	750	< 750	< 750	< 750
Gate-Metals (as Cu, E=2 x 10 <sup>-5</sup> )	?	0,3	0,3	0,25	0,2	0,2	0,15	0,1	0,07	< 0,07	< 0,07
Gate-Organics (as molecular weight >= 250, E=1 x 10 <sup>-3</sup> )	1000	200	170	130	100	90	80	70	70	50	< 50
Organics (as -CH <sub>2</sub> )	–	3600	3000	2400	1800	1620	1440	1260	1260	900	< 900
Salicidation contact-acids (as Cl <sup>-</sup> , E=1 x 10 <sup>-5</sup> )	180 / 50	10	10	10	10	10	10	10	10	10	10
Salicidation contact-bases (as NH <sub>3</sub> , E=1 x 10 <sup>-6</sup> )	13000	40	32	24	20	16	12	10	4	< 4	< 4
Dopants (P or B, As Sb)	0,1*	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10

- Trace sources (if possible).
- Eliminate point sources (if possible).
- Use chemical filtration to reduce diffusive sources within the fab to meet acceptable (or forecasted) limits for the process.
- Use chemical filtration to filter outdoor sources if necessary.
- Isolate the most sensitive processes in minienvironments and by using special chemical filtration solutions.

Actions and solutions concerning these steps will be discussed in more detail below.

### MEASUREMENTS, STEP 1

Before searching for solutions, the extent of the problem should be estimated by measurements. The available monitoring techniques for detection of AMC at ppb (parts per billion,  $10^9$ ) or ppt (parts per trillion,  $10^{12}$ ) levels can be divided into

- analyser techniques
- active sample collection techniques
- passive sample collection techniques.

The analyser techniques give “real time” data and can be used for surveillance but are often very expensive. One method in use is ion mobility spectroscopy (IMS), which gives the possibility of measuring multiple gases.

Active sample collection techniques use a pump to gather an air sample into a liquid or solid adsorption medium. Impingers and sorption tubes are the most common sampling techniques for inorganic and organic substances, respectively.

Passive sample collection techniques use diffusive sampling, i.e. the AMC substance is transported into the sampling device by natural diffusion. These techniques combine a good detection limit and ease of use, often at a very reasonable cost.

Both active and passive sample collection give a value averaged over the sampling period and can be used for both single- and multiple-substance analysis. Where to monitor is an important question, since the concentration may vary within the area of interest.

In order to serve the customer with a measurement tool suitable for screening a fab before chemical filter installation and also for checking working installations, Camfil has developed the Gigacheck™, shown in Figure 1. This uses a gas-specific diffusive sampling technique that provides analysis of a selected group of substances at ppb or lower detection limits.



Figure 1  
Photograph of Gigacheck™

The Gigacheck™ has some excellent advantages over other available techniques, such as better detection limits, ease of use, a holder design which makes the actual exposure controlled and repeatable, speedy analysis and a very reasonable cost. This method also discards chlorine from salt particles when gaseous  $\text{Cl}_2$  and  $\text{HCl}$  are measured. Both single and multiple set-ups are available. Exposure times are normally around two weeks for sub-ppb detection.

### IDENTIFICATION AND TRACING, STEPS 2 AND 3

The most detrimental AMC gases for a given process should be identified from in-house process knowledge together with the general guidelines given by the ITRS, etc. Sources can then be traced using screening measurements, e.g. Gigacheck™ for ammonia at several different locations within the room and ducts in order to map the average “topography” of ammonia. The AMC contamination found may often be a chemical used in production or a by-product thereof.

### ELIMINATING OR MINIMIZING DETRIMENTAL AMC, STEP 4

Any contamination by chemicals used in production can and should be confined or minimised by using “cleaner” processes and process equipment. Process people should naturally consider the possibility of process modification in order to eliminate these problems.

Another sound preventive step is to use materials with low outgassing levels or at least to consider this when retrofitting components or refurbishing a fab. For the

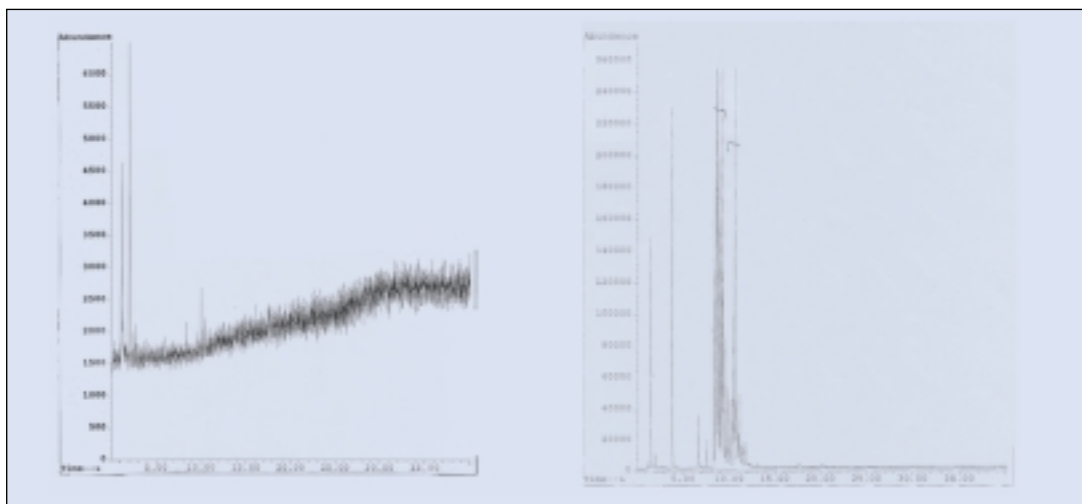


Figure 2  
Low and high outgassing from two samples of hot-melt adhesive

HEPA and ULPA air filters used in fabs today, we have developed excellent low-outgassing solutions in the form of low-boron and PTFE particle filtration media.

When comparing products it is important to evaluate the whole construction. A HEPA filter system consists of pleated media, a separation system, a potting material, a frame, and gaskets or a gel seal. In order to create a low-outgassing product each of these components should exhibit low outgassing characteristics. The material should be tested with TD-GC-MS. In Figure 2 one can see the difference between the chromatograms of relatively low- and high-outgassing hot-melt adhesives used for separators in a close-pleat filter.

In the chromatogram of the lower-outgassing hot-melt adhesive on the left, only the enlarged baseline is present; in the chromatogram of the higher-outgassing adhesive on the right, many peaks indicating outgassed organic compounds can be seen.

Contamination by boron originating from HEPA and ULPA filters as a result of a reaction between standard glass media and air contaminated with hydrogen fluoride, HF, has been reported. This can be avoided today by the use of low-boron media. A normal borosilicate

glass contains 8-11% of  $B_2O_3$ . Camfil can guarantee a low-boron product with less than 0.05%  $B_2O_3$ ; actual measurements show a  $B_2O_3$  content as low as 0.03%. For a completely boron-free and low-outgassing medium, our e-PTFE media should be used.

In addition to chemical resistance, e-PTFE media have the advantage of being resistant to physical damage. One can actually scratch a close-pleated e-PTFE medium with a fingernail without causing leakage. A chromatogram obtained from an e-PTFE medium is shown in Figure 3.

In summary, low-outgassing alternatives for filter components are available and these components are employed in specially developed products for the micro-electronics market.

In the case of an existing fab where large quantities of AMC exist owing to outgassing, chemical filtration is probably the best solution.

### CHEMICAL FILTRATION OF RECIRCULATING AIR, STEP 5

Typical examples of cases when chemical filtration of recirculating air is the only technologically feasible or cost-effective method to remove AMC gases are:

- contamination that originates from a large number of diffusive sources
- unavoidable process by-products
- operator-related leaks or spills.

Moreover, the large amount of recirculated air versus fresh make-up air will lead to an accumulation of substances generated inside the cleanroom.

For such a special application a chemical filter needs to be optimized accordingly. Camfil's Gigasorb™ filter series consists of spherical carbon beads, supported by an open grid of polyurethane foam contained in a frame system. A special bonding method makes it possible to cover the foam walls with a monolayer of beads, which results in an even sorption performance. The structure is shown in Figure 4.

For every site of a chemical filtration installation, different technical parameters will be of importance. The important parameters depend on a vast number of factors, including what type of air stream is handled (recirculating air or make-up air), the types of AMC present and, of course, the concentration levels acceptable for the process. To evaluate and optimise a chemical filter one can use the following factors:

- compatibility
- efficiency
- capacity
- energy loss
- cleanliness.

These terms will be explained and used to describe the performance of Gigasorb™ in recirculating air.

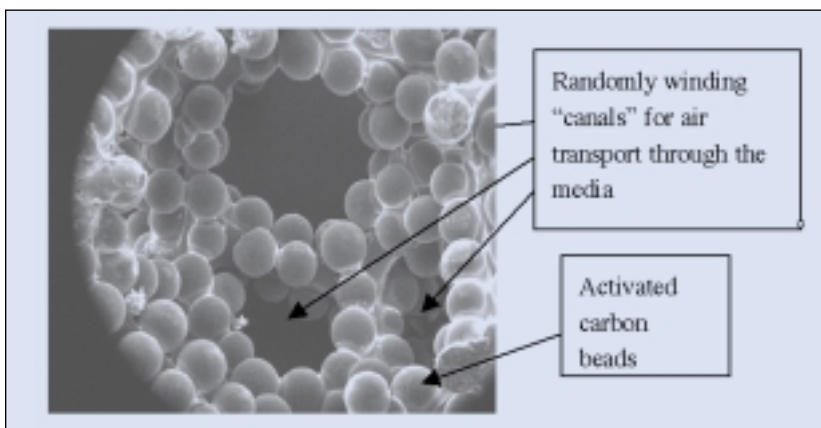
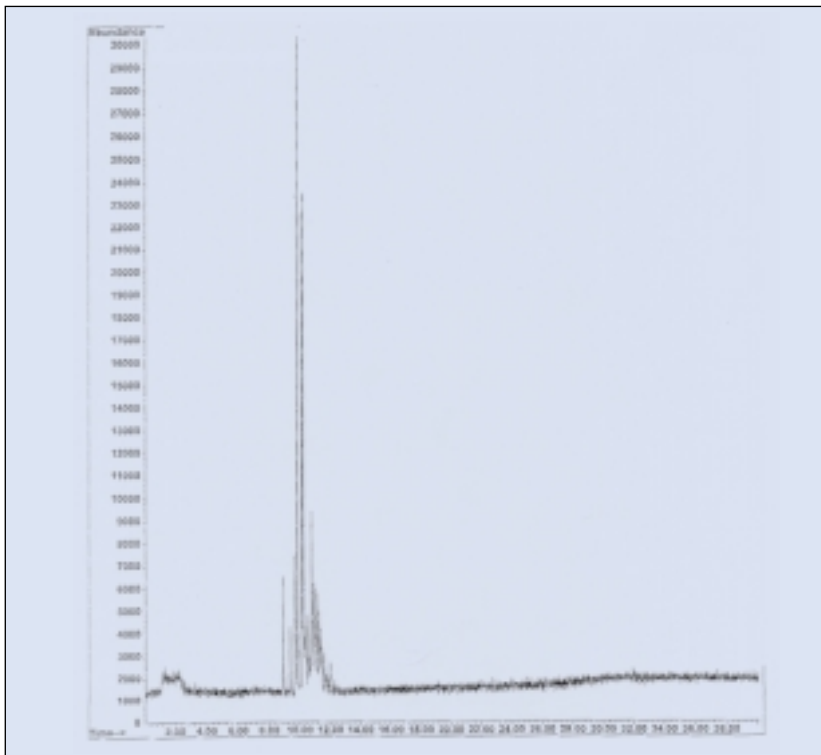
### COMPATIBILITY

A compatible chemical filter should be active towards the AMC or combination of AMCs that is present.

Depending on the type of AMC to be removed, different adsorption techniques and materials are used. An acid or base is removed by chemisorption (adsorption onto a surface followed by a chemical reaction), using different impregnants for acids and bases. Condensables and organic substances are removed by physisorption onto a high-surface-area adsorbent. The most widely used is activated carbon, which will collect a broad size range of organic substances.

Figure 3 (below)  
Chromatogram showing no outgassing from PTFE medium

Figure 4 (bottom)  
Structure of Gigasorb medium





The Gigasorb™ beads are made from a high-quality carbon and are available in three versions for removal of acids, bases and condensables. There is no special version for dopants. However, dopants will still be removed if the dopant gas has acidic, basic or organic properties. For instance the distribution of boron within a clean-room is believed to involve  $\text{BF}_3$ , which, chemically, is a weak acid and is therefore adsorbed as an acid. Ozone can also be effectively removed. Furthermore, the framing system adds a “mechanical compatibility” by being available in types suitable for both a plenum (panel type) and recirculation ducts (cell type), allowing up to four or two layers of exchangeable medium packs, respectively (see Figure 5). This makes it possible to adsorb acids, bases and condensables in one filter, or to increase the capacity for one or two AMC types. It is also possible to complement the filter with other media after initial installation, if needed owing to a production change. Also, certain designs feature the ability to replace or change the medium when it is consumed, without removing the frame.

## EFFICIENCY

The efficiency is defined as the percentage of the gas concentration removed and is mainly controlled by two factors: mass transport and contact time. Other physical parameters, such as temperature, pressure and relative humidity, will also influence the efficiency.

The mass transport involves all steps from the bulk flow of gas through laminar layers close to the carbon beads to diffusion within the pores of the beads and final sorption. Mass transport to the beads is maximised by the supporting grid of polyurethane foam, which gives a random flow pattern through the medium layer, as can be seen from Figure 6.

The next step is to maximise transport within the carbon beads. This is achieved by minimising the diffusion distances within the carbon using small-diameter beads (~0.5 mm). The contact time is often too dependent on the application to render an optimisation possible for a general case.

As an example, the initial efficiency at 0.12 sec of stay time for air containing 11 ppb  $\text{NO}_2$  (one medium layer), 300  $\mu\text{g}/\text{m}^3$  total organic content (TOC) (three medium layers), 7 ppb  $\text{NH}_3$  (three medium layers) and 16 ng/ $\text{m}^3$  of boron (one medium layer) is shown in Figure 7.

## CAPACITY

For an impregnated carbon the amount of impregnant is normally 2–15%(w) of the medium. From the carbon weight, percentage of impregnant and molar relationship (impregnant versus the AMC compound in question), the theoretical adsorption capacity can be calculated. This corresponds to the maximum amount of the AMC that the filter can remove, and thus the lifetime of the filter. However, when this endpoint is reached the efficiency is actually 0%. For this reason the practical adsorption capacity is determined by the degree of separation necessary, i.e. the lowest acceptable efficiency. The capacity is also dependent on many other factors, including the actual compound and its concentration, other compounds present, the engineering of the adsorption medium and the amount of it present. The temperature, pressure and relative humidity will also influence the capacity.

The Gigasorb™ activated-carbon beads use 10–15%(w) of impregnant and the lightest grade has a weight of more than 3500 g/ $\text{m}^2$ . Since the practical adsorption capacity is determined by many factors depending on the actual installation, a special calculation is made in each case and no general data will be presented here.

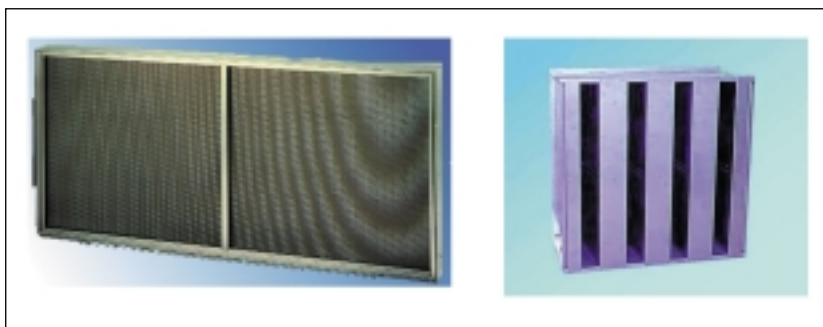


Figure 5 (above)  
Panel and cell types of filter

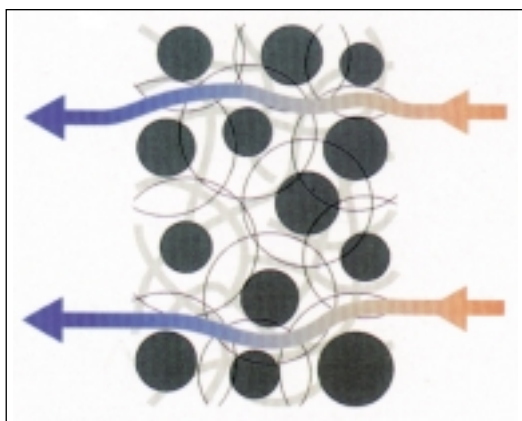


Figure 6 (left)  
Illustration of randomised flow  
in order to achieve high mass  
transport

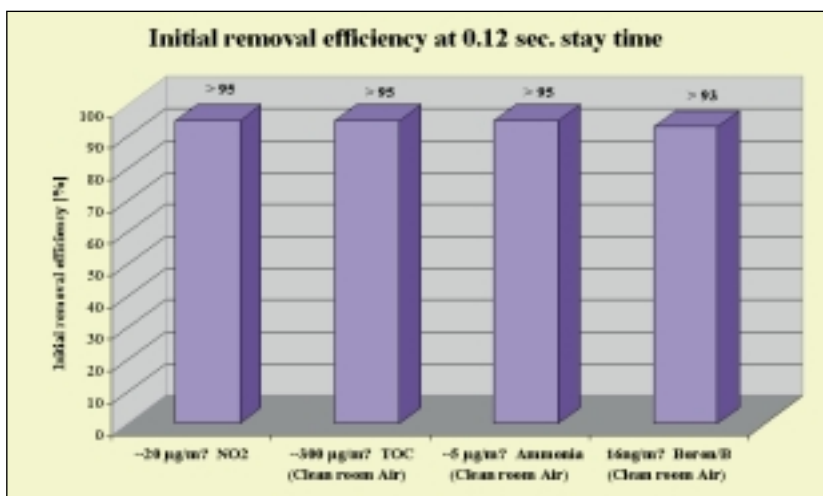


Figure 7  
Initial removal efficiency of  
Gigasorb

## ENERGY LOSS

After achieving the necessary chemical performance in an installation in terms of compatibility, efficiency and capacity, the next step is to minimise running costs, where the cost of energy is one of the major factors. The energy cost is directly dependent on the pressure drop  $\Delta P$  across the chemical filters. The Gigasorb™ filter series is optimised for a minimum pressure drop. The open, permeable foam structure features an extremely low pressure drop and the frame adds only a minor flow resistance. A panel filter for plenum or FFU use with three layers of medium packs adds only ~20 Pa at a face velocity of 0.3 m/s. A cell-type (610 × 610 mm frame) filter for recirculation ducts with one layer of medium adds ~50 Pa at a flow of 3400  $\text{m}^3/\text{h}$  (one-layer type). These figures represent extremely low pressure drops for chemical filtration, which also permit retrofitting of chemical filters into cleanrooms and minienvironments where the available fan capacity is limited.

## CLEANLINESS

A chemical filter should not release detrimental amounts of particles or chemical outgassing. This can be controlled by using special grades of adsorption media and construction materials selected for low outgassing characteristics.

The unique combination of very hard carbon and special production methods results in no broken beads, and therefore the emission of particles is minimal. A lab study reveals only a few particles ( $>5\ \mu\text{m}$ ) per cubic foot of air. The organic outgassing of the media is also very low, as can be seen in the chromatogram in Figure 8. Actually, the only peaks seen originate from solvents used to clean the sample packaging (A) and from instrument noise (B).

## CHEMICAL FILTRATION FOR MAKE-UP AIR, STEP 6

In the case of make-up air the demands are different from those for recirculation, and the optimum chemical filtration factors are different. For this case we have constructed the Camcarb™ system, which is a modular system that adapts a cost-effective granular carbon medium to different air duct sizes. The repetitive unit is a filter with a concentric-cylinder design, where the air enters the end plate of the inner cylinder, passes through a perforation in the cylinder wall into a concentric slot containing the carbon and leaves through a perforation in the outer cylinder wall. Once the system is installed, you can then replace the medium for a more cost-effective long-term, environmentally friendly solution.

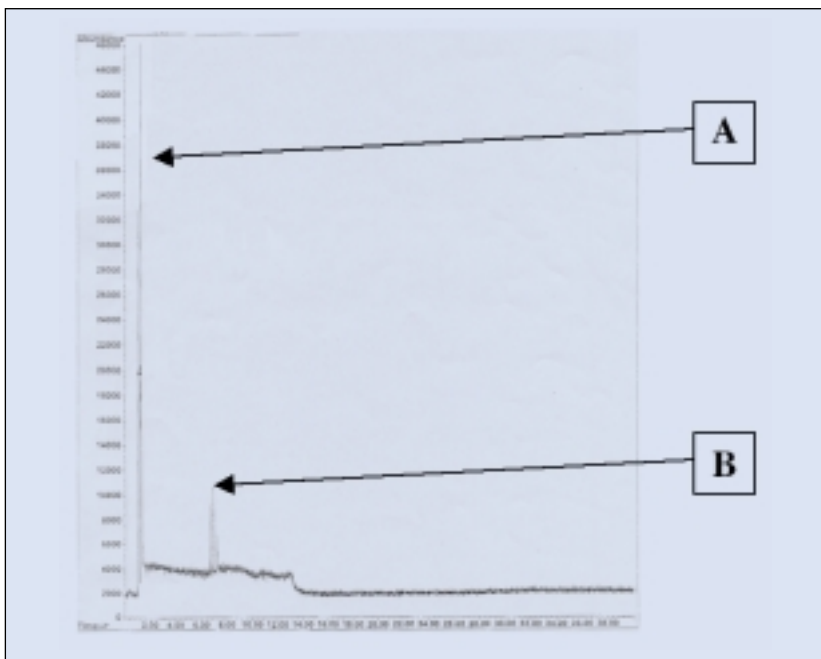
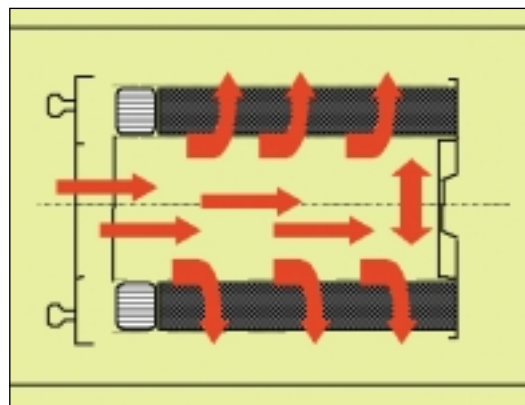


Figure 8 (above)  
Outgassing characteristics of  
Gigasorb

Figure 9 (right)  
Sectional view illustrating the  
flow pattern through a Camcarb  
cylinder



Another very important advantage of this system is its excellent attenuation values; we have independently tested the system and found that the noise reduction is quite the same as that of the silencers in an AHU. This gives three major cost-saving factors:

- space (in the AHU)
- Cost (saving in pressure drop for the attenuator and major reduction in pressure drop if you remove the attenuator)
- As more fabs start with addressing AMC problems with installing chemical filtration in the MUA (make up air), the ability to remove the attenuator and replace with the Camfil Camcarb System can be an ideal solution.

A cross-sectional view of the cylinder is shown in Figure 9.

Using the same chemical filtration factors as above, we need *compatibility* with the normal outdoor pollution such as sulphur dioxide, nitrogen oxides, ozone, ammonia and various natural and man-made volatile organic compounds. This can easily be achieved with a selection of different impregnants in the system. The *efficiency* is dependent on the contact time. *Capacity* is high thanks to a large amount of carbon, for example more than 20,000 g of carbon per 610 x 610 mm module. The energy *loss* can be customized to suit the end-user demand, with different bed depths and lengths to suit the given concentrations and allowable space. The *cleanliness* will of course be typical of granular carbon and therefore will only be acceptable before the particulate filtration steps in the make-up air system. This system is therefore ideally suitable for application to the make-up air of a fab.

## SPECIAL CHEMICAL FILTRATION FOR MINIENVIRONMENT AND TOOL APPLICATIONS, STEP 7

In order to meet the increasing demands of cleanliness, one important route is the use of ECDs or minienvironments. These terms describe a clean space separated from the rest of the cleanroom and containing no people. There are obvious benefits from separating the most sensitive processes from the rest of the cleanroom and at the same time including an extra stage of particle filtration. Many types of minienvironments are in use today, and if there is any possibility of AMC damage to the enclosed process, chemical filtration should be installed. Often the available space for chemical filtration is limited, especially in the case of retrofitting an existing construction, and also the available fan power is often limited.

For these kind of installations a customized Gigasorb filter can be the ideal solution. Thanks to the special medium structure, filters can be produced in virtually any size, from  $20 \times 20\ \text{mm}$  up to  $1200 \times 1200\ \text{mm}$  or as large as required. Or in any shape: round, square, triangular or whatever suits the minienvironment or tool in question. The built-in height can be as low as 25 mm and the pressure drop as low as 7 Pa. Types of media can also be combined in any order to remove acids, bases, condensables, dopants or oxidants.

Another possibility is to construct a combination filter that fits into the already available space for particle filters in a minienvironment and provides the combination of both HEPA/ULPA and AMC filtration in one product. This combination filter is marketed as the GIGALAM. Depending on requirements, standard, low-boron or e-PTEF particle media can be chosen in combination with one type of Gigasorb medium. A filter of this type is shown in Figure 10.



## CONCLUSIONS

Fighting AMC problems is teamwork! There is a need to include the efforts of all specialist groups within a fab, together with measurement and filtration specialists, in order to find optimal solutions. Using advanced techniques and the latest available materials, specially profiled products have been developed for the micro-electronics industry. This article has demonstrated some products that have been developed to minimise AMC emissions and provide AMC control in any cleanroom-based production process.

Some examples of the solutions are:

- the use of outgas-controlled materials for cleanrooms and equipment
- low-boron, low-outgassing alternatives for HEPA glass filters
- boron-free, low-outgassing and chemically resistant e-PTFE HEPA filters
- chemical filtration systems for recirculating cleanroom air that remove acids, bases and condensables, optimised for low pressure drop penalty (20 Pa at 0.3 m/s face velocity) and high cleanliness
- chemical filtration systems for make-up air that remove acids, bases and condensables, at a low pressure drop penalty.
- special combination filters for HEPA/ULPA particle filtration and for AMC- and tool-specific filtration solutions
- customised minienvironment filters with low pressure drop, high cleanliness and minimum form factor in order to avoid costly redesign of existing constructions.

## REFERENCES

- [1] Semiconductor Equipment and Materials International, SEMI F21-95.
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- [3] Semiconductor Industry Association, "International Technology Roadmap for Semiconductors", 1999 edition. International SEMATECH, Austin, TX, 1999.

## ABOUT THE AUTHORS

Dr Mikael Forslund is a member of the R&D department of Camfil AB, which is the central research facility within the Camfil group. The scope of his work includes building up knowledge on the effects of pollution and on the measurement of AMC and outgassing, together with responsibility for new product development and technical support within the area of chemical filtration in cleanrooms. Dr Forslund is a member of the Electrochemical Society and also of Working Group Eight (WG8) for molecular contamination within ISO/TC209. He has a background in corrosion research and holds a PhD in corrosion science and an MSc. chemical engineering.

Sean O'Reilly is Cleanroom Segment Manager for the Camfil Group, currently based in Malaysia. Sean has worked for Camfil for over 17 years, first in production, then sales, then went on to work for Camfil in the UK. He is responsible for ULPA and chemical filter business from a technical and commercial point of view, and co-ordinates Camfil's global cleaning activities.

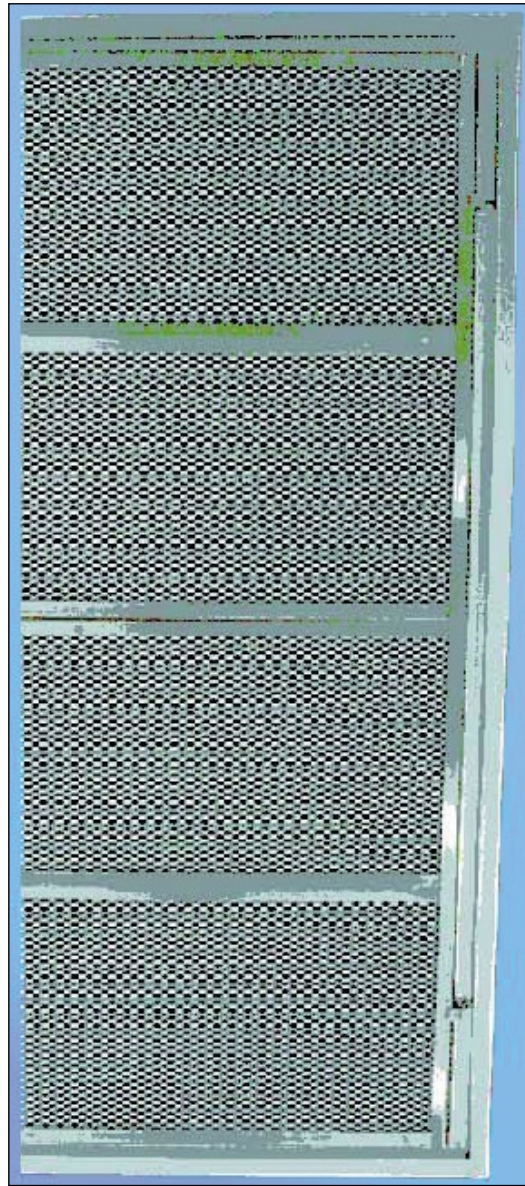


Figure 10  
Filter for a minienvironment

IF YOU HAVE ANY ENQUIRIES REGARDING THE CONTENT OF THIS ARTICLE, PLEASE CONTACT:

**Sean O'Reilly**  
**Camfil Air Filter**  
**Plot 17b**  
**Lorong**  
**Bemban 2**  
**Bemban Industrial Estate**  
**31000 Baru Gajah**  
**Perak Darul Ridzuan**  
**Malaysia**

**Tel: +60 53668888**  
**Fax: +60 53668880**  
**E-mail: Sean.oreilly.my@camfil.com**

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