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Chemically Clean Air: An Emerging Issue in the Fab Environment

Smaller semiconductor geometries move air cleanliness from the realm of particles to the realm of molecules.

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Key Technologies:

- **Contamination control**
- **Particle measurements**
- **Clean air**

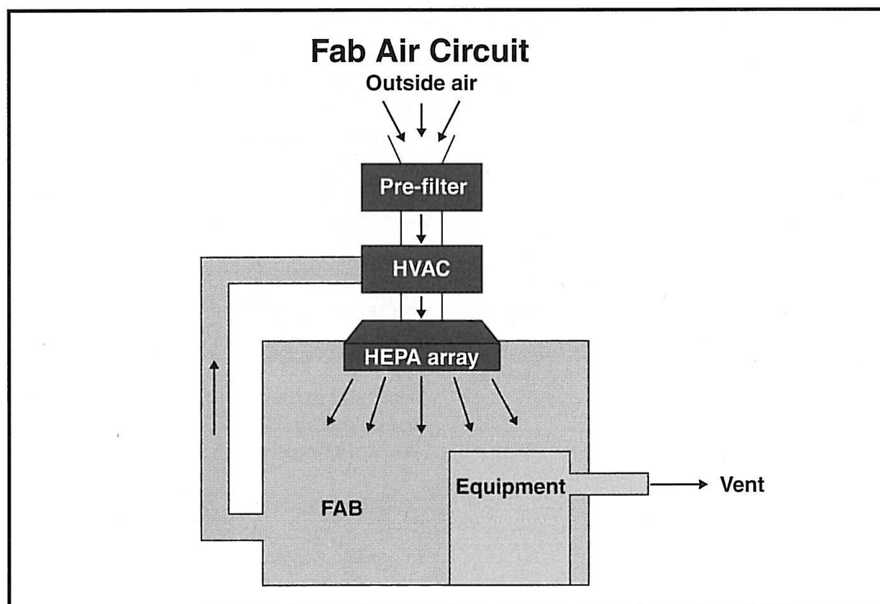
At A Glance:

New process chemistries and their associated contamination sensitivities will increase the need to control airborne chemical contamination, moving it from the study of particle distributions to that of molecules. Identifying and eliminating airborne molecular contaminants, which are dispersed by the airflow in a cleanroom, can improve wafer processing yields.

The smaller geometries planned for the future will move air cleanliness from the realm of particles to that of molecules — chemically clean air. Quantifying the cleanliness of cleanroom air has been focused on particle count and control. Limiting the view of air cleanliness to that of classical particle definitions will not be adequate in the future.

Air transport in the fab

A simplified model of air transport in the fab is shown in Fig. 1. Outside air is drawn into the air handling system, usually through a significant pre-filter system. The air is then tempered by the heating, ventilating and air conditioning (HVAC) equipment, mixed with re-circulated air and sent on its way to the ceiling high efficiency particulate air (HEPA) filter array for delivery to the cleanroom. Once inside the cleanroom, the air moves downward and out of the room for eventual re-circulation. Also in the air circuit are various venting systems which remove exhaust air from processing equipment. As the air moves through this entire air handling circuit, chemical contamination can be introduced or removed at any point. While



1. Outside air is mixed with inside air before it passes through the HEPA filters.

conventional air handling systems effectively minimize particle contamination, many do little to address the issues of chemical contamination.

Because of the high airflow rates in contemporary cleanrooms, air handling systems are actually very efficient transporters of chemical contamination. The air in the cleanroom is changed rapidly and mixed vigorously by the air handling system. As a result, contamination introduced into the air circuit at one point quickly disperses throughout all the cleanroom sectors served by a common air handling system. Adjacent sectors can also be contaminated by air leakage through doors, chases and pass-throughs. The shear volume of air movement can result in the wafer being exposed to significant contamination. Even at low concentrations, the net mass arrival rate of airborne molecular contamination can be very high due to the large amount of air involved. The footprint of a 200 mm wafer horizontally positioned will be washed by almost a cubic meter of air every minute in a 100 ft/min air stream. Since many airborne contaminants exhibit concentrations of tens, hundreds or even thousands of ng/m^3, a short time in such an air stream can easily expose the wafer to significant amounts of contamination.

Air contamination levels

Various authors have reported on studies of molecular contamination in fab air. While results vary, patterns are beginning to emerge with respect to the types and levels of contaminants. These molecular contaminants can be divided into three broad categories: metals, other inorganic compounds and organic compounds. The metallic contaminants (Table 1) include those typically of concern in semiconductor processing, while the nonmetals (Table 2) are generally the vapors of acids and bases common to the fab. The list of potential organic contaminants is lengthy and can only be characterized in broad classes of compounds (Table 3). These levels represent the typical range; in many cases, however, some observations of significantly higher or lower levels have been made. In particular, much higher concentrations would be expected in the immediate vicinity of a contamination source. The unit used to quantify these contaminants is ng/m^3, which refers to the total weight of the subject analyte found in a cubic meter of air. The analyte may exist in its basic form or as a constituent of some more complex compound.

Note that metals tend to have concentrations in the range of 1-100 ng/m^3, with most being well below 100 ng/m^3. The exception is boron, which forms compounds that are easily vaporized or sublimed and which is found in abundant quantities in the fab. In most situations, the boron level has the highest concerns due to its ability to dope the wafer. The exact form of these metal contaminants is uncertain — they may be very small particles or volatile compounds.

The range for nonmetals is 100 to 10,000 ng/m^3, with ammonium and nitrite commonly found in the highest concentrations. Currently, efforts are being made to lower the detection limit for fluoride to determine if appreciable concentrations of this highly active species are present.

By far, organic compounds are the most abundant type of molecular contaminants. Listed in the tables are the compounds of concern, which have typical concentrations in the range of 1000 to 100,000 ng/m^3. Some of these compounds are low molecular weight materials that easily desorb from the wafer surface, while others are much heavier compounds that attach much more securely. In addition to those listed, there are abundant quantities of even lower molecular weight compounds (i.e. methane); however, they do not adhere to the wafer surface and are not of concern.

For perspective regarding the importance of these molecular contamination levels, a Class 10 cleanroom might have little more than 2 ng/m^3 of particulate contamination compared to thousands of ng/m^3 of molecular contamination. From a contamination perspective, one can visualize cleanroom air as a rapidly moving fluid containing large amounts of molecular contaminants along with an occasional burst of particulate contamination.

Table 1. Metal Contaminants in Cleanroom Air

Analyte	Typical range (ng/m^3)	Typical detection limits (DL) (ng/m^3)
Aluminum	10 to 20	1 to 3
Boron	20 to 150	1 to 10
Calcium	Below DL	1 to 50
Chromium	Below DL	1
Copper	Below DL	0.5 to 3
Iron	1 to 20	1 to 3
Magnesium	1 to 10	0.5 to 1
Manganese	Below DL	1
Nickel	Below D	2
Potassium	1 to 5	0.5 to 10
Silicon	20 to 70	20
Sodium	1 to 10	1 to 2
Zinc	Below DL	2

Table 2. Nonmetal Contaminants in Cleanroom Air

Analyte	Typical range (ng/m^3)	Typical detection limits (ng/m^3)
Ammonium (NH_4^+)	1000 to 10,000	30 to 50
Bromide (Br^-)	Below DL	30 to 50
Chloride (Cl^-)	100 to 1500	20
Fluoride (F^-)	Below DL	600 to 1000
Nitrate (NO_3^-)	500 to 5000	30 to 40
Nitrite (NO_2^-)	1000 to 10,000	6 to 20
Phosphate (HPO_3)	Below DL	20 to 40
Sulfate (SO_4^+)	50 to 500	20 to 40

Impact on device processing

Impact studies defining the practical threats these airborne contaminants pose to wafer processing are just beginning to appear. When present on the wafer surface, these contaminants can act directly to impair device performance or indirectly by impeding intended processing steps. Some of the effects have been clearly demonstrated, while others are only hypothesized at this time. A summary of these effects follows:

Direct processing effects

- High levels of boron or phosphorus compounds can result in

unintentional doping of the wafer during processing.

- High levels of metallics may contaminate the wafer and reduce carrier lifetime and/or breakdown voltages.
- In very thin oxide structures, the presence of airborne organic contaminants on the wafer surface during oxide growth results in lower breakdown voltages.

Indirect processing effects

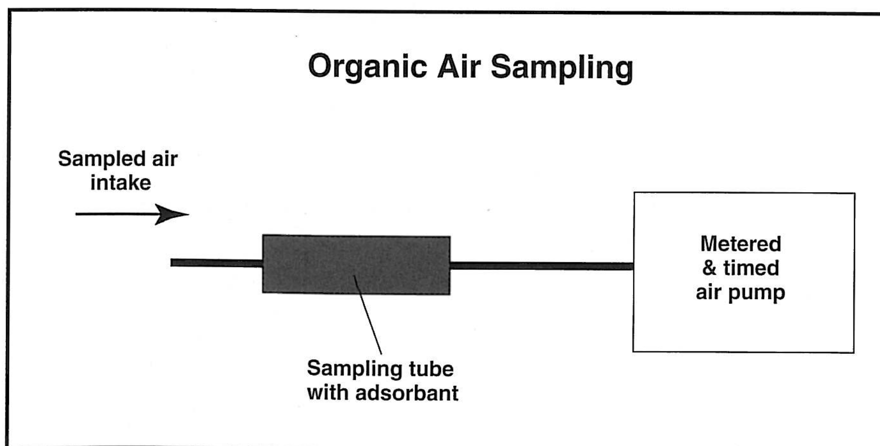
- Organic contamination on the wafer surface may impede the wetting abilities of various aqueous cleaning solutions or cause uneven etching or deposition.
- In epitaxial growth processes, organic contamination may nucleate faults in the crystal structure.
- Deep UV photoresists can be poisoned by the presence of both ammonia and NMP (N-methyl pyrrolidine) vapors.
- Organic residue can impede packaging operations such as lead bonding and encapsulation.
- Various optical measurements of the wafer surface can be distorted by the presence of organic films.
- Silicones can react with air ionizers in the cleanroom to form SiO_2 particles and/or they can adhere to the wafer surface, impeding wetting or subsequent deposition and bonding operations.

While the existence of airborne molecular contamination is undeniable, we lack a definitive correlation between airborne contaminant levels and those actually observed on the wafer surface. The mechanisms involved in this transfer mode are complex and dynamic in nature. The key factors are the concentration of the contaminant in the air, the diffusion rate to the wafer surface, the affinity of the contaminant for the wafer surface and the ability of the contaminant to spontaneously evaporate from the wafer surface when the equilibrium forces shift. Some authors have reported anecdotal results, but a full characterization of this mechanism remains the subject of ongoing research.

From a practical perspective, experience suggests that maintaining airborne contamination levels similar to those considered typical is adequate for today's technology (i.e. 0.5 mm devices). However, all are cautioned that this is a speculative conclusion that must be examined carefully in the context of any specific situation. The Semiconductor Industry Association's National Technology Roadmap has defined targets for wafer surface contamination levels for organic and inorganic materials and for molecular migration, projected out to 0.10 mm devices. However, the Roadmap also identifies the need to develop a reliable correlation between these two characteristics as a key priority; without this correlation, there is a risk that future facilities might be over- or under-designed.

Table 3. Organic Contaminants in Cleanroom Air

Analyte	Typical range (ng/m^3)	Typical detection limit (ng/m^3)
Aliphatics Examples: C-9 through C- 20 dimethyl pentane hexanone 4 propylheptane	1000 to 25,000	1000
Aromatics Examples: toluene xylene ethyl benzene trimethyl benzene	Toluene up to 300,000; others 5000 to 100,000	1000
Silicones Example: hexamethyldisiloxane	1000 to 10,000	500
Chlorocarbons Examples: tetrachloromethane dichlorobenzene	1000 to 50,000	1000
Others Examples: butyl acetate 2 ethyl 1 hexanol acetone	5000 to 50,000	1000



2. A six-hour sampling period is typically required for collecting organic contaminant samples in air.

Measuring airborne molecular contamination

The fundamental technique for measuring airborne molecular contaminants consists of drawing the fab air through a collection media for a specified number of hours and subsequently extracting the contaminants from the media for identification and quantification. This multi-hour sampling regimen is required to collect a sufficient volume of analyte to provide useful detection limits. For metals, the total sampled air volume is in the range of three cubic meters, while for organic compounds the sampled volume can be reduced to 0.05 m^3. This is consistent with the relative contaminant levels present. The two basic media consist of adsorptive filters for organic compounds and scrubbing solutions for inorganic compounds.

Figure 2 schematically depicts the process for collecting and measuring organic contaminants. A small pump draws air through the adsorptive filter array at a rate of about 0.1 liter/minute; a six-hour sampling period is typical. The filter array, consisting of a metal tube filled with carbon or Tenax (Akzo

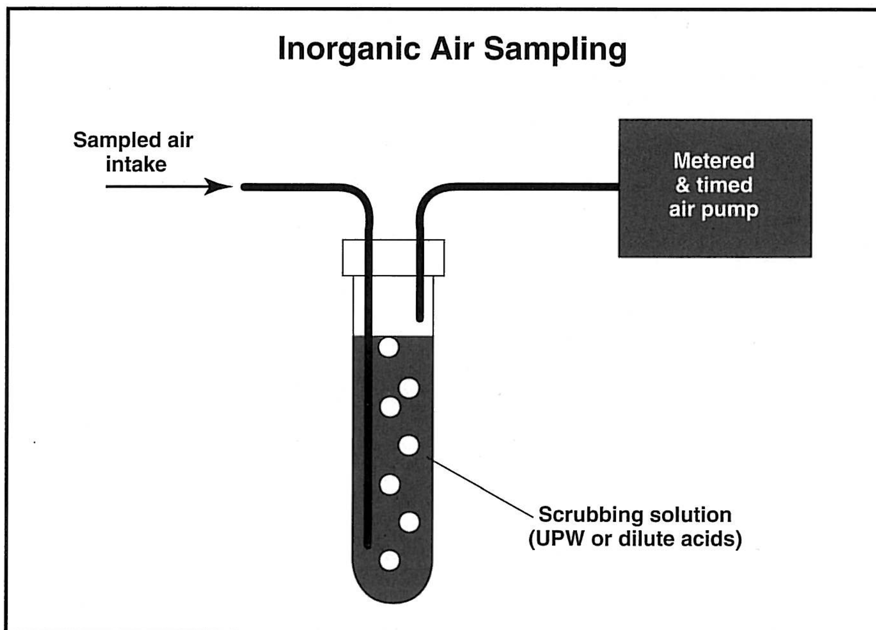
Corp., volatile organic filter) adsorbant, must be carefully prepared to ensure accurate testing. The key properties include an ability to reliably adsorb the target compounds with a known efficiency combined with the capability to subsequently release the contaminants during the later desorption step. Given the broad range of potential contaminants, a composite filter array of multiple media types is generally required (Fig. 3).

After the collection step, the tube is heated to 200-400°C while an inert carrier gas (typically He) passes through the tube and carries the contaminants to a gas chromatograph-mass spectrometer (GC-MS) instrument for identification and quantification. The technique is similar to that routinely used for regulatory air quality measurements, but is highly refined for this application due to the lower concentration levels (ppb vs. ppm), the much broader range of potential contaminants at issue (50 or so for air quality measurements vs. potentially hundreds for fab air measurements) and the need to detect trace high boiling compounds. Once the GC-MS spectra are obtained, they are compared to reference libraries and standards to allow identification and quantification.

In the case of inorganic compounds, the sampled air is drawn through various scrubbing solutions, usually ultrapure water or mild acid solutions, at a rate of about 1 liter/minute (Fig. 4).

3. A typical organic air sample collection apparatus uses multiple media types to collect samples.

Collection periods are in the range of 24 to 72 hours depending upon the target analytes and the concentration of the impurities in the air. A unit developed by Balazs Analytical Laboratory for conducting these measurements is shown in Fig. 5. The contaminant levels in the scrubbing solutions are subsequently measured and the airborne contamination is calculated based on the total volume of air sampled. Recovery studies have been conducted on the scrubbing solutions to demonstrate that accurate determinations can be made. For metal contaminants, the solutions are analyzed using inductively coupled plasma-mass spectrometer (ICP-MS) techniques while non-metallic species are measured with ion chromatograph (IC) methods.



4. Inorganic samples are usually drawn through scrubbing solutions.

Sources of airborne contamination

The sources of airborne chemical contaminants can be divided into five groups:

- **Outside air:** Normal urban air contains a variety of organic and inorganic molecular species. Unless special filtering methods are used, they will typically pass through the air handling system into the fab operating environment. This is in contrast to the excellent performance of contemporary air handling systems in removing particulate matter from outside air. Typical measurements have shown, however, that the volatile contaminants generated and released within the fab generally far outweigh those introduced by outside air.
- **Air handling systems:** The entire air handling circuit is a potential source of molecular contamination. These systems are mostly metal in construction, comprising steel, zinc, copper, and aluminum with numerous platings and coatings applied to the base metals. Any eroding surface in the system can emit metallic contaminants. Corrosive fumes from the outside air or from the air re-circulated from the fab attack the metal surfaces and produce corrosion products that are then drawn into the air stream. A classic example of this case is the gradual decomposition of borosilicate glass fibers in high efficiency particulate air (HEPA) filters by HF fumes generated in the fab. Typical filters might be as much as 10 percent boron compounds by weight. Once dissociated from the glass fibers, the boron compounds will leave the HEPA filter and enter the cleanroom. Some fabs are moving to fluoropolymer or silica based HEPA filters to remove this potential contamination source. In addition to metallic components, numerous elastomers and sealants are present in air handling systems and they can produce a variety of organic contaminants.
- **Construction materials:** The many polymer products used in fab construction are a common source of molecular contaminants. Other than a few fluoropolymers, virtually all polymeric materials contain various additives — flame retardants, anti-oxidants, catalysts, plasticizers, color concentrates and residual processing agents. The plasticizers and processing agents usually are organic compounds while the

others tend to be inorganic. Many flame retardants are phosphorus, antimony or halogen based compounds. The organic additives often are low molecular weight compounds, relative to the base polymer, that easily volatize. Paints, coatings, wire insulations and adhesives are another typical source of airborne organic contaminants, especially the solvents used in their formulation. Each material and its respective manufacturer tend to have unique formulations, so materials in the same generic class can have markedly different contamination signatures.

- **Fab equipment:** For protection from corrosive solutions, polymeric materials are used routinely in fab equipment, cleanroom garb, containers and the like. These items can generate similar contamination effects as do the construction materials noted above.
- **Processing chemicals:** Inherent in the semiconductor fabrication process are various chemicals with volatile components, especially cleaning solutions and photolithographic materials. These contaminants tend to be concentrated in the immediate vicinity of the workstation where they are used. However, the air handling system will often cause them to diffuse throughout the fab. Even if well vented, sometimes wind direction changes can cause them to be sucked back into the air handling system by downstream air intakes.

The dynamics of the effusion of these contaminants can take a variety of forms: steady state, cyclic or transient. Process chemical fumes tend to have similar, steady state levels when tested repeatedly. Construction materials often have a transient pattern of a high initial level which then recedes as the contaminant levels reach an equilibrium between the source and the fab air.

The testing of contamination sources consists of measuring the air immediately adjacent to the item, either in situ or in a special test fixture. For example, air handling systems are usually evaluated by sampling at multiple locations and then comparing contamination levels upstream and downstream of a particular component. For contamination generated by process chemicals, the air is sampled directly at the workstation. For many of the polymeric materials, a convenient technique is to place a specimen in a small test chamber and then sample the headspace gas in the chamber. Ideally, this test is conducted dynamically, with a continuous stream of inert gas to simulate the dynamic conditions of a continuous air flow. In some cases, the specimen will be heated to accelerate the outgassing process.

5. The typical collection period for inorganic air sampling devices is 24 to 72 hours.

Mini-environments and containers

Mini-environments and closed wafer carriers represent a special subset of this issue. As confined spaces, the air flow within them may be stagnant or significantly reduced relative to the general airflow within the fab. As such, there is the potential that contaminants can concentrate to significantly higher levels than observed in the general fab environment. Also, depending on the thermal and equilibrium conditions, contaminants in these confined spaces may adsorb onto or absorb into the container walls only to re-evaporate when the equilibrium forces are reversed.

Conclusions

Airborne molecular contamination clearly exists at levels that might easily affect device properties or processing. Prescriptively, the following steps appear advisable:

- Evaluate new facility designs from the perspective of controlling this type of contamination.
- Evaluate construction materials used in any new facilities that are expected to meet enhanced contamination standards.
- Develop a baseline of airborne molecular contamination levels once a facility is completed to provide a basis of comparison for future measurements.
- Monitor airborne molecular contamination levels at regular intervals.
- Verify contamination levels when changing the parameters of the air handling system in ways that could affect vapor removal or the concentration of contaminants.

As research continues in this area, particularly on the correlation of airborne to wafer surface contaminants, more definitive strategies will be possible. Meanwhile, process engineers are well served to be mindful of this emerging issue and the effect it may have on yields of future products. □

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