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ORGANIC OUTGASSING FROM CLEANROOM MATERIALS INCLUDING HEPA/ULPA FILTER COMPONENTS: STANDARDIZED TESTING PROPOSAL

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BIOGRAPHIES

Mark Camenzind has been a research chemist at Balazs Analytical Laboratory since 1987 and is currently the organic analysis manager. He received his BS degree from MIT and Ph.D. from Univ. of Calif. at Berkeley in chemistry. He has been developing new methods for solving organic contamination problems in the semiconductor and disk drive industries. He is a member of IES working group 31 (WG 31) on outgassing, ASTM F1 on electronics and D22 on testing of atmospheres, and other committees for SEMI and IDEMA.

Anurag Kumar received his Ph.D. from Univ. of Roorkee, India, and did postdoctoral research at U.C. Santa Barbara. He has been a GC-MS Chemist at Balazs since 1996 and has been developing outgassing methods for cleanroom and disk drive components.

ABSTRACT

The outgassing of construction materials and polymers are major sources of organic contaminants in cleanrooms used for critical processes in the semiconductor, disk drive, optical and aerospace industries. Standardized outgassing tests are needed to control potential contamination sources and reduce yield losses that are still common. Existing outgassing test methods are reviewed, and two types of dynamic headspace GC-MS (Gas Chromatography-Mass Spectrometry) tests are proposed for screening FAB materials (FAB is short for cleanroom-based fabrication facility). One is a 100°C "screening method" and the other is a room temperature, 40% RH (relative humidity) "engineering test" that attempts to simulate actual conditions in the cleanroom.

An example of a HEPA filter potting compound outgassing an organophosphate that affected the yield of silicon wafers is reported in this paper. For silicone HEPA/ULPA (High Efficiency Particulate Air and Ultra Low Penetration Air Filters) gel seals, which are a common source of silicones in FAB air, tests by both the "screening" and "engineering" methods are presented. A screening program using these tests can reduce organic molecular contaminants in FAB's.

KEYWORDS

Cleanroom, Airborne Molecular Contamination, Silicone, Organophosphate, HEPA, ULPA, Outgassing, Dynamic Headspace, Thermal Desorption, GC-MS, Semiconductor, Disk drive

I. INTRODUCTION

New, billion dollar FAB's go to great efforts to control particles to very low levels. Yet the mass arrival rates of molecular contaminants at the wafer surfaces are orders of magnitude higher than the particle arrival rates.[1] HEPA and ULPA filters remove particles, but have little or no effect on molecular compounds. Most cleanrooms are dirtier than outside air for many molecular contaminants, especially organics, acids, bases and dopants.[1-3] Some of the molecular compounds can cause disastrous yield losses or degradation of electrical, mechanical, optical or other properties. Many contaminants come from outgassing of materials used in the cleanroom.[4] These contaminants need to be better controlled. For example, we commonly find silicones in the air for many cleanrooms,[2] and the silicones may come from silicone gel seals used to seal ULPA filters, or other silicone sealants.[3,5,6]

Balazs Labs and others have developed methods for identifying organic contaminants in cleanroom air[2-7] and for looking at their sources. For example, we identified organic compounds outgassing from gloves, wafer carriers and all FAB construction materials at relatively low temperatures.[2] Outgas testing that is sometimes done at higher temperatures (>100°C) becomes less representative of what outgasses at lower temperatures of actual use.[4] With more sensitive instrumentation, we can approach testing under ambient conditions for some materials, but higher temperatures are still used to increase the sensitivity to trace high-boiling organics that tend to be most detrimental to processing.

Nearly all semiconductor FAB's specify no organophosphates be used since they can n-dope silicon wafers. Yet we still encounter silicon wafers with n-doping problems, despite several previous reports warning of the problem. Organophosphates outgassing from HEPA filter potting compounds have upset processing at several semiconductor facilities.[8,9,10] Phosphates are especially common flame retardants or catalysts in urethane polymers used as foams and sealants, e.g., in HEPA filters. We will give examples of outgassing from two HEPA filter potting compounds we have evaluated in the last 6 months that have detectable outgassing of organophosphorus compounds. One was high enough to substantially impact the yield of silicon wafers being produced.

I.A. Effects of Organics on Processes

Organic contaminants can affect semiconductor and other processes in a variety of ways:[2,4]

- Organics can form particles or films
- Organics on surfaces affect wetting, etching & particle removal
- If wafers don't wet: cleaning with SC-1, SC-2, piranha, HF-peroxide are less effective; metal contaminants are not removed
- Uneven etch rates cause roughness
- Incomplete etching of metals or polysilicon can cause shorts
- Organic deposits can cause high resistivity or opens for contacts
- Contact corrosion (e.g., from halocarbons)
- Adhesion between layers is affected, usually adversely
- High temperature processing can form silicon carbide[11] (esp. during Rapid Thermal Processing, RTP)
- Photolithography defects (T-topping):[12] Amines, NMP, ammonia from HMDS or SC-1, and other bases can affect chemically-amplified photoresist at ppbM (parts-per-billion-molar) levels
- Affect surface analysis, charging, ellipsometry
- Organics can fog optics[4] of particle counters, lasers, steppers
- Streaking during application of SOG (spin on glass), photoresist, polyimide
- Silicones pass through HEPA filters: air ionizers make particles downstream.[5]

An atomically clean silicon surface is needed for many processes:

- Prior to gate oxide growth
- Any organic contaminant on surface can:
  - ◊ affect initial growth of thermal oxide,
  - ◊ cause interface roughness,
  - ◊ affect oxide density, GOI, V_{bd}
  - ◊ 60 Å gates must be very uniform or breakdown may occur.
- Polysilicon gate deposition:
  - ◊ organics affect grain size: lower V_{bd}
- Selective CVD:
  - ◊ loss of selectivity or nucleation
- Epitaxy - organics can cause crystal defects

Sematech has made estimates of the impact of condensable organics and other airborne molecular contaminants on specific process steps.[13] SEMI (Semiconductor Equipment and Materials International) has made a new classification of cleanrooms for molecular contaminants that includes compounds that outgas from cleanroom materials such as silicones, organics and organophosphates.[14]

High-boiling organics tend to adhere to wafer surfaces more strongly than lower boiling compounds.[8,9,15] The high-boiling organics can be the most detrimental to sensitive processes. A recent paper[15] used thermal desorption GC-MS analysis of organics adsorbed onto silicon wafers to demonstrate that it is the high-boiling compounds such as DOP (dioctylphthalate, bp 384 °C) that are actually found adsorbed onto the wafer surfaces, not the low boilers such as toluene (bp 110°C) that are present at much higher concentrations in air. They showed that the electrical properties worsened with exposure to cleanroom air and correlated with the amount of DOP on the wafer. They came to the conclusion that no more than 10 ng of DOP per wafer can be tolerated.

The disk drive industry is especially susceptible to organic contaminants in cleanroom air that can affect fluorolubricant application, such as phthalates and silicones.[16]

Sealed disk drives are very susceptible to organics outgassed internally in the drive since they can cause "stiction" of the heads to the media, buildup on the heads, head crashes and data loss or read-write errors.[16] For the above reasons, all disk drive companies perform outgas testing, and the disk drive standards organization, IDEMA (International Disk Drive Equipment and Materials Association), is considering developing standardized outgassing tests within the microcontamination committee.

Due to the detrimental effects silicones have on manufacturing, most disk drive manufacturers and some semiconductor FAB's, especially in Europe, do not allow silicones in their FAB's. Similarly, many FAB's specify no DOP should be used.

I.B. A balanced program of tests is needed to QC cleanroom construction materials

1. Need to understand each contaminant's impact on specific substrates or processes.
2. Need standard tests for contaminant levels on surfaces to set specifications, based on impact studies for each process and contaminant.
3. Assess contaminants in the air or gases to maintain at safe specification levels.
4. Quantitate levels of organics outgassed from materials onto nearby substrate surfaces; such as wafers, disks and optical surfaces.
5. Identify and quantitate compounds outgassed from materials, regardless of application.
6. Assess outgassing of materials for specific applications (Engineering studies) using actual geometries and ambient conditions.

IES working group 31 (WG 31, founded in May 1996) is attempting to standardize outgassing methods for cleanroom materials (items 4-6 above).

Our paper focuses on item 5 above, developing a practical screening program to test outgassing of each cleanroom material, regardless of the substrate these compounds might affect. An example of a preliminary "engineering test", (item 6), is also given. The users will need to assess which contaminants are likely to impact their particular processes. SEMATECH[13] has published estimates of the effects of specific molecular contaminants in air on specific wafer processes (item 1 above). A recent paper reviews the types of materials that are typically tested for new cleanrooms.[17]

We will first review standard outgassing methods, with emphasis on the limitations when applied to cleanroom materials. Then two new outgassing methods will be described along with some method development and problem solving examples. We will not include surface analysis methods since they have been covered elsewhere.[4,6]

II. AVAILABLE OUTGASSING METHODS

II.A. Outgassing from materials onto the substrate of interest

To determine which compounds may affect a process, substrates such as silicon wafers can be exposed to the material, then the substrate analyzed for contaminants added. These direct substrate exposure studies have proven invaluable for some processes, especially when coupled with impact studies on the process. For example, some wafer manufacturers or users have performed these tests by exposing silicon wafers with an oxide film to the candidate materials, then performing thermal desorption GC-MS analysis to identify the contaminants.[8,10,15] IES (WG31, task 3) is evaluating standardizing methods for this analysis.

SEMI E46-95, "Specification for Determination of Organic Contamination from Minienvironments" has been adopted by SEMI. This method stores a silicon wafer in a minienvironment to collect organic contaminants. The wafer is heated to desorb the organics into an Ion Mobility Spectrometer (IMS) for detection, but without identification. A contamination value is calculated by comparison with a hexaphenylbenzene standard. This test is extremely sensitive, but the instrumentation is expensive and not widely available. The method is not designed for identification of compounds, and identification by drift time can be attempted, but the only extensive drift time libraries are proprietary. For compounds at high enough levels, a quadrapole mass spectrometer can assist identification.[18]

While both of the above methods work well for silicon wafers with oxide surfaces, the contaminants may have dramatically different sticking coefficients onto the many substrate surfaces used in semiconductor manufacture. These surfaces include bare silicon, polysilicon, silicon with native oxide, hydrogen terminated silicon, thermal oxide, gate oxides, CVD oxides, spin on glasses, BPSG passivation films, metal conductors including Al, Cu, W, Ti and some silicides, silicon nitride, silicon oxyfluorides, titanium nitride, gallium arsenide, etc. An organic-free silicon oxide can be made by heating in air, but other organic-free substrates can be quite difficult to make and store (e.g., bare silicon).

Disk drive manufacturers also use very different films including carbon, fluorolubes, magnetic layers, head materials, nickel-phosphorus, etc.[16] For these users, some of the exposure tests should be useful for establishing impacts for their most critical process, but this is usually done in an R&D mode.

For a supplier providing materials to cleanrooms, or the companies designing and building cleanrooms for these critical industries, testing the impact of the outgassing of each building material on all of the above substrates would be very difficult and prohibitively expensive. Hence standard tests are needed for the outgassing of materials, independent of the substrate or application.

II.B. Available Vacuum Outgassing Methods

In general, vacuum methods are useful for vacuum systems, but are not very useful for screening fab materials. Still, large numbers of materials have been tested by vacuum methods[4] such as ASTM E595[19] (see below).

AVS (American Vacuum Society) has methods for outgassing and permeation of vacuum chamber components, with rates given in torr-L sec^{-1} cm^{-2} (e.g. AVS Standard 9.1, 1964, obsoleted). The outgassing is usually dominated by water, air or hydrogen. These compounds are irrelevant to cleanroom component outgassing. No identification of compounds is provided. RGA's (Residual Gas Analyzers) can be used for low molecular weight compounds such as air and water, but it is the larger molecules that cause problems. For large organics, good identification by RGA is difficult, especially for outgassed mixtures.

ASTM E-595-93 "Total Mass Loss (TML), Collected Volatile Condensable Materials (CVCM) from outgassing in a vacuum environment" does vacuum outgassing at 125°C for 24 hours. Values for TML, CVCM (collected onto a cooled substrate), and Water Vapor Regained (WVR) after the test are reported. This is a wonderful method to ensure satellites do not go off course due to mass loss, and to give an indication of what might condense onto surfaces such as lenses. This method is often dominated by water or low molecular weight solvent loss which is not of concern in cleanroom air. This method is not very sensitive to trace levels of high-boiling compounds which most dramatically affect wafer processing, nor does this method identify high-boiling plasticizers, phosphates, silicones and other compounds that are known to be detrimental at extremely low levels. Many plastics can be degraded at 125°C and compounds outgassing into a vacuum are not representative of what outgasses at atmospheric pressure or lower temperatures. A huge database is available from NASA,[19] which usually accepts materials with CVCM <0.1% and TML <1%. Any material that has outgassed condensables below the CVCM 0.01% (100 ppmw, parts per million by weight) detection limit of this method is usually considered acceptable for cleanroom use. Yet if all of the outgassing was due to organo phosphates, this could still be harmful to semiconductors. It would be a bigger problem for closed environments with static air, like wafer carriers, than for dynamic environments like the FAB's that have many air changes per minute. Many FAB materials have CVCM values >0.01%, yet are used in FAB's to keep construction economical. To assess whether the compounds are likely to impact specific processes, identification of individual components in the mixture of compounds outgassed is needed.

ASTM F1227-89 (1994), "Total Mass Loss of Materials and Condensation of Outgassed Volatiles on Microelectronics-related Substrates". Samples are heated to 25, 70, or 125°C for 24 hrs at 0.05 mbar (0.0375 torr). This was an improvement of the ASTM E595 procedure, since it is more sensitive, allows other lower temperatures to be used, and can condense materials onto a substrate of interest, such as a silicon wafer. Optional qualitative identification of the condensed material can be done by FTIR (Fourier Transform Infrared Spectroscopy), but individual compounds are not identified or quantitated.

ASTM E1559-93, "Contamination Outgassing Characteristics of Spacecraft Materials" does analysis of outgassing as condensable weight onto a sensitive quartz crystal microbalance (QCM). This is a complicated, expensive, slow analysis of outgassing, with poor identification of compounds, except gases, but is good for assessing relative boiling points of condensed materials.

II.C. Atmospheric pressure outgassing methods

ASTM D5116-90. "Small scale emission chamber for indoor material testing", in ASTM Vol. 11.03, by D22.05 committee on indoor air (currently undergoing revision/re-balloting). This is an excellent review of the parameters to consider for static- or dynamic headspace outgassing of material used indoors, but does not specify any of the parameters. This is a good starting point to review all of the parameters to be considered. This method uses small test chambers with a mixing fan. The throughput is low. A faster screening method is needed. This document would be referenced in any IES outgassing method developed, but appropriate parameters for testing cleanroom components need to be selected. This method is for small chambers in the liter range, and primarily looks for very volatile components, not the high boilers that affect most cleanroom processes. The concepts outlined in this method are considered in the method we propose, but we use either a smaller chamber or an automated thermal desorption system, with GC-MS for identification of compounds.

ASTM-DXXXX (unassigned). ASTM committee D22.05 on sampling and analysis of atmospheres, indoor air, is balloting an air sampling method using air sampling tubes followed by thermal desorption of the air sampling tubes. This method or modifications can be used for monitoring cleanroom air quality. This method can use the same instrumentation as the outgassing method we will propose, and most parameters for the analyses are described. Very similar methods are also being adopted by the US EPA (EPA method TO-17) and are being developed within ISO (ISO technical committee 146 on air quality). The current revision of the ASTM method does allow testing of air exiting test chambers used for outgassing, such as those in ASTM 5116 above. Once approved, future extensions of this method could include outgassing analysis as described here. This method was not designed to look for high-boiling compounds.

IES WG-31 outgassing committee. Task 4 is to develop a dynamic headspace method for outgassing of cleanroom components. We propose this group consider standardizing several methods that will identify individual components and quantitate them by boiling range for QC, and as individual components for troubleshooting. We need first to understand the differences between more common static headspace, and newer dynamic headspace methods.

III. FACTORS TO CONSIDER FOR NEW ATMOSPHERIC OUTGASSING METHODS

III.A. Static vs. Dynamic Headspace

Static headspace measures the concentration in air after heating a sample in a sealed container for a fixed time. A typical test might heat a 0.2 gram sample in a sealed 20 mL headspace vial for 1 to 24 hours, then sample 1 mL of the gas phase into a GC. The big advantage is convenience and the availability of many brands of autosamplers. Static headspace methods are useful for looking for very volatile solvents and are commonly used for residual solvent analyses in the pharmaceutical industry.

Static headspace is ineffective for analyzing reactive compounds that outgas since they may polymerize in the hot vials during the long sampling times, to form non-volatile compounds that will not be detectable by GC. These reactive compounds that go undetected can react on substrate surfaces and lead to failures.

The amount of outgassing into the static headspace can be partly under kinetic control, or could be near equilibrium vapor pressures. For example, some samples will give a constant outgassing result whether heated for 1 or 24 hours (since they rapidly reach equilibrium). Other viscous materials may have diffusion control, in which case up to 24 times more could be outgassed in 24 hours, than in one hour. Outgassing of organic compounds can continue for more than 24 hrs. For long time period tests, the chance of the sampling vials leaking increases.

Static headspace is relatively less sensitive than dynamic headspace to high-boiling organics (bp >>200°C) since high boilers have very low vapor pressures, so very little will equilibrate into the 1 mL of headspace sampled. Higher boiling compounds (DOP, BHT [butylated hydroxy toluene], organophosphates, silicones) can have the biggest impacts on processing. Static headspace is dramatically less sensitive than dynamic headspace for these compounds. High boilers can often condense and carryover within the instrumentation.

III.B. Advantages of Dynamic Headspace

For this method, outgassed compounds including reactive compounds are swept out of the sampling vessel onto an adsorbent as soon as they are outgassed, minimizing the chance that they will polymerize and go undetected.

High-boiling compounds with low vapor pressures can outgas at low rates, but they will be continuously swept onto the adsorbent for analysis. When the adsorbent is analyzed, we can state a precise outgassing rate under the experiment conditions. This method is especially sensitive to high-boiling compounds. The cleanroom is a dynamic environment where air is continuously swept over the FAB materials, not kept in a static room. Hence, dynamic outgas rates are the most relevant to dynamic cleanrooms.

Automated instruments for dynamic headspace are now available, e.g. we use two Perkin-Elmer ATD 400 automated thermal desorbers connected to Hewlett Packard GC-MS systems. Use of other equivalent instruments is possible. Other instruments with autosampler capacity are now available.

IV. WHY USE GC-MS ANALYSIS?

GC can separate complex mixtures of compounds, and can give a response for most, or all compounds. However, most GC detectors do not uniquely identify the compounds, which are extremely varied for FAB construction materials. The impact of specific compounds varies dramatically with structure. Identification is needed so that the worst compounds can be eliminated, without worrying about other compounds at higher levels that cause few problems, e.g. hydrocarbons or low-boiling alcohols. Identification also greatly assists tracking down sources of contaminants since many materials have unique outgassing fingerprints. The TD-GC-MS (Thermal Desorption GC-MS) method has the unique ability to separate complex mixtures, then use MS to unambiguously identify each compound for the majority of the compounds detected. The amounts of individual compounds can be easily "semiquantitated" by comparison with a known standard such as n-decane, or more accurately calibrated using authentic target compounds when needed.

A GC-FTIR could also be used in principle, but with much lower sensitivity and specificity. The compound libraries are much smaller, e.g. 7,000 compounds for gas phase IR spectra vs. 275,000 spectra for MS, and GC-FTIR instrument are much less common.

V. PROPOSED DYNAMIC HEADSPACE GC-MS OUTGASSING TESTS

V.A. Screening Tests at 100°C for 30-Minutes

This in-instrument screening method first thermally desorbs the sample at 100°C for 30 minutes, then uses GC-MS for separating and identifying individual compounds. It outgasses using dynamic headspace, as we have discussed above.

This test can be performed using a variety of commercially available thermal desorber instruments or custom built machines. For productivity reasons, use of an autosampler-based instrument is recommended. We have tested over 300 materials by this method. A small sample of the material to be tested (ideally a single piece) weighing about 0.2 grams is placed into a stainless steel tube 8.9 cm (3.5") long x 6.4 mm (¼") O.D. x 5 mm I.D. with a retaining screen in one end. The sample tube is purged to remove air, then thermally desorbed over a 30-minute period at the selected temperature. The default temperature for the test is 100°C, but other lower temperatures for selected materials can be used when they have a high level of outgassing. In special cases of materials that need to be used in reactors at higher temperatures, tests up to 300-400°C have been performed. During the thermal desorption, all of the volatiles are swept from the sample using an inert carrier gas, such as helium, and the compounds are trapped on a cold trap cooled to an appropriate temperature to recover the compounds of interest. Cooling to -30°C is usually more than adequate to capture compounds of interest, since it is the higher boiling compounds that tend to adhere most strongly to wafer, disk drive and optical surfaces. Low-boiling solvents, hydrocarbons, alcohols, benzene, etc., are common in urban and factory air, but are not believed to cause processing problems at low levels (sub ppmM). Hence we do not focus on low boiler analysis for the outgassing experiments.

After cryofocusing all the outgassing compounds, the cold trap is rapidly heated to desorb compounds into the GC-MS as a narrow band, which improves the chromatography and sensitivity. Temperature ramping of the GC oven is used to separate the compounds roughly by boiling point, and mass spectroscopy is used to identify each compound as it exits the GC column.

A standard is run daily to ensure that n-hydrocarbons from C7 (n-heptane, bp 100°C) to high-boiling compounds such as octacosane ($C_{28}H_{58}$, bp 432°C) and DOP (dioctyl phthalate, a plasticizer bp 384 °C) are recovered.

Detection limits are typically <1 ppmw for most compounds (based on a 0.2 gram sample), and lower detection limits are possible for selected compounds. In practice, we have not found that materials that outgas compounds <1 ppmw at 100°C have created any processing problems when used at ambient temperatures within cleanrooms.

We have studied several hundred materials and have been able to eliminate many materials that outgas contaminants that can affect processing. We have also worked with a variety of coating, plastic, elastomer, sealant, garment, and wafer carrier manufacturers to reduce outgassing levels for cleanroom use. Based on these studies, several vendors have developed special products for cleanroom use, whereas competitive formulations not improved are continuously causing problems in cleanrooms. Examples of products improved are HEPA potting compounds, HEPA gel seals and coatings. One recent report found that screening >100 materials by thermal desorption-GC-MS eliminated 60% of the materials planned for use in a new state-of-the-art FAB in Oregon.[17] When the FAB was completed, no high-boiling, detrimental compounds such as phosphates, silicones, phthalates or other plasticizers were found in the air (<1 ng/L for any one compound).

In contrast, we and others monitor air in FAB's worldwide and many still have these contaminants that come from cleanroom components. Many FAB's have detectable levels (>1 ppbM) of high-boiling (>C20 retention index) silicones, phthalates, phosphates or hydrocarbons.[2,3,6,7] Production at a few FAB's has been set back for months due to molecular contaminants.[8] The usefulness of the procedures has been demonstrated. The outgassing test sensitivities are adequate (detection limits <1 ppmw) that contaminants can be detected at levels that will not give a detectable contribution to the FAB air (Detection limits for air sampling are <1 ppbM, parts per billion molar, equivalent to parts per billion by volume, ppbv).

A key question is whether this outgassing test is sensitive enough to detect contaminants that can shut down FAB's or at least impact production. We will give two examples.

Example 1. Organophosphates from two HEPA filter potting compounds by 100°C screening method.

We will give two examples for organophosphates outgassed from HEPA potting compounds. We recently installed a HEPA filter at our facility. Air sampling found no detectable phosphates in the air (e.g. <0.05 ppbM triethyl phosphate, TEP). A sample of the potting compound used to seal the HEPA filter pleats to the filter body was heated to 100°C for 30-minutes and analyzed by dynamic headspace GC-MS. **Figure 1** shows the GC-MS chromatogram for the outgassing from the potting material. A very small peak corresponding to 0.2 ppmw TEP is seen at 13.6 minutes. **Figure 2** shows the mass spectrum for this small peak, along with the best match from the GC-MS library of 275,000 spectra. Despite being a small peak, the best computer match to a Wiley library of 275,000 reference spectra was 93%. The molecule was unambiguously identified based on its fragmentation pattern (**Figure 2**). In addition, each compound can be confirmed based on its retention time. This low level of organophosphate outgassing (<1 ppmw) is not considered a significant problem.

In contrast, we sampled the air at a major semiconductor FAB using our air sampling method[2,7] and found a different organophosphate, tris(chloropropyl) phosphate (TCPP), at 0.07 ppbM in air (**Figure 3**). Detection limits for selected organophosphates such as triethyl phosphate, tributyl phosphate and tris(chloropropyl) phosphate in air are below 0.05 ppbM by GC-MS. This FAB had been having anomalous doping problems for the last 3 wafers in each batch, suggesting airborne n-dopants. Wafer die yields for the last wafer, #25, varied between 0-90%, and were worse for longer air exposures. The previous two wafers also had reduced yields for the die on the periphery. Yield losses were about 10% and increased with air exposure. The problem began when HEPA filters were replaced and continued for several months. Hence we outgassed the potting compound from the HEPA filters. A huge peak (531 ppmw) of tris(chloropropyl) phosphate was detected (**Figure 4**).

Thus, under the same outgassing conditions, the filter that was causing problems in a FAB was found to outgas 2700 times more organophosphate than another brand of filter used elsewhere. Based on these results, we have established that the 100°C outgassing screening method is sensitive enough to detect semivolatile organophosphorus compounds even when they are below levels that are likely to affect processing, and that when samples are tested that are affecting production, the contaminants can be easily detected. Testing at lower temperatures could be performed, but the test would then become less sensitive to the harmful contaminants. Based on these results, the HEPA filters should be replaced. We can work with filter suppliers and their vendors to QC potting compounds in the future.

Similar results have been reported previously at Eastman Kodak where 0.2 ppbM TCPP in air inverted the doping of a CCD device,[8] and in Japan where tris(chloroethyl) phosphate was detected.[9] For both of these studies, the phosphates were demonstrated to adsorb onto the wafers. In both cases, the source was found to be phosphates used as flame retardants in the polyurethane HEPA potting compounds.

Example 2. Silicone gel seals 100°C screening method.

Other materials that have caused multiple problems are HEPA/ULPA filter gel seals used to seal the filter box edges into the ceiling U-grids.

An example of the 100°C outgassing of a silicone seal that has been cured for 70 days is given in **Figure 5.** For the screening test, medium- to high-boiling cyclic and linear polydimethylsiloxanes (PDMS) were detected. These could adhere to wafers or disks. This method can be used to compare competitive products, QC batches of products, or ensure that the gels were mixed and applied properly. If incorrect mixing ratios are accidentally used, outgassing can go up dramatically, potentially leading to FAB shutdowns. This test is also applicable to urethane gels, but can not be used for petrolatum gel seals since they melt and contaminate the instrument.

Sample preparation and cure time

For materials like plastics, the materials can usually be tested as received. For solvent-based paints, coatings, two-part mixtures such as epoxies and sealants, we recommend curing for the following time periods as defaults:

- One month if the material will only be used in FAB construction, since it will often be several months between application and FAB use, and outgassing rates should decrease substantially by the time any products are made in the completed FAB.
- If a material will be used for maintenance of a running FAB, testing after a shorter cure is recommended. We recommend one week so that a consistent database can be developed, even though some FAB's may continue running during maintenance
- In rare instances, if materials used for maintenance cause unusually high concerns, they can be tested after a short period such as a one day cure.

Coatings are usually coated onto organic-free aluminum foil prior to curing and analysis. The coating should be applied at a thickness representative of what will be used in the FAB.

Ideally, an MSDS sheet for each sample should be consulted to assess what materials might be present and aid in selection of test conditions. Materials should not be tested above their melting points. The report should document the sample type, lot numbers and details of sample preparation, curing, and size, shape, area and weight of the sample tested, since all of these parameters can affect the outgassing results.

Although testing at the temperature of intended use is ideal, e.g. room temperature, the sensitivity of the test for detecting detrimental compounds would be greatly reduced, often to where compounds would not be detected, even though they outgas at levels that impact production. The 100°C desorption temperature increases the ability to detect high boilers in a short time. The 30-minute desorb time is a practical constraint of the software for the most common automated thermal desorption instrument, the Perkin Elmer ATD-400. Longer times would significantly reduce the throughput of the analysis, increasing it's cost.

For materials with high levels of outgassing, lower temperatures can be used. Examples of outgassing gloves at 50°C and wafer carriers at 75°C have been published previously.[2] To avoid developing a scattered test database with all possible temperatures being used, which would limit the usefulness of the database, we recommend testing be performed with the following temperatures as defaults:

- Gloves: 50°C
- Carriers: 75°C if polyolefin (PP, PE)
  100°C if higher temp. materials
- 100°C for all other materials

If materials outgas too much, alternative materials are usually sought. If all the alternatives outgas at high levels, yet one must be used, we suggest first identifying all components outgassed using the 100°C test. The materials are then retested at the lowest temperature (either room temperature, 50 or 75°C) at which the compounds of most concern can be detected. In some cases, which candidate material outgasses more can change with temperature.

Select the lowest outgassing material if all other factors are equal. However, it is not the total outgassing that is important. Most failures described in the literature are due to high-boiling compounds. Generally speaking, the best materials are those that outgas the least amount of high-boiling compounds. For this reason, the proposed test gives compounds summed by "boiling" range (more technically, by retention index range) for QC.

It is important not to use outgassing rates as the only parameter to select or reject a material. Sometimes the lowest outgassing materials may loose a desirable property such as flexibility, impact resistance, thermal- or photostability, adhesion, electrostatic dissipation, particle shedding or retention, cleanability, chemical resistance, flame retardant properties or affordability. All the parameters required of the material for its intended function must be considered and balanced against their cost. In addition, the amount used in the FAB must be considered. One label for a pipeline in a chase might outgas slightly more than a specification, but if few are used, they are required for safety, and no economical alternative is available, it may be allowed. In contrast, a thick material like a floor tile that outgasses moderate amounts of a high-boiling plasticizer like DOP, will probably outgas at low levels for a very long time, and the many tiles used can give detectable amounts in the cleanroom air. One paper has estimated 10 ng of DOP can be enough to affect silicon wafer processing.[15]

Another paper has described the process used for selecting low outgassing FAB materials.[17]

V.B. Room temperature "engineering tests"

Some materials outgas enough organics that the outgassing testing temperature can be lowered to ambient conditions. An example is silicone HEPA gel seals. For these, we recommend what we call an "engineering test". The sample is cured one week to one month at room temperature in a channel designed to mimic a U-grid used in the false ceilings of FAB's. Then the sample is placed into a glass tube and purged at room temperature with 40% RH (relative humidity) air (since the outgassing may be moisture-dependent) to equilibrate the samples. The purging is then continued while the compounds are collected on an air sampling tube containing appropriate adsorbents. From most silicone sealants, adequate silicones are outgassed at room temperature to yield excellent chromatograms with distinct peaks from each of the outgassed silicones (**Figure 6**). Each silicone is unambiguously identified by its mass spectrum and retention time. The amount of outgassing in these engineering tests does depend highly on the flow rates used and the geometry of the test apparatus. Hence any standardized test will need to exactly specify the conditions to be used. We propose a standard test of thoroughly mixing then pouring the gel ½" (1.27 cm) deep into an aluminum channel that is ¾" (1.9 cm) wide, 6" (15.2cm) long, and ¾" (1.9 cm) deep, then curing on a lab bench for one week at room temperature. The channel is then placed into a glass tube with 28 mm I.D. x 18 cm inner length equipped with a gas inlet and outlet. Clean air humidified to 40% RH (this is typical of many semiconductor FAB's) is passed through the glass tube at 200 mL/minute for 1 hr to equilibrate, then an air sampling tube is connected. The effluent gas is collected for an appropriate sampling time, typically from a few minutes to a few hours, depending on the sensitivity of the analytical instrument used. The tube is outgassed as in the air sampling methods. The results of outgassing as a function of the gas flow rate are shown in **Figure 7**. It can be seen that the amount of outgassing per time is highly dependent on the flow rate, but levels out after 200 mL/minute. Based on this, we recommend using a standard flow rate of 200 mL/minute to be relatively insensitive to minor variations in test conditions.

The cure time prior to the tests does affect the results. For example, a gel seal cured in a simulated U-grid for 7 days, then outgassed using the "engineering tests" at room temperature and 40% RH, outgassed the equivalent of 12 mg/day per HEPA filter unit. After a 70-day cure, the outgassing per HEPA dropped dramatically to 0.7 mg/HEPA per day. Drops for the amounts of silicones in cleanroom air vs. time have been documented by others for actual FAB's.[6]

This test is especially important for gel seals since many are two component mixtures that can be improperly mixed, improperly formulated, or may age. Many FAB's have not come into production on-time or have had yield busts due to problems with outgassing of gel seals. Silicone, urethane and hydrocarbon seals can all be tested at room temperature by this method. Note that the hydrocarbons cannot be tested by the 100°C screening method since they would melt and flow into the instrument. The "engineering test" will allows all materials to be tested under identical conditions.

VI. REPORTING

The amounts of each compound are estimated by integrating the area under each peak, then using the total ion count response factor of a n-decane standard to "semiquantitate" the amount of each compound. Standards for specific compounds of interest can also be run, but it is not practical to find actual standards for the millions of organic compounds known.

Results are usually reported in units of μg/g (ppmw) outgassed for most materials. For coatings or materials used on an areal basis, results should be reported as $\mu g/cm^2$ outgassed. The outgassing results are given as total outgassing, and are also broken down into boiling ranges. Typical boiling ranges are defined based on when compounds come out in the chromatogram vs. n-hydrocarbon references, using a capillary GC column with a non-polar polydimethylsiloxane bonded phase. Organic compounds with boiling points less than n-hexane are not normally quantitated since they have not been implicated in disk or semiconductor failures. "Low-boiling" compounds are defined as those with retention times between n-hexane and n-decane ($C_{10}H_{22}$), "medium-boiling" have retention times from beyond n-decane to n-eicosane ($C_{20}H_{42}$), and "high boiling" are compounds with retention times beyond n-eicosane up to at least n-triacontane ($C_{30}H_{62}$). The use of the same column type, e.g., poly(dimethylsiloxane), standard (e.g., n-decane) and indexing scheme (described above) worldwide is essential to making this method a reproducible standard.

VII. SUMMARY & RECOMMENDATIONS

1. Draft TD-GC-MS methods are now available for screening the outgassing of cleanroom materials. The methods have adequate sensitivity (<1 ppmw) to detect the types of high-boiling organic compounds (e.g. phosphates, silicones, phthalates, plasticizers) that are most likely to affect processing of sensitive substrates.

2. When cleanrooms are being designed and constructed, all plastic or elastomeric materials should be screened for outgassing, to eliminate compounds harmful to production. A surprising number of materials still outgas organophosphates, some at very high levels. All urethanes and especially HEPA filter potting compounds, should be tested to be sure no phosphates are present. DOP or other plasticizers outgas from many plastics, especially PVC and many floor tiles, and the outgassing of these high boilers can continue for years.

3. All new and existing FAB's should do an air sampling baseline to ensure no harmful compounds are present. When they are found, an outgassing database combined with air sampling data can be used to assess whether the contaminants are from outgassing, outside air or process chemicals. An outgassing screening program combined with process effluent control can eliminate compounds harmful to sensitive substrates, yielding molecularly clean cleanroom air.[17] Some FAB's have been shut down, delayed in startup or had production impacted due to silicones, phthalates and phosphates.[8]

4. For those materials that have high outgassing rates, yet have unique properties that make substitution difficult (e.g. HEPA gel seals),

practical engineering tests have been developed that closely simulate actual use conditions. These tests can be used to select the lowest outgassing material available, and to QC each lot so that formulation or mixing variations do not upset production. In principle, multiplying the engineering method outgassing rates of materials by the amount used in the FAB can be used to assess the biggest contributors to FAB contamination. If the total projected FAB outgassing is divided by the FAB air flow and multiplied by the recirculation ratio, predictions of airborne contaminant level contributions for each material can be made.

5. Eventually, correlations will be made between the sources of organic contaminants, how much is being transported in the air, how much is deposited on the substrate, and how much specific organics affect specific processing steps. Only then can rational contamination limits for specific materials and processes be specified. The proposed standard test methods described here could allow formation of an outgassing database that will aid making these correlations. By having one screening test, the cost of each vendor qualifying components for multiple users will be greatly reduced.

6. If a screening program for outgassing is implemented, and process chemical contamination is controlled, molecular contamination can be greatly reduced. Some yields will go up, some processes will allow longer hold times between processes without re-cleaning, and it is conceivable that some cleaning steps might be eliminated. This would give the biggest return on investment since it would reduce scrap, cycle times, cost of equipment and process footprints.

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FIGURE 1. GC-MS ANALYSES OF COMPOUNDS OUTGASSED FROM POTTING MATERIAL AT 100°C/30 min, SHOWING TRIETHYL PHOSPHATE (0.2 ppmw).

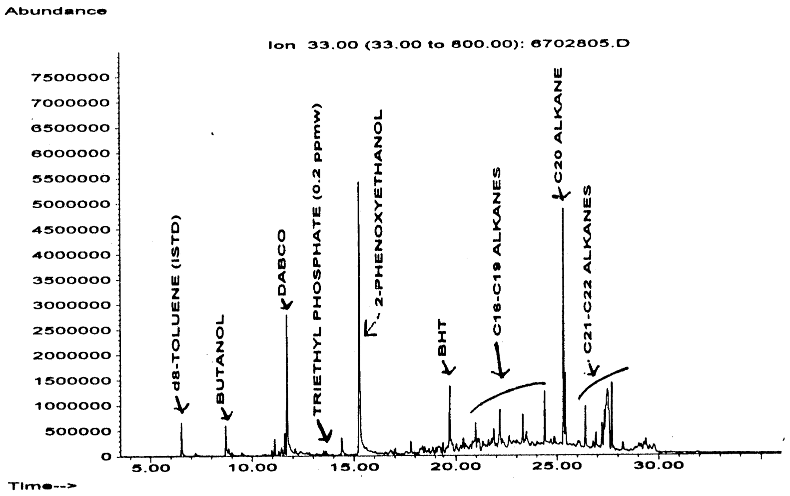


FIGURE 2. MASS SPECTRA OF TRIETHYL PHOSPHATE ALONG WITH THE BEST MATCH FROM GC-MS LIBRARY.

```
Library Searched : C:\DATABASE\wiley275.L
Quality          : 93
ID               : Phosphoric acid, triethyl ester (CAS) $$ Triethyl phosphate $$ TRIETHYL ESTER O
                   F PHOSPHORIC ACID $$ Ethyl phosphate $$ triethyl-phos
```

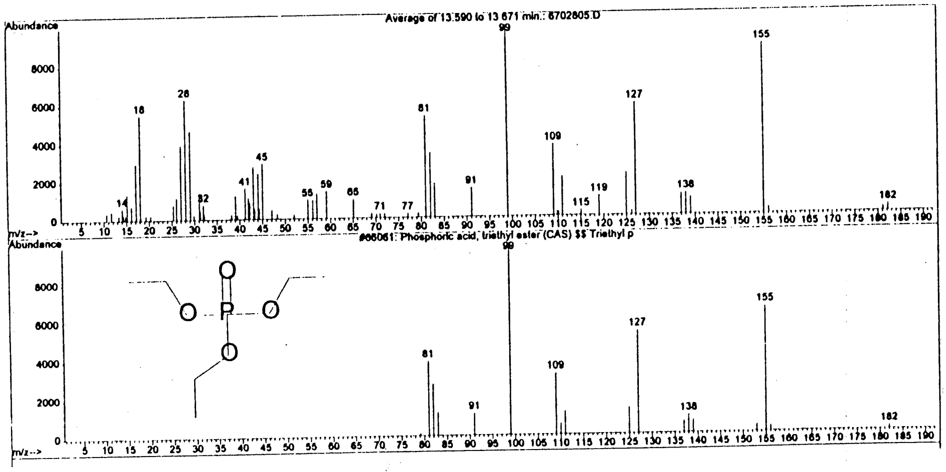


FIGURE 3. GC-MS ANALYSES OF COMPOUNDS IN FAB AIR SHOWING TRIS(CHLOROPROPYL) PHOSPHATE (0.07 ppbM or 0.9 ng/L).

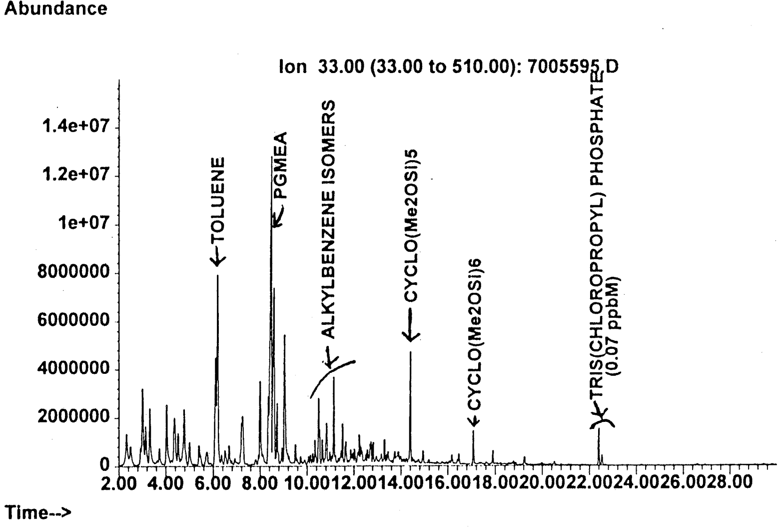


FIGURE 4. GC-MS ANALYSES OF COMPOUNDS OUTGASSED FROM POTTING MATERIAL AT 100°C/30 min, SHOWING TRIS(CHLOROPROPYL) PHOSPHATE (531 ppmw).

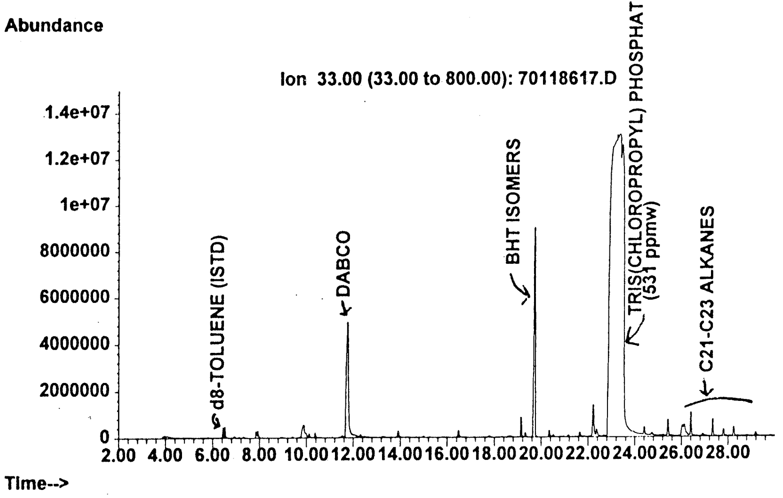


FIGURE 5. GC-MS ANALYSES OF COMPOUNDS OUTGASSED FROM HEPA GEL SEAL AT 100°C/30 min, CURE TIME 70 DAYS.

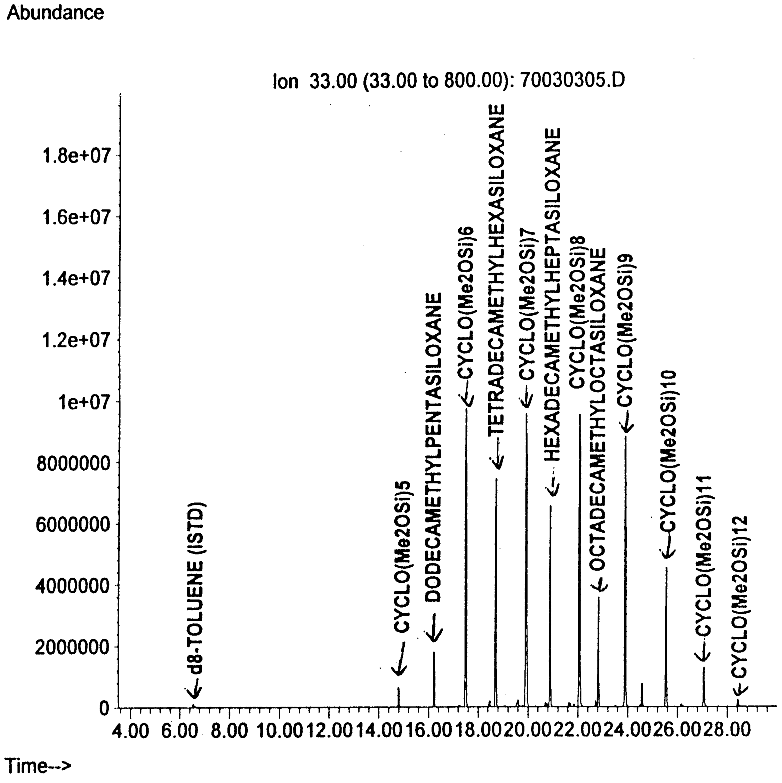


FIGURE 6. GC-MS ANALYSES OF COMPOUNDS OUTGASSED FROM HEPA GEL SEAL AT 23±1°C, FLOW RATE 100 mL/min, 40% RH AIR, CURE TIME 70 DAYS.

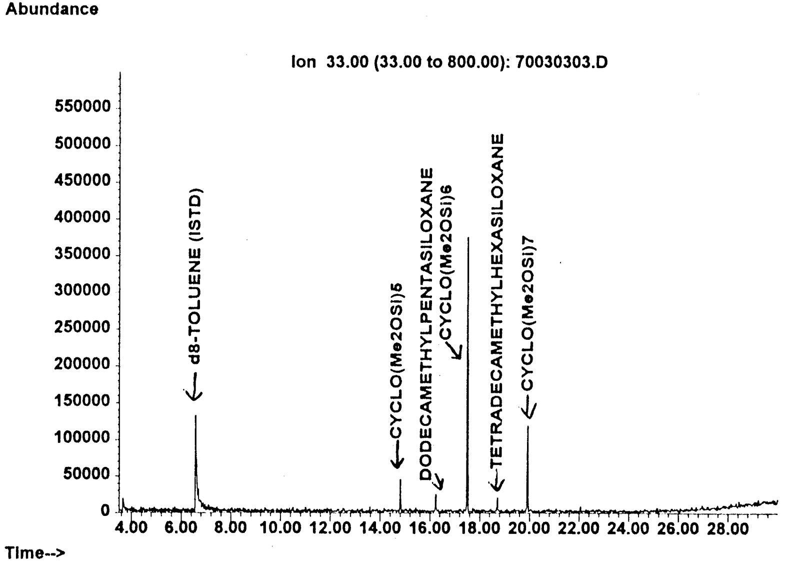
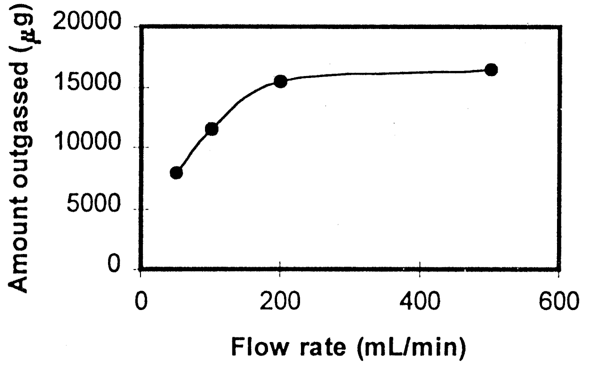


FIGURE 7. ENGINEERING STUDY FOR SILICONE HEPA GEL SEAL IN U-GRIDS: Effect of flow rate on measured outgassing values, units μg/day per 2'x4' HEPA (12' perimeter). Gel cured 7 days prior to test. Test using 40% RH air at 23±1°C.



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