Identification of Organic Contamination in Cleanroom Air, on Wafers and Outgassing from Gloves & Wafer Shippers

by

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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 molecular contaminants, especially organics, acids, bases and dopants. Some of the molecular compounds can cause disastrous yield losses or degradation of electrical properties. These contaminants need to be better controlled.

Organic contaminants can affect semiconductor processing in a variety of ways:

- Organics can form particles or films
- Organics on surfaces affect wetting, etching & particle removal
- If wafers don't wet: reduced effectiveness of cleaning with SC-1, SC-2, piranha, HF-peroxide. Metal contaminants are not removed.
- Uneven etch rates cause roughness of surfaces
- Incomplete etching of metals or polysilicon can cause shorts
- Organic deposits can cause high resistivity or opens for contacts
- Contact corrosion (especially for halocarbons)
- Adhesion between layers is affected, usually adversely
- High temperature processing can form silicon carbide[2] (esp. during RTP)
- Photolithography defects:
  - ◊ Amines, NMP (N-Methylpyrrolidinone), ammonia from HMDS (hexamethyldisilazane), and other bases can affect chemically-amplified photoresist at ppb levels ("T-topping")[3].
- Amines can react with acids to form ammonium salts = particles, TDH (time-dependent haze): affects PWP (particle per wafer pass) studies, Particle mapping
- Affect surface analysis, charging, ellipsometry
- Streaking during application of SOG, photoresist, polyimide
- Organophosphorus compounds in air or from carriers can n-dope wafers[4]

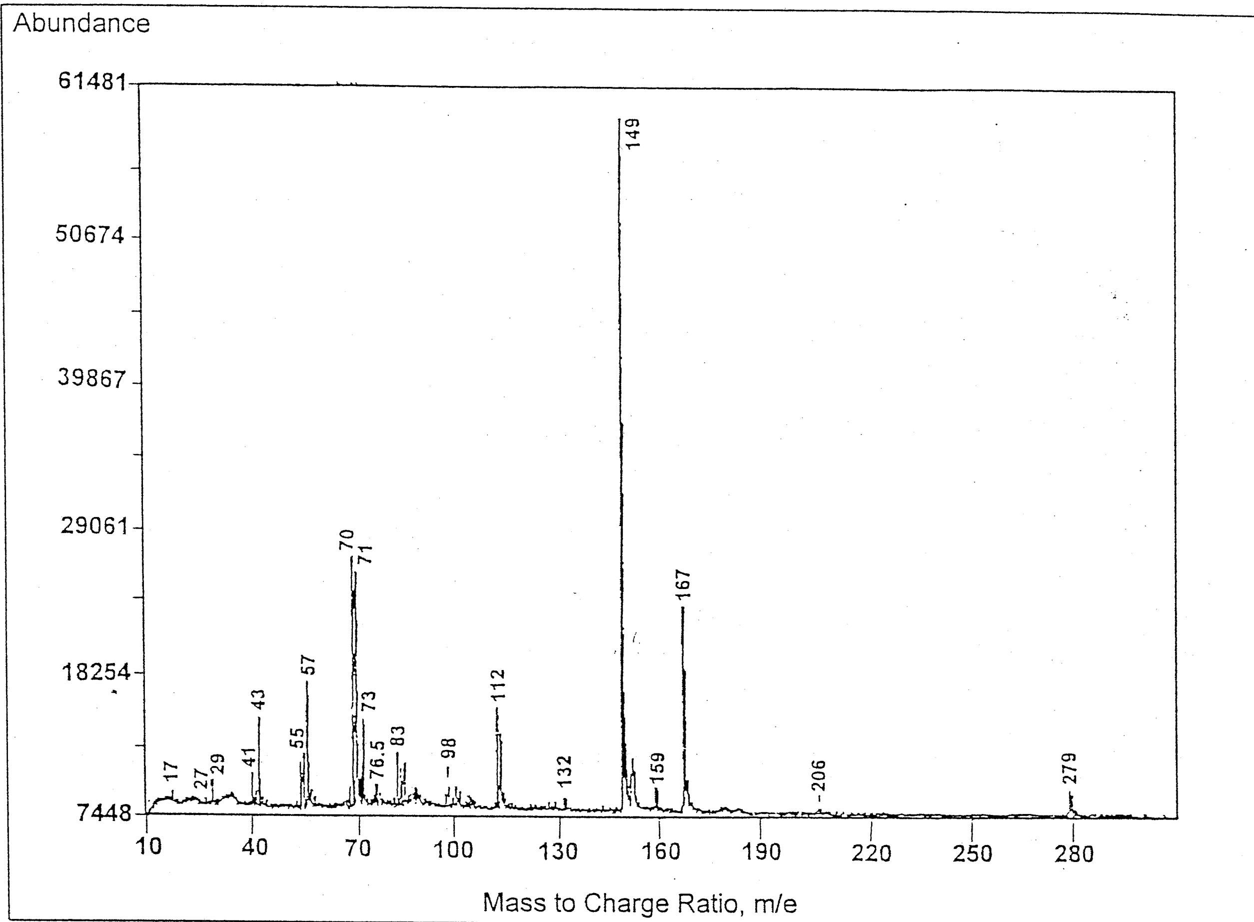


FIGURE 1. Single photon ionization SALI[12] analysis of a piece of an 8" wafer with organic contamination. The mass spectrum is that of a phthalate ester, possibly DOP (dioctylphthalate)

The single photon ionization SALI technique shows promise of having less fragmentation than TOF-SIMS and possibly of being more readily calibrated since compounds are ionized with near unit efficiency.

Other methods such as TD-GC-MS and TD-IMS can address whether lower boiling compounds are also adsorbed. The TD-GC-MS method has the unique ability to ID and quantitate each compound in a complex organic mixture.

Sources of Wafer Contamination

Wafers can get contaminated by molecular contaminants from a variety of sources such as: cleanroom or minienvironment air, gases, UPW (ultra pure water), process chemicals, reactors and outgassing from FAB construction materials or components.

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:
  - ◊ polysilicon grain size: can lower breakdown voltage
- Selective CVD:
  - ◊ loss of selectivity
  - ◊ loss of nucleation
- Epitaxy - organics can cause crystal defects
- Salicides

Some estimates of the impact of condensable organics on specific process steps have been made.[5]

High boiling organics tend to adhere to wafer surfaces more strongly than lower boiling compounds[6]. The high boiling organics can be detected at monolayer levels or below by a variety of techniques including:

- TOF-SIMS (Time Of Flight-Secondary Ion Mass Spectrometry)[7]
- TD-GC-MS (Thermal Desorption-GC-MS) [8]
- TD-IMS (Thermal Desorption-Ion Mobility Spectrometry)[9, 10]
- FTIR (Fourier Transform Infrared spectroscopy, especially polarized grazing angle) [11]
- XPS = ESCA (X-ray Photoelectron Spectroscopy, Electron Spectroscopy for Chemical Analysis)
- SALI (Surface Analysis by Laser Ionization, with either single- or multiple-photon ionization)[12]

Of these, single photon ionization SALI is a new technique that has been investigated by this laboratory. An example of identification of organics on a bare silicon wafer by SALI is given in **Figure 1**. Note that it is the high boiling compounds that are found by SALI and other vacuum techniques. Since low boiling compounds may be lost into the vacuum system prior to analysis, it is difficult to tell whether they stick to the wafer surface under ambient conditions.

measurement, little useful information is obtained for a typical FAB with << 1 ppm of higher boiling organics.

The organics can be concentrated onto an adsorbent, followed by GC (Gas Chromatography) analysis which separates compounds approximately by boiling point range. GC gives greatly improved detection limits for the types of compounds that are likely to cause processing problems. GC can be used to track the approximate boiling ranges of compounds in cleanrooms. However, compounds detected cannot be positively identified.

Using a mass spectrometer (MS) as the detector for the GC analysis is currently the most practical for identification and quantitation of complex mixtures of organics in air at trace levels (ppb). GC-MS has been used to identify volatile organics in FAB's.

Existing Standardized Tests Of Organics In Air

Procedures developed by OSHA[13] and NIOSH[14] already exist for monitoring organics in workplace environments. These procedures do not use GC-MS and the detection limits are generally high, in the ppm range. In addition, OSHA regulates toxic materials, and many materials with low toxicity can be quite detrimental to processing at low levels. Examples include: organophosphates that can dope wafers; silicones, hydrocarbons, and phthalate plasticizers that can adhere strongly to wafer surfaces; and amines. Hydrophobic organic compounds can prevent effective wetting, etching and cleaning of wafer surfaces.

EPA GC-MS methods exist for detecting trace organics in the atmosphere that can cause air pollution in urban environments (TO = toxic organic methodsand[15]) other methods for identifying trace organics in indoor air (IP = indoor air pollutant methods[16]). These methods do have ppb detection limits, but emphasize the analysis of low boiling compounds including solvents. For many semiconductor and disk drive industry processes, low boiling compounds are less likely to cause problems than the higher boiling compounds that adhere strongly to the wafer surface.

We have developed methods for identifying organic contaminants in cleanroom air, 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, i.e. 50-100°C. Testing that is often done at higher temperatures is not representative of what outgasses at lower temperatures. With more sensitive instrumentation, we can approach testing under ambient conditions.

Airborne Contamination

To address airborne molecular contamination problems, SEMI has approved a new standard, SEMI F21-95, "Classification of airborne molecular contaminant levels in clean environments" that classifies cleanrooms for molecular acids (HF, HCl, etc.), bases (includes NMP, ammonia, amines), condensable (organics including silicones and hydrocarbon compounds with bp's > 150°C), and dopants (e.g., boron, phosphorus and arsenic compounds).

This standard does not specify methods or calibration guidelines to make concentrations determined by different labs or methods comparable. Since no lab can be calibrated for all of the thousands of organic compounds that are used in FAB's, it is possible that two labs sampling side by side and using appropriate methods can legitimately come up with different results. Some standardization of the calculations of results is needed.

Measurement of Organics In Cleanroom Air

Total organics in air can be determined using a Flame Ionization Detector (FID), but identification of each individual compound is needed if you are to track down the source of the contaminants.

Using an FID detector alone, you can achieve a reliable measurement of the total organics in the air as THC (Total HydroCarbons, calibrated with methane). Since the main organic in FAB air is usually methane (typically >2 ppm in air worldwide) and the methane usually dominates the

Air is pulled into an adsorbent tube for 6-8 hours. The tubes are thermally desorbed so that nearly all of the analytes go into the GC-MS system, giving excellent detection limits (typically < 1 ng/L, 0.01 ppbv achievable). Based on the levels of contaminants currently seen in FAB's, the detection limits of <1ng/L are more than adequate when compared with the higher levels of contamination currently found in FAB's.

Figure 2 shows that this method recovers hydrocarbons with boiling points well above EPA and OSHA methods (these methods typically cover compounds with boiling points under 215° C only). A typical GC-MS chromatogram for a standard is shown, in Figure 2, where it can be seen that compounds with a wide boiling point range are recovered by one analysis.

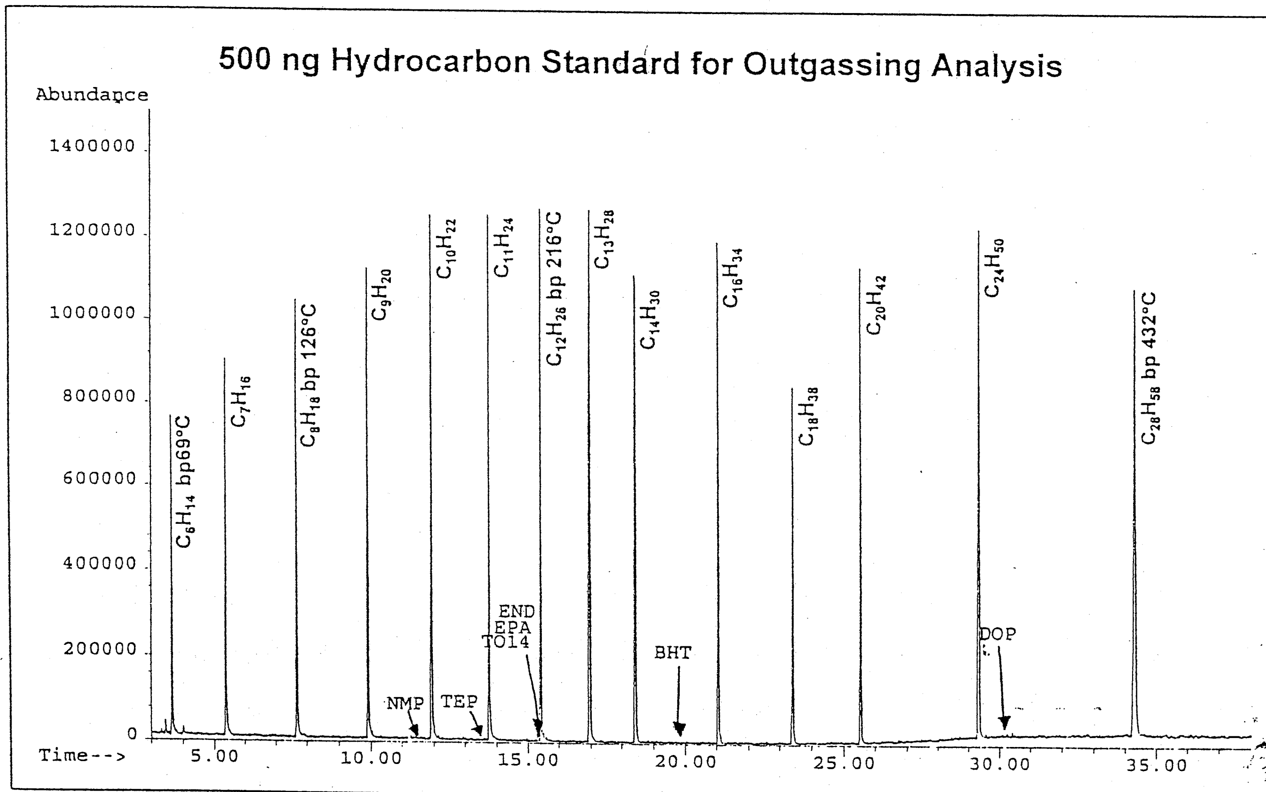


FIGURE 2. GC-MS instrument calibration with a hydrocarbon standard demonstrating recovery of C_6 to C_{28} hydrocarbons. For comparison, EPA method TO-14 only covers compounds to C_{12} at best. EPA methods would not see high boilers such as DOP plasticizers or BHT antioxidants. Nor are compounds such as NMP or TEP (triethylphosphate) on EPA target lists. Both of these compounds have mass 99 peaks and would often be mistaken for hydrocarbons.

A typical baseline study of FAB's would test the outside air and the recirculation air in each FAB area, e.g., diffusion, lithography, wet cleaning, inspection, etc. The lithography area is generally the most contaminated with organics. Figures 3-6, shows some results from a typical new FAB.

Methods are needed for high boiling organics

A recent paper[6] 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). 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.

We have also looked at organics on wafer surfaces and found high boilers present, such as DOP, TXIB (a plasticizer, Texanol isobutyrate) and silicones. These results were obtained using TD-GC-MS, and a newer technique called SALI (Surface Analysis by Laser Ionization). Other groups have found the same types of molecules using other techniques including TD-IMS and TOF-SIMS.

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, some FAB's specify no DOP should be used. The EPA methods do not look for these compounds.

Nearly all semiconductor FAB's specify no organophosphates since they can dope the silicon wafers. Yet we still encounter silicon wafers with N-doping problems. Phosphates are especially common flame retardants in urethane polymers used as foams and sealants, e.g., in HEPA hoods[4].

Air Monitoring By GC-MS

A modification to the EPA methods was developed by Balazs Analytical Laboratory in 1995. This procedure uses tubes containing a proprietary mixture of adsorbents that trap compounds from C7 (heptane) to high boiling compounds such as octacosane ($C_{28}H_{58}$) and DOP (dioctyl phthalate, a plasticizer bp 384° C).

Figure 3 is a typical example of air coming into a FAB. The compounds detected were typical of urban air. They included:

- Aromatics:
  - ◊ benzene, toluene, xylene, trimethylbenzenes: from autos, paints, etc.
- Aliphatic hydrocarbons:
  - ◊ pentanes, hexanes, octanes, nonanes, decanes, undecanes
- Chlorocarbons:
  - ◊ TCE from dry cleaners
  - ◊ TCA, possibly from degreasing, paint stripping

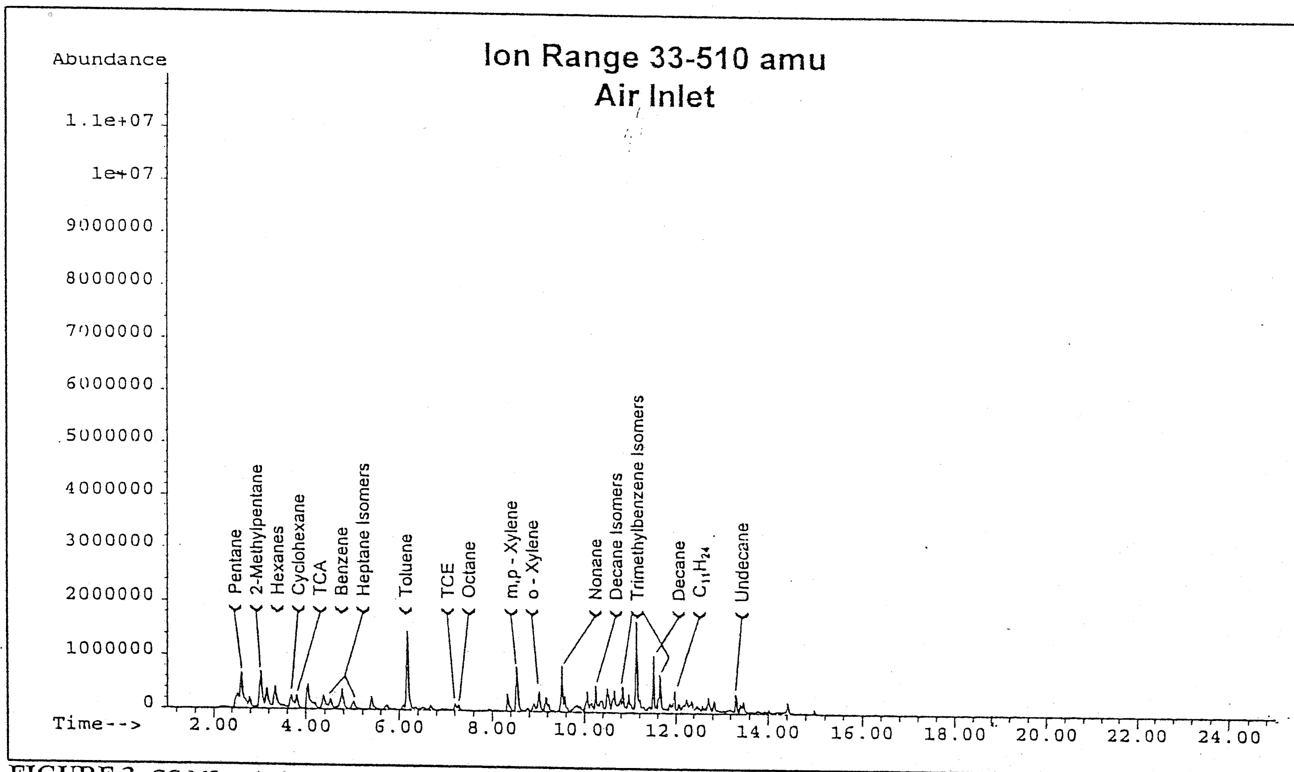


FIGURE 3. GC-MS analysis of outside air coming into a FAB. Low levels (ppb) of organics common in urban environments were detected.

These compounds have been detected throughout the FAB. Increases in their levels over outside air are due to their use in the FAB.

Figure 4 shows the mass spectrum used to identify the small tetrachloroethylene (TCE) peak in Figure 3. Despite being a small peak, the best computer match to a NIST library of 75,000 reference spectra was 96%. The molecule was unambiguously identified based on its fragmentation pattern. In addition, each compound can be confirmed based on its retention time.

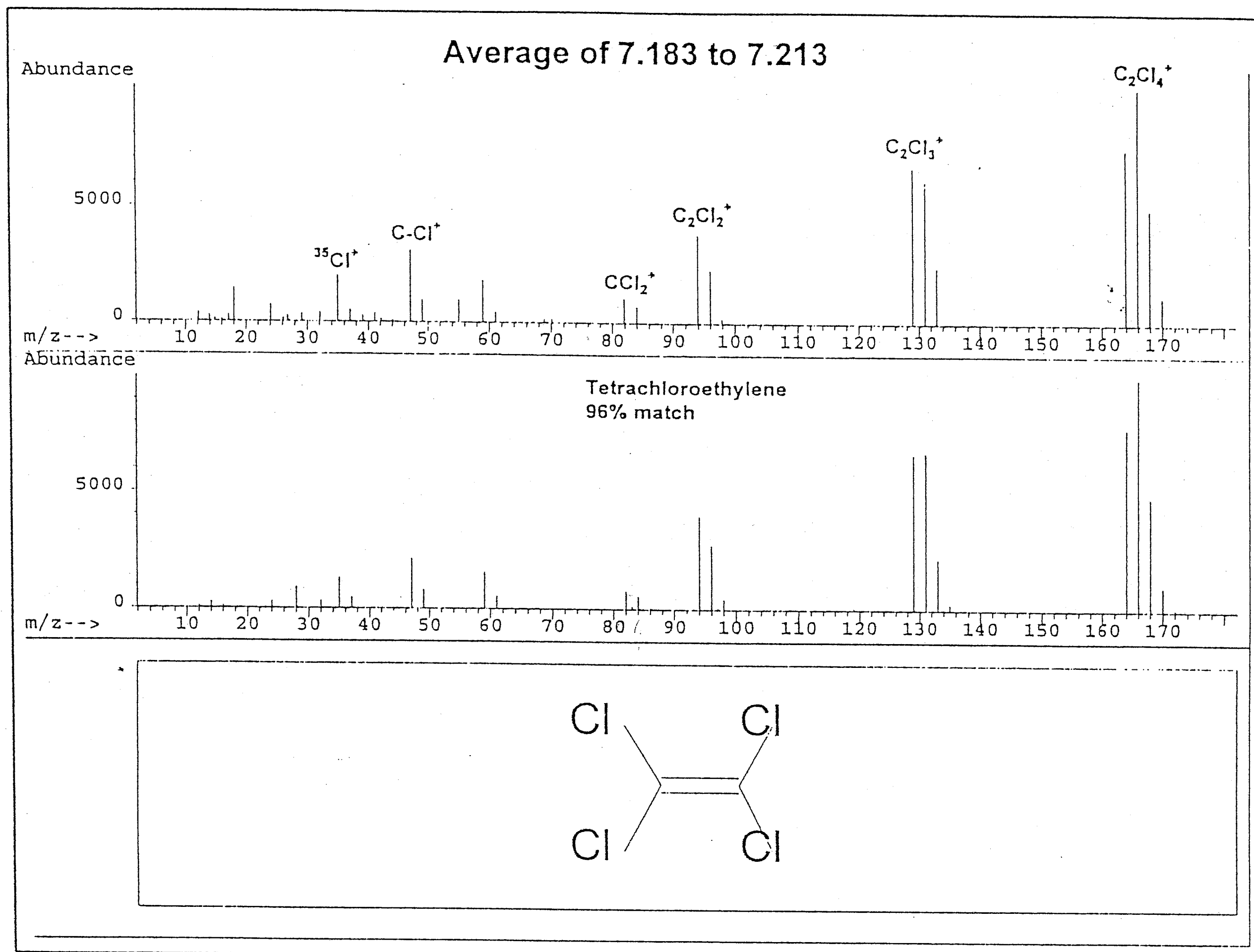


FIGURE 4.

A second GC-MS analysis of the makeup air after filtration and humidification (not shown) was identical to that shown in Figure 3. This demonstrated that the HEPA filters, while removing particles, have no effect on the molecular organics. The humidifier can affect polar molecules such as IPA, but IPA was not observed in the outside air for this study.

Outside air can often have other solvents present that are specific to industries in your area. The amounts present can vary dramatically with wind velocity, wind direction, and depending whether operations such as painting, roof tarring or road paving are in progress.

Many FAB's are a significant source of their own incoming contamination due to incomplete scrubbing. HMDS hydrolysis products trimethylsilanol and hexamethyldisiloxane are often seen:

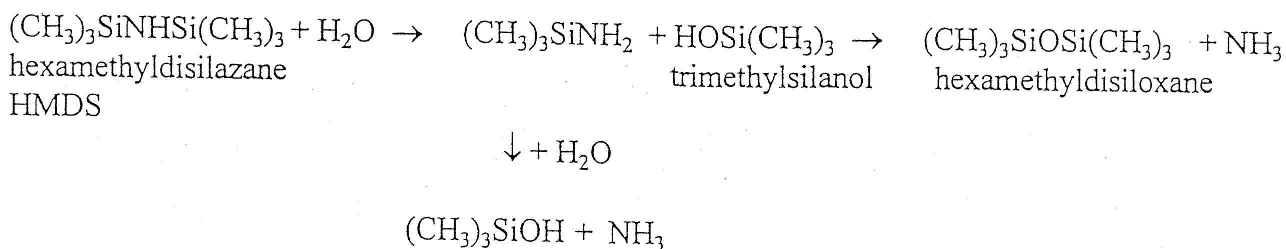


Figure 5 shows the GC-MS analysis of the air in one photolithography area. The analysis of two other lithography areas gave nearly identical results, indicating that the FAB is the source of many ubiquitous organic compounds found in FAB air. Siloxane byproducts from HMDS, photoresist solvents, NMP and cyclic silicones, possibly from a HEPA gel, were detected.

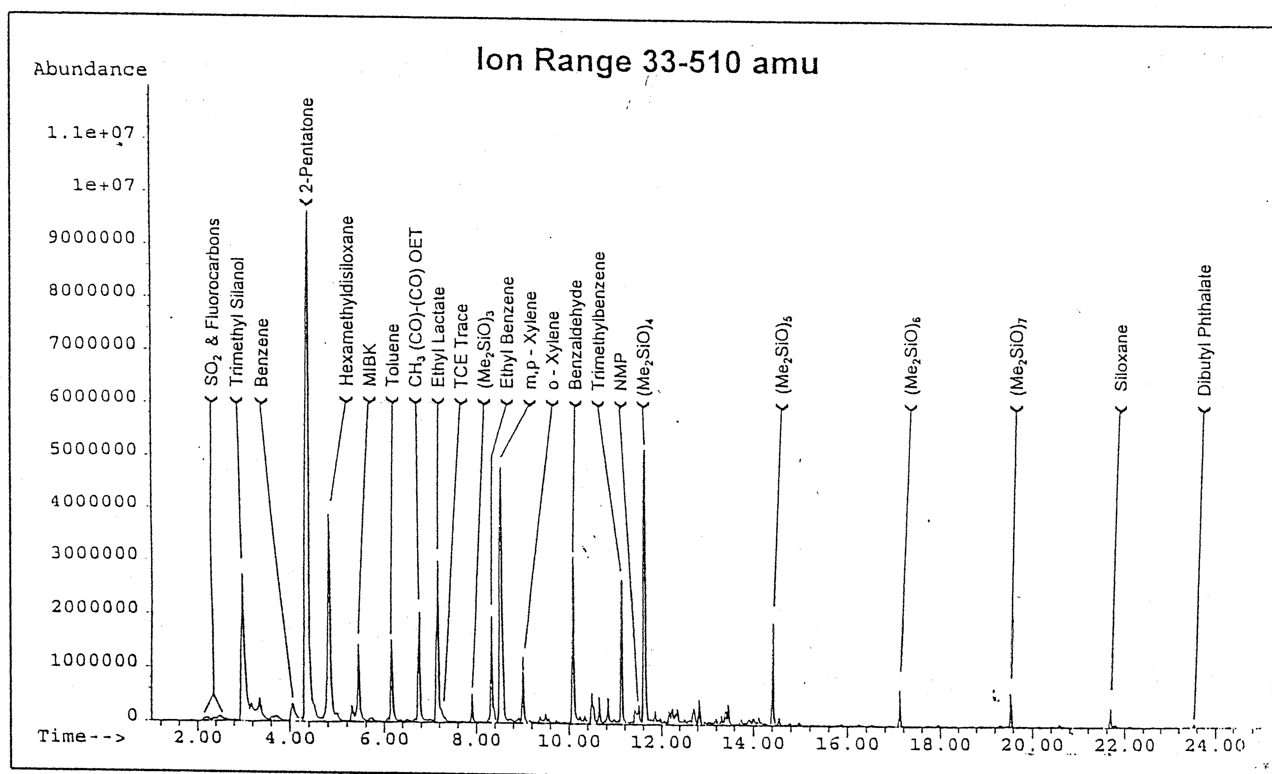
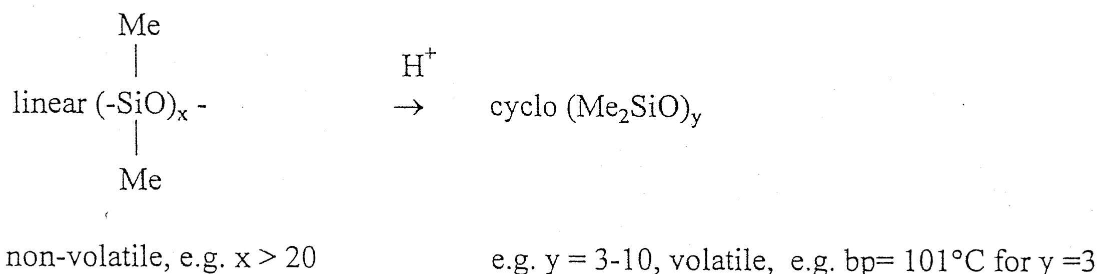


FIGURE 5.

The SO_2 is probably from the use of piranha baths, or possibly due to the photoresist itself. The 2-pentanone and MIBK solvents are ketones that might be used, e.g., as edge bead removers or post stripper rinses. The fluorocarbons might be from RIE (Reactive Ion Etching). The amount of toluene was very similar to that seen for the makeup air, suggesting most comes from the outside air. The ethyl lactate is a common solvent for photoresists, and its oxidation product was

also seen. Trace TCE was probably from outside air. It was detected by mass spectroscopy despite having a large peak superimposed over it. This is one huge advantage of GC-MS over other GC techniques. More xylenes were observed than for outside air. Xylenes may be used as negative resist developers or as solvents. The benzaldehyde may be from positive photoresist oxidation. NMP is commonly used as a stripper. NMP is known to have disastrous effects on some chemically amplified photoresists ("T-topping") even at ppb levels[3]. It is important that NMP be kept below ppb levels for some new photoresists. NMP is sometimes used as a solvent for polyimides, paints or other materials. A series of cyclic polydimethylsiloxanes were detected. They could come from silicone sealants or possibly from silicone gel seals used to seal the edges of the HEPA/ULPA filters. In a running FAB, it is possible that some acidic vapors catalyze the decomposition of low volatility polymeric silicones to form the more volatile cyclic compounds:



$$\text{linear } (\text{-}\underset{\text{Me}}{\overset{\text{Me}}{\text{Si}}}\text{O})_x\text{-} \xrightarrow{H^+} \text{cyclo } (Me_2SiO)_y$$

non-volatile, e.g. $x > 20$ e.g. $y = 3$-10, volatile, e.g. bp= 101°C for $y = 3$

A small amount of dibutylphthalate (a plasticizer) was detected, but no higher boiling phthalates (e.g., DOP) were found at this FAB. Some FAB's that have large amounts of PVC curtains do have detectable amounts of airborne DOP which is known to strongly adhere to wafers.

If any carbon filters are installed as a means of trapping organic compounds in air, they should be tested upstream and downstream to assess their efficiency versus time. Carbon filters might prove useful for controlling NMP, higher boiling amines, and high boiling antioxidants and plasticizers. The ammonia created by HMDS hydrolysis and amines can be removed by acidic filters, but one should test to ensure that no acidic compounds (e.g., phosphoric acid), or products of their reactivity (e.g., POF_3) come out of these filters to cause worse problems.

Figure 6 shows the GC-MS analysis of the air in the chemical mechanical polishing area. The lithography chemicals are no longer observed. Some xylenes and some proprietary solvents unique to this area were detected. As with the lithography area cyclic silicones, possibly from HEPA gels and trace dibutylphthalate were detected. The diffusion area was similar except a proprietary solvent was absent.

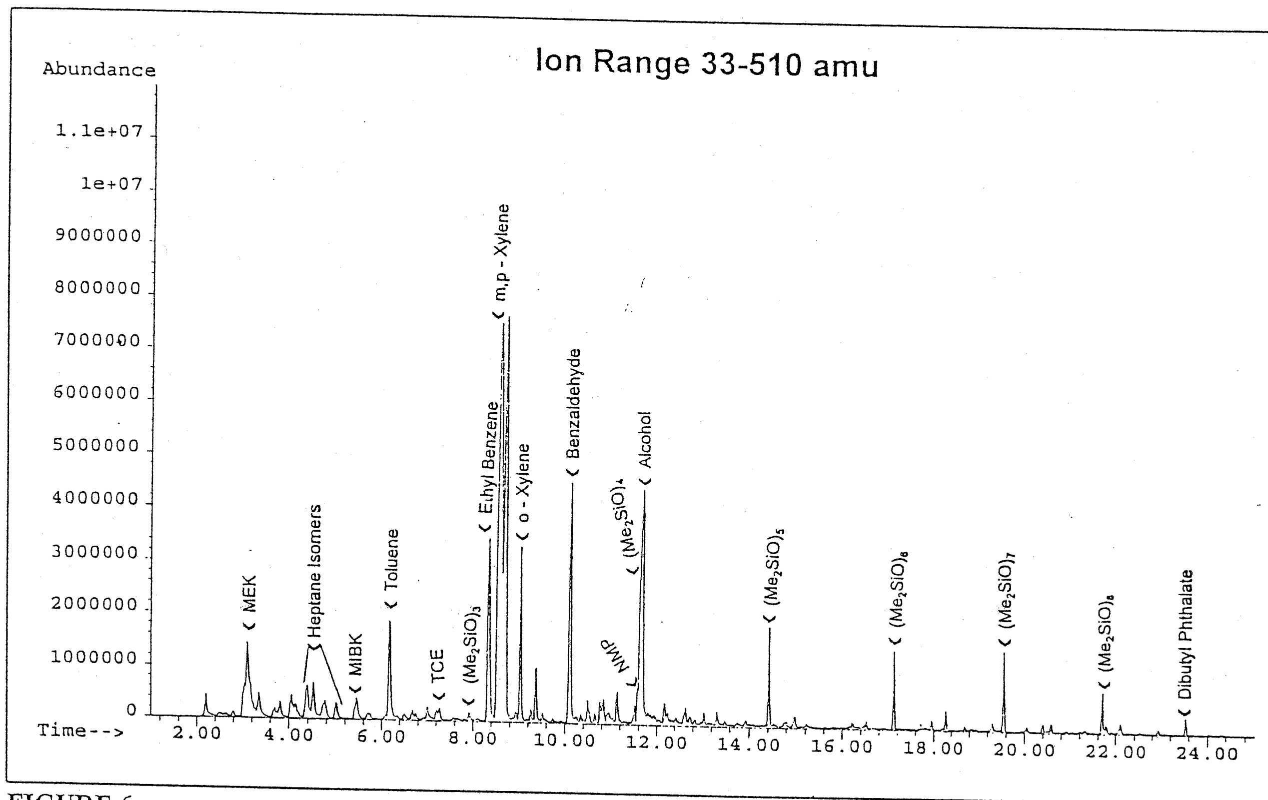


FIGURE 6.

Types Of Studies That Can Be Performed On Cleanrooms.

All cleanroom should have a baseline analysis to assess what types of compounds are present. The study should be repeated periodically to assess how much the contaminants vary in type and concentration. The variations can be dramatic and often times controllable. If contaminants of potential concern are found, they should be identified, and their sources eliminated. This can be accomplished by better venting of process chemicals, better scrubbing of the FAB's effluents, changing the chemistries used (e.g., eliminating NMP or phosphate use) or if needed, by using gas phase adsorber cells when practical.

Any gas phase adsorber cells can be evaluated by installation in a single grid and testing for the removal efficiency versus time. An annual change-out may be acceptable, but a weekly change probably will not. The filter lifetime when installed in the actual area where they will be used needs to be determined, e.g., by sampling upstream and directly downstream of the filter after 1 day, 1 week, 1 month, 4 months and a year. Some common solvents may break through quickly (e.g., IPA), but the lifetime of the filter for more detrimental, high boiling compounds such as DOP and TEP may be much longer. The lifetime depends on the concentrations present and the maximum contamination limits needed.

The highest levels of contamination are often during maintenance or mishaps. Few impact studies correlating specific organics with device problems have been made. If sampling is performed during startup, after any maintenance painting, HEPA installation, or after a spill of organics, data will finally be available to assess at what level these compounds may have an impact on processing. For example, the baseline level of some silicones might be 2 ppb. After installing new HEPA's using a silicone gel seal, the silicones might hypothetically go up temporarily to 20 ppb for two days. If wafers were produced during this period without any negative effect on the processes in this area, you could conclude that 20 ppb of silicones in the FAB was tolerated, and you might attempt to keep the silicones below this level to be conservative. In contrast, if a crash was experienced, you could conclude which process failed and you could make a specification for silicones << 20 ppb, or possibly use other sealants in the future. Silicones were picked strictly as an example, and the same logic could be applied to other seals including hydrocarbons, urethane gels or gasket seals.

FAB air has been monitored during the time that the FAB was being painted. For some paints, the amount of volatile organics from the paint were minuscule compared to the amounts of organics already in the FAB, e.g., due to lithography. In this case, it was concluded that the particular paint being used should not pose a problem to wafer production.

Other sources of contamination in cleanroom air include all of the FAB construction materials. We have a standard program for determining the relative outgassing of all FAB materials at selected temperatures, e.g., 50, 75, or 100° C. A mass spectral library of the results has been compiled and used as a reference. This library resulted in more positive identifications leading to more rapid contaminant source identification.

A surprising number of materials still outgas organophosphates, some at very high levels. All urethanes should be tested to be sure no phosphates are present. DOP or other plasticizer's outgas from many plastics, especially PVC and many floor tiles, and the outgassing of these high boilers can continue for years.

By using the same instrumentation for outgassing as for air sampling, correlation can be made between outgassing of FAB materials with the compounds found in the cleanroom air.

Wafer Box Outgassing

One of the materials most likely to contaminate wafers is the wafer storage, transport and shipping boxes since they are polymeric and the wafers are stored in a static environment where the organics can build up over time. To illustrate this point, three wafer carriers were heated at 75° C for 1/2 hour and the volatile organics analyzed by dynamic headspace GC-MS. The results are shown, in Figures 7-9, using identical conditions.

Figure 7 shows that only a small amount of chlorobenzene outgassed from an 8" polycarbonate single wafer holder. This solvent is known to be present in the pellets used to make the wafer holders. No plasticizers or antioxidants were found.

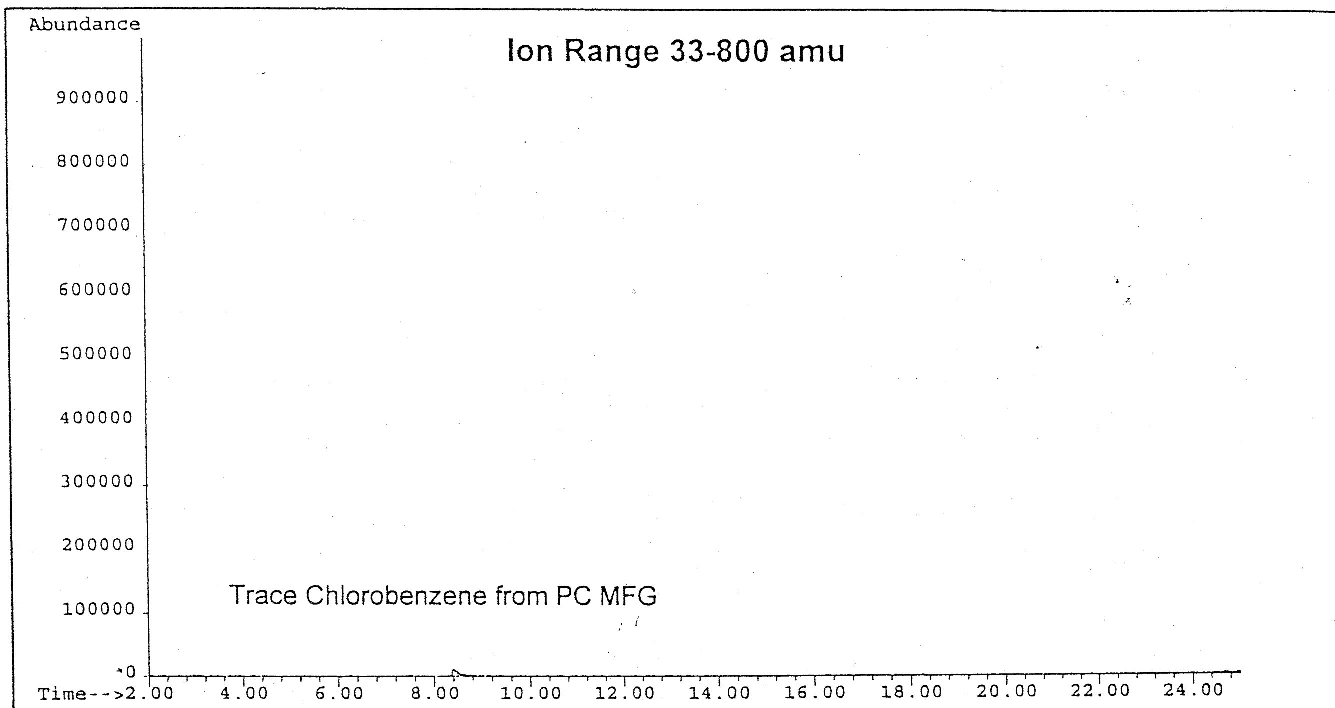


FIGURE 7. GC-MS analysis of outgassing from polycarbonate carrier when heated to 75°C for 1/2 hour.

Figure 8 shows the outgassing of a polypropylene single wafer holder from Vendor "A". Small amounts of a variety of polypropylene oligomers were detected, some with fairly high boiling points, e.g., 330° C. The presence of many oligomers suggests this polypropylene was made via a gas phase polymerization process.

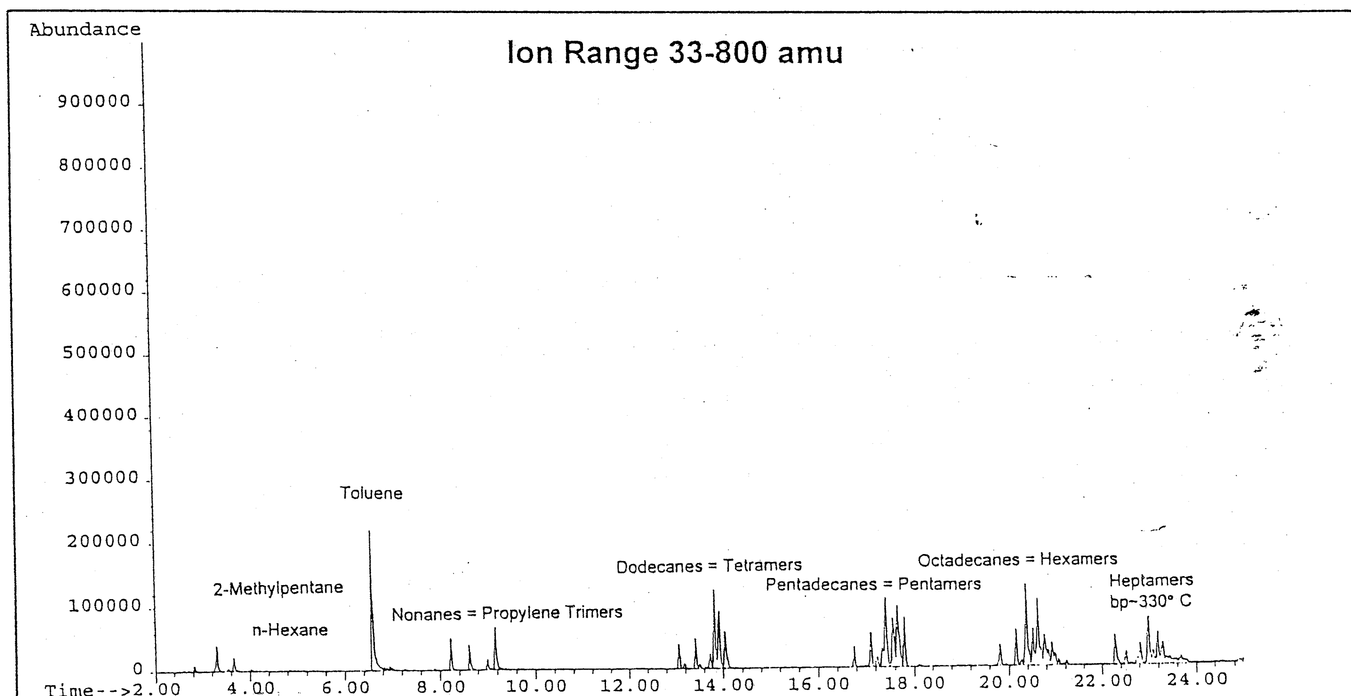


FIGURE 8. GC-MS analysis of outgassing from polypropylene wafer carrier from Vendor A when heated to 75°C for 1/2 hour.

Figure 9 shows the outgassing from a different polypropylene carrier. The lack of outgassing oligomers, and the presence of a variety of heptane solvents may suggest this polypropylene was made via a solution polymerization process.

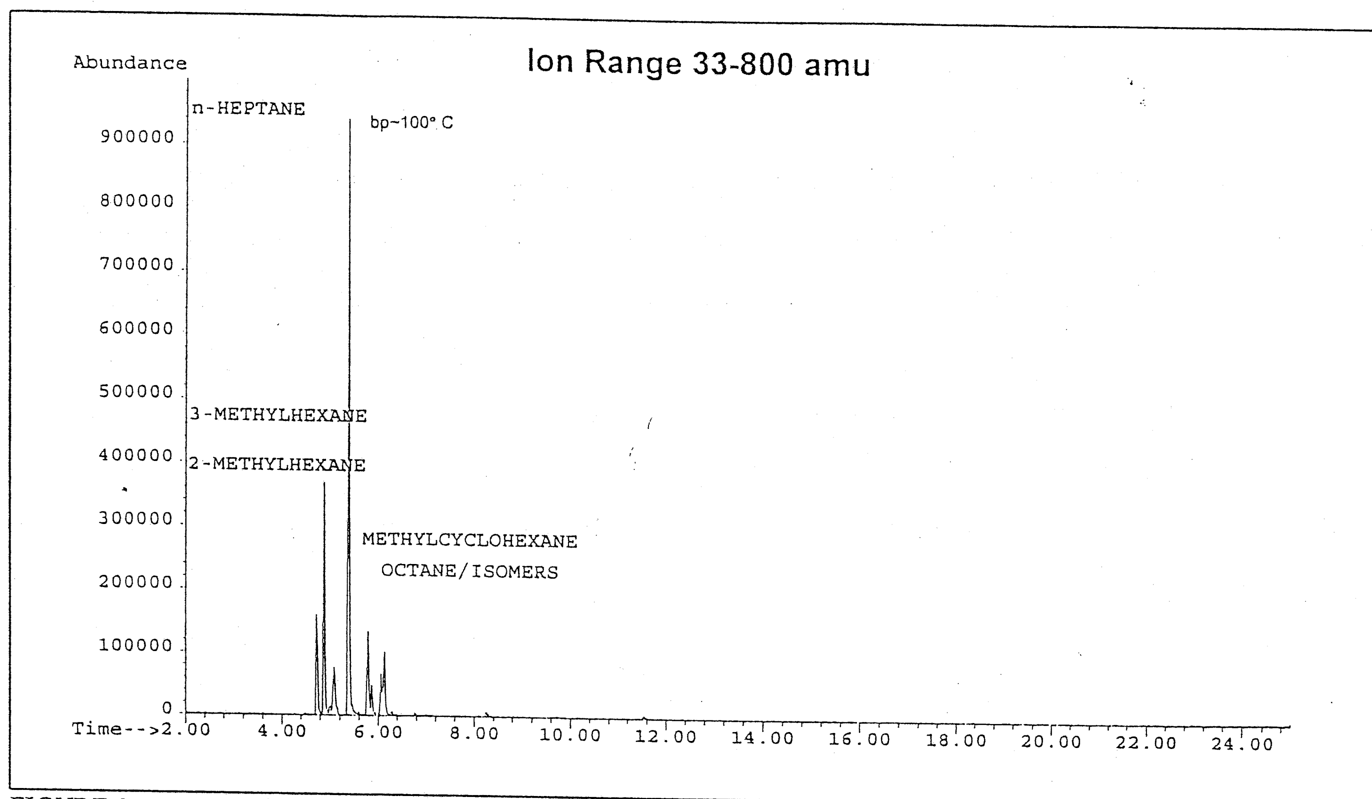


FIGURE 9. GC-MS analysis of outgassing from polypropylene wafer carrier from Vendor B when heated to 75°C for 1/2 hour.

Although the total organic outgassing from the polypropylene in Figure 9, was more than from the polypropylene in Figure 8, the polypropylene in Figure 8 is more likely to cause problems because the compounds are higher boiling and are more likely to adhere strongly to wafer surfaces. Thus it is not only how much and the types of compounds that outgas, but also their volatility that is important.

After use, some carriers can get grossly contaminated due to absorption of process chemicals. Segregation of carriers to a single area and periodic analysis for contamination buildup can prevent carryover of process chemicals from one area to another area where they can have disastrous consequences. Photoresist strippers based on amines or NMP are particularly prone to absorption into some carriers.

Gloves

Another source of potential wafer contamination is gloves, since they can get quite close to the wafers or wafer handling equipment. Outgassing studies of several gloves were conducted by heating them in a dynamic gas flow at 55° C for 1/2 hour. All analyses were performed under identical conditions and results were plotted to the same scale for easy comparison.

Many PVC gloves contained DOP plasticizer. After many episodes of contamination by DOP, some users have specified no DOP in their gloves. **Figure 10** shows the outgassing of a PVC glove. No DOP was found. Instead a large amount of TXIB, an alternative plasticizer, was detected. It is not known whether this will actually be any better than the DOP. Be aware that when users make a specification, vendors can reformulate to meet that specification, but the new product is sometimes worse than the original. The user will not know unless they or the vendor test all new formulations. Some gloves are now available that have essentially no outgassing of high boiling compounds.

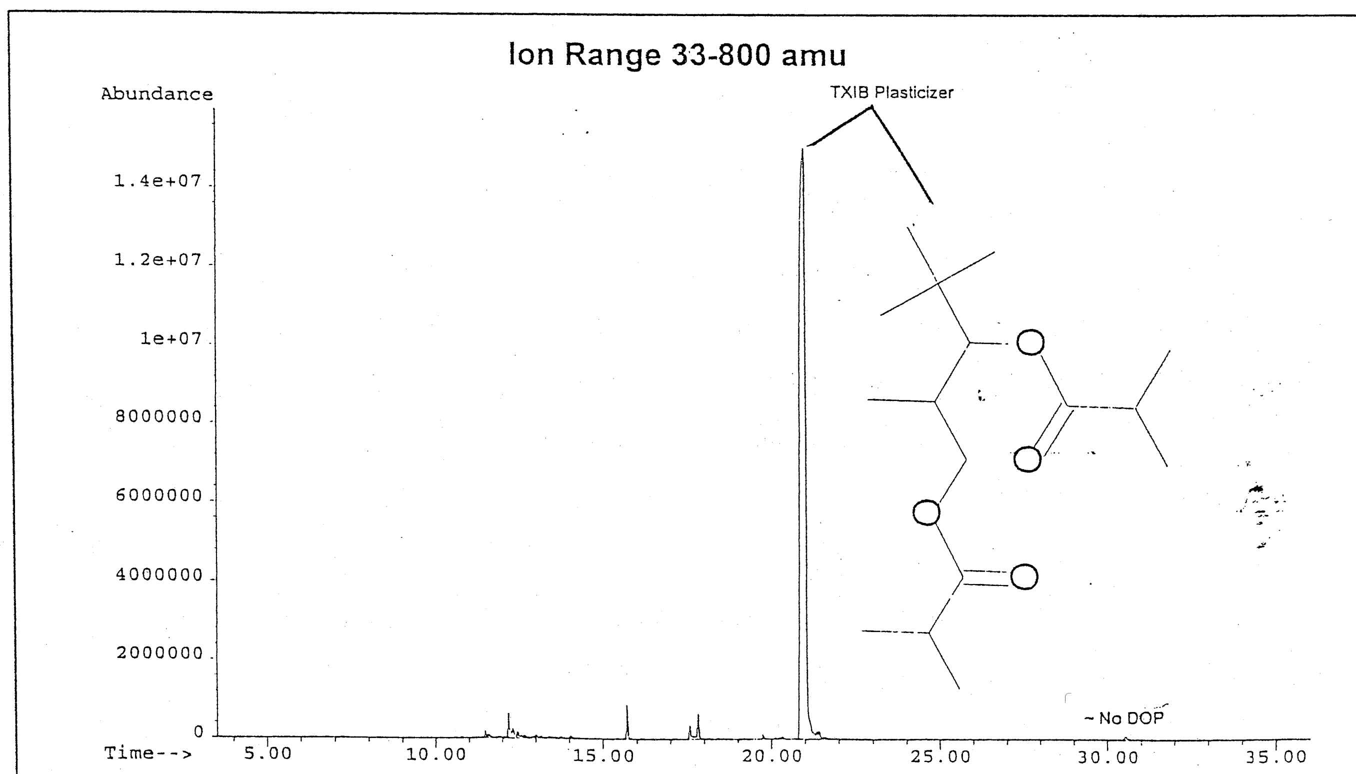


FIGURE 10. GC-MS analysis of outgassing from a PVC vinyl glove when heated 55°C for 1/2 hour. Almost no DOP was detected, but an alternative plasticizer (TXIB, 2,2,4-trimethyl-1,3-pentanediol Diisobutyrate) was detected.

Other gloves were studied, and each gave off characteristic compounds. The relative amount of outgassing from gloves decreased in the order PVC >>Nitrile > Latex > Nylon (Figures 11&12 respectively, Nylon not shown). While the PVC gloves outgassed the most, selection of gloves should include consideration of other properties such as particles, metals, and chemical resistance.

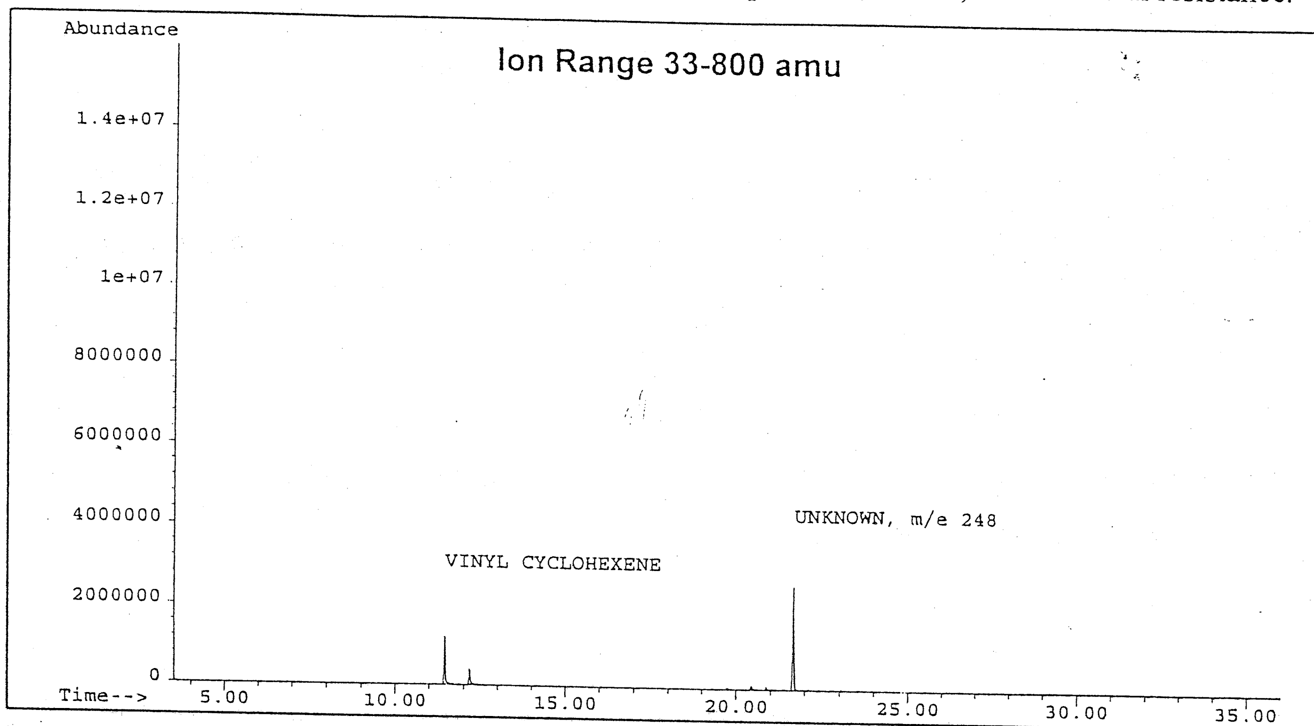


FIGURE 11. GC-MS analysis of outgassing from a Nitrile rubber glove when heated to 55°C for 1/2 hour.

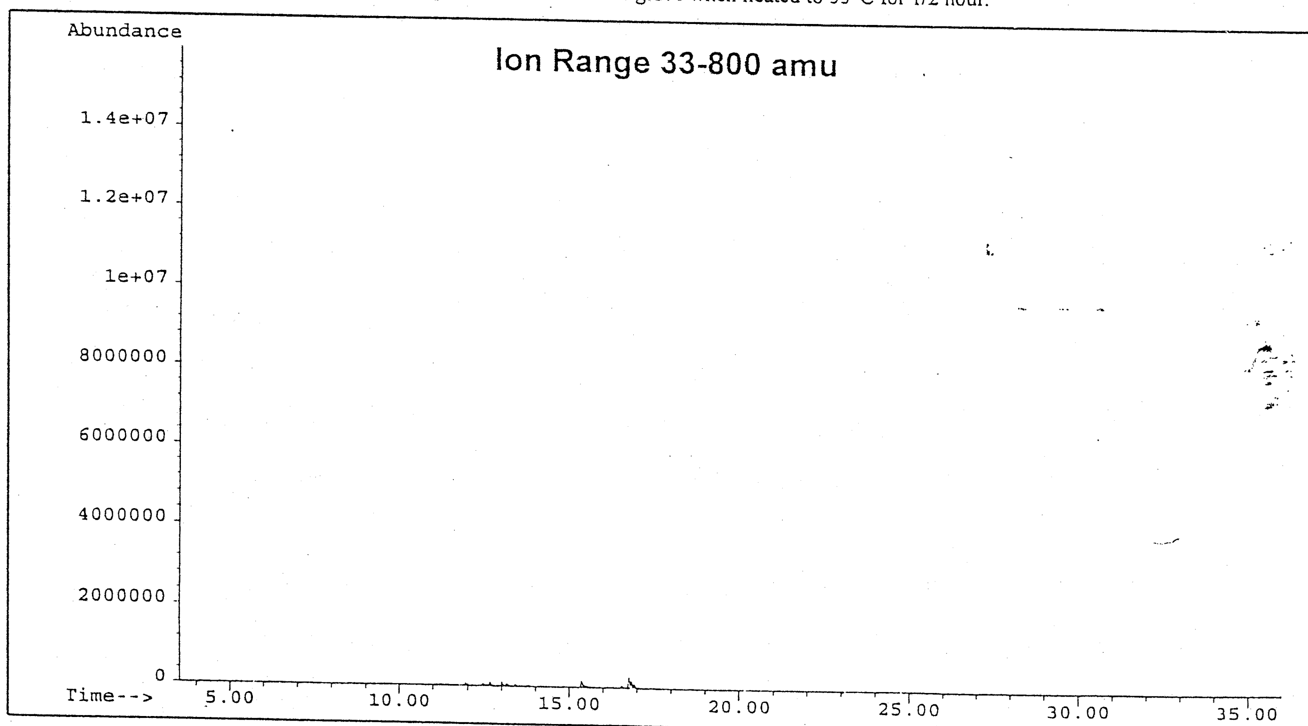


FIGURE 12. GC-MS analysis of outgassing from a Latex glove when heated to 55°C for 1/2 hour. Other Latex gloves were similar.

Summary

1. Methods are now available for looking at trace levels of a broad range of organics in FAB air, including high boiling compounds and compounds not on target lists.

2. Based on the compounds identified and levels found, assessments can be made whether the known contaminants are likely to be detrimental to specific processes.

3. Impact studies can be performed when doing routine maintenance, e.g., painting or HEPA installation with gel seals, to find out what is present under worse scenario conditions and whether this impacts any phase of production.

4. By monitoring the concentrations of organics during upsets, spills, etc., it is possible to establish relationships between concentrations of specific compounds and failures or lack of failures to develop control limits for specific processes.

5. Gas phase adsorber cells can be assessed for controlling specific contaminants. A single gas phase adsorber cell should be monitored vs. time to assess whether it is likely to have a useful lifetime for the contaminants present. A year lifetime is probably practical, but weekly changes would probably not be. Test a single unit before retrofitting the FAB. Note that the filter lifetime will be longer if the whole FAB is retrofitted.

6. Controlling odors, especially around Lithography, can reduce employee exposure. In many cases, ID of compounds demonstrates that better venting or scrubbing is needed for a given process.

7. Careful selection of polymers used in carriers, gloves, and other FAB materials can reduce exposure of the wafers to high boiling organics or dopants such as phosphates.

8. Eventually, correlation's will be made between the sources of organic contaminants, how much is being transported in the air, how much is deposited on the wafer, and how much specific organics affect specific processing steps. Only then can rational contamination limits be specified.

Author Biographies

Dr. Mark Camenzind has been a research chemist at Balazs Analytical Laboratory since 1987 and is currently the organic analysis manager. Mark received his B.S. in organic chemistry from MIT, his Ph.D. in inorganic chemistry from UC Berkeley, and did postdoctoral research at the University of British Columbia. He has been developing analytical methods for determining the composition of organic mixtures, detecting trace organic contaminants in chemicals, on wafers, and in cleanroom air or minienvironments, and identifying compounds outgassing from all components going into new cleanrooms, minienvironments and semiconductor processing equipment. Techniques used include TOC (total oxidizable carbon), GC, GC-MS, thermal desorption GC-MS and others as needed. Mark is a member of the American Chemical Society, ASTM, IES, AVS and serves on SEMI and ASTM committees. He is also a member of Sematech's organic contamination PTAB.

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[4] Erik Mori, J. Dowdy, Larry Shive "Correlating Organophosphorus Contamination On Wafer Surfaces With HEPA-Filter Installation", Microcontamination, Nov. 1992, pp. 35. Triethylphosphate was found outgassing from urethanes used in HEPA's.

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Author Biographies

Dr. Mark Camenzind has been a research chemist at Balazs Analytical Laboratory since 1987 and is currently the organic analysis manager. Mark received his B.S. in organic chemistry from MIT, his Ph.D. in inorganic chemistry from UC Berkeley, and did postdoctoral research at the University of British Columbia. He has been developing analytical methods for determining the composition of organic mixtures, detecting trace organic contaminants in chemicals, on wafers, and in cleanroom air or minienvironments, and identifying compounds outgassing from all components going into new cleanrooms, minienvironments and semiconductor processing equipment. Techniques used include TOC (total oxidizable carbon), GC, GC-MS, thermal desorption GC-MS and others as needed. Mark is a member of the American Chemical Society, ASTM, IES, AVS and serves on SEMI and ASTM committees. He is also a member of Sematech's organic contamination PTAB.

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