Characterization of Organic Contaminants Outgassed from Materials Used in Semiconductor Fabs/Processing

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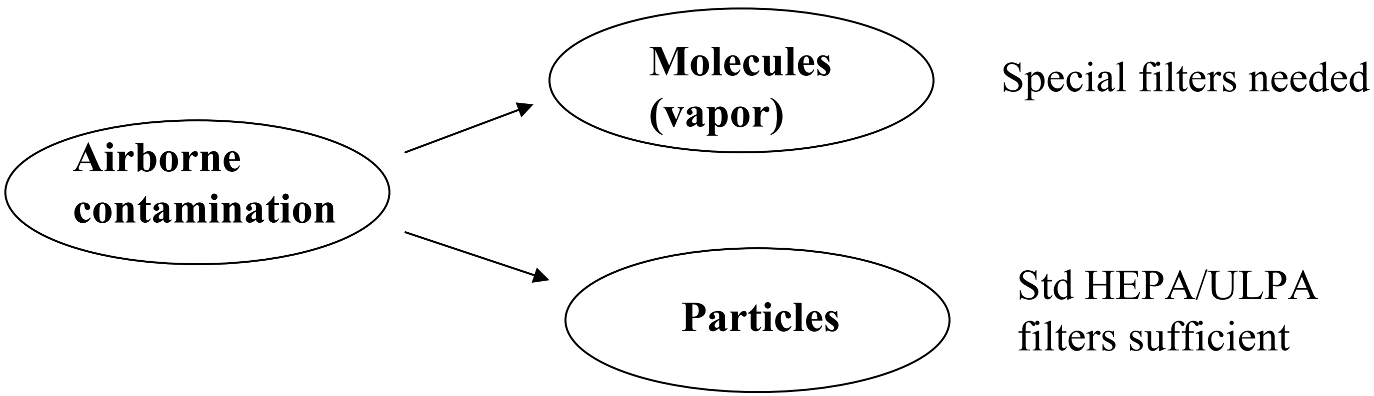
Outline

- Introduction
- Analytical Methods for Materials' Outgassing Measurements
- Characterization of Outgassed Organic Contaminants Using Thermal Desorption-Gas Chromatography-Mass Spectrometry (TD-GC-MS)
- Ammonia/Amines' Outgassing
- Summary

Introduction: Airborne Molecular Contamination (AMC)

Airborne contaminants that:

- Are smaller than particles, << 0.01 um or 100 Å, typically: 2-50 Å.
- Are in the form of molecular vapor.
- Pass through HEPA/ULPA filters.



- **Note:** Most cleanrooms are clean for particles, but contaminated with AMC. HEPA/UPLA filtration systems can be AMC sources.

Introduction: Airborne Molecular Contamination (AMC)

- AMC Classification (SEMI F21-95):
  - **A**cids: HCl, HF, HNO3, H2SO4
  - **B**ases: NH3, amines, NMP
  - **C**ondensables: organics with boiling point (bp) > 150 ^{o}C
  - **D**opants: P, B, As compounds
- Material outgassing is one of the major sources of AMC.

- **Notes:**

1. Some compounds belong to more than one class.
2. Some compounds are not covered by this classification.
3. NMP: N-methyl-pyrrolidinone, photoresist stripper or polyimide solvent.

Introduction: Molecular Condensables (MC)

- Known Problematic Organic Contaminants:
  - Flame retardants, e.g. organophosphorus
  - Siloxanes
  - Polymer/plastic additives, e.g. plasticizers, antioxidants
  - Amines/amides (such as NMP)
  - Decomposition compounds

- Effects of Organic Contamination:
  - Surface properties (e.g. hydrophobicity)
  - Lower breakdown voltage
  - Unintentional doping
  - Haze degradation
  - Oxide growth rate and quality
  - Post-CVD defects
  - Delamination
  - Optic and mask hazing

Introduction: Effects of Organic Contamination - Unintentional Doping Due to Outgassing

Sheet resistance map of a contaminated wafer

Phosphorus contamination vs. exposure time of witness wafer to cleanroom contaminated by Fyrol

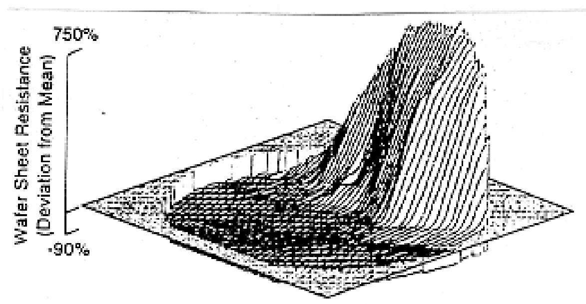


Fig. 2. Sheet resistance map of a contaminated wafer showing increased resistivity from contamination in the region opposite the flat.

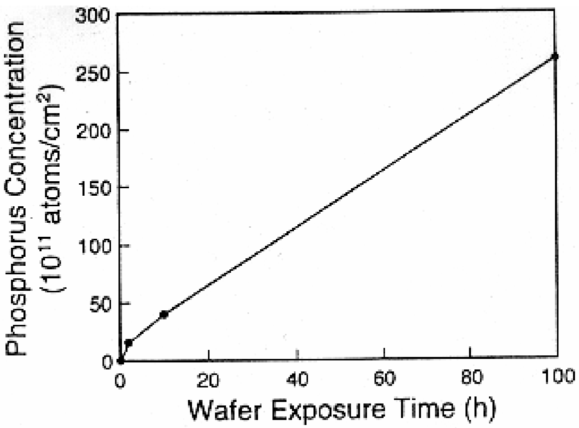
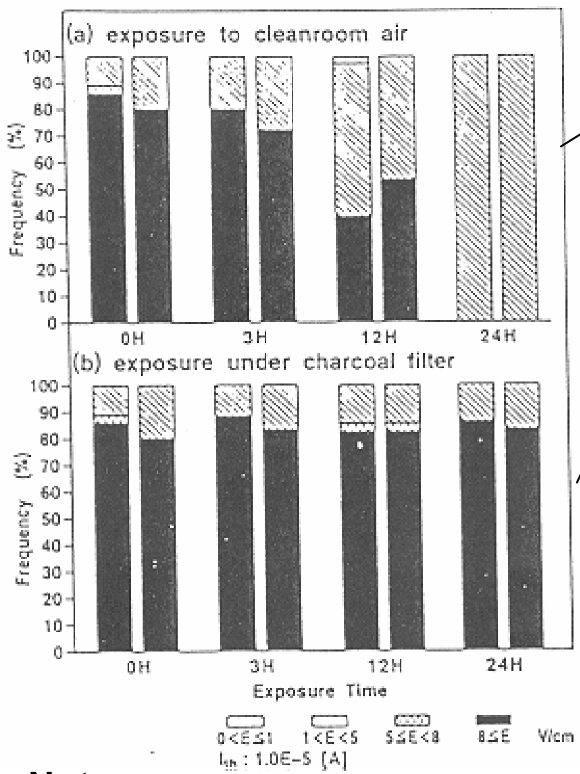


Fig. 4. Phosphorus contamination measured on witness wafers as a function of exposure time to Fab 1 air.

- Unintentional doping on Si device wafers during furnace operation was observed.
- Witness wafer test showed that phosphorus contamination on witness wafers was roughly linear with exposure time.
- TD-GCMS analysis of various components of HEPA filters identified that the contaminant as Fyro PCF flame retardant outgassed from the HEPA polyurethane potting material.

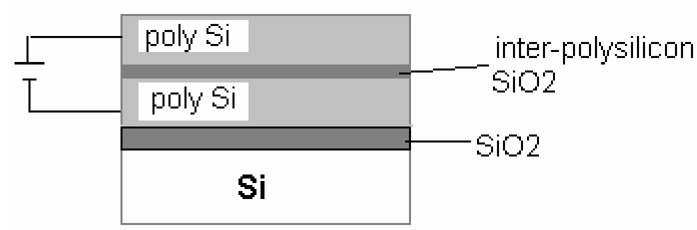
Reference: J.A. Lebens, *et al.,* "Unintentional doping of wafers due to organophosphates in the cleanroom ambient", J. Electrochem. Soc., 143(9), 2906-2909 (1996).

Introduction: Effects of Organic Contamination - Breakdown Voltage Reduction



Wafers exposed to cleanroom w/o chemical filters

Wafers exposed to cleanroom with chemical filters



Device structure used to measure breakdown strength of inter-polysilicon SiO2

- **Notes:**
  1. Organic contamination on the first SiO2 surface causes degradation in the polysilicon layer, resulting in breakdown field strength reduction.
  2. Storage time in cassettes prior to the first polysilicon deposition can affect breakdown field strength.

Reference: M. Tamaoki, *et al.*, “The effect of airborne contaminants in the cleanroom for ULSI manufacturing process”, 1995 IEEE/SEMI Advance Semiconductor Manufacturing Conference, 322-326 (1995).

Introduction: Sources of Organic Outgassing Contamination

- sealants
- adhesives
- paints
- lubricants
- plastics
- HEPA/ULPA filtration systems
- floor tiles
- wafer carriers
- cleanroom consumables: gloves, garments, tapes, cleaners…
- process chemicals
- people …

Introduction: ITRS Roadmap for Wafer Surface Organics

Wafer surface organic contamination: Carbon atoms/cm^2:

	2001	**2002**	**2003**	**2004**	**2005**	**2006**	**2007**
Technology (nm):	130			90			65
‘99 edition:	6.6×10^{13}	5.3×10^{13}	4.9×10^{13}	4.5×10^{13}	4.1×10^{13}	2.1×10^{13}	**(2008)**
‘02 edition:	2.6×10^{14}	2.1×10^{13}	1.8×10^{13}	1.5×10^{13}	1.3×10^{13}	1.1×10^{13}	1.0×10^{13}

- Trend: Tighter wafer surface organic contamination requirements due to increasing sensitivity to organic condensables’ contamination.

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Analytical Methods for Outgassing Measurements

- Most widely used methods in semiconductor industry:
  - Direct Outgassing
    - Weight loss method
      - for total outgassing assessment
    - TD-GC-MS method
      - for outgassing compound identification and quantification
  - Indirect Outgassing Measurement Using Witness Wafers
    - TD-GC-MS analysis of witness wafers
      - full wafer analysis
    - Time-of-flight Secondary Ion Mass Spectrometry (TOF-SIMS) analysis of witness wafers
      - spot analysis

Analytical Methods for Outgassing Measurements

- Industry Standards:
  - ASTM F1227-89, "Standard Test Method for Total Mass Loss of Materials and Condensation of Outgassed Volatiles on Microelectronics-Related Substrates"
  - IEST WG-CC031 Recommended Practice: "Method for Characterizing Outgassed Organic Compounds from Cleanroom Materials and Components" (to be published in 2003)
  - SEMI Environmental Contamination Control (ECC) WG: SEMI E108-0301: "Test Method for The Assessment of Outgassing Organic Contamination from Minienvironments Using Gas Chromatography/Mass Spectroscopy"
  - ASTM F1982-99: "Standard Test Methods for Analyzing Organic Contaminants on Silicon Wafer Surfaces by Thermal Desorption Gas Chromatography"

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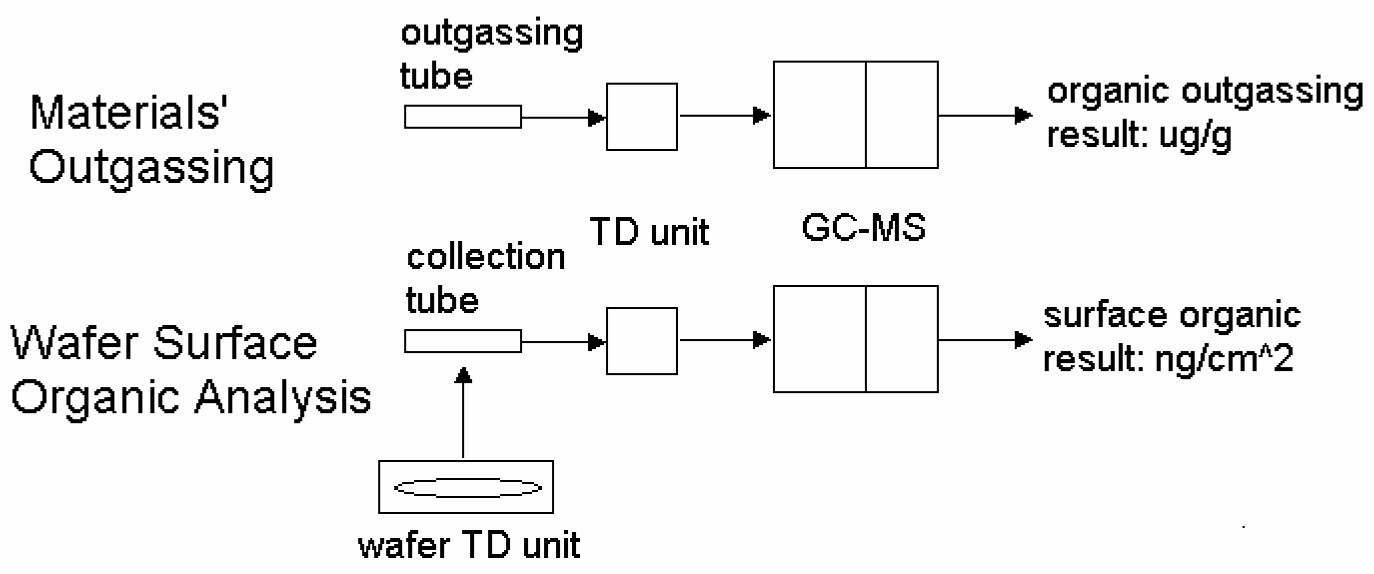
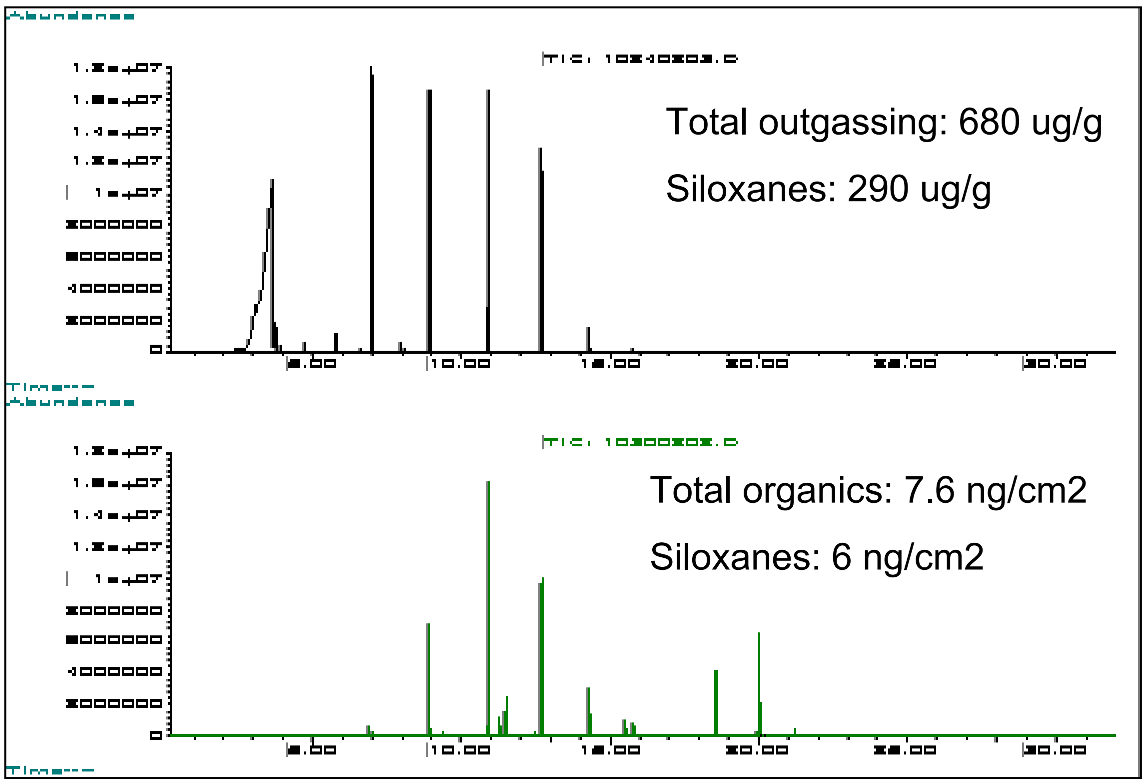
Characterization of Outgassed Organic Contaminants Using TD-GC-MS

- Schematic Diagram of TD-GC-MS Technique:



Detection of Outgassed Polycyclodimethyl-siloxanes from a Cleanroom Sealant

- TD-GC-MS Analysis Results:



Retention Time (min)

Direct outgassing of a sealant

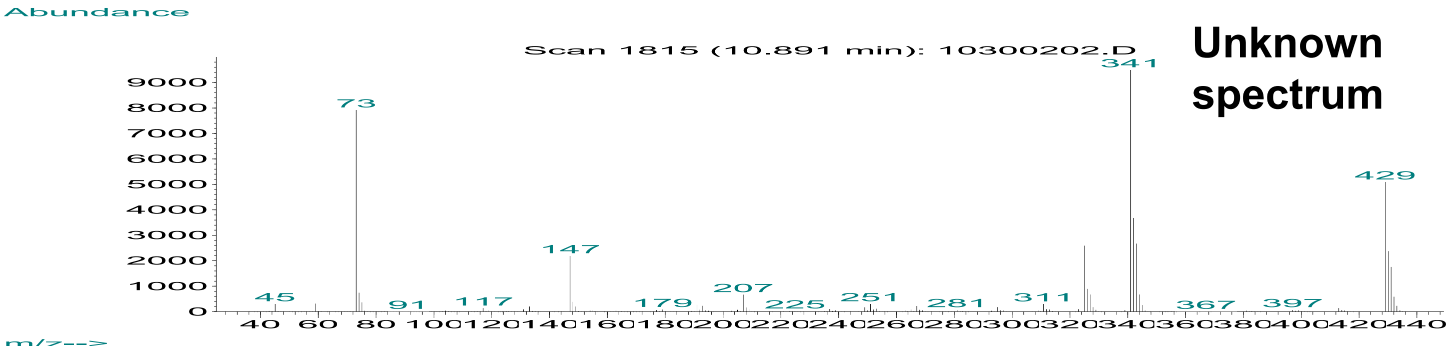
Surface analysis of a witness wafer exposed to the sealant:

Siloxane: 2.5E14 Carbon atoms/cm2, 10x > ITRS requirement (1.8E13)

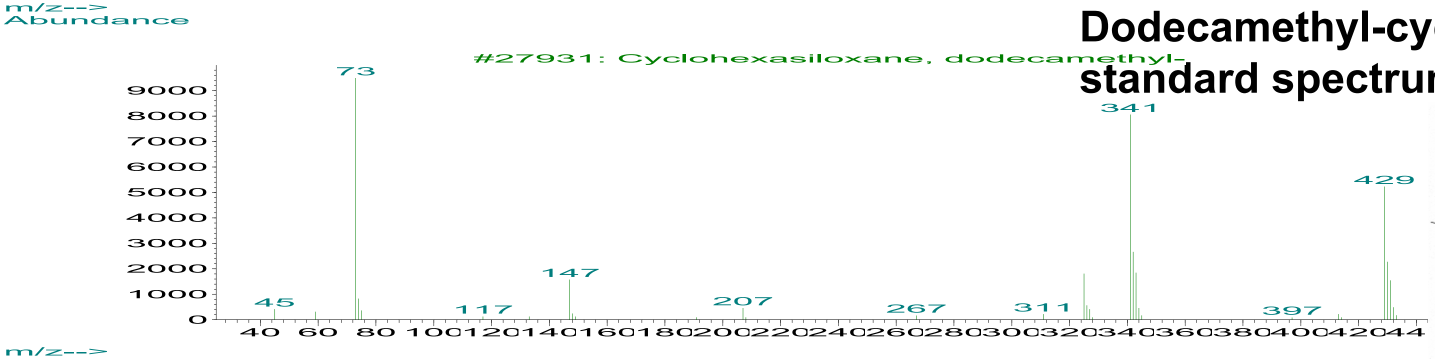
ug = microgram, ng = nanogram

Detection of Outgassing Poly-Cyclodimethylsiloxanes

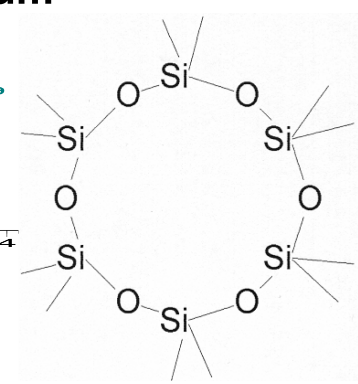
- Identification of Dodecamethyl-cyclohexasiloxane:



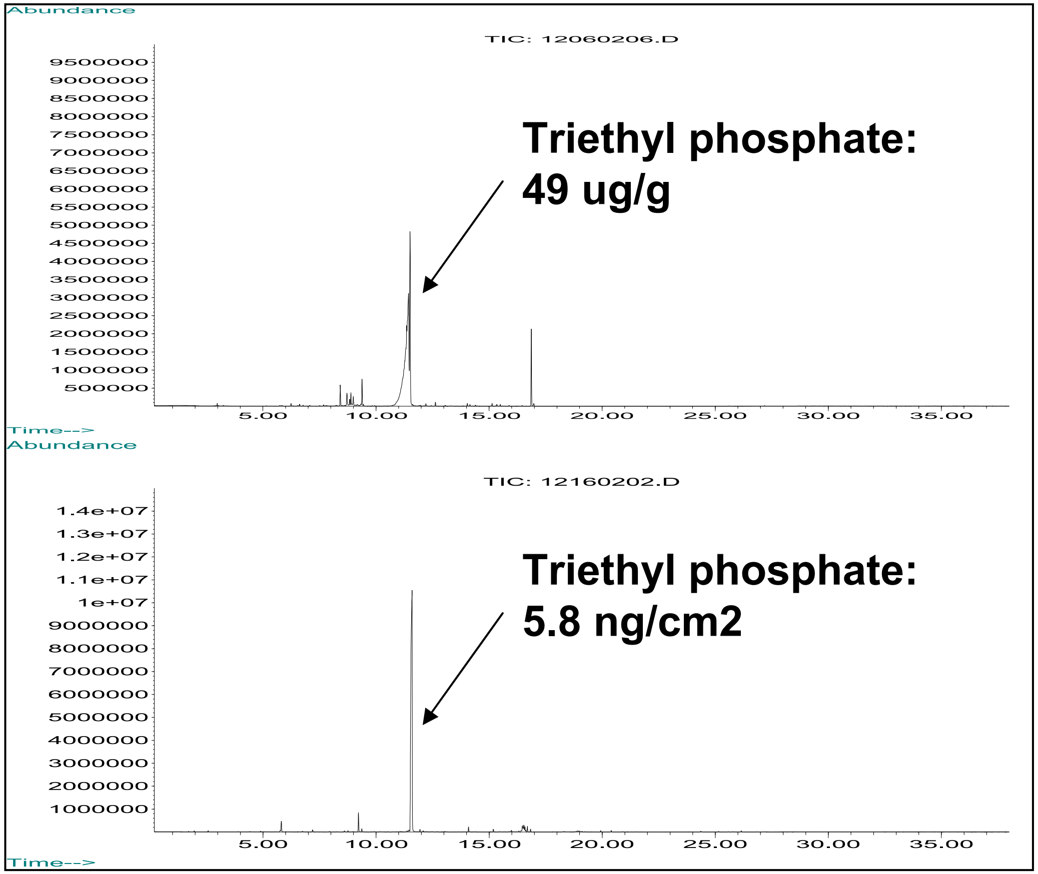
Unknown spectrum



Dodecamethyl-cyclohexasiloxane standard spectrum



Detection of Triethyl Phosphate (TEP) Outgassed from a Cleanroom Sealant



Retention Time (min)

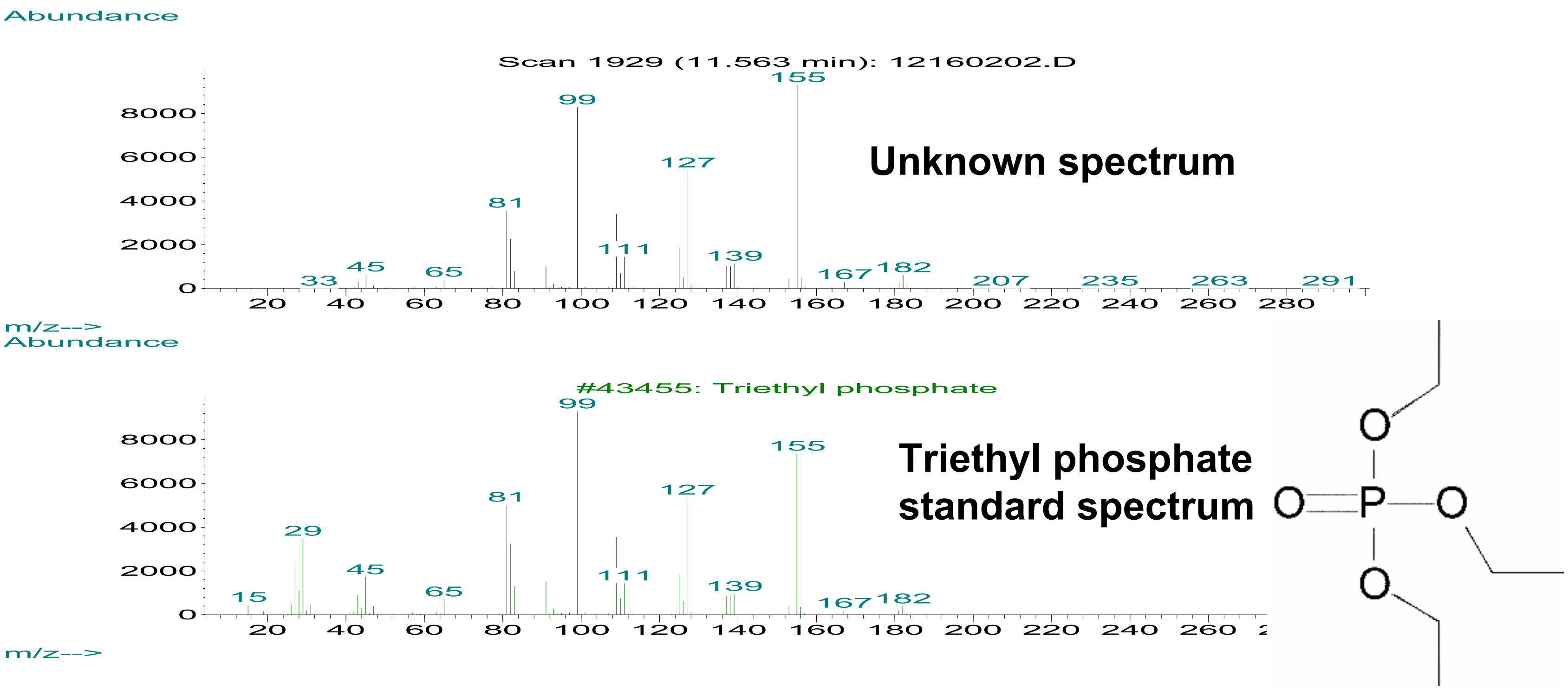
Direct outgassing of a cleanroom sealant

Surface analysis of witness wafer exposed to the same sealant

~2E13 P atoms/cm2, >> critical level: 1E12

Detection of Triethyl Phosphate (TEP) Outgassed from a Cleanroom Sealant

- Identification of Triethyl phosphate (TEP):

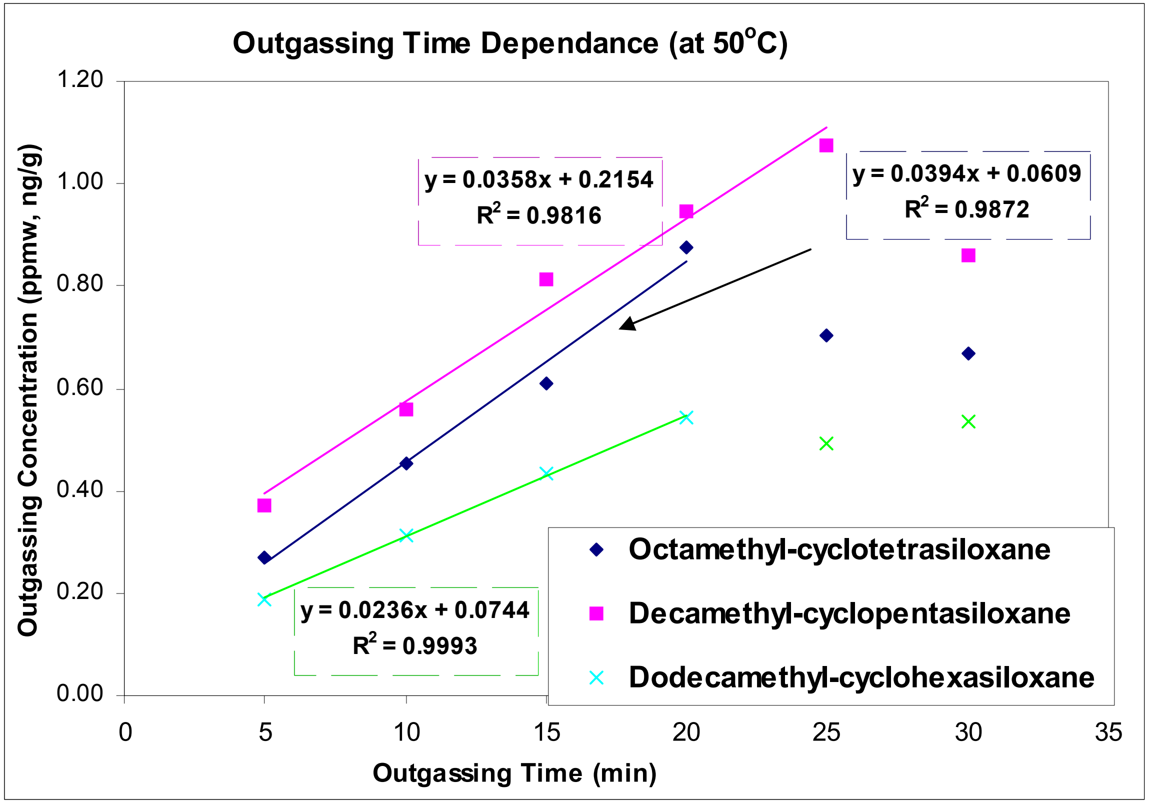


Characterization of Outgassed Organic Contaminants Using TD-GC-MS

- Polymer materials chosen outgas organic contaminants commonly seen in semiconductor Fab cleanrooms. Organic contaminants monitored included:
  - polycyclodimethylsilocxanes
  - Dibutyl phthalate (DBP)
  - Butylated hydroxytoluene (BHT)
  - 2-Ethyl-1-hexanol
  - Methylstyrene
  - Naphthalene

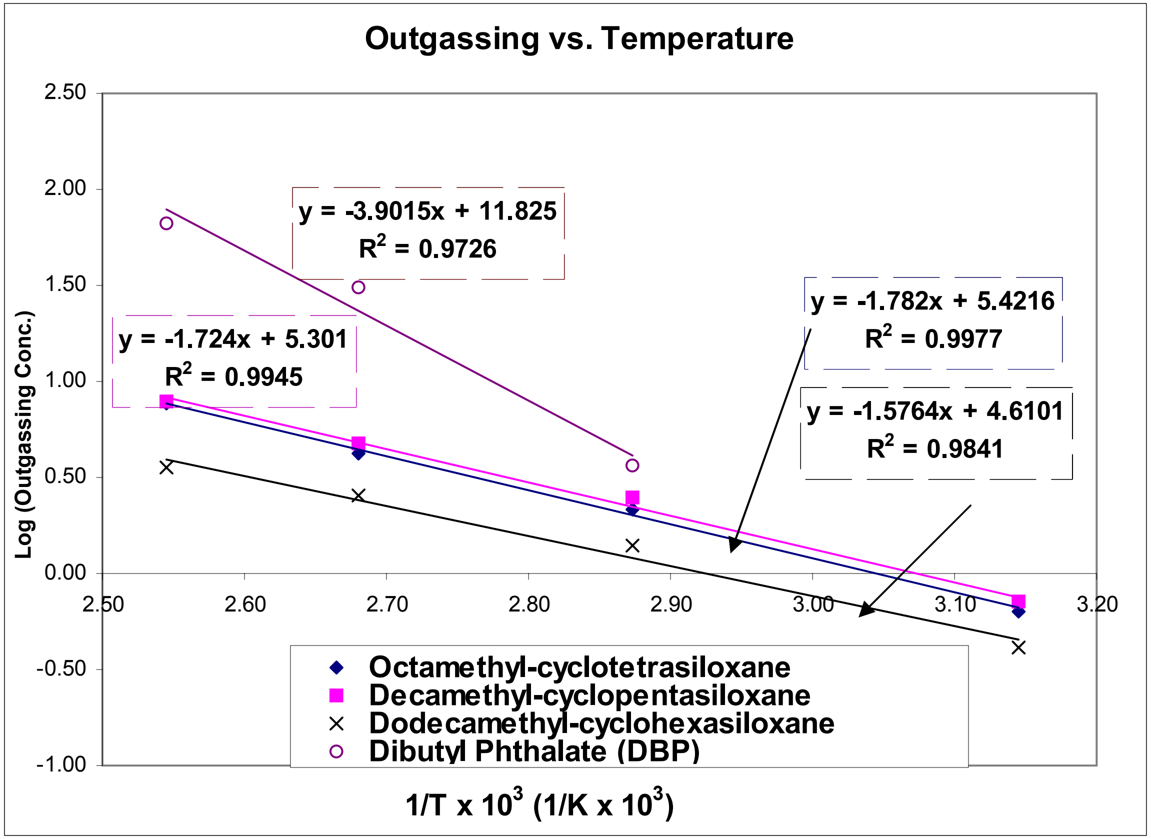
- Outgassing behaviors of selected contaminants were studied by varying the following parameters:
  - outgassing time
  - outgassing temperature
  - surface area
  - weight

Outgassing Concentration vs. Outgassing Time: Siloxanes



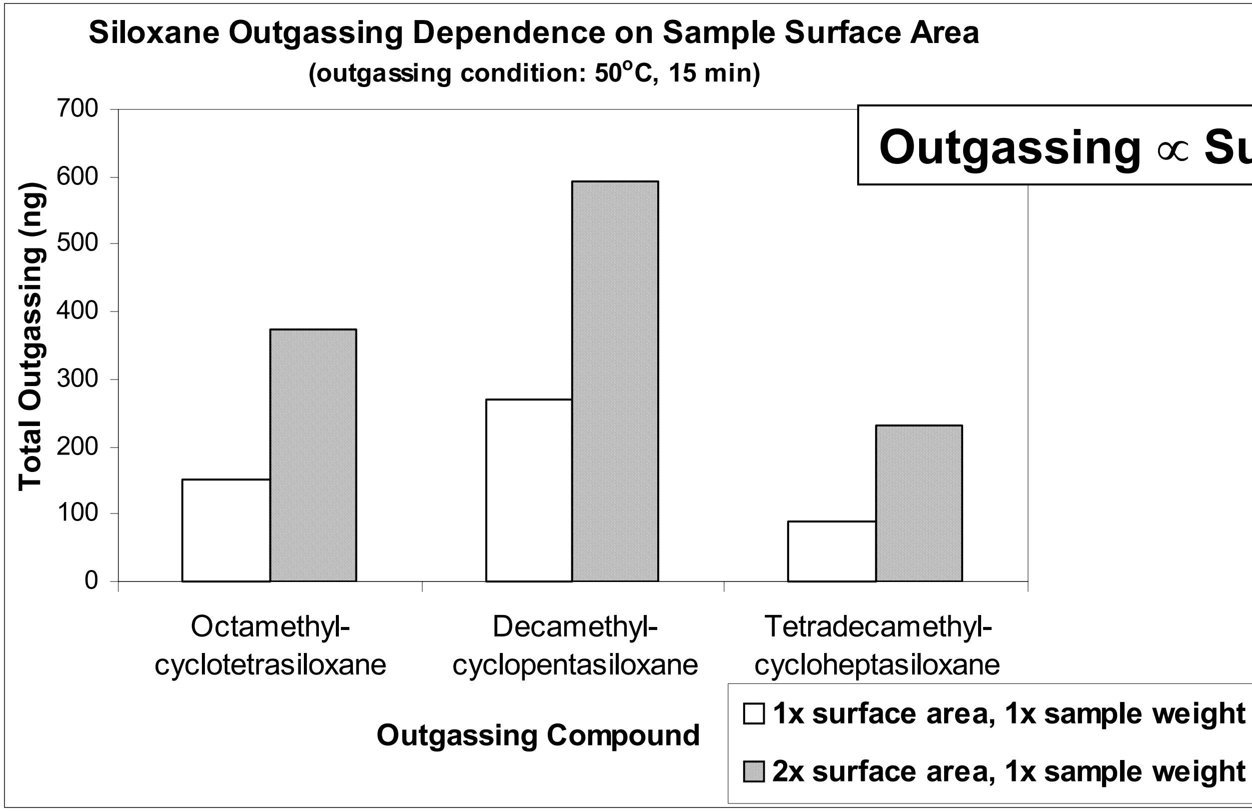
- Linear relationship between outgassing concentration and outgassing time within a time range. Outgassing rate can be estimated from the slope.
- Same findings for Dibutyl phthalate (DBP) and Butylated hydroxytoluene (BHT)(not shown).
- Linear relationship was also observed at 75 °C with higher slope values, indicating higher outgassing rate at 75 °C.

Outgassing Concentration vs. Temperature: Siloxanes and DBP



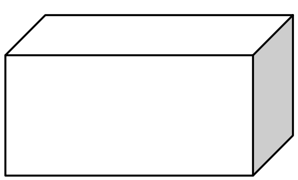
- **Linear relationship between Log (Outgassing Conc.) and inverse of outgassing temperature (1/T).**
- **In agreement with findings reported by K. Takeda, et al., IEST 2000 ESTECH Proceedings, pp. 71-77 (2000).**
- **Same result was observed for Butylated hydroxytoluene (BHT) (not shown).**

Outgassing Quantity vs. Surface Area: Siloxanes

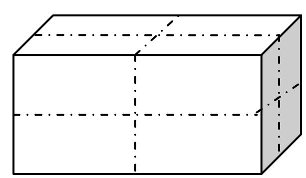


Outgassing ∝ Surface Area

- Outgassing quantity ∝ surface area when sample weight is constant.

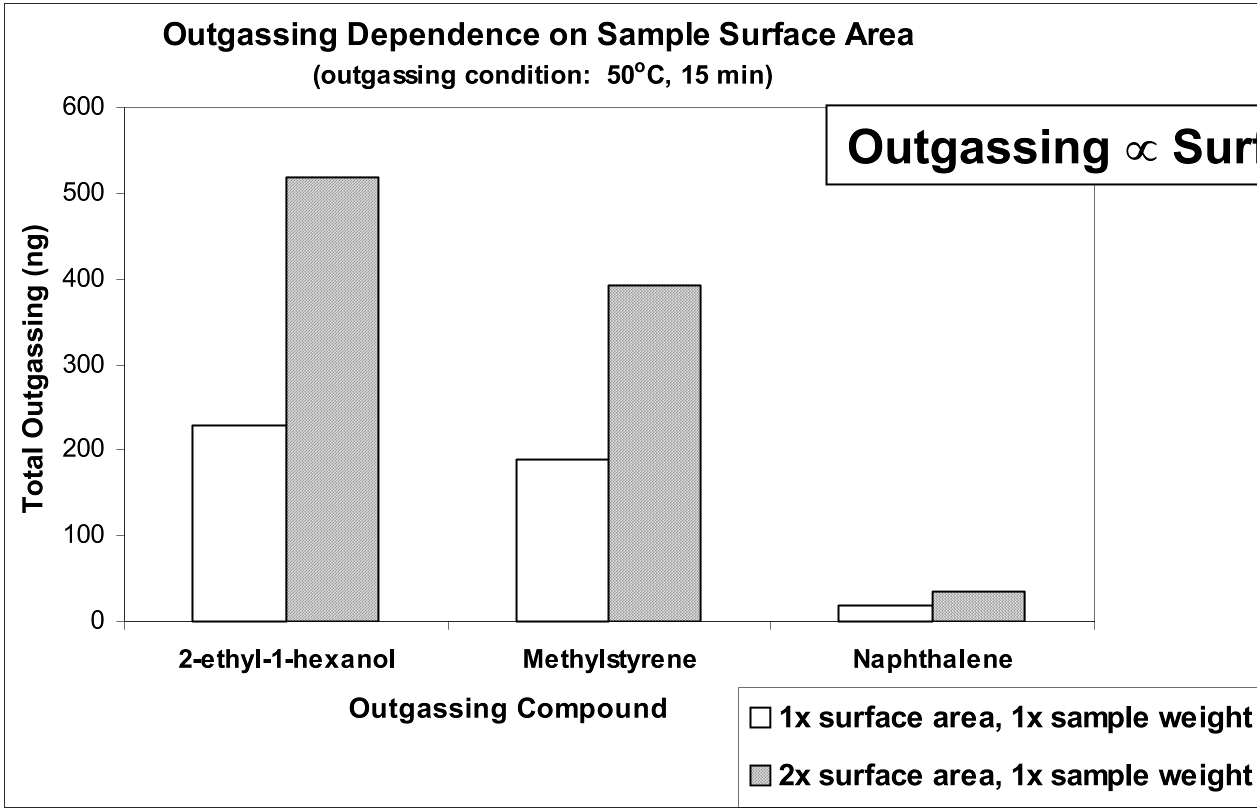


1x surface area
1x weight



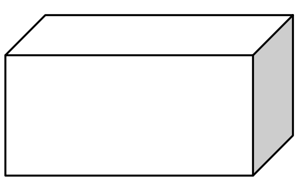
2x surface area
1x weight

Outgassing Quantity vs. Sample Surface Area

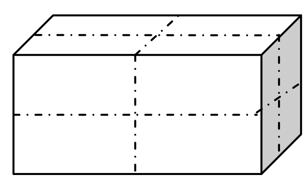


Outgassing $\propto$ Surface Area

- Outgassing quantity $\propto$ surface area when sample weight is constant.

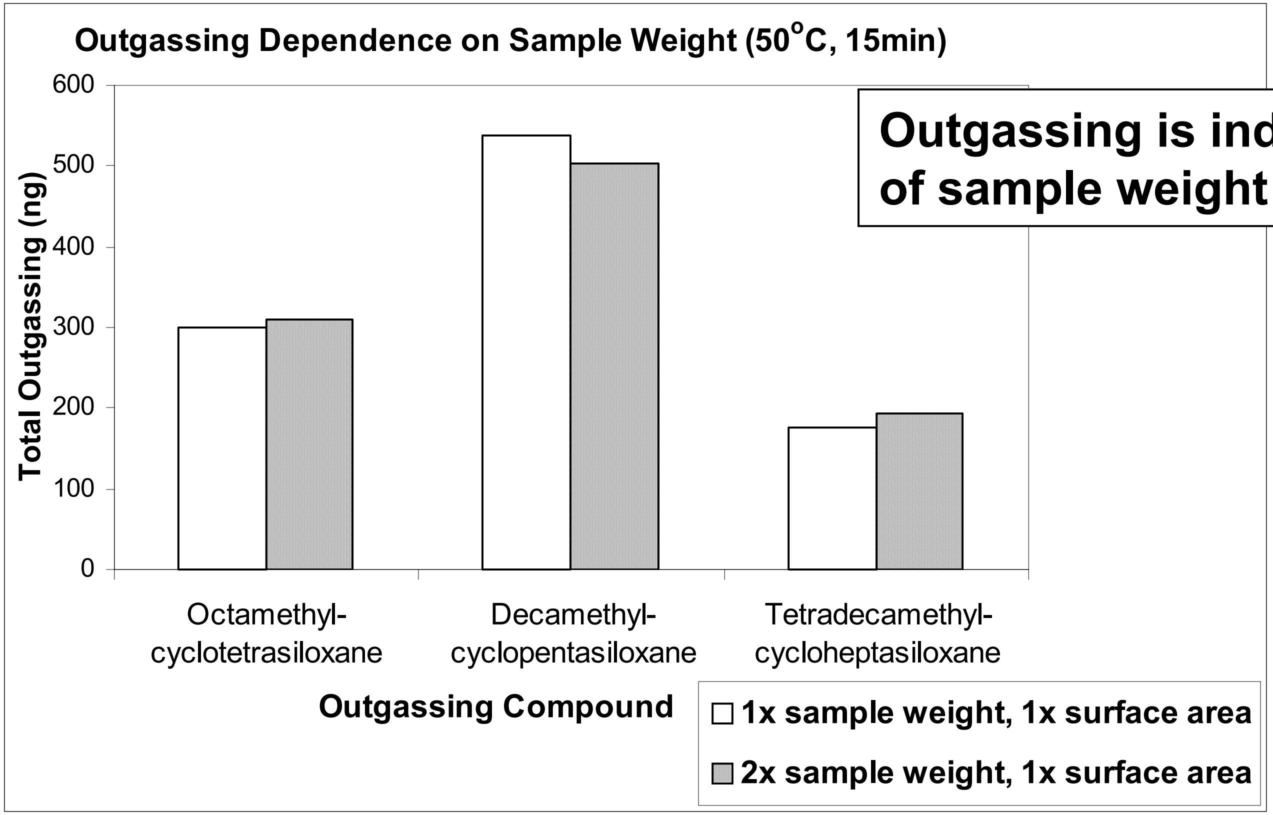


1x surface area
1x weight



2x surface area
1x weight

Outgassing Quantity vs. Sample Weight



Outgassing is independent of sample weight

- Outgassing is independent of sample weight when surface area is constant.
- Same results for methylstyrene, 2-ethyl-1-hexanol and naphthalene (not shown).

Conclusions: Characterization of Outgassed Organic Contaminants Using TD-GC-MS

- Linear relationship between outgassing concentration and outgassing time in a certain time range.
  - where the slope equals the outgassing rate.
- Linear relationship between logarithm of outgassing concentration and 1/T; where 'T' is the absolute outgassing temperature.
- Outgassing amount $\propto$ sample surface area.
- Outgassing is independent of sample weight when surface area remains constant.
  - Suggests that outgassing is indeed a surface phenomenon.

Note: These findings are based on the limited number of contaminants tested.

- Materials' outgassing can be far more complicated due to large number of variables in the physical and chemical properties of different materials used in cleanrooms.

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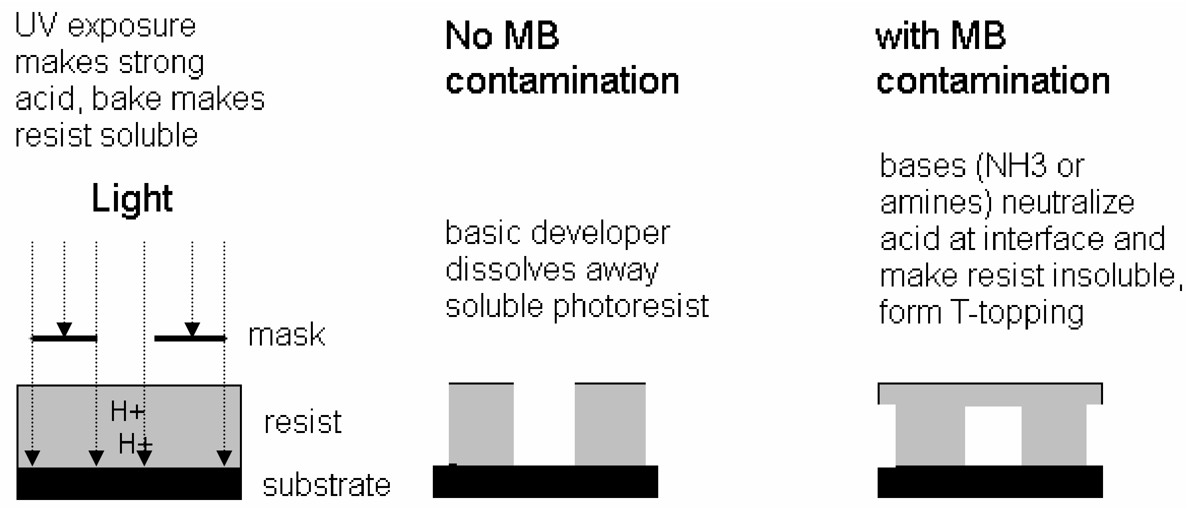
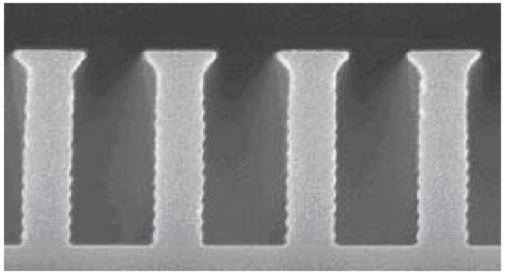
Ammonia/Amines' Outgassing

- T-topping defect caused by NH_3/amines' Outgassing:



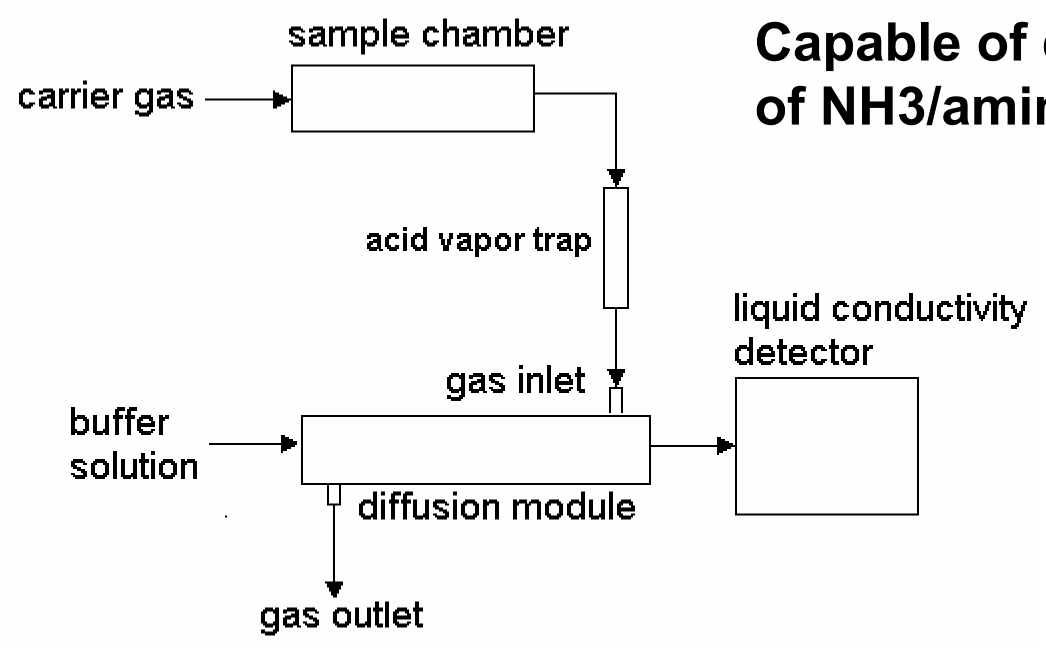
T-topping SEM image



- Airborne bases outgassed from cleanroom materials can neutralize the photo-generated acid during the time delay between the exposure and post-exposure bake, generating insoluble products, which cannot be dissolved by developer solvent. A lip forms at the top of the developed resist profile, known as "T-topping".

Ammonia/Amines' Outgassing

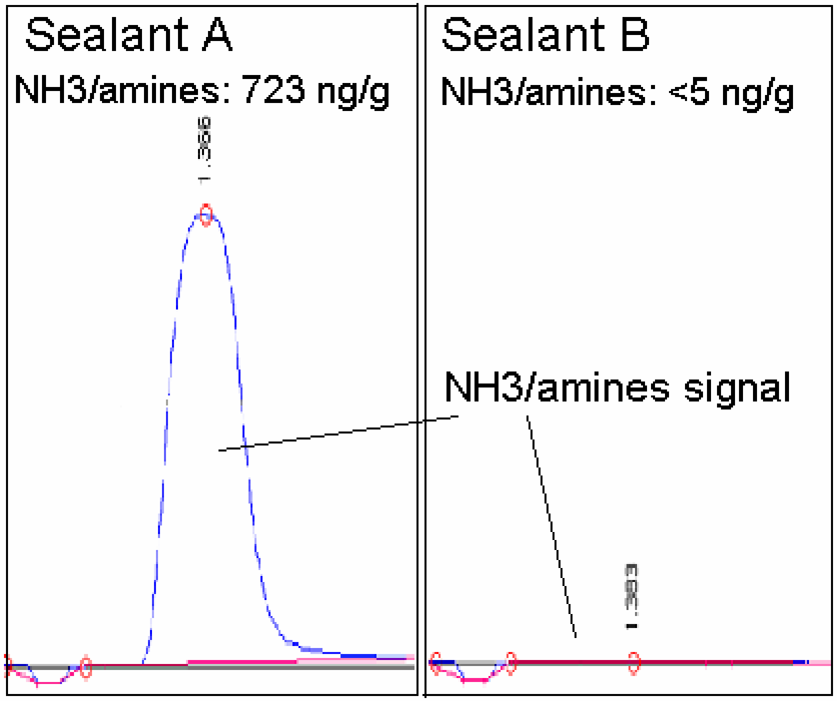
- Gas Diffusion-Conductivity Detection-based NH3/Amines' Outgassing Method:



Capable of detecting 1 ng/g (ppb) of NH3/amines' outgassed

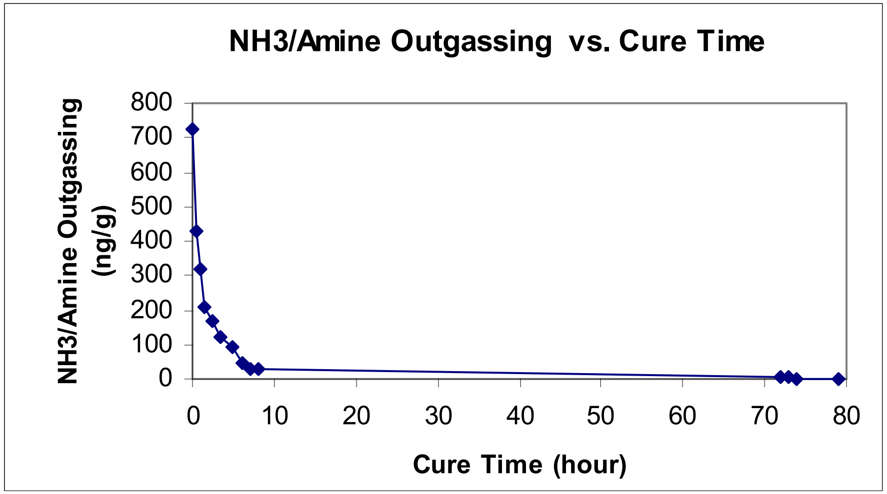
ppb = parts per billion

NH3/Amines Outgassing of Two Cleanroom Sealants

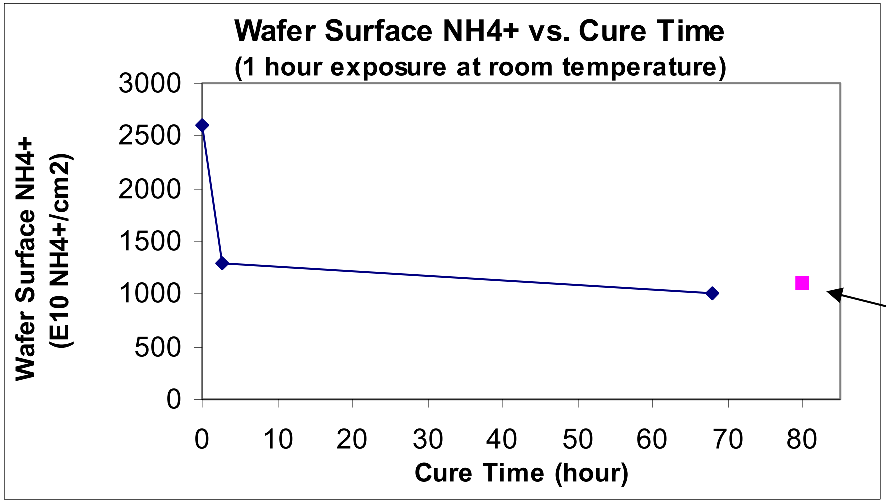


Sealant A caused significant T-topping defects in E0 delay photoresist test due to its high NH3/amine outgassing.

Time Dependence of NH3/Amines' Outgassing



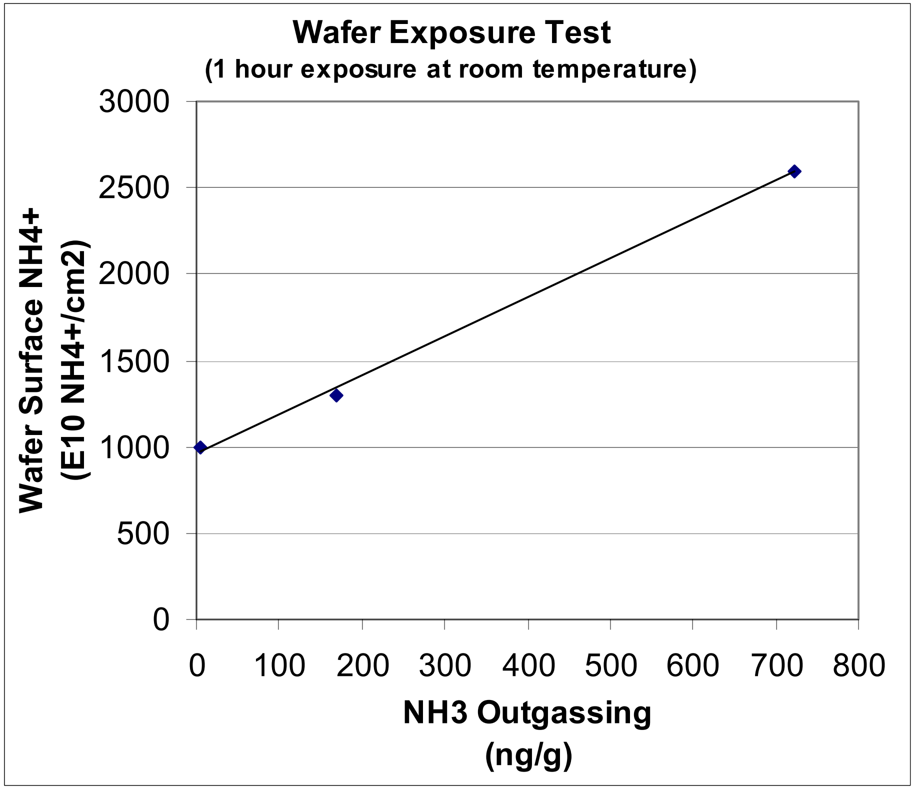
Time dependent NH3/amine outgassing of a sealant: room temperature



Surface NH4+ of witness wafers exposed to same sealant: room temperature

control wafer

NH3/Amines' Outgassing vs. Wafer Surface NH4+



Linear relationship between witness wafer surface NH4+ and sealant NH3/amines' outgassing concentration

Summary

- Many AMC contaminants found in semiconductor Fabs come from outgassing of cleanroom materials. Outgassed contaminants can adversely affect many processes, resulting in yield loss, shortened tool life and reduced long-term device reliability.
- The large variety of cleanroom materials and numerous outgassing contaminants combined with the complexity of process steps makes understanding detrimental levels of specific contaminants in particular processes very challenging.
- Screening materials for both condensable and NH3/amines' outgassing prior to bringing them into Fabs can be used as a first-line-of-defense against molecular contaminants such as organophosphorus, siloxanes, plasticizers and ammonia/amines.

Summary

- New microelectronic fabrication processes with decreasing device geometries are increasingly susceptible to AMC.

- As processes and chemistries change, requirements for monitoring, control and analysis of materials' outgassing will evolve as well.

- Cooperative efforts among manufacturers of integrated circuit, materials and analytical tools are needed to better understand the impact of molecular contaminants and to properly define specifications applicable to new ULSI technologies.

Acknowledgements

- Yaacov Maoz of Intel Fab 18 for providing the “T-topping” defect SEM image.
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