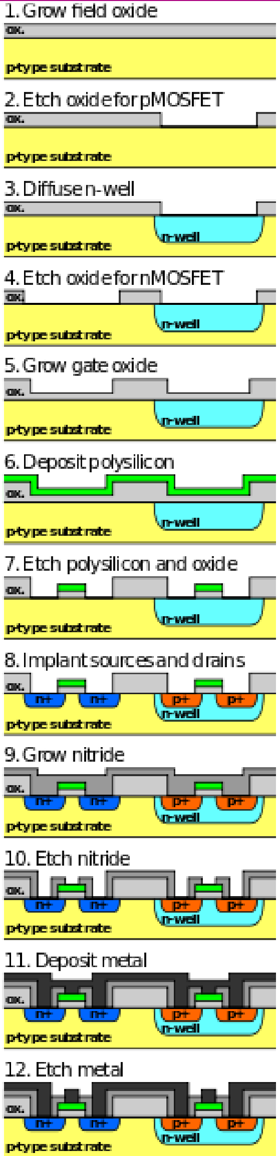
Analytical Toolbox for Technology Enabling and Troubleshooting

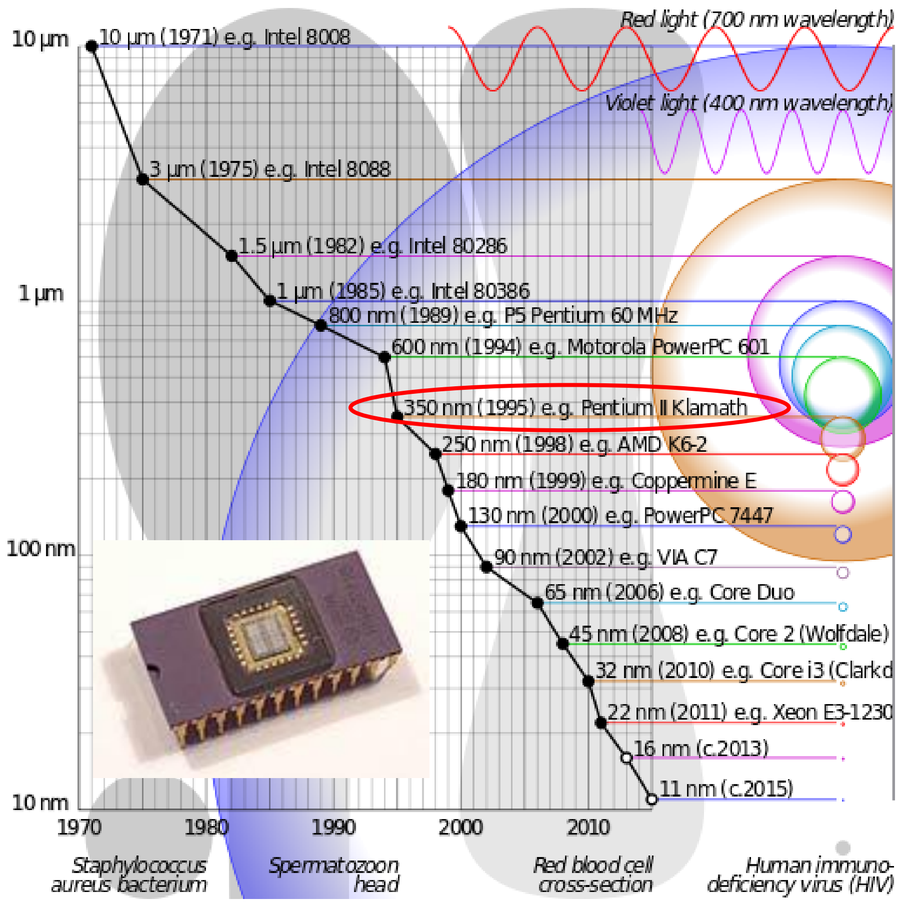
SEMATECH SPCC2016

Agenda

- The Problem Statement
- Airborne molecular contamination becoming Surface molecular contaminants
- Industrial standard methods as tools
- The Toolbox
- Trouble shooting guides

Semiconductor Integrated Circuit (IC) Chip





IC chips getting smaller and smaller

Semiconductor manufacturing processes (gate length/line width)
10 µm — 1971
3 µm — 1975
1.5 µm — 1982
1 µm — 1985
800 nm (.80 µm) — 1989
600 nm (.60 µm) — 1994
350 nm (.35 µm) — 1995
250 nm (.25 µm) — 1998
180 nm (.18 µm) — 1999
130 nm (.13 µm) — 2000
90 nm — 2002
65 nm — 2006
45 nm — 2008
32 nm — 2010
22 nm — 2012
14 nm — approx. 2013
10 nm — approx. 2015
7 nm — approx. 2020
5 nm — approx. 2022

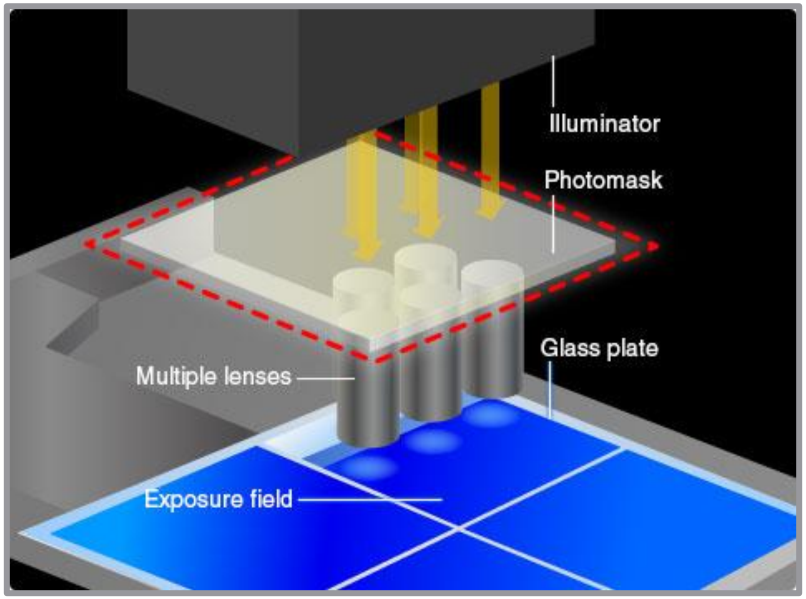
Cleanroom Surface Cleanliness

IEST-RP-CC043: SURFACE MOLECULAR CONTAMINATION

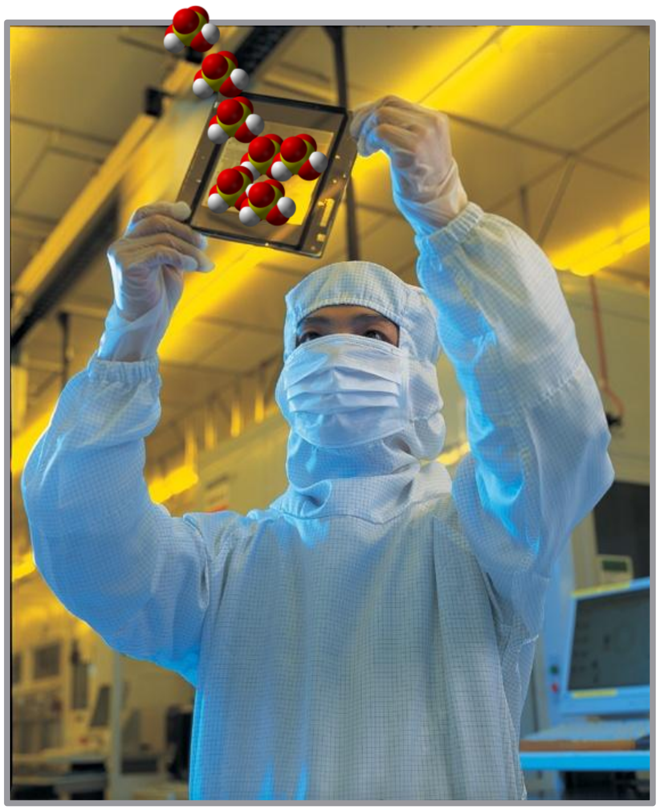
- This Recommended Practice (RP), IEST-RP-CC043 describes the types of surface molecular contamination (SMC) that may affect critical surfaces and processes
- Types of SMC include organic and inorganic contaminants that may be adsorbed or reacted onto the surface
- Effects are manifested in the physical, electrical, chemical, or optical properties of the surface
- The document also describes sources as well as measurement and control methods

Cleanroom Surface Cleanliness

- SMC (surface molecular contamination)
  - AMC can form particles leading to SMC
  - If > monolayer, SMC can make films, homogeneous or islands
  - SMC is often < ML (~5Å) or approximately 10^{15} atoms or ions/cm^2



Flat panel display (FPD) lithography system and photomask



AMC Sources

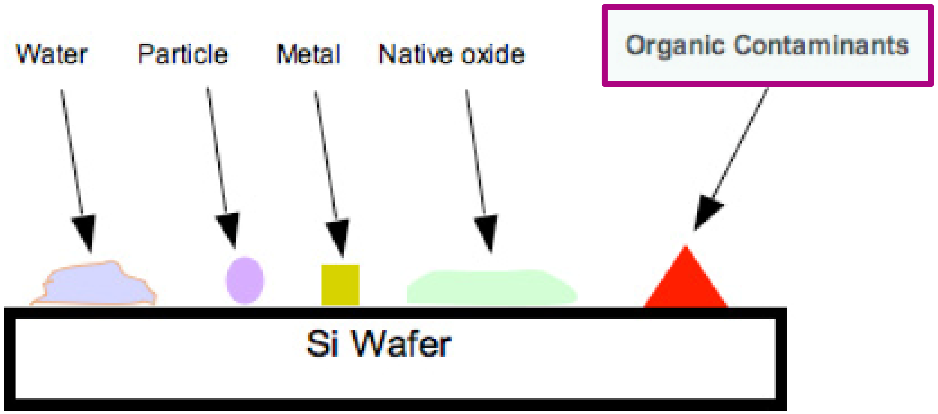
- Outside air: autos, power plants, smog, industry, roofing, paving, fertilizers, pesticides, farming, sewers, fab exhaust, ocean/saline water
- Process chemicals (esp. hot), reaction by-products, reactor exhaust
- Wet cleaning, wet- and dry-etching, electroplating baths
- Solvents: lithography, cleaning solutions
- People: ammonia, sulfides, organics
- Equipment outgassing: robots, motors, pumps, fans, electronics, computers, heaters
- Materials outgassing into air or onto sealed products
- Disasters, internal or external:
- Spills, leaks (coolants), accidents, fires, power outages
- Failures of air handlers and scrubbers
- Recirculating air between areas
- FOUPs, Pods, shippers, carriers, minienvironments

SMC Effects

- DUV photoresist T-topping
- Uncontrolled boron or phosphorus doping
- Surface issues: adhesion, wafer bonding, delamination, electrical conductivity, high contact resistance, shorts, leakage currents, wetting, cleaning, etch rate shifts, spotting, particle removal, electroplating defects
- Wafer hazing: time dependent haze
- Optics hazing: hazing by adsorption, reactions, etching or photochemistry on lenses, lasers, steppers, masks, reticles, pellicles - especially for 157 and 193 nm lithography
- Corrosion: process wafers (Al, Cu), flat panel displays, equipment, instruments, wiring and facility (over many years)
- SiC/Si3N4 formation following pre-oxidation clean
- Threshold voltage shifts
- Nucleation irregularities

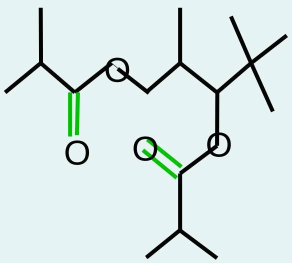
Airborne Molecular Contamination

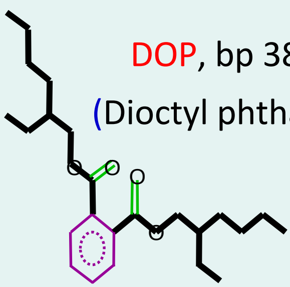
Molecular Condensable (AMC-MC) Leading to SMC



Plasticizers

TXIB, bp 280 °C (Texanol isobutyrate)

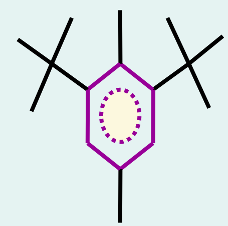




DOP, bp 384 °C (Dioctyl phthalate)

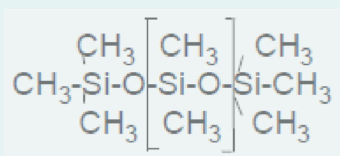
Antioxidants

BHT, bp 233 °C (Butylated hydroxytoluene)

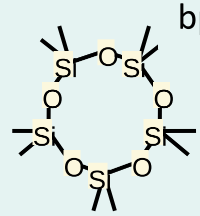


Silicones / Siloxanes

PDMS Poly(dimethyl silicone)

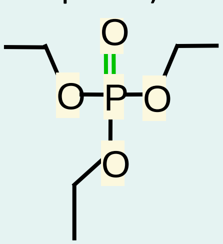


Decamethylpentasiloxane bp 211°C



Phosphates

TEP, bp 215°C (Triethyl phosphate)

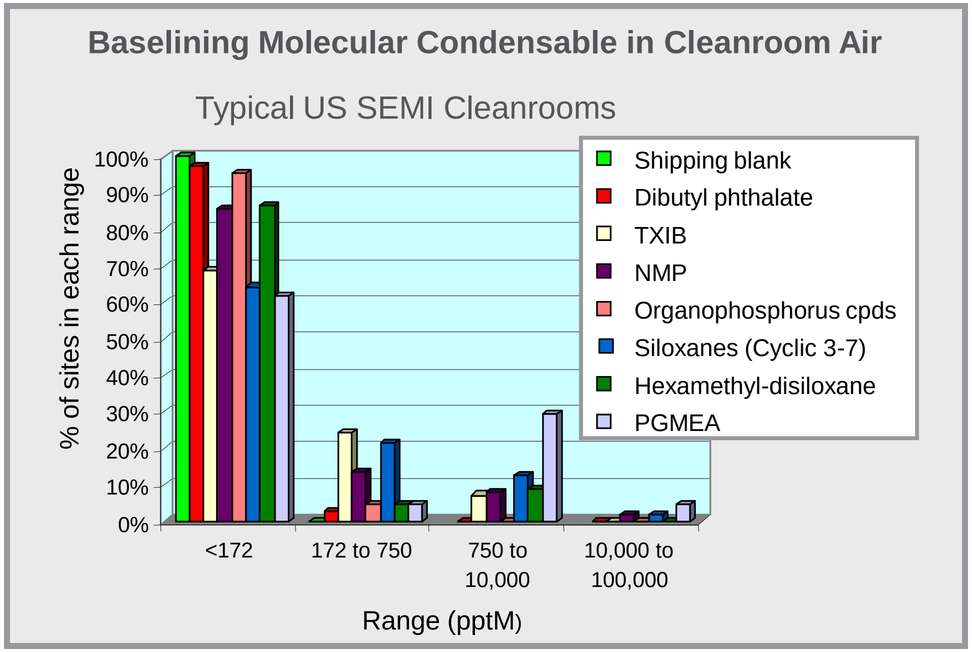


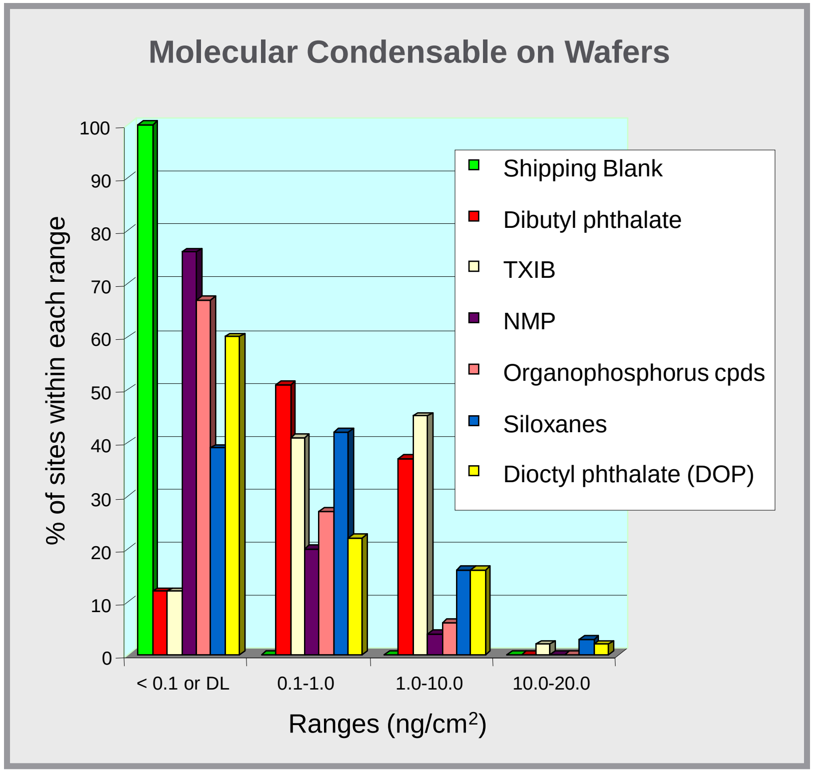
Sources of Molecular Condensables

Classification	Compound	Comments
ITRS wafer recommendation for >C7 is targeting 2 ng/cm2 (~ 0.1 ML) for 24 h exposure.		
Plasticizers	Phthalates	Phthalates are plasticizers and present in organic contruction materials.
	TXIB	TXIB (texanol isobutyrate) is commonly observed on wafers and is from airborne deposition from outgassing vinyl materials in the cleanroom.
	Diethyl phthalate	Common source may be from the wafer carrier or from outgassing of copolymers used in flexible cable housing, ties, etc. Problem is phthalates affects gate oxides and can decompose to make SiC.
	Diisobutyl phthalate	
	Butylbenzyl phthalate	
	DOP (dioctyl phthalate)	DOP is from cleanroom flooring material outgassing and from vinyl and plastic type materials such as wafer carriers and flexible duct connectors. Presence not acceptable in most fabs.
Antioxidants	Butylated hydroxytoluene	BHT is common on wafers from wafer carrier outgassing. BHT found in urethane foam sealants for HVAC, vinyl curtain, and floor sheet.
Silicones	Cyclo-dimethylsiloxane	Compound used in silicon HEPA gel seal.
Organometals	Organophosphates	Its presence can be an issue as phosphorus could be a counter n-dopant resulting in 10-15% yield loss. Common phosphates in the cleanroom such as TEP (triethyl phosphate) used in urethane foam sealants for HVAC and HEPA gel seals, TBP (tributyl phosphate) found in vinyl materials, and TCPP (tris{beta-chloroisipropyl} phosphate or Fyrol PCF used as a fire retardent.
	Organoborates	Would not expect this in a tool unless it was a reactive ion etcher using BBr_3. Boron could be a p-dopant and an issue for ion implantation.
Base Compds	NMP (N-methylpyrrolidinone)	Presence would affect lithography (DUV) and also cause hazing. Found in paints and strippers.
Alkyl Esters		Present in many materials including solvents, lubricants and oil.

Molecular Condensables in Air and Wafers

- Can cause delamination or irregular spin-on thickness
- Vacuum degradation in process tool and inspection tool chambers
- Organics may carbonize producing graphite, SiC and carbides resulting in electrical shorts





Notes:
- *PGMEA, HMDSO not found on witness wafers*
- *Silicones, phosphates, TXIB, DBP, DOP found on wafers*
- *Both air and wafer tests recommended. Improved detection sensitivity using Si wafers for some compounds.*

Material Outgassing Test Methods

Dynamic Headspace GC-MS (IEST-RP-CC031)

- Method for semi-qualitative analysis of outgassed compounds from cleanroom materials and components

IDEMA M11-99 DHS GC-MS method

- Approved for disk drives and used for cleanrooms
- Good for detecting high boiling compounds outgassed from cleanroom components, disposables

ASTM F1982-99: Analysis for organics on a silicon wafer by TD-GC-MS

Assorted materials for outgasssing characterization

Outgassing onto a substrate of interest

- SEMI E46: Outgassing of pods onto wafers, then IMS analysis
- SEMI E108: Outgassing onto wafer method, GC-MS analysis by ASTM 1982-99

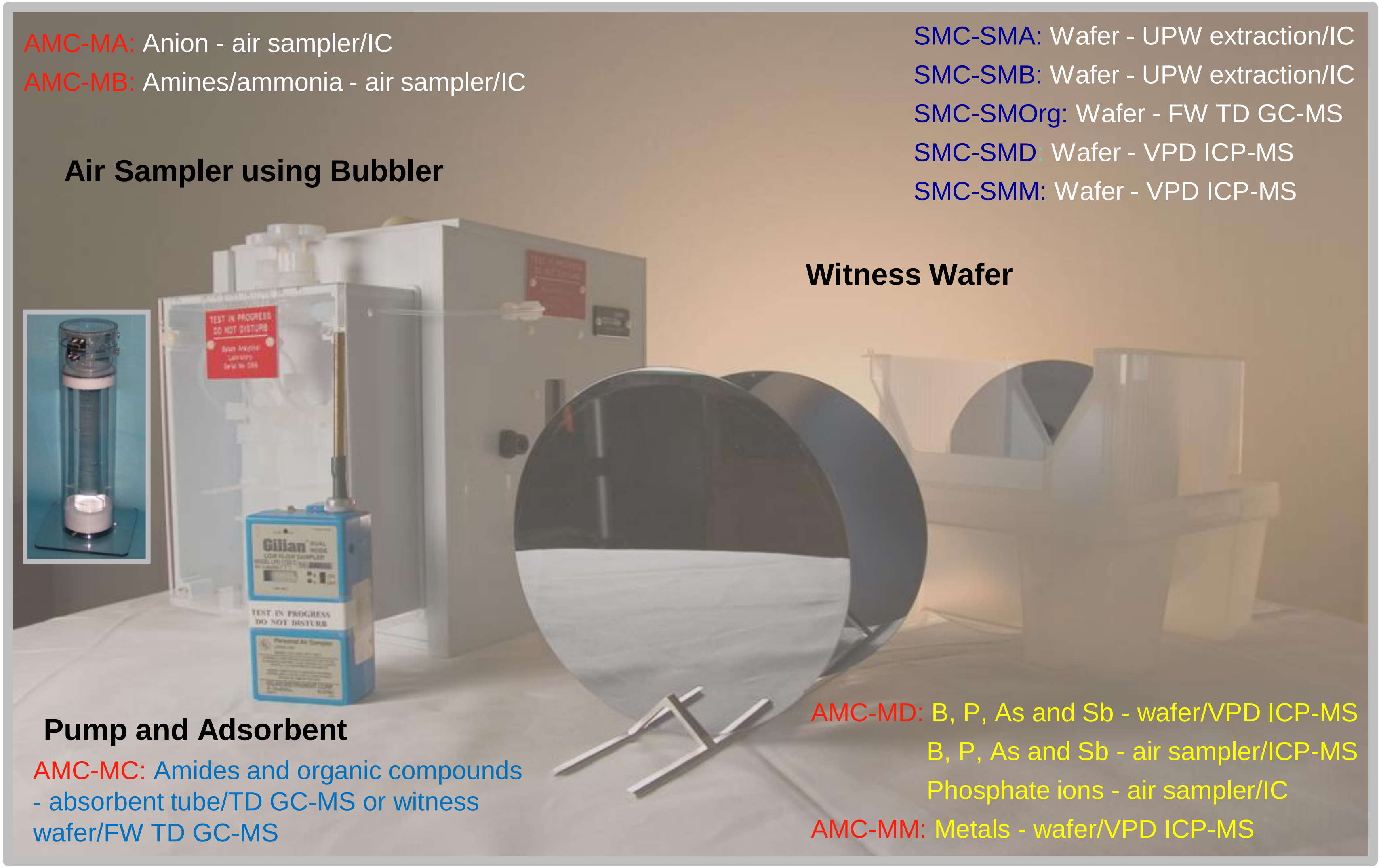
Airborne Molecular Grab Test Methods

- Grab sampling provides excellent sensitivity and specificity
- It is required for determining specificity, i.e. the source of the AMC

MOLECULAR ACIDS (MA)	**METHOD**	**COMMENTS**
HF HCl HNO_3 H_2SO_4	Impinger followed by ion chromatography (IC)	Very specific, low DLs
MOLECULAR BASES (MB)		
NH_3 Amines Urea	Impinger followed by ion chromatography (IC)	Very specific, low DLs
NMP	GC-MS	
MOLECULAR CONDESABLES (MC)		
Organic compounds (e.g. silicones and plasticizers)	Adsorbent tubes followed by TD GC-MS	Survey, low DLs
MOLECULAR DOPANTS (MD)		
P, B and As compounds in air	Impinger followed by ICP-MS	Very specific, low DLs
MOLECULAR METALS (MM)		
All metals (e,g, Al, transition metals, alkali)	Witness wafers followed by VPD ICP-MS	Survey, low DLs

Note: MD detection limit best using witness wafer and VPD ICP-MS

AMC and SMC Monitoring Methods



AMC-MA: Anion - air sampler/IC

AMC-MB: Amines/ammonia - air sampler/IC

SMC-SMA: Wafer - UPW extraction/IC

SMC-SMB: Wafer - UPW extraction/IC

SMC-SMOrg: Wafer - FW TD GC-MS

SMC-SMD: Wafer - VPD ICP-MS

SMC-SMM: Wafer - VPD ICP-MS

Air Sampler using Bubbler

Witness Wafer

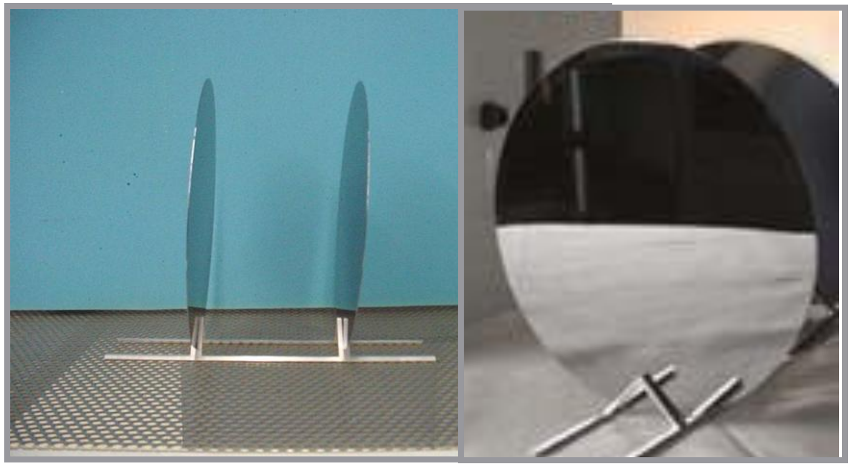
Pump and Adsorbent

AMC-MC: Amides and organic compounds - absorbent tube/TD GC-MS or witness wafer/FW TD GC-MS

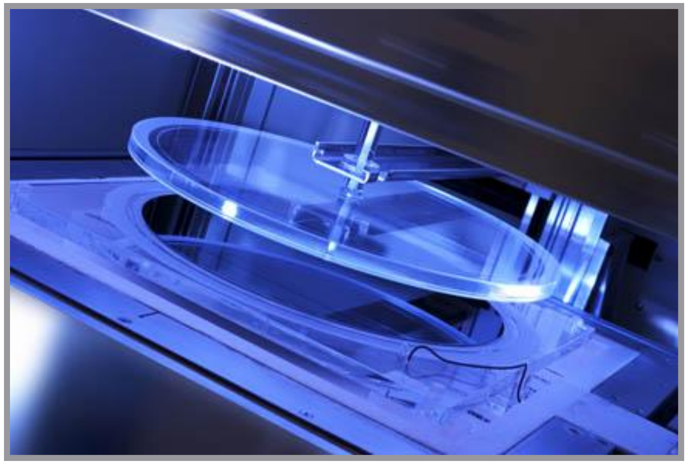
AMC-MD: B, P, As and Sb - wafer/VPD ICP-MS
B, P, As and Sb - air sampler/ICP-MS
Phosphate ions - air sampler/IC

AMC-MM: Metals - wafer/VPD ICP-MS

Surface Molecular Test Methods



Organic-free wafers on Al rack



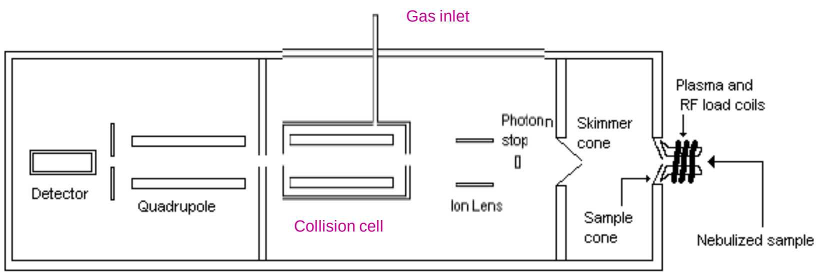
Full wafer outgassing unit

- **SME (metal / particles):** VPD ICP-MS
- **SMD:** Drop scan etch for B, P, As and Sb followed by ICP-MS
- **SMOrg:** Full wafer thermal desorption GC-MS, SEMI MF1982-1103

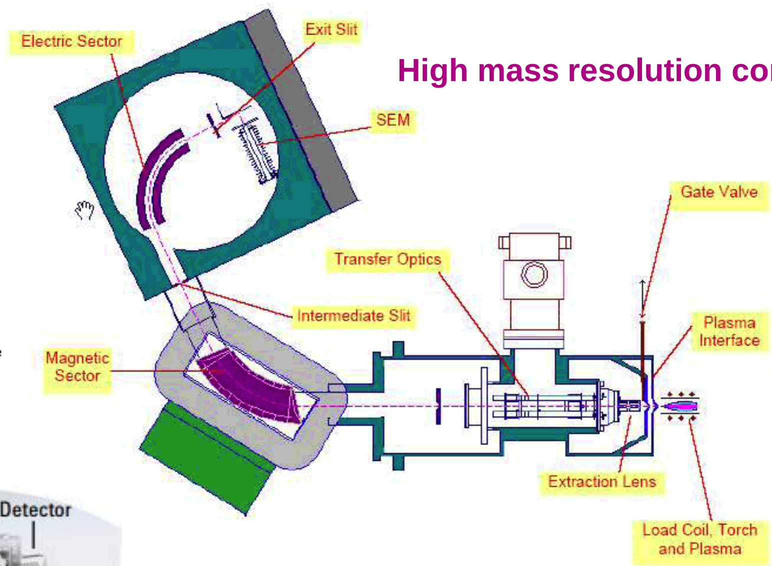
Trace Metals Analysis by ICP-MS

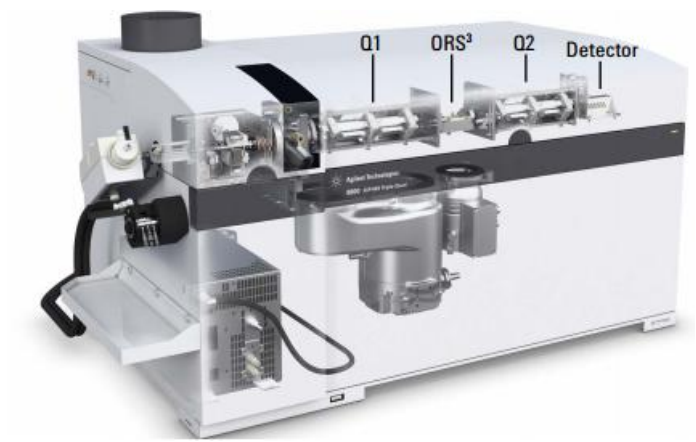
- There are several ICP instrument configurations available; Quadrupole ICP-MS, Collision Cell-Quadrupole ICP-MS, HMR ICP-MS and Triple Quad ICP-MS

Quadrupole configuration



High mass resolution configuration

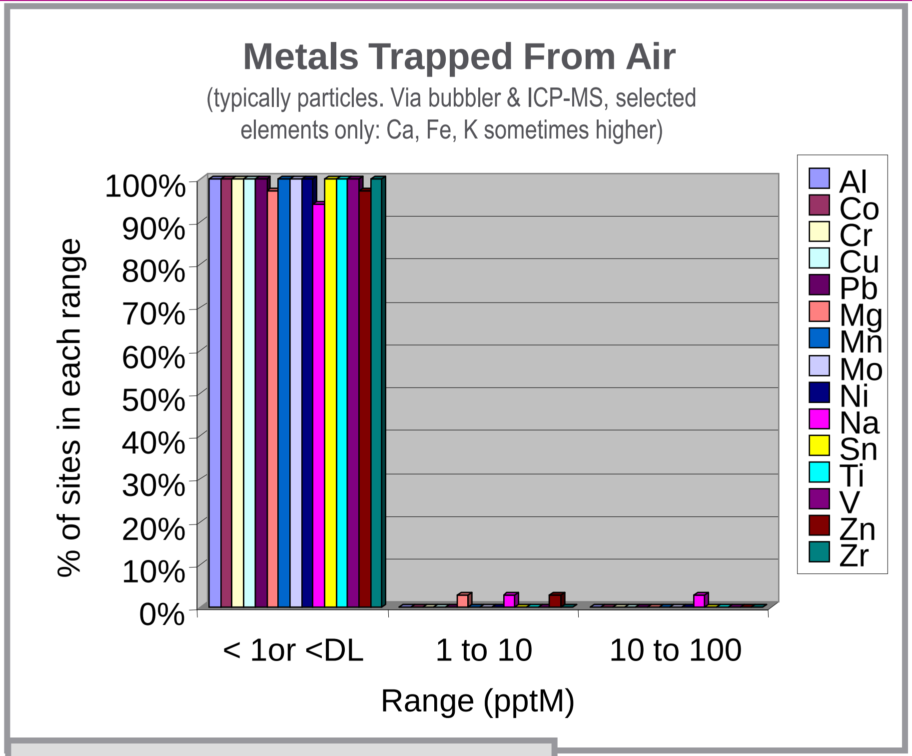


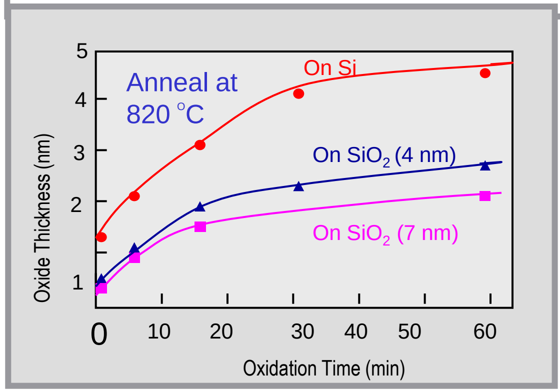


Triple Quadrupole configuration

Molecular Elements (AMC-ME)

- Metals in air may be molecular in some cases
  - $AlCl_3$ (bp 183 ºC)
  - WF_6 (bp 18 ºC, used for W plugs)
- In the future, more metal problems are likely
  - ALD Organometallic Precursors (organo-Cu, Al, Ti, Ga, As, Ge, In, Ba, Sr, Ta, Zr, Hf, Bi, Nb, La) and hydrides for MOCVD are volatile
  - Etch by-products may also be volatile



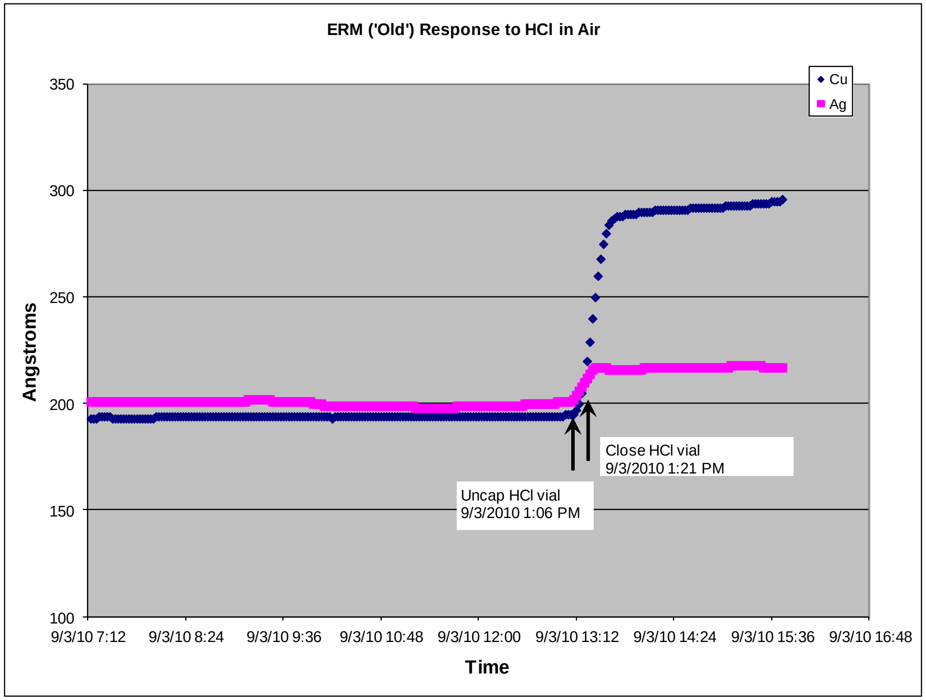


Experiments by Ohmni has shown that 100 ppb Al residue on a wafer surface after a SC1 (NH_4OH : H_2O_2 : DIW) cleaning process can accelerate oxidation of bare silicon wafers

T. Ohmori, N. Yokoi, and K. Sato, UCPSS, p. 25, 1996

Environmental Reactivity Monitor (ERM)

- Reactivity monitors are capable of estimating AMC concentration levels as low as 1 ppb
- Their main limitation is their inability to provide continuous AMC characterization

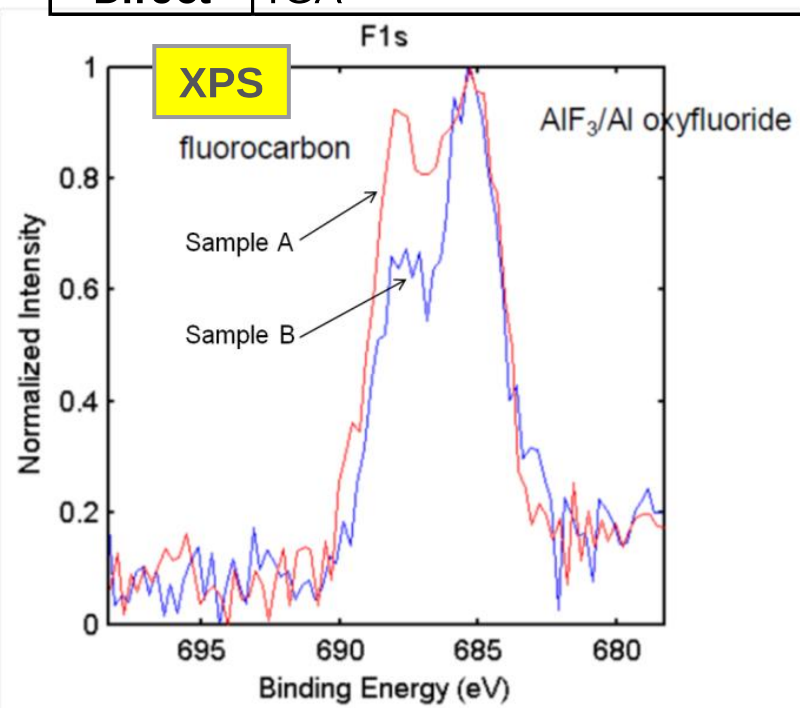


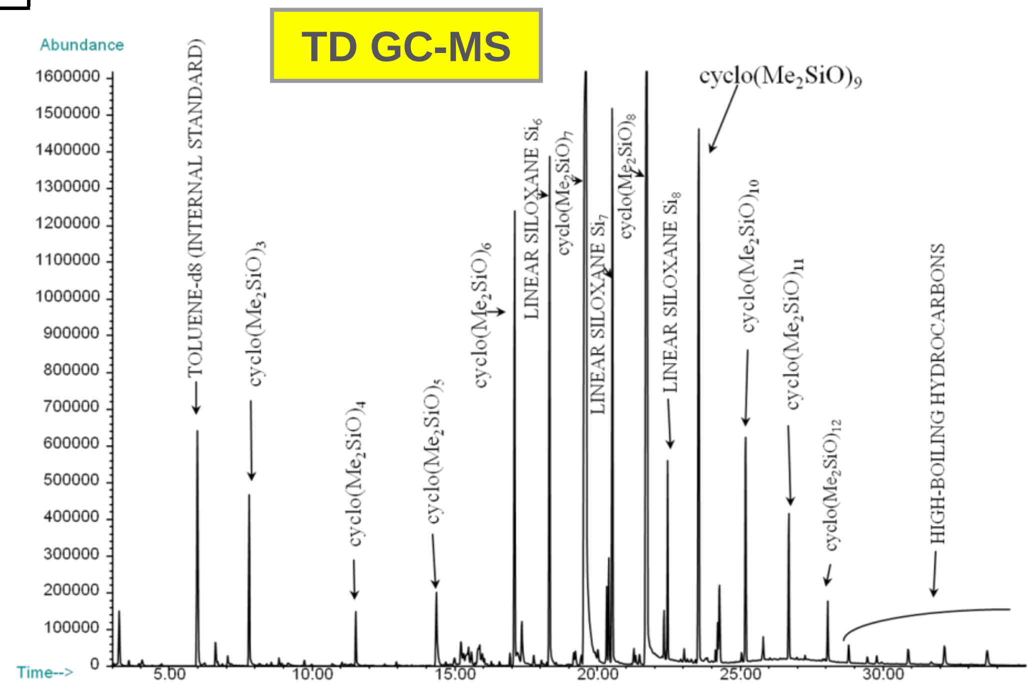
ERM response to HCl in air, 50-ppbV HCl challenge

Reactivity monitors are made of Cu or Ag metal strips

Residue Characterization for Organics

Indirect	Solvent extraction / GC-MS
Indirect	Solvent extraction / NVR/FTIR
Direct	TOF-SIMS
Direct	XPS
Direct	TD GC-MS
Direct	FTIR
Direct	Raman
Direct	TGA





Wafer Exposure Experiments

Experiment

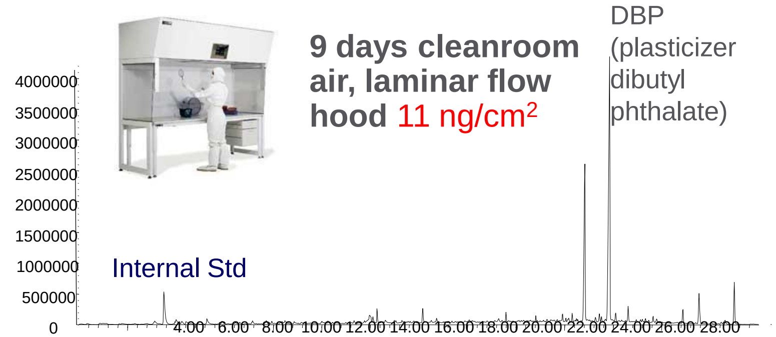
- Organic-free wafers exposed in various environments. Wafers analyzed using TD GC-MS, SEMI MF 1982-1103 Method-B

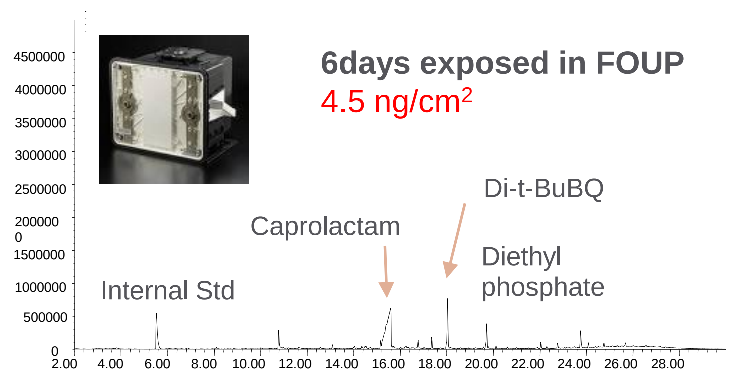
Results

- Individual shipper provided the best protection – less surface area exposed to the wafer

Conclusion

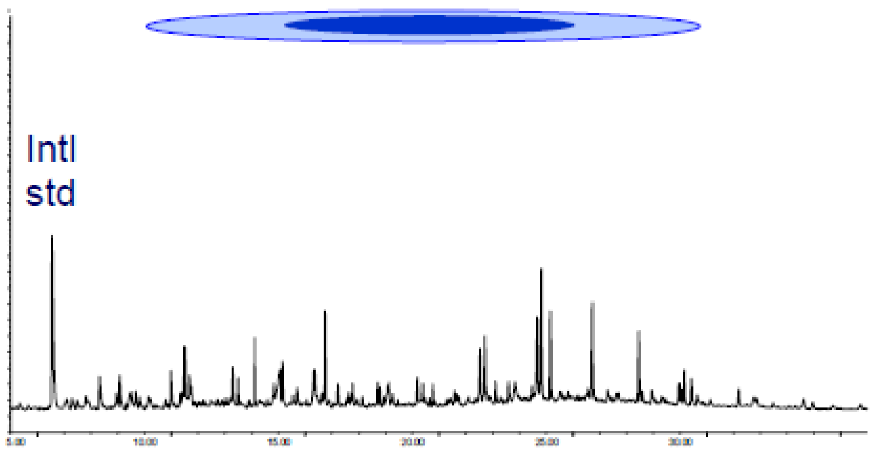
- Individual shippers provide protection from outside AMC
- FOUP outgassing/carryover issues possible; especially for hot wafers
- Keep wafer exposure in LFH to a minimum



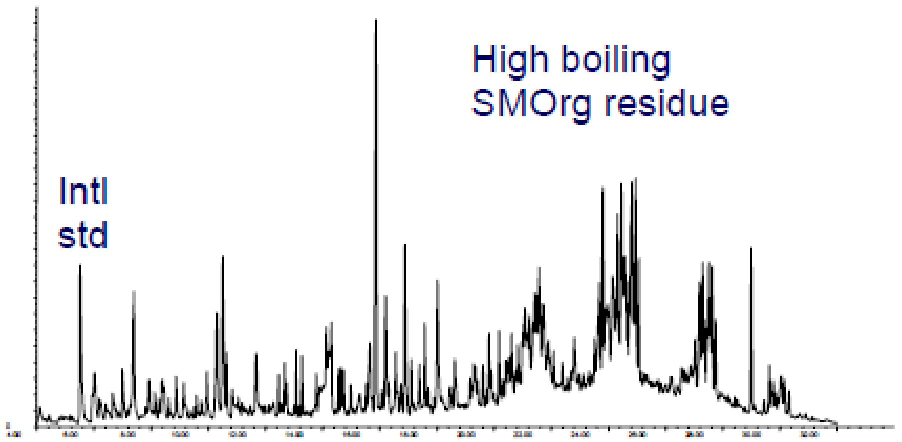


Simulation of Surface Cleaning Procedures

- IPA solvent residue vs. residues from wiping



- 8 g IPA (Gigabit)
- **5.3 µg SMOrg residue left**
- 0.67 ppmw SVOC's
- DL <0.05 ppm



- 6 g polyester wipe + 6 g IPA (Gigabit) + 8 g Nitrile glove

  <u>Wafer wiped 1 min</u>
- **19.3 µg SMOrg residue left**
- 61 ng/cm2 ~ 3 ML
- Most residue from glove/wipe and some IPA

Summa Canister

- A Summa Canister is an evacuated canister that is used to collect an instantaneous air sample. Air sample may be collected over 4 to 24 hrs

- The subsequent analysis by a cryo-focus GC-MS for volatiles identifies the chemical constituents present in the sample often in concentrations to sub-ppbV levels
  - Volatile organics
  - ~165 compounds reported
  - Detection limits in the order of 0.1 to 0.3 ppbV
  - Specific
  - Semi-quantitative

Photo-Ionization Systems

- Portable Photo-ionization Detectors (PID) systems contain built-in correction factors for 100's of compounds.
- This tool is not specific and does not identify the individual volatile material.
- The ppbRAE 3000 measures the presence of VOC's and inorganic gases from 1 ppb-10,000 ppm with widely varying sensitivities.
- System calibrated using standard gas mixture or a specialty custom gas mixture
  - Specifications (Mixture):
    - 10 ppm Isobutylene, Balance Air

ppbRAE 3000

Dräger-Tubes

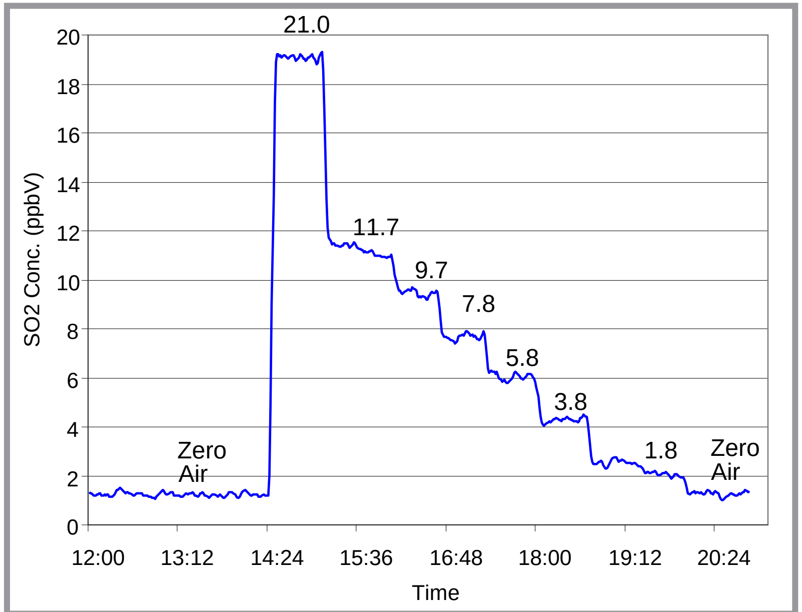
- The Dräger-Tubes are glass vials filled with a chemical reagent or media that reacts through adsorption or chemisorption to a specific chemical or family of chemicals
- Air is drawn through the tube with a pump
- If the targeted chemical is present the reagent in the tube changes color and the length of the color change typically indicates the measured concentration
- Reagents used in Dräger-tubes enable the removal of potential interfering gases (e.g. aromatic hydrocarbons) to enhance specificity of the targeted chemical
- Measuring range:
  - Fluorine 0.1-2 ppm
  - Chlorine 0.3-10 ppm
  - Ammonia 0.25-3 ppm

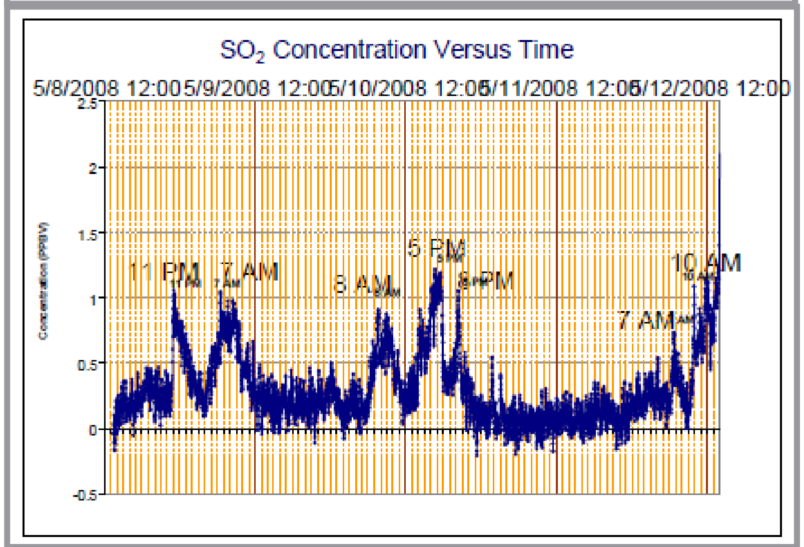
Dräger tubes and pump

Ultra-Sensitive Sulfur Detector

SO_2 and total-sulfur analyzer

- Reporting limit is 200 pptV for SO_2 and/or total sulfur
- Instrument challenge of SO_2 to determine its sensitivity (top right)
- SO_2 concentration in cleanroom make-up air (MUA) over a period of time (lower right)





Case Study Using Total Sulfur Monitor

Problem: Experiencing sporadic but confounding problem with substrates hazing

- Analyzed hazed wafers (DIW leach + IC) and found ammonium / sulfate in 2:1 ratio
- Air was sampled using DIW bubblers and identified high concentrations of ammonia and sulfate; suspected wafer TDH due to ammonium sulfate
- TS/SO_2 monitor operated on-site to assess cleanroom air, recirculation air, MUA, that pointed to one MUA unit as the source of contamination

Contamination source: Identified as sodium metabisulfite drums stored outside, but near the building air intake

Remedy: Drums bagged and removed. TS measured in cleanroom air immediately reduced significantly

Lesson learnt: Combination of real-time monitors and highly-sensitive, species-specific methods, are powerful tools for contamination early warning, identification and mitigation

Chemiluminescence (CL)

- Sensitive and mature method for the in-situ analysis of NO_x and many organic molecular bases such as NMP and amines; cannot be applied to most MC and MA compounds
- Can potentially generates ozone, which is undesirable in the cleanroom environment
- The basic chemiluminescence chemistry is:

$$NO + O_3 \rightarrow NO_2^* + O_2$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2^* \rightarrow NO_2 + hv \text{ photons } (\sim 600 \text{ to } 3{,}000 \text{ nm})$$

- Light emission with intensity linearly proportional to the concentration of NO

0-50 ppb to 0-20,000 ppb full scale with independent NO, NO_2, NO_X ranges and autoranging EPA's NO_x Reference Test Methods 20 and 7E were based on and written for chemiluminescence NO_x analyzers

AMC Monitoring System

- Tiger Optics' gas phase AMC analyzer is currently available in two platforms; Tiger-i 1000 and the Tiger-i 2000 with parts per trillion (ppt) levels detection
  - The Tiger-i 1000 HF and HCl analyzers employ a split architecture that allows users to place sensor modules up to 50 m away from the central analyzer; employs Tiger Optics' patented Continuous Wave Cavity Ring-Down Spectroscopy (CW-CRDS) technology
  - The Tiger-i 2000 NH_3, HF, HCl, H_2S, CO and CO_2 analyzers provide a compact, integrated architecture for enhanced analysis with a smaller footprint, and is based on HALO line of mini-CRDS analyzers

Tiger – i 2000

Ion Mobility Spectrometry (IMS)

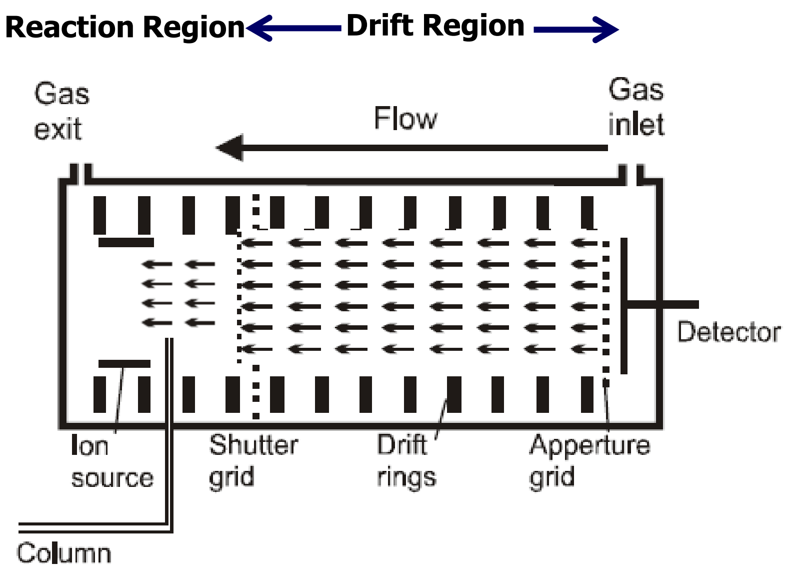
- Fundamental papers on ion mobility in electrical fields published around 1905, but IMS is considered to be one of the relatively new analytical methods

$$AB + h\nu \rightarrow AB^* \rightarrow AB^+ + e^-$$

$$AB^* \rightarrow A + B^-$$

$$AB^* + C \rightarrow AB + C$$

$$AB^+ + e^- + C \rightarrow AB + C$$



- Advantages of IMS is its capacity to operate at atmospheric pressure with no moving parts
- The IMS cell within the AirSentry® II chloride analyzer provides part-per-trillion (ppt) sensitivity and alerts users to small concentrations or changes in ambient Cl_2 and HCl levels

End of presentation

Thank you for your attention

Hugh Gotts, Ph.D.

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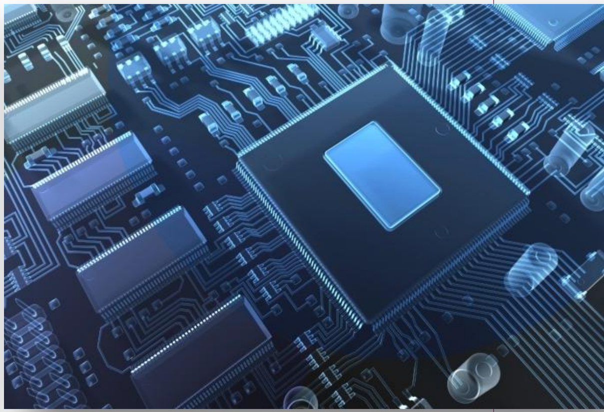


Back-Up Slides

Trouble Shooting Guides

Troubleshooting Guide

- Process impact from building and cleanroom construction materials

Problem or Effect Observed	Target Compound	Categories	Material Component
SiC formation, oxide growth variation	DOP (dioctyl phthalates) TXIB (texanol isobutyrate) BHT (butylated hydroxy toluene) Carbon	Plasticizer Plasticizer Anti-ageing, anti-oxidant Conductive filler	Flooring materials and vinyl tiles
Adhesive failure, surface hydrophobic	Poly dimethyl silicone Hexamethyl tri-silicone Octamethyl tetra-siloxane	Cyclic siloxanes (silicone bi-component)	Fluid seal (ceiling grid), cauking sealant
SiC formation	BHT (butylated hydroxy toluene)	Anti-ageing, anti-oxidant	Cleanroom walls, gaskets
Unintentional doping, surface hazing	Phosphate ester Antimony (Sb) Butyl phthalate	Crossliking agent Plasticizer Anti-oxidant	Fexible connectors and ductwork
CD control, hazing, optics degradation, SiC and SiN parasitic layer formation	Amines Ammonium DBP (dibutyl phthalate) BHT (butylated hydroxy toluene)	Crossliking agent Plasticizer Anti-oxidant	Polyuethane adhesives
CD control, hazing, optics degradation	Amines, polyimides	Crossliking agent Surfactants	Paintings, coatings, concrete fillers
Unintentional doping	TEP (tri-ethyl phosphate) TCEP (tri-chloro ethyl phosphate) TCPP (tri-chloro propyl $BF_3B(O\text{-}R)_3$, boron	Fire retardant Fire retardant Fire retardant Borosilicate fiberglass	ULPA/HEPA filters (media and potting materials)

Troubleshooting Guide

- AMC impact and recommended tests

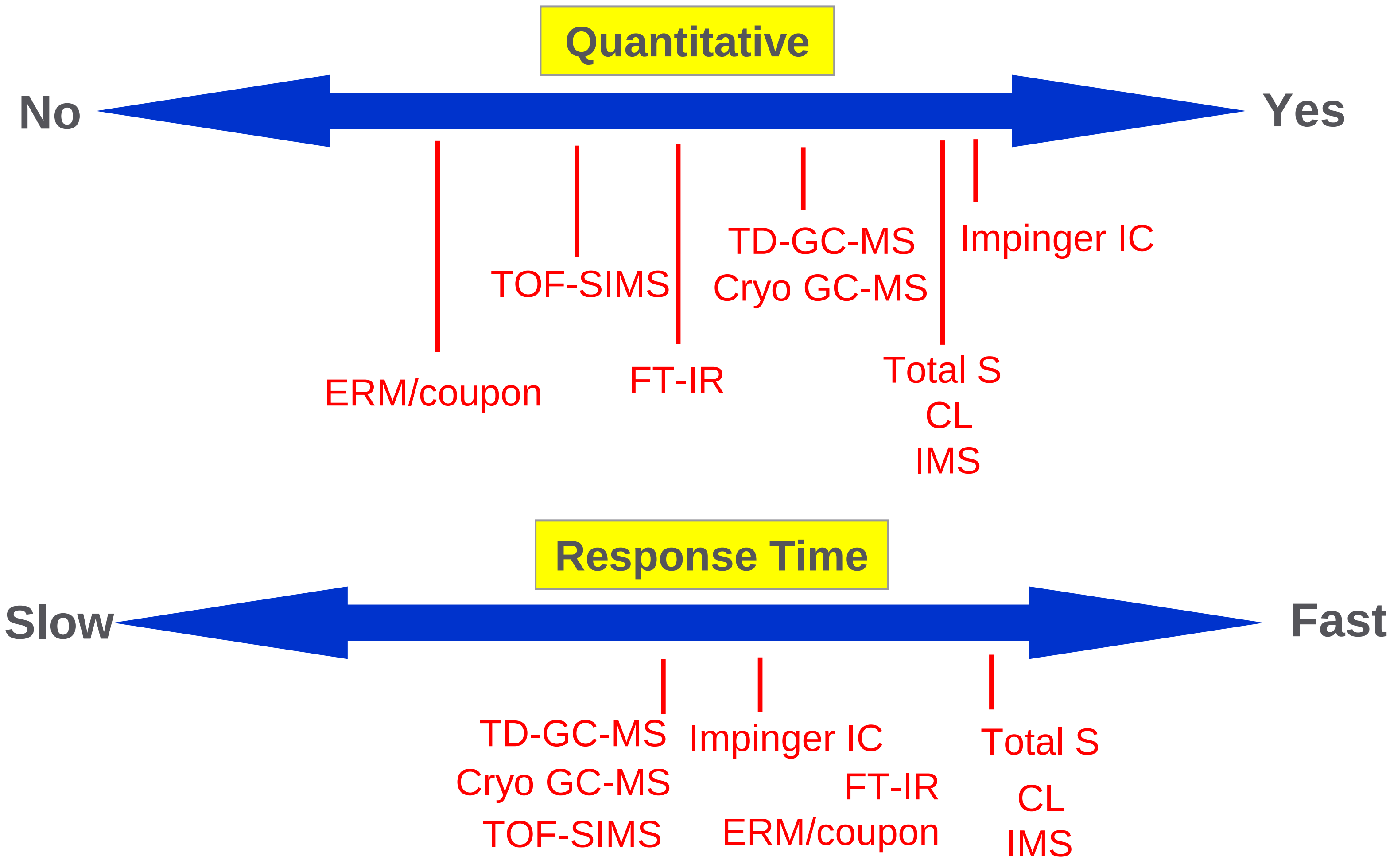
Problem or Effect Observed	Recommended Test/Source	Other Possible Tests/Comments
High contact resistance, open interconnects	Acids in air	Extractable anion tests from wafer surface (e.g. post RIE, post CMP)
	Ammonia in air	
	Organics on wafers	
Air ionizers (need frequent cleaning >3 times quarterly or "fuzzballs" form)	Acids, bases and organics in air as this is a string indicator of an AMC problem	Identification by EDS on ionizer tip (esp of Si containing)
		Ammonium salt identification by extraction and analysis by IC
SAW mass build-up	Organics on witness wafers	Note that reversible binding of water due to humidity changes and binding of alcohols or other
	Acids and bases in air for specific contamination identification	
High particle counts in cleanroom or MENV	Acids and bases in air since ammonium aerosols may from particles on witness wafers	
	Metals on witness wafers by VPD ICP-MS	
High particle counts on wafers	VPD ICP-MS for metals	Anions, cations or organics on wafers may sometimes be needed

Troubleshooting Guide

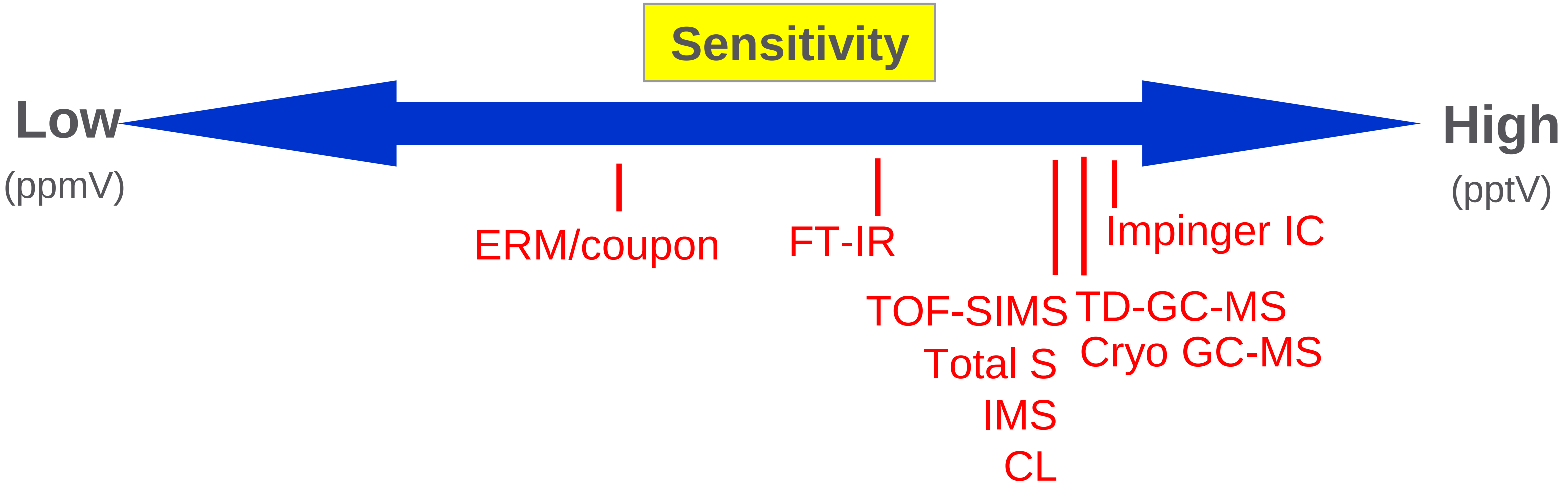
- AMC impact and recommended tests

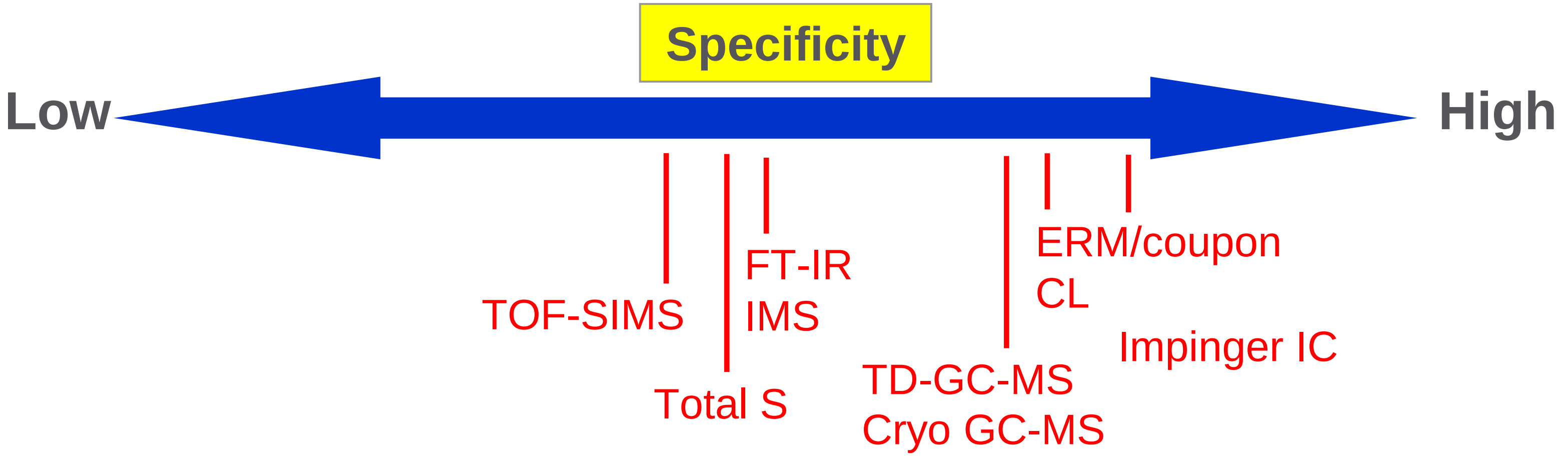
Problem or Effect Observed	Recommended Test/Source	Other Possible Tests/Comments
Odor complaints	Solvent smell; test for organics in air by GC-MC Irritating smell; test for acids in air by IC Fish-like smell; test for amines in air by IC	If testing needs to be performed for EHS or compliance monitoring appropriate OSHA, NIOSH, or EPA methods may need to be used
Delamination of photoresist,	Organics on wafers at the process	This exposure test is typically 24
Gate oxide thickness measurement variation or Ellipsometry errors	Organics on 24-hwitness wafer by GC-MS	Minimize air exposure time between gate oxidation and Ellipsometry
Metal corrosion on wafers,	Acids and ammonium in air near	Corrosion test via coupon exposure
Electrical tests: poor recombination lifetimes, SPV or leakage currents	Trace metals on witness or process wafers by VPD ICP-MS	May need to test both front and back side of wafers if Cu is used as Cu is fast diffuser
Unwanted doping, resistivity changes, threshold or flatband voltage shifts	Boron and phosphorus in air Boron and phosphorus on air Organics on wafers by GC-MS to assess organophosphorus compounds Metals on wafers by VPD ICP-MS may also be of value	B, P and other dopant profiling by SIMS can be used. Note: if boron is found, recommend testing the air for fluoride and other anions since borosilicate filters may have been attacked and can lead to boron contamination

AMC Comparison Technique Guide



AMC Comparison Technique Guide





Sources of Molecular Condensables

- **Plasticizers**, such as DOP and TXIB, are used in flooring material, vinyl curtains, flexible duct connectors, wafer carriers
  - TXIB, chemical name is trimethylpentanediol diisobutyrate.
  - TXIB is a Eastman trademark and is a common plasticizer found in PVC (polyvinyl chloride)

Si wafer exposed to the cleanroom environment for 30 days

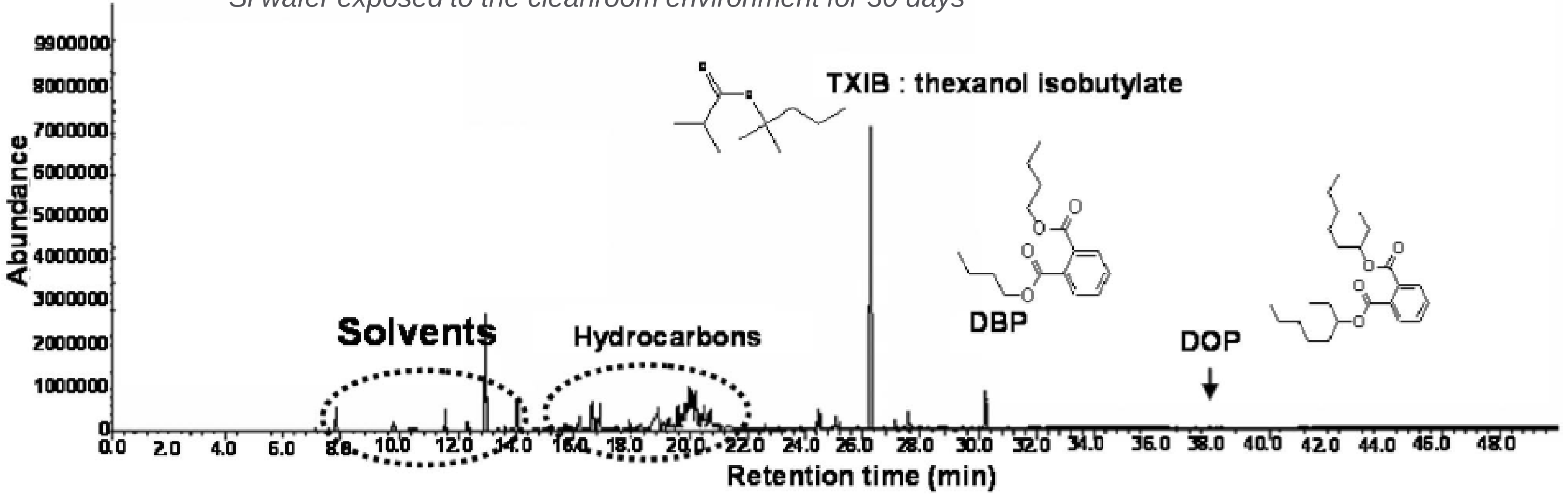


Photo-Ionization Systems

- Portable Photo-ionization Detectors (PID) systems contain built-in correction factors for 100's of compounds.
- This tool is not specific and does not identify the individual volatile material.
- The ppbRAE 3000 measures the presence of VOC's and inorganic gases from 1 ppb-10,000 ppm with widely varying sensitivities.
- System calibrated using standard gas mixture or a specialty custom gas mixture
  - Specifications (Mixture):
    - 10 ppm Isobutylene, Balance Air

ppbRAE 3000