ERC Teleseminar

An Update of ESH Regulations Affecting Semiconductor Chemicals

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May 1, 2003

INTERNATIONAL SEMATECH

Outline

- Global ESH Trends
- PFOS, Pb, HMDS, HAPs, others
- EPA's Chemicals Strategy
- European Chemicals Initiative
- SEMATECH's Current ESH Focus
- Summary

Global ESH Trends

- **Four relatively long-standing trends**
  1. Targeting chemical categories of concern
  2. Forcing producers to take responsibility for full life cycle of products
  3. Increased emphasis of public's "right-to-know"
  4. More documentation and verification
- **Latest trends**
  1. Japan consumers want "energy-efficient, green products"
  2. Europe wants to regulate product content and the process to design and manufacture these products
  3. Europe wants to regulate the use of chemicals in the Periodic Table

Major Challenge Resulting from Global Trends

- **Managing chemical risks -- real or perceived**
- **Chemicals of most concern:**
  - ***Persistent, Bio-Accumulative Toxics (PBTs)***
  - ***Persistent Organic Pollutants (POPs)***
  - ***Carcinogenic, Mutagenic, Reproductive hazards (CMRs)***
  - ***PFOS/PFAS chemicals***
  - ***Lead***
  - ***Hexamethyldisilizane (HMDS)***

Persistent, Bio-accumulative Toxics (PBTS) and Persistent Organic Pollutants (POPs)

- **Resulted in "POPs Treaty"**
  - Official name: "Stockholm Convention on Persistent Organic Pollutants"…to protect human health & the environment
  - Requirements:
    - Eliminate production and use of 12 listed POPs chemicals
    - Reduce, minimize and, "where feasible", eliminate the "unintentional" release of 4 of the 12 listed POPs chemicals
  - Effective Date: 90 days after Treaty is ratified by 50 countries (could happen in 2004)
  - USA signed treaty on May 23, 2001
  - Ratified by about 30 countries so far (EU, Japan, but not U.S.)
  - Working on implementation document; contains terms such as "**best available techniques**" and "**best environmental practices"**

Chemicals Listed in POPs Treaty

- **The so-called the "Dirty Dozen"**
- **Includes:**
  - Eight (8) pesticides (e.g., aldrin, chlordane, DDT, dieldrin, mirex, endrin, heptachlor and toxaphene)
  - Two (2) industrial chemicals (polychlorinated biphenols and hexachlorobenzene)
  - Two (2) by-products of combustion and industrial processes (dioxins and furans)
- **Treaty has provisions for addition to this list in the future** (PFAS, lead and HMDS may be prime candidates)

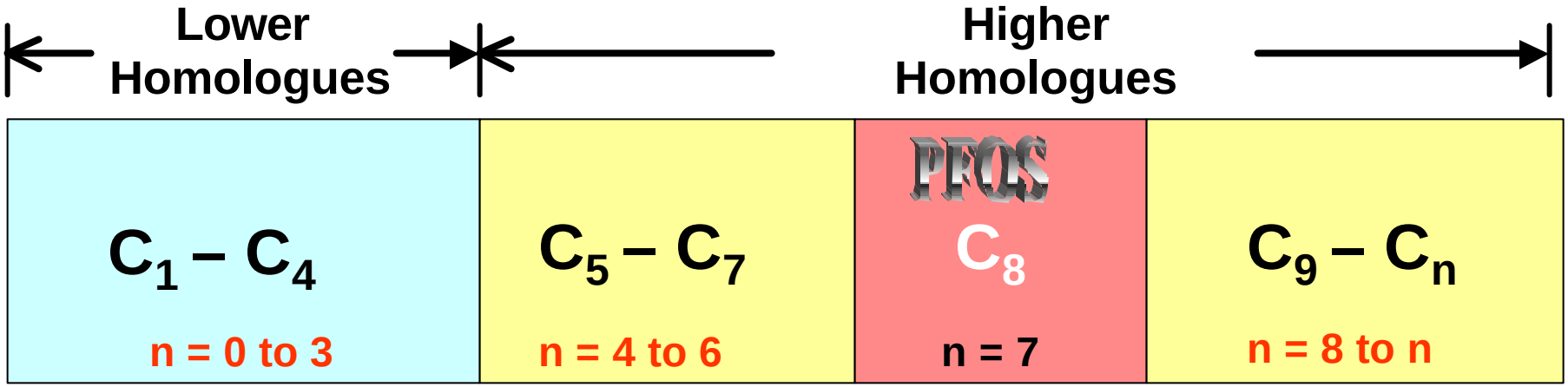
PFAS Issue

- **U.S. EPA issued proposal to restrict manufacture, import and use of certain PFAS containing compounds**
  - Due to concerns with environmental persistence and bio-accumulation
- **Principle use is in consumer products such as Scotchgardä made by 3M, which proposed voluntary phase-out of 90 PFAS materials over two-year period**
- **PFAS offer unique characteristics critical to lithography photo-resists – no known replacements exist**

PFAS Homologue Family

$CF_3(CF_2)_nSO_2X$

Per**f**luoro**a**lkyl **s**ulfonate moiety



PFOS is the homologue normally found in the chemicals used by the semiconductor industry

Courtesy: Murrae Bowden-Arch Chemicals

EHS Concerns with PFOS

• **Persistence and Bioaccumulation:** Ultimate degradation product is PFOSA (Perfluorooctanesulfonic acid) - extremely stable substance; resists chemical or biological breakdown processes and is transported in the water

• PFOS found in:
  - **•fish, eagles and wild birds in U.S, Korea, Japan, the Baltic Sea and the Mediterranean**
  - **•polar bears in Alaska**
  - **•penguins and seals in Antarctica**
  - **•children**
  - **•blood banks world-wide**

• Mean elimination half-life ≅ 4 years
  - **•Rat and primate studies identify potential toxicity effects and developmental effects**

• EPA concerned that low volume exemption (<10 tons/year) of PFOS has resulted in widespread human and animal bioaccumulation and that continued PFAS production and release will result in adverse effects on people and wildlife

Identification of PFOS Uses

•**SIA/SEMI identified PFAS in following chemicals:**

- **Photoresists**
- **TARCs**
- **BARCs**
- **Developers**
- **Polyimides**
- **Wet Etchants**
- **Plating baths**
- **Strippers**
- **Cleaners**
- **Low-k dielectrics**
- **Anisotropic Conductive Films**

Litho Processes

Other Processes

- **Initial Industry Focus has been Lithography**

Implications for SC Manufacturing

- **Photo Acid Generators (PAGs) in Advanced Photoresist Systems**
  - No known substitutes
  - Essential to the next several generations of semiconductor manufacturing; ban would stop 157nm resist development
  - This would seriously impact the US semiconductor industry
- **Surfactants in anti-reflective coatings**
  - Suppliers investigating polymeric replacements
  - At least two years needed to replace them
- **Surfactants in photoresist**
  - Replacements available but existing products require reformulation and re-qualification
  - Alternatives contain silicon. (Si converts to SiO_2 in etching/ashing – removal difficult plus quality issues)

Rationale for Exemption

- **Joint SIA/SEMI working group sent formal request for an exemption to the EPA in September 2001**
- **Requested an unlimited exemption for PFOS use as PAG precursors and ARC in photolithography**
  - The exemption was justified by the criticality of the materials and by the very small amounts that enter the environment via waste water
  - Developers were not included in the request
  - Understood that ARC should not be disposed of in wastewater
- **No exemption requested for aqueous and non-lithographic uses of PFOS in electronic applications**
  - Substitutes, even for critical applications, are more readily available
  - Orderly re-qualification of replacement materials may present problems

PFAS/PFOS Exemption Status for Semiconductor Industry

- **PFAS SNUR (Significant New Use Rule)**
  - EPA issued proposed rule on March 11, 2002
  - Scales down manufacturing (and importation) during 2001 and 2002
  - Bans manufacturing (and importation) after 2002
  - Future actions on a broader scale anticipated
- **Includes exemption for photolithography uses of 75 PFAS chemicals**
- **Public comment period ended on July 9, 2002 without any substantive challenges to proposed rule**

EPA Ruling on PFAS/PFOS Issue

- **Resist and ARC have been granted an exemption!!!**
- **Final PFAS SNUR published December 9, 2002**

"(3) Manufacture or import of any chemical listed in Table 2 of paragraph (a)(1) of this section for the following specific uses shall not be considered as a significant new use subject to reporting under this section:

"(ii) Use as a component of a photoresist substance, including a photo acid generator or surfactant, or as a component of an anti-reflective coating used in a photmicrolithography process to produce semiconductors or similar components of electronic or other miniaturized devices

"(iv) Use as an intermediate only to produce other chemical substances to be used solely for the uses listed in paragraph (a)(3)..(ii)… of this section"

Federal Register/ vol.67, no. 236

SNUR = Significant New Use Rule

Continued S/C Industry Actions on PFOS

- Further regulation of PFOS still a threat (e.g., Europe)
- Therefore, S/C Industry is pursuing the following activities:
  - **Elimination of PFOS from developer**
    - Largest single use of PFOS in lithography
    - Developer supplier is removing product voluntarily
    - This usage is not covered by the SNUR exemption
  - **Elimination of PFOS from resists**
    - Surfactant replacement underway at every supplier
    - Replacement in PAGs has also begun
  - **Elimination of PFOS from ARC**
    - ARC is a small use for PFOS

Lead (Pb)

- Lead-containing solder is used to bond chip to printed wiring board (PWB)
- Most solder balls are made of a eutectic Pb-Sn alloy; low melting point, excellent wetting characteristics & strength
- Legislation under way in Europe, Japan and USA to restrict or ban the use of Pb in electronic packages
  - In Europe, lead ban in place = 1 July 2006
- Many different lead-free solders are being considered, but problem is the higher temperature required for processing
- EPA is currently doing a life cycle analysis (LCA) to compare the impact of conventional vs lead-free solders
- At one time, Pb-containing precursors were considered for advanced gate stacks

Hexamethyldisilizane (HMDS)

- HMDS is used as a photo-resist adhesion promoter
- HMDS has been placed on the EU's OSPAR* list of chemicals considered hazardous to marine environment
- France is performing a risk assessment of HMDS. If not proven harmless and removed from list, it will be banned as of 2020
- Dow Corning did study and found statistically significant increase in Leydig cell tumors in rats
- Chance that it could be classified as carcinogen based on this study

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***OSPAR is a treaty among European Countries that addresses discharge of "dangerous" compounds into the North Atlantic**

Other S/C Compounds under Scrutiny

- **Indium compounds**
  - Used in assembly & packaging
  - Replacement for Pb in solder
  - Potential lung carcinogens
- **1-Bromopropane** and **2-Bromopropane**
  - Often used as substitute for CFC, HCFCs and methylene chloride
  - Under review for reproductive effects

EPA MACT Rule for Semiconductors

- MACT = Maximum Achievable Control Technology
- Provides standards for controlling hazardous air pollutants (HAPs); Federal HAPs list contains 183 compounds
- Common semiconductor HAPs:
  - Inorganic HAPs: arsine, phosphine, HCl, HF and chlorine
  - Organic HAPs: methanol, xylenes, ethyl benzene, ethylene glycol, MEK, MIBK and glycol ether compounds
- Process vent standards:
  - Organic HAP standard: 98% (by wt.) reduction or < 20 ppmv outlet concentration
  - Inorganic HAP standard: 95% (by wt.) or < 0.42 ppmv outlet concentration
- Rule was signed into law on February 28, 2003; SC industry failed to get exemption

EPA's Multimedia Strategy

- National Action Plans for "Dirty Dozen"
- Screen/Select More PBTs for Action
- Prevent introduction of new PBTs
- Measure progress through Toxic Release Inventory (TRI) data
- Children's Chemical Evaluation Program
- Endocrine Disruptor Screening

TSCA

- **Toxic Substances Control Act (TSCA) is the primary means of restricting chemical use in the U.S. (enacted in late 1970's)**
  - Administered by EPA; provides broad regulatory authority
  - All chemicals & components must be on TSCA inventory to be used
  - EPA requires risk assessment of health and environmental impacts before new chemical can be listed
  - May require data on health effects and toxicity
  - Low volume exemption (limited to <10,000 Kg/yr aggregate) can be granted for new chemical

EPA Regulatory Initiatives

- **Developing PBT list for regulatory/voluntary action (includes the "Dirty Dozen")**
- **Setting up Policy for Screening New Chemicals**
  - Persistence (transformation half-life)
  - Bio-accumulation (in fish)
  - Determines restrictions on commercialization
- **Toxic Release Inventory (TRI) Rules**
  - Lowering reporting thresholds for many chemicals
  - E.g., For lead (Pb), went from 25,000 to 100 lbs/year

High Production Volume (HPV) Chemicals

- Voluntary testing program covering over 2000 chemicals
- Testing for toxicology; physical and chemical properties; and environmental fate and effects
- Timing: Next three years, with 1/3 of the testing to be completed by 2001 and remainder by 2003
- Driver: the lack of publicly available data
- Federal Register states: “data obtained….will be used to develop initial risk assessments that will allow EPA and others to set priorities…identify chemicals of lesser concern”

Voluntary Children's Chemical Evaluation (VCCEP) Program

- Children's health is a"hot button" political issue
- EPA evaluation program, which includes toxicological study for developmental neuro-toxicity
- 23 chemicals identified for study based on bio-monitoring data:
  - acetone, benzene,vinylidenechloride, methyl ethyl ketone, trichlorethylene, a-pinene, o-xylene, ethylbenzene, p-dichlorbenzene, ethylene dibromide, ethylene dichloride, m-xylene, toluene, chlorobenzene, n-dodecane, p-dioxane, decane, tetrachlorethylene, m-dichlorobenzene, decabromodiphenyl ether, pentabromodiphenyl ether, octabromodiphenyl ether

Endocrine Disruptor Screening Program

- Endocrine system controls a variety of functions including reproductive, immune, respiratory and digestive functions
- Examples of endocrine disruptors: bisphenol A, phthalates, PCBs, DDT
- EPA testing to begin in 2004, but some manufacturers will start screening earlier
- High level of activism by groups such as “Friends of the Earth”

Canadian Initiative

"DSL Screening"

- Under the Canadian Environmental Protection Act (CEPA) approximately 23,000 substances on the Canadian Domestic Substances List (DSL) will screened by 2006
- To identify those that:
  - Present the greatest potential for human exposure
  - Are persistent or bio-accumulative and inherently toxic
- Chemicals so identified by modeling (primary screening tool) will be subject to a screening level risk assessment

European Initiatives

"WEEE Directive"

- EU legislation deals with "*waste from electrical and electronic equipment*",
- Sets requirements for take back of electronic products including collection, separation/disassembly and recycling
- A big deal for OEMs

European Initiatives (cont'd)

"RoHS Directive"

- RoHS = Restriction of Hazardous Substances
- Restricts use of Cd, Pb, Hg, Cr compounds and two flame retardants in Electronics [polybrominated biphenyls (PBB) and their ethers/oxides (PBDE)]
- Date of implementation likely to be Jan. 1, 2006
- Electronics industry lobbying for Lead exemptions:
  - Lead in high melting solders (Sn/Pb >85% and 260 ^{o}C MP)
  - Lead in electronic ceramic parts
  - Lead in glass of CTRs and fluorescent tubes

European Initiatives (cont'd)

EU Chemicals Strategy "White Paper"

- In early 2001, European Commission prepared a "white paper" for revision of laws governing "new" and "existing" chemicals
- "White Paper" contained concrete suggestions for introducing legislation, provided policy strategy, but no legislative details
- Introduction of the **"REACH System"** – i.e., Registration, Evaluation, Authorization of CHemicals
- Special focus on PBTs, carcinogens, neurotoxins, with "high concern" chemicals banned after a certain due date
- Downstream users impacted for the first time

European Initiatives (cont'd)

Legislative Timeline for EU Chemicals Strategy:

- In July 2001, European Parliament issued report strongly endorsing "white paper"
- Strong opposition by chemicals industry, but unlikely to derail Commission's push for new law/regulation
- Business Impact Study - May 2002
  - Number of substances and intermediates are big concern
  - Cost of testing, registration, implementation: ~2-8 B Euro
  - Impact on innovation (esp. for specialty chemicals)
  - Disclosure of confidential information / IP
  - International competitiveness
- Legislative process likely to take 4 years

European Initiatives (cont'd)

"CMR List"

- European Union is developing a consolidated list of "CMR" substances
- "CMR" = carcinogens, mutagens and toxic to reproduction
- The list currently contains about 1000 compounds that are suspected to fall into one of these categories
- Official legislation for this list is expected in 2003
- Outcome may vary from ban (in the worst case) to authorized use (with minimal exposure, i.e., in closed systems)

SEMATECH ESH Program

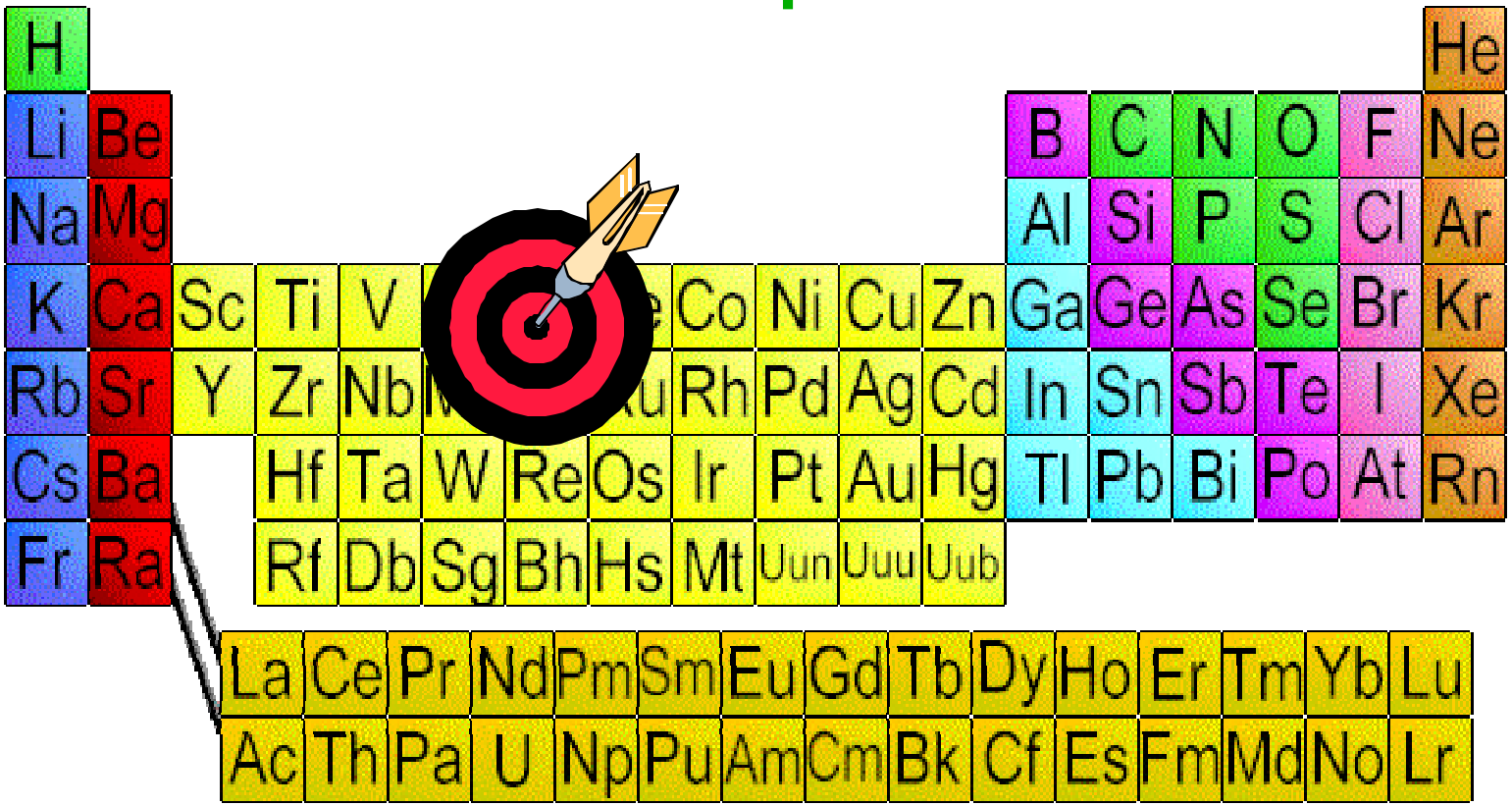
Our Vision: “Greener”, Safer Semiconductor Fabs

Our Goal:

- Prevent potential ESH showstoppers
- Minimize negative ESH impacts and costs
- Avoid cost due to ESH risk
- Reduce fab cost through reductions in energy, water, and chemical consumption
- Allow member companies greater flexibility in considering technology options and making strategic business decisions

New Materials Everywhere!

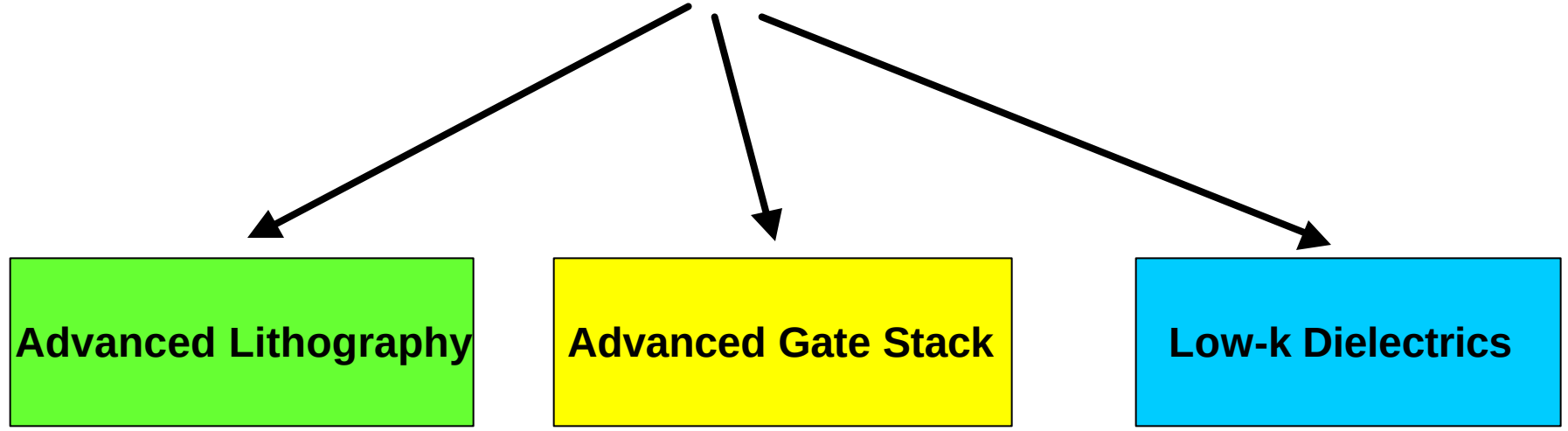
New materials & processes are being introduced at an unprecedented rate



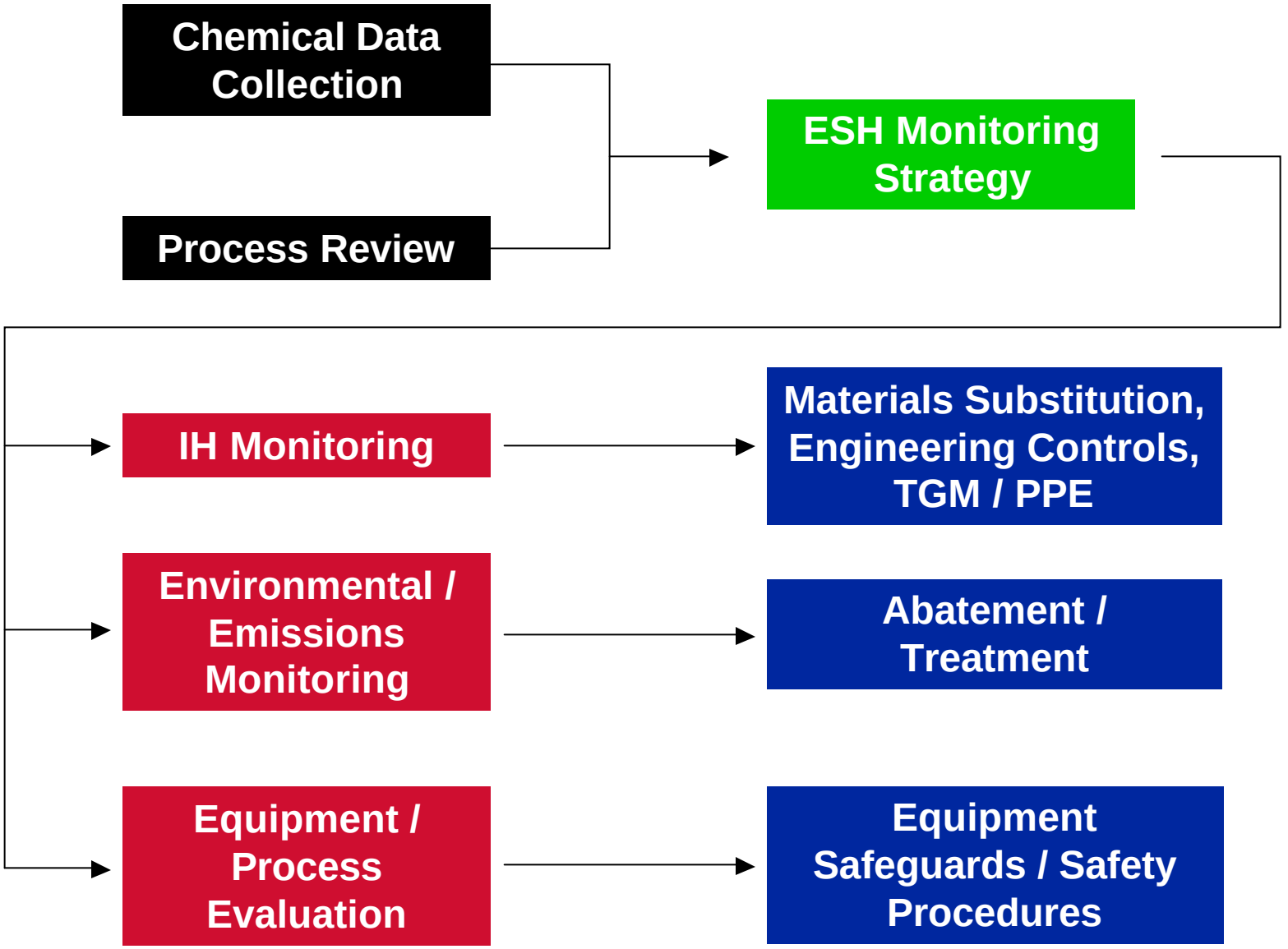
Laura Mendicino-Motorola

ESH Impact Assessment

Objective: Early Identification of ESH issues associated with new chemicals prior to insertion into manufacturing



ESH Assessment / Evaluation Process



ESH Assessment – What's Involved?

- Identify candidate chemistries through close collaboration with technology thrusts
- Evaluate using "Chemical Data Matrix" (75 data types)
    - Start with MSDS
    - Utilize many data bases
    - Request additional data from suppliers
- Identify how the chemicals are being applied, deposited, etched and processed
- Perform emissions characterization
- Perform industrial hygiene (IH) survey

ESH Assessment Results

- Provides early information on potential ESH risks/issues associated with new chemicals/materials/processes
- Avoids potential delays in process development/ implementation
- Allows selection of:
  - Personal protective equipment (PPE) appropriate to risk
  - Most cost-effective emissions control and waste handling/treatment

Summary

- Both the U.S. EPA and the EU have programs under way for screening all chemicals for health and environmental effects.
- Chemicals facing highest regulatory scrutiny are persistent, bio-accumulative toxics and lead
- Chemicals with the “highest concerns” will likely be banned from use or importation
- Introduction of so many new chemicals for next generation chips makes early assessment of ESH impacts very important

Acknowledgement

- Julia Hatcher of Latham & Watkins

  (Washington law firm supporting SIA)
- Coleen Miller, TI assignee to SEMATECH
- Jeff Heaps, Motorola assignee to SEMATECH