Perspectives on PFOS*

***P**er**F**luoro**O**ctyl **S**ulfonate

Jim Jewett

Steve Harper

Bob Leet

Robert Meagley

SIA PFOS WG

27 January 2005

Overview

- Background
- Semiconductor Technology Perspective
- Opportunities for University (ERC) research

Classical Train Wreck Problem

- Concern regarding the **potential** environmental and human health **impacts** attributed to [*target chemical*] drive regulatory actions by governments.

- Continued success of the global semiconductor industry depends on the **availability** of [*target chemical*] for critical uses.

Public Policy Context

- Increasing tendency of public and governments to focus on intrinsic properties of substances *(hazard)* rather than likelihood of exposure *(risk)*

- Gaining popularity of *precaution* as basic regulatory approach

- Analytical ability to detect chemicals at extremely low concentrations

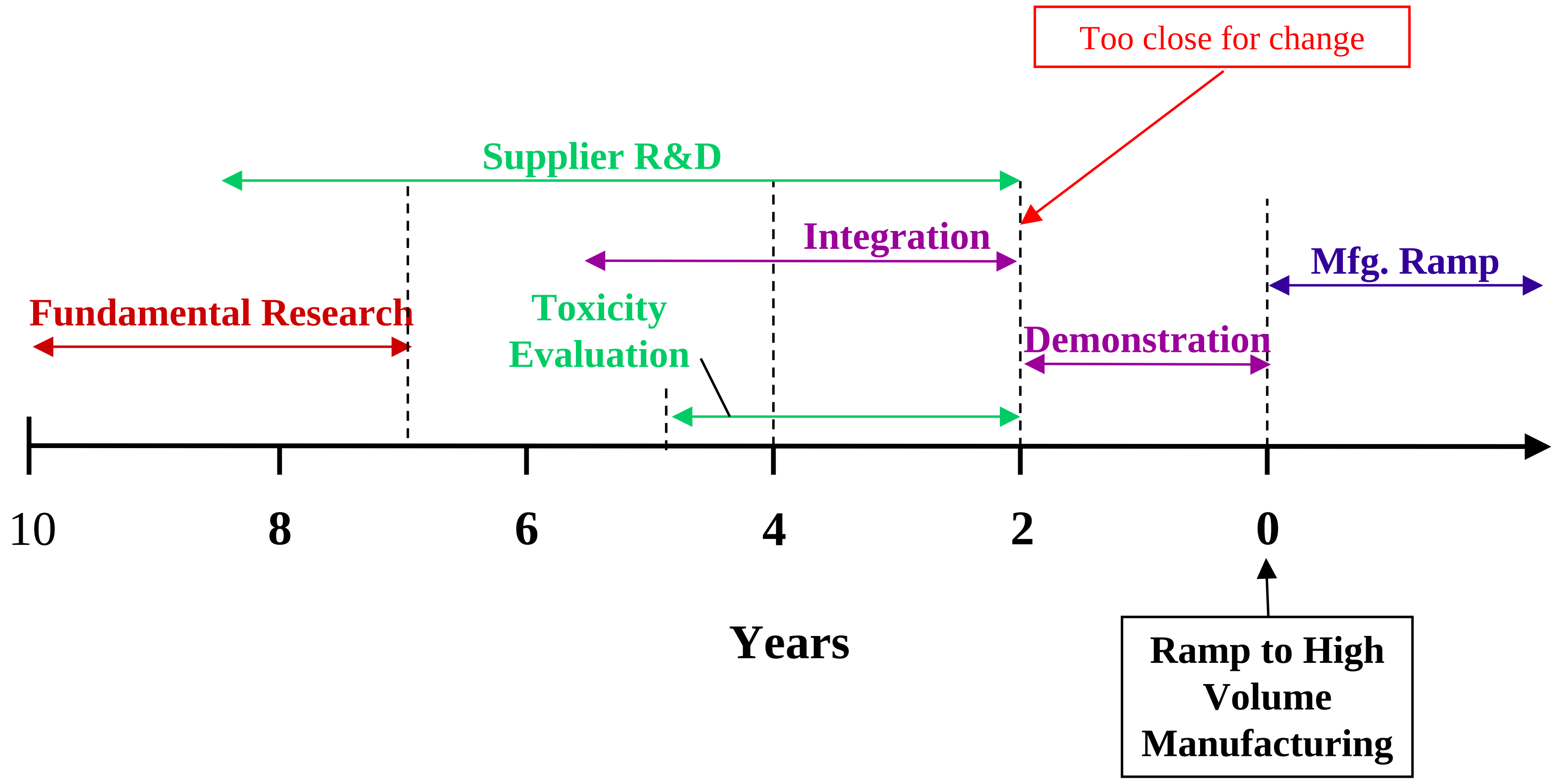
Technology Planning Context

- As circuit widths continue to decrease, novel chemicals become more important to our ability to maintain Moore's Law
- Bans and phase-outs reduce our product and process design flexibility
- Need to get regulatory approvals for chemicals threatens cycle time delays

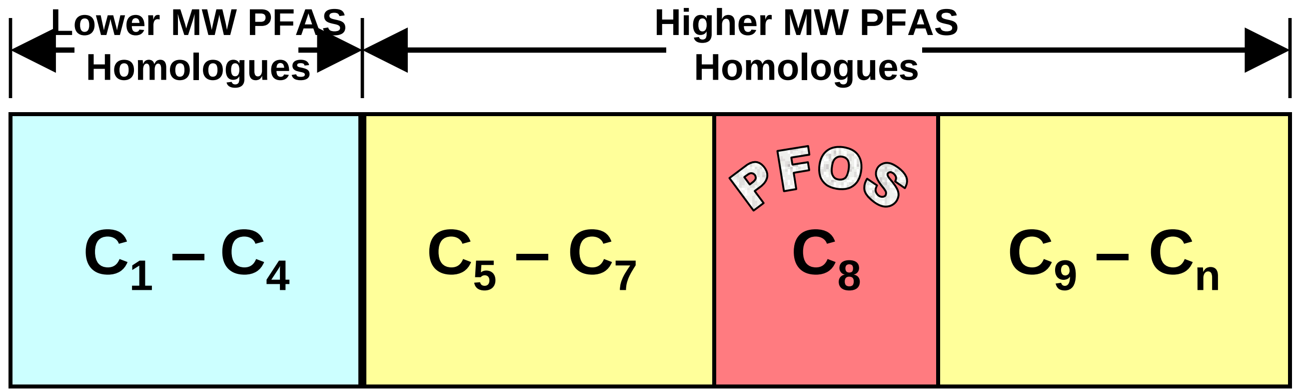
The Semiconductor Technology Development Cycle

- The semiconductor manufacturing process is highly complex
- As circuit features get ever smaller, specialty chemicals like PFOS become ever more important
- Chemicals and materials must work precisely with advanced equipment (“tools”) to accomplish high-yield, high-volume manufacturing
- The process for developing new chemicals, new tools, and to ensure that the two work together in a manufacturing environment can take 10-15 years to complete
- Substitution of new materials into an existing process cannot happen quickly

Technology Development Cycle



Definitions



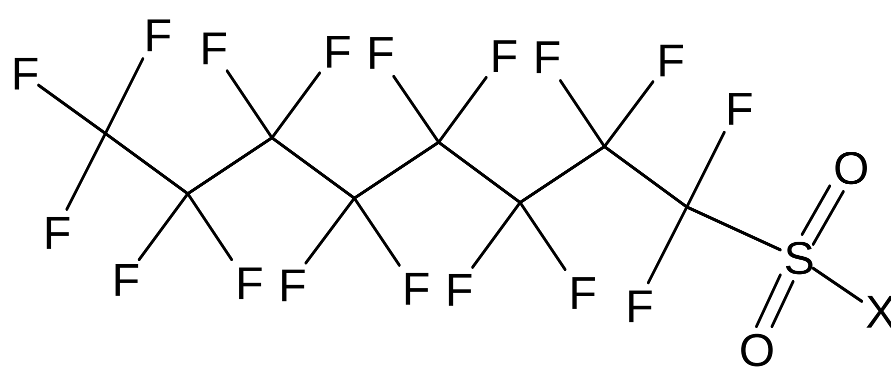
- PFAS is….

$$CF_3(CF_2)_n SO_2 X$$

- PFOS is…

$$CF_3(CF_2)_7 SO_2 X$$

PFOS Chemical Structure



MW = Molecular Weight

Policy Actions RE: PFOS

- Supplier withdrawals from the market due to concern over environmental persistence and bioaccumulation plus potential for toxicity
  - 3M (2000), DNI (2003)

- EPA issued a SNUR (Significant New Use Rule) covering PFOS compounds (2000)
  - Bans manufacturing (importation) after 2002
  - Limited exemption for “critical” photolithography uses in the semiconductor industry – photoresists, ARCs, and surfactants

- Further Regulatory/governmental actions
  - PFOA risk assessment (EPA)
  - PFOS risk assessment (EPA) – timing uncertain, but on slow track
  - UK Risk Reduction Strategy – restrictions/exemption by end of 2005
  - EU Commission (Marketing & Use Exemption)
  - OSPAR – follow UK result
  - SNUR II rule – (Potential incorporation of PFAS)

Industry Response

- End all non-critical uses of PFOS
- Work towards phase-out of PFOS in critical applications
- Undertake research and development to identify potential PFOS substitutes outside the universe of **organic** perfluorinated chemistry
- Insure that releases to the environment are *de minimis*

“Critical” vs. “Non-Critical” PFOS Uses

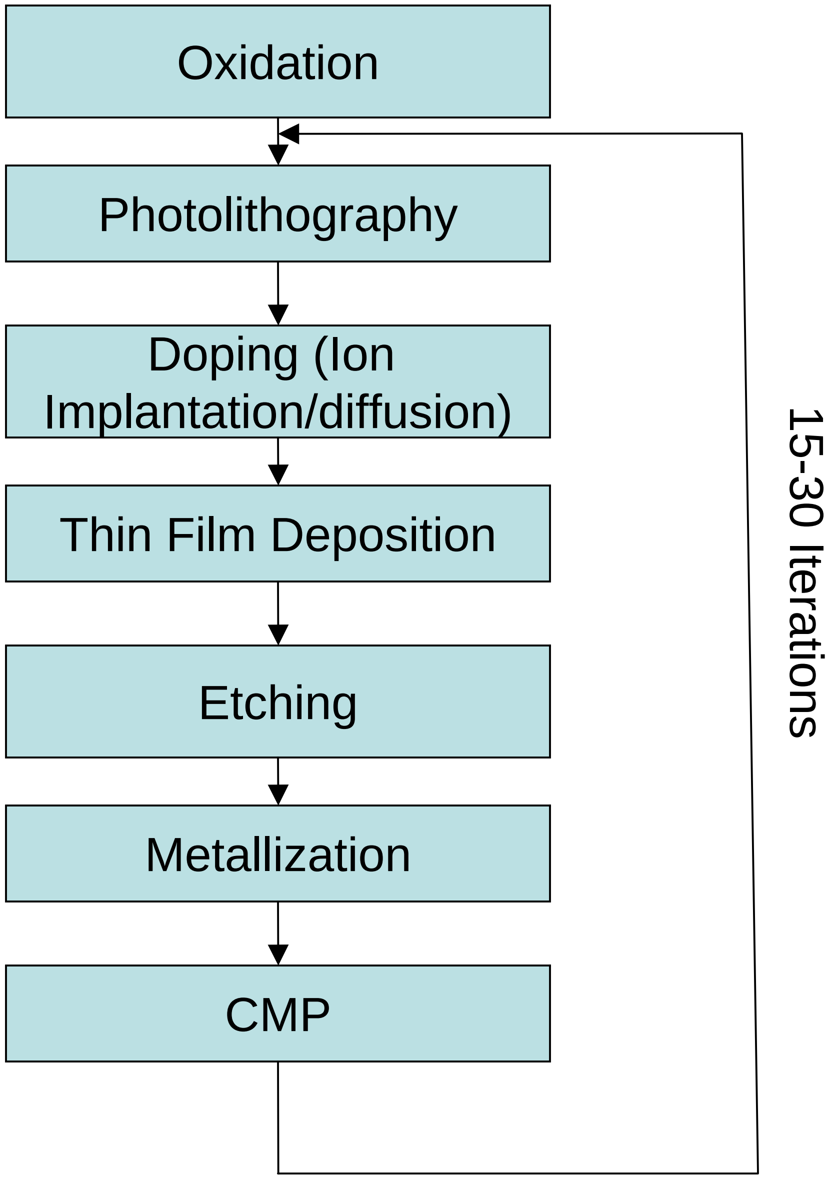
- The distinction between “critical” and “non-critical” revolves around the availability, or expected availability, of technically-adequate substitutes *where PFOS makes a unique contribution to the manufacturing process*

- Remaining PFOS uses in semiconductor manufacturing are those for which there are no readily available substitutes, e.g., PAGs and ARCs

.

- Finding substitutes for all critical PFOS uses will take many years of basic research through to qualification and high-volume manufacturing
  - Among the issues to be faced
    - Highly competitive industry;
    - Confidentiality issues;
    - Information not readily available
    - Because of low volumes, supplier interest mixed

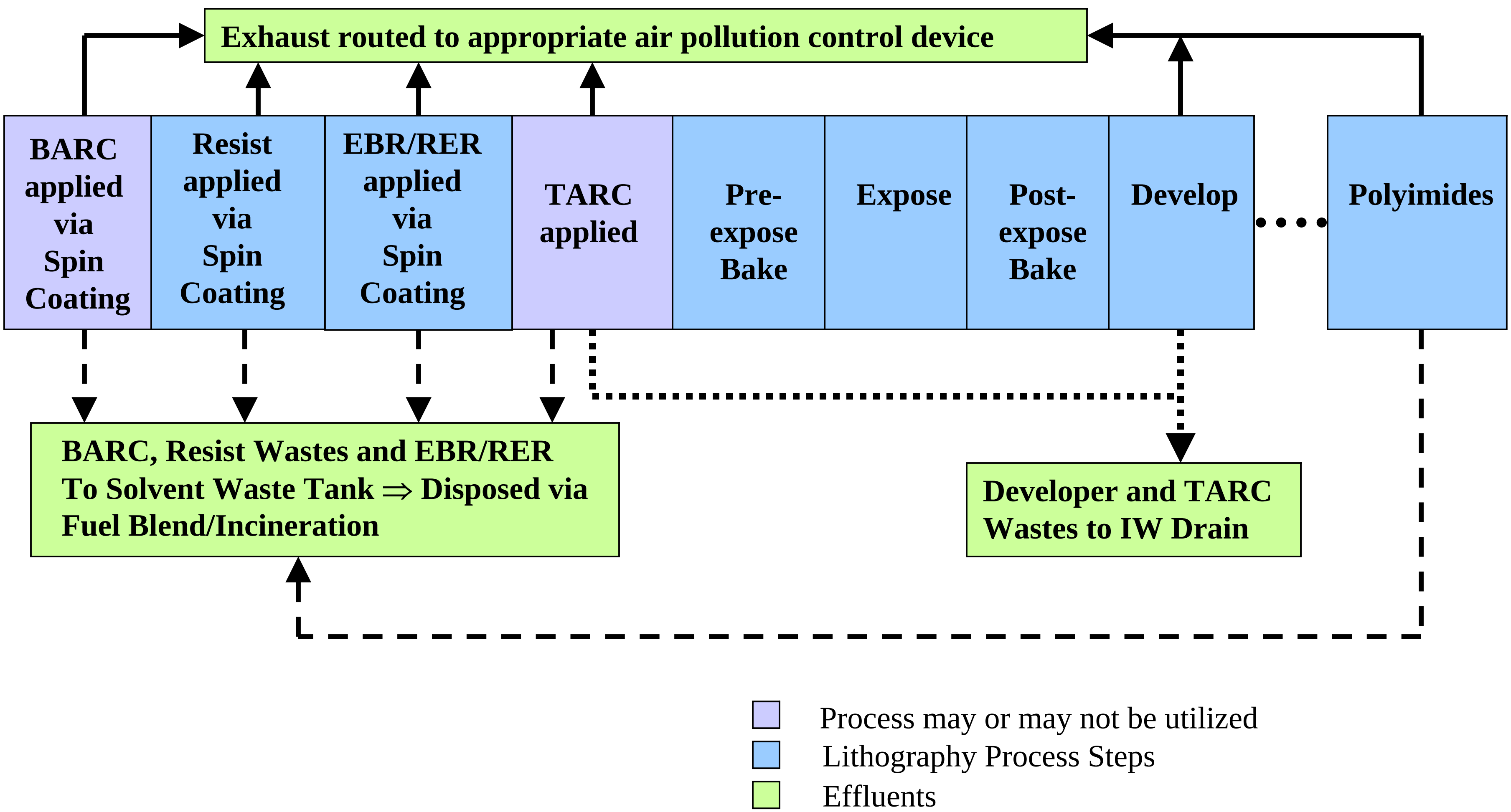
Basic Steps in Semiconductor Manufacturing



Why Are PFOS Compounds Used in Photolithography

- Photoacid Generators
  - Photoresists for 248nm and shorter wavelengths rely on chemical amplification
  - During exposure the photo-acid generator forms an acid catalyst which aids in creating the desired image
  - Photo-acid generators used for this purpose are typically sulfonic acids
  - PFOS is currently the ONLY chemical that can provide the necessary acidity
- Anti-Reflective Coatings
  - Refractive index (RI) must be as close as possible to the square root of the photoresist RI.
  - Only fluorinated materials can meet this requirement
- PFOS-based Surfactants
  - Surface tension can produce thickness variations that emanate from the center of the wafer during the spin-on application of the resist
  - PFOS-based surfactants are particularly effective in:
    - Lowering the surface tension
    - Reducing thickness variation
    - Creating more uniform films

Typical Photolithography Process Life Cycle



The PFOS Substitution Process

Considerable engineering is required to make the PFOS-free alternatives work in manufacturing; they are not “drop-in” replacements.

- A semiconductor process technology is a combination of 100-400 steps that are all somewhat dependent on each other. A technology is unique from another technology because any or all of the steps are different, as well as their processing parameters (e.g. feature size)
- Thus, a lithography step in one technology is not equivalent to another technology, although sometimes they are a little similar.
- Introducing a new resist requires an extensive qualification for each technology use. Up to 20 different resist uses could exist in one technology.
- This qualification is costly and involves many engineers.
  - If development engineers are working primarily on legacy resists, they cannot work on the newest technologies and the total technology development timeline will be impacted.

TECHNICAL CHALLENGES

- Finding and qualifying non-PFOS substitutes for use in critical applications (PAGs and ARCs)
  - Initially mostly PFAS materials

- Finding non-perfluorinated substitutes

- Implementing waste stream segregation and treatment technology to eliminate all PFOS/PFAS/PFOA effluents
  - This will increase prospects for continuing exemptions while we exit perfluorinated chemistry
  - Support obtaining broad regulatory exemption for our chemical use based on “highly-controlled industrial process” model

Sample Problem - PAGs

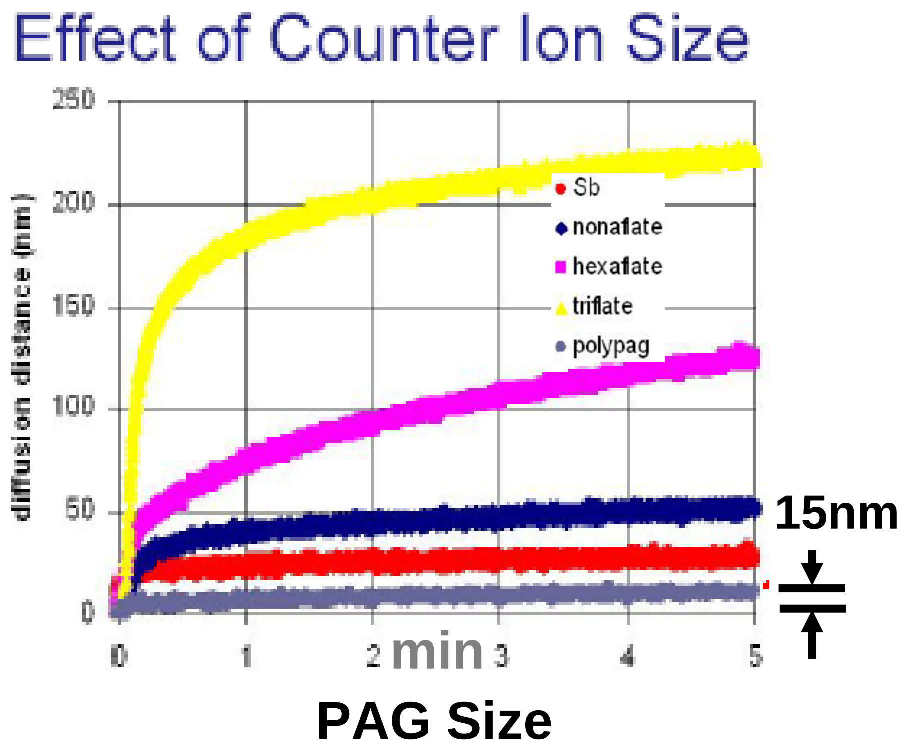
PFOS PAG Technology Issues

Why PFOS PAG?

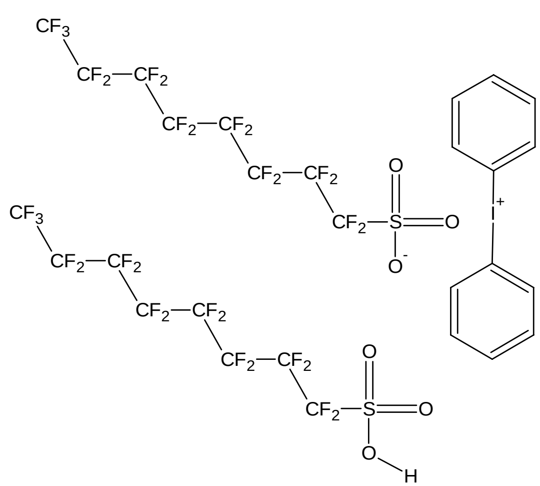
- •Strong Acid
- •Miscible with many materials
- •Big

Why not PFOS?

- •POP concern
- •Fluorous Self Assembly
- •EUV transparency
- •15nm diffusion for even larger



Willson, 2003 SRC/DARPA Review, reproduced by permission



Salt

Acid

PFOS PAG Replacement Technology options

Why is PFOS good for resist catalyst?

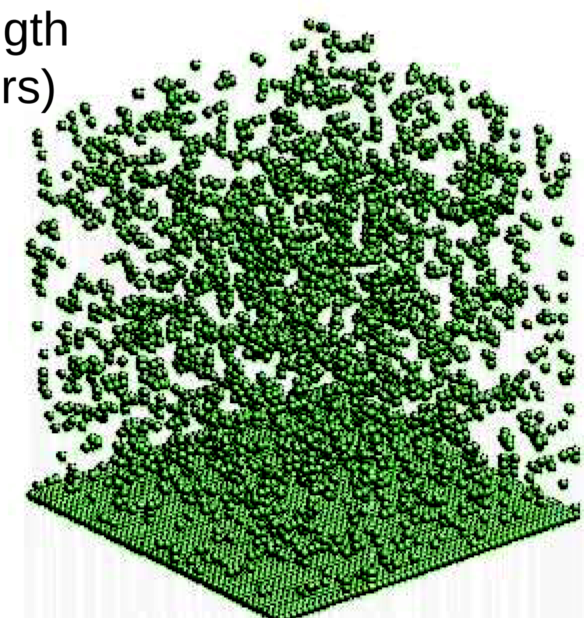
- •F increases strength of sulfonic acid
- •Nonpolar tail (C7F15) associates with polymers like acrylates & styrene

Why is PFOS not good for environment?

- •Perfluoro- compounds don't degrade easily
- •PFOS associates with protein in the blood
- •Polar bears, Cormorants, EU ministers

What else instead?

- •Other electronegative atoms/groups for acid strength
- •Re-engineer resist to bind acid (15nm limit, clusters)
- •Re-engineer resist so a weaker catalyst is ok
- •Remove the PFOS from the waste (stop-gap)



PFOS Clusters Modeled by Willson