

*Engineering Research Center for  
Environmentally Benign Semiconductor Manufacturing*



# **Manufacturing in Nano-Scale: Environmental Challenges and Opportunities**

**University of Utah  
March 15, 2011**

# ERC Members and Participants

**Founded in 1996 by NSF & SRC; now almost entirely industry funded**

## Founding Universities

- U Arizona
- U California – Berkeley
- MIT
- Stanford

## Other University members

- Arizona State U (1998 - )
- Columbia (2006 - 2009)
- Cornell (1998 - )
- Georgia Inst. of Tech. (2009 - )
- U Maryland (1999-2003)
- U Massachusetts (2006 - 2009)
- U North Carolina (2009 - )
- Purdue (2003 - 2008 )
- U Texas - Dallas (2009 - )
- Tufts (2005 - 2008 )
- U Washington (2008-)
- U Wisconsin (2009- )

## **Cumulative Data:**

- 16** Core member Universities
- 241** PhD and MS
- 205** Undergraduates (reported)
- 13** Academic disciplines

**> 80% of graduates joined SC industry  
& suppliers (mostly ERC members)**

- 10** Current member universities
- 28** Current PI/Co-PIs
- 37** Current graduate students

# A Formidable Economic Ecosystem

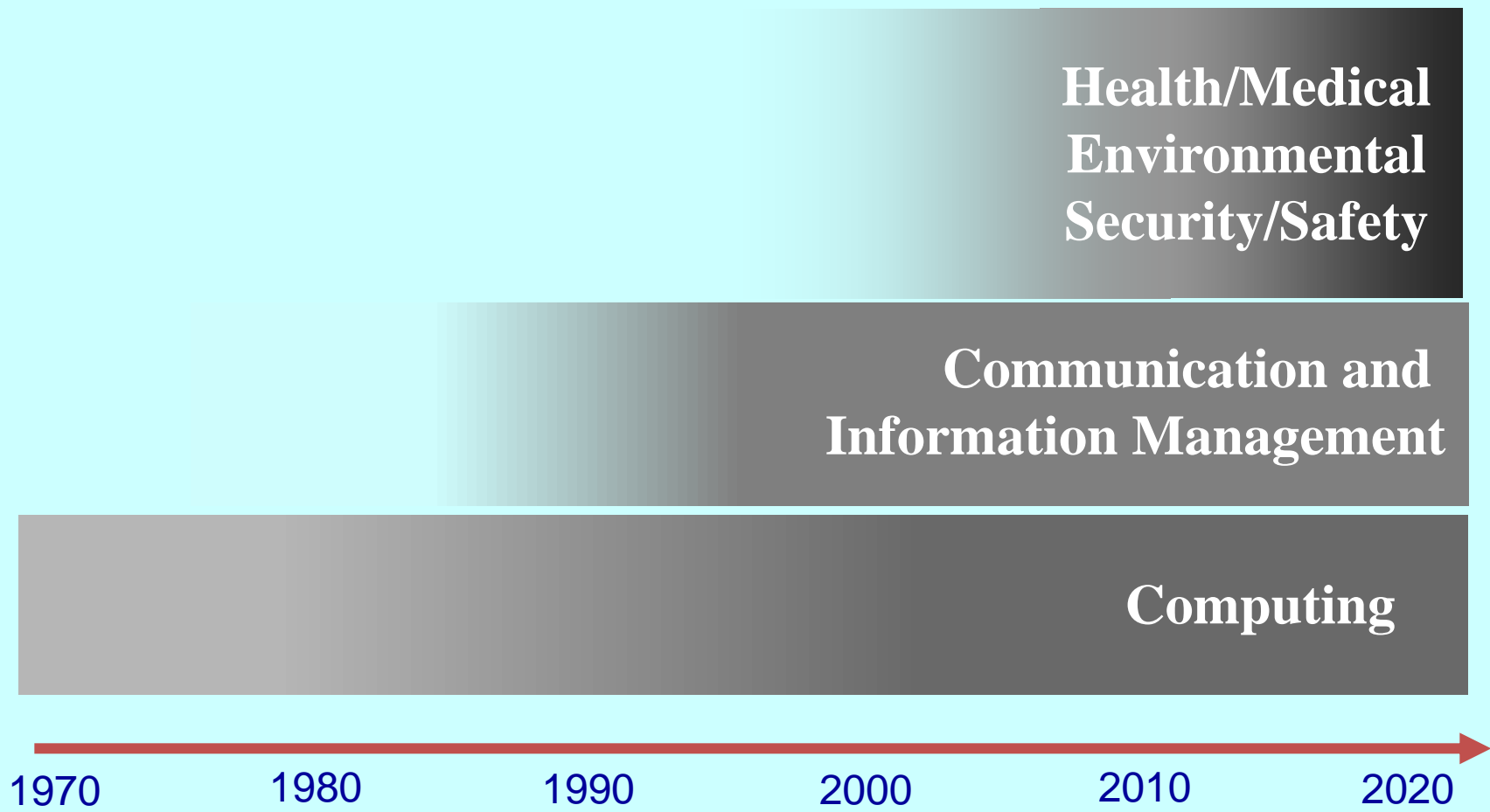
**IT-Enabled Services ~ \$5.5T**

**Electronics ~ \$1.2 T**

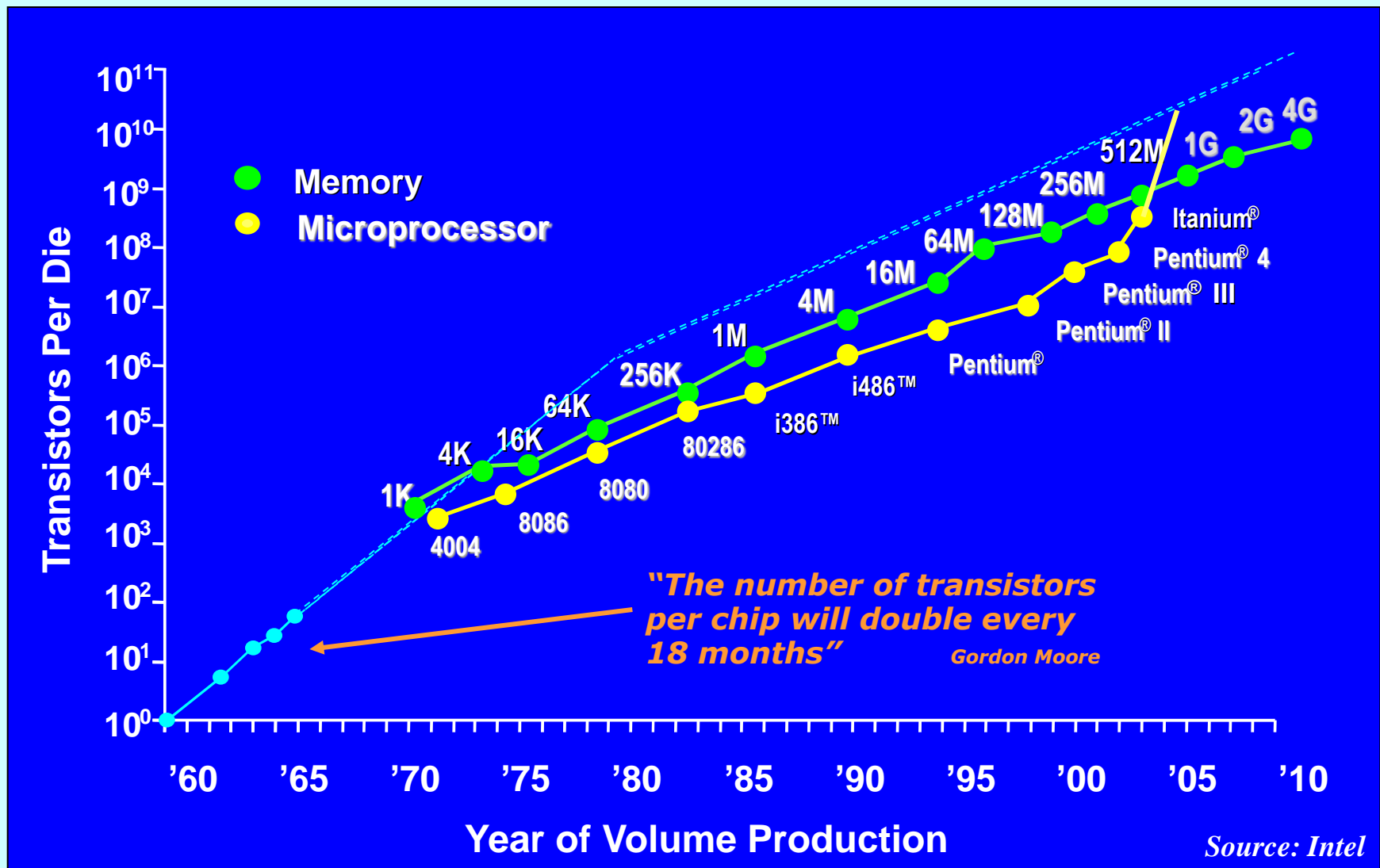
**Semiconductors ~ \$250B**

**Suppliers ~ \$60B**

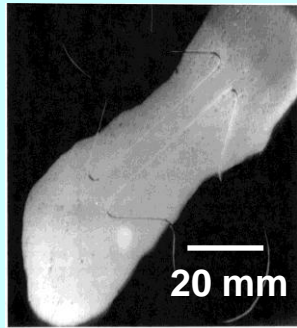
# Applications that Have Changed Our World



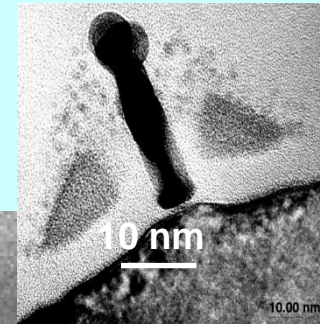
# Unprecedented Growth



# Shrinking of Device Dimensions

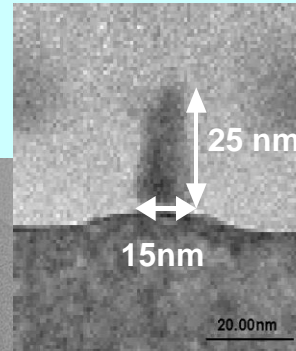


**First MOSFET  
(1960)**

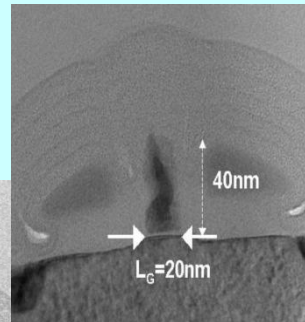


**MOSFET in 2008**

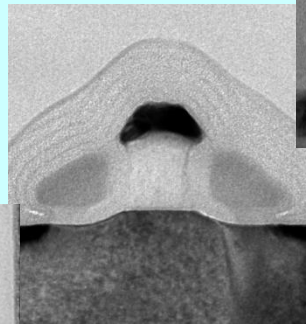
**Gate thickness <1 nm  
Channel Length <10 nm  
Junction depth < 50 nm**



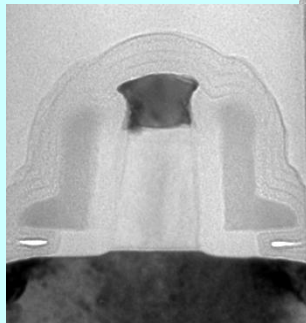
**15 nm**



**20 nm**



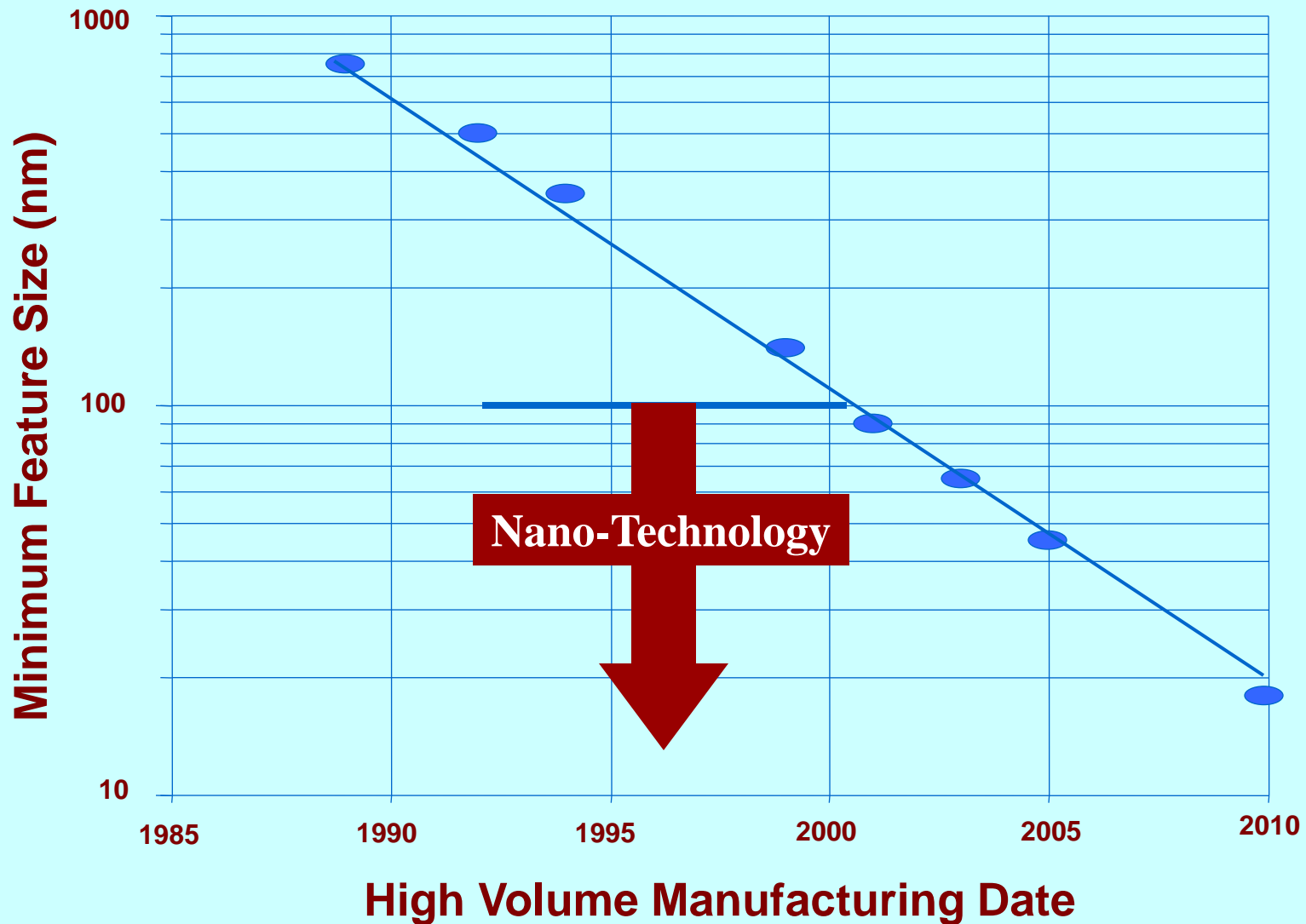
**30 nm**



**50 nm length**

*Size of an atom ~ 0.5 nm*

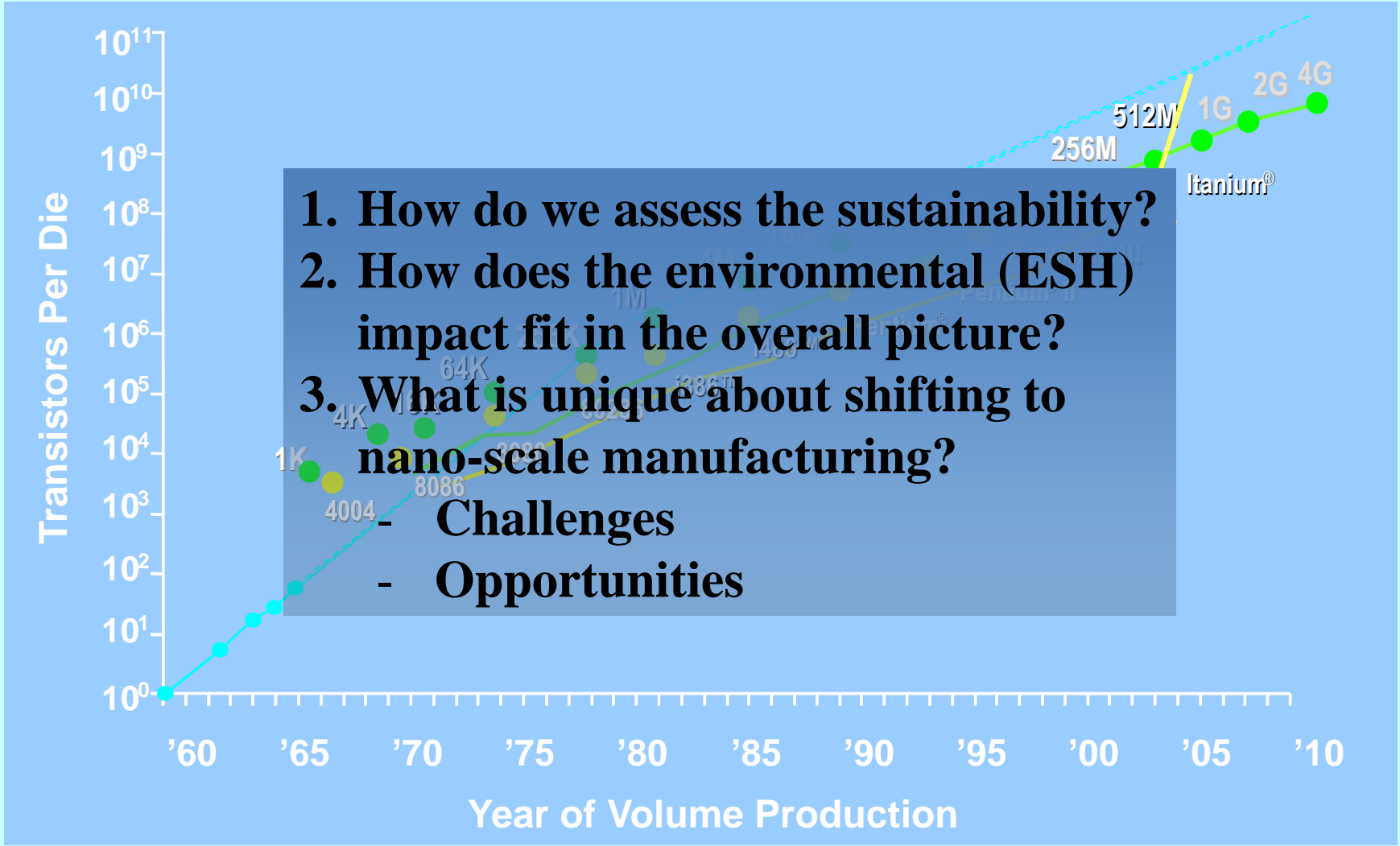
# Trends in Feature Size







# Is this Growth Sustainable?



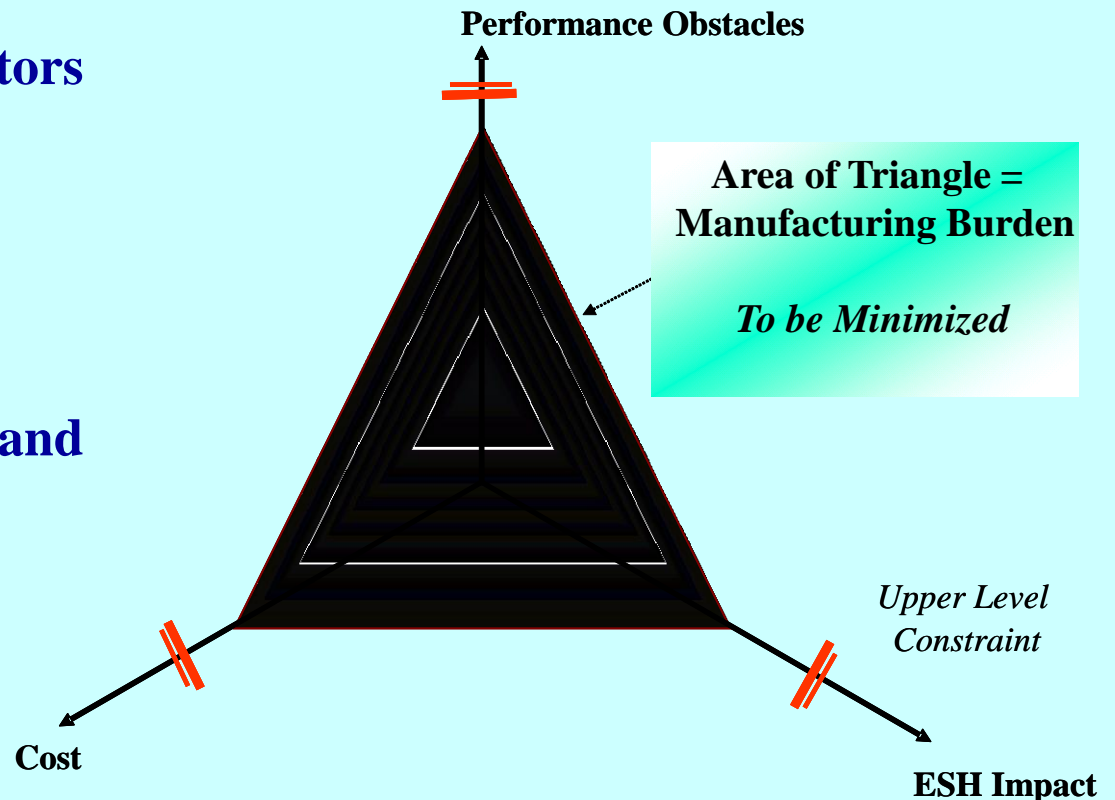
# Definition of Sustainability

**“*SUSTAINABILITY*” is like “*PEACE*”:  
it enjoys a universal appeal and full agreement;  
the disagreement is **ONLY** in what it means and how  
to implement it.**

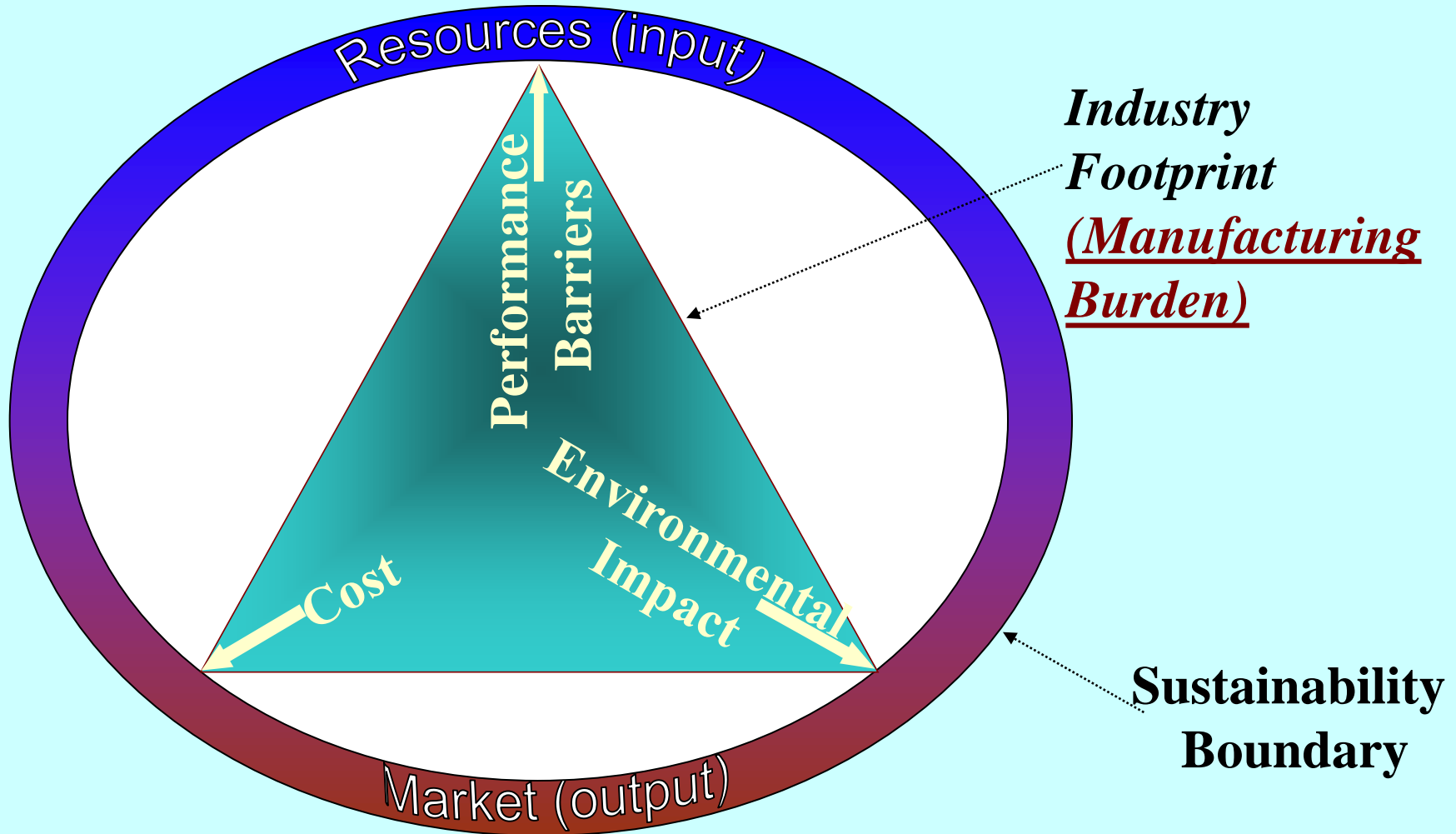
# Sustainability Factors

Factors that determine the sustainability of a product, a process, a manufacturing operation, or an industry:

1. Product performance
2. Cost and economic factors
3. Environmental impact
  - Safety and Health
  - Social factors and compatibility
  - Resource utilization and availability



# Sustainability Illustrated



# Sustainability Challenges

## Environmental, Safety, and Health (ESH)

### Aspects of Nano-Manufacturing

#### 1. Nano-Particles in Manufacturing

- Workers exposure to nano-particles in the fabs
- Emission of nano-particles through fab waste streams

#### 2. Impact on Resource Utilization

- Increase in water, energy, and chemical usage

#### 3. Introduction of New Materials

- New device materials, new processing fluids, etc.

#### 4. Positive Environmental Impact

- Opportunities for major ESH gain

# Functionalized Fabricated Nano-Particles

New name for some old materials



**Aerosil = fumed  $\text{SiO}_2$**

**Particle size:**

**4-20 *milli-micron* (nanometers)**

**New additive for coating industry**

**Colorants & Coatings**

**(*Farbe & Lack Journal*; April 1949)**

# What is Unique About Nano-Particles?

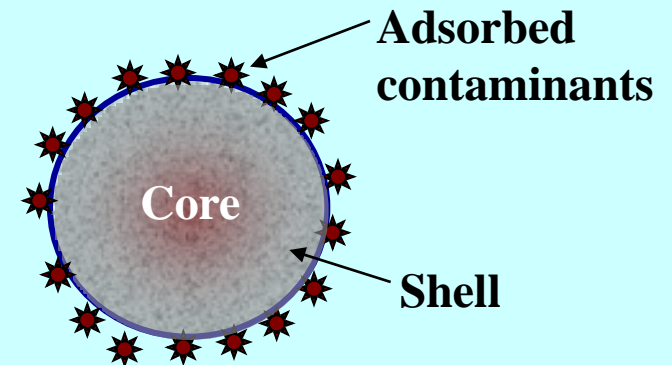
## Treatment problem:

- Nano-particles cannot be effectively removed by *agglomeration, settling, and filtration*; they also clog membranes.

## Synergistic ESH impact of nano-particles:

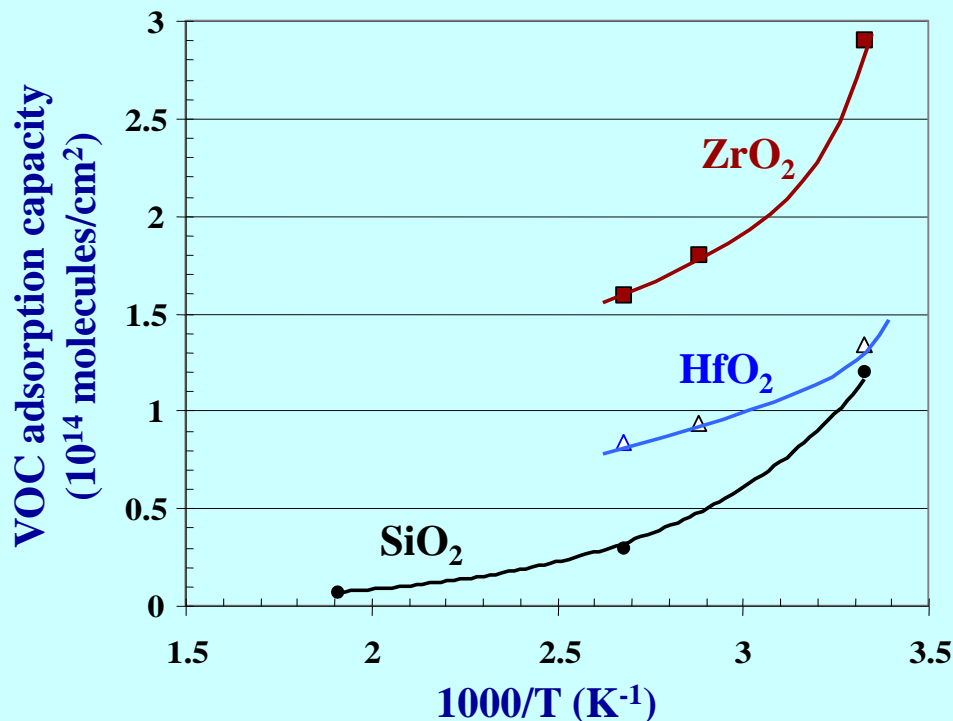
- *Active surface*
- *Selective adsorption*
- *Pore condensation (Kelvin Effect)*

Consequence {  
◦ *Concentration*  
◦ *Facilitated transport*  
◦ *Enhanced life-time*



# Toxicity Enhancement in Nano-Particles

a) Nano-particles in the gas phase  
15ppb VOC; 40 nm particles



b) Nano-particles in the wastewater

- 10 ppb of Cu<sup>++</sup> in CMP wastewater results in  $3 \times 10^6$  ppb of adsorbed copper on 90 nm CeO<sub>2</sub> nano-particles
- 10 ppb of PFOS in wastewater results in  $2.8 \times 10^4$  ppb of contaminated 10 nm carbon nano-particles



# ESH Aspects of Nano-Manufacturing

## 1. Nano-Particles in Manufacturing

- Workers exposure to nano-particles in the fabs
- Emission of nano-particles through fab waste streams

## 2. Impact on Resource Utilization

- Increase in water, energy, and chemical usage

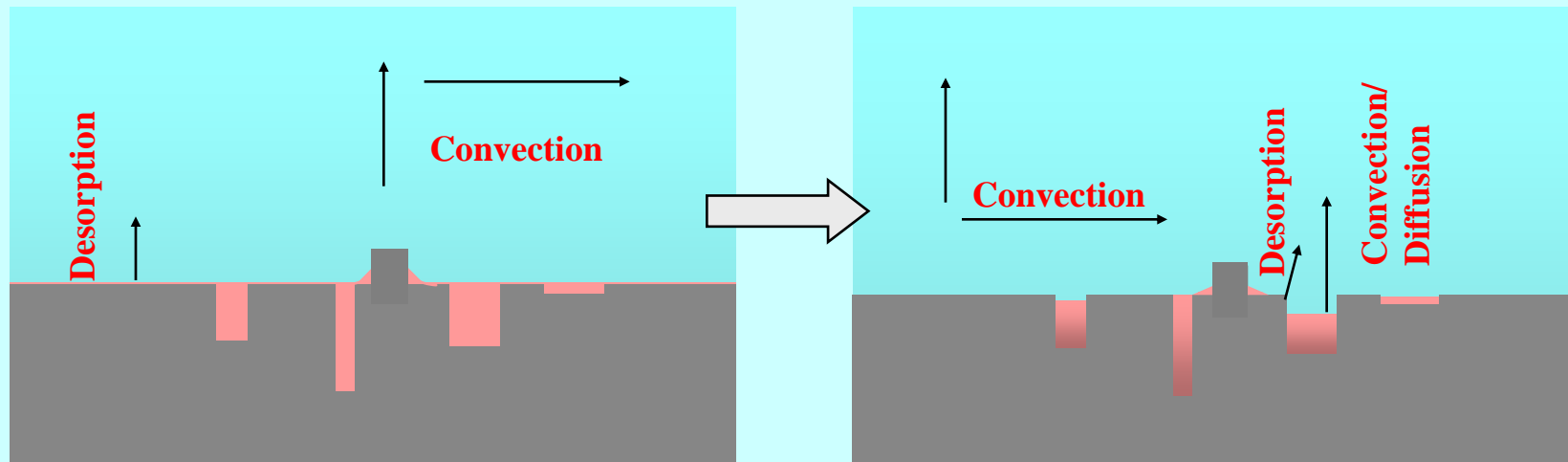
## 3. Introduction of New Materials

- New device materials, new processing fluids, etc.

## 4. Positive Environmental Impact

- Opportunities for major ESH gain

# Issues in Cleaning of Nano-Structures

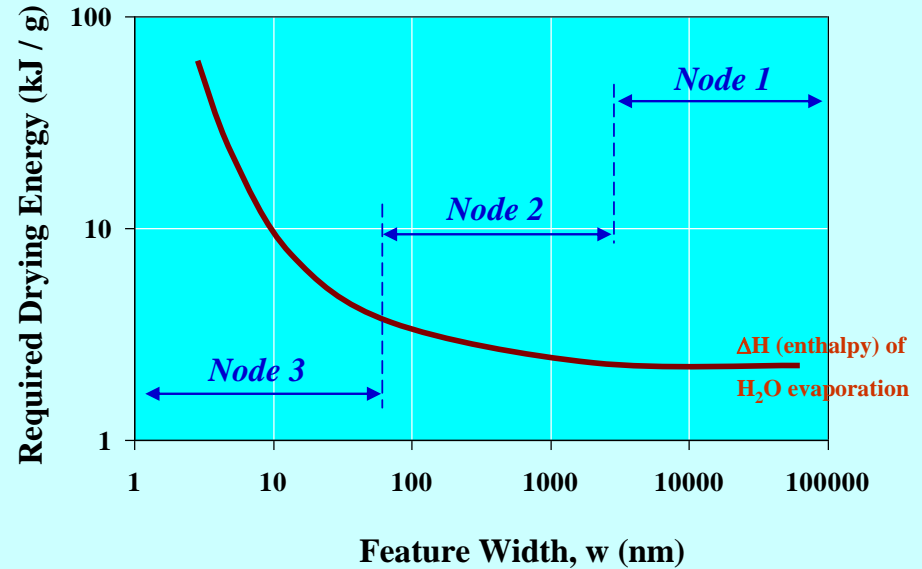
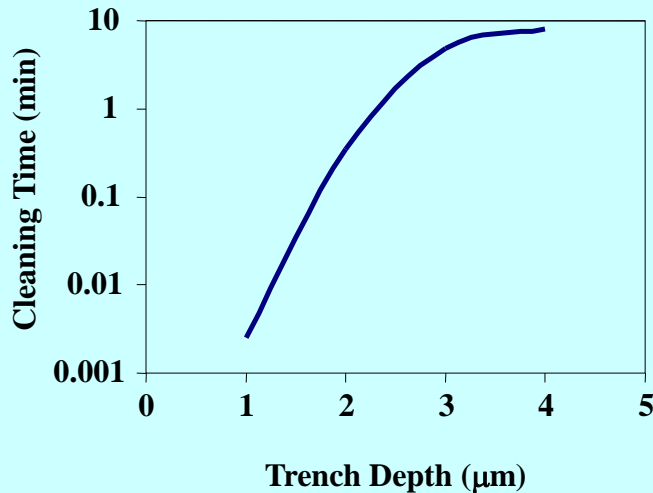
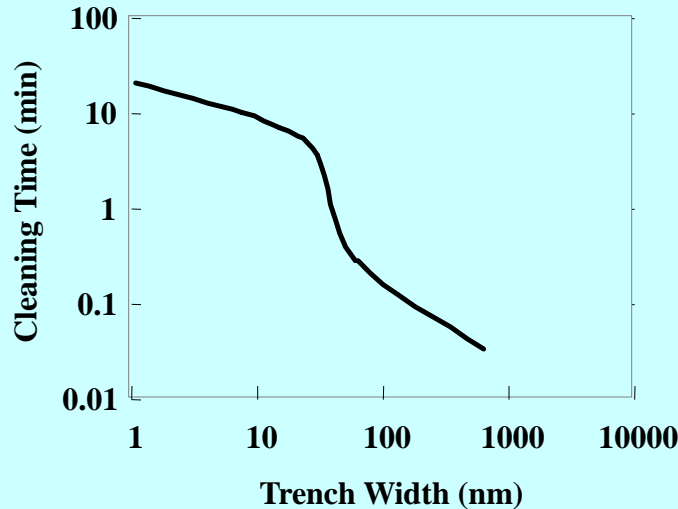


Mechanism	Time Scale	Flow Effect
Boundary Diffusion	$d^2/D \sim 10 \text{ s}$	Indirect, mild
Convection	$d/u \sim 1-3 \text{ s}$	Direct, strong
Desorption	$1/k_d \sim 0 - 10^5 \text{ s}$	No effect

**Needs:** → **New metrology methods**  
**New cleaning chemistries**

# Large Wafers and Small Features

## ESH Challenges



**ERC results show large increase in water, chemicals, and energy usage in various nano-manufacturing processes as feature size decreases and wafer size increases.**



# ECRS: Winner of 2009 Product of the year Award

6...



## Semiconductor International Announces 2009 Editors Choice Best Product Award Winners

Wed Jul 15, 8:32 AM

[Email Story](#) [IM Story](#) [Printable View](#)

OAK BROOK, Ill.--(BUSINESS WIRE)--*Semiconductor International* bestowed its 2009 Editors' Choice Awards for excellence in semiconductor manufacturing on 15 commercially proven industry products. These awards will be presented at a ceremony in San Francisco on Wednesday, July 15, during SEMICON West. The 2009 winners exemplified state-of-the-art equipment and materials installed and used in numerous fabs around the world.

The 2009 Editors' Choice Best Product Award winners are:

AMEC	Primo D-RIE dielectric etcher
Applied Materials Inc.	SEMvision G4 defect review platform
ASM Technology Singapore	IDEALcompress encapsulation system
ATMI Inc.	AutoClean ion implant cleaning process
ATMI Inc.	Safe Delivery Source (SDS) cylinder
Cabot Microelectronics Corp.	Epic D100 CMP pad
Carl Zeiss SMT AG	ULTRA plus field-emission SEM
CI Semi	WetSpec200 in-line chemical analyzer
Environmental Metrology Corp.	Electro-Chemical Residue Sensor (ECRS)
Linde Group	Generation-F 80 on-site fluorine generator
Nikon Precision Inc.	NSR-S610C ArF immersion scanner
Nova Measuring Instruments Ltd.	NovaMARS optical CD software
Qcept Technologies	ChemetriQ 3000 inspection system
Tec-Sem AG	Pr@ctor 300 mm single wafer management
W.L. Gore & Associates Inc.	GORE ultrapure water filters

"The Editors' Choice Best Products awards program acknowledges products, materials and services that are proven in the manufacturing environment," said Laura Peters, Editor-in-Chief of *Semiconductor International* (SI). In the evaluation process, SI's editors consider the products based on feedback from

INTELLIGENT TECHNOLOGY  
**Forbes**  
 WHERE WILL TECHNOLOGY TAKE YOU AND YOUR COMPANY NEXT?  
 Visit the new Intelligent Technology section  
 Featuring: Video, White Papers, Blogs and more

**Forbes**  
 U.S. EUROPE ASIA  
 Search:  [Forbes.com](#) [Quotes](#) [Video](#) [Advanced](#) [Investing for College](#)  
 Video [ForbesWomen](#) [CEO Network](#) [Org Chart Wiki](#) [People Tracker](#) [Portfolio Tracker](#) [Blogs](#) [E-mail Newsletters](#) [Special Reports](#)  
 HOME PAGE FOR THE WORLD'S BUSINESS LEADERS [Restore Results](#)  
 HOME BUSINESS TECH MARKETS ENTREPRENEURS LEADERSHIP PERSONAL FINANCE FORBESLIFE LISTS OPINIO

### Press Release Semiconductor International Announces 2009 Editors' Choice Best Product Award Winners

07.15.09, 08:30 AM EDT

**BusinessWire** - Semiconductor International bestowed its 2009 Editors' Choice Awards for excellence in semiconductor manufacturing on 15 commercially proven industry products. These awards will be presented at a ceremony in San Francisco on Wednesday, July 15, during SEMICON West. The 2009 winners exemplified state-of-the-art equipment and materials installed and used in numerous fabs around the world.

The 2009 Editors' Choice Best Product Award winners are:  
 AMEC Primo D-RIE dielectric etcher Applied Materials Inc.  
 SEMvision G4 defect review platform ASM Technology  
 Singapore IDEALcompress encapsulation system ATMI Inc.  
 AutoClean ion implant cleaning process ATMI Inc. Safe Delivery Source (SDS) cylinder Cabot Microelectronics Corp. Epic D100 CMP pad Carl Zeiss SMT AG ULTRA plus field-emission SEM  
 CI Semi WetSpec200 in-line chemical analyzer Environmental Metrology Corp. Electro-Chemical Residue Sensor (ECRS)  
 Linde Group Generation-F 80 on-site fluorine generator Nikon Precision Inc. NSR-S610C ArF Immersion scanner Nova Measuring Instruments Ltd. NovaMARS optical CD software  
 Qcept Technologies ChemetriQ 3000 inspection system Tec-Sem AG Pr@ctor 300 mm single wafer management system W.L. Gore & Associates Inc. GORE ultrapure water filters

"The Editors' Choice Best Products awards program acknowledges products, materials and services that are proven in the manufacturing environment," said Laura Peters, Editor-in-Chief of *Semiconductor International* (SI). In the evaluation process, SI's editors consider the products based on feedback from actual customers in the field and only the most highly recommended ones are honored each year.

Semiconductor International, published by Reed Business Information and a part of Reed Elsevier's global array of information products, is the leading technical publication servicing the global semiconductor manufacturing industry. SI boasts the industry's most experienced full-time technical editorial team. Additional information about SI and its many products and activities are available at [www.semiconductor.net](http://www.semiconductor.net).

For more information about the Editors' Choice Product Awards program, go to [www.semiconductor.net/awards](http://www.semiconductor.net/awards).



#### Article Controls

- EMAIL
- PRINT
- REPRINT
- NEWSLETTER
- COMMENTS
- SHARE
- WIDGET BLEZ

# Cleaning of Nanostructures

## Process Simulation

Multi-component species transport equations :

$$\frac{\partial C_i}{\partial t} = \nabla \cdot (D_i \nabla C_i + z_i F \mu_i C_i \nabla \phi)$$

Change in tank concentration :

$$V \frac{\partial C_b}{\partial t} = Q(C_{in} - C_b) + A \cdot Flux$$

Surface adsorption and desorption:

$$\frac{\partial C_{S2}}{\partial t} = k_{a2} C_2 (S_{02} - C_{S2}) - k_{d2} C_{S2}$$

Poisson equation:  $\nabla^2 \phi = -\frac{\rho}{\epsilon}$

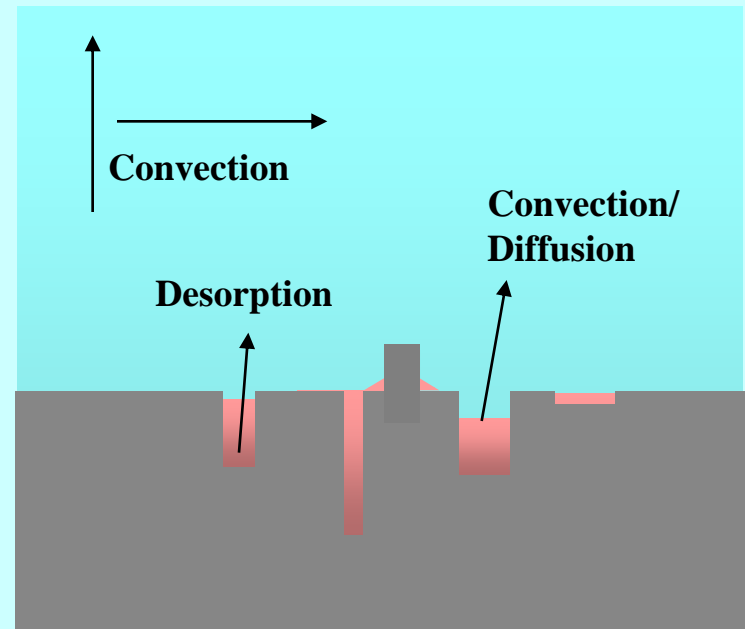
where charge density:  $\rho = F \sum_i z_i C_i$

Ohm's law:  $\vec{J} = \sigma \vec{E} \quad \nabla \times \vec{E} = 0$

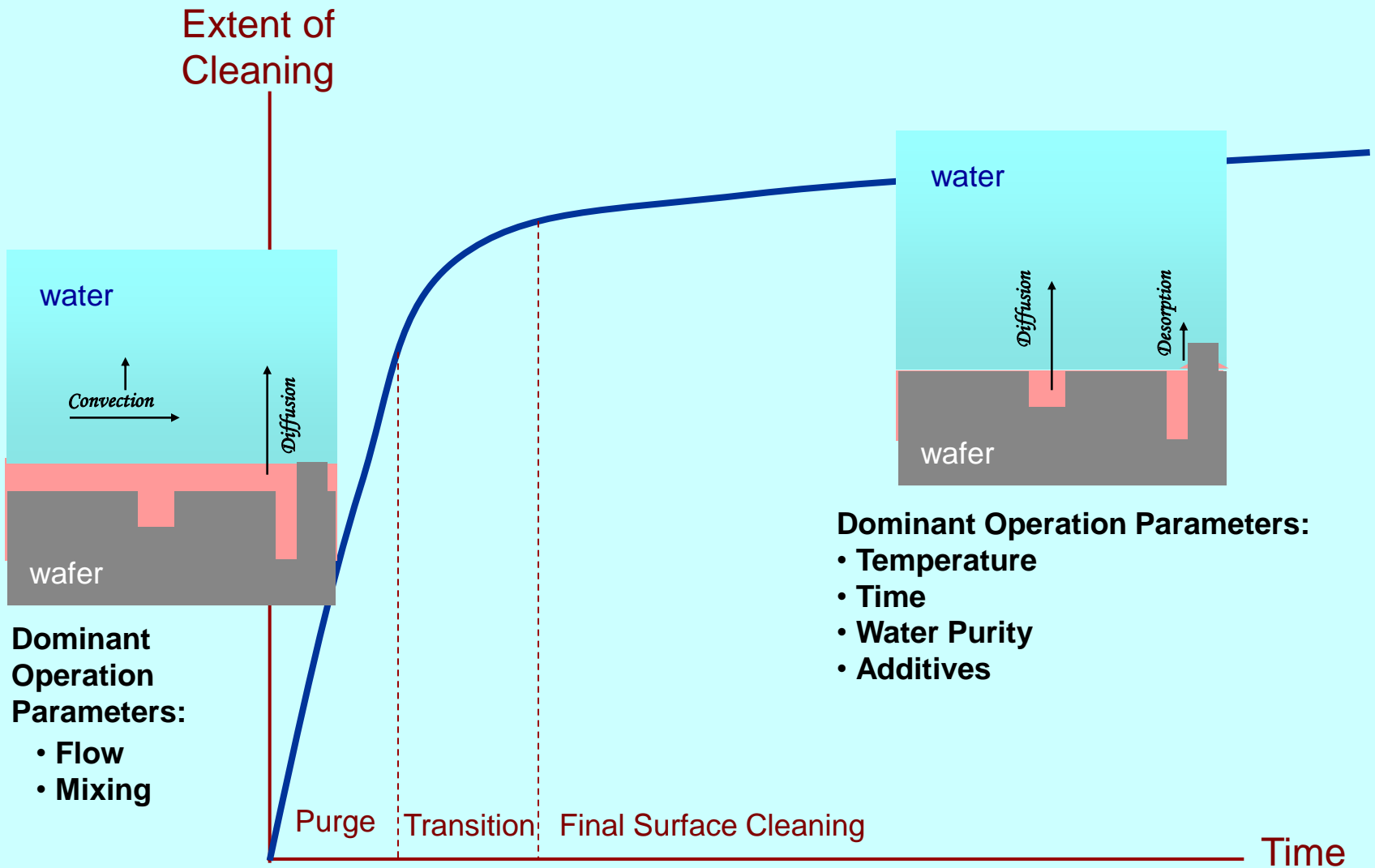
where electrical conductivity:

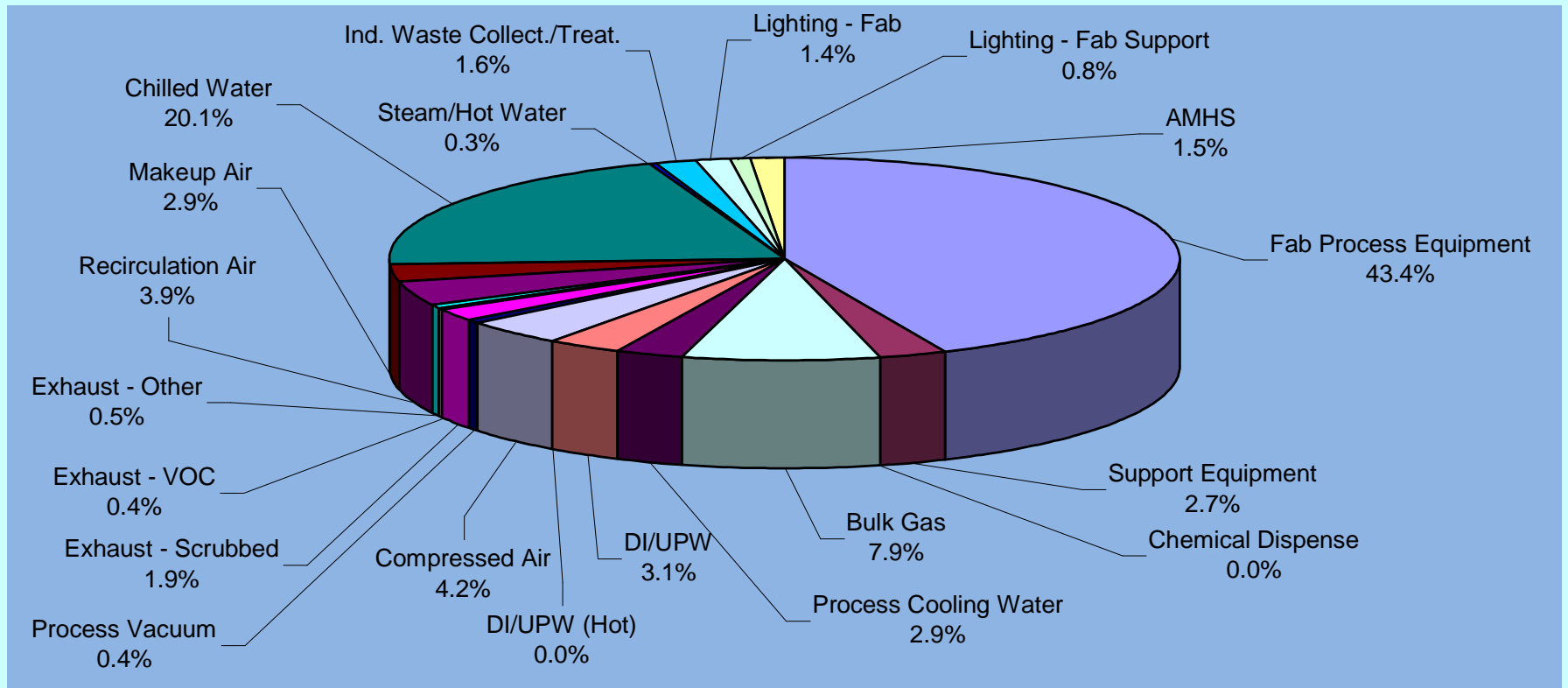
$$\sigma = \sum_i \lambda_i C_i$$

- Surface Charge
- Diffusion
- Surface reaction
- Ionic transport



# A Novel Staged Rinse Process







# ESH Aspects of Nano-Manufacturing

## 1. Nano-Particles in Manufacturing

- Workers exposure to nano-particles in the fabs
- Emission of nano-particles through fab waste streams

## 2. Impact on Resource Utilization

- Increase in water, energy, and chemical usage

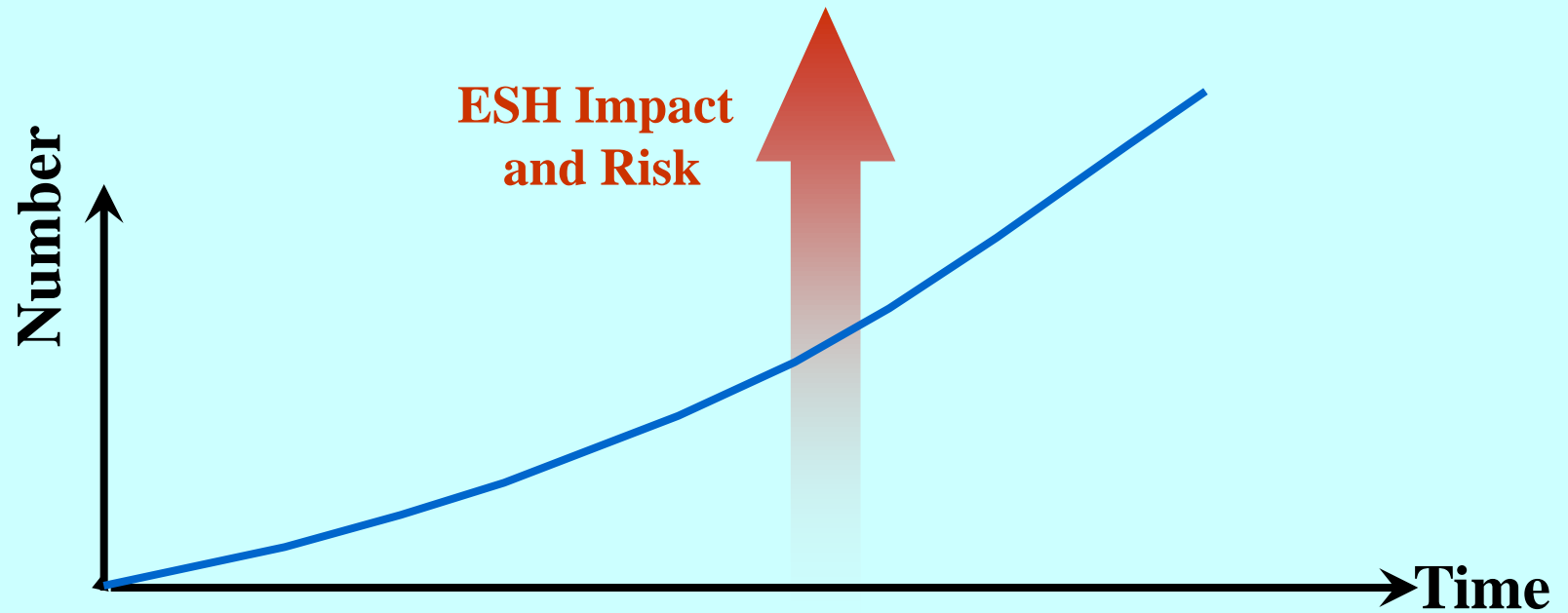
## 3. Introduction of New Materials

- New device materials, new processing fluids, etc.

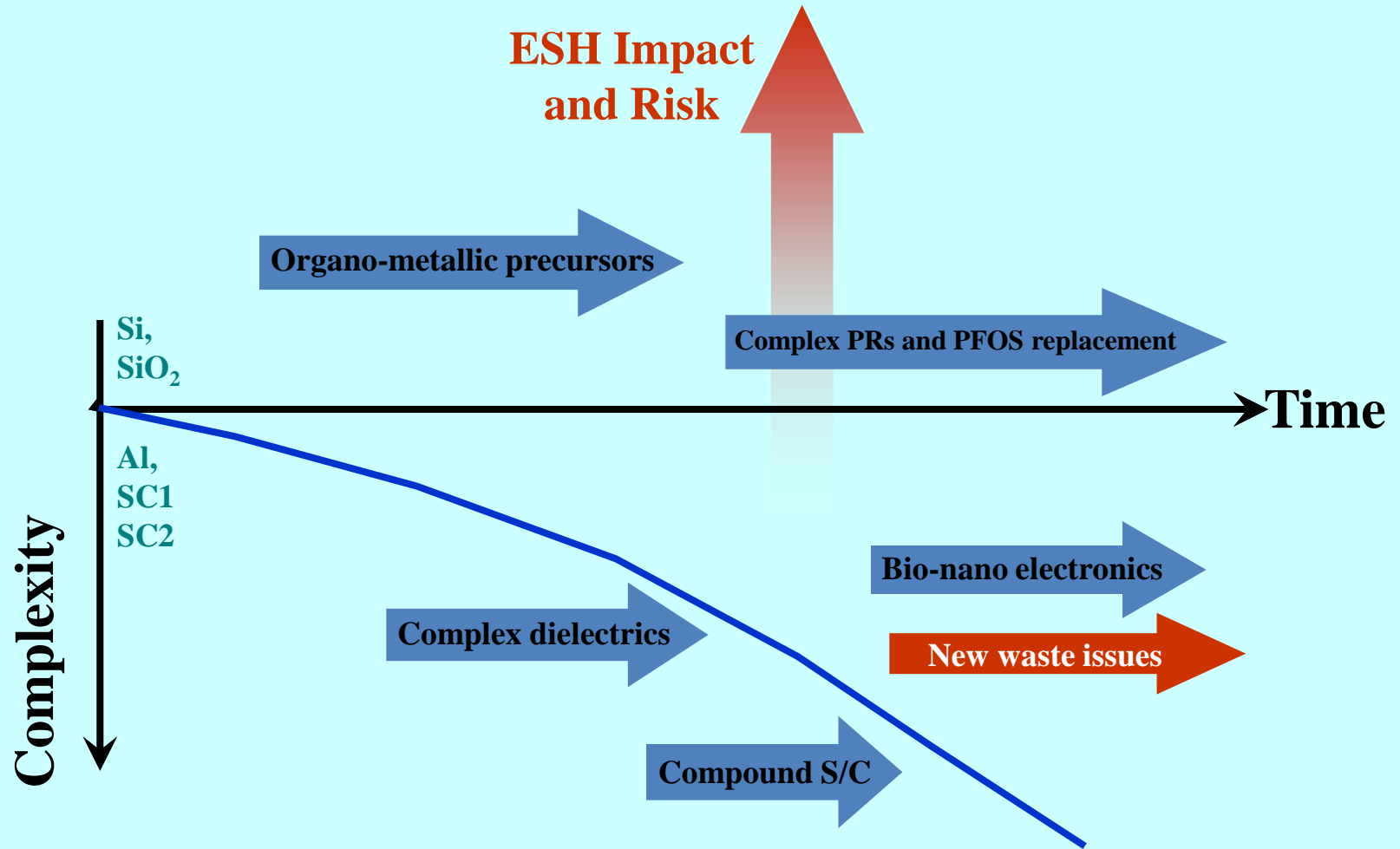
## 4. Positive Environmental Impact

- Opportunities for major ESH gain

# Introduction of New Materials

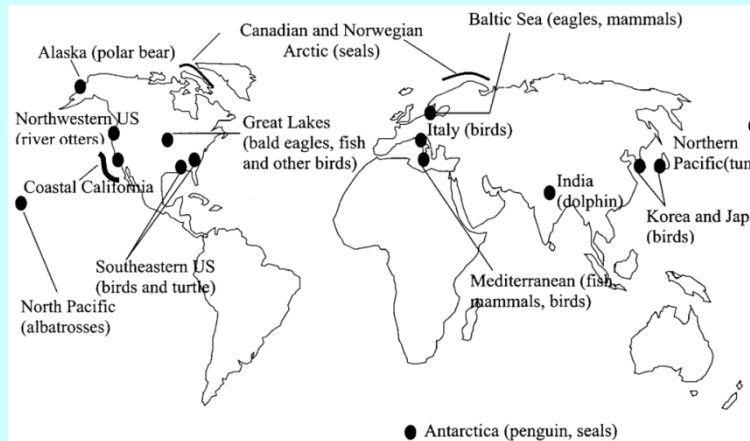


# Introduction of New Materials



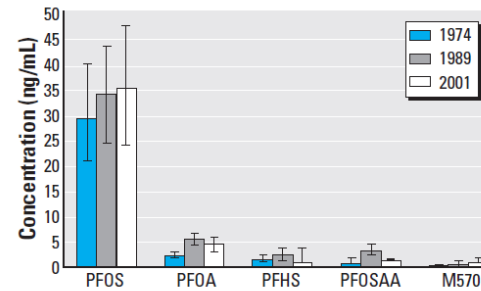
# Example: Challenge of Replacing PFOS

## Global Distribution of PFOS in Wildlife



*Environ. Sci. Technol.* 2001, 35, 1339.

## PFOS in human blood



**Figure 1.** Median fluorochemical concentrations and IQRs for blood samples collected in Washington County, Maryland, from adults living in proximity in 1974 ( $n = 178$  serum samples) and 1989 ( $n = 178$  plasma samples) and in the county in 2001 ( $n = 108$  serum samples; Olsen et al. 2003c).

*Environ. Health Perspect.* 2005, 113, 539.

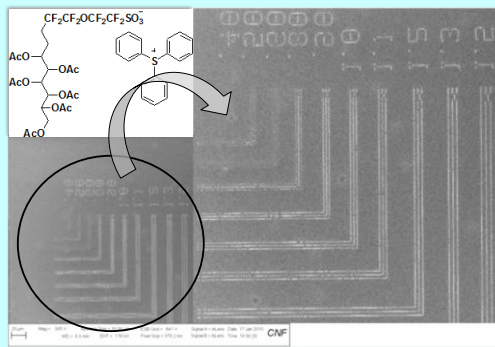
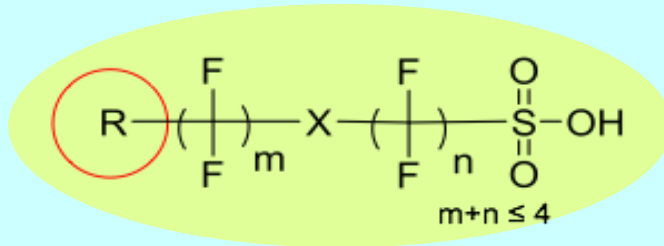
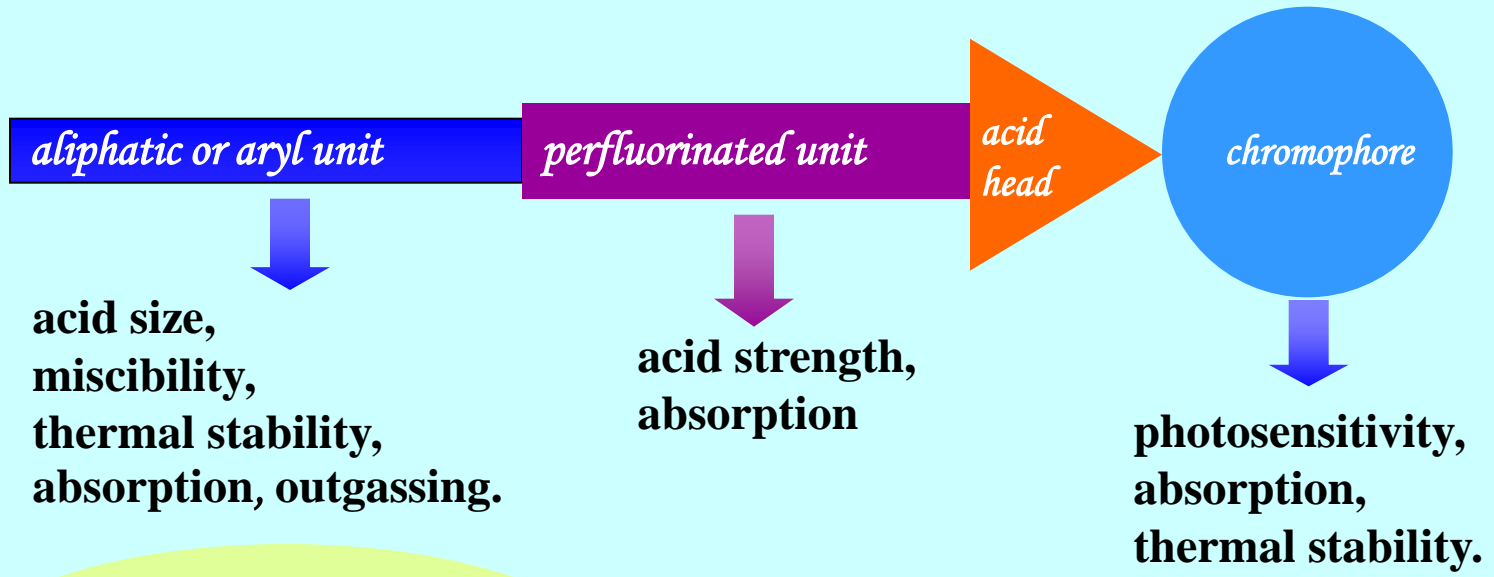
## PFOS in drinking water



PFOS and other PFCs detected in drinking water resources worldwide

- **PFOS banned for most application is the US and EU.**
- **PFOS listed as chemical for regulation within the Stockholm Convention on Persistent Organic Pollutants (POPs)**
- **EPA Provisional Health Advisory Levels for PFOS 200 ng L<sup>-1</sup>**

# Molecular Design of PFOS-Free PAGS



Polar	Hydrophilic	Aromatic	Linear
Nonpolar	Hydrophobic	Aliphatic	branch ring

Sugar based "Sweet" PAG

Natural molecules based Biocompatible/ Biodegradable PAG

# ESH Aspects of Nano-Manufacturing

## 1. Nano-Particles in Manufacturing

- Workers exposure to nano-particles in the fabs
- Emission of nano-particles through fab waste streams

## 2. Impact on Resource Utilization

- Increase in water, energy, and chemical usage

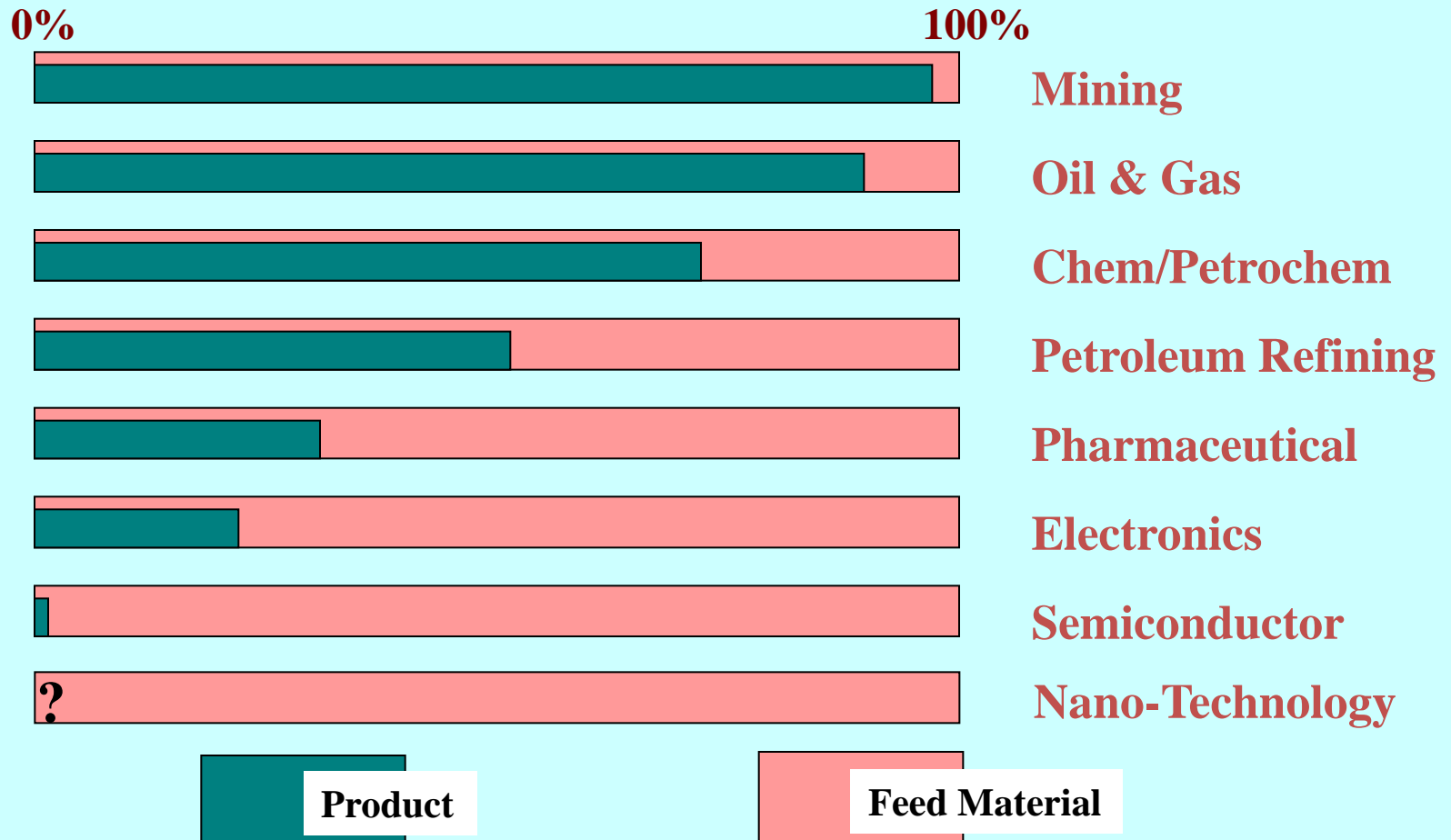
## 3. Introduction of New Materials

- New device materials, new processing fluids, etc.

## 4. Positive Environmental Impact

- Opportunities for major ESH gain

# Material Usage Index in Various Industries

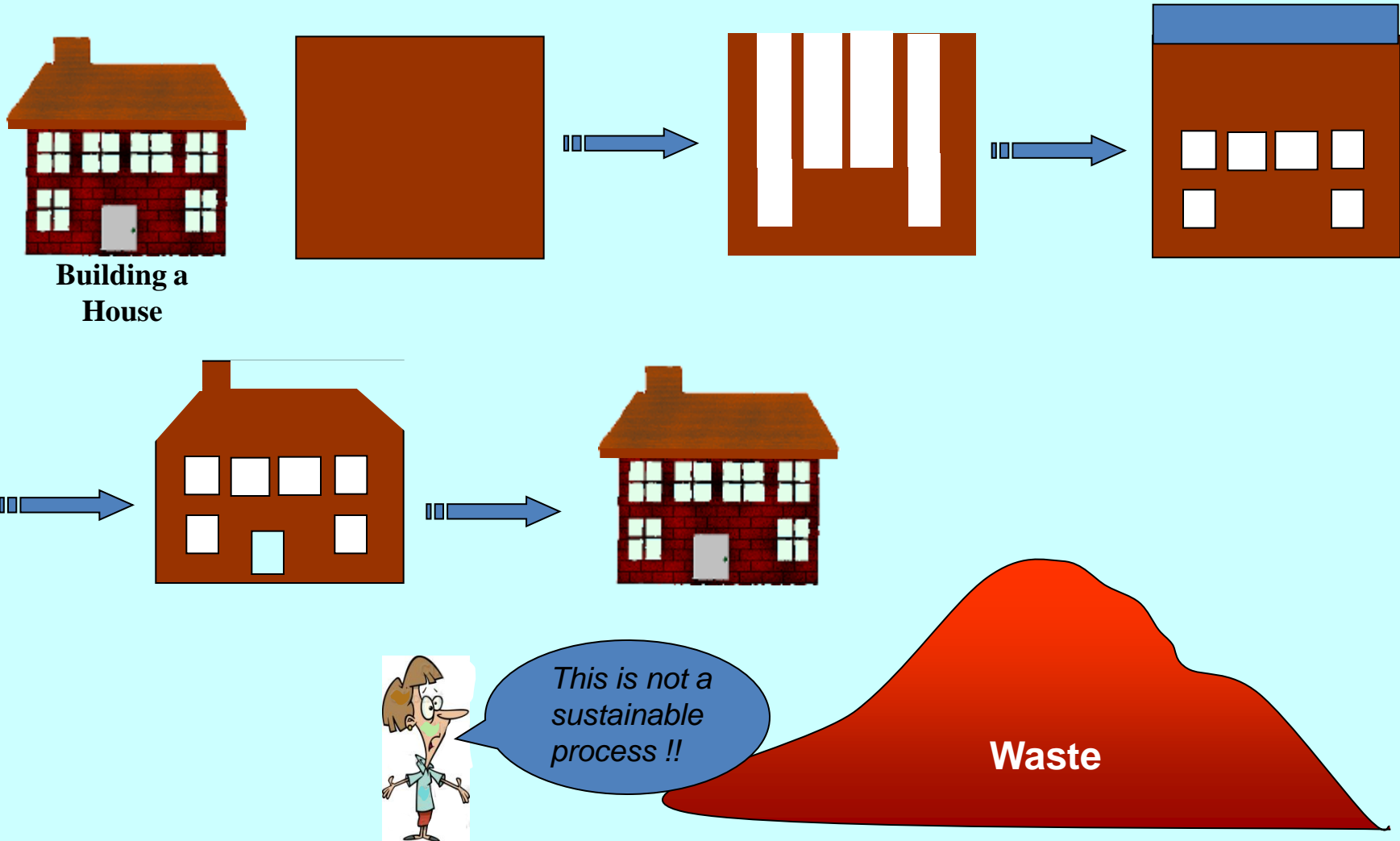


# Two Basic Approaches to Manufacturing Structures

1. *Subtractive*: Carve the structural details in a solid block or solid deposited layers
2. *Additive*: Place the final materials only in places where they are needed.

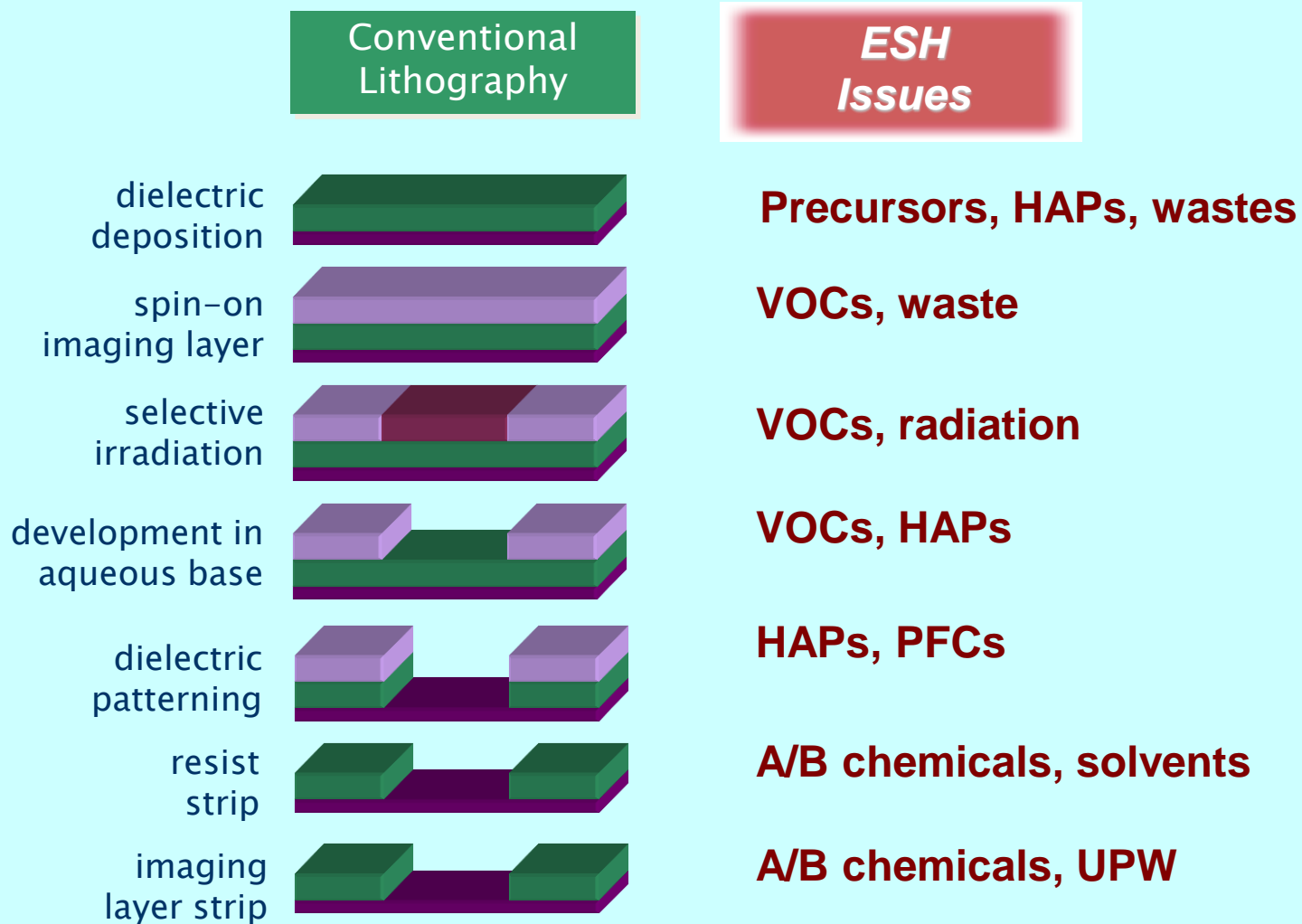


# Subtractive Fabrication *(where it does not work)*

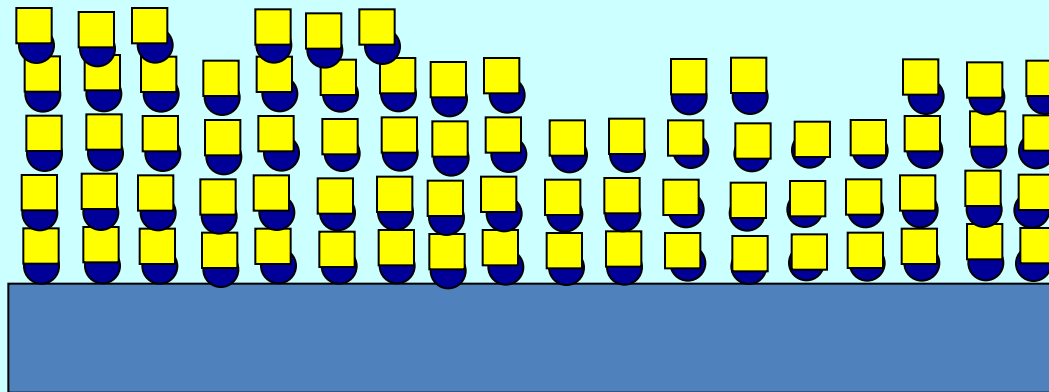
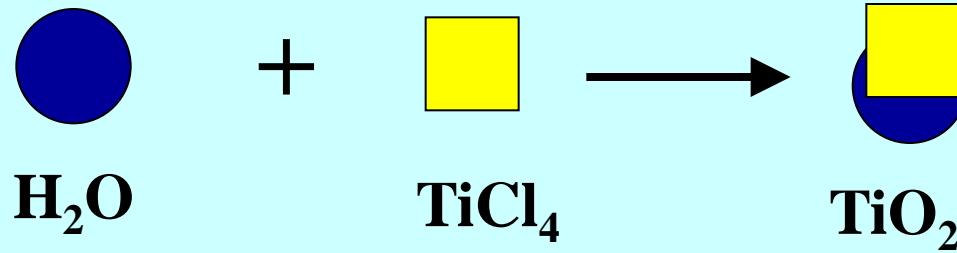


# An Example of Subtractive Processing

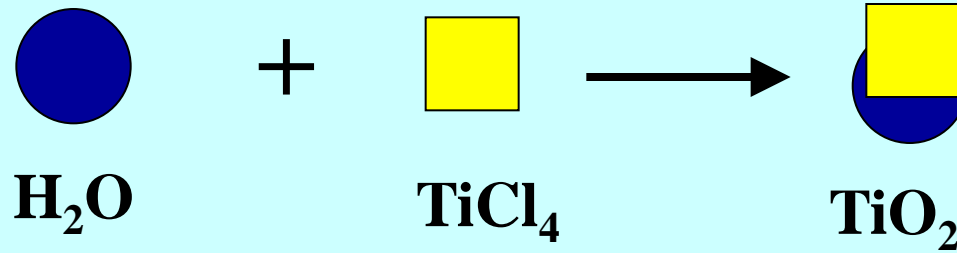
## Deposition and Patterning of Dielectrics



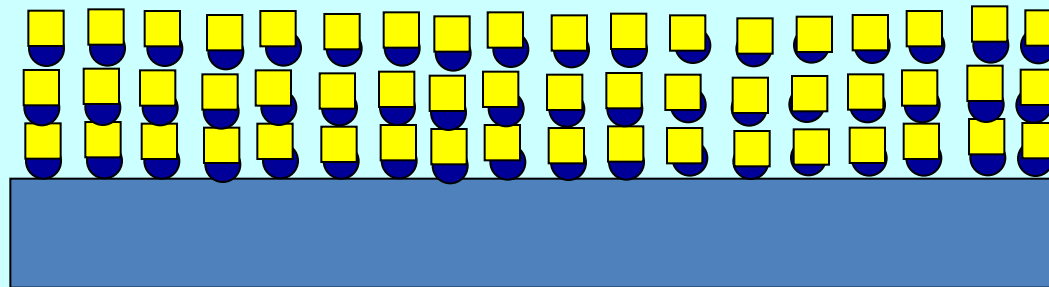
# Conventional Subtractive Processing Deposition



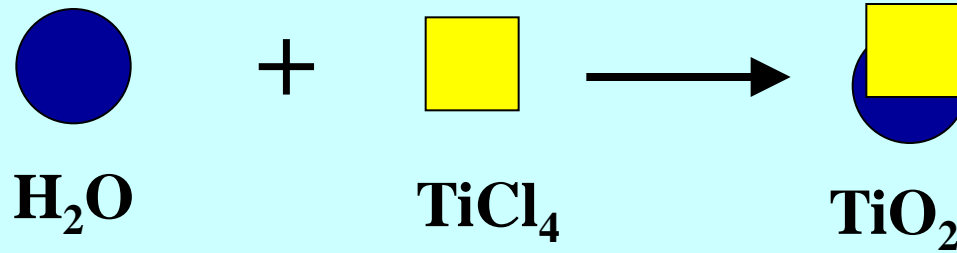
# Conventional Subtractive Processing Planarization



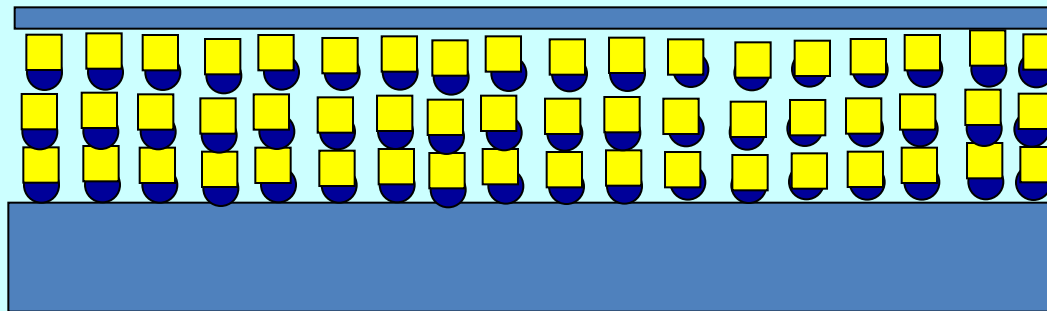
**Waste**



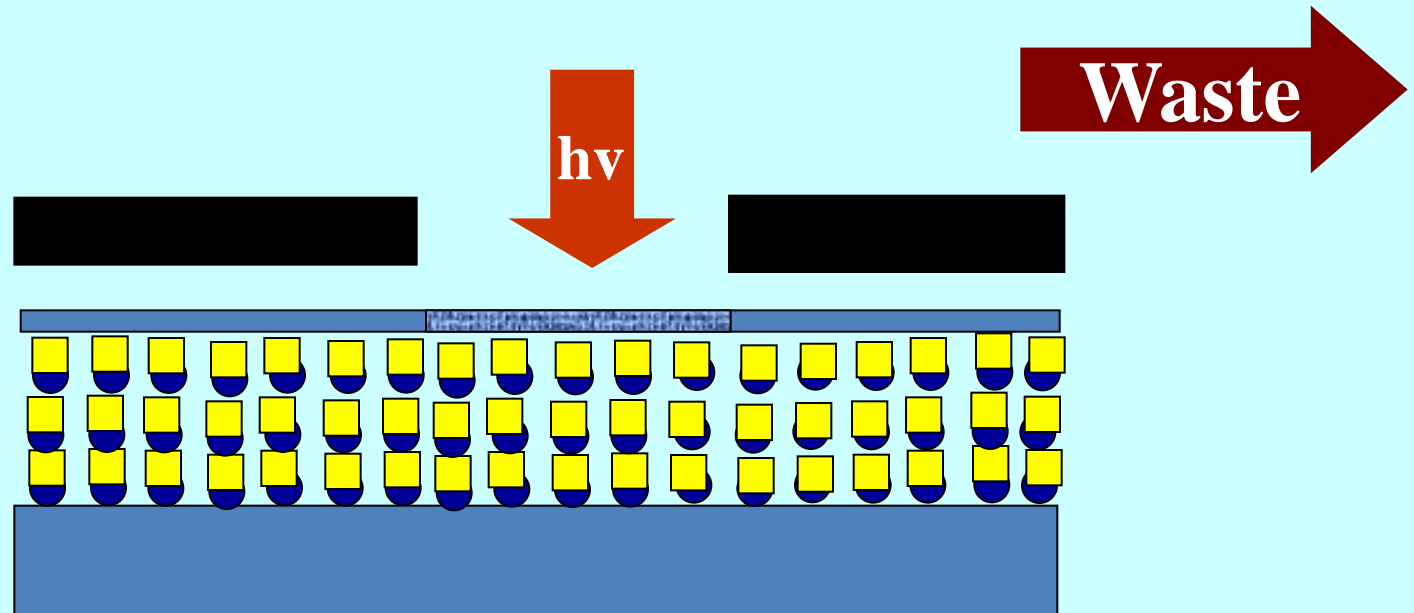
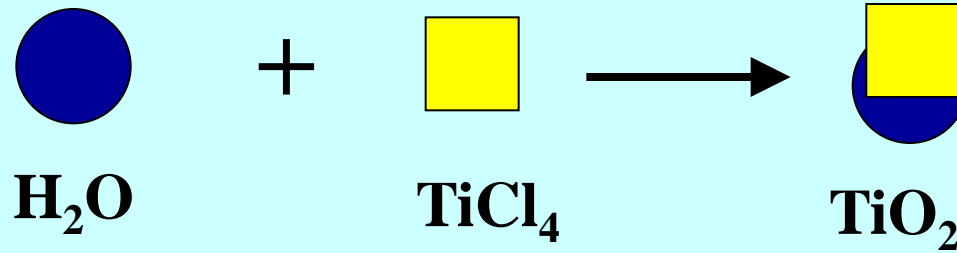
# Conventional Subtractive Processing Photo-Resist



**Waste**

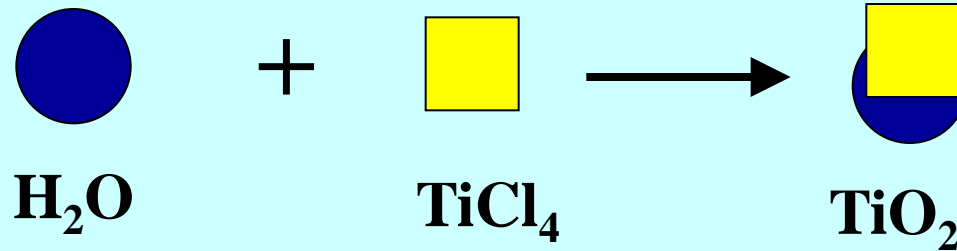


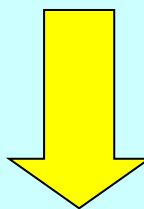
# Conventional Subtractive Processing Lithography



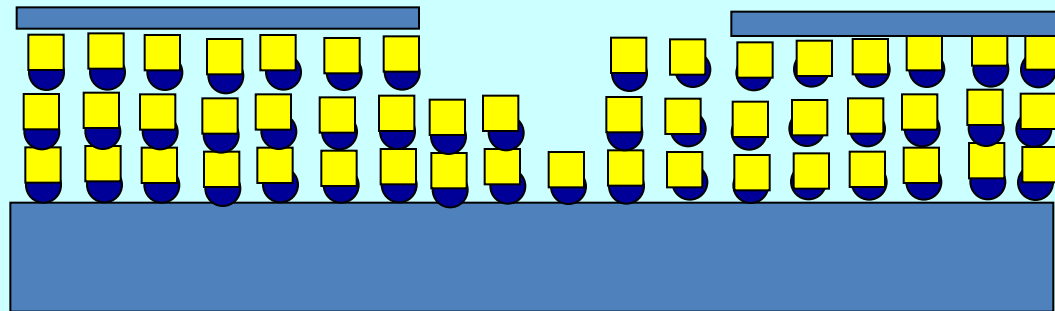
# Conventional Subtractive Processing

## Etch

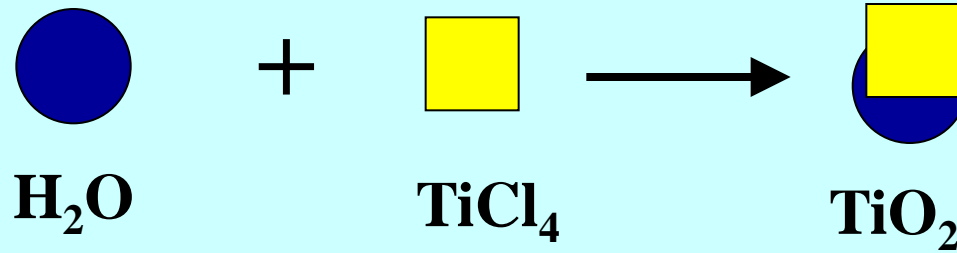


 **Etch**

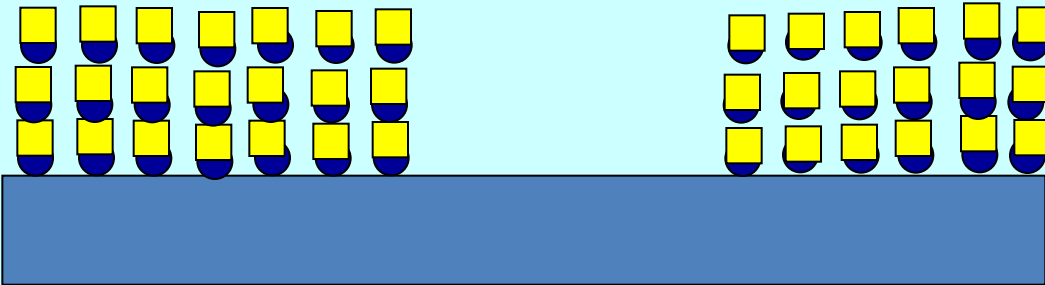
 **Waste**



# Conventional Subtractive Processing Cleaning

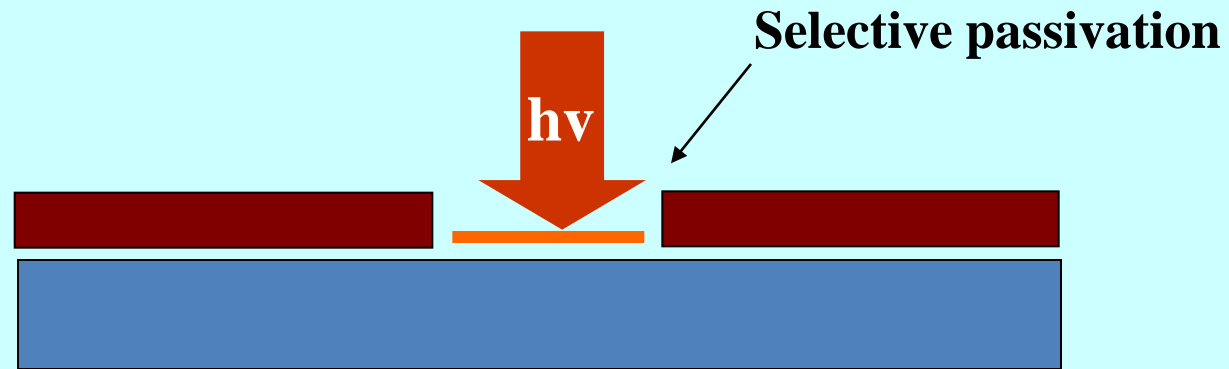


**A lot of  
water and  
chemical  
waste**

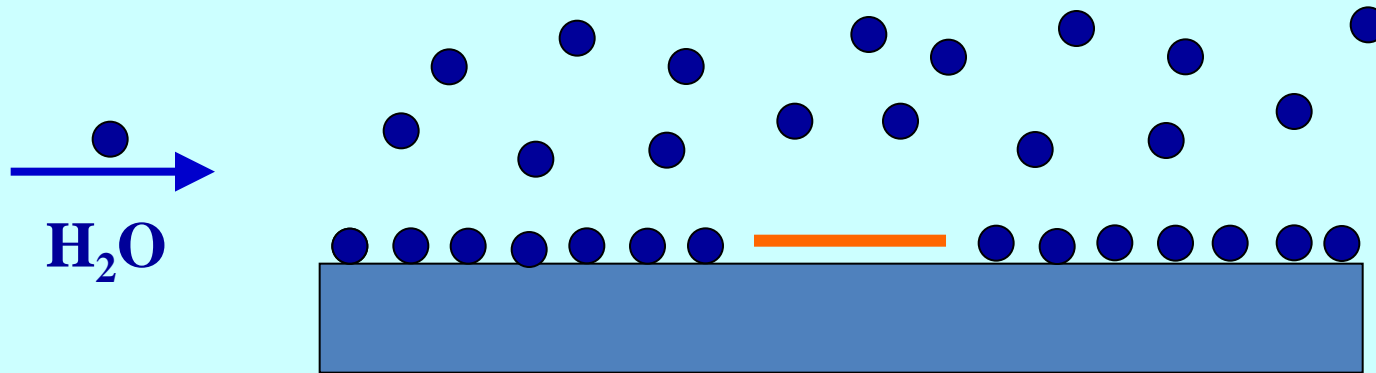




Additive Processing:  
Patterning and Selective Passivation



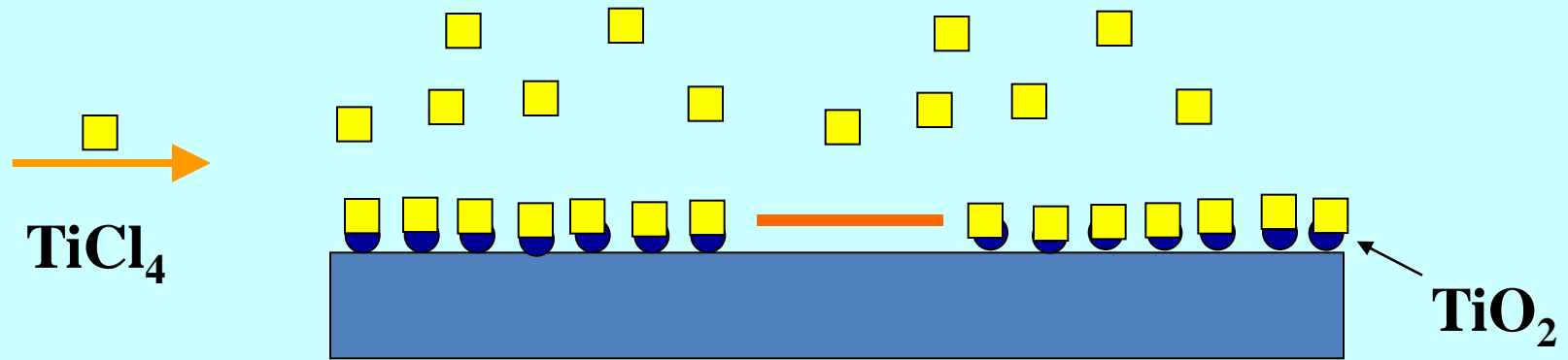
Additive Processing:  
Selective Atomic Layer Deposition (ALD)



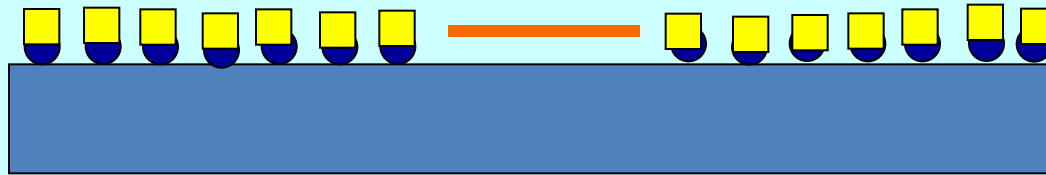
Additive Processing:  
Selective Atomic Layer Deposition (ALD)



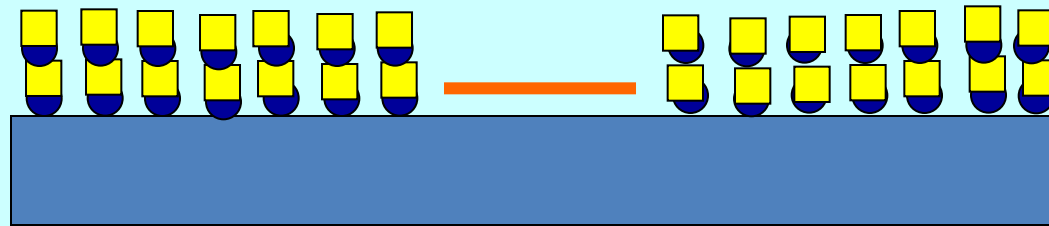
# Additive Processing: Selective Atomic Layer Deposition (ALD)



Additive Processing:  
Selective Atomic Layer Deposition (ALD)



# Additive Processing: Selective Atomic Layer Deposition (ALD)



# Best Examples of Additive Processing

*Dan Herr and Victor Zhirnov (SRC)*

	<b>EUV Lithographic Subtractive Patterning 32 nm</b>	<b>Growth of a Baby [Bio-Assisted Self- Assembly]</b>	<b>Bio Advantage</b>
<b>Bits patterned per second</b>	<b>8.59E+09 bits/s/masking layer</b>	<b>7.53E+17 amino acid equivalents/s</b>	<b>8.77E+07</b>
<b>Energy required per bit</b>	<b>1.46E-12 J/bit/masking layer</b>	<b>1.29E-20 J/amino acid equivalent</b>	<b>1.13E+8</b>

*A Lot to Learn from Nature*

# Thank you

**ERC Website**  
**[www.erc.arizona.edu](http://www.erc.arizona.edu)**

**Email:**  
**[Shadman@erc.arizona.edu](mailto:Shadman@erc.arizona.edu)**