PFAS in Electronics Industry

Applications and Replacement Strategies

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6 Nov 2024

MERCK

Over 350 years of curiosity

- **1668** Friedrich Jacob Merck lays the **foundation** for our company
- **1827** Emanuel Merck begins production on an **industrial scale**
- **1904** Start of **liquid crystal** research
- **1995** Merck KGaA **goes public**
- **2003** Entry into **targeted cancer therapies**
- **2007** Acquisition of **Serono**
- **2010** Acquisition of **Millipore**
- **2013** Acquisition of **AZ Electronic Materials**
- **2015** Acquisition of **Sigma-Aldrich**
- **2017** **Regulatory approvals** for drugs in the areas of cancer and chronic progressive diseases of the immune system
- **2018** **350th anniversary** Opening of the new **Innovation Center** in Darmstadt
- **2019** Acquisition of **Versum Materials & Intermolecular**
- **2023** Acquisition of **Mecaro**

We have 3 high-tech business sectors competing in attractive markets

Healthcare

Leading in specialty pharma markets

- Biologics and small-molecule **prescription medicines** against cancer, multiple sclerosis, infertility
- **Research** focus: Oncology, Immunology & Immuno-Oncology

Life Science

Leading in life sciences

- Tools and services for **biotech research & production**
- **Tools and laboratory supply** for academic research and industrial testing

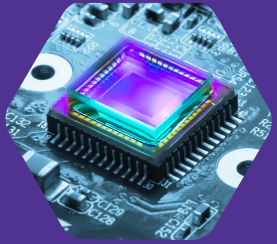
Electronics

Leading in high-tech solutions

- High-tech solutions and materials for **electronics**
- Broad portfolio of **decorative and functional solutions**

our Businesses

Semiconductor Solutions



Semiconductor Materials

are at the heart of Electronics and enable the transformation of communications, mobility and healthcare. We unlock the potential for smaller, faster, and more powerful devices.

Delivery Systems & Services

safely guards the molecule of semiconductor and display materials. We provide high-quality delivery and storage of specialty chemicals and gases.

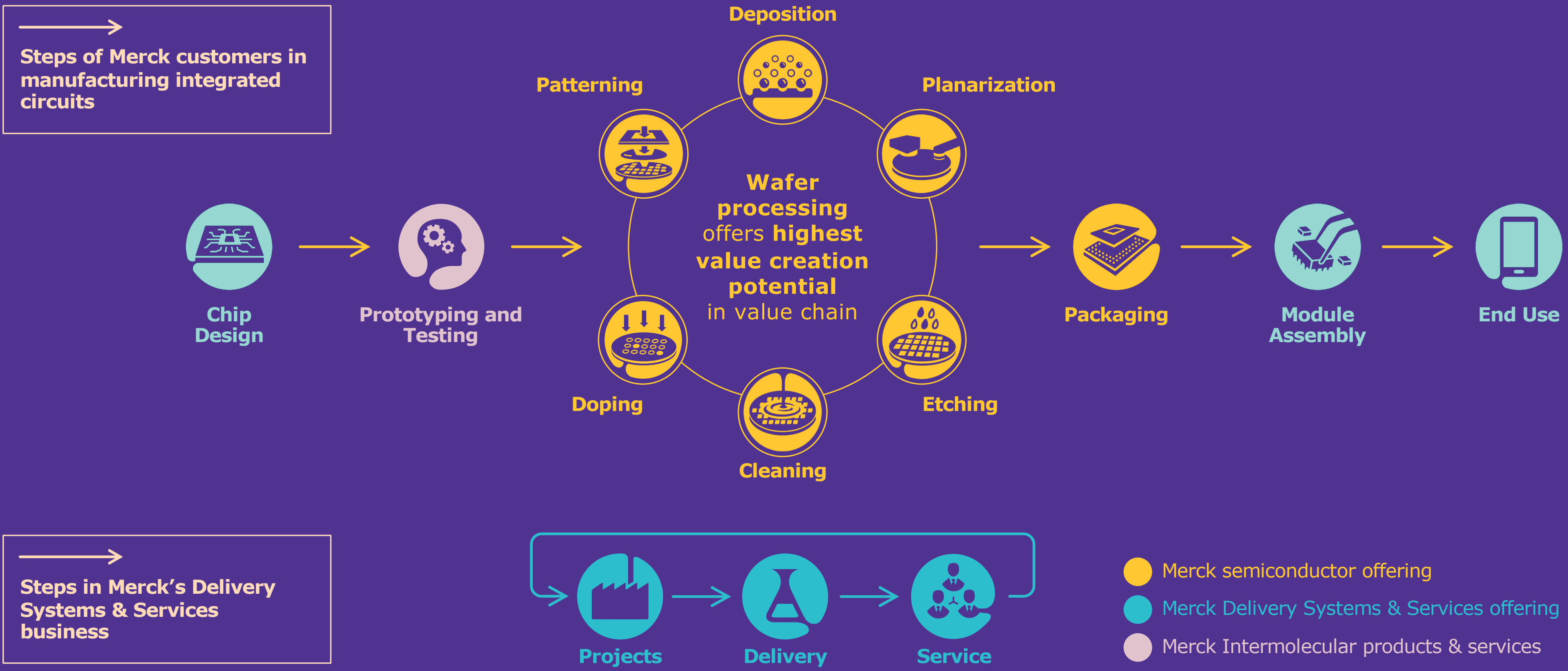
Display Solutions

offers next generation material, equipment systems and services that revolutionize Electronics. We help to connect the intelligence inside devices with human experience.

Surface Solutions

helps redefine the use of color in modern living. Our broad portfolio of pigments and active ingredients continue to drive value in the Automotive, Cosmetic and Industrial industries.

We cover the entire value chain and provide customers with end-to-end solutions



Steps of Merck customers in manufacturing integrated circuits

Chip Design

Prototyping and Testing

Deposition

Planarization

Etching

Cleaning

Doping

Patterning

Wafer processing offers **highest value creation potential** in value chain

Packaging

Module Assembly

End Use

Steps in Merck's Delivery Systems & Services business

Projects

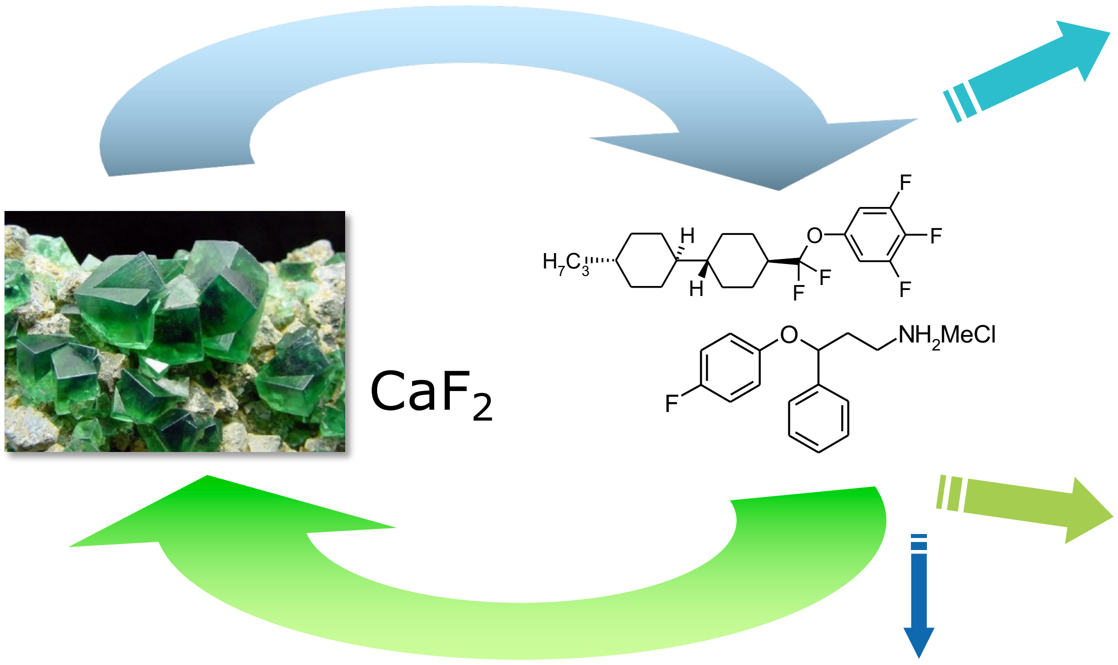
Delivery

Service

- ● Merck semiconductor offering
- ● Merck Delivery Systems & Services offering
- ● Merck Intermolecular products & services

Environmental Impact of Fluorochemicals
Lifecycle

Industrial processes



CaF_2

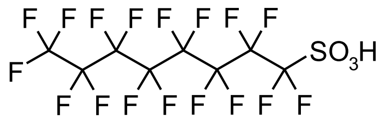
CFC, fluorocarbons

- Global warming
- Ozone depletion (CFC)

too stable

Fluorosurfactants, fluororepellents

- Bioaccumulation
- (Eco)toxicty



biological and abiotic degradation: mineralization not always possible

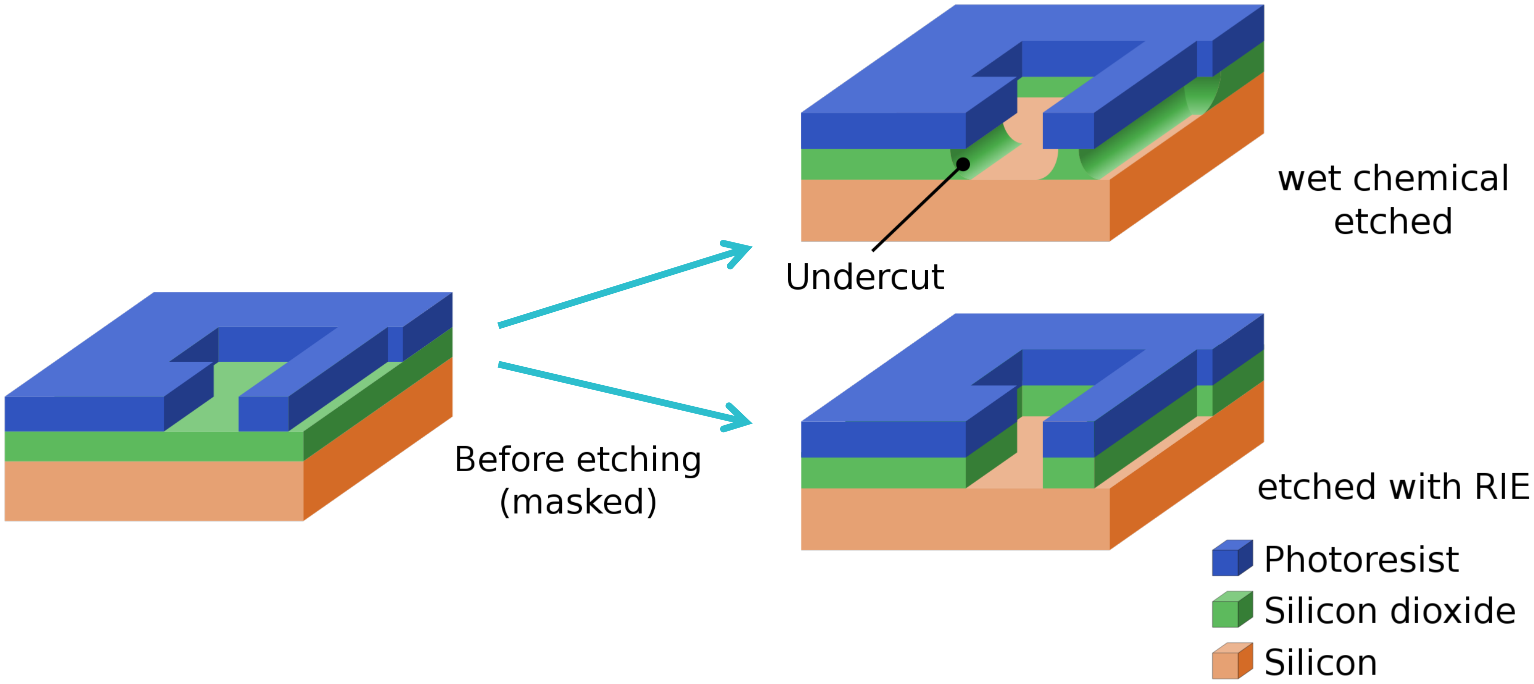
CF_3COOH

01

plasma etch gases

Application in Electronics Industry
Reactive Ion Etching (RIE)

- **NF_3**, CF_4, C_2F_6, SF_6, C_4F_8, etc., as etching gases for photolithography, chamber cleaning



wet chemical
etched

Undercut

Before etching
(masked)

etched with RIE

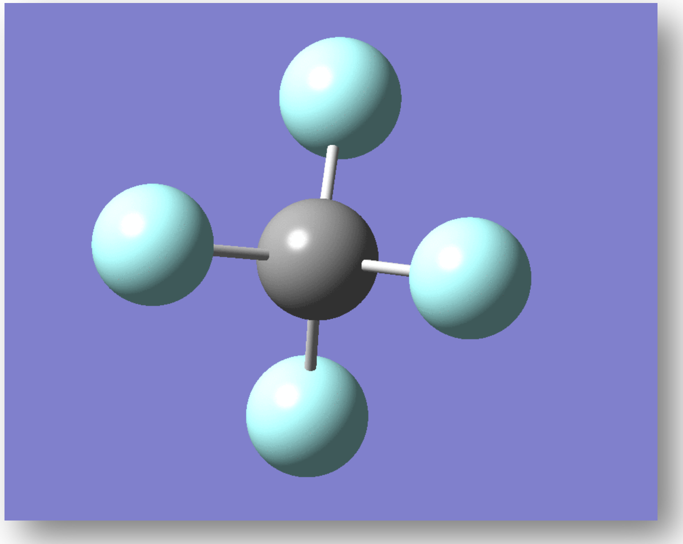
🟦 Photoresist
🟩 Silicon dioxide
🟧 Silicon

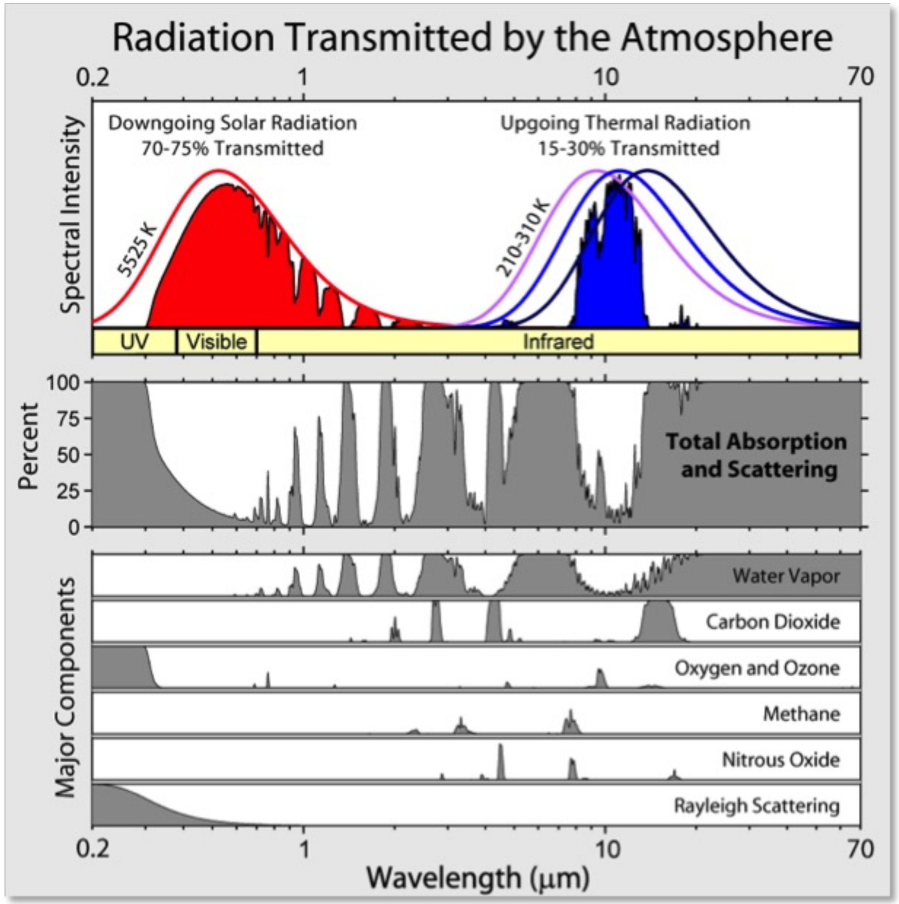
Source: Wikipedia (https://en.wikipedia.org/wiki/Reactive-ion_etching; accessed on Oct 28, **2024**)

Environmental Impact of Plasma Etch Gases
Global Warming

Critical Factors

- Infrared absorption
- Atmospheric lifetime

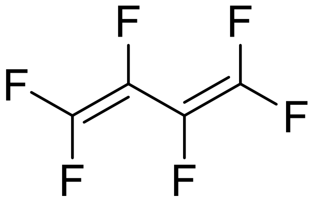




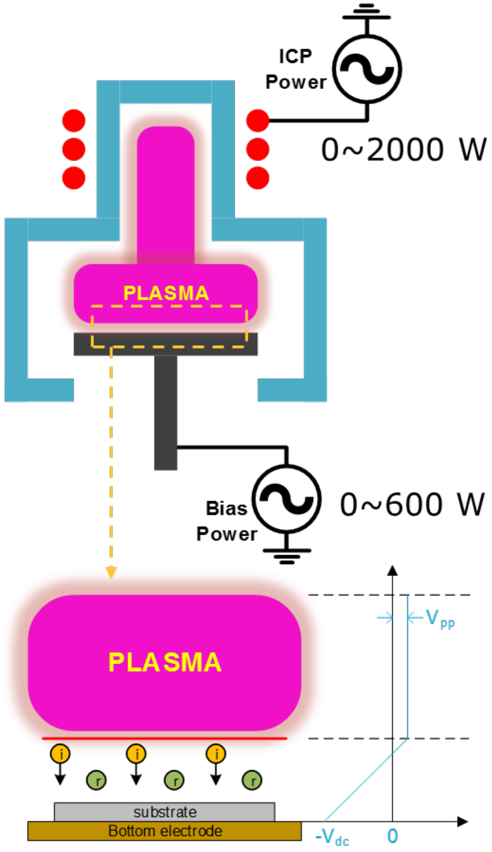
Source: GHG Management Institute (https://ghginstitute.org/2010/06/28/what-is-a-global-warming-potential/; accessed on Oct 28, **2024**)

Fluorocarbon Plasma Etching
Sources of Greenhouse Gas Emissions

etch gas



- material design



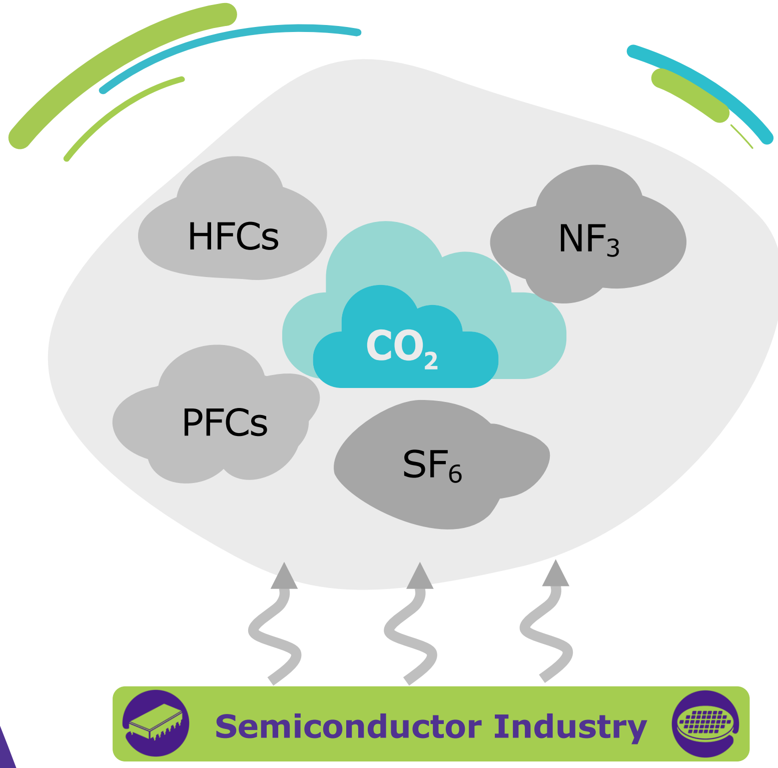
DC bias=$-V_{dc}+V_{pp}$

effluent

CF_4, CHF_3

- process optimization
- abatement
- material design

Fluorinated Etch Gases in Semiconductor Industry
Etch Gases as Driver of Scope 1 Emissions



>600.000 t CO_2e
emissions in the
US only due to
NF_3!*

corresponds to
emission of
131.000 cars

*data source: „2020 US EPA Emissions Figures" of semiconductor industry

etch and clean gases
are responsible for **74%** of all
Scope 1 emissions in
semiconductor industry

Compound	GWP
CO_2	1
SF_6	23.500
CF_4	7.390
NF_3	16.100
CHF_3	12.400
C_4F_8	10.300

GWP = Global Warming Potential
HFC = (Hydro)fluorocarbon
PFC = Perfluorocarbon

Development of Sustainable Etch Gases at Merck Electronics
Design and Synthesis of Low GWP Materials

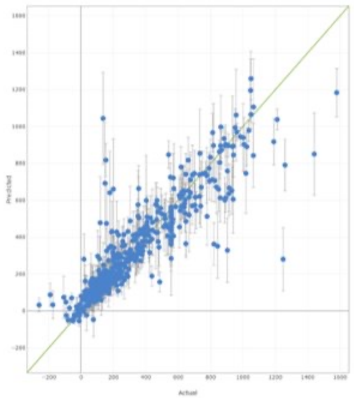
In Silico **Materials Design**

Computational simulation as screening tool for new molecules.

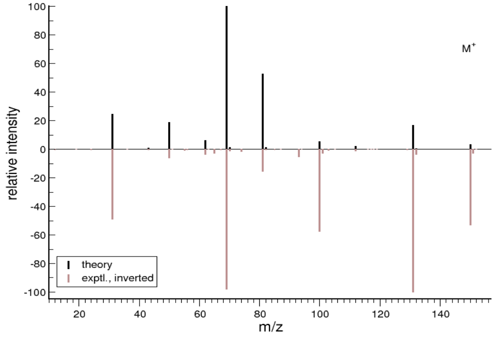
Approximation of molecular fragmentation during plasma etch process by simulation of mass spectra.

Models for prediction of GWP, etch rates and selectivities:

- Identification of structure-property relationships.
- Selection of most promising synthetic targets.



Correlation of simulated with experimental etch rates

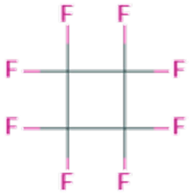


Correlation of simulated with experimental mass spectra

Lab-Scale Synthesis of New Molecules

Design strategy for low GWP:

Reactive compounds which will be completely decomposed under plasma conditions.



High GWP

$GWP_{100} = 10.300$

No structural "weak point"

High stability

Low GWP

$GWP_{100} < 1$

Double bonds as potential attack points for decomposition

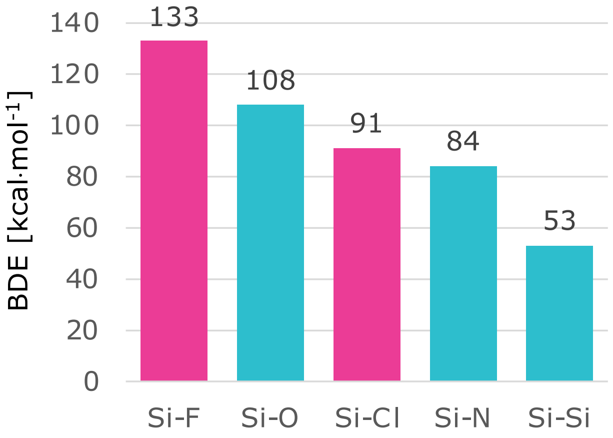
Highly reactive material

data source: Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2018, Annex 6, US EPA

Reactive Ion Etching without Fluorine?
Stoichiometry and Energetics

$$SiO_2 + CF_4 \longrightarrow SiF_4 + CO_2$$

$$Si_3N_4 + 4\ CHF_3 \longrightarrow 3\ SiF_4 + 4\ HCN$$



- Reaction products must be volatile!

Reference: Huheey, pps. A-21 to A-34; T.L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed., Butterworths, London, **1958**; B. deB. Darwent, "National Standard Reference Data Series," National Bureau of Standards, No. 31, Washington, DC, **1970**; S.W. Benson, *J. Chem. Educ.* **1965**, *42*, 502.

02

Liquid crystals

MERCK

2002

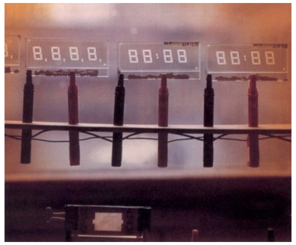
2010

2000

1995

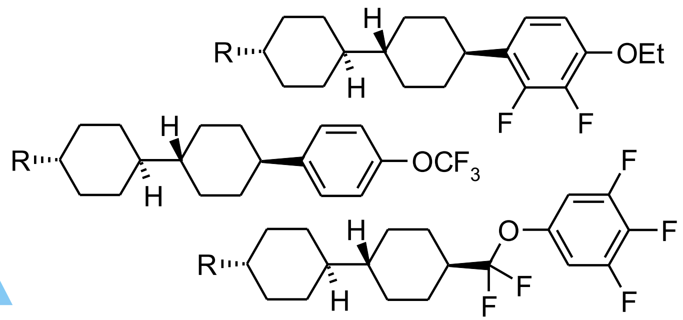
1990

1973



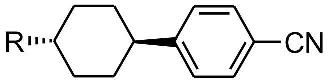
1968

1966

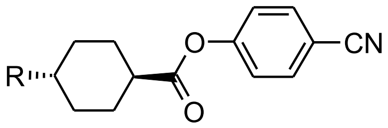


PFAS?

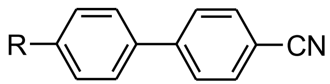
"Super Fluorinated Materials" (SFM), **1985**+



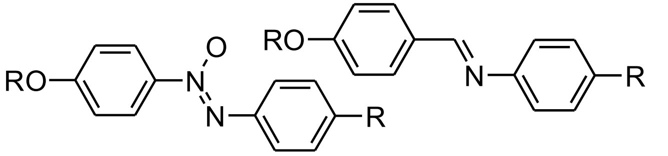
R. Eidenschink *et al.*, **1976**

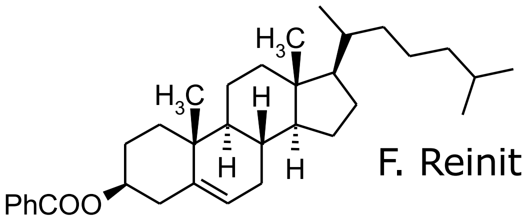


D. Demus *et al.*, **1975**



G. W. Gray *et al.*, **1972**



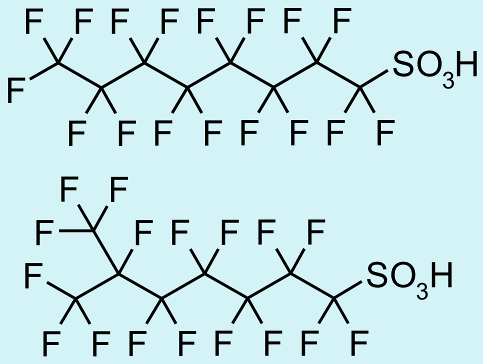


F. Reinitzer, **1888**

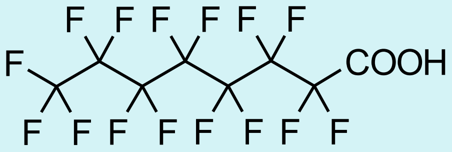
03

(Bio)degradable fluorosurfactants

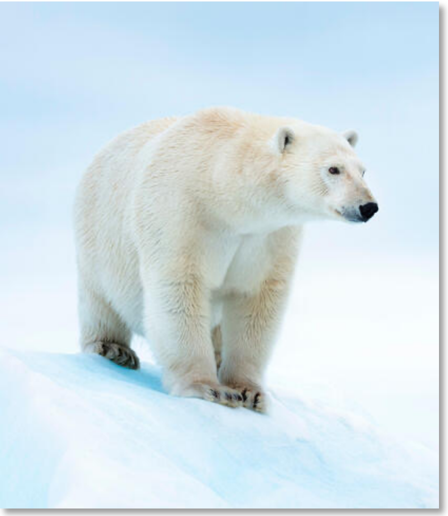
Fluorosurfactants
“Forever Chemicals“



Perfluorooctane sulfonic acid (PFOS)



Perfluorooctanoic acid (PFOA)



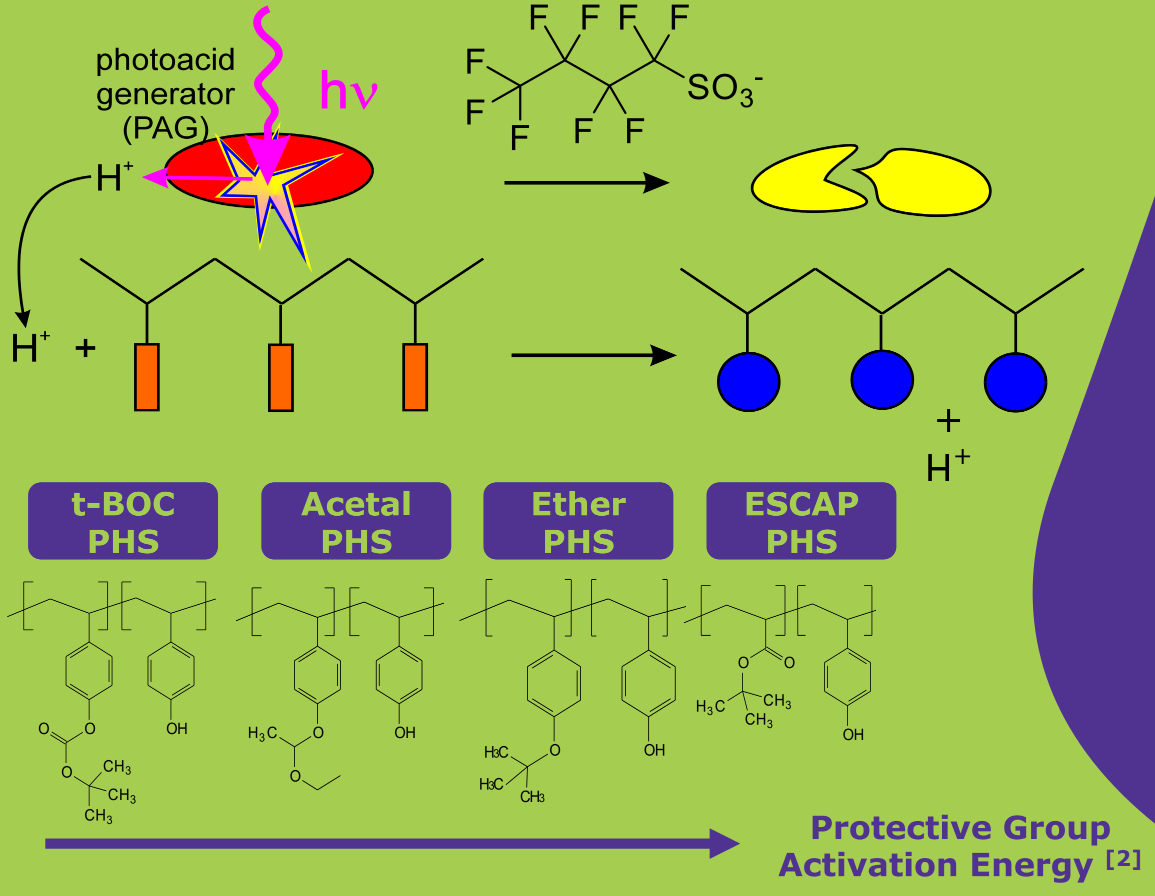
- Bioaccumulative, not degradable
- Toxic, possibly cancerogenic
- Ubiquitous, even in remote areas

- **PFOS**: Banned in the US in **2002** and in the EU in **2007**, except for a very limited range of applications
- **PFOA**: 2010/15 PFOA Stewardship Program (Jan **2006**): Commitment to reduce PFOA emissions until 2010 by 95% (*vs* 2000) and eliminate PFOA until 2015

L. Ahrens, M. Bundschuh, *Environ. Tox. Chem.* **2014**, *33*, 1921-1929 (doi: 10.1002/etc.2663)

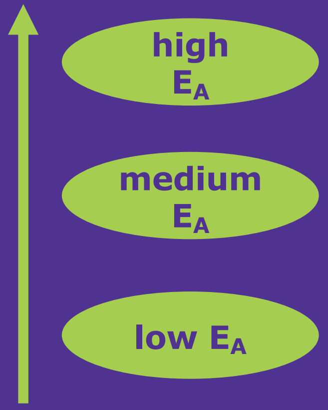
M. G. Evich et al., *Science* **2022**, *375*, eabg9065 (doi: 10.1126/science.abg9065)

PFAS in Photolithography
Chemically Amplified Photoresists



Protective Group Activation Energy [2]

Influence of Activation Energy on Performance: [1]



➔ higher resolution

➔ reduced defectivity

➔ higher stability

➔ shorter tact time

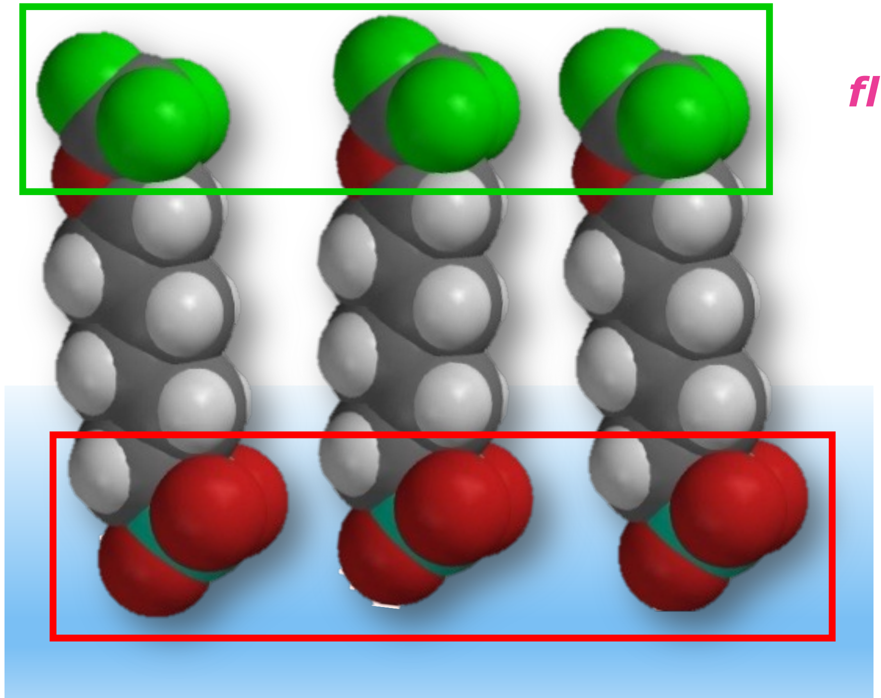
➔ reduced production cost

[1] H. Ito, "Chemical Amplification Resists for Microlithography", *Adv. Polym. Sci.,* Vol 172 (2005).

[2] D. K. Lee, G. Pawlowski „A Brief Review of DUV Resist Technology" J. Photopolym. Sci. Technol., Vol 15 (2002).

Design for Degradability
How to Make Fluorosurfactants (Bio)degradable?

$^{-}O_3S-(CH_2)_n-OCF_3$



fluorous group

polar group

Mineralizable
short fluorocarbon
head group

(bio)degradable
hydrocarbon moiety

M. Peschka, N. Fichtner, W. Hierse, P. Kirsch, E. Montenegro, M. Seidel, R. D. Wilken, T. P. Knepper, *Chemosphere* **2008**, *72*, 1534-1540