PFAS in Electronics Industry

Applications and Replacement Strategies

Prof. Dr. Peer Kirsch, Merck Electronics KGaA & TU Darmstadt
7 Apr 2025

MERCK

Over 355 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 that eventually make us a leader in the Display market

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** to further position our Performance Materials portfolio into Electronics

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®** to offer solutions in every critical area of wafer processing

2024 – Acquisition of **Mecaro**

Acquisition of **Unity SC** adding Metrology & Inspection to broad portfolio

We offer innovation-critical materials, services, and equipment for both the Semiconductor and Display industries

Thin Films*

- A leading portfolio of thin film materials and related deposition processes
- Capability to solve complex integration challenges on atomic level

Formulations*

- High-performance materials for optimum wafer results
- Set a new standard in chemical mechanical planarization and pattern transfer performance

Specialty Gases*

- High-purity specialty gases for semiconductor manufacturing
- Customized solutions to empower our customers with speed and efficiency

DS&S*

- Safe delivery and storage of specialty chemicals and gases
- System design for fab building
- Onsite expertise and management of gas and chemical supplies with highly trained technicians

Display Solutions

- Next generation material solutions that revolutionize key interfaces between humans and electronics devices
- Connects the intelligence inside devices with human experience

* Combined for financial reporting and reported as Semiconductor Solutions

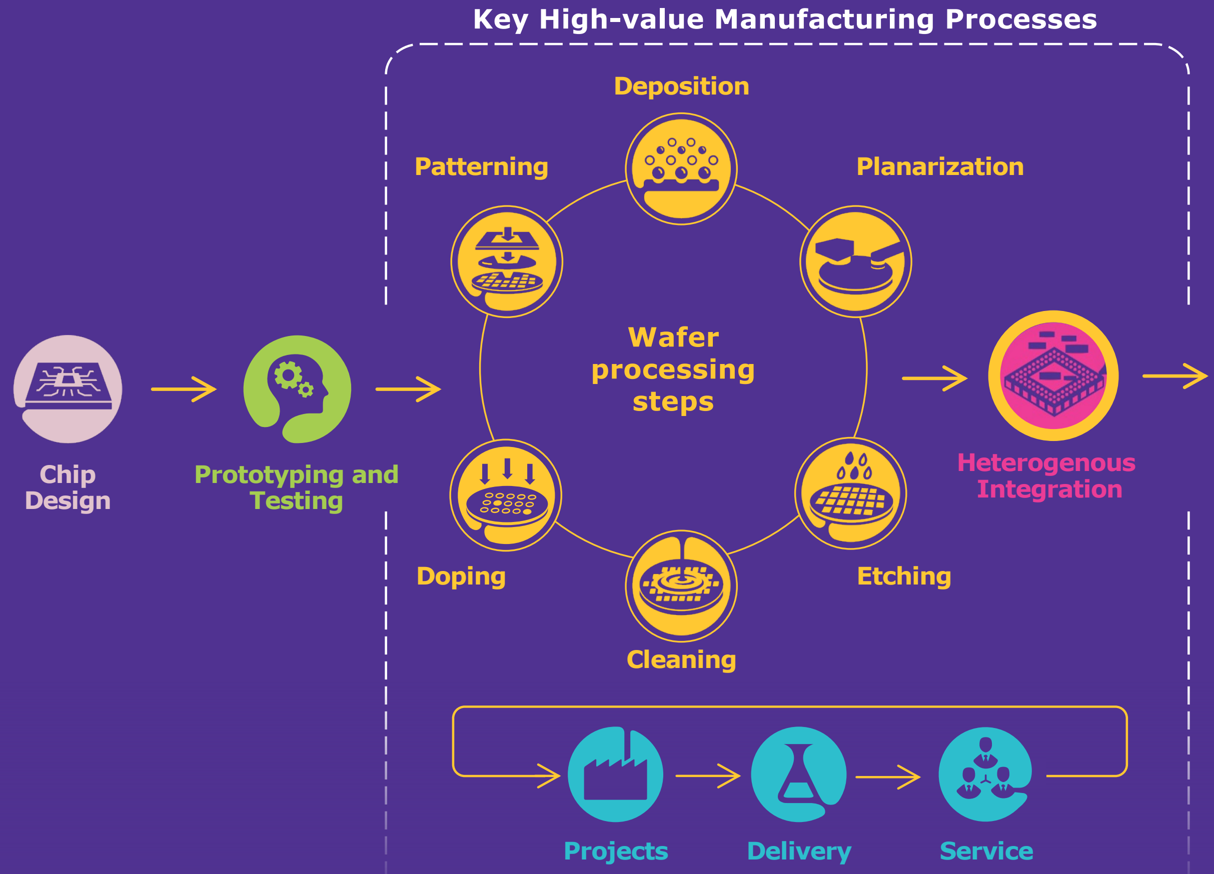
The Logic Manufacturing Process Flow

Ernest Levine- Prof.-College of Nanoscale Science and Engineering, University at Albany---

***Format obtained from presentation by Conrad Sorenson of Prax Air. Modifications in Power Point done by Jobert Van Eisden. Build sequence represents a typical build of any no of different manufacturers at 90 nm node or smaller.**

Source: E. Levine, U. Albany SUNY

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



Four levels of ecosystem integration:

- Metrology and inspection offering
- Merck semiconductor offering
- Merck Delivery Systems & Services offering
- Intermolecular® products & services

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Environmental Impact of Fluorochemicals
Lifecycle

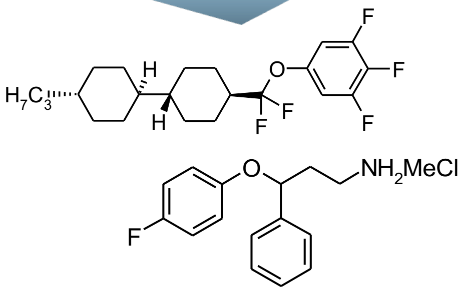
industrial processes

CFC, fluorocarbons

- global warming
- ozone depletion (CFC)

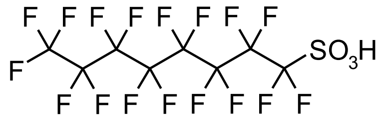
too stable

CaF_2



Fluorosurfactants, fluororepellents

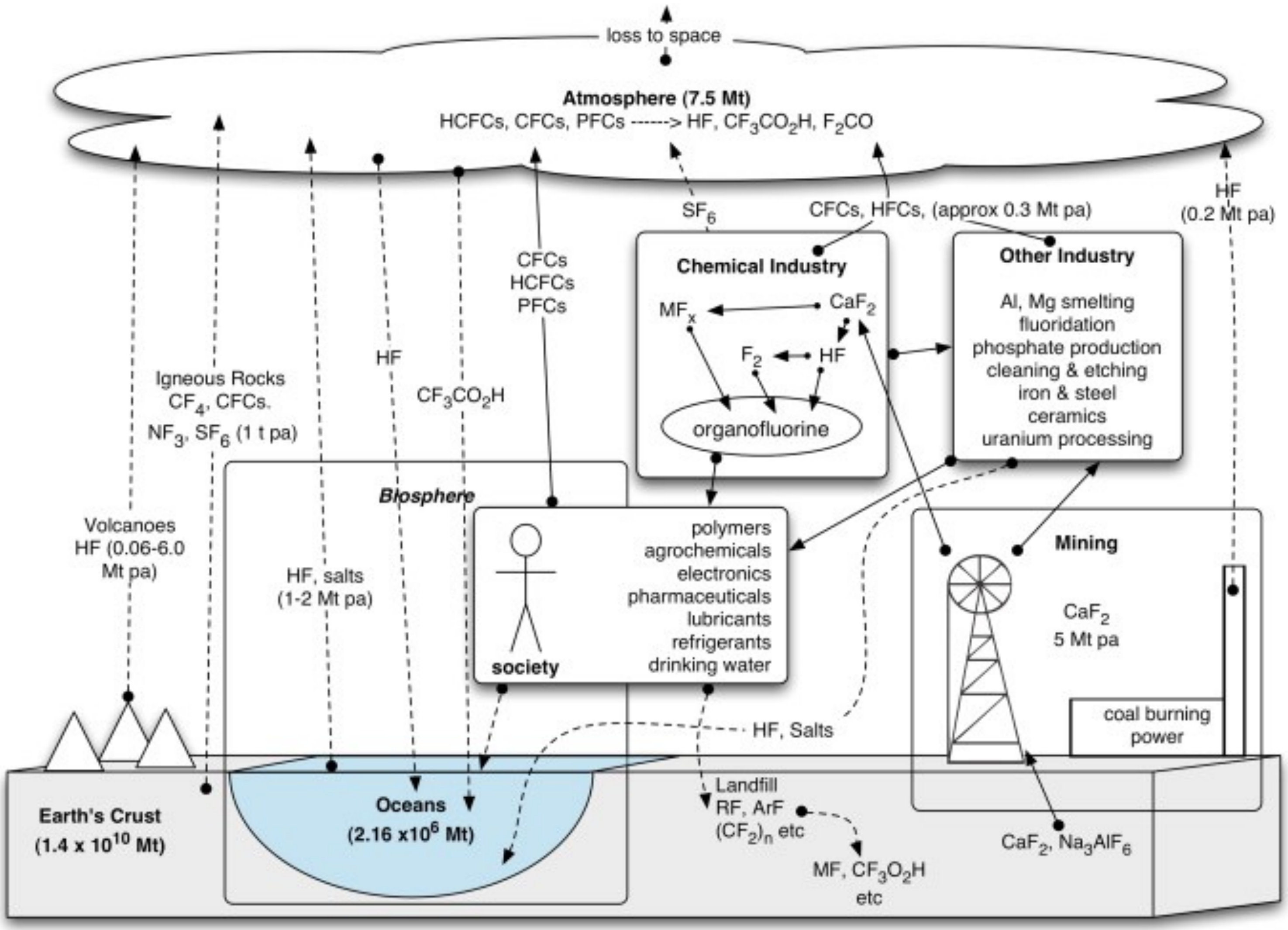
- bioaccumulation
- (eco)toxicty



CF_3COOH

biological and abiotic degradation: mineralization not always possible

MERCK



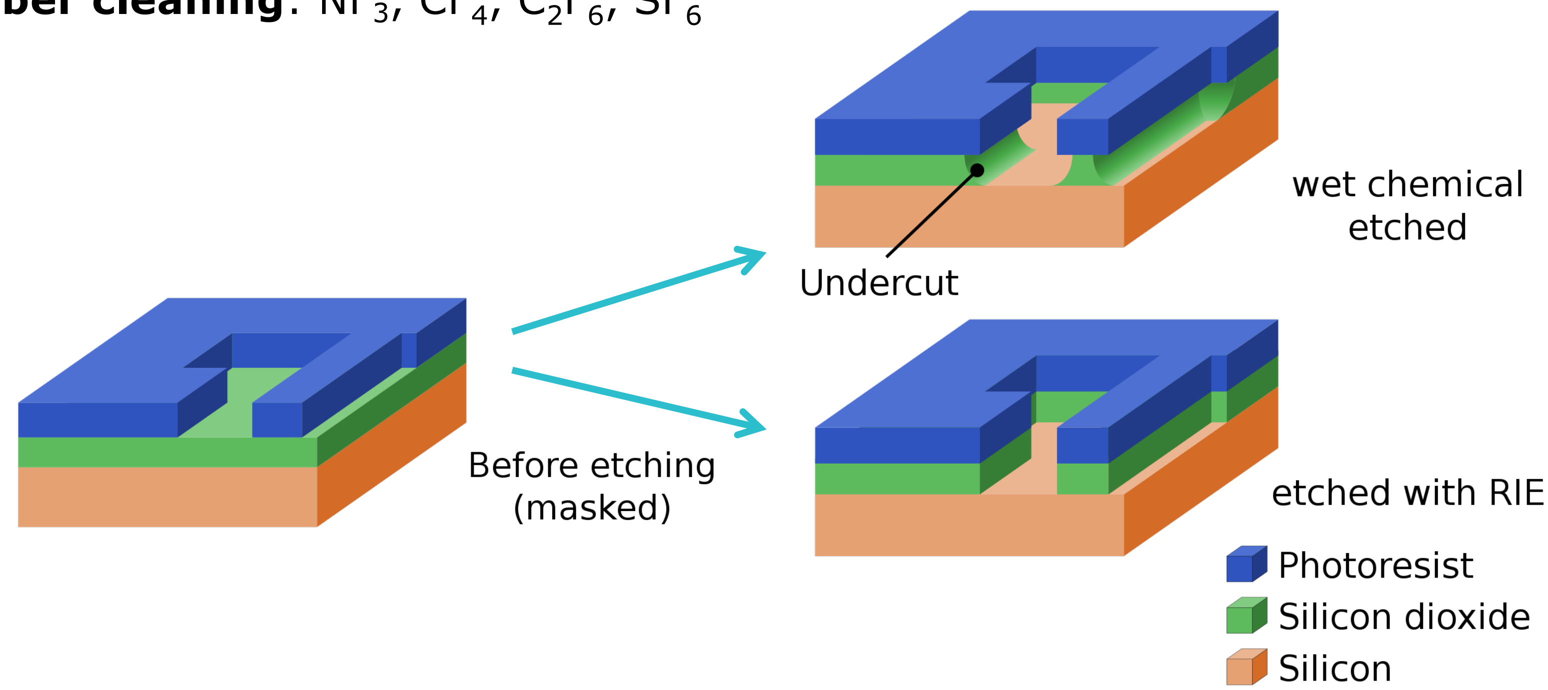
S. J. Taverner, J. H. Clark, *Fluorine: Friend or Foe?* in *Fluorine and the Environment*, Elsevier, **2005** (doi: 10.1016/S1872-0358(06)02005-7)

01

plasma etch gases

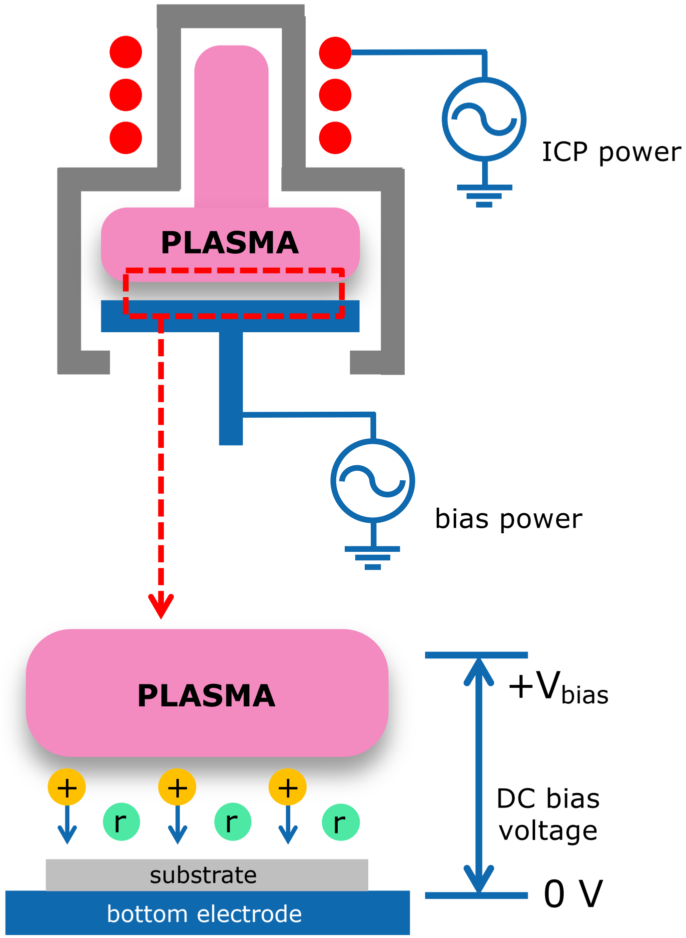
Application in Electronics Industry
Reactive Ion Etching (RIE)

- **Materials to be etched**: Si, SiO_2, SiN_x, many others throughout the whole periodic system
- **Structural etch**: C_4F_8, C_4F_6
- **Chamber cleaning**: NF_3, CF_4, C_2F_6, SF_6



Source: Wikipedia (https://en.wikipedia.org/wiki/Reactive-ion_etching; accessed on Jan 21, **2025**)

Fluorocarbon Plasma Etching



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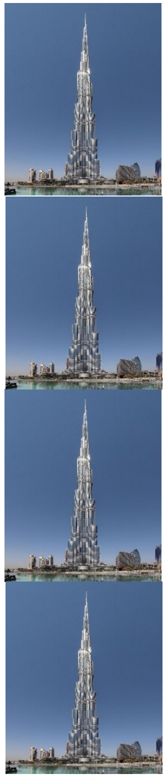
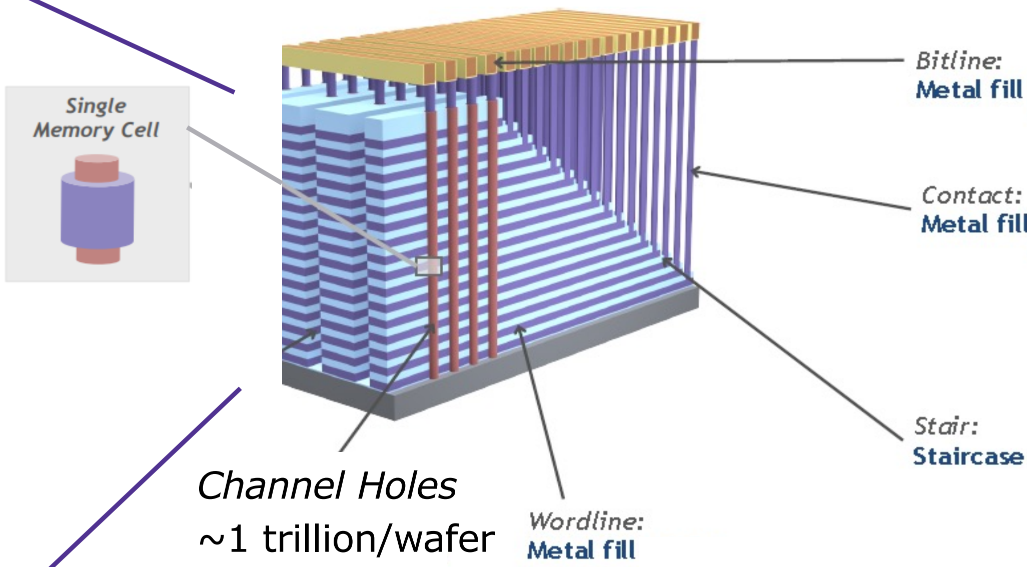
Moore’s Law
The Path is Up!



Burj Khalifa:
aspect ratio 9:1



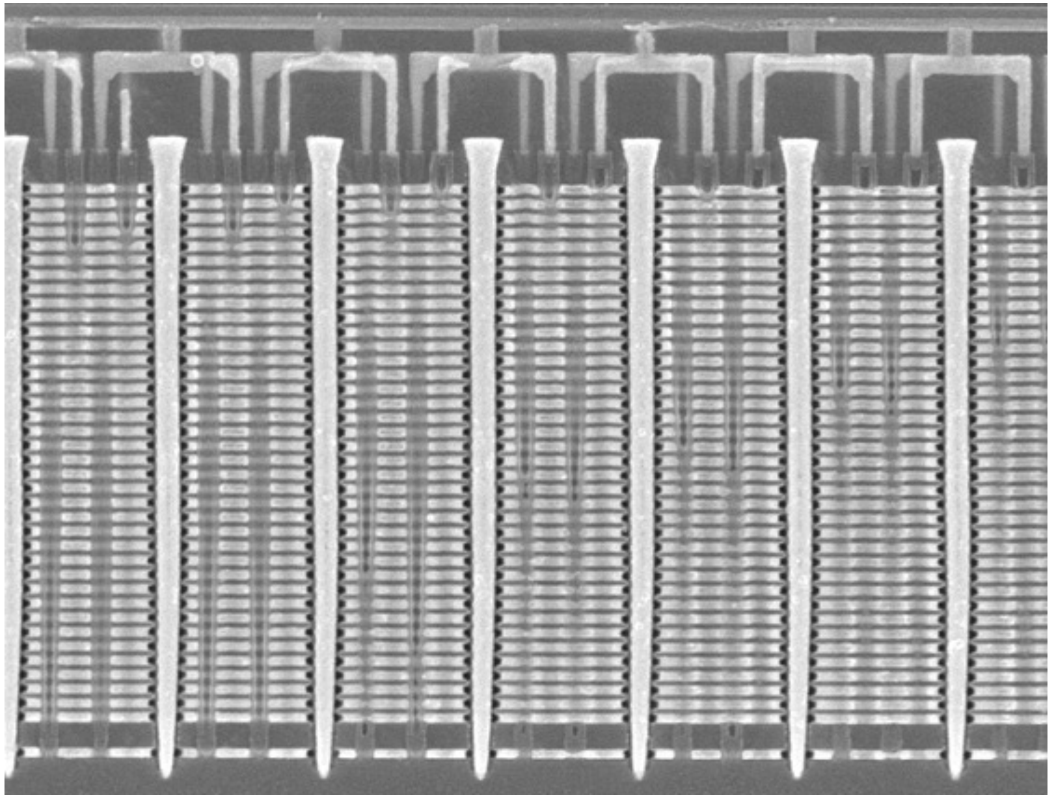
Channel Holes
~1 trillion/wafer

3D NAND stack:
aspect ratio >40:1

- 3D NAND manufacturing has relaxed patterning size requirements but adds challenges in etch and deposition that open opportunities for new materials

Data Storage

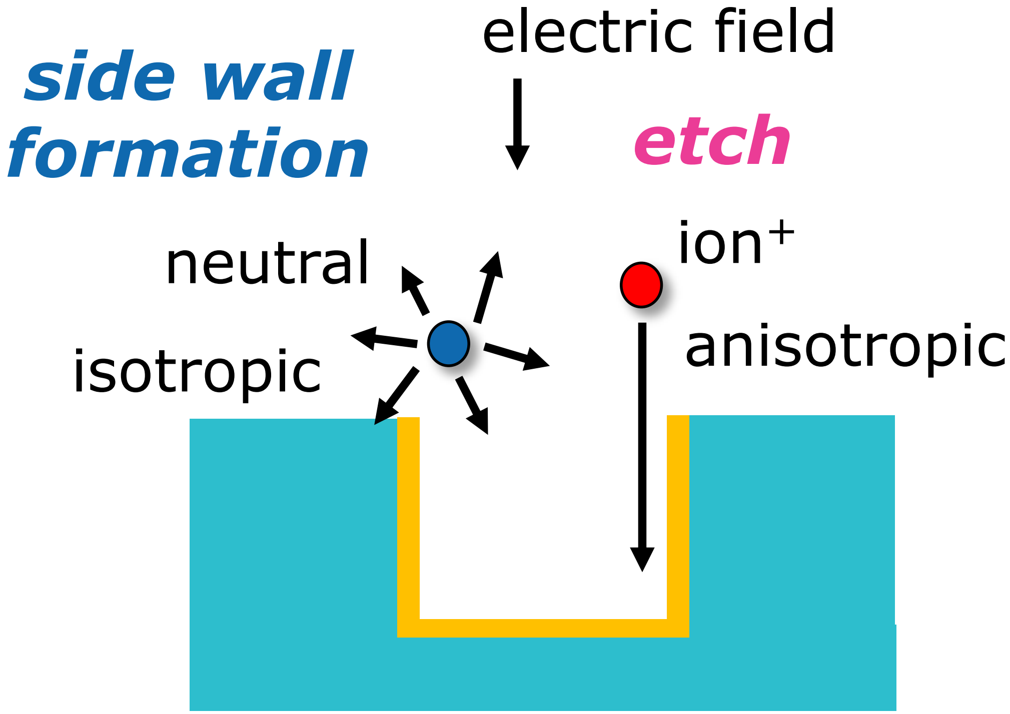
Flash Memory – 3D Stacking



- Alternating stacks of **SiO_2** and **Si_3N_4**

Source: Cross section of Samsung's 86 Gbit 32-layer 2nd generation V-NAND flash array;
cf. Chipworks (https://www.3dincites.com/2014/08/samsungs-3d-vnand-flash-product-spires-el-dorado/; accessed on Jan 24, **2022**)

Fluorocarbon Plasma Etching
High Aspect Ratio Etching



- Etch plasma contains typically **10% ions** and **90% neutral** particles
- **Ions** are accelerated by electrical field and **provide directionality** of etch
- Neutral species contribute to **polymer** formation on side walls

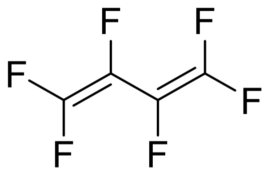
D. Humbird, D. B. Graves, "Fluorocarbon plasma etching of silicon: Factors controlling etch rate" *J. Appl. Phys.* **2004**, *96*, 65-70

High Aspect Ratio - Deep Reactive Ion Etching
Bosch Process

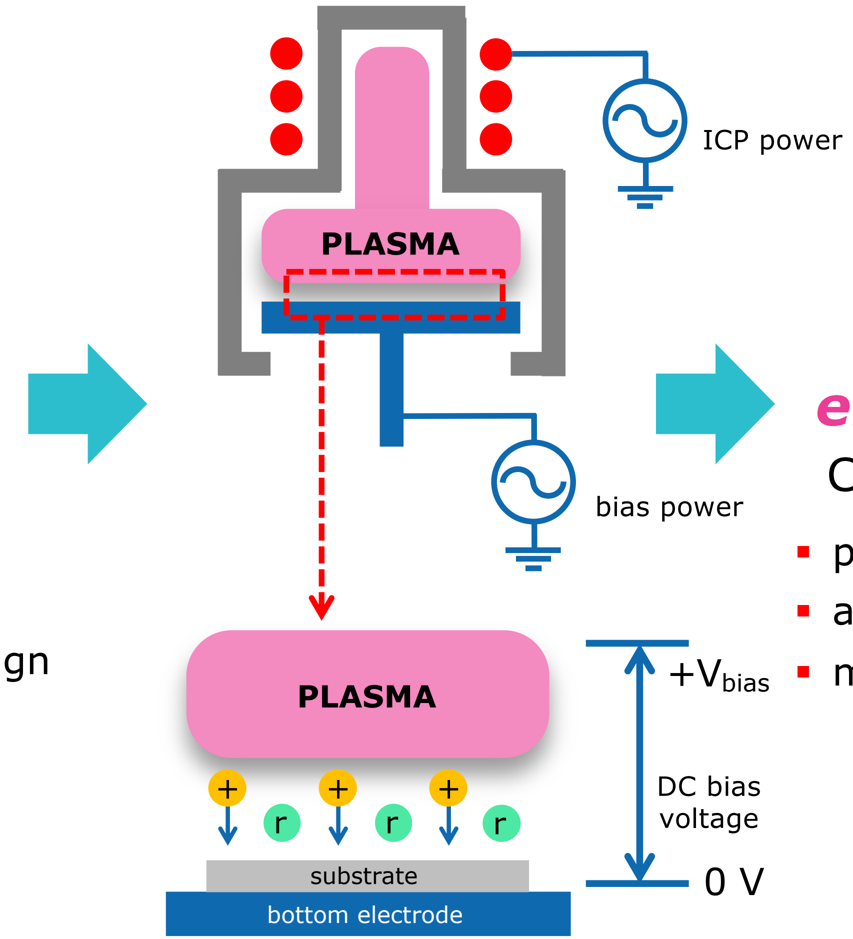
Source: Oxford Instruments (https://plasma.oxinst.com/technology/deep-reactive-ion-etching, accessed on Jan 25, **2022**)

Sources of Greenhouse Emissions

etch gas



- material design



effluent

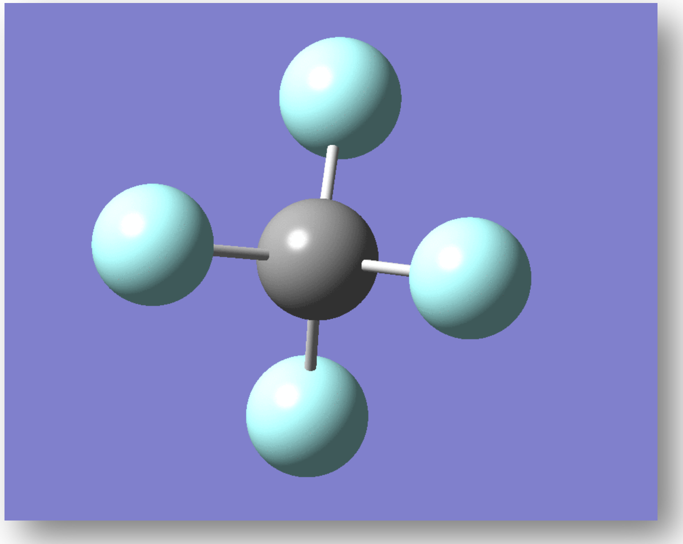
CF_4, CHF_3

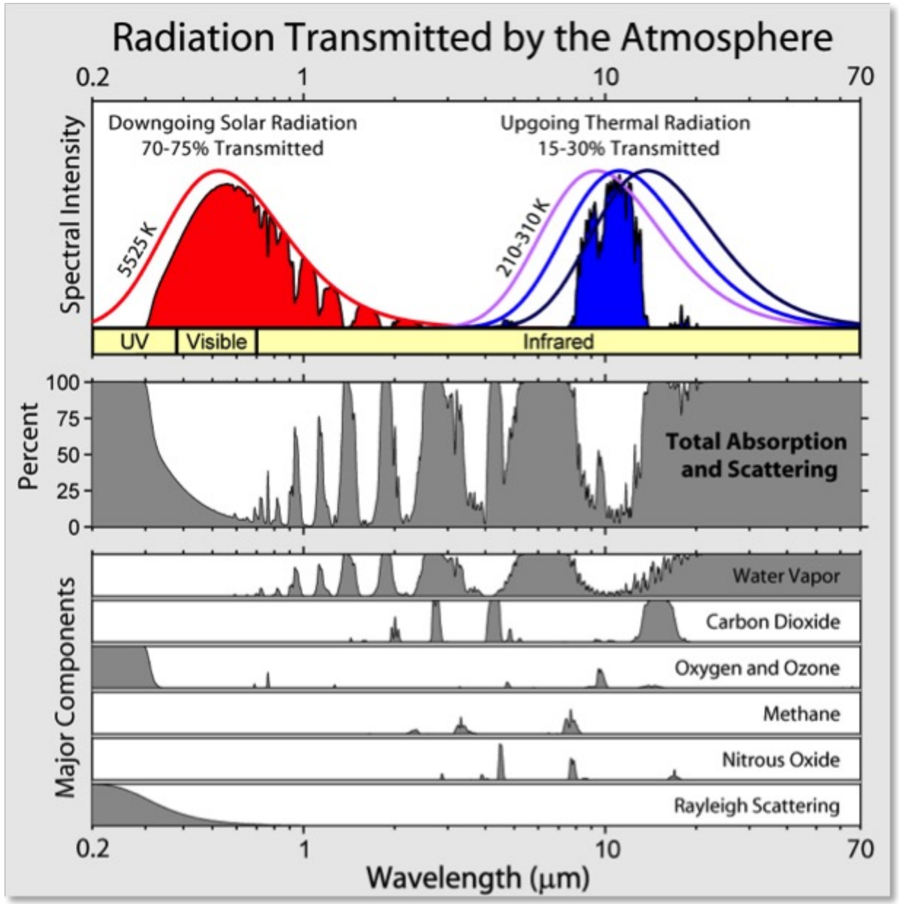
- process optimization
- abatement
- material design

Environmental Impact of Plasma Etch Gases
Global Warming

Critical Factors

- Infrared absorption
- Atmospheric lifetime

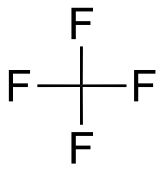




Source: GHG Management Institute (https://ghginstitute.org/2010/06/28/what-is-a-global-warming-potential/; accessed on Jan 25, **2022**)

Molecular Stability

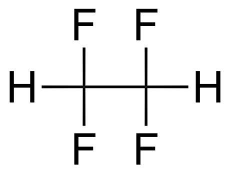
Atmospheric Lifetime Dictates GWP



CF_4

lifetime: 50,000 years

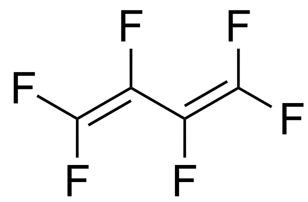
GWP_{100}: 7,390



$C_2H_2F_4$

lifetime: 10.6 years

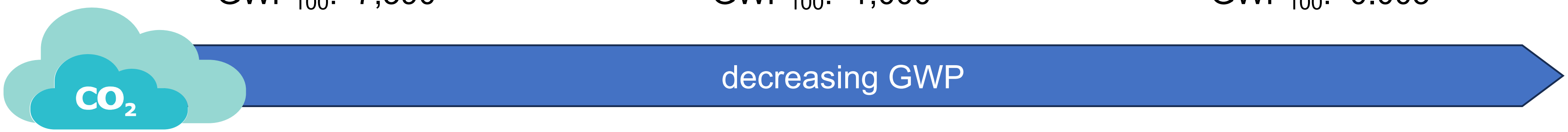
GWP_{100}: 1,000



C_4F_6

lifetime: 1.1 days

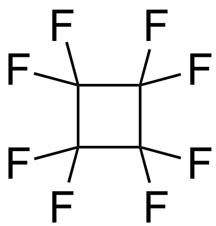
GWP_{100}: 0.003



C_4F_8

lifetime: 3,200 years

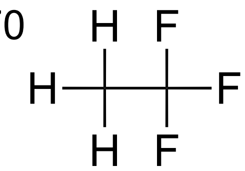
GWP_{100}: 10,300



$C_2H_3F_3$

lifetime: 52 years

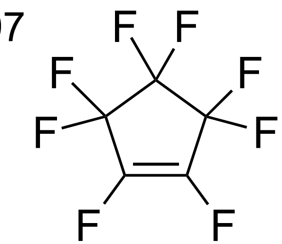
GWP_{100}: 4,470



C_5F_8

lifetime: 31 days

GWP_{100}: 1.97



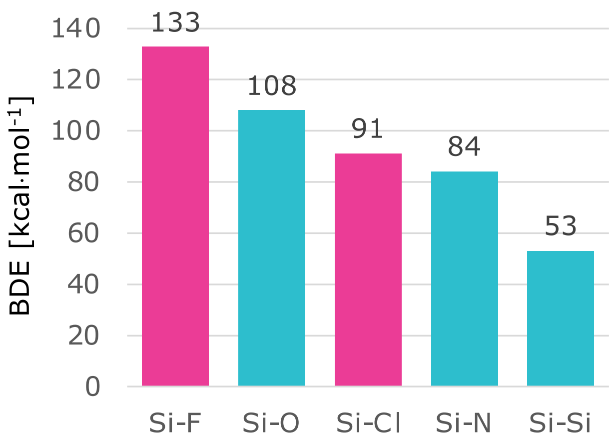
Data Source: Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2018, Annex 6, US EPA

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.

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

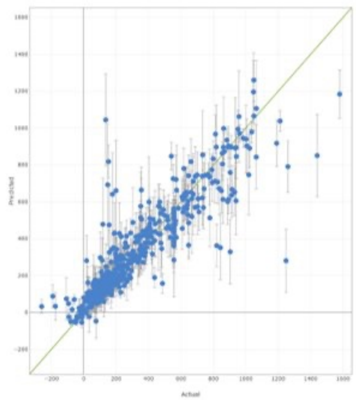
In Silico Materials Design

Computational simulation as screening tool for new molecules.

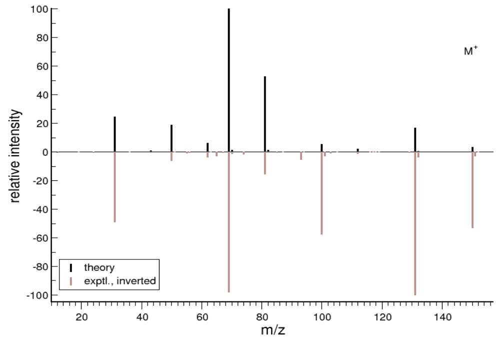
Approximation of molecular fragmentation during plasma etch process by simulation of mass spectra.

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:

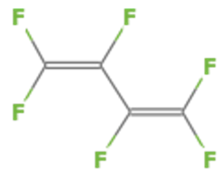
Reactive compounds which will be completely decomposed under plasma conditions.

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

02

Liquid crystals


2002

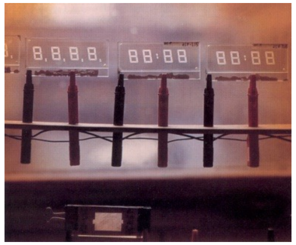

2010+


2000

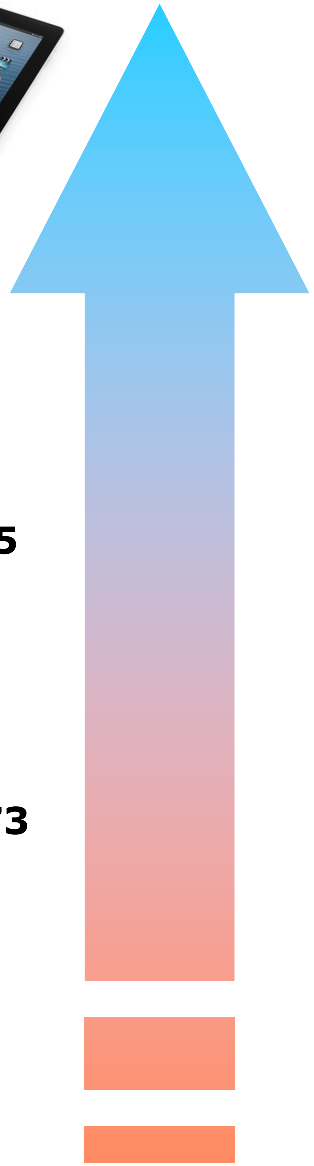

1995

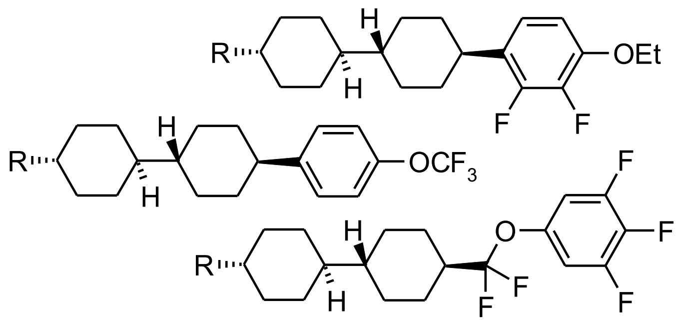

1990

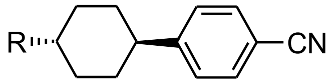
1973

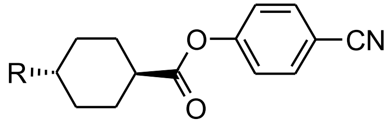

1968

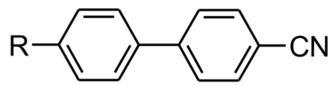

1966

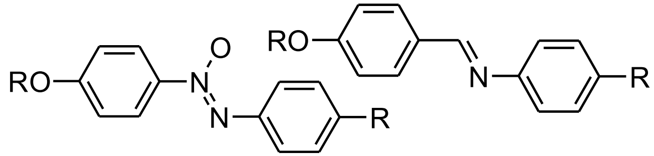


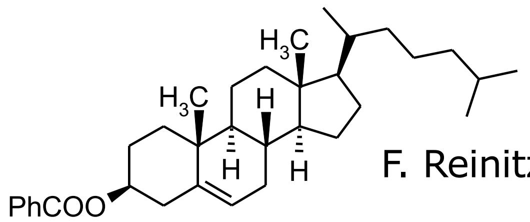

"Super Fluorinated Materials" (SFM), **1985+**


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


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

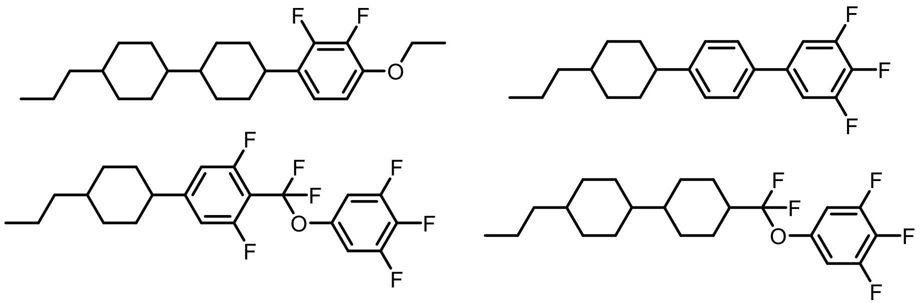

G. W. Gray *et al.*, **1972**




F. Reinitzer, **1888**

Fluorine in Liquid Crystals
Essential to achieve required properties, but alternatives already exist

- modern LC displays contain 10-20 single LC compounds
- fluorinated substituents are essential to achieve the required properties



- Merck can provide PFAS-free LC-mixtures without significant performance loss

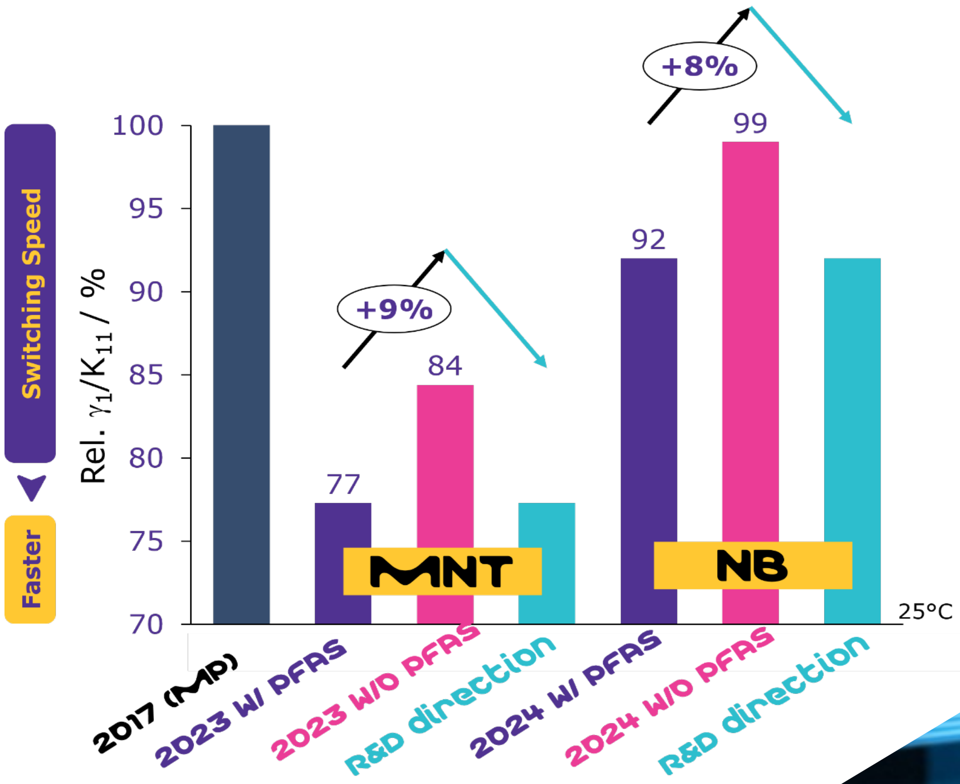
References:

Chem. Soc. Rev., 2007, 36, 2070-2095

Angew. Chem. Int. Ed., 2013, 52, 8880-8896

Fluorine in Liquid Crystals
PFAS-free Liquid Crystals

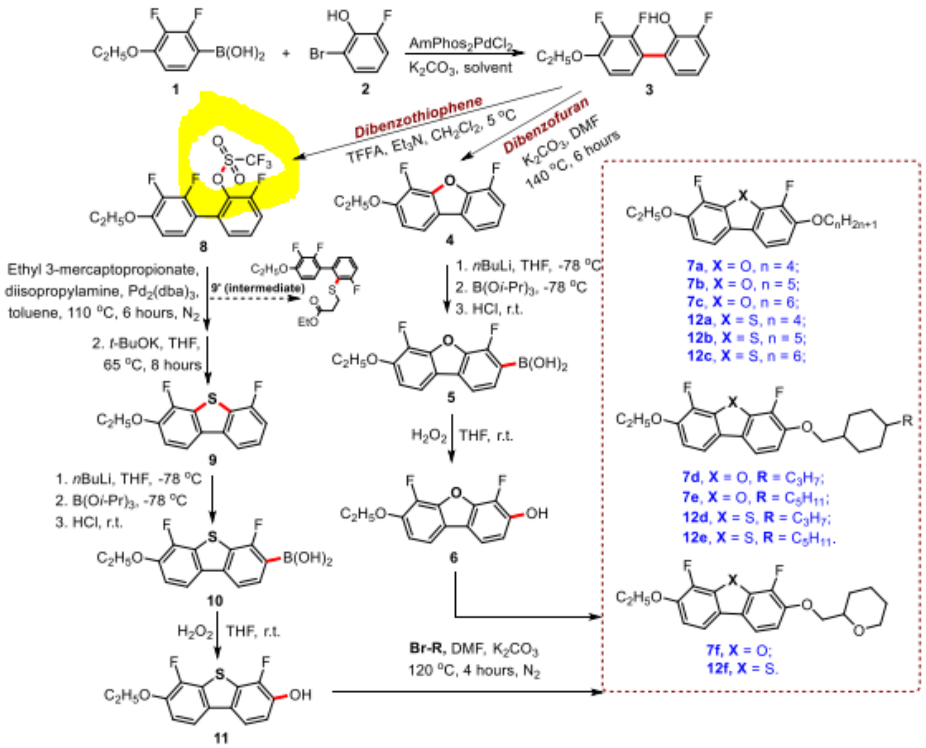
<u>Performance Impact* of EU PFAS-Ban:</u>



* exemplary data, not universally valid

- There are PFAS-free LCs already available without significant loos in performance
- Whenever possible, we substitute PFAS material by PFAS-free materials

Fluorine in Liquid Crystals
PFAS in synthesis procedure



Scheme 1. Synthetic route to the newly designed liquid crystals with negative dielectric anisotropy.

- Triflates, allow an efficient and selective functionalization of abandoned phenols.
- → A targeted research to find competitive alternatives to triflates for phenol coupling would be useful.

References:

J. Mol. Liq. 2024, 405, 125061

03

photolithography

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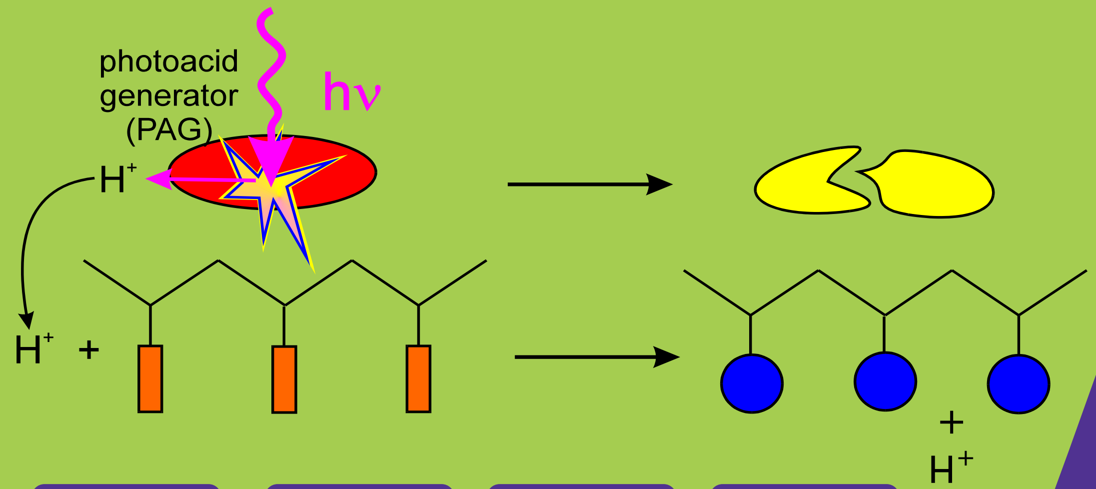
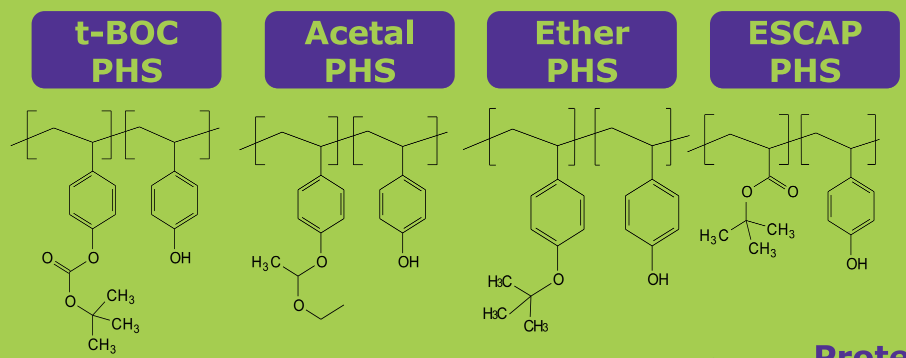
PFAS in Photolithography
Chemically Amplified Photoresists





Protective Group Activation Energy [2]

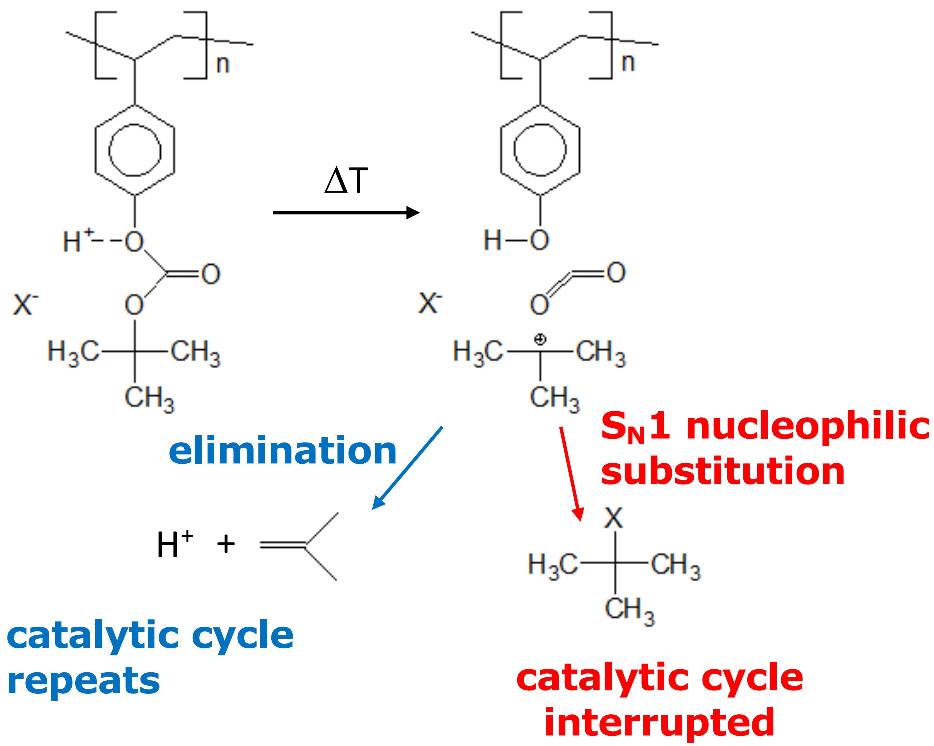
Influence of Activation Energy on Performance: [1]

➔ higher resolution
➔ reduced defectivity
➔ higher stability
➔ shorter tact time
➔ reduced production cost

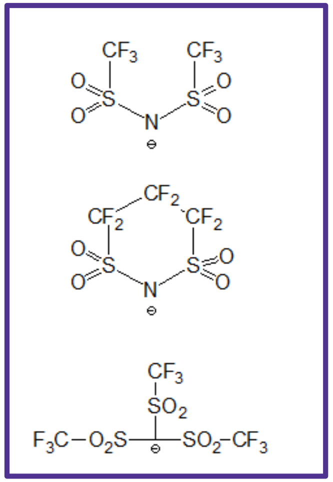
[1] H. Ito, "Chemical Amplification Resists for Microlithography", *Adv. Polym. Sci.,* Vol 172 (2005).

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

PFAS in Photolithography
Photo Acid Generators (PAG) for Chemically Amplified Photoresists

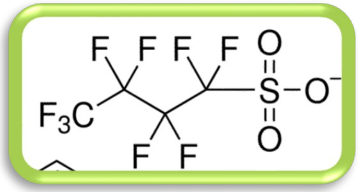


PAG anion	nucleophilic	other issues
PF_6^-	no	dopant
AsF_6^-	no	toxic
SbF_6^-	no	toxic
Cl^-, Br^-, I^-	yes	---
$R\text{-}SO_3^-$	no	---



$F_3C-SO_3^-$	Triflate
$F_9C_4-SO_3^-$	Nonaflate
$F_{17}C_8-SO_3^-$	PFOS

"Work Horse" of semi-conductor industry

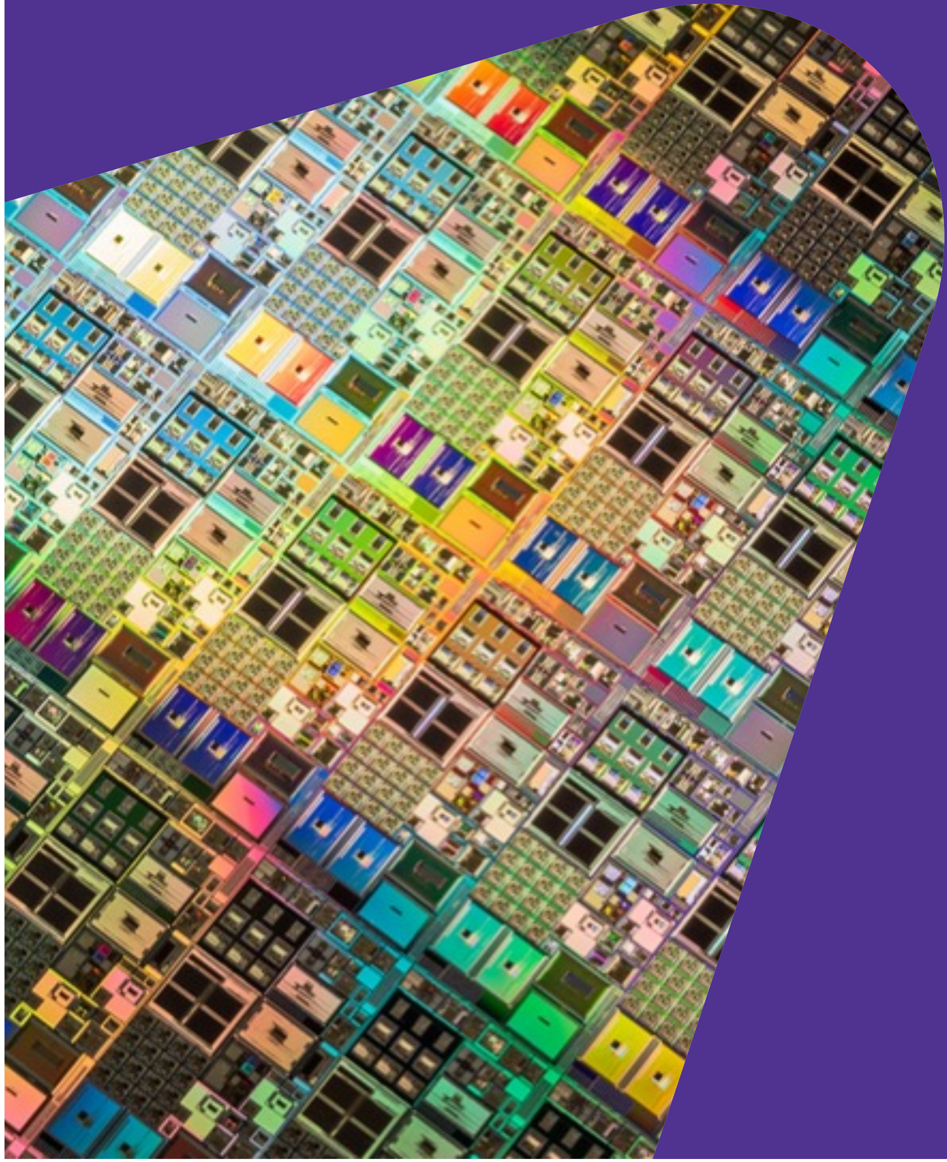


C. K. Ober, F. Käfer, J. Deng, "The essential use of fluorochemicals in lithographic patterning and semiconductor processing", *J. Micro/Nanopattern. Mater. Metrol.* **2022**, *21*(1), 010901.

Where are PFAS materials used in Semiconductor Photolithography?
Whenever possible we aim to replace PFAS in Semi applications

PFAS use application	Function	Replacement status
Photoacid Generators (PAGs)	• Precursor for the photoacid catalyst needed for CARs and BARCs	Mid-Term
Photoresists – polymers	• Control pattern profile in EUV	Mid-Term
EUV anti-collapse rinses	• Prevent pattern collapse	Available
Top anti-reflective coatings (TARCs)	• Control of thin film interference effects in resists	Mid-Term
Immersion barriers (immersion topcoats)	• Protection of the resist from immersion liquid and of the exposure tool from contamination • Prevent water film pulling and resist component leaching in immersion topcoats	Difficult
Surfactants	• Improved coating uniformity in photoresists and BARCs	Available
Barrier Layer Polymers (PBO/PI)	• Provide electrical, thermal, and mechanical protection for the semiconductor device • Also protects the device components from the impact of moisture	Mid-Term

Merck has R&D programs in all product categories that we are servicing today



04

(Bio)degradable fluorosurfactants

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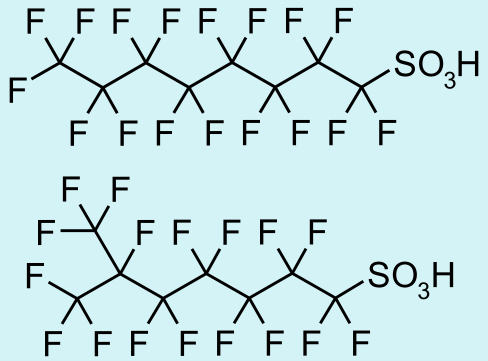
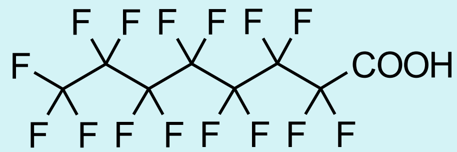
Fluorosurfactants



Perfluorooctane sulfonic acid (PFOS)



Perfluorooctanoic acid (PFOA)

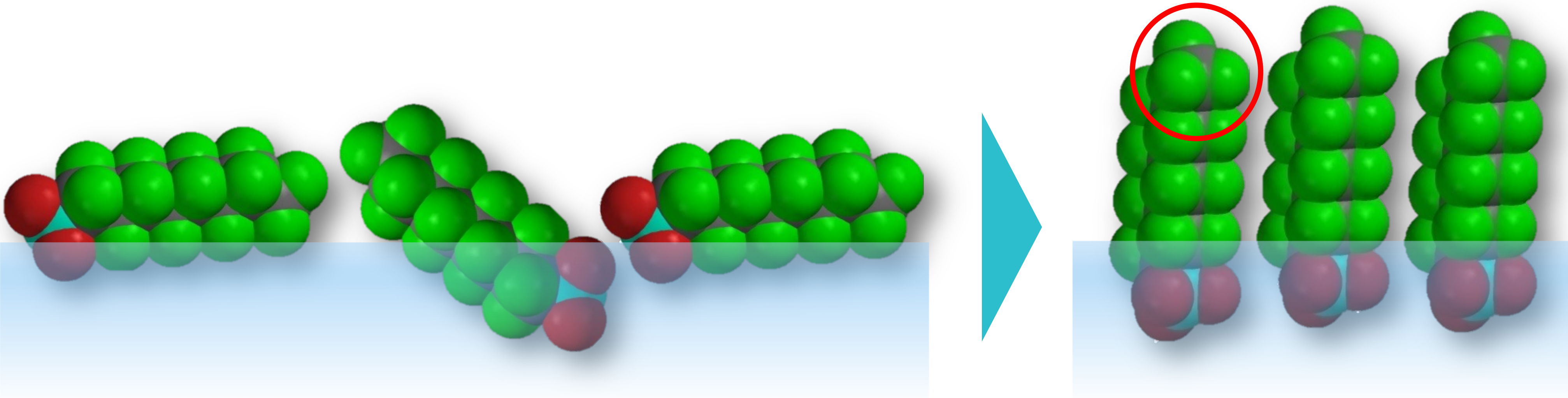
- Unique property profile: provides surfaces with **ultra-low surface energies** at lowest concentration; not only **hydrophobic** but also **oleophobic**
- Until the early 2000s widely used as a **all-purpose surfactant**

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)

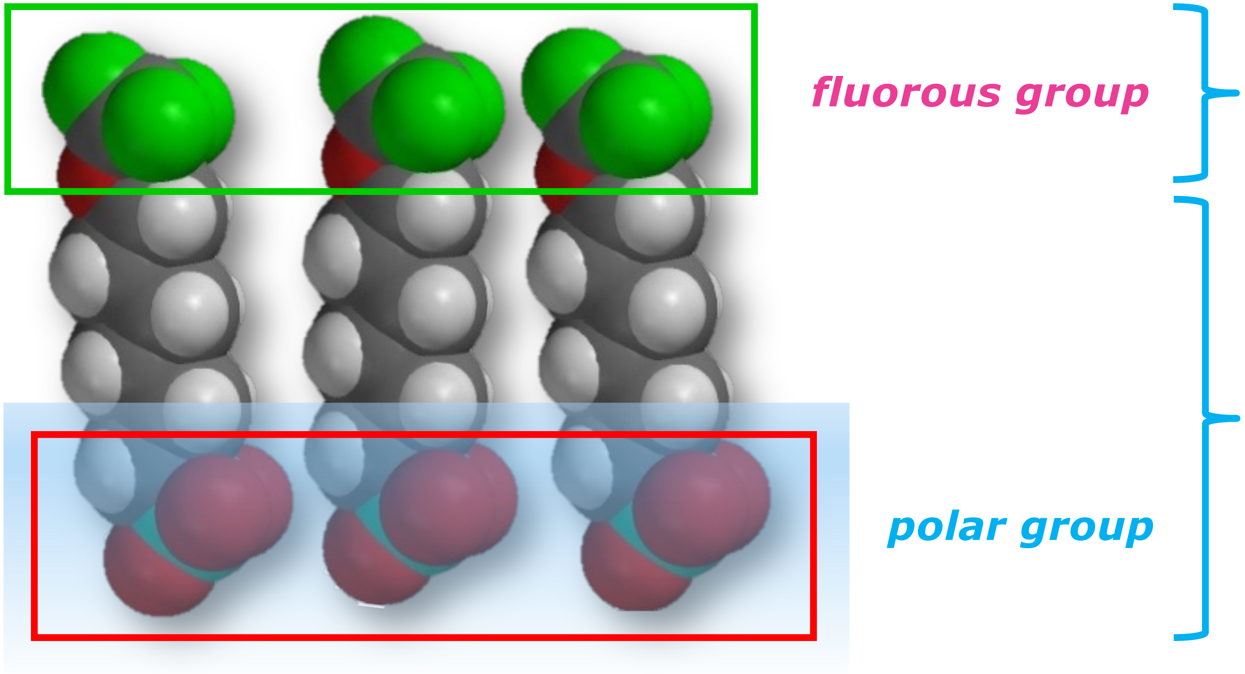
Fluorosurfactants – Replacement Strategies
Short, Labile Terminal Perfluoroalkyl Moiety

- In a surfactant monolayer only the **ω-trifluoromethyl group** of a perfluoroalkyl surfactant is really exposed to the water-air interface, contributes disproportionally to to performance
- **Small fluorous terminal group** give (per)fluorosurfactant-like performance at least in higher concentration



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

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



mineralizable

- short fluorocarbon head group

(bio)degradable

- hydrocarbon moiety
- via β-oxidation

M. Peschka, N. Fichtner, W. Hierse, P. Kirsch, E. Montenegro, M. Seidel, R. D. Wilken, T. P. Knepper, *Chemosphere* **2008**, *72*, 1534-1540 (doi: 10.1016/j.chemosphere.2008.04.066)

Design for Degradability

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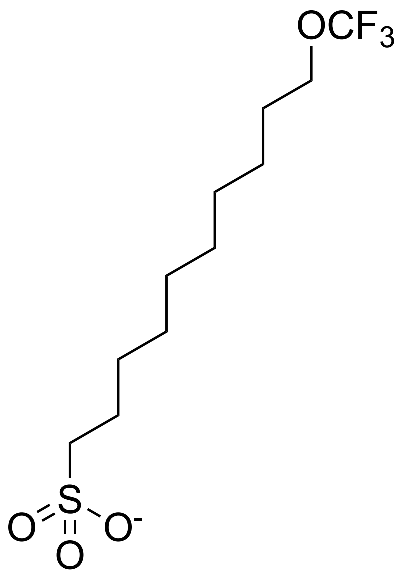

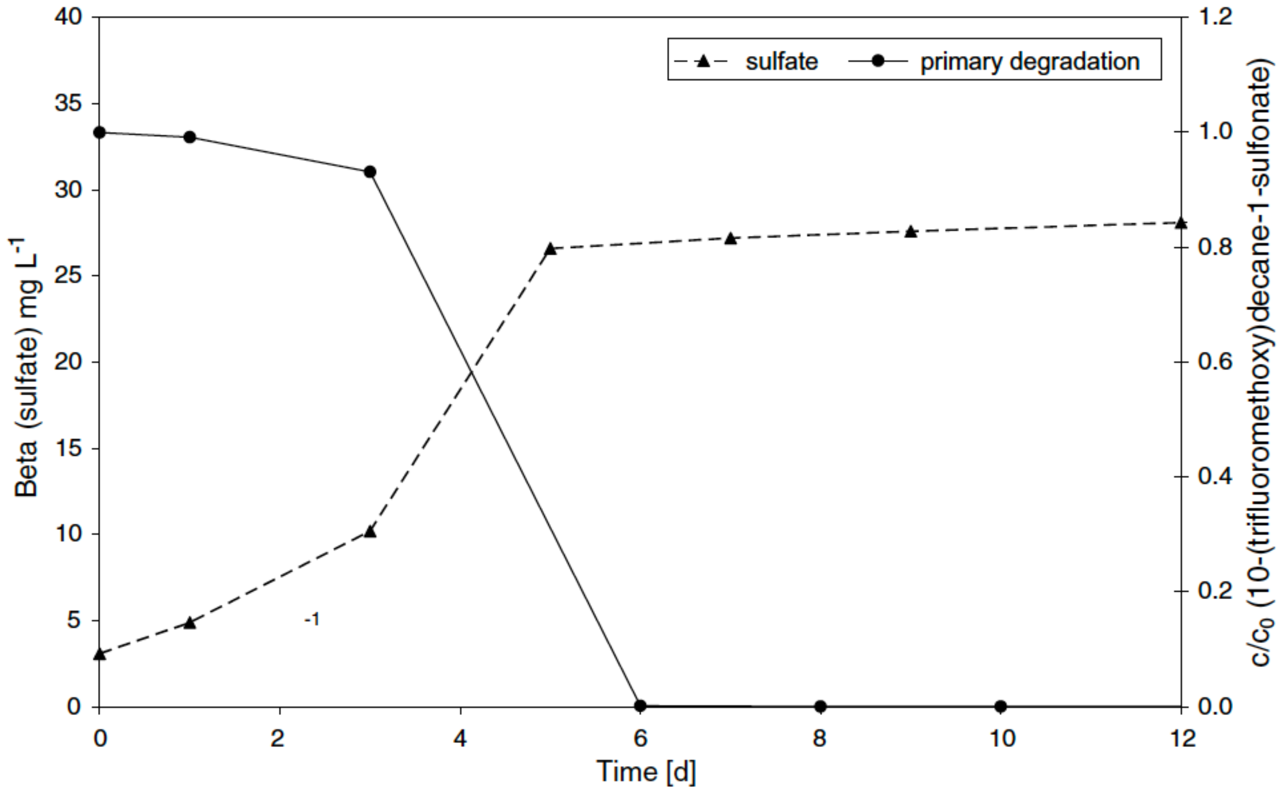

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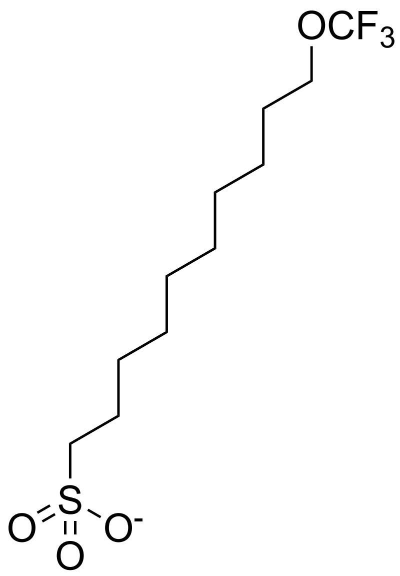

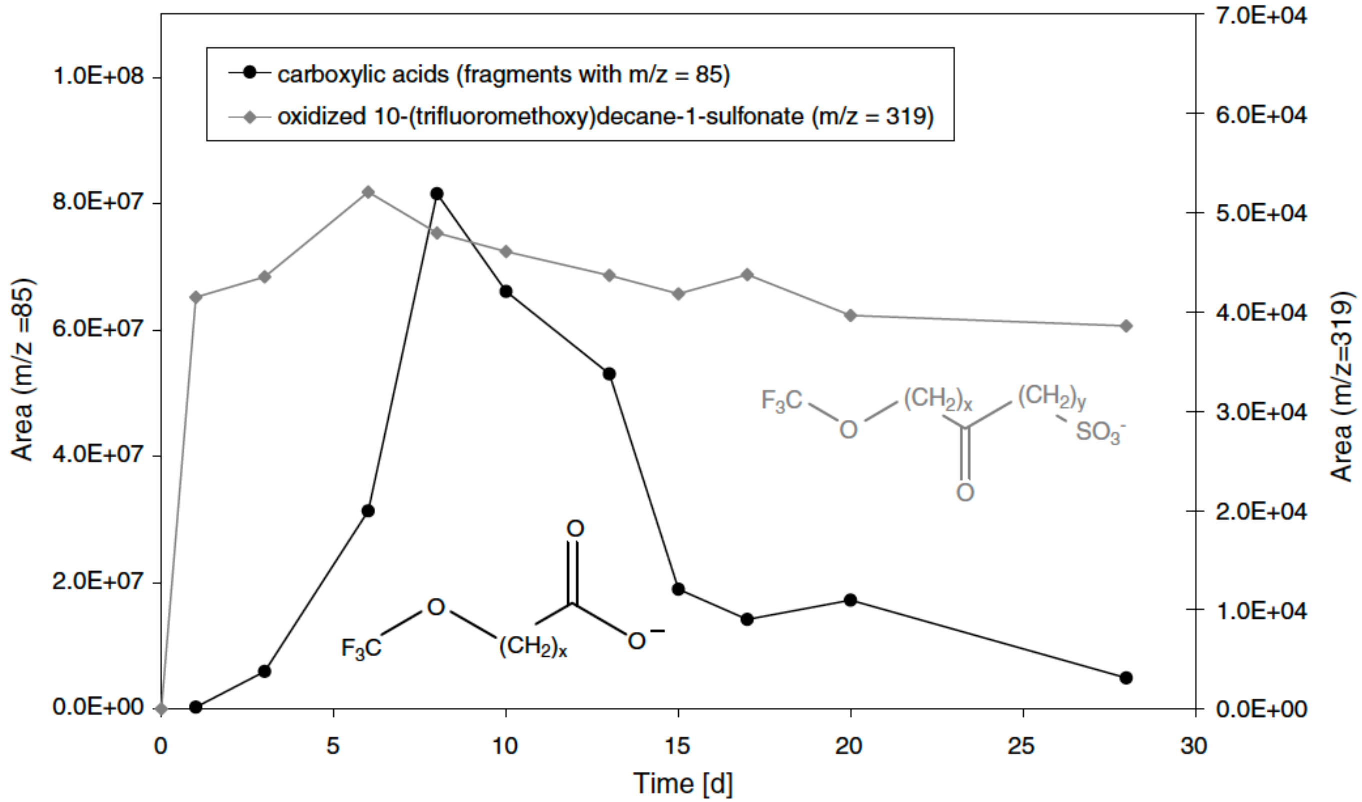

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