PFAS Replacement in the Semiconductor Industry

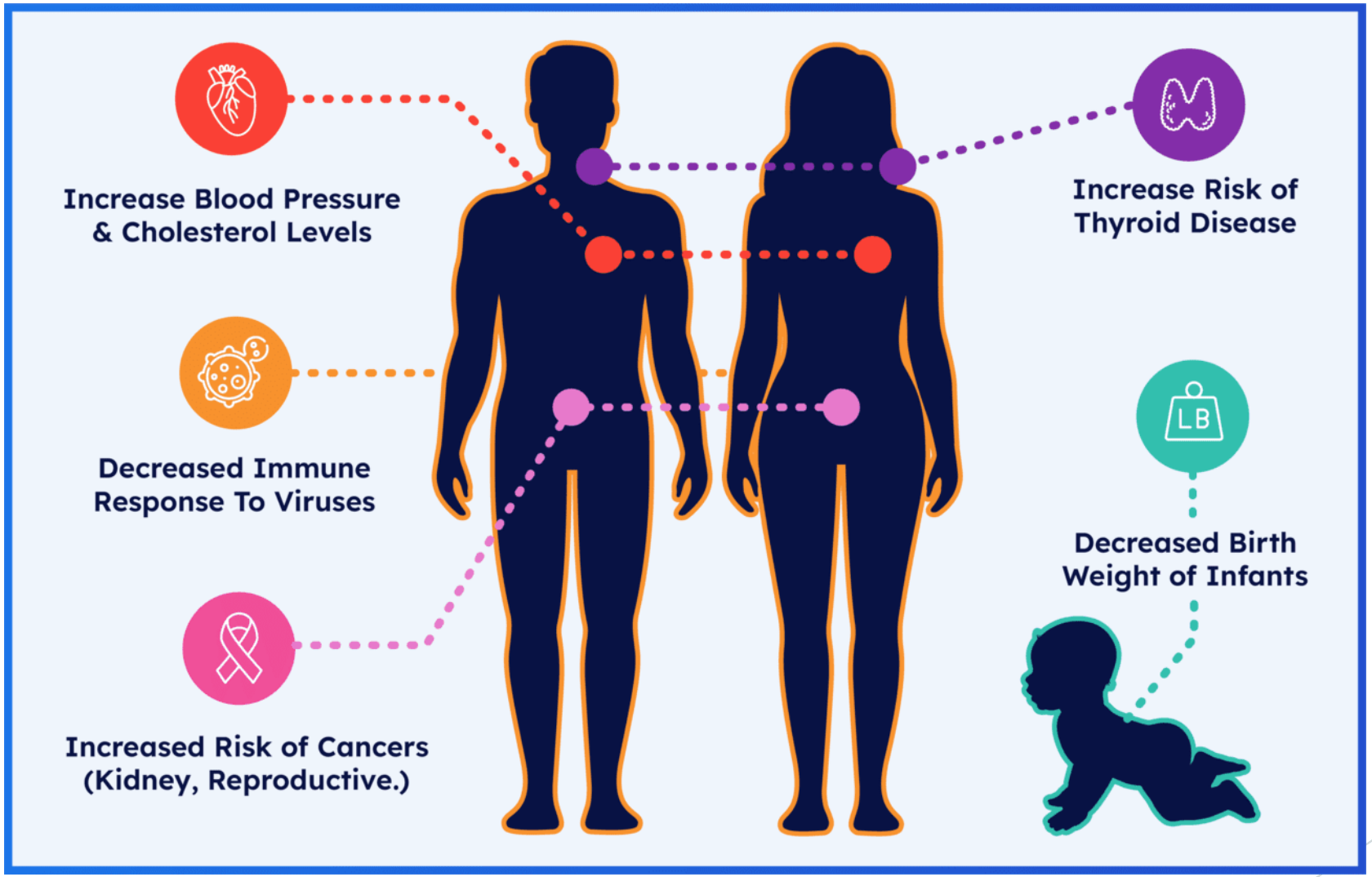
April 12, 2023

PFAS almost everywhere!

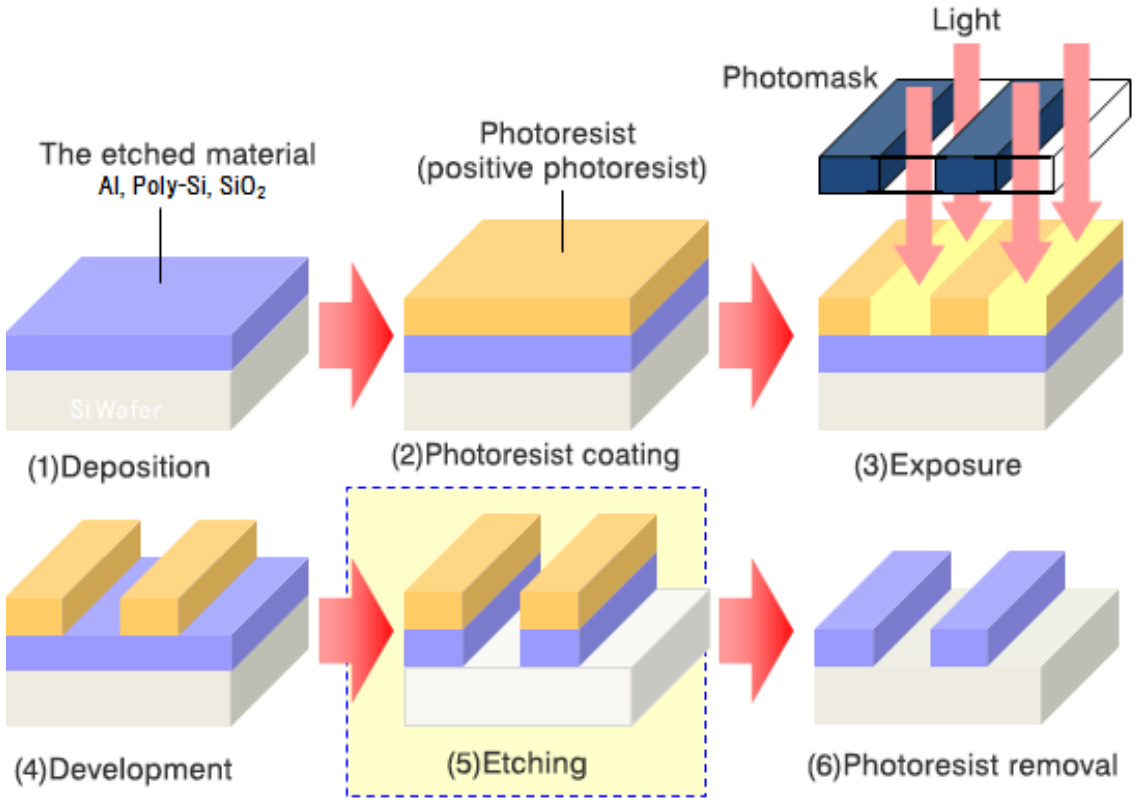
Poly and Perfluoroalkyl substances

- Used in industry and consumer products worldwide since the 1950s
- Food packaging, carpets, grease, Omniphobic textiles, nonstick pans, firefighting foams, and numerous other applications
- Highly toxic, persistent forever chemicals

PFAS Dangers



PFAS surfactants in the semiconductor Industry



PFAS surfactants:

- Increase the wettability of the etching solution
- Effective at low concentrations
- Used for wetting complex geometries of the substrates

Problem Statement

- **Transene Inc.** – a Massachusetts-based supplier of chemical etchants, photoresists, dielectrics, etc. for the electronics and aerospace industry
- PFAS is used as a surfactant to improve the wettability of the chemical etchants

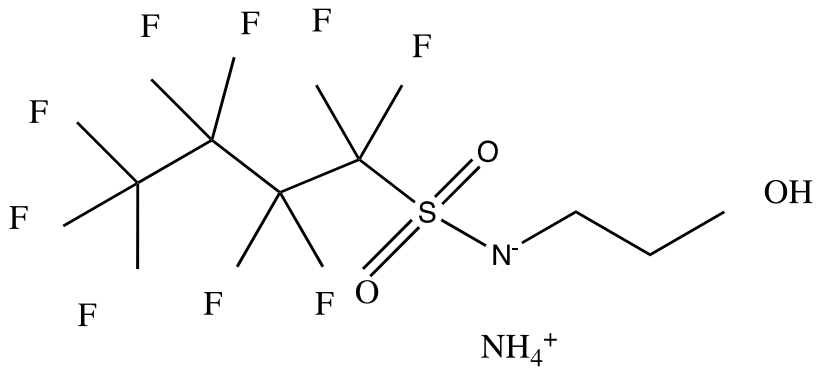
- The alternative surfactants must:

  - **Be compatible with**: Strong acidic/oxidizing solutions – nitric acid, phosphoric acid, etc.
  - **Reduce the etchant's surface tension:** Etching solutions' surface tension reduction should be comparable to PFAS surfactants for better wettability of the substrate (less than 0.1 wt.% consumption)
  - **Be less hazardous and toxic (No sodium Ions)**
  - **Stability**: > 1-year shelf life

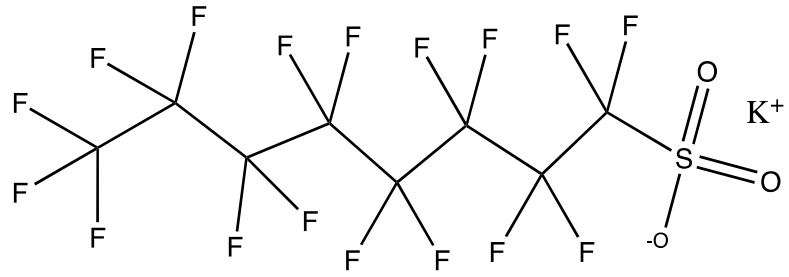
Etching Solutions

Parameter	Buffered Oxide Etchants (BOE)	Chrome Etchant	PAN	TMAH
Composition	NH_4HF_2 : HF mixture **6:1**	Ceric ammonium nitrate + acid (perchloric/nitric/ acetic)	Phosphoric, Acetic & Nitric Acids	Tetramethyl ammonium hydroxide (2.38%)
pH	pH = 3-5	pH = 3-4	pH < 1	pH =13-14
Color	Colorless	Orange	Colorless	Colorless
PFAS used	Novec 4200	FC95	Novec 4300	Novec 4200
Substrate	Glass	Chromium	Aluminum	Photoresist

PFAS surfactants



NOVEC4200



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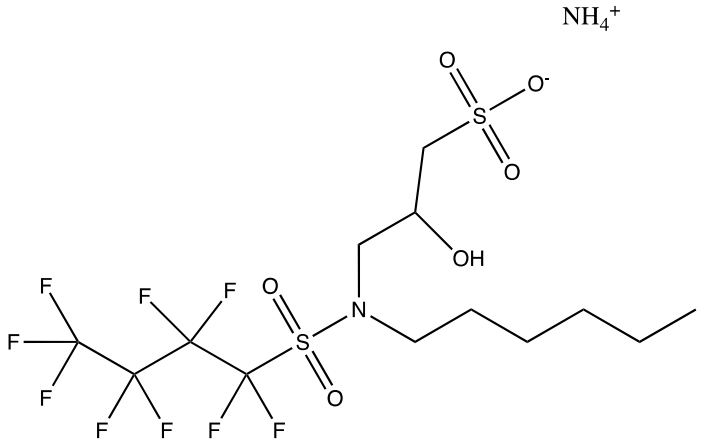


FC-95

Replacement Methodology

1) HLB Values

2) Surfactant-Etchant compatibility test

3) Etchant Surface tension/CMC

4) Measuring SFE of the substrate &

The Contact angle of etchant-substrate

5) Toxicological Measurements

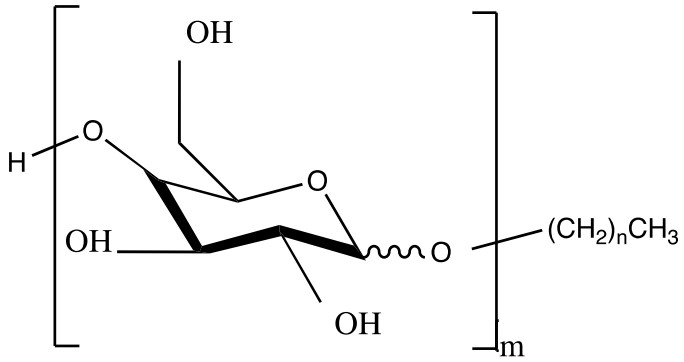
6) Industrial Trial

1) Hydrophilic-Lipophilic Balance

- HLB value, a metric for comparing surfactant performance in a solution
- Ranging from 0 to 20, higher HLB shows higher water or polar media solubility
- Etching Solutions are aqueous (up to 75% for TMAH, BOE, and chrome etchants)
- or highly polar (PAN etchant which is a mixture of phosphoric acid, acetic acid, and nitric acid)
- PFAS surfactants are highly soluble in etchants
- Alternatives must perform similarly
- Having HLB values of 13 and above are desirable (Primary criterion)

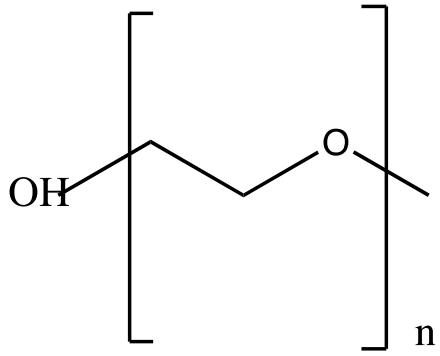
Potential alternatives: No fluorine, HLB>13

Alkyl polyglucosides



BG-10, CG-50, CG-110,…

Polyoxyethylenes

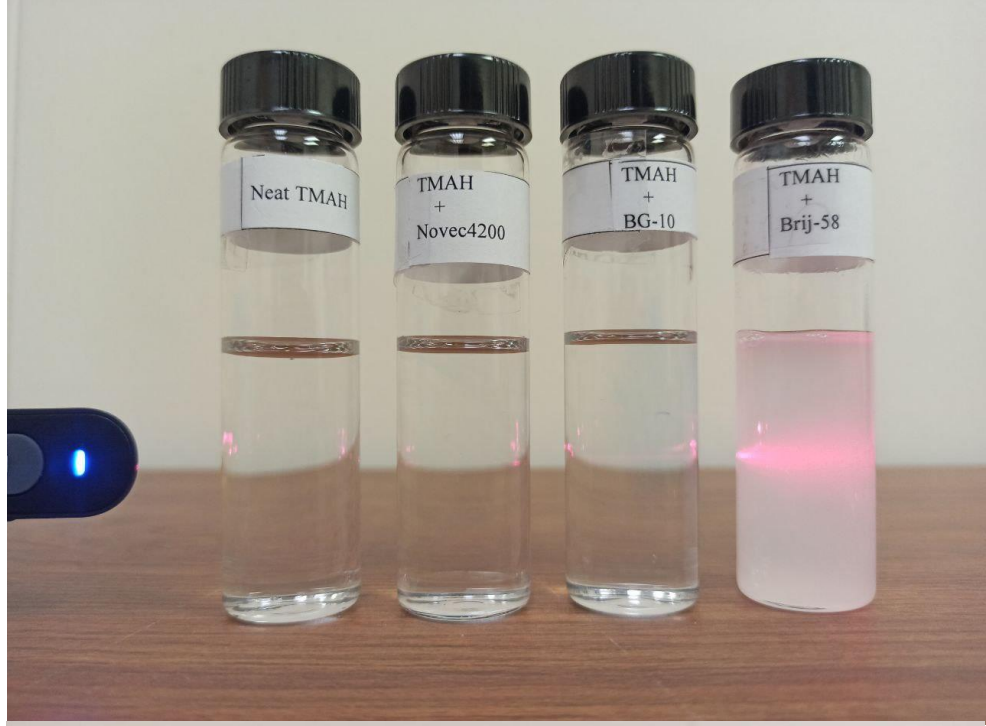


$CH_2(CH_2)_mCH_3$

Brij-35, Brij58, Brij S100, …

2) Compatibility test:

- PFAS surfactants are highly compatible with etching solutions
- We conducted a three-month compatibility test
  - Solutions of 0.1 and 0.01wt.% of the alternative surfactants in the etching solutions
- Maintaining a clear solution without any observation of phase separation was the desired result for indication of better compatibility



Top: left to right: Neat TMAH etching solution, stable TMAH etching solution with 0.01 wt.% of (PFAS surfactant Novec 4200, safer alternative BG-10), and TMAH solution with Brij 58 (incompatible)

Bottom: left to right: Neat chrome etchant, stable chrome etching solution with 0.01 wt.% of (PFAS surfactant FC-95, safer alternatives Brij 35, and Brij S100) and chrome solution with Brij 58 (incompatible)

Compatibility test results

Parameter	Buffered Oxide Etchants (BOE)	Chrome Etchant	PAN	TMAH
Composition	NH_4HF_2: HF mixture 6:1	Ceric ammonium nitrate + acid (perchloric/nitric/ acetic)	Phosphoric, Acetic & Nitric Acids	Tetramethyl ammonium hydroxide (2.38%)
pH	pH = 3-5	pH <1	pH < 2	pH =13-14
Color	Colorless	Orange	Colorless	Colorless
PFAS-based surfactant	Novec 4200	FC95	Novec 4300	Novec 4200
Substrate	Glass	Chromium	Aluminum	Photoresist
Compatible Alternative Surfactant	CG-50	Brij 35 Brij S100	BG-10	BG-10

3) Surface tension measurements

- According to the data obtained from the compatibility test, PFAS and alternative surfactants were added to etching solutions in different concentrations (0.01 to 2 wt.%)

- Du Nüoy ring method as described in ASTM D1331-11 ‘Standard Test Methods for Surface and Interfacial Tension of Solutions of Surface-Active Agents’- Method A

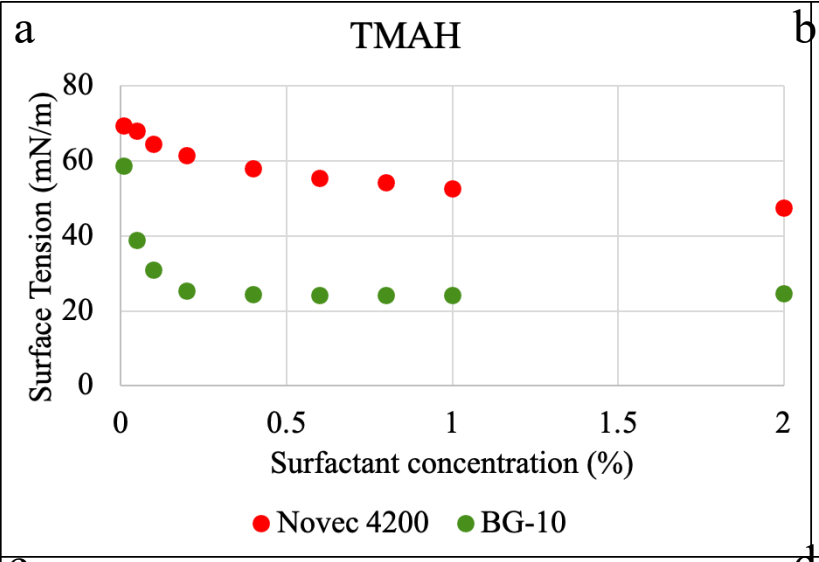
- KSV Sigma 70 surface tensiometer that was calibrated with deionized water

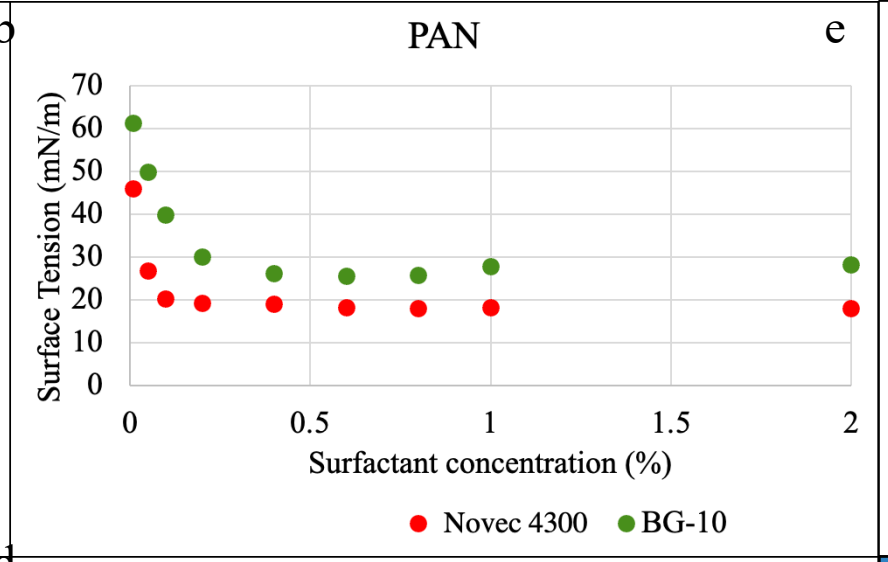
Critical micelle concentration (CMC)

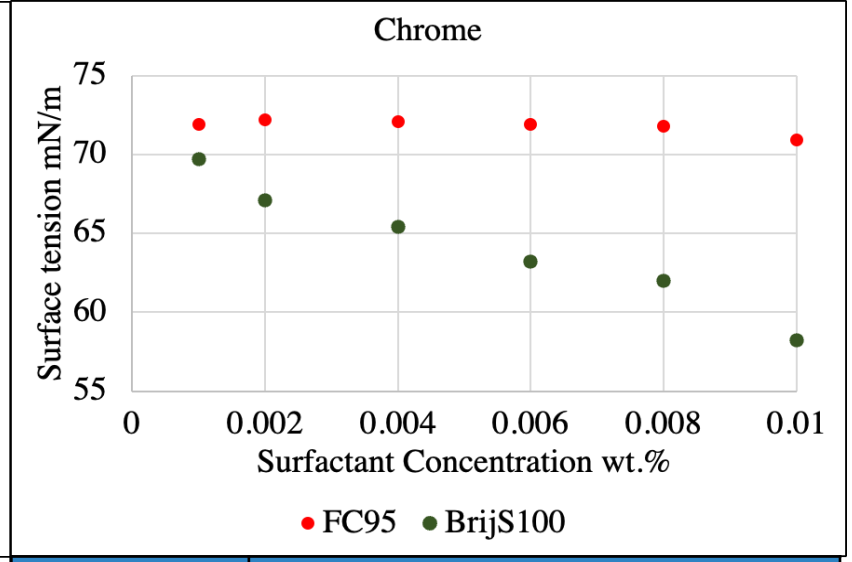
- CMC: the intersection of the baseline of lower surface tension and the slope where surface tension declines linearly in the surface tension plot vs. the surfactant concentration.

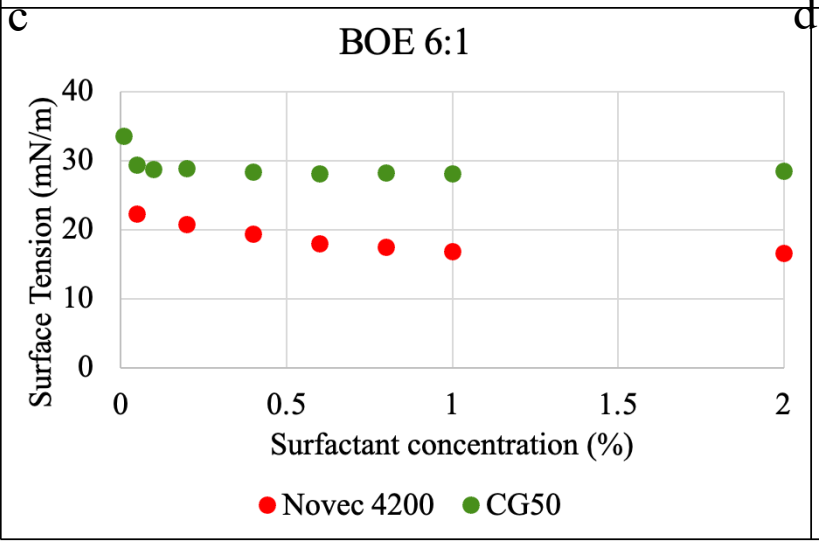
- At the CMC of a surfactant, the surface tension of the solution ceases to decrease

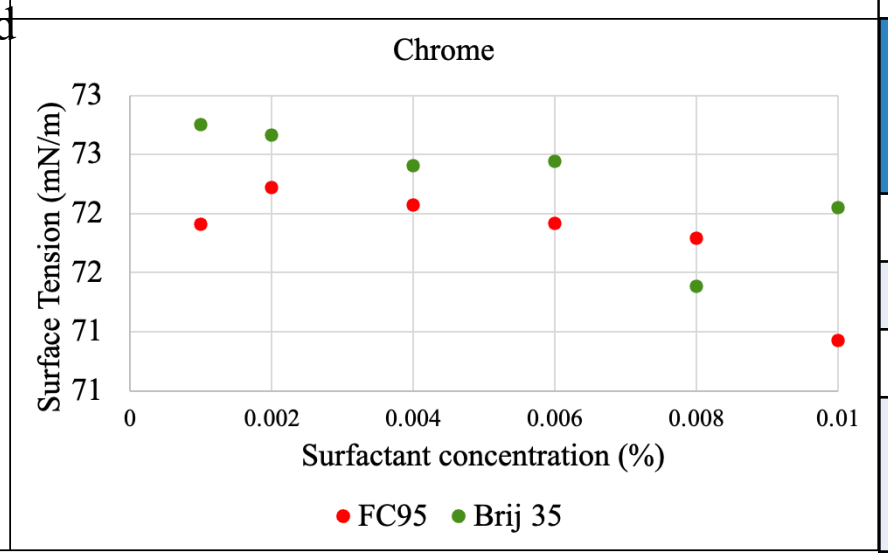
- Less CMC can be a criterion of less consumption for surfactants











Etchant	CMC (mg/ml)			
	PFAS		Alternative	
TMAH	Novec 4200	5.33	BG10	3.21
PAN	Novec 4300	6.14	BG10	4.72
BOE	Novec 4200	5.13	CG50	1.90
Chrome	FC-95	0.02	Brij35 Brij S100	0.04 0.1

The surface tension of the etching solution in various PFAS and Alternative surfactant concentrations for (a). TMAH (b). PAN (c). BOE 6:1 (d) & (e). Chrome etching solutions

CMC values for PFAS and alternative surfactants in the different etching solutions

Surface tension and CMC Results

- Bio-based surfactant BG-10 outperformed PFAS surfactant Novec 4200 in surface tension reduction of the TMAH etching solution (S.T from 60 to 21 Mn/m)
- BG-10 in PAN and CG-50 in BOE etchants were less effective in the reduction of the surface tension but the surface tension reduction for both alternatives was comparable to PFAS (Proceed to industrial trial)
- Polyoxyethylene-based surfactants, Brij-35, and Brij S100, also effectively reduced the surface tension, Brij S100 outperformed PFAS FC-95 (0.01 wt.% of Brij S100 reduces the surface tension of the chrome etchant from 74.6 to 57 mN/m
- To investigate the effect of the surfactants on the wettability of the etching solutions on selected substrates, the contact angle measurements were provided
- CMC concentration of all surfactants were used for contact angle measurements

Contact angle measurements for PFAS and Alternatives

Substrate	Etchant	PFAS surfactant	Alternative	SFE* of substrate (mN/m)	Contact angle etchant and substrate at CMC of surfactant	
					PFAS	Alternative
Al-oxide coated	PAN	Novec 4300	BG-10	53.9	27.6	33.4
Chrome-coated	Chrome	FC-95	Brij 35	72.9	-	-
			Brij S100			
Photoresist-coated	TMAH	Novec 4200	BG-10	35.4	61.1	32.1
Glass	BOE	Novec 4200	CG-50	61.52	30.7	31.3

Alternative surfactants improve the wetting of the substrates by etching solutions, comparable to PFAS

Comparative Hazard Assessment

Color	Level of Hazard	Score Range
	Low (L)	2.0 to 3.9
	Medium (M)	4.0 to 5.9
	High (H)	6.0 to 7.9
	Very High (VH)	8.0 to 10.0

According to P2OASys alternative surfactants are less toxic as compared to the PFAS surfactants

Chemical	P2OASys Score 10 – Very High Hazard 2 – Low Hazard	Role
3M Novec 4200 Perfluoroalkyl substance (CAS# 484024-67-1)	7.3 High Hazard	Baseline, PFAS chemical to be replaced
Brij 35 Laurel polyethylene glycol ether (CAS# 9002-92-0)	5.9 Medium Hazard	Safer alternative to evaluate
Brij S100 Polyoxyl stearyl ether (CAS# 9005-00-9)	5.3 Medium Hazard	Safer alternative to evaluate
Triton BG-10, Triton CG-50, and Triton CG-110 Decyl octyl glucoside (CAS# 68515-73-1)	4.5 Medium Hazard	Safer alternative to evaluate

Industrial Trial

- Transene Company, Inc. currently has over 50 customers using PFAS surfactant replacements in their semiconductor etching processes
- The safer alternatives are finding great success at the academic and government research level
- Stability and etch performance appear to be identical between the PFAS products and the alternative products without PFAS

Conclusion

- A novel methodology to identify and evaluate safer and effective alternative surfactants to replace PFAS surfactants was developed
- Surface chemistry, surfactants' intrinsic chemical and toxicological properties, and interfacial interactions between etching solutions and solid substrates were used.
- This methodology of PFAS surfactant replacement was utilized for four types of etching solutions (TMAH, BOE, PAN, and chrome solutions), containing three PFAS surfactants in etching products named Novec 4200, Novec 4300, and FC95.

Conclusion

- Safer and effective alternatives were investigated through HLB values, CMC analysis, compatibility tests, measurement of contact angles in different substrates with different surface free energies, and chemical hazard assessment.

- Alkyl polyglucoside surfactants of BG-10 and CG-50 were selected as the alternatives in TMAH, PAN, and BOE etching solutions to replace Novec4200 and Novec 4300 PFAS surfactants

- Polyoxyethylene surfactants, Brij 35 and Brij S100 were determined to be viable alternatives for FC95 in the chrome etching solution.

Conclusion

- Safer alternative Surfactants demonstrated compatibility with etching solutions and simultaneously reduced the etchants' surface tension to improve the substrates' wetting capabilities.
- Toxicity comparison suggested less hazardous human health effects for the alternatives as compared to the PFAS surfactants.
- Eventually, industrial trials were carried out on the safer alternatives, and currently, approximately 50 semiconductor manufacturers, governments, and educational consumers are using the safer and effective non-PFAS alternatives in the etching solutions

Acknowledgements

- Toxics Use Reduction Institute for funding this project
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Questions

Thanks for your attention