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# Safer and effective alternatives to perfluoroalkyl-based surfactants in etching solutions for the semiconductor industry

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ABSTRACT

Surfactants based on poly and perfluoroalkyl substances (PFAS) such as Fluoroalkyl sulfonamide, fluoroalkyl sulfonyl amino propane sulfonic acid, and potassium perfluorooctane sulfonate surfactants are widely used in etching solutions in the semiconductor industry to improve the wetting characteristics of the etchant and substrates.

Their excellent stability in strongly acidic, alkaline, and oxidizing etching solutions such as Tetramethyl ammonium hydroxide (TMAH), perchloric acid/ceric ammonium nitrate aqueous solution (chrome), ammonium hydrogen fluoride solution, or buffered oxide etchant (BOE) and a mixture of phosphoric, acetic, and nitric acid etchant (PAN), has warranted their continuous use as a surfactant.

The toxicity and extremely high persistence of PFAS necessitate their replacement with less toxic and effective alternative surfactants.

A generic methodology is described for the identification of safer alternative surfactants and the experimental validation of properties to facilitate the drop-in replacement of these safer surfactants in etching solutions for the semiconductor industry. Hydrophilic-Lipophilic Balance (HLB) values, critical micelle concentration (CMC), compatibility, and wetting characteristics of etchants were analyzed on substrates relevant to the semiconductor industry.

Biobased *BG10* alternative surfactant outperformed PFAS surfactant in improving the wetting characteristics of the TMAH etchant on substrates of interest as evidenced by the significantly lower contact angle. The wetting characteristics of the PAN and BOE etchants containing *BG10* and *CG50* surfactants were comparable to PFAS surfactants.

Toxicity comparisons indicated that these alternatives are far less hazardous to human health than PFAS. These safer alternatives have been tested successfully by over 100 semiconductor companies. These companies have provided positive feedback with no reported deleterious effects on the final products. This successful approach opens new possibilities for the replacement of PFAS in numerous other applications where PFAS is commonly used as a surfactant. Using this methodology, alkyl polyglucosides with trade names *BG10* and *CG50* and polyoxyethylene surfactants of *Brij35* and *BrijS100* were identified as alternatives to PFAS surfactants.

## 1. Introduction

**P**oly and **P**er-**f**luoro**a**lkyl **s**ubstances (PFAS) refer to a large class of more than a hundred distinct compounds that contain at least one fluorine atom (Buck et al., 2011). Due to their unique characteristics, PFAS are widely used in the production of various consumer goods such as food packages, firefighting foams, omniphobic textiles, paints, sealants, and pesticides (Glüge et al., 2020; Kissa, 2001).

Fluorinated surfactants, which constitute a prominent subgroup of PFAS, consist of hydrophobic fluorinated chains and hydrophilic

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headgroups. The remarkable properties of PFAS surfactants stem from the high electronegativity, low polarizability, and reduced size of fluorine atoms, resulting in robust C–F bonds, feeble intermolecular forces within –CF2–, and potent hydrophobic interactions. As a consequence, these surfactants exhibit exceptional traits, such as high chemical and thermal stability, strong surface activity, high wetting ability, and incompatibility with both water and hydrocarbons (Kancharla et al., 2022). Fluorinated surfactants lower the surface tension of water (from around 72 mN/m to less than 16 mN/m) beyond the threshold at which hydrocarbon-type surfactants cease to function (Alexander et al., 2014). The hydrophobic group being extremely resistant to chemical attack, the fluorinated surfactants may be used in conditions where conventional surfactants do not survive (Gaines, 2022). Fluorosurfactants are far more expensive per unit volume compared to conventional hydrocarbon surfactants due to their high production costs (Farn, 2006), therefore, they are frequently used in situations where other substances cannot provide the desired performance or where PFAS can be used in much smaller amounts while still maintaining the same performance as a larger amount of a non-fluorinated chemical (Buck et al., 2012).

The many advantageous characteristics of PFAS have led to their extensive use as surfactants in etching solutions within the semiconductor industry (Ober et al., 2022) where PFAS surfactants are used to improve the wettability of the etching solutions and the substrates while remaining stable in a strong acidic to alkaline etching solutions (Tansel, 2022).

However, PFAS exhibit exceptional stability for extended periods, potentially spanning hundreds of years (Mahinroosta and Senevirathna, 2020), which accounts for their ubiquitous occurrence in various disposable products like cosmetics (Whitehead et al., 2021), agricultural commodities (Scher et al., 2018), and abandoned food packages (Cousins et al., 2020). Additionally, PFAS have been detected in different environmental segments, including drinking water (Quiñones and Snyder, 2009), rainwater, and groundwater (Guardian et al., 2020; Daly et al., 2018), promoting bioaccumulation and biomagnification in many existing species (Genualdi et al., 2022) as well as humans (Carrizosa et al., 2021; Zhou et al., 2021). Studies have investigated the health effects of human populations unknowingly exposed to PFAS, with complications ranging from premature skin aging (Mousavi et al., 2021), malignancies, higher cholesterol levels, and impaired immunological and liver functions, to serious birth abnormalities (Bonefeld-Jørgensen et al., 2014).

Numerous industries have transitioned from utilizing long-chain fluorosurfactants, specifically perfluoro octane sulfonic acid (PFOS), to shorter-chain fluorinated surfactants in order to decrease the persistence of the surfactants (Wang et al., 2013). Nevertheless, this substitution strategy is not sustainable given that the shorter-chain per-and polyfluoroalkyl substances (PFAS) are also deemed hazardous to human and environmental health (Brendel et al., 2018). Further studies have demonstrated that short-chain PFAS are even more mobile in the environment and more difficult to remove from drinking water than long-chain PFAS (Sun et al., 2016; Cousins et al., 2016). The revelation of these human health problems has prompted the Stockholm Convention to prohibit the manufacture of long-chain PFAS (Radley-Gardner et al., 2016), which highlights the urgency of finding safer alternatives for these substances.

In this study, the aim is to develop a methodology for the replacement of PFAS surfactants utilized in etching solutions in the semiconductor industry. In pursuit of this objective, the safer alternatives identified should perform similarly to the PFAS surfactants that are being replaced.

The hydrophilic-lipophilic balance (HLB) of surfactants was considered the primary criterion for the preliminary selection of potential replacements for PFAS. (Sassi et al., 2020). The surfactants must be compatible with the etching solutions for prolonged times. Therefore, a three-month compatibility test was performed to assess stability in and compatibility with etching solutions. Subsequently, the surface tension of the etching solutions containing alternative surfactants was measured, to evaluate their ability to reduce the surface tension of the etchants, effectively. The critical micelle concentrations were calculated from the surface tension versus concentration plot. This was compared to etchant solutions containing PFAS as the surfactant (Perinelli et al., 2020). The main objective of using surfactants in the etching solutions in the semiconductor industry is to improve the wettability of the etchants and substrates. Therefore, contact angle measurements were carried out to evaluate the performance of the alternative surfactants in improving the wettability of substrates. (Nasalapure et al., 2021; Abdullah et al., 2022). Since the replacements are aimed to be less toxic than PFAS surfactants, preliminary toxicity assessment comparisons were carried out using the P2OAsys toxicity assessment tool. The safer alternative was designed to be a 'drop-in' replacement for PFAS surfactant that can be utilized at the industrial scale. Industrial trials were performed using a quality-tracking method with manufacturers in the semiconductor industry - the main consumers of these etching solutions.

Fig. 1 illustrates a generic methodology for the identification of safer and effective alternative surfactants for etching solutions in semiconductor industry, based on the fundamental characteristics of the surfactants employed and their intended application as described in the method section.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Etching solutions

Four different types of etching solutions were used to examine the alternatives for PFAS surfactants. Tetra methyl ammonium hydroxide or TMAH (2.38% w/v aqueous solution) with the trade name of *Novo Developer 342*, prepared with a low metal grade TMAH concentrate from Transene Company Inc. with a weight ratio of 25% w/w was used.

Perchloric acid/ceric ammonium nitrate aqueous solution, commercially available as *Chrome Etchant 9051*, prepared by Transene Company Inc., with the perchloric acid content of 5.2% w/w from ACS Reagent and ceric ammonium nitrate content of 7.5% w/w from Ganzhou Wanfeng Advanced Materials Technology Co., Ltd was also included.

Buffered oxide etchant commercially available as *BOE Etchant* is referenced as BOE X: Y where X is the volume ratio component of Ammonium Fluoride 40% (w/w) (Transene low metal grade), and Y is the volume ratio component of Hydrofluoric Acid 49% (w/w) (Transene low metal grade) was used. In this study, the alternative surfactants were tested in a 6:1 vol ratio.

PAN Etchants, or Phosphoric Acid-Acetic Acid-Nitric Acid solutions, was used with the trade name *PAN Etch Special,* with the ratio of 17-1-1-2, where numeric values are based on volumes of digit 1: 85% Phosphoric Acid (w/w) Transene low metal grade, digit 2: Acetic Acid Transene low metal grade, digit 3: 69–70% Nitric Acid (w/w) Transene low metal grade, digit 4: Deionized Water were all used as received.

#### 2.1.2. PFAS surfactants

The PFAS-based surfactants Fluoroalkyl sulfonamide (*Novec 4200*), fluoroalkyl sulfonyl amino propane sulfonic acid (*Novec 4300*), and potassium perfluorooctane sulfonate surfactants (*FC95*) were all purchased from 3M Company and used as received.

#### 2.1.3. Alternative surfactants

Alkyl polyglucosides or APG-based surfactants - *Triton BG10, Triton CG50,* and *Triton CG110* were purchased from DOW Chemicals and were used as received. *Brij 35*, a lauryl polyethylene glycol ether-based surfactant, was obtained from ThermoFisher Scientific Company and was utilized without any further processing. Other polyoxyethylene surfactants *Brij 58* (polyethylene glycol hexadecyl ether) and *Brij S100* (polyethylene glycol ether of stearyl alcohol) were obtained from Sigma-

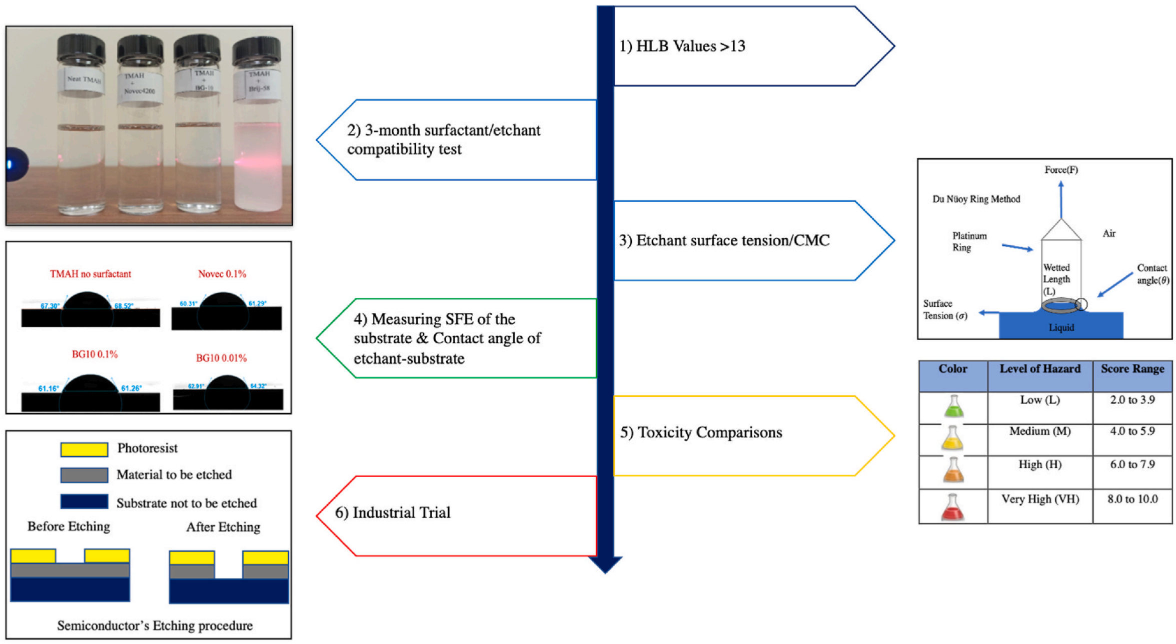



**Fig. 1.** Schematic of the methodology for finding safer and effective alternative surfactants for PFAS surfactants.

Millipore USA and were used as received.

*2.1.4. Semiconductor substrates*

Four substrates, commonly used in the semiconductor industry, were obtained to carry out the surface free energy measurements. Photoresist-coated silicon wafers, the aluminum oxide-coated and chromium-coated silicon wafers as well as the glass substrates were provided by Kemlab™ Inc., and Transene Company, Inc. respectively. The substrates were all used as received and were selected based on the recommendations of Transene Company Inc.

## 2.2. Test methods and parameters

*2.2.1. HLB values*

Hydrophilic-lipophilic balance (HLB) is one of the most commonly used metrics for comparing surfactants and their performance. The values range from 0 to 20 from highly lipophilic in the range of 0–6, and highly hydrophilic for higher than 13. The values for commercially available alternative surfactants that were investigated for this work have been obtained from technical data sheets of the vendor websites. Surfactants for etching solutions in semiconductor industries must be compatible with aqueous and polar systems. Therefore, for this work, surfactants with HLB values higher than 13 are chosen.

*2.2.2. Compatibility test*

A three-month compatibility test was carried out to make sure the alternative surfactants exhibit similar properties including stability in these etching solutions. For this purpose, etching solutions containing 0.1 and 0.01 wt% alternative surfactants were prepared. Maintaining a clear solution without phase separation was the desired result for ensuring compatibility. A semiconductor laser beam was passed through vials containing etching solutions with surfactant alternatives to observe if there was the scattering of light (due to turbidity) caused by potential incompatibility.

*2.2.3. Surface tension and critical micelle concentration (CMC)*

Surface tension measurements were conducted using the 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. Measurements were carried out at room temperature (24 °C) using a KSV Sigma 70 surface tensiometer that was calibrated with deionized water before use. Each test was repeated five times. The reference value for the interfacial tension of water/air at 24 °C is around 72 mN/m. Before use, the Du Noüy ring and the glass container were thoroughly cleaned by rinsing in deionized water, and finally, the ring was flame dried using a propane gas burner. Surface tension was measured three times for each concentration. The average error of <0.5 mN/m was regularly obtained. The CMC is calculated as the point where the baseline surface tension intersects with the linearly declining slope.

*2.2.4. Surface free energy (SFE) and wettability through contact angle measurements*

Owens-Wendt-Rabel-Kaelble (OWRK) method was utilized to calculate the surface free energy of the substrates. This was achieved by measuring the contact angle of multiple distinct liquids using ASTM D5946. This method sums up the polar dispersive components of the interaction (K. L. Mittal, 2009) and provides information on the overall surface free energy and its constituents.

The liquid surface tension, $\gamma_{LV}$, is the sum of a dispersive component ($\gamma_{LV}^{D}$ e.g., London dispersion forces) and polar component ($\gamma_{LV}^{P}$, e.g., hydrogen bonding) such that $\gamma_{LV} = \gamma_{LV}^{D} + \gamma_{LV}^{P}$. Likewise, the solid SFE, $\gamma_{SV}$, is the sum of dispersive and polar components such that $\gamma_{SV} = \gamma_{SV}^{D} + \gamma_{SV}^{P}$. The relationship between liquid surface tension, solid surface free energy, and the contact angle between the liquid and the solid is described by the Owens-Wendt-Rabel-Kaelble (OWRK) equation (K. L. Mittal, 2009):

$$\gamma_{LV}(1+\cos\theta) = 2\left[\left(\gamma_{SV}^{D}\gamma_{LV}^{D}\right)^{1/2}+\left(\gamma_{SV}^{P}\gamma_{LV}^{P}\right)^{1/2}\right]$$

where θ is the contact angle between the liquid and the solid. It should be noted that the polar and dispersive parameters used to calculate the surface free energy of the solid in equation 1, were determined by the Biolin Scientific apparatus. These were used in the OWRK equation to obtain the final surface free energy of the substrates.

It should be noted that the Photoresist-coated silicon wafer substrate is etched by TMAH etching solution, while etching of the aluminum oxide-coated silicon wafer is carried out using PAN etchant. The chrome etching solution is utilized to etch a chromium-coated silicon wafer and BOE etchant for the glass substrate.

To measure the contact angle of the etching solutions on substrates and estimate the surface free energy of the substrates, the Biolin Scientific Attension Theta Flex apparatus was used, and the ASTM D5946 test method was followed. Diiodomethane, glycerol, and deionized water were used to measure the surface free energy of the substrates.

*2.2.4.1. Statistical analysis of the contact angle measurements.* The contact angle measurements were subjected to statistical analysis to determine the significance of the observed variations. An initial one-way analysis of variance (ANOVA) (Zar, 2010) was employed to compare the means of the contact angles across the three groups of etching solutions with no surfactant, with PFAS surfactants, and with alternatives. ANOVA is a robust statistical technique used to assess differences between groups and determine the presence of statistically significant variations. Subsequently, post hoc comparisons were conducted using Tukey's Honestly Significant Difference (HSD) (Fowler et al., 1998), and a test significance level of $p = 0.05$ was adopted to establish statistical significance. Analyses were conducted using the statistical package SPSS v. 20.0.

### 2.2.5. Toxicological assessment

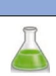
To evaluate the safety of the alternative surfactant chemicals, a chemical hazard assessment using the P2OASys tool was conducted. The P2OASys tool evaluates data from the following eight categories: acute human effects, chronic human effects, ecological hazards, environmental fate/transport, atmospheric hazards, physical properties, process factors, and life cycle factors.

Each category includes several subcategories. For instance, the "Acute Human Effects" category includes the following nine subcategories: inhalation toxicity, oral toxicity, dermal toxicity, respiratory irritation, dermal irritation, eye irritation, exposure limits, IDLH, and health. Under each subcategory, there are various endpoint options to be completed, for example, a toxicity value from animal studies, a GHS category, or an authoritative body's designation. The tool rates each category based on the information entered for each endpoint within the category. For subcategories that have multiple endpoints, the tool chooses the endpoint with the highest hazard score and assigns that score to the subcategory. At the category level, the tool calculates the average of the two highest hazard values from the subcategories. This average becomes the numerical rating for the category. The overall P2OASys product score is an average of each of the eight categories (Toxics Use Reduction Institute, 2021). This ranking is shown in Table 1.

## 2.3. Industrial trial

The performance of safer alternative surfactants was evaluated at the industrial scale in collaboration with Transene Company, Inc. The results were followed over several months in a quality-tracking program with consumers in the electronics industry. The quality-tracking procedure is a 'drop-in' method that involves the complete replacement of the PFAS surfactants with safer alternatives in a pass-or-fail approach. This means that if any key characteristics of the etching solutions including the wettability of the etchant and substrate, shelf-life, or even the physical appearance of the etching solution is impaired by using the PFAS-free surfactants, the alternative surfactant is considered to be a failure.

**Table 1**
P2OASys Scoring Scale.

| 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 |

# 3. Results

## 3.1. HLB values

HLB values for *BG10, CG50,* and *CG110* are above 13, and for *Brij 35, Brij 58* and *Brij S100* are 16.9, 15.7, and 18.8 respectively, as shown in Table 2.

## 3.2. Compatibility of alternative surfactants with various etchants

The results of a 3-month compatibility test are presented in Table 3, which examines the performance of surfactants used in etching solutions. PFAS surfactants remained transparent and clear throughout the test, indicating compatibility. *BG10* in PAN and TMAH, *CG50* in BOE and *Brij35,* and *BrijS100* in chrome etchant remained transparent and clear. As shown in Fig. 2, *Brij58* was cloudy, in TMAH, PAN, and BOE and with suspending precipitates in the chrome etching solution.

## 3.3. Surface tension measurements

The surface tension measurement data for each surfactant (PFAS and alternatives) are depicted in Fig. 3. Both PFAS and alternative surfactants reduced the surface tension of the etching solutions.

The surface tension reductions for all etching solutions were compared at 0.1 wt% of PFAS and alternative surfactants.

As shown in Fig. 3a, *BG10* reduced the surface tension of the TMAH etching solution to 31.1 mN/m, while *Novec 4200* reduced it from 73.4 mN/m to 64.5 mN/m.

Fig. 3b demonstrates that *Novec 4300* decreased the surface tension of PAN etchant from 61.5 mN/m to 31.0 mN/m while *BG10* reduced it to 40 mN/m.

Fig. 3c reveals that *CG50* surfactant reduced the surface tension of BOE from 85.7 mN/m to 28.8 mN/m, while *Novec 4200* surfactant reduced it to 22.1 mN/m.

Fig. 3d demonstrates that the surface tension of chrome etchant was decreased from 74.6 mN/m to 31.8 mN/m, using *Brij 35*, while *FC95* reduced it to 61 mN/m.

As shown in Fig. 3e, *Brij S100* reduced the surface tension of the chrome etching solution from 74.6 mN/m to 36.37 mN/m while *FC95*, it was reduced to 70 mN/m.

## 3.4. Critical micelle concentration values

The CMC values for *Novec 4200* in TMAH and BOE etchants were 5.33, and 5.13 mg/ml, respectively, for *Novec 4300* in PAN was 6.14 mg/ml, for *BG10* it was 3.21 mg/ml in TMAH and 4.72 mg/ml in PAN respectively, and for *CG50* in BOE was1.9 mg/ml. In the chrome etching solution, it was 0.04 mg/ml, 0.1 mg/ml, and 0.02 mg/ml for *Brij35*, *Brij*

**Table 2**
HLB values of the potential alternative surfactants.

| Surfactant Family | Surfactant Trade Name | HLB value |
|---|---|---|
| Polyoxyethylene | Brij 35 | 16.9 |
| | Brij 58 | 15.7 |
| | Brij S100 | 18.8 |
| Alkyl Polyglucoside | BG10 | 13 |
| | CG50 | 13.5 |
| | CG110 | 13.5 |

**Table 3**
Etching solutions and their compatible surfactants.

| Parameter | Etchant | | | |
|---|---|---|---|---|
| | BOE | Chrome | PAN | TMAH |
| 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 |
| Compatible Alternative Surfactant | CG50 | Brij 35 Brij S100 | BG10 | BG10 |
| Incompatible alternative surfactant | Brij35, Brij58, BrijS100 BG10, CG110 | Brij58, BG10, CG50, CG110 | Brij35, Brij58, BrijS100, CG50 CG110 | Brij35, Brij58, BrijS100 CG50, CG110 |

*S100* and *FC95* respectively (see Table 4).

### 3.5. Contact angles of etchant-substrates containing PFAS and alternatives at CMC values

As shown in Fig. 4 the addition of surfactants to the TMAH decreased the contact angle values. 0.1 wt% of *Novec 4200* and *BG10* decreased the contact angle from 68° with no surfactant (Fig. 4a) to 61° as shown in Fig. 4b and c. The addition of 0.01 wt% of *BG10* surfactant reduced the surface tension of the etching solution to 63°.

As shown in Table 5, the contact angle of TMAH decreased from 65.1° with no surfactant to 61.1° with *Novec4200*, while *BG10* reduced it to 32.1°. The contact angle for the PAN etchant with no surfactant was 37.2° and reduced to 28.6° and 33.4° with the addition of *Novec4300* and *BG10*, respectively.

The contact angle for the BOE etchant were measured to be 34.5° with no surfactant and was reduced to 30.7° and 31.3°, upon addition of *Novec4200* and *CG50* respectively.

### 3.6. Surface free energy comparison for the semiconductive substrates

Table 6 illustrates the data accumulated on the surface free energy of each substrate.

The highest surface free energy is for the chromium-coated silicon wafer with 72.6 mN/m and the lowest surface energy is shown by the glass substrate which is 35.4 mN/m. The surface energy of the Aluminum oxide-coated, and photoresist-coated silicon wafers are 53.9 mN/m, and 61.1 mN/m, respectively.

### 3.7. Chemical hazard classification of the potential alternative surfactant chemicals

The P2OASys scoring system ranks chemicals on a scale between 2 and 10, with lower scores given to safer chemicals and higher scores for more hazardous chemicals.

The toxicity scores shown in Table 7 are 7.3 for *Novec 4200*, 4.5 for *BG10, CG50* and *CG110*, 5.9 for *Brij 35* and 5.3 for *Brij35* and *BrijS100*.

### 3.8. Industrial trials

Over 100 semiconductor companies have conducted drop-in replacement of the PFAS surfactants with alternatives *BG10* in TMAH and PAN etchant, *CG50* in BOE etchant, and *Brij35* and *BrijS100* in the chrome etchant, and reported no adverse effects on the final products.

## 4. Discussion

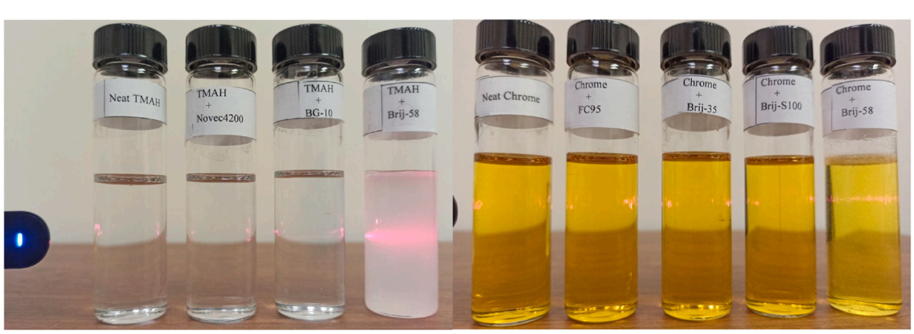
### 4.1. Selection of potential safer alternative surfactants

The HLB value is proportional to the ratio of polar to nonpolar sites of the molecule (Golodnizky and Davidovich-Pinhas, 2020) and indicates the surfactant's solubility preference in either oil or water, resulting in the formation of either a water-in-oil or oil-in-water emulsion. Surfactants with low HLB numbers exhibit a higher solubility in oil, while surfactants with high HLB numbers demonstrate a greater solubility in water (Kunjappu and Rosen, 2012). The etching solutions commonly used in the semiconductor industry are predominantly aqueous-based (up to 75% for TMAH, BOE, and chrome etchants) and highly polar in nature (PAN etchant which is a mixture of phosphoric acid, acetic acid, and nitric acid). PFAS-based surfactants are quite soluble in the etching solutions. The alternative surfactants must exhibit similar behavior in these etching solutions. As higher HLB values indicate higher solubility in water or polar solutions, the alternative surfactants must preferably have HLB values higher than 13 (Cheng et al., 2020). Therefore, alkyl polyglucoside surfactants *BG10, CG50*, and *CG110*, along with the polyoxyethylene surfactants *Brij35, Brij58,* and *Brij S100*, were selected to undergo etchant compatibility testing based on their higher hydrophilicity and improved solubility in polar and aqueous etching solutions.

In the 3-month compatibility test, it was observed that the biobased surfactant *CG50* exhibited transparency and demonstrated compatibility with the BOE etching solution. Notably, the polyoxyethylene surfactants *Brij35* and *Brij S100* formed stable solutions in the chrome etchant. Furthermore, the biobased alkyl polyglucoside surfactant *BG10* showed compatibility with TMAH and PAN etching solutions.

Surfactants that exhibited incompatibility, as indicated by turbidity or precipitation in all etching solutions, (e.g., *Brij58* and *CG110*), were excluded from further consideration as potential alternatives.

Fig. 5 shows the molecular structure the potential alternative surfactants from the HLB value and compatibility data results.




(a) (b)

**Fig. 2.** a. left to right: Neat TMAH etching solution, stable TMAH etching solution with 0.01 wt% of (PFAS surfactant *Novec 4200*, safer alternative *BG10*), and TMAH solution with *Brij 58* (incompatible). b. left to right: Neat chrome etchant, stable chrome etching solution with 0.01 wt% of (PFAS surfactant *FC95*, safer alternatives *Brij 35*, and *Brij S100*) and chrome solution with *Brij 58* (incompatible).

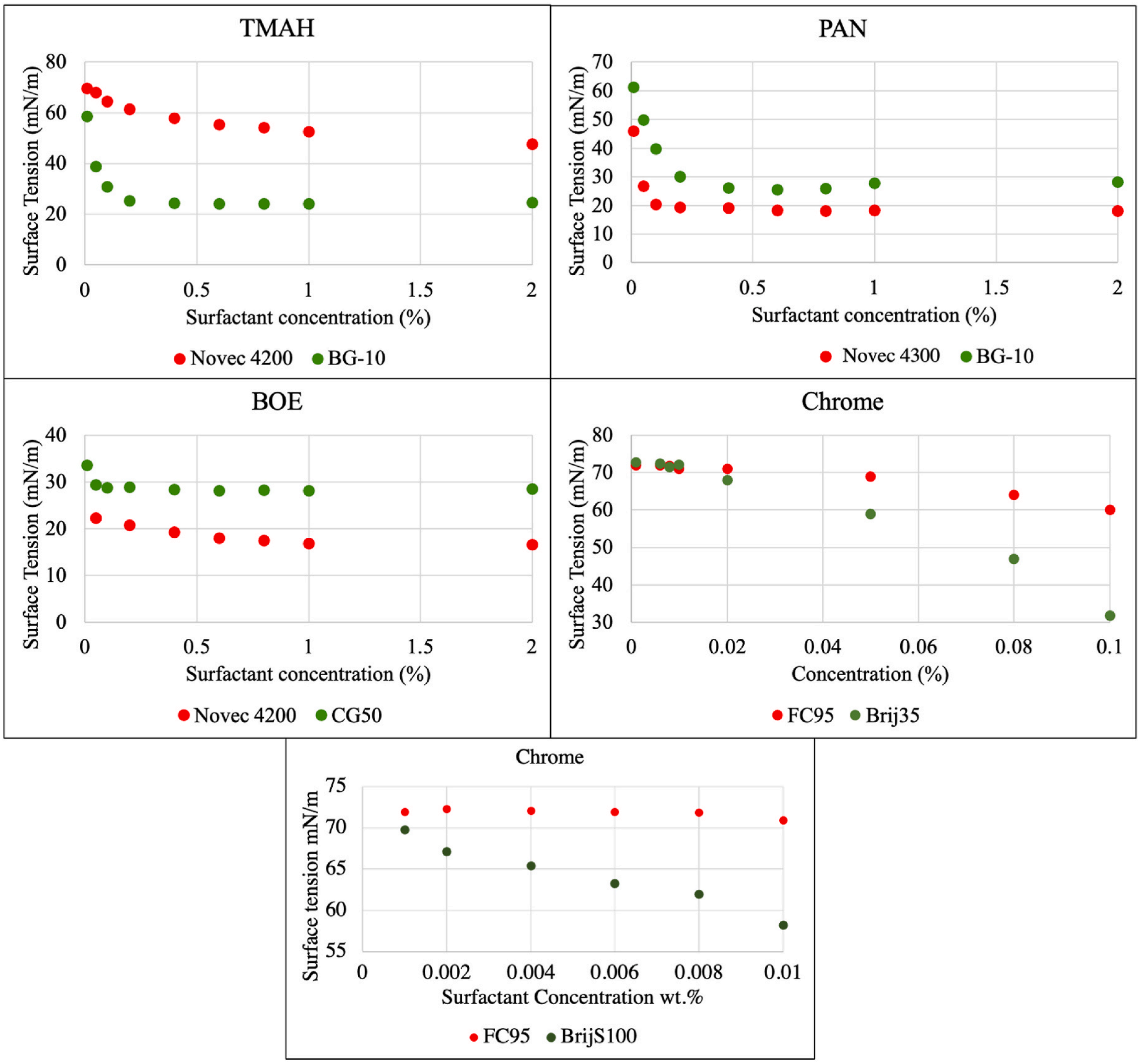



**Fig. 3.** The surface tension of the etching solution in various PFAS and Alternative surfactant concentrations for (a). TMAH (b). PAN (c). BOE (d) & (e). Chrome etching solutions.

**Table 4**
CMC values for PFAS and alternative surfactants in the different etching solutions.

| Etching solution | CMC (mg/ml) | | | |
|---|---|---|---|---|
| | PFAS | | Alternative | |
| TMAH | Novec 4200 | 5.33 (0.05) [a] | BG10 | 3.21 (0.07) |
| PAN | Novec 4300 | 6.14 (0.06) | BG10 | 4.72 (0.07) |
| BOE | Novec 4200 | 5.13 (0.07) | CG50 | 1.90 (0.04) |
| Chrome | FC95 | 0.02 (0.002) | Brij35 | 0.04 (0.002) |
| Chrome | FC95 | 0.02 (0.002) | Brij S100 | 0.1 (0.01) |

[a] Data represent the mean and ± the standard error.

### 4.2. Evaluation of the alternative surfactants

Substrate wettability is a key component of etching solutions especially when etching complex geometries or high aspect ratio structures. Etching a straight line might be accomplished using an etchant without a surfactant. But if the chip design necessitates a 90° turn, many etch solutions cannot penetrate the sharp corners. Surfactants can assist in achieving better wettability and coverage of the substrate. Similarly, it may be necessary to etch the sides and bottom of a via or hole in a chip. If the via has a high aspect ratio (depth vs. diameter), it may be difficult for the etchant to penetrate the via for complete etching. The surfactant in this case is critical in allowing for full etching of the sides and bottom of the via. To ensure that the etching solution wets the solid substrate, the surface free energy of the substrate must be higher than the surface tension of the etching solution and the contact angle between the etchant-substrate must be lower than 90°. (Jothi Prakash and Prasanth, 2021). In this study, since the surface free energy of the substrates are constant, the ability of the surfactant in reducing the surface tension and the contact angle is critical for improving the wettability.

Among alternative surfactants, *BG10* in TMAH, Brij35, and BrijS100 in chrome showed superior performance in regard to reducing surface tension compared to PFAS surfactants. As shown in Fig. 3a, the addition of *BG10* brought the surface tension down by 57% compared to that of *Novec 4200*, which affected it only by 12%. *Brij35* and *BrijS100* in chrome also outperformed PFAS surfactant, *FC95*. As demonstrated in Fig. 3d the same concentrations of the surfactants *Brij 35* and *BrijS100* lowered the surface tension by 42% and 52%, respectively compared to that of *FC95* which lowered it by only 18%.

In other conditions, such as *BG10* in PAN and *CG50* in BOE are marginally or less effective compared to that of PFAS. *BG10* reduced the surface tension of the PAN solution by 35% while *Novec4300* reduced it

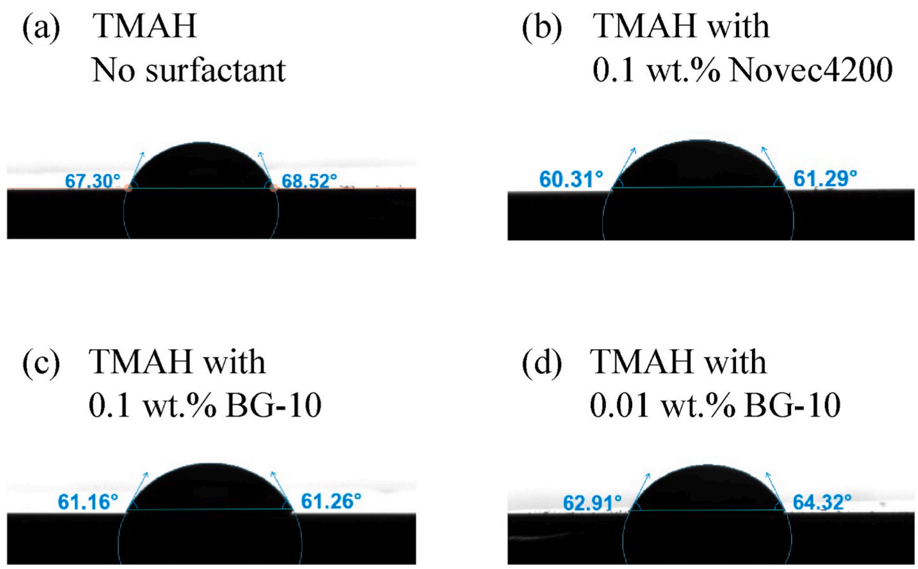



**Fig. 4.** The contact angle between the photoresist-coated substrate and TMAH etching solution: a. with no surfactant, b. with 0.1 wt% PFAS surfactant *Novec 4200*, c. with 0.1 wt% safer alternative *BG10*, d. with 0.01 wt% *BG10*.

**Table 5**
The contact angle between the etchants and substrates at CMC values of the surfactant.

| Etching Solution | Contact Angle (°) | | | | |
|---|---|---|---|---|---|
| | PFAS surfactant | | Alternative surfactant | | No surfactant |
| TMAH | Novec4200 | $61.1^{b}$ | BG10 | $32.1^{c}$ | $65.1^{a*}$ |
| PAN | Novec4300 | $28.6^{b}$ | BG10 | $33.4^{ab}$ | $37.2^{a}$ |
| BOE | Novec4200 | $30.7^{b}$ | CG50 | $31.3^{ab}$ | $34.5^{a}$ |

*Means analyzed with ANOVA and differences separated with Tukey HSD. Values not sharing the same letter indicate a significant difference ($P < 0.05$).

**Table 6**
Surface free energy of the substrates.

| Substrate | Etchant | Surface free energy of the substrates (mN/m) |
|---|---|---|
| Aluminum oxide coated silicon wafer | PAN | 53.9 (2.1) [a] |
| Chromium-coated silicon wafer | Chrome | 72.9 (3.1) |
| Photoresist-coated silicon wafer | TMAH | 35.4 (4.3) |
| Glass | BOE | 61.52 (3.3) |

[a] Data represent the mean and ± the standard error.

**Table 7**
P2OASys scoring scale.

| 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 BG10, Triton CG50, and Triton CG110 Decyl octyl glucoside (CAS# 68515-73-1) | 4.5 Medium Hazard | Safer alternative to evaluate |

by *48%*. *CG50* was comparable to the performance of *Novec 4200* in BOE. As shown in Fig. 3c *CG50* affected the surface tension by 66% while *Novec 4200* brought it down by 73%.

Reducing surface tension lowers contact angle resulting in better wettability. The contact angle measurements of etching solutions containing PFAS surfactants, and the alternatives demonstrate the effect of those surfactants on the wettability of the etching solutions and substrates of interest.

*BG10* outperformed *Novec4200* in the TMAH etching solution, with a contact angle value of 32.1° compared to 61.1°. The analysis of variance calculations for the TMAH etching solution with no surfactant compared to *Novec4200* and *BG10* resulted in different superscript letters for all three groups. *BG10* superscript letter is "c" compared to "b" for PFAS which confirms that *BG10* performs significantly better than *Novec4200* in improving the wettability of the TMAH.

*CG50* performed comparable to *Novec4200* in the contact angle measurements of BOE etchant. The contact angles for the BOE containing *Novec 4200* and its alternative *CG50* were found to be 30.7° and 31.3°, respectively. The superscript "ab" on the contact angle of BOE etchant including *CG50* suggests that the means of contact angle for the BOE including the *Novec4200* and *CG50* are statistically similar to each other, but both groups are statistically different from the contact angle mean of the etchant-substrate without surfactant (Lukas Meier, 2023).

The contact angle for the PAN containing *BG10* was measured to be 33.4°, while was 28.6° for *Novec 4300*. The variation in contact angles observed between the PAN with *Novec 4300* and *BG10* is not substantial enough to justify the exclusion of the alternative surfactant. The superscript "ab" is used to indicate that the means of the two groups, in this case, PAN including PFAS surfactant and PAN including *BG10* surfactant, are not significantly different from each other, but they are both significantly different from the PAN etchant without surfactant(Lukas Meier, 2023).

The contact angle for the chrome etching solution is not reported due to the etchant wetting the substrate instantaneously (contact angle of <5° in 5 s).

As depicted in Fig. 6, at a constant surface free energy of the substrate, the surfactants play a crucial role in reducing the surface tension of the liquid to improve wettability. Higher wetting between the etching solution and substrate leads to improved etching of the substrate. The more the surface tension of the etching solution is reduced by the surfactants, the greater the difference between the surface free energy of the substrate and the etching solution becomes, thus leading to

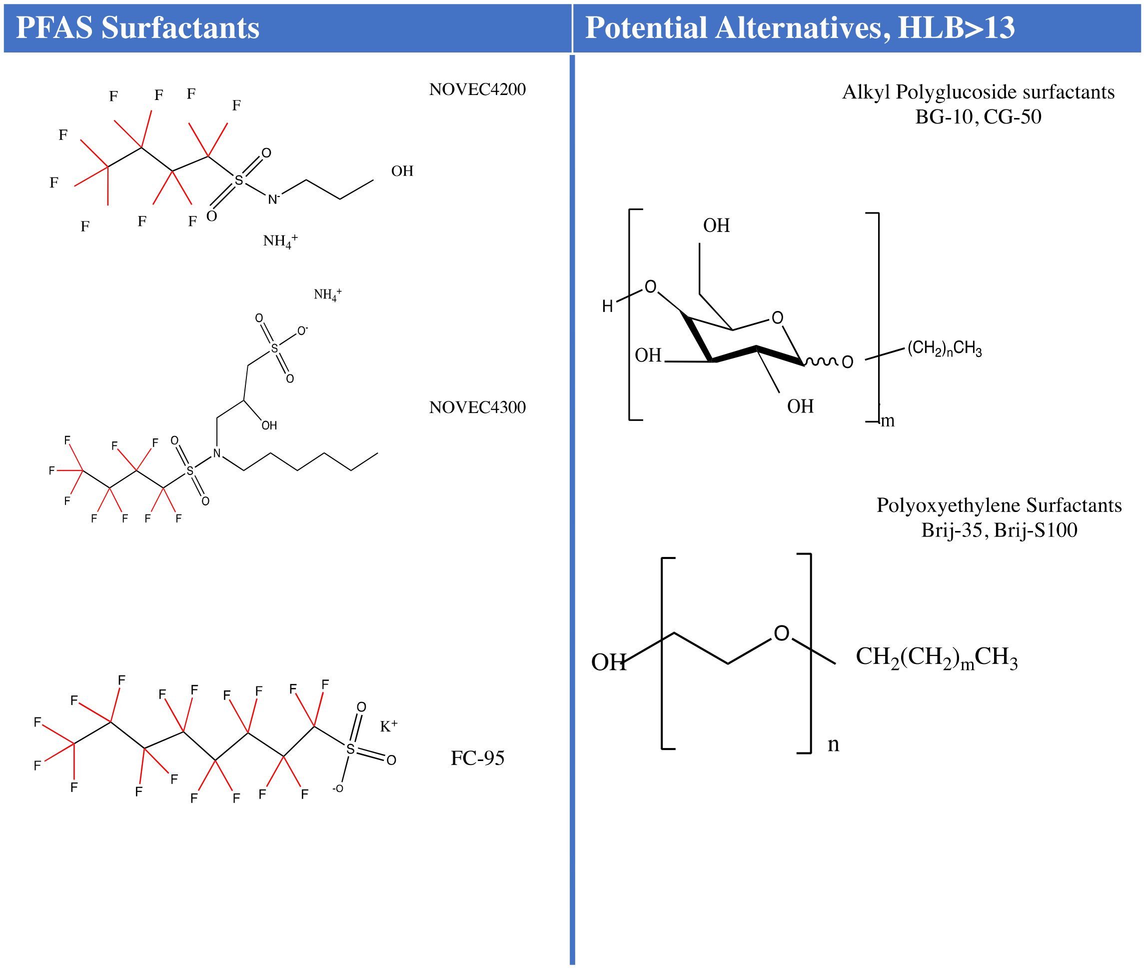



**Fig. 5.** The molecular structures of the PFAS-based surfactants and the potential alternatives.

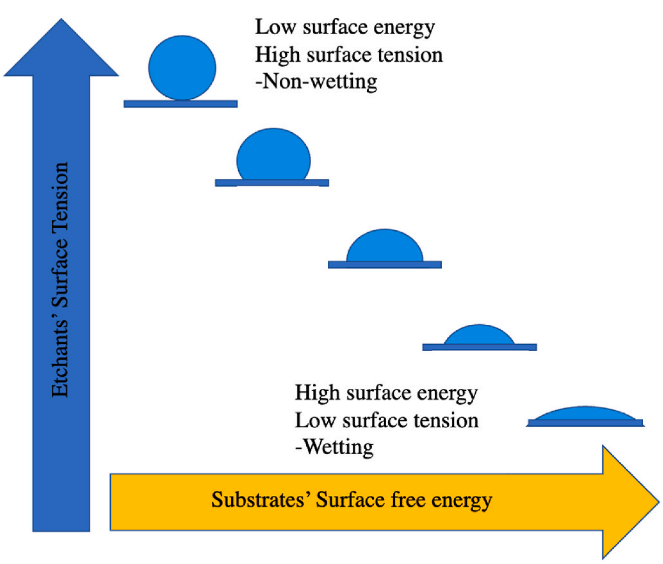



**Fig. 6.** Relation between Surface tension of the liquid and surface free energy of the substrate in wettability.

improved wetting of the substrate by the etching solution (Jothi Prakash and Prasanth, 2021).

Moreover, the alternative surfactants, namely *BG-10, CG50, Brij 35*, and *Brij S100*, exhibited lower P2OASys toxicity scores in comparison to *Novec4200* indicating that these alternative options are less toxic than the PFAS surfactants.

## 5. Conclusions

Safer and effective alternative surfactants were successfully identified utilizing a novel methodology for the replacement of PFAS surfactants in semiconductor etchants using surface chemistry, surfactants' intrinsic chemical and toxicological properties, and interfacial interactions between etching solutions and solid substrates. The chosen potential alternative surfactants, *BG10*, *CG50*, *Brij 35* and *Brij S100* were investigated using HLB values, surface tension measurements and CMC calculations, compatibility tests, measurement of contact angles in different substrates with different surface free energies, and chemical hazard assessment in four different etching solutions. Biobased alkyl polyglucoside surfactant *BG10* was selected as the preferred alternative in TMAH, and PAN, while *CG50* was the less toxic alternative in BOE etching solutions to replace *Novec4200* and *Novec 4300* PFAS surfactants. polyoxyethylene surfactants, *Brij 35* and *Brij S100* were determined to be less toxic alternatives for *FC95* in the chrome etching solution. Safer alternative Surfactants, *BG10, CG50, Brij 35,* and *Brij S100* 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. Industrial trials were carried out on the safer alternatives, and currently, approximately 100 semiconductor manufacturers, governments, and educational consumers that are using the safer and effective non-PFAS alternatives in the etching solutions.

The replacement of PFAS surfactants with safer alternatives is imperative to address the significant health risks and environmental contamination associated with these highly toxic fluorinated substances. Future research should focus on identifying effective and sustainable alternatives to PFAS surfactants in various industrial applications, such as the paint and coating industry where PFAS are widely utilized.

## CRediT authorship contribution statement

**Rashmi Sharma:** Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft. **Shreyas Shelke:** Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft. **Mohammad Bagheri Kashani:** Conceptualization, Methodology, Formal analysis, Investigation, Writing – original draft. **Gregory Morose:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition. **Christopher Christuk:** Formal analysis, Writing – review & editing, Supervision, Resources. **Ramaswamy Nagarajan:** Conceptualization, Writing – review & editing, Supervision, Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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