Developing TSV wet cleaning chemistry for quantum computing application

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I. Abstract

New 3D-integration routes for superconducting Josephson junction qubits include the development of an interposer die with through-silicon vias (TSV) for vertical and compact interconnections. Since fluoropolymer dielectric residues remaining in the vias may be detrimental for subsequent processes or qubit functionality, they must be removed without damaging the structure or other materials. Therefore, we developed a new O_2 plasma-free, selective and not-toxic wet cleaning solution that can remove both the fluoropolymer from the vias and the photoresist used for TSV patterning from the surface. Formulation key physico-chemical properties are discussed based on cleaning results obtained by scanning electron microscopy (SEM) and electron dispersive spectroscopy (EDS). Also discussed is evidence of the dissolution and removal of fluoropolymer formed during Bosch etching. Finally, SEM and time-of-flight secondary ion mass spectrometry (ToF-SIMS) analyses confirm complete removal of fluoropolymer residue from the vias. These encouraging results confirm a viable, manufacturable one-step wet cleaning process for TSVs designed for 3D packaging of qubits and other applications.

II. Introduction

Quantum computing based on superconducting Josephson junction qubits is an attractive technology path for performing ultra-fast and efficient calculations. One of the main challenge of qubit integration is to reduce variability while preserving the qubit coherence [1,2]. New packaging systems that comprise an interposer wafer connecting the qubit and the readout wafers appear promising [3]. Within the interposer, materials stacks compatible with cryogenic conditions are required [4], especially for under bump metallization (UBM), solder bumps [5] and through-silicon vias (TSV). TSV is a key enabling technology for 2.5D and 3D integrated circuit (IC) packaging schemes, as it enables several dies to be interconnected in a same package [6]. TSV aims at replacing bonding wires by vertical interconnects, minimizing internal signal connection lengths, and thus allowing faster operation, less heat production and lower power consumption. TSVs are high-aspect ratio structures (commonly with 1:10 aspect ratio) that are obtained by a deep reactive ion etching (DRIE) approach, such as the Bosch process [7–9], which consists of three steps repeated in a cycle: i) isotropic etching of the Si with SF_6; ii) depositing a passivating fluoropolymer layer with a fluorocarbon (C_xF_y gas); and iii) anisotropic etching of fluoropolymer at the bottom of the vias (Ar bias).

Following standard Bosch dry etch, high aspect ratio TSV sidewalls are covered with an inert fluoropolymer which is detrimental due to its roughness, poor conformality and weak adhesion. It can cause, among other issues, discontinuity, or delamination of subsequent layers (such as a barrier layer) and an increased thermal stress. For quantum applications, this could create loss mechanisms that can

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lower the coherence time and quality factor of qubits, thus reducing device yield [10,11]. Furthermore, dielectric residues in the TSV, at the interface between the Si and the superconductor filling the TSV, might impact the electrical and superconducting properties of these interconnections [12]. The design of narrow TSV with high-quality material bottom-up plating will thus require efficient surface preparation and complete removal of chemically resilient post etch residues (see Figure 1).

Current processes of record are either dry (*in-situ* O_2 ashing), wet or a combination of both [13–16]. Performing *in-situ* plasma cleaning directly following the Bosch process is tempting as it is efficient for removing organic species, but it is also an aggressive process with low selectivity and organic residues may remain that necessitate a subsequent wet cleaning. In addition, minimization of process times on costly DRIE equipment is favourable for CAPEX cost control and maximizing throughput. Qubits coherence can be impacted by plasma treatment, so a full wet solution is preferred for cases where TSV's are formed after qubit fabrication on the same wafer [2,17].

Industry-standard post-etch residues removers have been proposed to remove post-Bosch etch fluoropolymer, but they can contain hazardous compounds: for example, hydroxylamine, which is considered carcinogenic under REACH [13]. Hydroxylamine-based solutions are also aggressive toward metallic copper, while a good compatibility is required with exposed materials that can be revealed by forming TSV (possible for TSV-middle or -last approaches) [11]. Solvent alternatives have been proposed, such as organo fluoro solvents [14,16], which seem to demonstrate good fluoropolymer removal efficiency, but are not able to remove photoresists, have a high global warming potential, and are expensive and volatile.

To the best of our knowledge, no wet cleaning solutions are capable of both complete sidewall fluoropolymer and photoresist removal while i) remaining chemically compatible with exposed materials, especially metals; ii) maintaining a long effective bath life; and iii) avoiding the use of hazardous chemical components that are not bioaccumulative nor CMR (Carcinogenic-Mutagenic-Reprotoxic)-listed.

Facing these requirements and with Technic expertise in post etch residues removers [18], we developed TechniClean D-BOS series, wet cleaning solutions extensively investigated with partners on various structures patterned using a standard Bosch dry etch. In the present work, a comprehensive data set, including SEM images, thin-film metrology, and surface analyses such as ToF-SIMS validating post-Bosch etch cleaning efficiency and benchmarking new versus legacy cleaning candidates (wet and ash/wet) is presented and discussed.

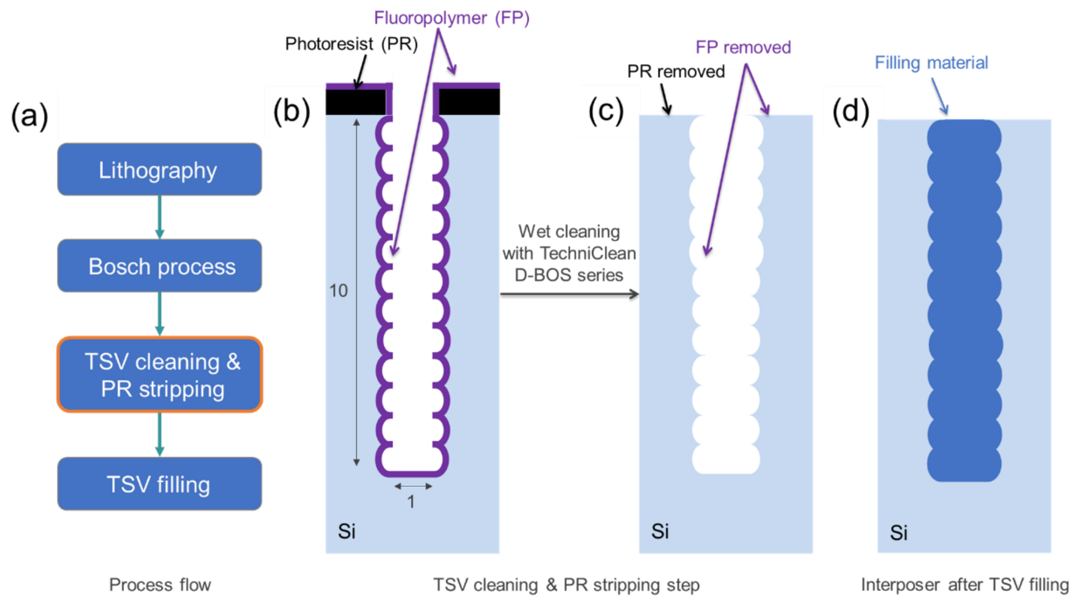

Figure 1 – (a) Process flow; (b-c) Before and after TSV (ratio 1:10) wet cleaning step with fluoropolymer removal and photoresist stripping; (d) example of a partial single side process interposer structure (zoom on 1 TSV) with connecting bumps.

III. Materials and methods

Chemistry

TechniClean D-BOS products were freshly produced at Technic France facility before each test conducted in the frame of the MATQu project. All chemical compounds were obtained from Sigma Aldrich, Alfa Aesar or provided by chemical supply companies. During the formulation development stage, all cleaning experiments were conducted in beakers with a gentle stirring (≈500 rpm). Samples were rinsed with water (immersion and spray), except when an organo fluoro solvent was used, for which the water rinse was preceded by an immersion in propan-2-ol. Finally, the samples were dried with dry air.

Materials

Most of the formulation development was conducted using plasma singulated wafers based on a silicon substrate glued on a polyisoprene-based tape (PlasmaTherm). The silicon was etched with a typical industrial Bosch process employing SF_6, C_4F_8 and Ar gases, with dies measuring 1 x 1 mm² and patterned with either Megaposit SPR220 or AZ12XT-20PL 50KA P-type photoresists. The cavities were 15-20 µm wide and 190-200 µm deep with sidewalls covered by the fluoropolymer left by the Bosch process. The silicon wafers were unglued and cleaved in coupons with typical size of 1.5 cm x 2 cm for the cleaning experiments. After cleaning, visual inspection was performed while cleaving the coupons along the streets (no sidewalls from the outer parts were observed) for observing the sidewalls in SEM.

For ion chromatography analyses, large silicon wafers (300 mm) covered with a thin film of fluoropolymer were employed. Coupons of size 2 cm x 1.5 cm were cleaved and immersed in the solution before ion chromatography experiments.

Etch rates were determined on blanket thin films either at 65 or 75 °C with a 10 to 30 min long immersion and with stirring.

Table 1 – Thicknesses and deposition method of the oxide and metals thin films used for this study.

Material	SiO_2 (TEOS)	Al	Cu	Au	Ti	Nb	Ag
Thickness (nm)	500	400	300	250	400	200	250
Deposition method	CVD	PVD	PVD	Evaporation	PVD	PVD	Evaporation

Silicon wafers patterned with TSVs were provided by imec and CEA, with respective dimensions: 5 µm x 50 µm (10 µm pitch) and 10 µm x 100 µm, the first number standing for the TSV diameter and the second for their depth. The photoresist patterned on the surface of the wafers from imec was a 2-4 µm-thick TX 1311 from AZ (Merck) while the photoresist was already removed for CEA wafers. The wafers were cleaved into 2 x 2 cm^2 coupons for visual inspection and 3 x 3 cm^2 coupons for ToF-SIMS analyses.

Surface Analysis

Surface inspection was performed with an Amscope metallurgical microscope connected to a digital camera. SEM images were acquired at Technic France with a Hitachi S-4500 with an acceleration voltage mainly at 10 kV. Charging samples were coated at Technic France with a thin AuPd layer deposited with a Emitech K550 sputtering system. Sheet resistance was measured with a four-point probe Pro4 from Lucas Lab and voltage was varied with an IMR-B-R020 system produced by Isabellenhütte. Ion chromatography analyses were performed with a ThermoFisher Dionex AQUION with autosampler ThermoFisher DV on samples diluted in water with a ratio 1:100 in mass. Calibration samples that contained 0.5, 1.5 and 20 ppm of fluoride anions were used for external calibration to run a quantitative analysis. Since the fluoride peak position in the chromatogram depends on specie retention time on column, which is different according to the column type used, the calibration allows fluoride peak identification and determination of their concentration. When coupons with photoresist on the surface were immersed in D-BOS solutions, the solution samples were filtered with a membrane that retains organic matter in suspension to minimize capillary contamination with residues and to avoid interferences with matrix effects during ion chromatography analysis. A TOF-SIMS IV from ION-TOF GmbH was used for probing elements from the surface of the sidewalls and in the depth. Depth profiles were acquired in negative polarity, using Bi^+ ions (15 keV) for analysis and Cs^+ ions (2 keV) for sputtering. ToF-SIMS analyses were done roughly 5-7 µm below the top of TSV.

IV. Results and discussion

I. Formulation development for fluoropolymer removal

As a starting point, compounds that are known to be incompatible with PTFE/Teflon, legacy products similar solutions and currently commercialized TechniClean solutions were studied [10]. Iterative formulation modifications intended to enhance fluoropolymer (FP) removal while removing the photoresist (PR) were conducted. Depending on the chemical nature and the physico-chemical properties of the mixtures, results varied significantly. While there is a thick and homogeneous FP coating on the reference sample (see Figure 2(a)), fragments on sidewalls showing partial attack of the FP were often observed (see Figure 2(b)). In some cases, the PR was completely removed (see Figure 2(b)), while in others, the sidewalls were perfectly cleaned whereas the PR was not removed (see Figure 2(c)). Based on visual inspection, the chemical nature and the physico-chemical properties of the cleaning mixtures were modified to remove both the FP and the PR as shown in Figure 2(d).

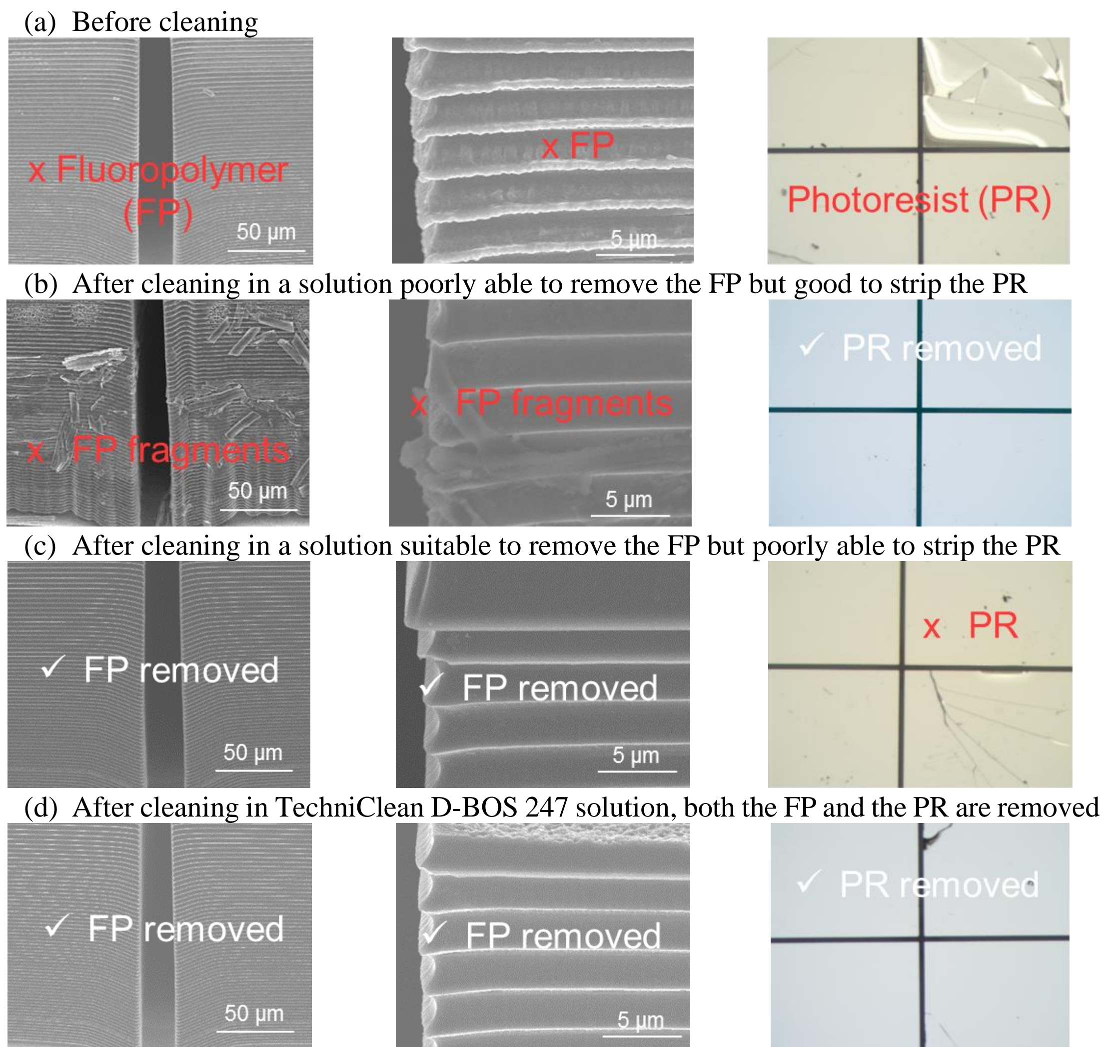

Figure 2 – SEM pictures and optical microscope pictures (x10) depicting partial or complete removal of the photoresist (PR) and/or the fluoropolymer (FP) after wet cleaning for (a) Reference sample; (b) Solutions that are poorly able to remove the FP but good to strip the PR; (c) Solutions that are able to remove the FP and not the PR; (d) Solutions that are suitable to remove both the FP and the PR.

Significant attention was paid to the relationship between a given formulation's physico-chemical properties and its FP/PR removal capability. Fluorinated polymers are known to be hydrophobic, so low surface tension mixtures are essential to wet these materials (reference). Therefore, wettability was especially considered as a crucial parameter to enable the mixtures to penetrate deeply in the trenches of post-singulated dies, and into the high aspect ratio TSV's. Thus, molecules from the same chemical family, but having a range of surface tension, were compared. These molecules were diluted in an otherwise identical formulation with equivalent number of moles, and cleaning was performed with the same process: 10 min at 80 °C. The blue data points illustrated in Figure 3 shows the results obtained for these molecules, while the green data points show the results obtained with an organo fluoro solvent of a different chemical class for 20 min at room temperature. Based on SEM observations, FP removal efficiency was evaluated from 0% (no difference with the reference sample) to 100% (complete FP removal on the sidewalls). The data showed that by lowering the main reagent surface tension, FP removal can be enhanced.

While with the organo fluoro solvent the PR was not removed, PR stripping occurred with most other formulations tested. This was expected and did not constitute a setback owing to the many drawbacks of organo fluoro solvents as discussed previously. As Figure 3 illustrates, the best reagents were determined to be those demonstrating FP removal efficiency of 80%, while at the same time being capable of stripping the PR. None of these best reagents were toxic nor flammable.

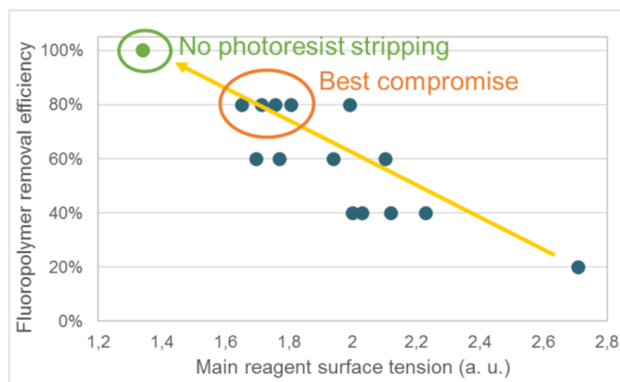

Figure 3 – Fluoropolymer removal efficiency as a function of the main reagent surface tension. Surface tension values are given in an arbitrary unit.

To further enhance FP removal, many chemical compounds were tested in combination, and reagent concentrations were optimized. Strong improvement was observed by utilizing two different main reagents with equivalent total number of reagent's moles in the whole formulation (see Figure 4).

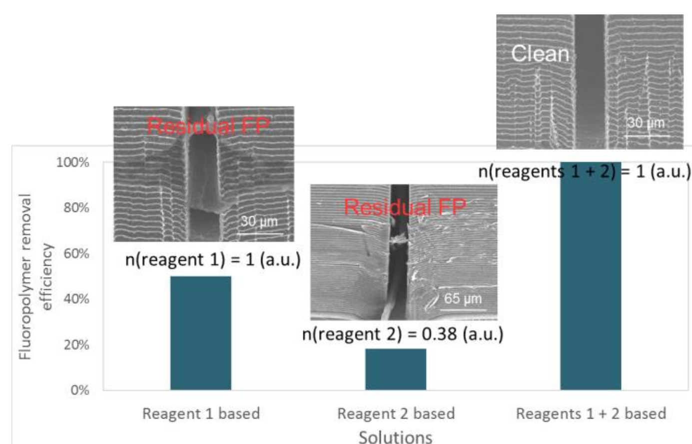

Figure 4 – Reagent combination that enhanced the fluoropolymer removal.

The newly developed solutions (see Table 2) are organic nucleophilic based mixtures. They can remove both the PR and the FP, as confirmed by EDS analyses (see Figure 5), in less than 10 minutes at 75 °C with a gentle stirring and with water rinsing.

Table 2 – Comparison between the TechniClean D-BOS series products.

Solutions	Organic nucleophilic based mixtures
D-BOS 247	Standard solution
D-BOS 347	With additive that optimize the physico-chemical properties for industrial use
D-BOS 390	Solution with a lower risk for raw material supply

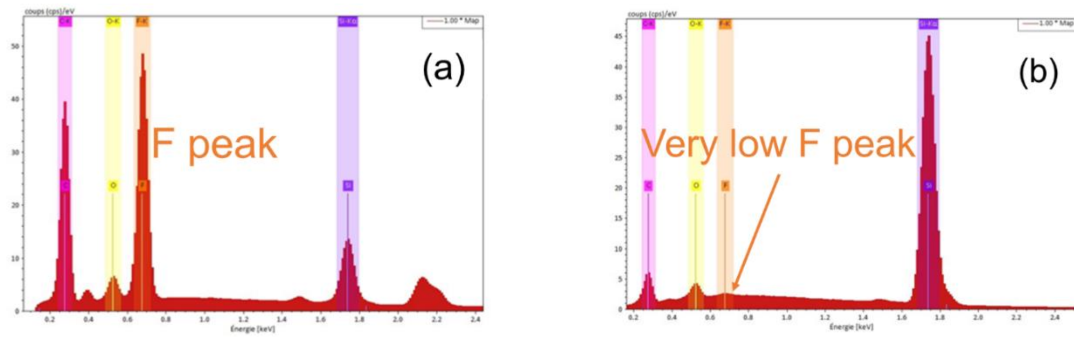

Figure 5 – EDS spectra (a) for a reference sample: (b) for a sample cleaned in TechniClean D-BOS 247 solution.

II. Fluoropolymer removal mechanisms study

After the wet cleaning process, no residues were left visible in the solution, and PR was completely dissolved, which was not surprising for these P-type photoresists in these removal solutions. However, the highly-effective FP removal was more surprising, so experiments were designed and executed to gain insights into the mechanism by which FP was removed and broken down. It is known that the energy of the C-F bond is high compared to other simple organic chemical bonds (513.8 ± 10 kJ/mol) [19]. Thus, fluorinated polymers are strongly reticulated and hard to dissolve. Therefore, we decided to perform ion chromatography to check fluoride concentration ([F^-]) in TechniClean D-BOS 347 solution after wet cleaning of FP covered samples.

First, ion chromatography was performed after immersion in TechniClean D-BOS 347 (5 min at 75 °C with gentle stirring) of six coupons from the wafer with plasma singulated dies. The six coupons were determined to be properly cleaned according to SEM analyses (see Appendix A). It was then assumed that the amount of FP removed was six times higher than what would have been obtained for wet cleaning of only one sample. As compared with a standard sample (black spectrum for 0,5 ppm in solution), no fluoride ions were detected in the fresh TechniClean D-BOS 347 (orange spectrum) as expected (see Figure 6). After wet cleaning of the six, a fluoride peak appeared (blue spectrum). The low value of the F^- peak was not surprising as the FP layers are very thin, and dilution was used before analysing the sample. Meanwhile, another peak arose for a longer retention time (approximately 3.3 min), that did not correlate with the standards. This was tentatively ascribed to an unknown anion that was solvated while dissolving the PR. For ion chromatography analysis, the anion peak position may rely on the matrix composition if its concentration is too high. To validate the fluoride presence in the used TechniClean D-BOS 347, the diluted sample was deliberately spiked with a significant amount of fluoride standard. The new spectrum (purple) showed clear enhancement of the fluoride conductance signal, for the same retention time as before. Thus, it was concluded that fluoride anions were leached in the solution during the wet cleaning of the plasma singulated dies.

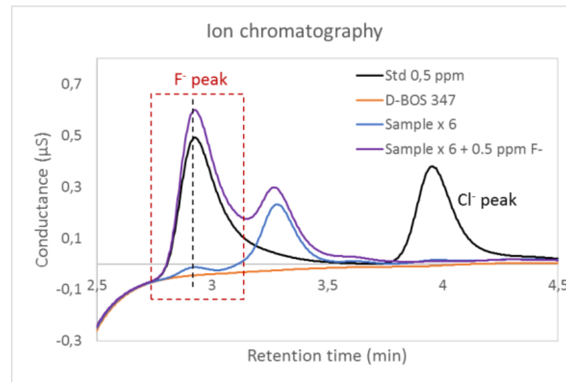

Figure 6 – Ion chromatography study to detect anions in TechniClean D-BOS 347 after wet cleaning of six patterned samples containing fluorinated polymer.

As the PR on top of the coupons was also dissolved in the TechniClean solution, the origin of the fluor could be yet questioned. To confirm the FP dissolution, ion chromatography was then performed after immersion in TechniClean D-BOS 347 (10 min at 75 °C with gentle stirring) of various numbers of coupons (0, 3, 6 and 9) covered by a thin film of FP and without PR. Compared with standard samples (black spectrum), the same peak that confirmed the presence of F^- species also appeared for the three solutions used for wet cleaning, but not for the fresh TechniClean solution (see Figure 7). Absence of the peak at a retention time of 3.3 min aligned with the hypothesis that another anion species is produced during PR dissolution. Finally, it was concluded that fluoride species can be found in TechniClean solution after FP removal, which may be ascribed to FP dissolution. Fluoride concentration was also determined quantitatively, and a well-defined linear relationship ($R^2 = 0.997$) was found between the concentration of fluoride in solution and the total wafer surface immersed in the TechniClean solution.

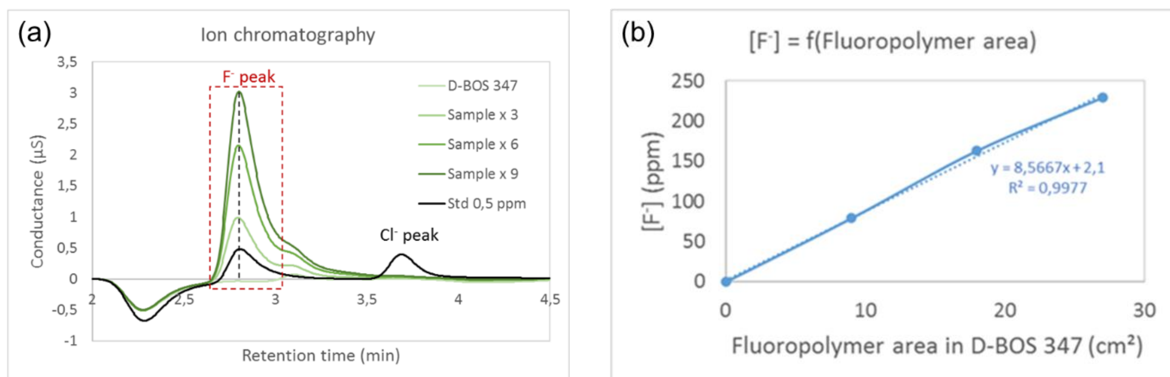

Figure 7 – (a) Ion chromatography study to detect anions in TechniClean D-BOS 347 after wet cleaning of various number of blanket samples; (b) F^- species concentration as a function of the fluoropolymer area immersed in TechniClean D-BOS 347.

III. Materials selectivity study

For via-middle formation, materials selectivity with potential metals in contact with cleaning solution is critical. Thus, corrosion inhibitors were included as components in this study in order to protect metals. Experiments were performed at 65 °C and 75 °C; the former chosen to increase bath life and reduce etch rates should cleaning prove sufficiently facile. Etch rates for all materials studied were less than 4 Å/min, and some (Au, Nb, SiO_2 at both temperature, and Al at 65 °C) are even lower than 0.1 nm/min, within experimental error (see Figure 8). These results validate the corrosion inhibitor efficiency and

demonstrate the possibility to use TechniClean D-BOS 347 for via-middle cleaning in the presence of a wide array of metals.

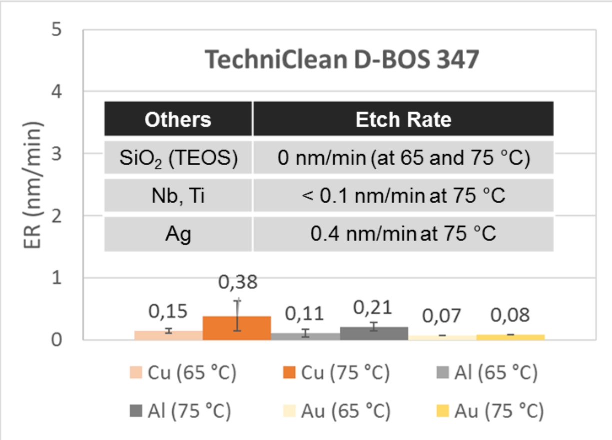

Figure 8 – Etch rate values for metals and silicon oxide, obtained with a four-point probe (for metals) and a reflectometer (for oxide), after immersion in TechniClean D-BOS 347 at 65 and 75 °C.

IV. TSV Cleaning

In parallel with the formulation work, TechniClean D-BOS solutions were tested with the TSV designed in the frame of the MATQu project. The visual inspections pre- and post-wet cleaning with TechniClean D-BOS 247 are shown in Figure 9 and Appendix B. The clearest difference consists of a surface colour change observed under optical microscope. It can be ascribed to the complete PR stripping. SEM pictures also show complete disappearance of this layer. It proved more challenging to discern removal of sidewall polymer, which appeared scalloped and rough in both cases, without any clear visual difference, even for lower acceleration voltage (1-5 kV) and coated samples. That was not surprising; others researchers have reported requiring EDS [14], Auger Electron Spectroscopy [20], fluorescence microscopy after labelling polymer residues with a fluorophore [21], or electrical testing [20] as techniques to detect cleaning. Therefore, elemental analysis was considered necessary for FP removal examination.

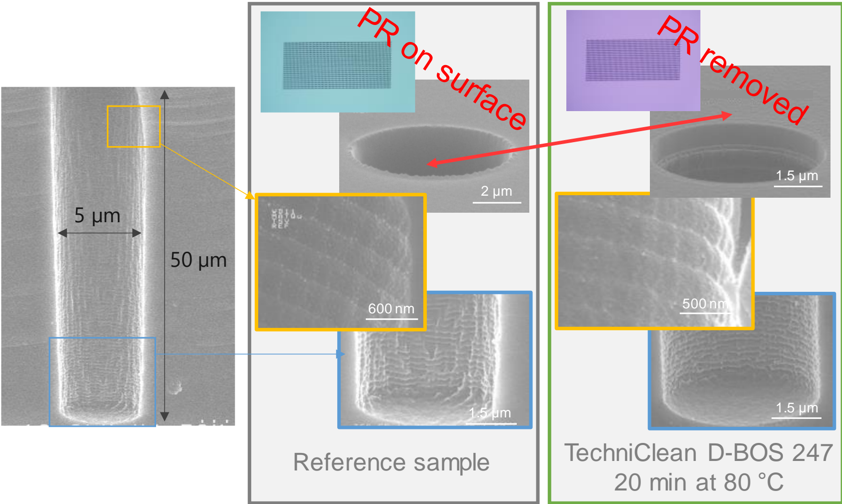

Figure 9 – Optical microscope and SEM images of TSV with dimensions 5 µm x 50 µm, before and after wet cleaning with TechniClean D-BOS 247.

ToF-SIMS depth profiling was chosen to study and detect F and C after cleaning. It is an extremely sensitive surface analysis method, particularly useful to study composition of thin surfaces. This in-depth analysis was performed while etching the sidewalls, and four elements were probed (see Figure 10). The result obtained for the reference sample showed relatively high intensity of F^- and C^{2-} signals at the beginning of profiling, correlating with a FP layer thickness of 20 nm. Those signals then decreased in intensity as a function of thickness, while the intensity of the Si signal increased as silicon bulk was reached. O^- signal intensity was low except at the top interface, indicating the presence of a native oxide layer on top of Si.

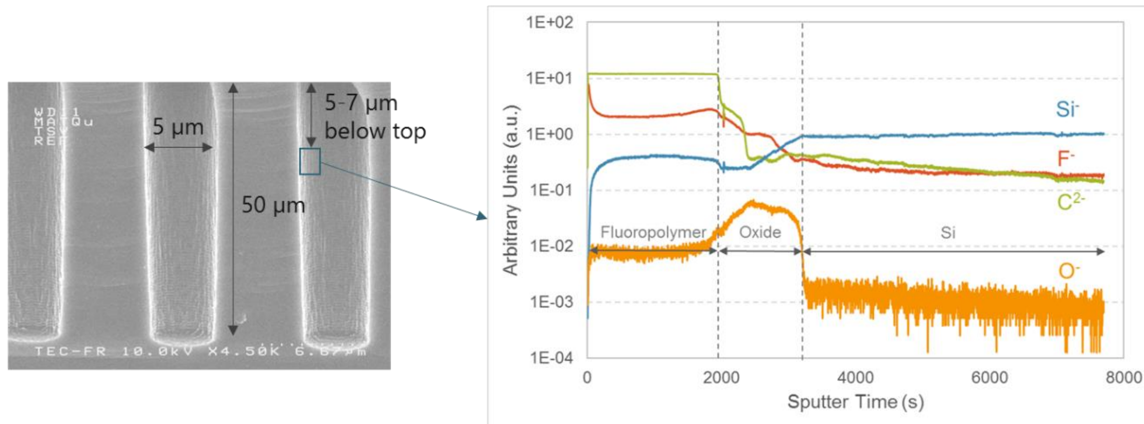

Figure 10 – SEM picture and ToF-SIMS of reference sample uncleaned depicting F^-, Si^-, C^{2-} and O^- signals.

ToF-SIMS was then employed to compare two processes for samples wet cleaning (see Figure 11):

1. One-step TechniClean D-BOS 247 for 60 min in immersion at 80 °C with gentle stirring.
2. Two-step imec POR composed of a 3 min-long O_2 ashing with a 500 W plasma power, followed by a 3 min-long wet cleaning in a single wafer clean tool.

First, a significant intensity reduction of the F^- and C^{2-} signals was observed for the one step and the two-step processes indicating that the FP was mostly removed during the cleaning processes. The silicon bulk seemed to be reached after a shorter sputtering time, as the 30Si$^-$ signal step gain occurred at a shallower depth for the cleaning processes. The O^- signal showed a higher intensity at the initial stage of the profiling, which may be evidence of either oxidation of the silicon surface deprotected from the FP or simply removal of the FP that revealed the FP/Si interface that was already oxidized. Finally, the C^{2-} signals were 3-4 orders of magnitude lower for the cleaned samples compared to the reference, consistent with complete removal of the FP. Thus, the FP removal efficiency of both cleaning processes was validated. The C^{2-} signal was one order of magnitude higher when the one-step process in TechniClean D-BOS 247 was used, so the wet cleaning of the two-step imec POR may be more efficient to remove all the organic residues. That said, the significance of this difference is questionable, as the ToF-SIMS chamber may be contaminated from one sample to another. Furthermore, for quantum computing, using oxygen plasma may degrade the device performance therefore developing single wet cleaning step is necessary for this application.

Overall, the differences between the two processes are minimal and may be ascribed to measurement artifacts. Therefore, it was demonstrated that the FP deposited during the Bosch process can be removed in a one step process with TechniClean D-BOS 247 in immersion.

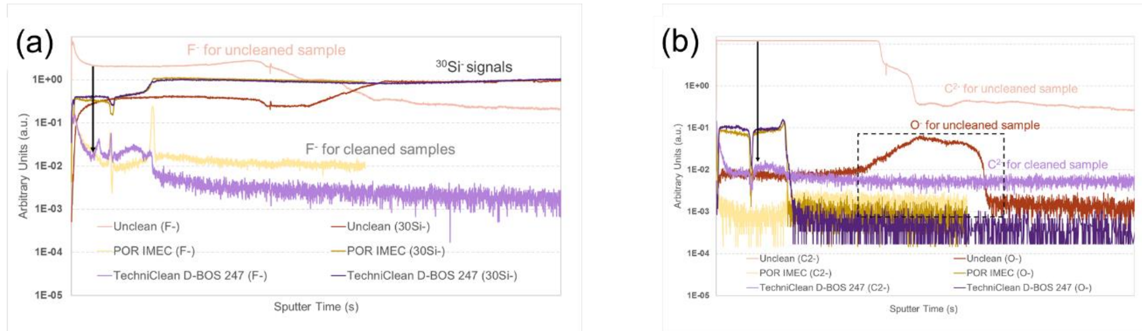

Figure 11 – Spectra comparison of ToF-SIMS analyses obtained for an uncleaned sample and for processed samples with imec POR and TechniClean D-BOS 247 wet cleaning solution (a) F^- and $30Si^-$ signals; (b) C^{2-} and O^- signals.

Immersion time reduction was then investigated by comparing a third process:

3. One step TechniClean D-BOS 247 for 20 min in immersion at 80 °C with a gentle stirring

ToF-SIMS results were compared with the sample cleaned for 60 minutes (see Figure 12). Although the $30Si^-$ signals are superposed, the F^- and C^{2-} signals are shifted to higher values (less than one order of magnitude) for the sample cleaned during the lowest immersion time. That may be ascribed to a non-complete FP removal on sidewalls surface. Residues ionization in the whole ToF-SIMS chamber may also explain why there is no clear intensity reduction for F^- and C^{2-} signals at the interface with the Si bulk. As a conclusion, it can be stated that optimal wet cleaning with TechniClean D-BOS 247 in such system require an immersion time comprised between 20 and 60 minutes. Further improvement may be enabled by using a mechanically-assisted process, such as a soak and high-pressure spray process, or with megasonics [22]**.**

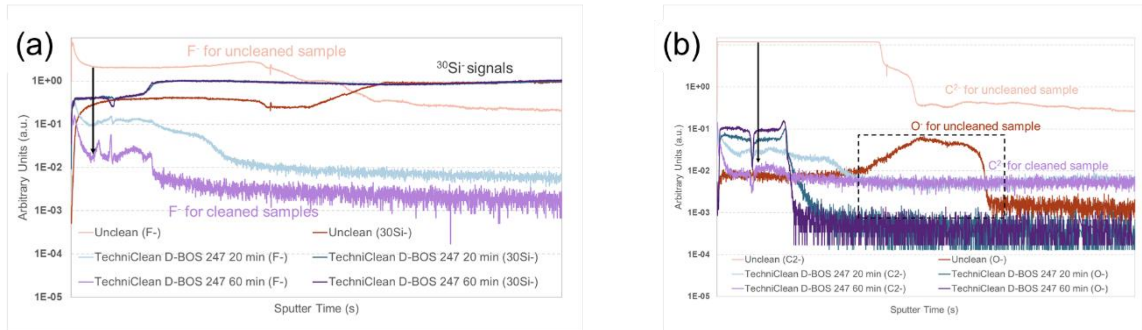

Figure 12 – Spectra comparison of ToF-SIMS analyses obtained for an uncleaned sample and for processed samples with TechniClean D-BOS 247 wet cleaning solution during 20 and 60 min in immersion (a) F^- and $30Si^-$ signals; (b) C^{2-} and O^- signals.

V. Conclusions

A new solution that removes the fluoropolymer deposited during the DRIE Bosch process was developed and presented specifically for quantum computing integration flows. TechniClean D-BOS series products demonstrated a dual function, *i.e.* they can remove the photoresist from the surface and the fluoropolymer from the sidewalls of the features etched with the Bosch process. A lowered surface tension of the formulation main reagent was shown to enhance the fluoropolymer removal. A synergy between two reagents was also evidenced. Dissolution of the fluoropolymer was demonstrated by ion chromatography results as a F^- peak was observed after cleaning which grows proportionally with the number of treated coupons. ToF-SIMS analyses verified Through Silicon Vias cleaning in a one-step process with TechniClean D-BOS 247 in immersion. The result is similar to what is obtained for a conventional dual process with O_2 ashing followed by a wet cleaning process. It is believed that further optimization is possible with industrial equipment and processes, that provide mechanical assistance to the wet cleaning.

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Appendices/Supplementary Materials

Appendix A

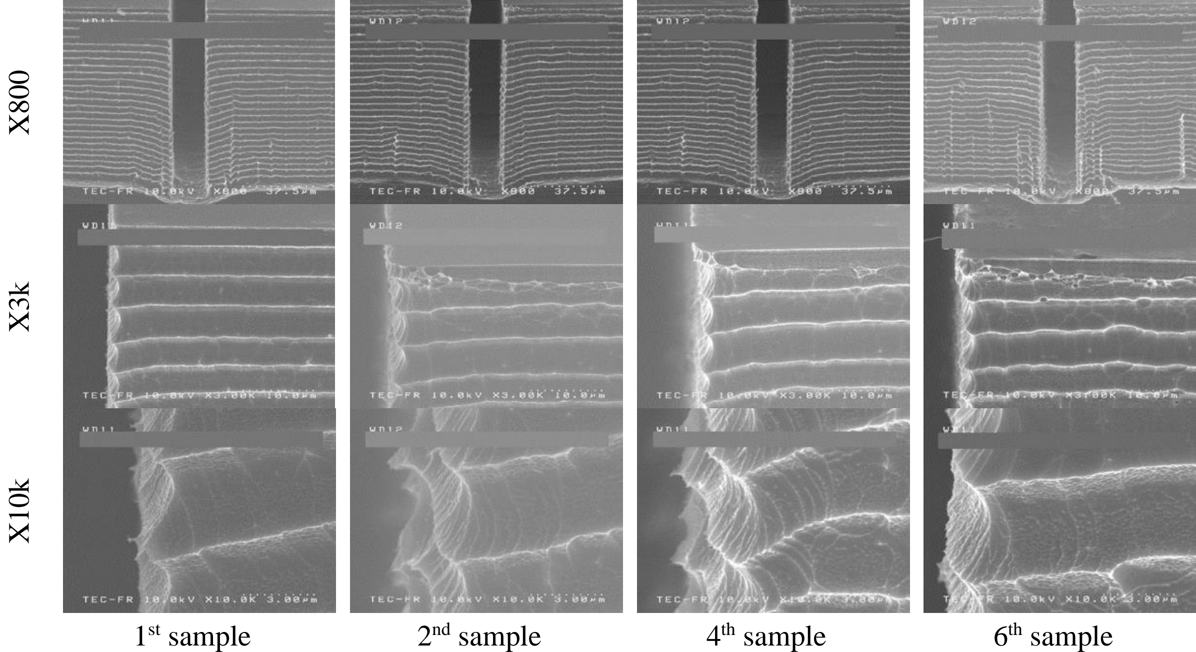

Figure 13 – (Appendix A) SEM images of samples with scalloped sidewalls that were immersed successively (six in total, four depicted) in the same TechniClean D-BOS 347 solution for 5 min at 75 °C with gentle stirring and water rinsing. Three magnifications are depicted to evidence samples cleanliness.

Appendix B

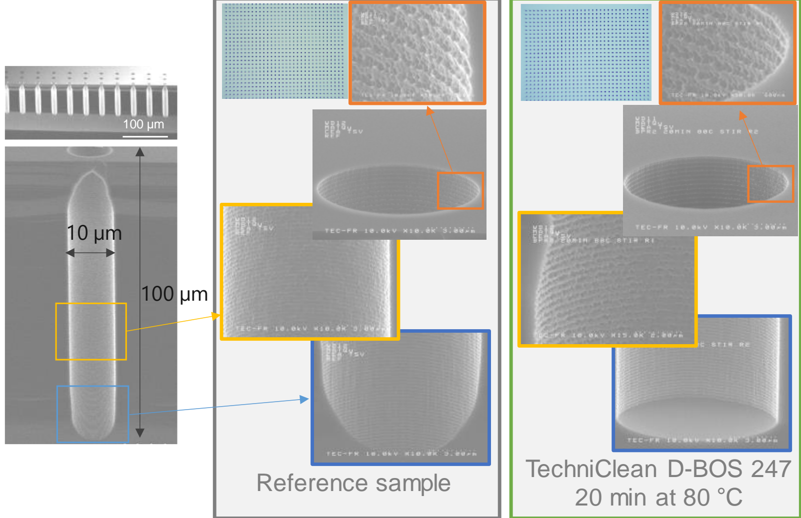

Figure 14 – (Appendix B) Optical microscope and SEM images of TSV with dimensions 10 µm x 100 µm, before and after wet cleaning with TechniClean D-BOS 247.