Where to apply sustainability optimizations in process flows?

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ABSTRACT

Future advanced semiconductor manufacturing processes are introducing significant patterning challenges. These challenges are coming together with additional requirements for sustainable, low Global Warming Potential/ low toxicity /low fine particle emissions. As a result, new solutions in terms of process integrations, molecules used for patterning modules, and overall stack of materials will have to meet those requirements while staying compatible with high-volume manufacturing (cost, availability, throughput, and overall patterning performance). Although specific process steps such as capacitor patterning for DRAM or 3D NAND high aspect ratio oxide etch are heavily scrutinized steps in terms of emissions and patterning challenges, many applications, including logic, integrate hundreds of steps where the patterning of 10-30 nm-thick layers requiring fluorine-containing gases. Although independently accounting for a modest amount of emissions, their sheer counts makes them a major contributor to CO_2 equivalent emissions. In this work, the cumulative impact of these low aspect-ratio patterning steps will be modelled through the imec.netzero program model. Then, the impact of a few sustainability-optimized solutions, such as low temperature etching for ultra-thin layer or stack optimization will be assessed.

Keywords: Sustainability, dry etching, optimization

1. INTRODUCTION

The majority of semiconductor manufacturing processes tend to use halogenated gases while globally there are sustainability and health hazard concerns arised towards these gases. This is due to the fact that halogenated gases can either be spontaneously reactive with organic materials (i.e. toxic) or can be extremely stable molecules capable of absorbing large amounts of energy (i.e high Global Warming Potential - GWP) contributing to climate change ref.[1]. So advanced patterning challenges are coming together with additional requirements for sustainable, low Global Warming Potential/ low toxicity / low fine particle emissions. Amongst the different process areas for chip-making manufacturing it is evident that dry etch processing is the area that contributes the most in direct emissions related to Scope 1 (Fig.1) and even with abatement systems there is are still GHG related emissions as can be estimated (Fig.2) by imec.netzero data [2,3].

In dry etching, halogenated and mostly fluorine-based gases are used regularly during processing. These gases tend to give reactive species that form volatile products making themselves very important to dry etch processing. Fluorocarbon can both deoxidize (carbon) and react with the other element of the oxide/ nitride (fluorine). We can take as an example the reaction in between silicon oxide (SiO2) and CF4 gas as described in ref. [4]. In dry etch processing, it has been a common practice to use high Global Warming Potential (GWP) fluorine-based gases that belong to the group of halogenated gases (Table 1) and that can have an accumulative environmental impact (Fig.3).

Considering the challenges mentioned above and the environmental impact of dry etch processing in direct emissions, process integration molecules used for patterning modules, and overall stack of materials will have to meet environmental requirements while maintaining with high-volume manufacturing (cost, availability, throughput, and overall patterning performance). Environmental requirements and standard cost saving strategies can be aligned under the scope of sustainability following a few practices. Saving resources such as e.g, reducing gas and/or power consumption or reducing the thickness and/or the number of layers in stacks on different patterns, usage of low-GWP gases, avoiding wasting wafers can be followed to potentially reduce emissions and to apply a cost-effective model [2]. To maintain these elements (power, performance, area, cost, environment) a methodology needs to be followed in order to identify targets suitable for sustainable optimizations. This methodology and examples of different sustainable optimizations will be described in the following paragraphs.

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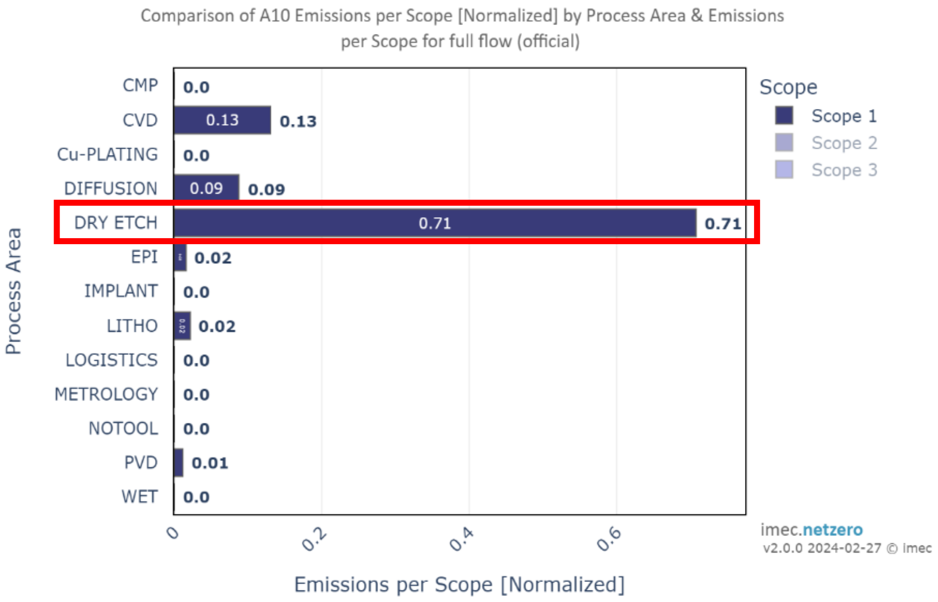


Fig.1: Top contributors bar plot for emissions per Scope by process area on A10 technology node focusing on Scope 1 using normalized values, source of data: imec.netzero. Emissions are modelled based on GHG gases input following the IPCC Tier2C methodology.

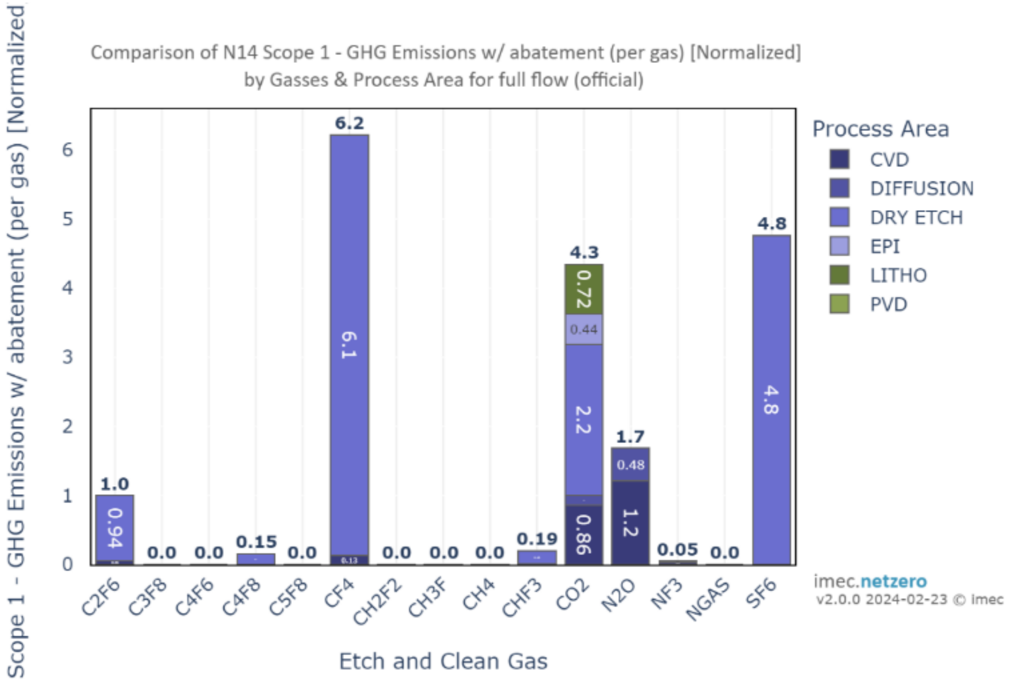


Fig.2: Top contributors bar plot for GHG emissions w/ abatement per gas by gas and process area on N14 technology node focusing on Scope 1 using normalized values, source of data: imec.netzero, Emissions are modelled based on GHG gases input following the IPCC Tier2C methodology.

Table 1: GWP values of top Scope 1 climate change contributors according to AR6 report.

Gas	***SF6***	***NF3***	***C2F6***	***C4F8***	***CHF3***	***CF4***	***CCl4***
GWP100 [kgCO2eq-AR6]	*25200*	*17400*	*12200*	*10200*	*14600*	*6630*	*2200*

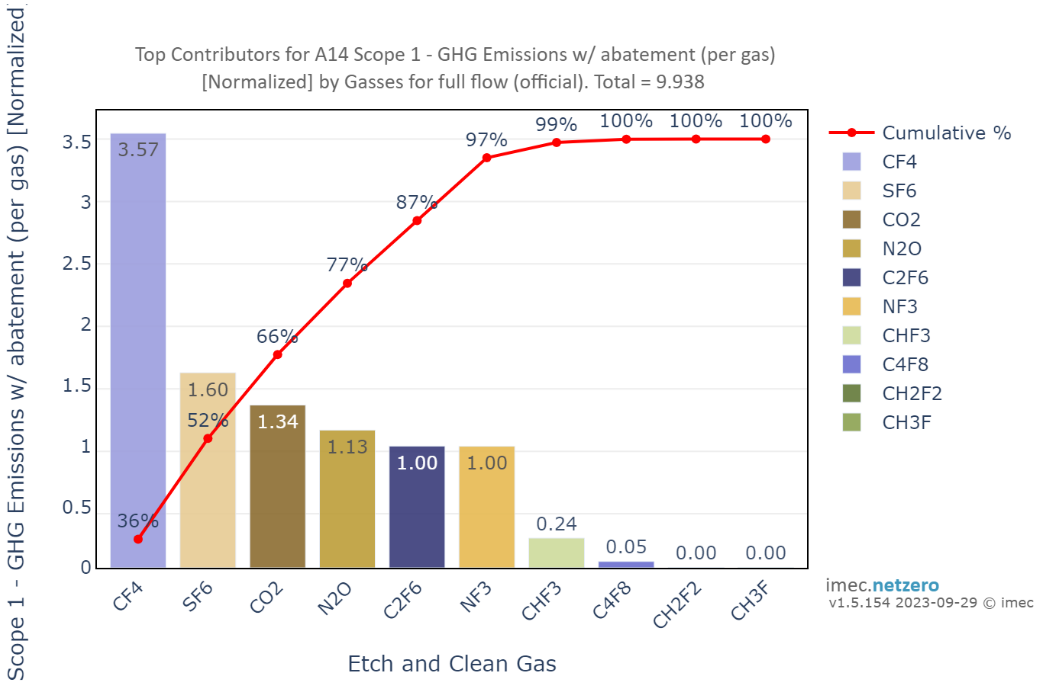


Fig3: Pareto table of climate change impact of high-GWP gas contributors used for etch and cleaning for A14 logic processes with burn-wash abatement (imec.netzero) using normalized values. Emissions are modelled based on etch gas input following the IPCC Tier2C methodology.

2. METHODOLOGY

As a starting point, process flows can be compared and adapted to minimize the need for polluting steps while maintaining performance and cost. Then, the stack of sacrificial materials used for the patterning of complex devices can be designed to exclude as much as possible the usage of materials requiring problematic gases to be etched.

2.1 Focusing on process flows

Firstly, we can focus on the different process flows and we need to structure our steps to identify the targets. To begin with, what type of fluorine-chemistries are used and where? Two main type of F-based chemistries are identified for process design: one group of SF6, NF3 or C4F8 chemistries and another one based upon CHF3, CH2F2, CF4.The former can be found in used for cleaning and deep etch and the latter found for ultra-thin films such as the ones found in logic applications. A typical case where the first mentioned family of chemistries is used is in specific process steps such as capacitor patterning for DRAM or 3D NAND high aspect ratio oxide where SiO2 is etched using a mixture of C4F8/C4F6/Ar/O2. The high-aspect ratio oxide etch is usually a long step with high-GWP gas (See Table 1) and a low-GWP fluorine based gases (C4F6 GWP100<1yr kgCO2 equiv, AR6 report) but with high toxicity. On the other group of chemistries, many applications, including logic, integrate hundreds of steps where the patterning of 10-30nm-thick layers require fluorine-containing gases. Related to the latter applications, a very standard and repetitive process would be the oxide hard mask opening which contains problematic layers as the spin-on-glass (SoG) and SiO2 layer etch. Both are small duration steps using a high concentration of CF4/CHF3 gases (GWP values: 6630 and 14.600 kg of CO2eq respectively) that are taking place almost after every lithography step.

Now, it is defined the frequency and the duration of the targeted process and as well as the comparison in between the different applications going towards the next phase, to sustainable optimization.

2.2 Sustainable optimization strategies

As the suitable process flows are identified the in-practice development should take place. In sustainable optimization strategies the final product requirements (power, performance, area, cost), as mentioned earlier, need to be maintained while reducing the carbon impact of a process. A good strategy to do it without have to sacrifice anything, would be to separate sustainable optimization into two: i. Design of patterning (stack optimization) and ii. Process optimization.

i. Stack optimization:

In this strategy, effort needs to be focused on avoiding including layers that require the usage of high-GWP gases by replacing them with materials that could be able to be processed with low-GWP gases. If it is not possible to try to make them as thin as possible so they can be etched using less gases and potentially faster.

Another interesting point would be to try to minimize the usage of passivative gases by going into low density plasma. In high-density plasma there are many volatile products and there is the need for passivation to protect the sidewalls, typically, by using high-GWP fluorine-based gases while in low density plasma there are more non-volatile etch products and less passivation is needed [2].

Finally, patterning a template and the then selectively grow back these layers, typically in dielectrics, can be followed as a rule to reduce gas consumption, as demonstrated in [5] for P28 CAR etch to TiN, using hybrid ALE (atomic layer etching) and selective deposition. In this work, using selective deposition a film of Si-based precursors was deposited on top of SoG. This process is giving us the capability to grow a HM on top of an ultra-thin-layer of 10nm of SoG, which as mentioned before, is a layer that requires high-GWP fluorine-gases to be etched. Basically, by following this practice, the defectivity on aC was reduced, on the same time less GHGs were used as etchants for the opening of the HM.

ii. Process optimization:

Special focus will be given in this work in process optimizations strategies. It is possible to etch efficiently by using heavy N2 dilution whilst maintaining the etch rate but reducing the amount of fluorocarbons used. This approach is taking advantage the synergistic effects between the gases and the N2 is acting as an accelerator of the etch by the fluorocarbons [2]. In that way both the concentration of the fluorine gases added and the processing time could be greatly reduced when comparing those used during standard processing.

Another method that could be followed without sacrificing the performance could be using low temperature etch. According to Ohiwa et al. [6] in low temperature conditions the etching rate (ER) could be increased for SiO2 etch using CHF3/Ar chemistry. This is happening due to the fact that in low temperature conditions there is the adsorption of fluoro-polymers by the oxide. The optimal thickness of this deposited film is around 10nm for -70◦C. This film can be pierced easily using Ar plasma and enhances the etching because it provides sidewall protection, while avoiding lateral etch and providing good performance in vertical anisotropic etch. To make sure that we do not polymerizing too much we need to keep low flow rate of the fluorine components which could be beneficial for reducing fluorine high-GWP gas usage whilst maintaining the performance.

3. DEMONSTRATIONS

For the SoG patterning a process in heavy dilution using N2/CF4 has already been proved to etch efficiently, in ref.[2] showing impact reduction. Correspondingly, the SiO2 opening can be done in low temperature conditions as referred in [3] and achieving higher etching speed. The amount of fluorocarbons used in the process recipe might be the same but the speed of the etch is much faster as Ohiwa et al. demonstrates in his work. In Fig. 2 the total consumption of CF4/CHF3 and CF4/N2 in kg is calculated and it is multiplied by the number of times the etch of SoG is repeated in every technology node in the BEOL. The target of this plot is to compare the impact on both chemistries demonstrating the impact in both cases. In the case where there is the necessity of reducing the processing time this practice can be followed and reduce impact on the direct emissions.

3.1 SoG etch: Standard chemistry vs alternative chemistry in heavy N2 dilution.

For this exercise calculations are made based on the gas consumption between a standard chemistry for SoG 10nm opening. The chemistry of the standard chemistry would be using CF4/CHF3 (190/50 scmm) and an alternative chemistry would be N2/CF4 (80/20 scmm). The etching rate of these two chemistries is comparable (~2.5nm/s) that is used to estimate the etching time for 10nm of SoG. In this exercise the consumption of CF4 has been calculated for 1 time processing and accumulatively for the total number that this process is repeated per technology node, data extracted by imec.netzero platform. The following calculations have been made to estimate the CF4 gas consumption in both cases:

- Gas consumption for 1 time processing:

$$Cons = \frac{etch\ time\ x\ density\ gas\ x\ flow}{6000000},\ (\text{kg})$$

- Total gas consumption for n times of processing:

$$Total\ consumption = \left(Cons_{gas1} + \cdots + Cons_{gasi}\right) x\ nb\ of\ times$$

- % of total consumption between standard and alternative recipe:

$$\Delta \text{Cons}\% = \frac{Totalcons_{standard} - Totalcons_{alter}}{Totalcons_{standard}} \%$$

3.2 SiO2 etch: Standard RT chemistry vs alternative chemistries in low temperature conditions

For this exercise the SiO2 etching rate has been studied compared to a standard with alternative low temperature condition recipes. It is worth paying attention to this study since SiO2 is a material that is vastly used in many applications, such as basic oxide/metal hard mask to high-aspect-ration applications. In this case we are comparing a standard chemistry of CF4/CHF3/N2 (70/45/60 scmm) in room temperature conditions to alternative one’s CF4/N2 and CHF3/N2 in low temperature conditions (-40◦C). Blanket SiO2 wafers have been etched on standard and on the alternative chemistries for 60 seconds. The following flow rate conditions (Table 2) were applied for the study of the alternative recipes:

Table 2: Flow rates of alternative chemistries studied on blanket SiO2 etch wafers on low temperature conditions.

Chemistries	**CF4/N2**	**CHF3/N2**
Flow conditions (scmm)	10/90	10/90
	30/70	30/70
	50/50	50/50

The thickness of the wafers was measured via ellipsometry tools before and after etching to calculate the average etching rate using the following equation:

$$\overline{ER} = \frac{\overline{Depth}}{Etch\ time}\ \left(\frac{nm}{s}\right)$$

The consumption of the fluorine gases was calculated:

$$Cons = \frac{etch\ time\ x\ density\ gas\ x\ flow}{6000000},\ (\mathrm{kg})$$

Etching rate and consumption of the usage of fluorine gases between the standard and the alternative recipes was compared:

$$\Delta ER\ \% = \frac{ER_{standard} - ER_{alter}}{ER_{standard}}\ \%$$

$$\Delta cons\% = \frac{mass, cons_{standard} - mass, cons_{alter}}{mass, cons_{standard}}$$

Moreover, it was calculated the consumption of fluorocarbons needed per nm and the ratio between the alternative recipes and the standard one to find the optimal conditions in terms of consumption and etching rate.

$$gas\ consumption\ per\ nm = \frac{mass\ gas\ consumption\ for\ 1\ sec}{ER}\ \left(\frac{kg}{nm}\right)$$

$$ratio = \frac{gas\ consumption\ per\ nm_{standard}}{gas\ consumption\ per\ nm_{alternative}}$$

As a next step, using the etching rate of SiO2 calculated above, the etching time and the fluorine consumption needed were calculated for the etch of 10nm of SiO2 using the conditions of the recipes mentioned on this exercise.

4. RESULTS

4.1 SoG etch: Standard chemistry vs alternative chemistry in heavy N2 dilution.

Following calculations mentioned in previous paragraph 3.1 the total consumption of fluorine-based gases multiplied by the number of times this process is repeated per technology node in a standard chemistry for 10nm of SoG etch vs an alternative chemistry of N2/CF4 is depicted in Fig 4.

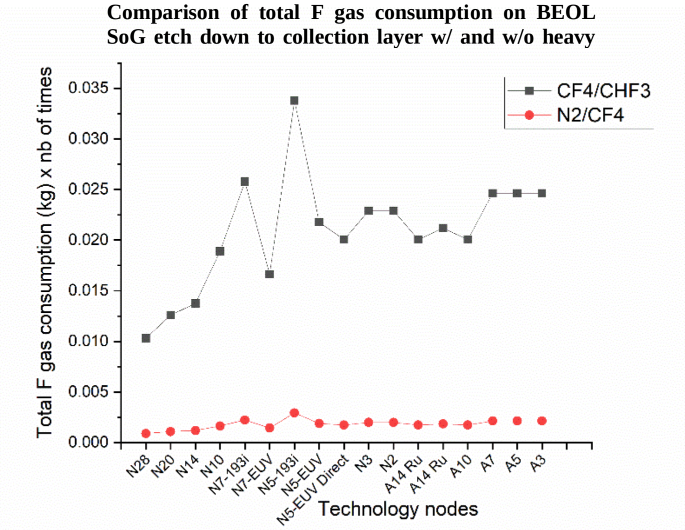


Fig 4: Plot demonstrating the total kg of consumption of two different chemistries for the etch of SoG. The black one is a standard chemistry of CF4/CHF3 and the red one is N2/CF4. The total consumption of the two different chemistries has been multiplied by the number of times the same process step is repeated within a process flow in the BEOL for every technology node according to imec.netzero data.

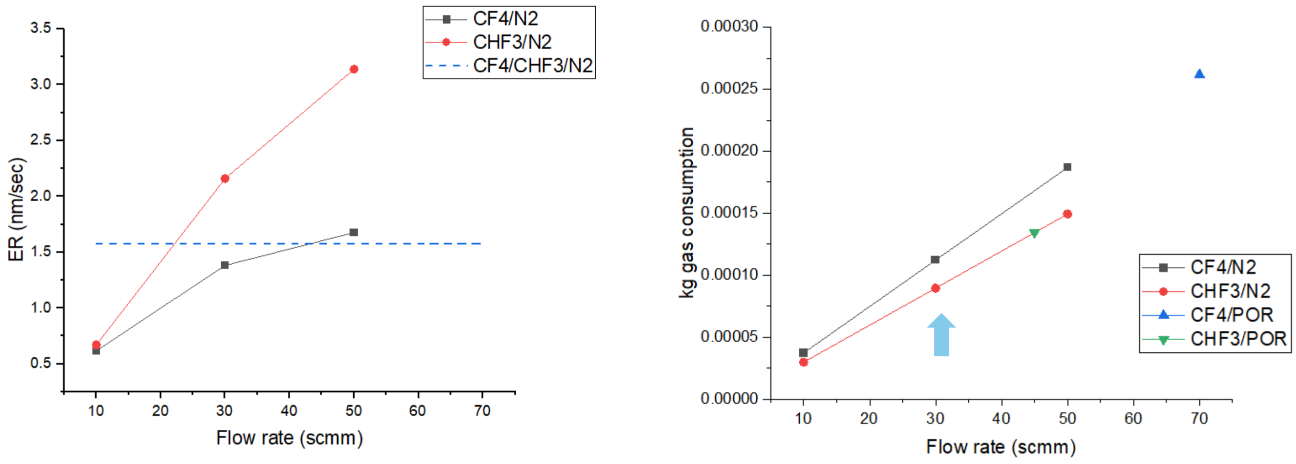
The total consumption of fluorine gases decreased by ~94% in the case of N2/CF4 chemistry compared to the POR, while no CHF3 gas was used.

4.2 SiO2 etch: Standard RT chemistry vs alternative chemistries in low temperature conditions.

After calculations have taken place as mentioned in the paragraph 3.2 above it is evident that the ER of the alternative chemistries is increased, as depicted in Table 3 and Fig.5a below. More specifically, for the CHF3/N2 chemistry, an increase from ~37% till 99% of the etching rate is observed for 30/70 scmm and 50/50 scmm respectively.

Table 3: Comparative table of standard vs alternative chemistries for SiO2 blanket etch.

Chemistry	**Flow**	**Temp (◦C)**	**ER mean (nm/sec)**	**ER%**
CF4/CHF3/N2	70/45/60	RT	1.58	NA
CF4/N2	50/50	-40	1.68	6.28
CHF3/N2	**30/70**	**-40**	**2.16**	**36.94**
	50/50	**-40**	**3.14**	**98.96**



(a): ER standard vs alternative chemistries for SiO2 60sec etch.

(b): Fluorine gas consumption on different (standard and alternative) chemistries vs flow rates

Fig 5: (a) Comparison of SiO2 etch using the standard (Process Of Reference – POR) vs alternative chemistries (low temperature & different flows) during 60sec. The blue dashed line demonstrates the ER of the POR chemistry in RT conditions while the black line corresponds to CF4/N2 chemistry and the CHF3/N2 chemistry both in low temperature conditions in different flow rates,

(b) Gas consumption of fluorine gases used for SiO2 blanket 60 second etch on different (POR and alternative) chemistries vs flow rates of different. The black and red lines demonstrate the gas consumptions for the CF4/N2 and CHF3/N2 respectively and the blue and green spots demonstrate the gas consumption of the CF4 and the CHF3 or the POR respectively.

In between the chemistries that show an increase on the ER compared to the standard chemistry, the one that has lower gas consumption compared to the POR would be CHF3/N2 30/70 scmm (Fig.5b). The amount of CHF3 used was decreased by 33% while no CF4 was used. Even though in the CHF3/N2 with 50/50 ratio we have a better ER compared to the POR, there is an increase in the gas consumption, which is calculated around ~11%. The % of reduction has been calculated and it is presented in Table 4 below:

Table 4: Comparative table of POR vs alternative chemistries on gas consumption and ER.

Chemistry	**Flow of FC (scmm)**	**kg CF4%**	**kg CHF3%**	**%ER**
CF4/N2	50	-28.6	0	+6.28
CHF3/N2	**30**	**0**	**-33.3**	**+36.94**
	50	0	+11.1	+98.96

For each alternative chemistry it was calculated the amount of fluorine gases needed per nm of layer and the ratio of etching rates of the POR and the alternative chemistries. In the Table 5 below it is evident that the CHF3/N2 chemistry with the 30/70 ratio has the lowest gas consumption per nm and the most satisfying ER increase. For that reason, the CHF3/N2 chemistry can be considered as the optimal spot and relation in this study.

Table 5: Comparative table of POR vs alternative chemistries on gas consumption/nm and ER

Chemistry	Flow	Kg/nm of fluorine gas	ER (nm/sec)	Ratio of ERs POR and alternatives
CF4 (POR)	70	2.76E-06	1.58	1
CHF3 (POR)	45	1.42E-06	1.58	1
CF4/N2	10/90	1.01E-06	0.62	2.74
	30/70	1.35E-06	1.38	2.04
	50/50	1.86E-06	1.68	1.49
CHF3/N2	10/90	7.43E-07	0.67	1.91
	30/70	**6.91E-07**	**2.16**	**2.05**
	50/50	7.93E-07	3.14	1.79

As a next step, the etching time and the gas consumption were calculated for 10nm of SiO2 for both standard and alternative chemistries in different flow rates. It is proved once again that the chemistry CHF3/N2 is beneficial in terms of reduction of gas consumption and etching rate performance because the etching time for 10nm of SiO2 using the POR recipe is around 6.34 sec while in the CHF3/N2 is at 4.63sec for the 30/70 scmm flow rate ratio. The etching time is lowest on the CHF3/N2 and 50/50 ratio, it is around 3.19sec. In parallel, the chemistry that shows the lowest gas consumption is the CHF3/N2. If we focus on this case only in the CHF3, it is observed that the gas used in the standard chemistry for 10nm etch would be around 4.75cm3 while for CHF3/N2 with the 30/70 ration 2.31 cm3 and for the 50/50 ration 2.66 cm3 (see Table 6 and Fig. 6 below).

Table 6: Comparative table of POR vs alternative chemistries on gas consumption, flow rate and etching time.

Chemistries	Flow	Time (sec)	Cons (cm3)
CF4 POR	70	6.34	7.40
CHF3 POR	45	6.34	4.75
CF4/N2	10/90	16.19	2.70
	30/70	7.24	3.62
	50/50	5.97	4.97
CHF3/N2	10/90	14.93	2.49
	30/70	**4.63**	**2.31**
	50/50	3.19	2.66

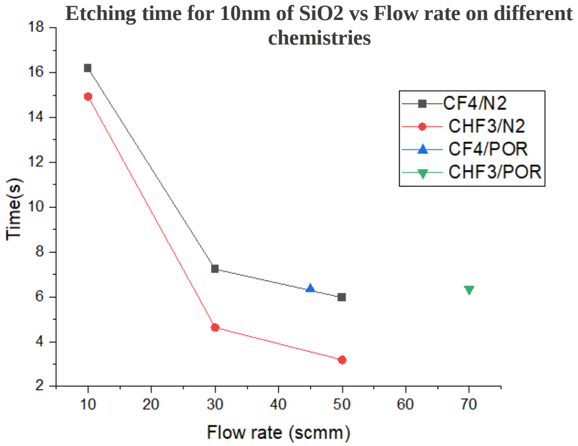


Fig 6: Calculated etching time of POR and different flows on low temperature conditions for SiO2 10nm etch vs flow rate. The black and red line correspond to the alternative chemistries of CF4/N2 and CHF3/N2 respectively. The blue and green spots correspond to the time for CF4 and CHF3 gas flows for the POR.

5. CONCLUSIONS

Focusing on reduction of the usage of gas resources can be beneficial for the different environmental targets and even for the performance and cost of the final products. This can be done by following reduction consumption strategies on dry etch processing paying attention to process optimization. Throughout 2 different exercises that are followed in this work it is evident that it is possible to use heavy dilution in N2 and low temperature conditions combined with heavy dilution without sacrificing the performance.

In the case of 10nm of SoG etch a reduction of 94% of the total fluorine gas consumption has been observed using the N2/CF4 chemistry compared to a standard CF4/CHF3 chemistry having comparable etching rates. Another advantage of this alternative chemistry would be the fact that 0% of CHF3 is used.

In the second case, the impact on the performance and the reduction of gas consumption on low temperature conditions on SiO2 blanket wafers was studied. Between the standard CF4/CHF3/N2 chemistry and two alternatives of CF4/N2 and CHF3/N2 the one that presents the best relationship of performance and reduction of gas consumption would be the CHF3/N2 using 30/70 scmm flow ratio with improve etching rate by ~37% and a reduction of CHF3 consumption by ~33% with 0% of CF4 added.

Both the heavy N2 dilution demonstration that depicts the advantages of synergistic effects and the low temperature etch show their capabilities and their advantages in terms of increase of performance, decrease of high-GWP gas usage and decrease of processing time. Similar practices can inspire future optimizations for sustainability in dry etch processing.

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References:

[1]: Shingo Nakamura et al 2003 Jpn. J. Appl. Phys. 42 5759

[2]: Gallagher E., Bezard P., Boakes L., Firrincieli A., Rolin C., Ragnarsson L-A., SPIE Advance Patterning + Lithography (2023)

[3]: Beu L, Raoux S, Chang YC, et al. Refinement to the 2006 IPCC guidelines for national greenhouse gas inventories, Volume 3: industrial processes and product use, Chapter 6: electronics industry emissions. Geneva, Switzerland: Intergovernmental Panel on Climate Change (IPCC); 2019 [cited 2022 Sep 27] Available from: https://www.ipcc-nggip.iges.or.jp/public/2019rf/pdf/3_Volume3/19R_V3_Ch06_Electronics.pdf

[4]: K. Nojiri, Dry Etching Technology for Semiconductors,

[5]: R. Vallat & all, AVS69, (PS+NS+FrM-3), Break Healing and LER Mitigation for Low Dose EUV Exposure

[6]: T. Ohiwa, K. Horioka, T. Arikado, I. Hasegawa, H. Okano, Jpn. J. Appl. Phys. 31 405 (1992)