Carbon footprint of PECVD chamber cleaning

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ABSTRACT

The use of perfluorinated gases such as NF_3, CF_4 or SF_6 for PECVD (plasma enhanced chemical vapor deposition) chamber cleaning has a much higher impact on global warming than does the use of onsite-generated F_2. This holds true even when supposing that in the future much more effort is paid for the correct abatement and a leak-free supply and take-back chain. This paper will discuss the steps available to the PV industry for control and reduction of carbon emissions in the chamber cleaning process.

Introduction

Fluorine and fluorine-containing gases are widely used in semiconductor, flat panel, and recently also in the solar industry to etch silicon, silicon nitride or silicon dioxide, respectively, in gas phase plasma reactors. An especially widespread application is the so called chamber-clean, a process that cleans SiO_2 residues from chamber inner surfaces by application of the cited gases. Historically, the nontoxic and noncorrosive CF_4, C_2F_6 and others were used, because of the convenience in flow control and storage. After much discussion about the global warming effects, specific abatements were developed and more reactive gases like C_4F_8 and NF_3 were introduced to allow higher depletion of the gas during application and thus arrive at lower emissions. Subsequently, gases without a GWP, such as ClF_3 and F_2, were used or introduced to industrial use [1,2]. SF_6 has been and is still widely used in the flat panel industry because of its relatively lower price compared to NF_3. Recently,

Chemical species	Formula	Lifetime years	100-yr GWP kg CO2-eq
carbon dioxide	CO_2	170-200*	1
methane	CH_4	12	25
nitrogen trifluoride	NF_3	740	17,200
nitrous oxide	N_2O	114	298
perfluoromethane	CF_4	50,000	7,390
perfluoroethane	C_2F_6	10,000	12,200
sulfurhexafluoride	SF_6	3,200	22,800

*the lifetime of CO_2 is a function of its concentration [4], pp. 212-213

Table 1. Global warming potential of certain greenhouse gases [4].

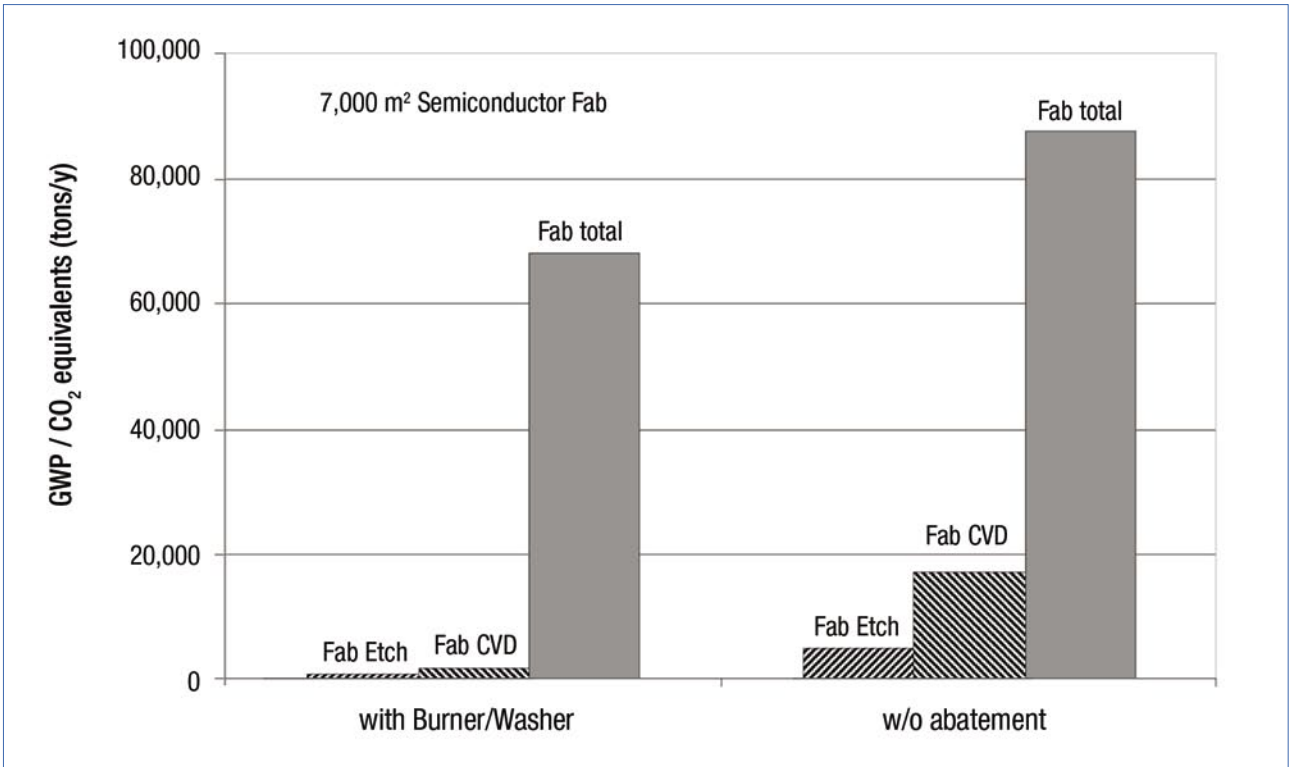

Figure 1. CO_2 equivalent emissions of a typical semiconductor fab [1].

• Chemical synthesis
• Distribution, transport, and connection to the users' system
• Application for the intended use, including emissions without abatement
◦ emissions due to no abatements for PFC being installed
◦ emissions resulting from abatements installed not being 100% reliable and lacking backup
• Return of the container for refill, and refilling.

Table 2. Principal contributions to carbon footprint of PFC and F_2 onsite.

some emerging technologies (thin-film Si) in solar cell production have started to use massive amounts of SF_6 (or NF_3) for the chamber clean application.

In a semiconductor fab, unfiltered PFC (perfluorocarbon) emissions with standard 200 or 300mm technology, although low on a kg/h basis, may represent as much as one quarter of the fab's total CO_2 equivalent emissions [3].

This difference is laid out in Figure 1, where the 'with burner/washer' columns represent the scenario utilizing a suitable abatement, whereas the others use no abatement ('unfiltered'). In the latter case, a reduction of the incoming (purchased) PFC gas is still carried out by the application (plasma cleaning of the reaction chamber and etch processes), but less efficiently than with an abatement. In the cited calculation, the respective etch and CVD areas were associated with emissions typical for 200/300mm technology, using a mix of different fluorine-containing gases. In conclusion, it is recognized that PFC emissions form a significant part of the global warming emissions, but that the major part is contributed by electrical power usage for tools and cooling purposes.

In the solar industry, two major groups of production technology are in use today: crystalline silicon, which represents the major part of the installed production capacity, and thin film technologies, which are emerging. While the former use minor amounts of PFC gases and tend to phase them out, some of the latter introduce increasing amounts of SF6 and NF3. The effect of this introduction is highlighted below.

Contributors to the emissions problem

The most important issue driving this investigation is that of the total life-cycle emissions of the respective application in terms of the cited global warming gases. The total CO_2 equivalent associated with the use of any global warming gas is more than just the combined physical emissions encountered during the application. Contributions are as shown in Table 2.

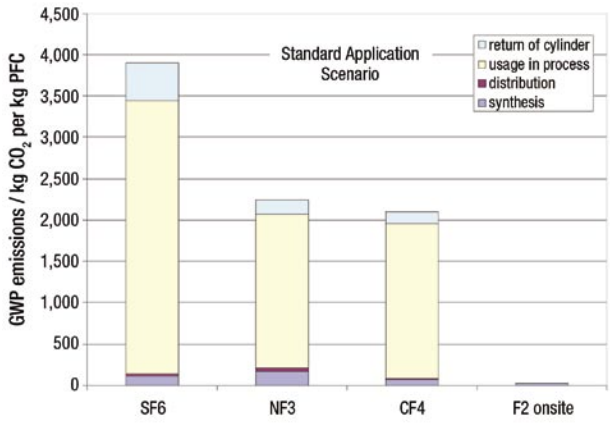

Figure 2. Carbon footprint of the investigated gases for chamber clean applications [5].

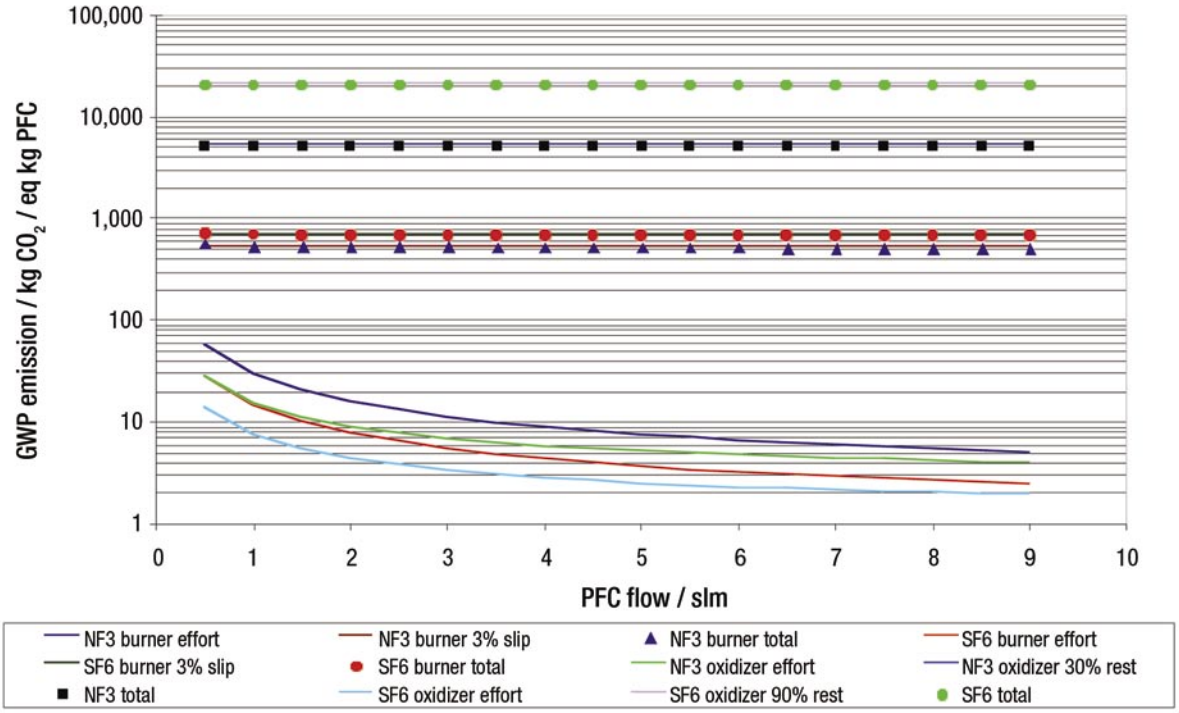

Figure 3. Determination of a typical abatement effort.

Users worldwide = 100%		100%=365 d/a Downtime of abatement	PFC input total worldwide = 100% VCovered by reduction	Not covered by reduction
No PFC reduction	15%	N.A.	0%	15% = fab input x fraction x users
Reduction concept "major streams (80% of PFC)"	65%	5%	49.4% = 80% (covered) x 0.95% (uptime) 65% (fraction of users)	15.6% = 20% (not covered) x 65% + 80% (covered) x 5% (downtime) x 65%
Reduction concept "all streams"	15%	5%	14.25% = 95% (uptime) x 15%	0.75% = 5% (abatement down-time) x 15%
Reduction concept as above including redundancy	5%	0%	5% = fab input	0%
			Sum covered 68.65%	Sum uncovered 31.35%

Table 3. Worldwide averaged user profile (semiconductors).

Chemical synthesis is associated with diffuse emissions, as there may remain traces of the global warming gas trapped during the steps of chemical reaction and subsequent purification, e.g. distillation. Also, as a significant amount of primary energy is associated with chemical synthesis, both contributions must be assessed.

Distribution and transport are considered to be major contributing factors, not only because of the use of fuel for transportation, but also due to undesired loss from leaking containers. The latter phenomenon is especially frequent with gases containing corrosive traces such as HF. The connection to a fab's distributions system implies vented volumes of the global warming gas, which is often not cleaned.

While the fab application may be equipped with abatement, it is quite common that there is no redundancy available; as a result, every abatement downtime leads to unfiltered PFC emission. The container or cylinder return can also lead to unfiltered emissions in case the filling station is not equipped with an abatement system suitable for fluorinated gases. In most cases, the system is absent.

Each of these steps is thus associated with CO_2 equivalent emissions, because of undesired unfiltered emissions, or because of the use of fuel or another primary energy source to perform the respective step. All possible contributions must be considered to yield a correct assessment of the CO_2 equivalent emissions.

CO_2 equivalent emissions / kg CO_2 per kg PFC used					
		CF_4	SF_6	NF_3	F_2 onsite
1 Outside Fab	Synthesis	81	118	180	35
	Transport/Distribution	8	23	35	0.2
	Cylinder/Container return	48	456	172	0
	Total	237	597	386	35
2 Inside Fab	Unfiltered Emissions	Calculated by user or taken from diagram as an estimate			
	Abatement efforts	From Diagram			

Table 4. CO_2 equivalent emissions (kg CO_2-eq/kg PFC) for the use of a compound without process application.

Scenario setup

Of all the gases involved, CF_4, SF_6, NF_3 and F_2 were chosen for this detailed

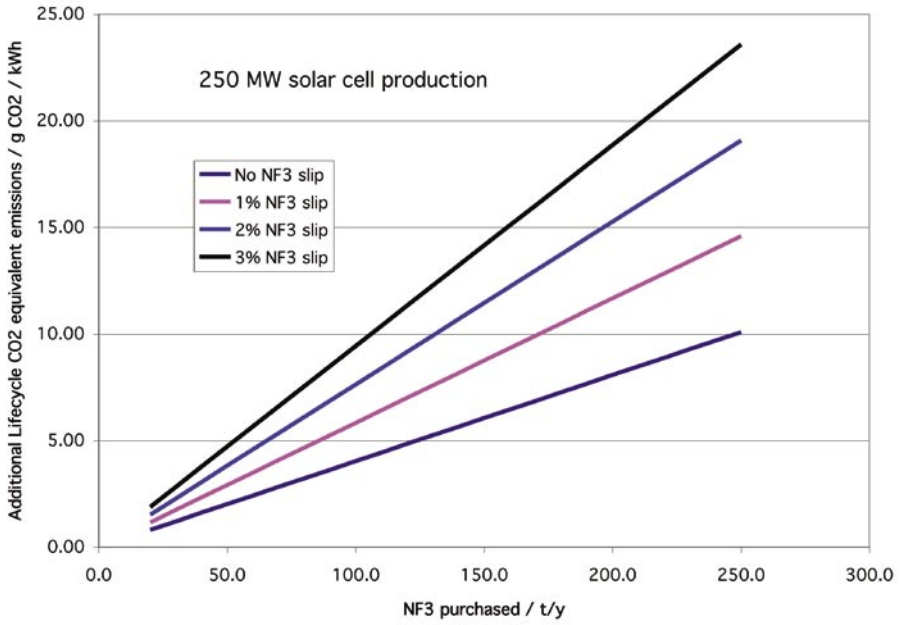

Figure 4. Effects of a 250MW thin film Fab consuming NF_3.

inspection. F_2 itself has no global warming potential, but its synthesis and disposal are associated with CO_2 equivalent emissions. These emissions are different for bottled F_2, F_2 generated offsite or F_2 generated onsite, the latter exhibiting larger emissions. However, since the only technically reasonable application of F_2 in the large scale is based on onsite generation, this type of generation is taken into consideration rather than that associated with bottled F_2 in this scenario setup. The determination of the level of these contributions, or by which scenario construction they have been derived, is given in [5].

Assessment of the CO_2 equivalent emissions requires the calculation of the kg CO_2 emitted per kg PFC used, with each additional contribution under consideration brought to this same scale. This format led to the result shown in Figure 2 for the CO_2 equivalent emissions, the values of which are balanced in a way that global averages are assumed to be obtained [5].

Moreover, the breakdown of different contributions is comparable for all gases except F_2. The intended use in process is most important, because there may be no abatement or no redundancy for abatements. F_2, however, features only 'important' contributions from the act of chemical synthesis.

Average Irradiation:	1,700 kW/m².y
Solar Module lifetime:	30 years
Module efficiency:	8% (not to be confounded with cell efficiency)

Table 5. CO_2 equivalent emissions payback calculation.

Results and discussion

Since abatement structure and performance is most important, driving factors for the overall effectiveness turn out to be more customer-specific than gas-specific. The different approaches of the respective different users' contributions are summarized in Table 3, data for which are taken from the M+W Zander installation database [3].

For the equipment uptime, a pessimistic figure of 95% was introduced. This implies a slip of 5% of the PFC as time-average, although the abatement could potentially reduce the PFC by 99%. Uptime and slip are not only dependent on the technical features of the abatement, but also on maintenance quality and intervals. Slip may be less than 5%, but this figure falls to virtually zero in cases where full backups of the abatement systems are installed. This refers to the last line of Table 3, but the investment required of such an abatement setup means that only 5% of the worldwide users have such a system installed.

The 'average user' as supposed in both Figure 2 and Table 3 is therefore mathematically represented by a mix of 'no abatements' (or non-PFC-effective abatements); 'abatements without backup'; and to a minor extent 'abatements with full backup'. So, for a customer having an installation different from average and wishing to calculate the actual CO_2 equivalent emissions of his application, another subset of numbers is required.

Table 4 illustrates the effort in kg CO_2 per kg PFC 'outside fab', i.e., all contributions without the use of the respective PFC in production. Unfiltered emissions resulting from either a slip in the abatement stage, or from a lack of abatements, can only be calculated on an individual basis by the user. In both cases, the depletion in the respective process application is taken into account. A further contribution in this same context is the abatement effort, which, if not easily calculable by the user, may be taken from Figure 4.

In converting kWh electrical power to CO_2 equivalent emissions, the ratio of 0.484 kg CO_2 per kWh was used. This supposes a power mix, which is, in this case, typical for Europe [6]. It is usually the case that the abatement efforts are a minor contribution, whereas the unfiltered emissions form a major part (see Figure 3).

Figure 3 shows the respective CO_2 equivalent emissions of both abatement effort and slip or rest of untreated PFC in a range of five decades. ('Slip' refers to the fraction not being treated because of installation up- or downtime, respectively, whereas 'rest' refers to the fraction not being treated because of the limited efficiency of the abatement.)

Two important types of abatement are considered in Figure 3: burner-type equipment using an oxygen-driven burner, thus reaching sufficiently high decomposition temperatures; and an electrically-heated oxidizer (without flame) reaching typically 800°C, which is too low for complete decomposition. In the semiconductor and solar industries, these two types of abatement play the dominant role in PFC abatement.

The burner-type abatements are usually very efficient, providing 99% or more abatement in the case of PFCs, meaning that the overall PFC emission is dominated by the slip. The oxidizer, however, does not show decomposition for a number of important PFCs, and a limited decomposition for NF_3, so the overall PFC emission is dominated by the other PFCs.

This difference is depicted as solid lines accordingly in Figure 3. Because the demand in primary energy and other facility media is higher with burners than with oxidizers, this part, the abatement effort, is generally lower for the oxidizer than for the burner (represented by four solid lines in the lower part of the diagram of Figure 3).

The overall (total) CO_2 equivalent emission is represented as dots in the upper part of the diagram, the resulting line for which is almost identical to the solid lines showing slip or rest. In the case of low PFC flow, a slight difference is discernible.

The total contribution of application of abatements is dominated by the slip or rest of unreacted PFC, both for the more effective burner-based and especially for the classical non-flame oxidizers. Nevertheless, the contribution of the pure abatement effort is given separately, so that users with very reliable abatements capable of less than 0.5% downtime, or having full backup installation, can do the proper calculation as shown in Table 4.

The PFC flow on the x-axis spans a wide range from 0.5 to 9slm (standard litres per minute). Whereas the former can be regarded as typical for 200mm semiconductor applications, the latter value reflects the demand of solar thin-film processes. In most cases, there is not one single abatement equipment serving the whole range, but different abatements of different generations of development.

These will be used for the different sectors of application. Therefore, the resulting effort curve will not be ideally smooth, but will show 'jumps' at the point where a switch from one abatement machine to another occurs. Figure 3, however, represents a generic average curve, showing the dependencies of the entire range required.

Estimation of the ecological effect of NF_3 chamber clean

For a long time, silicon solar module fabrication has not been influenced by the usage of PFC, or only to a minor extent. Emerging thin-film techniques, however, introduced significant amounts of SF_6 or NF_3 for the CVD chamber clean process. Since the use of this technology is still young, many installations are designed with high-performance burner-type abatements in all relevant emission points; a future trend prediction shall be derived based on this scenario. To come to a short and simple evaluation, the g CO_2 emitted per kWh solar energy produced by the respective cell is calculated. This expresses the relation of ecological effort and benefit.

Since a complete assessment of the CO_2 equivalent emissions is still not finished for the technology in question (Si thin film), only the additional CO_2 equivalents can be given, which are purely due to the usage of NF_3.

According to recent results, it was a relation of 38,250 kWh produced in cell lifetime per kWp produced has been used for conversion [7], and the assumption that the thin film fab shall have a capacity of 250MW(el) production per year.

Figure 4 gives the ecological cost of the usage of NF_3 in terms of additional CO_2 equivalent emissions per kWh produced. This is depending on the amount of NF_3 used per year and depending on the assumed slip, that is the rest of NF_3 remaining and emitted after abatement. In the best case, this is zero, but it may be higher, in the single digit percent range.

Even for completely effective abatement (0% slip) there is additional CO_2 equivalent emissions because of the efforts associated with the chemical synthesis of NF_3 according to Tab. 3. Since this additional CO_2 equivalent emissions come on top of the other equivalent emissions to be considered for the use of other resources than NF_3, like electrical energy, water, or chemicals, this impact is an environmental burden to those thin film technologies making use of PFC, even in the case of very effective abatement.

The values obtained are in a range of 5 to 15 g CO_2 per kWh. This additional contribution to the effort linked to NF_3 usage may be compared to the total CO_2 equivalent emissions for a polycrystalline Si solar cell, which are 30g/kWh [7]. So the NF3 contribution is significant.

It is out of question, that the use of less effective abatements, today unusual in solar industry, is a real threat to the ecological efficiency of Si thin film solar cells using NF_3 in production.

Conclusions

For the solar industry, it is clear that the recommendations are the use of abatements that are able to destroy PFC with better than 99% efficiency, and with full backup, or the avoidance of the use of PFCs. Better still is the introduction of F_2 for the same purpose.

Although the results are very much in favour of the F_2 onsite application, there remain a number of practical barriers. A qualification has to be carried out prior to replacement of a cleaning gas by another. In the flat panel industry, this process is already underway and replacement is ongoing. For the semiconductor and solar industries, however, there is still a need for action.

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