THE CARBON FOOTPRINT OF PECVD CHAMBER CLEANING USING FLUORINATED GASES

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ABSTRACT: Fluorinated gases like CF_4, C_2F_6, SF_6, NF_3, F_2 by on-site generation can be used by the semiconductor and photovoltaic industry for etching silicon wafers and (PE)CVD chamber cleaning. Avoidance of the emission of the gases CF_4, C_2F_6, SF_6 and NF_3 is required because they have a high global warming effect and high atmospheric life-time. In this work a comparison is made of the carbon footprint from the use of these gases in chamber cleaning. The carbon footprint is calculated as the total greenhouse gas emissions over the whole life-cycle of the gases.
The steps in the life cycle are the following: production of the compounds, transportation, distribution in the fab (connection of cylinders), use in the process, abatement to destroy the unreacted gases and take-back of cylinders. Emissions from each step can be direct (from emission of the fluorinated gases) or indirect (from energy use).
Preliminary results (excluding SF_6 onsite recycling), partly based on best guesses, indicate that the life-cycle greenhouse gas emissions are dominated by rest emissions of the fluorinated gases after abatement in the usage phase, followed by fugitive emissions during downtime of the abatement system and cleaning of the not completely empty returned cylinders.
The use of on-site generated F_2 turns out to be clearly in advantage over the other fluorinated compounds because F_2 has a global warming potential of zero. Possible improvement options to minimize the use and emission of fluorinated gas are (1) strict procedure for connection of cylinders, (2) complete usage or reliable abatement of the gas from the bottle, (3) the recovery or reliable abatement of unused gases from the process and (4) good end-point detection of the process.

Keywords: amorphous silicon, microcrystalline silicon, manufacturing and processing, environmental effect

1 INTRODUCTION

Fluorinated gases like CF_4, C_2F_6, SF_6, NF_3, ClF_3 and F_2 by on-site generation are used by the semiconductor, flat panel and photovoltaic industry for etching silicon wafers and (PE)CVD chamber cleaning. The emission of the gases CF_4, C_2F_6, SF_6 and NF_3 is unwanted because they have a high global warming effect and high atmospheric life-time. Much discussion has taken place about the replacement of the first-generation perfluorinated carbon gases (PFCs) CF_4 and C_2F_6 by more modern compounds like C_3F_8, C_4F_8, but also NF_3 and - recently - SF_6 [1]. The lack of a common basis for comprehensive comparison initiated this study. For a case study, the compounds CF_4, C_2F_6, NF_3, and SF_6 were selected. For comparison, F_2 generated onsite was also taken into account, although not feasible for all the cited applications, but already in steadily increasing use in the flat panel industry [2] .

This contribution is intended to give an estimate for the life-cycle CO_2 equivalent emissions (carbon footprint) of the use of different PFCs in use in semiconductor, flat panel and solar industry. It comprises the contributions of synthesis, handling and distribution, intended use in the production tool, including different abatement scenarios, and return of the emptied transport vessel.

2 SYNTHESIS

2.1 General

Classical chemical synthesis is characterized by a sequence of synthesis and purification steps [3]. A generic flow diagram is shown in figure 1.

All figures shown are hypothetical, but typical. The typical issues are: the energy input required in synthesis step is low compared to the purification step; energy may come as waste heat from an exothermic synthesis reaction suitable for secondary use. In practice, this is used in case of energy integration in a large chemical site. Reaction waste is created in the synthesis step, which is usually easily separated from the rest. Waste heat from purification steps are less often used in an efficient way and may be smaller. Traces from the raw product are contained in all waste streams, both from synthesis and purification. The dedicated purification step is necessary to come to levels of purity required by the application. Very often, this is a distillation step.

The losses are in most cases unavoidable either by physical or by economical reasons: no better selectivity of the synthesis process available, no efficient separation process known or investment for better separation not justified by the price of the product are possible reasons.

The respective synthetic pathways of the considered compounds are all classical in the sense that they are in accordance with the flow diagram in figure 1. Moreover, the installation base (worldwide) shows then all the characteristics of classical process industry, operated by the players of process industry.

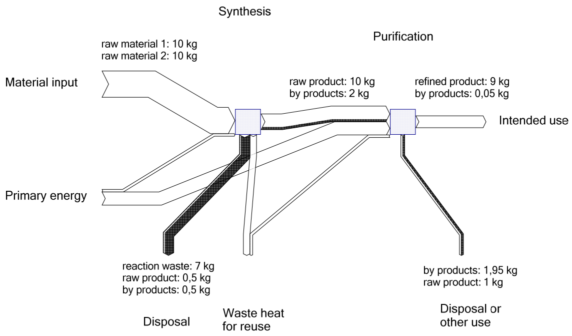

Figure 1: Flow diagram of a chemical synthesis

2.2 PFC synthesis

Data from the suppliers suggested that loss during production can be expected in a range from about 0.5% to a single-digit percent range. Staying as close to the few supplier data available, the following estimates were derived (Table 1).

Table I: Data on synthesis of PFCs and F_2.

	Synthesis	Reaction	Purification	PFC loss	Energy (1) kWh/kg PFC	CO_2 equivalents (2) kg CO2-eq/kg PFC
SF_6	Direct fluorination	$S + 3 F_2 \rightarrow SF_6$	(a) thermal decomposition at 400°C (b) caustic scrubbing (c) pressure distillation	0.5%	8.3	4.4
NF_3	Ammonia fluorination	$NH_3 + 3 F_2 \rightarrow NF_3 + 3 HF$	(a) scrubbing (b) distillation	1%	23	12.4
	Electrolytical fluorination	$NH_3 + 3 HF \rightarrow NF_3 + 3/2 H_2$	(a) purification (b) distillation		13.7	7.3
CF_4	Exchange reaction	$CF_2Cl_2 + 2 HF \rightarrow CF_4 + 2 HCl$	(a) scrubbing (b) distillation	1%	17.0	9
F_2	Electrolysis	$HF \rightarrow 1/2 H_2 + 1/2 F_2$	(a) purification	0	35.3	19

(1) Including energy spent for the precursors
(2) CO2 equivalent calculated with 0.53 kg CO2-eq / kWh (UCTE electricity mix; IPCC 2007)

Differences in the loss rate of the different PFCs shall not be discussed and are probably not real with view to the data quality. Energy required for synthesis is an estimate too, taking into account the raw materials as well as the efforts in the synthesis and purification steps themselves.

It should be noted that the precision of these data is not sufficient to serve as a reference, prior to a further confirmation. The influence of imprecise input data on the conclusion is given in the section "Discussion".

Since the reduction of global warming gases came to the political agenda, all players show remarkable efforts to demonstrate or improve compliance with political reduction goals. So in a scenario consideration for future development, improvement shall be included. However, if physical barriers exist, there will remain a residual loss.

3 HANDLING AND DISTRIBUTION

Classically, the "handling and distribution" comprises the contributions of transport, e.g. a truck running for a predefined distance.

For this it was assumed 1000 kg-km per kg PFC distributed with a corresponding CO_2 emission of 0.165 kg CO_2-eq/kg PFC (ecoinvent 1.3 database, IPCC2001 GWP100a).

The handling and distribution itself may be expected to show insignificant losses of the desired compound, because a valuable product is not expected to be subjected to a "leaking" distribution chain. However, also these losses are not zero and shall be included into the consideration additionally to the classical transportation scenario.

Two different cases are to be included: the regular emission during flushing the connection lines and the irregular major leakage of transport or storage vessels.

On the one hand, in high purity applications as the industries cited in the headline, flushing procedures are a standard after each new connection of a bottle or container to a distribution system (see figure 2). Non-corrosive and nontoxic PFC are not cleaned during flushing as a standard.

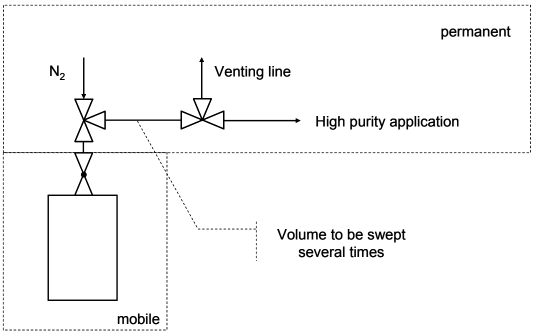

Figure 2: Connection and related emissions

These standardized and regular procedures lead to a maximum loss of 0.1% of the container's content, taking all connection steps in the course of the usage of the gas container together.

On the other hand, there are incidents, which are rare but regular events, where the content of a transport container is lost. Since no statistics about losses were accessible, an estimate was used. If every 1,000 to 5,000 connection processes one container is lost, the overall loss rate is similar to the regular loss considered above, around 0.1% of the content.

To stay conservative, 0.1% of the cylinder/container content (plus the truck's contribution) was used for the evaluation in this study. Any higher rate of failure for NF_3, which may be expected because certain impurities may lead to explosion of bottles [4], was also not included.

4 INTENDED USE

During the intended use in (dry or plasma) etching steps a major release may occur in the case there is no exhaust abatement available to decompose the PFC. Recycling as an exhaust purification step is under development since many years and recently again introduced for the cleaning of micromorphous silicon (µ-Si) PV module production.

However, the standard abatements of today are widely spread, and shall be considered in the following as a standard case, especially since the efforts to be invested to abate are no more than a few kg CO_2-eq per kg SF_6 abated. The differences between plasma, burner and catalytic abatements are not included for the sake of simplicity. Basically the efforts to abate are based on burner type abatements, representing a standard case and not the best case for efficient energy usage.

In a worldwide comparison four different types of abatement installations are observed [5] (Table II).

(1) No PFC abatement in place (only wet scrubber or cold absorbers): 15% of the users worldwide.

This results in 15% unfiltered PFC emission relative to the worldwide PFC input (100%).

(2) PFC abatement of major streams (80/20 rule): 65% of users worldwide. 80% of the PFC mass flow is covered by reduction, but 20% remain undestroyed. The abatements in use are supposed to have 5% downtime with no PFC reduction during downtime.

This results in 15.6% unfiltered PFC emission relative to the worldwide PFC input (100%)

(3) PFC abatement of all significant PFC containing streams: 15% of users worldwide. All PFC streams are reduced by suitable abatements, but the downtime of the respective abatements is supposed to be 5%.

This results in 0.75% unfiltered PFC emission relative to worldwide PFC input (100%)

(4) PFC abatement with redundancy of the abatements: 5% of the users worldwide. This covers not only 100% of the PFC fab input, but also reduces abatement downtime to virtually zero because of redundancy concepts. *This results in 0% unfiltered PFC emission*

Total estimated emission from application is therefore 15%+15.6%+0.75% = 31% unfiltered PFC emissions from the intended use, relative to the worldwide input set to 100%. The unfiltered emissions have to be reduced furthermore by an average consumption in the respective process steps. This reduction comes on top of the abatement performance. It may vary from 30 to 70% reduction, depending of the process tool, the recipe, the respective gas and the generation of the process.

Best case:	9% unfiltered emission
Worst case:	22% unfiltered emission

These percentages of abatement are relative to the kg PFC entering the plasma etch process.

In the scenario's presented in paragraph 6, the abatement is simply divided into a section "without abatement" showing the unfiltered emissions and a section "with abatement" using the abatement mix explained above.

The different process usage efficiencies are set to 30% for CF_4, 60% for SF_6 and C_2F_6, and 70% for NF_3, respectively.

Please note that neither the exact figure for abatement downtime nor the reduction in the process can change the outcome significantly because an important fraction of users simply emits all the gases unfiltered.

5 RETURN OF EMPTIED BOTTLES

The consideration of returning the emptied bottles is separated from the general discussion of "handling and distribution" because of the major impact in this step. A considerable amount of rest gas contained in the bottle is released prior to the refill, and it depends on the installations available in the filling center of the gas distributor, whether a PFC abatement is carried out during bottle refill or not.

Generally, for the nontoxic and non-corrosive gases SF_6, CF_4, and C_2F_6 an unfiltered release at this point of 2% of the vessel is assumed. This is an average of all countries and installations. For NF_3 a 1% unfiltered and 1% abated release is supposed. This is because NF_3 emissions are regulated in some countries. The efforts for the respective abatement are included, but unimportant compared to the rest of the contributions.

6 SUMMARY SCENARIO

Summarizing the contributions of general PFC usage, the following flow scheme is obtained (values generic) (figure 3).

Converting these values to a basis of kg CO_2 equivalent emission per kg PFC produced we obtain table III and figure 4.

It is obvious, that most of the GWP emissions are related to the intended use, and that the choice and operation of abatements is crucial.

Table II Estimation of PFC emission in the use phase

		100%=365 d/a	PFC input total worldwide = 100%	
	Users worldwide	**Downtime of abatement**	**Covered by reduction**	**Not covered by reduction**
No PFC reduction	15%	N.A.	**0%**	**15%** = fab input x fraction of users
Reduction concept "major streams (80% of PFC)"	65%	5%	**49.4%** = 80% (covered) x 0.95%(uptime) x 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 downtime) x 15%
Reduction concept as above including redundancy	5%	0%	**5%** = fab input	**0%**
	100%		Sum covered = **68.65%**	Sum uncovered = **31.35%**

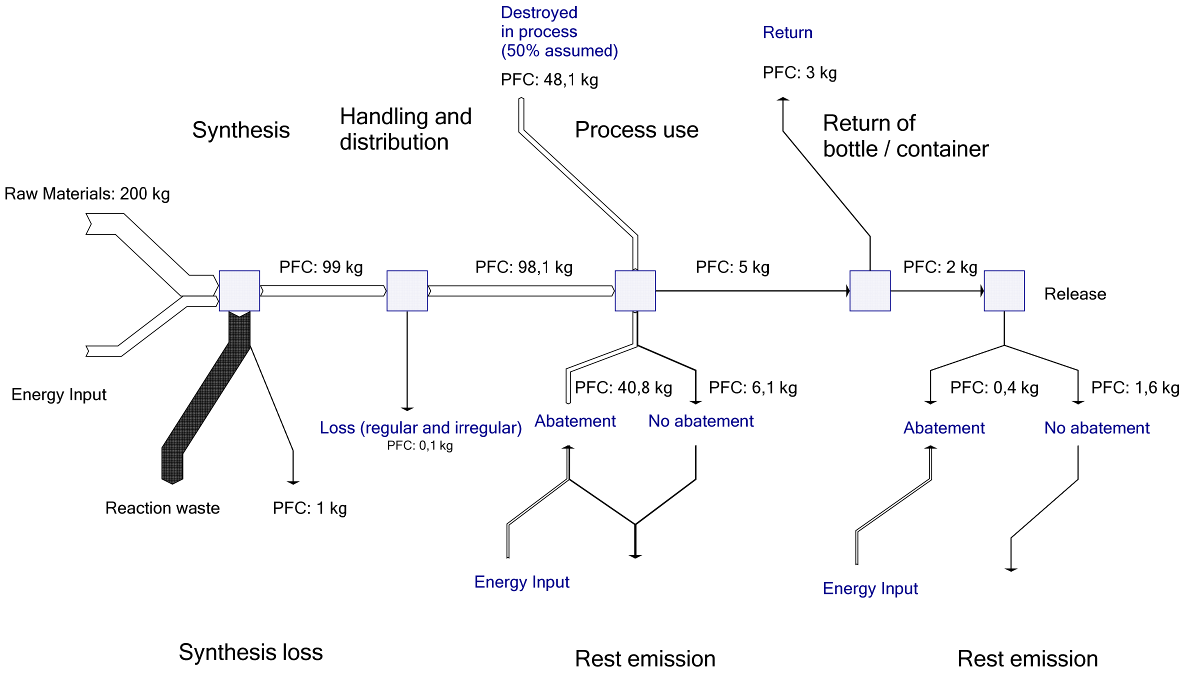

Figure 3: PFC usage chain

Table III: Summary of greenhouse gas emissions (kg CO_2-eq per kg PFC)

		SF_6	NF_3	CF_4	F_2 onsite
synthesis	raw material and energy input	4.1	7.9	7.5	35.3
	loss during production	114	172	74	0
distribution	handling, including transportation	23	35	7.6	0.2
usage in process	unfiltered emission because of no abatement	1,291	726	729	0
	rest emissions using abatements	2,010	1,130	1,134	0
	abatement efforts, total	2.6	5.2	4.5	2.5
return of cylinder	unfiltered emission because of no abatement	456	172	148	0
	abatement efforts, total	0	0.2	0	0
	Rounded sum	3,900	2,200	2,100	38

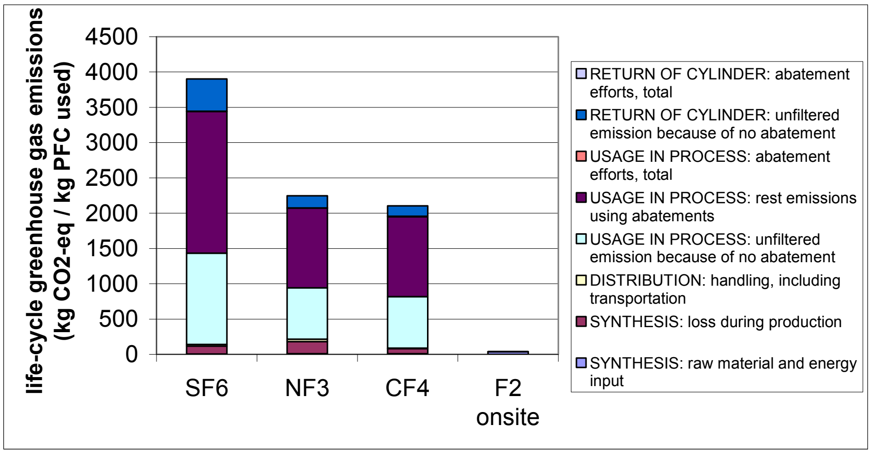

Figure 4: Summary of greenhouse gas emissions (kg CO_2-eq per kg PFC)

7 DISCUSSION & CONCLUSIONS

7.1 Data quality

Prior to drawing conclusions an estimate of the data quality of the input values used are given in table IV.

Table IV: Data quality

Step considered	**Subcategories**	**Data Quality**	**Impact to final result**	**Comment**	**Rank**
Synthesis	raw material and energy input	Fair	Low	(1)	6
	loss during production	Bad	Marked	(2)	4
Distribution	handling, including transportation	Bad	Negligible	(3)	5
Usage in process	unfiltered emission because of no abatement	Good	High		1
	rest emissions using abatements	Fair	High	(4)	1
	abatement efforts, total	Good	Low	(5)	7
Return of cylinder	unfiltered emission because of no abatement	Fair	Marked		3
	abatement efforts for above	Fair	Negligible		8

(1) It is not intended to create reference values in this categorie in the frame of this publication (Rank = 6)
(2) Diverging data from the producers
(3) No statistics for " rare events" like loss of a container
(4) Depending on maintenance of the abatements, thus may vary even for the same site over time
(5) Much depending on process conditions, values used here are for " large PFC flow" where effort

Since data are different for the different PFCs considered, only a qualitative ranking is given for data quality, impact of the respective category, and the resulting overall rank of the contribution to the cumulative result. Rank 1 is found two times, for unfiltered PFC emissions in the process and rest emissions after abatement. Rank 3 is the loss during bottle return and rank 4 is the loss during production. All the higher ranks are not truly stable. However, the major impacts can be regarded as stable, and the more uncertain contributions have been assessed conservatively. So the overall assessment is stable, also.

7.2 Results obtained

First of all, abatement matters. Not only it is worth to install it, but it is also of top priority to run it at maximum performance.

The fact that rest emissions with abatement are estimated to be superior to those without abatement is due to the fact, that the installation base using no PFC abatement is only 15% of total, whereas 65% are assumed to have at least a minimum PFC capable abatement installation. The environmental impact from abatement is always small under the conditions assumed here compared to the abated potentials, but also compared to the rest emissions. This is because in this study benchmark figures for applications with high flow of PFC are used (e.g. semiconductor CVD, µ-Si thin film deposition, etc.). It is no longer true, if streams become very dilute, like e.g. in semiconductor dry ash. The latter case is not included here.

The release during production and cylinder return are approximate, but conservative on the other hand. This may largely depend on how the design-, but also the maintenance status of the respective installation is. We tried to compile the data we regard close to the "un-avoidable" limit.

It is clearly pointed out that onsite F_2 generation is superior from the standpoint of GWP emissions. A similar picture is expected for ClF_3, not deeply analyzed in this contribution. The practical advantage of F_2 generated onsite over bottled ClF_3 is safety.

The precision of the conclusions is not dramatically affected by the lack of precise input data, because these belong to less important impacts. However, once the abatement and/or process optimization has made progress, bottle return, losses during production and even transportation, handling and distribution come into the focus. To proceed then, an improved set of data is mandatory.

8 ACKNOWLEDGEMENTS

This work was conducted in the German funded CO_2 reduction project 01LS05090.

Part of this research was conducted within the Integrated Project CrystalClear and funded by the European Commission under contract nr. SES6-CT_2003-502583.

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