

CONTROL OF LIFE-CYCLE EMISSIONS FROM CRYSTALLINE SILICON SOLAR CELL MANUFACTURING

Mariska de Wild-Scholten¹, Martin Schottler², Birgit Schlüter²

¹ECN Solar Energy, P.O. Box 1, 1755 ZG Petten, The Netherlands

²M+W Zander FE GmbH, Lotterbergstr. 30, 70499 Stuttgart, Germany

E-mail: m.dewild@ecn.nl

ABSTRACT

Reduction of life-cycle emissions are needed to improve the environmental profile of silicon photovoltaics. Most emissions are indirect via upstream processes and can be reduced for example by lowering the energy consumption for silicon feedstock and wafer production. The direct emissions from solar cell manufacturing must be reduced by implementing abatement strategies.

1 INTRODUCTION

In order to decrease the environmental burden and to comply with legislation, the emission of harmful gases into the biosphere needs to be controlled [1]. In this study, we investigate the direct and indirect emissions of NO_x, HF, NH₃, volatile organic compounds (VOC) from silicon solar cell production. Emission control is discussed in the frame of national and EU legislation.

Emissions of harmful gases are regulated in the European directive on Integrated Pollution Prevention and Control (IPPC) [2] and in the European Solvents Emissions Directive [3]. The IPPC Directive sets out the main principles for the permitting and control of installations based on an integrated approach and the application of best available techniques (BAT) which are the most effective techniques to achieve a high level of environmental protection, taking into account the costs and benefits. However it does not include emission limit values. The *emission limit values* are normally defined by regional or national authorities, taking site-specific conditions into account such as the technical characteristics of installations and the local environmental situation. Emission limit values for Germany will be presented and abatement technologies to control the emissions.

Accurate and up-to-date information on the *direct emissions* from cell manufacturing is not available in open literature. A European register (EPER) publishes detailed information on the industrial emissions into air and water from approximately 12 000 industrial facilities. However, information about volumes produced is not provided. Companies typically do not disclose this type of information. Our paper is based on measured emissions for a wide variety of gases associated with mono- and multi-crystalline silicon cell production.

The *indirect emissions* associated with upstream processes (i.e., silicon production, crystallization and wafer manufacturing) are determined using using Simapro 7.1 software with the ecoinvent 2.0 database and recent data.

2. CONTROL OF EMISSIONS

Control of emissions is needed to reach the emission limit values. The available abatement technologies are specific for the type of effluent to be treated. An overview is given in table I.

Table I. Overview of different abatement technologies

1 Acid and caustic gases						
Source	Texturing and etching benches	HF	HNO ₃	NO ₂	NH ₃	others
Treatment	Wet scrubbers / absorption towers / SCR for NO _x gases					
2 Acid and caustic waste waters						
Source	Texturing and etching benches	KOH	NH ₄ OH	others		
Treatment	Neutralization					
3 Fluoride containing waste waters						
Source	Rinsing water from benches, scrubbers	HF	HNO ₃	H ₂ SiF ₆	others	
Treatment	Precipitation and filtration					
4 Concentrated acid waste						
Source	Texturing and etching benches	HF	HNO ₃	H ₂ SiF ₆	others	
Treatment	External disposal					
5 Solvent exhaust						
Source	Printing, spray dopers	solvents, alcohols				
Treatment	Condensation, oxidation, biofilter					
6 Solvent waste						
Source	Condensation of exhaust, residues	solvents, alcohols				
Treatment	External disposal					
7 Silane containing gas						
Source	Silicon nitride deposition	SiH ₄	NH ₃			
Treatment	Oxidation, scrubbing					
8 Silicon dioxide waste						
Source	Side reactions (in chamber), scrubbers	SiO ₂				
Treatment	in situ or manual cleaning, external disposal					

Acid and caustic gases are usually treated by scrubber technologies (wet absorber, mostly based on packed tower systems). This neutralizes the acid or caustic gases. Selective Catalytic Reduction (SCR) is used instead of wet scrubbing of NO_x in case of high NO_x load. Subsequent treatments of HF rinse water, wet scrubber drain, and concentrate solutions include neutralization, and, in most cases, also precipitation of the liquid fluoride content.

For vapors and volatile organic compounds oxidation technologies or condensation can be used. Open flame burners are used as local or centralized installations. As central treatments also catalytic oxidizers, Regenerative Thermal Oxidation (RTO) or biofilters can be used.

Silane is usually oxidized in local installations, with open flame or flameless type. The ammonia associated with this control step is wet scrubbed (as above).

Most crystalline silicon solar cell Fabs are equipped with a central acid scrubber, because many sources of acid emissions are there not only from production, but also from support and service areas of the Fab.

Installations using "acid texturing" step also need NO_x scrubbing to comply with German legislation. These two abatement technologies (acid and NO_x scrubbers) are therefore included for calculating the environmental impacts.

Depending on process tools, additional abatement techniques might be necessary, e.g. to reduce fire risks, and emissions of ammonia. Some variations for scenario comparison include doping with an oven vs. spray doper, vacuum SiN deposition vs. oven techniques. Product performance is normally the driving force for selecting

industrial processes. Hence, environmental more favorable processes may be disregarded.

Printing produces a VOC exhaust gas that is difficult to handle because of condensation and polymerization processes. Three options are available: treatment with local burners, local condensers plus central thermal oxidation or biofilters.

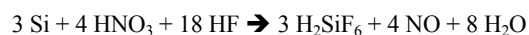
Perfluorocarbons with high global warming potential are in use only to a minor extent in crystalline Si production and will be phased out due to replacement of the dry edge isolation by laser or wet processing and because good alternatives exist for PECVD chamber cleaning.

The next paragraphs give information on NO_x, HF, NH₃ and volatile organic compounds (VOC):

- emission generation,
- environmental effects of the emission,
- German legal emission limit values,
- control of the emission and
- direct and indirect emissions.

3 NITROGEN OXIDES (NO_x)

NO_x is produced during etching (texturing) of silicon wafers with nitric acid. The oxidized silicon is solubilized in the form of H₂SiF₆.



Assuming that 10 micron of silicon is etched, 1.7 gram HNO₃ is consumed per 156 mm x 156 mm wafer and 0.81 g NO is produced. However, in practice it is found that NO_x emissions are less than the stoichiometric calculation indicates. For the modeling of the effluents, values based on measurement were used instead.

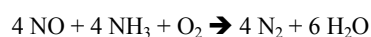
NO_x emissions have acidification and eutrophication effects.

The NO_x emission limit values in Germany (TA Luft) are 350 mg/Nm³.

30% reduction in concentration is possible when using a non-specific central scrubber. 60% reduction in concentration is possible when using local scrubber without H₂O₂. This usually meets German requirements. 90% reduction in concentration is possible when using local scrubber with H₂O₂.

All wet scrubbers bring the NO_x load to the waste water in form of nitrites and nitrates. Although nitrates are predominant, a significant fraction remains in the form of nitrite. Usually tight emission limits for nitrites exist, and a subsequent nitrite oxidation has to be included to convert nitrite to nitrate.

For high throughput nitrogen output of the fab also via the wastewater will be over the emission limits. Then a real conversion of all oxidized nitrogen to N₂ is required. This is provided by the Selective Catalytic Reduction (SCR) technique. This SCR local scrubber is based on reduction of NO_x to nitrogen N₂ and water using for example NH₃ as reducing agent:



10% of the life-cycle emissions are direct from the texturing of multicrystalline wafers. This means that the largest opportunity to reduce the impact is by lowering

the energy consumption of upstream processes for example by reducing the wafer thickness.

4 HYDROGEN FLUORIDE (HF)

The SiO₂ layer is removed by reaction with HF:



Moreover, acid texturing of raw silicon with mixtures of HF and HNO₃ generates significant emissions of HF by vaporization of the latter.

HF is toxic and impacts plants even at low levels in air. In the EU, immission is limited to 1 µg/m³. Accordingly, HF emission limits are usually strict: 3 mg/Nm³ in Germany (TA Luft).

HF process emissions are led to a central acid scrubber and then to precipitation of CaF₂. This is for landfill.

HF emissions are modeled according to source strength and usual removal rate of the scrubbing systems installed. Only 10% of the life-cycle HF emission is direct for monocrystalline silicon solar cell production whereas for multicrystalline silicon solar cell production the direct emissions are 40% of the total life-cycle emissions. Again this means that, especially for monocrystalline silicon, the major opportunity for improving the impact is to reduce the contribution from upstream processes.

5 AMMONIA (NH₃)

Crystalline silicon solar cell production uses ammonia in PECVD of silicon nitride to provide nitrogen sources. Silane is used as silicon source.

The NH₃ emission limit value is 30 mg/Nm³ in Germany (TA Luft).

Since silane (SiH₄) is the more critical gas in exhaust control, NH₃ treatment is designed on a case-by-case basis. Using either ambient or electrically heated flameless oxidation of the silane, ammonia is not affected by the oxidation step and is removed by subsequent water scrubbing. Using an open flame burner, ammonia is burnt to N₂ with some risk of secondary formation of NO_x. The latter are normally not treated.

Ammonia emissions have been calculated using the emission of the process, the removal rate of a local electrically heated oxidation with subsequent water scrubbing and no central installation to remove ammonia. 1% of the life-cycle HF emission is direct for monocrystalline silicon solar cell production whereas for multicrystalline silicon solar cell production the direct emissions are 10% of the total life-cycle emissions.

6 VOLATILE ORGANIC COMPOUNDS (VOCs)

Crystalline silicon solar cell production uses ethanol and/or isopropanol to dilute the spray of dopant, and for cleaning purposes. Some technologies use volatile

alcohols in heated baths in benches for cleaning or etching, thus inducing VOC emissions.

Metallization pastes contain VOCs such as aromatics, terpineol and softeners and others.

VOC's contribute to photochemical oxidant formation.

The VOC emission limit value in Germany (TA Luft) is 50 mg/Nm³ as total carbon.

There is a variety of concepts for VOC control. Since composition and concentration of VOC show large variation, more than one VOC collection and treatment system may be required. Low emissions, mostly from the printing, are treated by fixed bed carbon absorbers with external regeneration, while the polymerizing parts of the printer emissions have to be removed mechanically or by condensation. Local burners and central biofilters can be applied. High emissions can be treated by so-called "RTO" systems (flame-based oxidation with internal heat recovery), but also by direct flame based oxidation (including external heat recovery) or catalytic oxidation systems have been in use.

7 SUMMARY OF EMISSIONS

Table II shows the direct and life-cycle (from cradle to the solar cell factory gate) emission values for the production of crystalline silicon solar cells.

Table II. Direct/life-cycle emissions for crystalline silicon solar cell production (size 156 mm x 156 mm)

Mono	Multi	
0.0/4.8	0.3/4.0	g NO _x /cell
3/36	16/42	mg HF/cell
1/110	12/112	mg NH ₃ /cell

8 CONCLUSIONS

Reduction of life-cycle emissions are needed to improve the environmental profile of silicon photovoltaics. Emissions of NO_x, HF (mono Si) and NH₃ are mostly (>90%) indirect via upstream processes and can be reduced by lowering the energy consumption for silicon feedstock and wafer production. The direct emissions from solar cell manufacturing must be reduced to comply with legislation by implementing abatement strategies.

9 ACKNOWLEDGEMENTS

M+W Zander received funding in the frame of the "O₂ reduction" project FKZ 01LS05090.

10 REFERENCES

- [1] Fthenakis V.M., H.C. Kim, E. Alsema (2008) Emissions from Photovoltaic Life Cycles, Environ.Sci.Technol. 42(6) 2168-2174
- [2] Directive 2008/1/EC of the European Parliament and of the Council of 15 January 2008 concerning integrated pollution prevention and control (Official Journal of the European Union 29.1.2008)
<http://ec.europa.eu/environment/air/pollutants/stationary/index.htm>

- [3] Council directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations

<http://ec.europa.eu/environment/air/pollutants/stationary/solvents.htm>

- [4] TA Luft, Germany (24 July 2002)

http://www.bmu.de/files/pdfs/allgemein/application/pdf/taluft_engl.pdf