EVALUATION OF HIGH-EFFICIENCY mc-Si CELL PROCESSING TECHNOLOGIES REGARDING ENVIRONMENTAL IMPACT AND INDUSTRIAL APPLICABILITY

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ABSTRACT: Due to the impressive growth rate of the photovoltaic industry in the last years, it has become of increasing importance to assess solar cell production processes for its environmental impact. This work compares in detail the environmental impact of equipment, consumed materials and waste treatment in several high-efficiency mc-Si cell processing sequences developed within the European project TOPSICLE. Amongst others, we critically analysed the advanced isotextured process for up to 17% efficient cells based on screen-printing proposed by ECN, the angled buried contact (ABC) process and a hybrid buried contact / screen printing process, both proposed by the University of Konstanz. The evaluated data is compared with that of a state-of-the-art industrial screen-printing process. The publicly available results might serve as a useful decision tool for planning future solar cell production lines with respect to environmental impact and industrial applicability.
Keywords: Multi-Crystalline, Manufacturing and Processing, Environmental Effect

1 INTRODUCTION

Environmentally clean production and waste policy is becoming increasingly important especially for the rapidly-increasing European photovoltaic (PV) market. An overview of the European environmental legislation which is effective now or proposed and which may have implications for the PV industry is given in [1].

Within the TOPSICLE project [2] the developments of highest efficiency cell processing sequences were accompanied from the beginning by the industrial cell producers SCHOTT Solar and BP Solar to evaluate process technologies, sequences and equipment regarding costs, environmental impact and industrial applicability. In order to environmentally assess and compare the evaluated process steps we have focused mainly on the German legislation [3, 4] and the respective EC directives [5] as well as on a limited throughput of 1200 wafers per hour (i.e. ~20 MW_p/a production), because a generalization on European level as well on higher throughput would have gone far beyond the scope of this project due to the complexity of the laws and regulations on European, national and local level.

All partners contributed to a complete list of process steps and chemicals for all evaluated process sequences. Both involved cell producers SCHOTT Solar and BP Solar provided realistic cost and environmental data for each evaluated process step based on their production lines. This included material consumption as well as creation of emissions and waste. Supplementary publicly data on material consumption for some process steps were taken from the EU-funded Integrated Project CRYSTAL CLEAR [6, 7], see also [8, 9], as well as from the literature, see e.g. [10]. On this basis a comprehensive study was performed using different external databases [11] in order to get for each evaluated chemical as well as process step valid laws & regulations, limiting values for emissions and waste water contamination, toxicological data etc.

Detailed evaluated environmental data are publicly available as Excel file in an ECN report [12]. Concerning the economical assessment we will present in this paper just a summary of the main results, due to the confidentiality of the cost data provided by SCHOTT Solar and BP Solar. The focus of these assessments was to serve as a steering instrument for the development efforts.

2 PROCESS DEFINITION

Within the TOPSICLE consortium three industrially feasible high-efficiency solar cell processing sequences with low-cost potential were identified:

- Advanced isotextured process, based on newly developed in-line processes and screen printing technology (cell efficiency η = 16.5% at ECN) [13],
- Hybrid Buried Contact process with screen-printed Al-BSF (η = 17% at UKON) [14, 15],
- Angled Buried Contact (ABC) process (η = 18% at UKON) [16].

These process sequences will be compared in the following with a reference state-of-the-art industrial screen printing process (assumed cell efficiency 15.5%) concerning the economical and environmental impact as well as industrial applicability. The evaluated process flows are presented in Table I in more detail.

Table I: Evaluated process sequences

State-of-the-art industrial screen-print process	Advanced iso-textured process based on screen-print (ECN)	Angled Buried Contact (ABC) process (UKON)	Hybrid buried contact – screen print process (UKON)
		Groove formation	
Damage etch & cleaning	Advanced isotexturing	Isotexturing	Isotexturing
$POCl_3$ diffusion	Belt furnace emitter process (>70 Ω/sq)	Light emitter diffusion (~100 Ω/sq)	Light emitter diffusion (~100 Ω/sq)
PECVD SiN_x:H	Microwave PECVD SiN_x:H	PECVD SiN_x:H	LPCVD SiN_x
Screen-printed front and rear metallization	Screen-printed front and rear metallization		Plasma etch
Co-firing	Co-firing		Grooving front side and cleaning
		Deep groove diffusion	Deep groove diffusion
		Print Al and BSF formation	Print Al and BSF formation
		Electroless plating of Ni, Cu and Ag	Electroless plating of Ni, Cu and Ag
Edge isolation	Edge isolation	Edge isolation	Edge isolation

Figure 1 and Figure 2 show the structure of the hybrid buried contact / screen print and the Angled Buried Contact (ABC) solar cells, respectively, evaluated within this study.

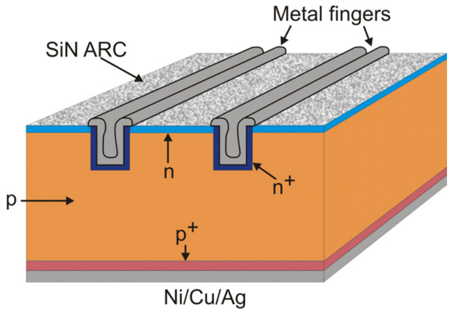


Figure 1: Cross section of the Hybrid buried contact / screen print cell design [15].

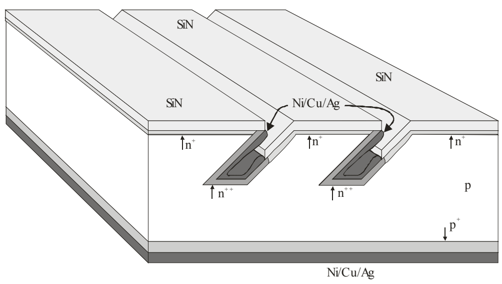


Figure 2: Cross section of the ABC (Angled Buried Contact) cell design [16].

3 SUMMARY ECONOMICAL EVALUATION

Base data was established for cost calculation so that labour rates, energy costs, depreciation rates etc. were the same for all processes. It was assumed that the factory would operate 24 hours per day for 350 days per year (typical for a high volume production process e.g. at SCHOTT Solar and BP Solar) with a throughput of 1200 wafers per hour. The factory up-time was set at 90%. A 10 year depreciation period was assumed for all equipment and a total factory fixed overhead cost for the cell fabrication process of yearly 3 million Euro. The confidential process costs delivered by SCHOTT Solar and BP Solar were adjusted in detail. Averaged publishable values were created in order to ensure a realistic comparison of the different evaluated process sequences.

The costs relative to an industrial process resulting in an efficiency of 15% are presented in Fig. 3. The ABC process is mainly more expensive than the state-of-the-art screen-print process due to the larger number of process steps. This first estimate shows that the ABC concept should result in about 2% higher efficiencies to be competitive on cell level compared to the screen-printed one. This higher efficiency should come from the absence of shading losses and possibilities to improve the front surface passivation.

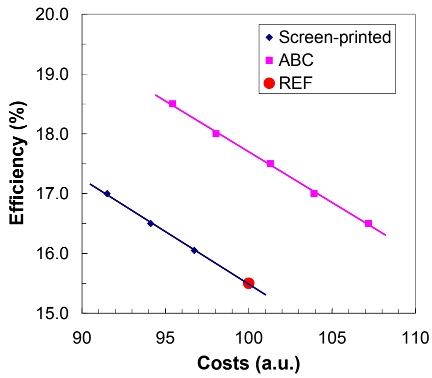


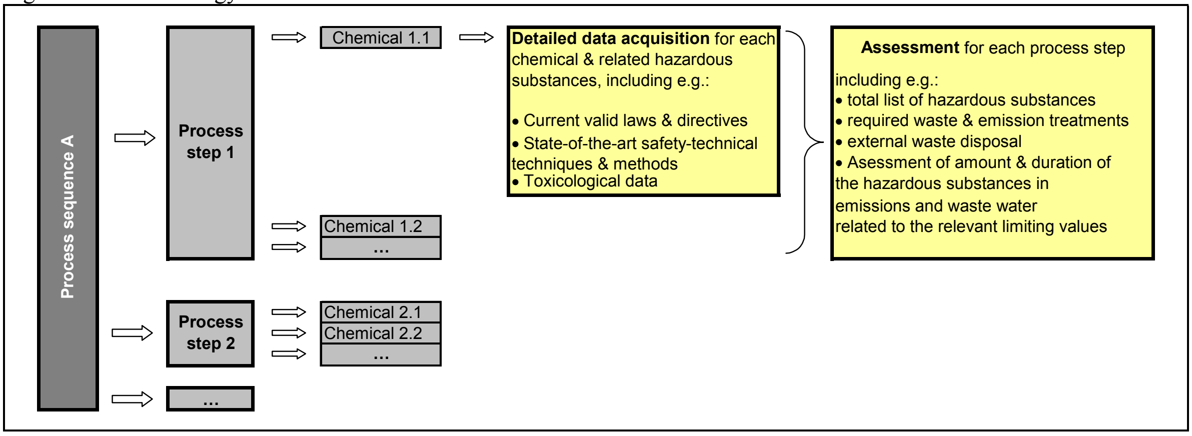
Figure 3: Costs per W_p for screen-printed and ABC process with respect to 15.5% industrial process.

4 METHOD OF ENVIRONMENTAL DATA ANALYSIS

Figure 4 shows a graphical overview of the methodology for the environmental assessment as developed by SCHOTT Solar within the TOPSICLE project. On the basis of the above defined process sequences, a comprehensive study was performed by collecting and analyzing relevant environmental data for each evaluated process step listing

- Type and amount (if known) of all chemicals for the evaluated process sequences, each assigned to the respective process step.
- Types and classification of the respective hazardous substances, emitted to air and/or contaminating waste water and solid waste.
- Reference to relevant German laws and EC directives.
- Required waste management as well as the

Figure 4: Methodology for the environmental assessment.



most important state-of-the-art safety-technical techniques and methods for preventing / minimizing the release of hazardous substances.

- Assessment of amount & duration of the respective emitted and water polluting substances and solid waste for each process step.

This tabular environmental assessment (see Table II as an example) is based on confidential production data from SCHOTT Solar and BP Solar (including qualitative and quantitative determination of hazardous substances in emissions and waste water) and related to the relevant legal limiting values (Spanish laws & EC directives for the specific buried contact process steps and on the German laws and EC directives for all other process steps). A graphical overview on the German legislation and the respective EC directives can be ordered at UB Media AG [17].

5 RESULTS ENVIRONMENTAL ASSESSMENT

A tabular summary of the economical and environmental assessment as well as the industrial applicability can be found in Table IV.

5.1 Reference process – industrial screen-printed mc-Si cell

In a 20 MW_p/a production line for a standard screen-printed Si solar cells typically the permanent emissions of the hazardous substances hydrofluoric acid (HF), total dust, ammonia (NH_3), organic solvents as well as alkaline and HF containing waste water exist. But the environmental impact of all these substances is small, i.e. the emissions are lower than 10% of the legal limit, if the following technical requirements are fulfilled:

- Usual condensers for the emission exhaust purification of the drying and sintering furnaces (metallization) in order to strip organic solvents.
- Exhaust treatment for all processes in order to prevent the release of emissions within the production facility.
- Neutralisation of the alkaline and HF containing waste water.

Most critical in the standard Si solar cell technology are the lead and solvent content of the metallization pastes [18, 19]. Looking at the legislation for electronic equipment manufacturing after 2005, the lead content of the solar cell metallization has to be reduced significantly. PV modules are not included in the WEEE and ROHS directives, but this may change in the future. For example, the lead content of the reference paste is above the RoHS 2002/95/EC [20, 21] concentration limit of 0.1 mass% in homogeneous material. The metallization pastes Ferro 3349 (silver conductor paste for the front metallization) and Ferro 5540 (aluminium conductor paste for the rear metallization and BSF formation) are used as reference for the metallization. The composition taken from the Material Safety Data Sheets (MSDS) [12].

In general, SCHOTT Solar and BP Solar undertake strong efforts in order to eliminate or minimise the usage of hazardous materials in their production lines. As an example, SCHOTT Solar carried out a lot of work in the previous EU-funded project EC2CONTACT [22], which had the objective to develop more environment-friendly metallization, e.g. lead-free and/or solvent-free front and rear side contact pastes. This goal is of major interest for the solar cell manufacturer SCHOTT Solar, because lead and solvent free metallization pastes with satisfying properties are not available on the market yet.

5.2 Advanced isotextured mc-Si cell process (ECN)

In the case of an isotextured mc-Si cell process, the additionally hazardous substance NO_x is formed, which can effectively be removed by state of the art gas scrubbers. The cost of the required gas scrubber is too low to have an effect on the cell product cost. Additionally the evaluated process sequence differs from the reference cell process in the replacement of the $POCl_3$ diffusion by a spin-on P deposition and belt-furnace diffusion. The additionally emitted organic substances due to the spin-on process should also be no problem, if a second gas scrubber is used for the emission exhaust purification. This process feature has a negligible effect on the total cell product cost. Hence, this high-efficiency process is very attractive for industrial production.

5.3 Angled Buried Contact (ABC) process

For the evaluated buried contact solar cell processes the screen printing metallization process is replaced by electroless plating, leading to an elimination of the above-described lead and solvent problem. On the other hand, the electroless plating process requires Ni-, Cu- and Ag containing bathes, which are toxic (Cu, Ag) or very toxic (Ni) for water organisms. In order to avoid water pollution the legal limits and regulations are especially in the case of plating processes very strict. Hence, the degree of optimisation of the effluent treatment at BP Solar is that high, that concerning waste water there is no effect on the environment. That means 100% recycling is realised by extraction of the metals. In more detail the bathes, rinse waters and effluents are treated at BP Solar as follows:

- The concentrated HNO_3 (30%) tank used in the second Ni process is collected and treated externally.
- The rinse water from rinses after Ag plating, Ni plating, Cu plating and HNO_3 cleaning passes through an ion exchange. The output is water that can be disposed off. Periodically the resins in the ion exchange have to be cleaned and this waste product is added to the evaporated metal wastes (see below) and is treated externally.
- The rinse water from rinses after HF cleans and the HF solutions (4% and 1%) are treated with CaO. The resulting clean water and the solid residue is treated offsite externally.
- Effluent treatment: all the nickel, copper and silver bath solutions are evaporated and the solid waste is treated off-site.

The emissions of the plating processes have a small effect on the environment, i.e. the emissions are lower than 10% of the legal limit. BP Solar as well as the chemical producer Rohm & Haas Electronic Materials Deutschland GmbH [23] confirmed that the presently used plating bathes are cyanid-free.

The additional required groove diffusion and laser grooving processes are from the environmental point of view identical with the standard $POCl_3$ diffusion and edge isolation process, respectively. Hence, they will not increase the effect on the environment. Further information on the industrial production of buried contact

Table II: Extract from the comprehensive environmental data collection & assessment showing the tabular summary of some exemplary processing steps. The complete table can be downloaded as EXCEL file [12].

Present Processes and their Components: process	components (chem. Symbol)	CAS-No.	Hazardous Substances: emitted hazardous substances	waste water	Waste Treatment: required waste & emission treatments	external waste disposal	Assessment: emissions	waste water	Currently valid German Laws and Directives: WHG (WGK)	GefStoffV	StörfallV	TA-Luft	31.BImSchV	MuSchRiV	Hazard symbol	Poison class CH
a) Standard mc-Si cell reference process																
Damage etch & cleaning	Di H_2O	7732-18-5	HF	HF, NaOH	neutralisation CaO		Cx	Cx								
	NaOH	1310-73-2							1						C	2
	HF	7664-93-3							1	■	■	<			T^+ C	1
$POCl_3$ diffusion	$POCl_3$	10025-87-3	HCl	-	exhaust		Cx	-		■	■	<			T^+ C	1
	O_2	7782-44-7													O	
	N_2	7727-37-9														
HF etch	Di H_2O	7732-18-5	HF	HF	exhaust, neutralisation CaO		Cx	Cx								
	HF	7664-93-3							1	■	■	<			T^+ C	1
PECVD SiN deposition	SiH_4	7803-62-5	SiO_2, NH_3	-	exhaust		Cx	-							F^+ X_n	
	NH_3	7664-41-7										<			T	
	N_2	7727-37-9														
Rear Ag/Al contact	Silver	7440-22-4	organic solvents, Pb	-	exhaust		Cx	-	3	■					N	F
	Aluminum	7429-90-5														
	Lead borosilicate glass	65997-17-3														
	solvents											<				
Rear Al area	Aluminum	7429-90-5	organic solvents (drying)	-	condensor, exhaust	condendate of organic solvents	Cx	-								
	Silicea	14808-60-7														as
	Terpineol	98-55-5										<		■		
	Trimethyl pentanediol monoisobutyrate ("ester alcohol")	25265-77-4										<	<	■		

Table III: Abbreviations used for assessing amount & duration of the release of hazardous substances related to the relevant limiting values.

Abbreviations			
A		strong effect on environment	- permanent exceeding of limiting values,
B		medium effect on environment	- short-time exceeding of limiting values,
			- emission of problematic hazardous substances
C		small effect on environment	- emission of small amounts of hazardous substanzes (< 10% of limiting values)
D		no effect on environment	- e.g for 100% recycling
x		permanent emissions from continuous industrial processes	
y		temporary, regular batch processes	
z		occasional, irregular processes	

solar cells at BP Solar can be found in [24, 25].

5.4 Hybrid buried contact / screen print process

In comparison with the ABC process additional etch and cleaning process steps are required for the evaluated Hybrid process, which are from the environmental point of view comparable with the respective processes of the reference cell processing sequence.

The Hybrid cell process requires a plasma etch process. When using fluorinated gases like CF_4 for plasma etching, it is very important that proper emission abatement equipment is installed. For information: a CF_4 consumption of 40 kg per MW_p which is emitted unabated, the total greenhouse gas emission of modules may increase by 20% (Alsema, de Wild 2005 [22]. But the creation of CF_4 should be either no problem if this gas is cracked after processing with state-of-the-art techniques.

5.5 Industrial applicability

All evaluated process steps have proven their industrial applicability either at SCHOTT Solar or BP Solar excepting:

Spin-on P deposition process,

which is used on laboratory equipment at ECN for the "Advanced ECN process", see [13]. In the near future this process will be replaced by another industrially suitable P deposition technique. Since there are several alternatives available on the market, the implementation of a suitable P deposition technique into a production line should not be a problem, in principle.

Angled groove formation,

which is processed on a laboratory dicing saw at UKON for the "ABC process", see [16]. In the future it should be evaluated if this process can be replaced by Laser grooving technique, which is already used at BP Solar for the industrial processing of buried contact solar cells. In this context it has to mentioned, that the fill factor (FF) problems of the laboratory ABC process have to be solved prior implementing this process sequence into a high-throughput production line.

PECVD SiN deposition for the BC cell process,

which is required for a directional SiN deposition in the ABC process, see [16]. In the future BP Solar has to introduce the PECVD SiN deposition in the buried contact cell process, if the ABC should be transferred to the BC production line.

6 CONCLUSIONS

Detailed economical analysis showed that a newly developed in-line process resulting in 16.5% cell efficiency and based on isotexturing and screen-printing could result in a cost reduction of about 6% compared to a reference process with 15.5% cell efficiency. For a 17% cell process the cost reduction will be 8-9%. The ABC concept is more complex, but will result in higher efficiencies. Based on the currently available data, it is estimated that the efficiency for the ABC cells should be about 2% absolute higher to achieve the same cost per W_p.

A comprehensive study on the developed processes was carried out with respect to the national legislation and the EC directives. For all newly developed processes a limited environmental effect is expected. All emissions will be below 10% of the limits when the exhaust of chemical and furnace processes is purified or recycled. All this can be done with state-of-the-art technologies.

TOPSICLE was a very relevant and successful project for the industrial cell producer BP Solar and SCHOTT Solar. Processes chosen for evaluation close to industrial applicability. Nevertheless, very promising high efficiencies were obtained with the evaluated

Table IV: Summary of the economical and environmental analysis.

Evaluated process sequences	cell eff.[1] (%)	potential to reach a €/Wp cost reduction	Cost saving / increase (%)	List and assessment of hazardous substances	Safety-technical and environmental requirements	Industrial applicability
State-of-the-art industrial screen-print reference process	15.5	-	-	Permanent emissions & waste water with small[3] environmental impact: HF, NH_3, total dust, organic solvents, lead in metallization pastes, alkaline and HF containing waste water	• Usual condensers for the emission exhaust purification of drying & sintering furnaces • Exhausts for all processes • Neutralisation of alkaline & HF containing waste water	All processes used in standard industrial cell production
Advanced isotextured process based on screen-print (ECN)	16.5	Significant potential due to • Lower consumables cost • Lower depreciation cost • Higher cell efficiency Most promising potential due to • Further increased cell efficiency additonal to the advantages of the isotexturing	6.8	Additional permanent emission of NO_x with small environ. Impact Spin-on P instead of $POCl_3$: + organic substances with small environ. impact	• Additionally gas scrubber for isotexture process • Additionally gas scrubber for emission exhaust purification	Isotexture already under development at SCHOTT Solar Evaluation of Spin-on P deposition or alternative
Angled Buried Contact (ABC) process (UKON)	18.0[2]	Promising potential due to • increased cell efficiency	1.6	Additional: Ni-, Cu-, Ag containing bathes for plating: Waste water = no effect on env. Emissions = small environ. Impact	• plating: 100% recycling, extraction of the metals by external company • Others: Similar to reference but without condensors	grooving with dicing saw = laboratory process
Hybrid buried contact – screen-print process (UKON)	17.0	Most expensive process due to • largest number of process steps • 18% average cell eff. needed to reach the ref product cost	- 7.1	Additonal: GHG CF_4 for plasma etching, but no environmental problem	• Plasma etch: state-of-the-art technology for cracking CF_4 directly after processing	Similar to industrial production of BC cells at BP Solar

[1] Obtained average cell efficiency, [2] Maximum cell efficiency, [3] (< 10% of the legal limit)

process sequences at the institutes [2]. Additionally fruitful and well designed common experiments were performed. From those, important fundamental process knowledge could be obtained in the frame of this project providing guidelines for future (at BP Solar) and near future (at SCHOTT Solar) development. That means that the transfer of the "Advanced ECN process" into the a production line for screen printed solar cells should be possible in the near future at least partly, while on the other hand further development is required for the industrial transfer of the advanced buried contact process sequences. The isotexturing process is already under development at SCHOTT Solar.

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[24] N.B. Mason, T.M. Bruton and M.A. Balbuena, *Laser grooved buried grid silicon solar cells from pilot line to 50 MWp manufacture in ten years*, Conference proceedings of PV in Europe – From PV Technology to Energy Solutions, 7.-11. October 2002, Rome, Italy.
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