



COOP-CT-2005-017586

**SOLARPLAS**

Development of Plasma-Chemical Equipment  
for Cost-Effective Manufacturing in Photovoltaics

Instrument: CRAFT, Co-operative Research

**Publishable final activity report**

Period covered: from 01.11.2005 to 29.02.2008

Date of preparation: 2008-05-21

Start date of project: 01.11.2005

Duration: 28 months

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Revision 2008-05-21

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# 1 Project execution

## 1.1 Summary description of project objectives

With typical growth rates of 25% p.a. the production of photovoltaic (PV) cells is nowadays developing very dynamically. Core technology for power production is (still) crystalline silicon based photovoltaics with a market share of > 90%. Taking into account that on longer term solar energy must take over a major share of the worldwide total energy production the photovoltaic industry is under strong pressure to reduce specific cost for electric power production and to increase production capacity substantially. In the near future the capacity of just one advanced production line will add-up to about 1GW-peak p.a., which is 4 – 10 times higher than the current capacity.

For modules in current PV systems solar electricity costs amount to 0.25 to 1.00 €/kWh. The PV technology development should decrease this value to about 0.10 € per kWh to realize a breakthrough. Thus, long term target is to reduce specific electricity production costs for photovoltaic by a factor  $\geq 5$ . Typical costs for PV system manufacturing distributes to 50% for silicon wafer manufacturing, 25% for solar wafer processing, and 25% for PV modules manufacturing.

The state-of-the-art production technology for crystalline silicon solar wafers is characterized by a combination of batch processing steps. As a result, wafer handling represents a significant additional cost factor. It leads to an increase of wafer break and thus decreases the throughput, limits the introduction of thinner wafers which would furthermore reduce materials costs, and increases the total processing costs by about 30%.

Strategic target for the project is to develop a complete in-line manufacturing concept to build up the technological platform for future production of crystalline silicon solar cells. It is proposed to introduce innovative atmospheric pressure plasma technologies into cell manufacturing lines to achieve such a step-change in production technology.

An additional objective of the consortium is to develop a multi-purpose technology with applications outside the PV area. This second strand will widen-out not only the technological basis of the SMEs involved but also potential routes for exploitation.

Main objective to meet the challenging cost and throughput targets in PV power production is to save raw material consumption by introducing thinner solar wafers with increased size (on mid term 210 x210 mm<sup>2</sup>, with < 150  $\mu$ m thickness) and to substantially increase throughput by introducing in-line technology (from about 2000 to several ten thousand wafers per hour).

The innovative field of atmospheric plasma technologies is currently under rapid growth, worldwide. Atmospheric pressure plasma (APP) techniques have the potential to combine low-cost, ease of application, continuous processing capability, cleanliness, uniformity, high energy density, and high throughput. The use of APP means that in-line deposition is feasible, and due to the

extra energy input by the plasma the deposition can take place at considerably reduced substrate temperatures. The past half-decade has shown that scalable homogeneous plasma sources can be potentially leading to a step-change in large area processing and thus in throughput. Key potential advantages of these technologies are high throughput; continuous in-line processing, and low running costs. Capital cost savings for both equipment and line space (foot print) and relative ease of integration are further benefits in comparison to low pressure technology approaches.<sup>1</sup>

The typical production chain for crystalline silicon based photovoltaic cells comprises a sequence of steps which may be characterized shortly as follows (see Figure 1): (i) wafer slicing from silicon ingot (wire sawing), (ii) removing saw damage layer from both wafer sides (wet etching), (iii) surface structuring to reduce front side reflectance (wet etching), (iii) p/n junction by phosphorous doping (spray pyrolysis, heat treatment), (iv) edge isolation (laser scribing, plasma etching or rear side wet etching), (v) removal of residual phosphorous silicate glass (PSG) layer (wet etching), (vi) anti-reflective silicon nitride coating with passivation properties (low pressure PE-CVD batch/continuous or PVD/ sputtering), (vii) front/back contacting (printing of metallic paste + firing).

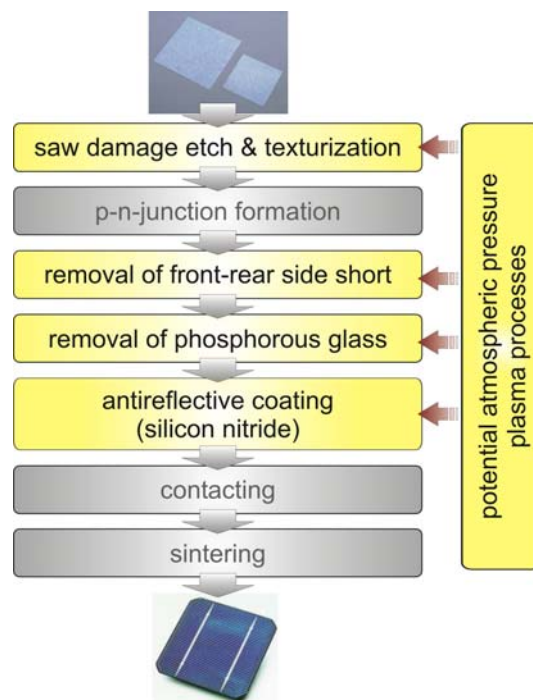


Figure 1: Scheme of c-Si solar cell production; potential steps for AP plasma processing are marked

This means, the current production process for crystalline silicon solar cells is characterized by a wide range of process conditions, varying between low and atmospheric pressure, wet and dry processing, and by a high number of handling steps, resulting in a high number of robots for wafer handling.

<sup>1</sup> V. Hopfe, R. Spitzl, I. Dani, G. Maeder, L. Roch, D. Rogler, B. Leupolt, B. Schöneich; „Remote Microwave PECVD for continuous wide area coating at atmospheric pressure,” Chem. Vapour Dep. 11-12 (2005) 510-522  
V. Hopfe, D. Rogler, G. Maeder, I. Dani, K. Landes, E. Theophile, M. Dzulko, C. Rohrer, C. Reichhold, „Linear extended ArcJet-CVD – a new PECVD approach for continuous wide area coating at atmospheric pressure,” Chem. Vapour Dep. 11-12 (2005) 497-509  
V. Hopfe, D. W. Sheel, “Atmospheric Pressure Plasmas for Wide Area Thin Film Deposition and Etching”, Plasma Process. Polym. 4(3) (2007) 253–265

When moving to thinner wafers, breakage during handling becomes a critical issue. Plasma based in-line systems for etching and deposition have until now been limited to vacuum conditions.

Targeting at an integrated concept for in-line production of solar cells, the introduction of atmospheric pressure plasma processes is a promising alternative route toward establishing cost-efficient production technologies. APP processing is expected to lead to reduced running costs because of reduced chemical waste (e.g. avoid NO<sub>x</sub> emissions from acidic etch) and reduced handling operation due to in-line processing. Furthermore, the technology can be applied for future very thin solar wafers which substantially save raw material usage but cannot be processed with conventional wet chemistry because of increased wafer break rate. High demands concerning throughput require equipment for large area processing with high etch rate. The technology has the potential to be implemented into different processing steps such as saw damage removal, reduction of front side reflection losses by both surface texturing and anti-reflection layers, PSG removal, edge isolation etc, see Figure 1.

Currently, the production of crystalline silicon solar cells is characterized by a series of non-compatible process steps operating at low and atmospheric pressure, and wet and dry atmosphere; resulting in a great number of handling steps. Decreasing wafer thickness of currently 160 µm results not only in material and therefore cost reduction, but also in increased wafer breakage. Therefore, an integrated concept for continuous processing of solar wafers with reduced number of handling steps is required. In-line wet chemical etching reduces the number of wafer handling steps, but leads to high water and chemical waste disposal. The risk of wafer breakage remains high. Plasma based in-line systems for etching and deposition are bound to vacuum, linked with high investment costs and large footprint.

In this project a continuous in-line concept for solar cell fabrication based on atmospheric pressure plasma technologies was developed. Process steps, potentially being replaced by these technologies, are saw damage etch, surface texturization, removal of front-rear side short (rear side etching), removal of phosphorous glass, and antireflective layer deposition (Figure 1).

Advantages of the plasma equipment used are the low footprint requirements and the ease of integration into both existing and newly designed production lines. Process development has been performed on continuous laboratory reactors with two complementary plasma sources for etching and coating.

## 1.2 Contractors involved

The project brings together companies and research centers from 4 European countries (Germany, Great Britain, Switzerland and the Czech Republic). The consortium ensures a balance of expertise, both technically and industrially, including process developers, equipment manufacturer, and end-users. It provides the critical mass to solve a problem of such a degree of complexity. No individual SME would be able to undertake such a challenging program of this size and degree of risk.

The **Fraunhofer Institute of Material and Beam Technology (IWS)** as co-ordinator of the project provides industrial oriented RTD mainly for laser materials processing, surface processing, and for thin film deposition.

The number of employees is 130. The main objectives of the department of CVD Thin Film Technologies involved in the project are technology development for high rate atmospheric pressure PECVD technologies, materials development for functional coatings with specific for selected application areas, computational fluid dynamic modeling for the design of CVD reactors and for process optimization, as well as the development of process control techniques by in-situ spectroscopy. Furthermore significant experience and equipment exists in layer and surface characterization by spectroscopic methods.

The task of the IWS inside the project is the development of atmospheric pressure plasma technologies for coating and etching of solar wafers and the design of dedicated coater heads for the targeted prototype equipment.

**Centrotherm Photovoltaics AG** is a member of the Centrotherm group with currently about 800 employees, which develops and manufactures equipment for heat treatment (diffusion, annealing), and for low pressure PECVD coating. Centrotherm Photovoltaics AG is one of the leading suppliers of complete turn key production lines for photovoltaic industry. The benefit for Centrotherm from the project is an increase of the market share on photovoltaic equipment.

The **REGATRON AG** with 55 employees has a remarkable potential for design and development. Since over 30 years REGATRON works successful in the development and manufacturing of industrial electronics, namely in the field of power electronics for railway illumination and accessory electronics, control and monitoring hard and software, and servo drives and accessories. In 1999, research, development and manufacturing of high power DC supplies were added to the existing line of AC power inverters.

Inside the project REGATRON simulates, develops and manufactures power systems, ignition modules, and overall process control system to operate atmospheric pressure DC linear extended arc plasma sources. REGATRON will finalize the product palette being necessary to operate the DC arc plasma sources for processing processes related to solar cell fabrication. The collaboration with RTD partners on the one side and end-users on the other side is essential to come to well industrialized and field-proven solutions.

**CVD Technologies LTD** is an SME with 8 employees dealing with the commercialization of CVD coating technologies via at atmospheric pressure. CTEC has many years experience in commercialize CVD processes and has recently been undertaking a laboratory evaluation of GDBD. In the project CTEC develops equipment and processes for the application of the glow dielectric barrier discharge (GDBD) technology to CVD processes developed in the project. By an improved surface treatment and an improved homogeneity of the surface properties an improved market share is expected.

**SOLARTEC s.r.o.** is an SME with 68 employees and plays a key role in promoting PV technology in Czech Republic. The company is focused on production of high-efficiency, high-quality mono-crystalline solar cells and the delivery of solar systems. The standard products are mat blue solar cells having conversion efficiency from 14.5% to 15.5%. Another field of activity of SOLARTEC is solar cells for special applications such as concentrator solar cells, small parts of cells, and sensors. Innovative processes developed within the project are evaluated for a transfer to individual technological steps for solar cell production. Furthermore, solar wafers being processed by RTD

partners within the project are measured and characterized. SOLARTEC is a potential end-user of the developed technologies.

The **Q-Cells AG** is a world-leading producer of high performance polycrystalline and mono-crystalline solar cells with 1800 employees. Beside the mono- and polycrystalline core business Q-Cells develop and produce thin-film modules, using different technologies. Inside the project Q-Cells was responsible for specification of process parameters, the test of electrical cell properties and the evaluation of processed solar wafers.

The Institute of Materials of the **University of Salford** has a widely recognized reputation in the field of fundamental research for CVD processes. Significant knowledge and state-of-the-art equipment exists for a range of atmospheric pressure CVD technologies, e.g. thermal CVD, combustion CVD, and PECVD. USAL produces materials by CVD methods, including conventional CVD, AP-PECVD, and liquid injection CVD. Significant experience and equipment exists in thin film characterization, i.e. surface/layer characterization by spectroscopic techniques and microscopy. Inside the project glow dielectric barrier discharges are used for coating on solar wafers and on plastic web.

### 1.3 Main results of work performed

Because of the strong pressure for cost reduction material-saving technologies were much quicker introduced into industry than originally expected by the consortium. The industrial roadmap targets on introduction of thinner wafers with increased size. After project launch it became obvious that the majority of the industrial tests would need to process solar wafers with a size of 156x156 mm<sup>2</sup>, and, on longer term, with 210x210 mm<sup>2</sup>. Against the originally planned wafer size this step change in wafer size needed a scale-up of both plasma source and prototype equipment. Additional resources outside of the project were necessary for providing this extra work.

#### Main tasks in the project included:

- (1) Exploration of low energy, direct plasma technology based on glow dielectric barrier discharge (GDBD) to demonstrate feasibility for deposition of specified functional layers on silicon (and polymers, as second strand).
- (2) Development of high throughput atmospheric pressure coating technology to demonstrate the feasibility of the manufacturing of homogeneous anti-reflective films with additional passivation properties for silicon solar cells
- (3) Development of technologies for continuous plasma chemical etching on solar wafers at atmospheric pressure, focus on substitution of current technologies by a high throughput in-line technology with significantly reduced environmental impact. Development of both process and equipment for:
  - saw damage etching on silicon solar wafers; etching rate > 100 nm/s
  - back surface etching of pre-processed wafers

- Feasibility study on phosphorous glass layer removal
  - front surface texturing
  - rear surface etching in combination with edge isolation.
- (4) Development of highly efficient power supply modules for scale-up of a linearly extended DC arc plasma source with respect to working width and consequently, throughput.

### 1.3.1 Plasma chemical etching

The plasma etch processes for crystalline silicon solar wafers studied in the project are based on a linearly extended direct current arc discharge operated at atmospheric pressure. Until now, the arc is operated up to a length of 250 mm; a further up-scaling is possible. However, within the project duration only 5" wafers can be processed (125 mm). Currently the scale-up to 6" wafers is underway.

The arc is stabilized by the gas flow, a magnetic field, and by the water cooled walls. The etch gases are injected into the plasma afterglow region close to the wafer surface (Figure 2). Purge gas curtains on the substrate entrance and exit avoid a leakage of etch gases or reaction products into atmosphere as well as contamination of the etch zone with air.

Aiming at higher etch rates and a higher utilization of the etch gas an improved design of the reactor was developed and is shown in Figure 3. This reactor includes a double-sided waste gas extraction for an enlarged etching zone and a reduced distance between plasma and substrate leading to a higher degree of dissociation of the etch gas.

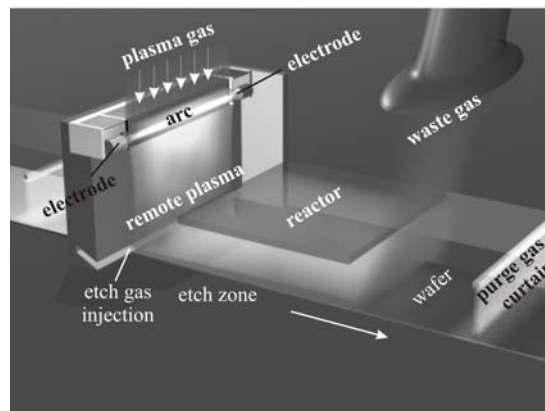


Figure 2: Scheme of the arc plasma enhanced etching technology

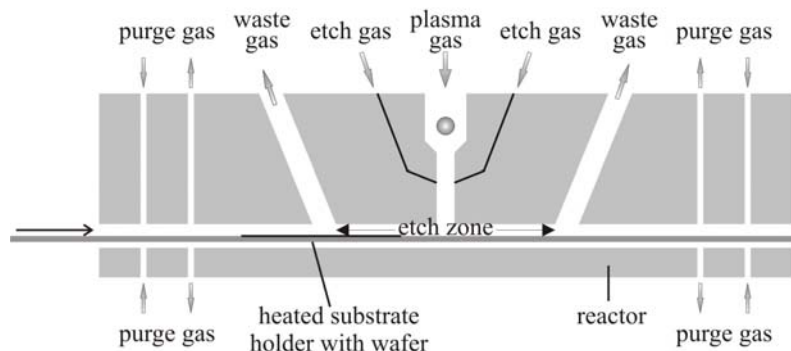




Figure 3:

Scheme of a remote AP-Plasma reactor for continuous air-to-air etching of PV cells. With an automatic control of purge gas flow rates and extraction flow rates the concentration of critical components ( $O_2/H_2O$ ) can be controlled down to  $< 1$  ppm

A wide range of fluorine-containing etch gases, namely  $CHF_3$ ,  $CF_4$ ,  $C_2F_6$ ,  $C_4F_8$ ,  $SF_6$ ,  $NF_3$  and the gas mixtures  $CHF_3/O_2$ ,  $C_2F_6/O_2$  and  $SF_6/O_2$  have been evaluated<sup>2</sup>. The etch rates cover a wide range over more than 2.5 orders of magnitude in dependence on plasma conditions and etch gas used. The most favourable etch rates have been obtained with  $SF_6$  and  $NF_3$  as etchants. Because of these results, optimization of etch processes has been carried out only for  $NF_3$  and  $SF_6$ .

Global dynamic etch rates have been calculated by gravimetry. The use of  $NF_3$  leads to the highest dynamic etch rates of  $3.6 \mu m \cdot m/min$ . In the case of  $SF_6$  the maximum etch rates are  $0.95 \mu m \cdot m/min$ . This allows a wafer throughput of over 865 wafer/hour (5" wafers) with just one plasma source.

The etch gas utilization as well as the composition of the waste gas were determined by in-situ-Fourier Transform Infrared (FTIR) absorption spectroscopy. The high degree of decomposition of  $NF_3$  (up to 99 %) in plasma decreases the costs of waste gas disposal in a potential industrialized etch step.

### **Saw damage etching**

The wire sawing of silicon ingots results in microscopic defects and in organic and inorganic impurities on both wafer surfaces. The material quality has to be improved by removal of the damaged surface. In a laboratory test, "as-cut" (100)-mono-crystalline silicon wafers with a saw damage depth of approximately  $5.5 \mu m$  have been plasma etched with  $SF_6$ . The etch rate is in the range of  $3 \mu m/min$ . The etch rate depends on the etch gas flow. The resulting surface after etching of  $6 \mu m$  shows no visible structuring.

### **Edge isolation**

Preventing short-circuits by isolating the edge of PV cells is an operation that increases cell efficiencies. Several technologies are today available to prevent these shunts. Each of these techniques has specific advantages and disadvantages. One main goal of the SOLARPLAS project was to lower the cost for industrial cell processing. Especially compared to other techniques using vacuum technology the AP plasma chemical dry etching has a big cost saving potential for cost of ownership. But there is another important cost saving potential that plays a big role. The efficiency of solar cells has large price per cell effect. At beginning of the project it was the main goal to achieve equivalent efficiencies as the industrial reference process. After the first test series it becomes clear that the AP chemical dry etching has the potential for higher cell efficiencies compared to the reference laser edge isolation.

Several industrial tests for the edge isolation / back surface etching of crystalline silicon solar wafers by atmospheric pressure plasma etching have been carried out to investigate the suitability of the process at high substrate velocities, leading to high wafer throughput.

<sup>2</sup> E. López, I. Dani, V. Hopfe, H. Wanka, M. Heintze, R. Möller, A. Hauser, paper 2CV.5.11, 21<sup>st</sup> European Photovoltaic Solar Energy Conference and Exhibition, Dresden, 2006

Five test series for edge isolation with  $\text{SF}_6$  and  $\text{NF}_3$  atmospheric pressure plasma were carried out in cooperation between IWS and QC. For the reference wafers edge isolation by laser at Q-Cells was chosen. Beside the atmospheric pressure plasma etching all wafers were processed at Q-Cells with standard process parameters.

In Table 1 test results for mono-crystalline Si wafers are shown. The best results show the dry etched cells with precursor gas  $\text{NF}_3$ . Compared to the Q-Cells reference this cells show an average gain in. This gain is caused mainly by a higher short circuit current ( $I_{sc}$ ).

Table 1: Parameters of AP-plasma etched solar cells referred to different standard industrial processes; Reference processes represent 100%

	Process 1	Process 2
Efficiency	$103.6 \pm 3.3\%$	$101.8 \pm 1.6\%$
Fill factor	$99.4 \pm 2.8\%$	$101.2 \pm 1.5\%$
$I_{sc}$	$103.2 \pm 0.7\%$	$100.0 \pm 0.5\%$
$U_{oc}$	$100.9 \pm 0.5\%$	$100.6 \pm 0.4\%$

Multi-crystalline silicon wafers have increased their market share continuously over the past few years and are now dominating crystalline silicon technology. Therefore optimisations of process parameters for multi-crystalline wafers were an important part of the project. Comparable to mono-crystalline cells the plasma etched multi-crystalline cells show a gain in short circuit current.

### Front surface texturisation

For improved absorption of the incoming sunlight the surface of the wafer has to be textured. The resulting surface structure of (100) mono-crystalline silicon wafers after plasma-chemical etching with different etch gases was studied. Nano-structured textures with high aspect ratio are achieved by use of  $\text{NF}_3$  or  $\text{SF}_6$  (Figure 4), the specular reflection of these surfaces is less than 5% in the wavelength range between 400 and 1000 nm.

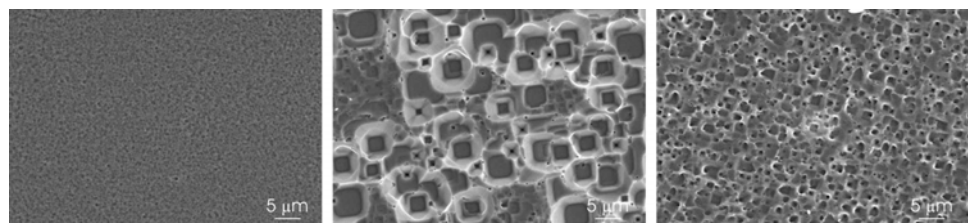


Figure 4:

Texturing of (100) mono-crystalline silicon wafers by atmospheric pressure plasma etching; SEM photographs, left: etch gas  $\text{SF}_6$ , centre: etch gas  $\text{NF}_3$ , etch rate  $<4 \mu\text{m}/\text{min}$ , right: etch gas  $\text{NF}_3$ , etch rate  $>4 \mu\text{m}/\text{min}$

### PSG etching

Phosphorous silicate glass (PSG) is formed on the surface of the solar wafer during the emitter diffusion using  $\text{POCl}_3$ . Under oxygen atmosphere phosphorous is driven into the silicon to form the  $n^+$  emitter of the solar cell. Typically, the resulting PSG is removed by wet-chemical etching based on hydrofluoric acid (HF). Thinner wafers and reduction of breakage losses as well as a short time between cell processes makes inline processing and the integration of different processes into one production machine attractive for solar cell manufacturers. Closing the gap between phosphorous glass (PSG) etching and in-line AP silicon nitride deposition an AP PSG removal system is a consequent choice. Plasma etching of PSG represents a very challenging process, since it has to show a high PSG etch rate without damaging the underlying emitter layer (i.e. under the same conditions a low Si etch rate is required).

Phosphor silicate glass (PSG) etching at atmospheric pressure has been studied using  $\text{CHF}_3$  and  $\text{C}_2\text{F}_6$  as etch gases. In the case of  $\text{CHF}_3$ , oxygen has to be added to avoid the deposition of undesired fluorocarbon polymer layers. A first industrial test series was carried out at QC. All AP PSG etched cells have losses in most electrical parameters due to incomplete PSG removal. Further process optimisations are needed to increase the homogeneity and stability of the PSG removal.

### **1.3.2 Silicon nitride deposition on solar wafers by microwave plasma enhanced CVD**

The development of a high throughput, continuously working atmospheric pressure coating technology to demonstrate the feasibility of the deposition of anti-reflective films with additional passivation properties for silicon solar cells was a further key objective of the SOLARPLAS project.

For silicon nitride deposition on crystalline silicon solar wafers, two plasma processes at atmospheric pressure are under investigation. A wide parameter study for plasma enhanced CVD of  $\text{SiN}_x\text{:H}$  using a linearly extended DC arc discharge (LARGE) has been performed. Films with a stoichiometry being close to specification and with a low oxygen content have been deposited. However, index of refraction of the silicon nitride films did not achieve values above 1.8 which is out of specification. Furthermore, film homogeneity and tendency for powder formation were problematic.

Therefore the consortium decided to pursue the introduction of a microwave plasma as an alternative approach for silicon nitride deposition (Figure 5). Films are characterized by a reduced powder formation tendency and improved film homogeneity. First experiments were provided based on a lab-scale equipment, which was substantially re-designed providing a heated substrate stage, wafer fixation, and an additional precursor line. Deposition experiments, using both organic silanes and mono-silane as precursor, produced coatings which closely meet specifications concerning chemical composition, optical and electrical properties.

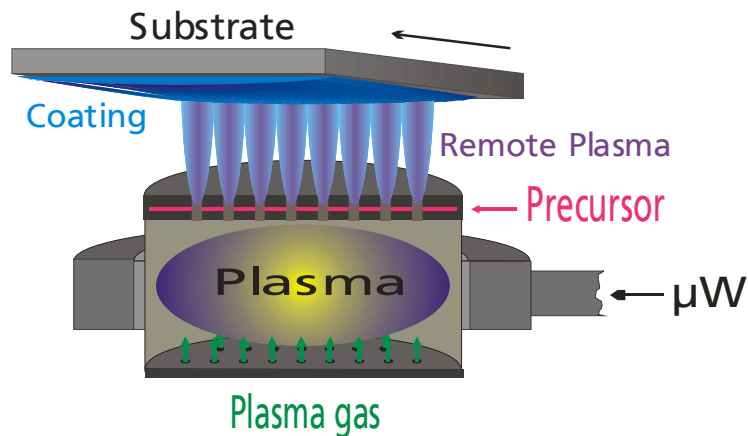


Figure 5: Scheme of the microwave PECVD at atmospheric pressure

Because of the rapid progress of photovoltaic industry, wafers with increased size have been introduced much quicker than originally expected by the consortium. After project launch it became obvious that any industrial test requires machine capacity for processing of wafers with a size of 156x156 mm<sup>2</sup>. This increase in wafer size needs a scaled-up microwave plasma source and a new coater head design.

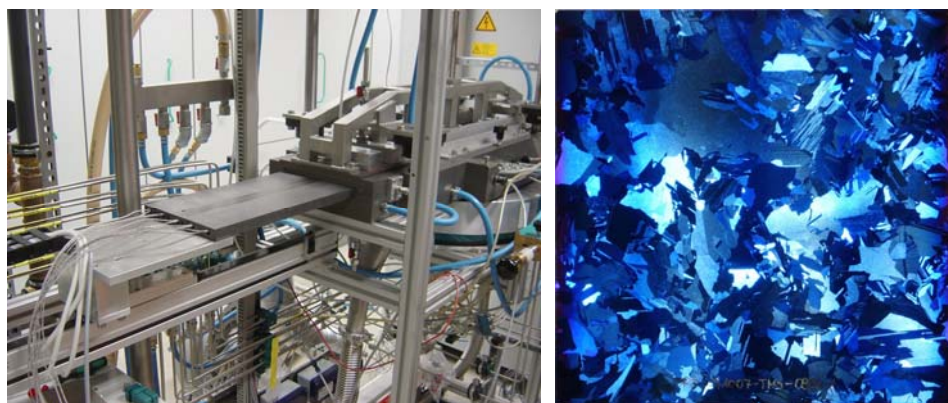
Main features of the microwave plasma enhanced CVD prototype equipment are:

- a plasma diameter of 240 mm allowing coating of substrates up to 156 x 156 mm<sup>2</sup>,
- vacuum fixed substrates,
- substrate temperature up to 450 °C,
- inert deposition zone realized by purge gas curtains, and
- a substrate velocity up to 100 mm/s for semi-continuous coating.

For supporting reactor design the flow dynamics and deposition profiles were simulated by computational fluid dynamics (FLUENT). Different arrangements of the nozzle arrays for precursor and plasma gas feed-in schemes were modeled. Furthermore a purge gas curtain system was re-designed from the existing lab-scale equipment and has been adapted to the larger substrate size.

Due to the well proven vacuum fixation of the wafers this principle was transferred to the prototype equipment. The requirements to a full continuous operation were established; based on these, two different designs combining true continuous processing and secure substrate handling could be identified.

To improve the film homogeneity, the coater head was modified leading to film thickness homogeneity better than 3% (Figure 6, right).



With respect to silicon nitride coating materials specification three key parameters need to be addressed:

- optical properties (index of refraction)
- passivation properties (i.e. minority charge carrier lifetime)
- homogeneity

The index of refraction could be tuned to values of 2.08 and can be considered as inside of the specification. Passivation properties could be proved in 2 successful test series; a third series tested at Q-Cells was not successful due to problems with contaminations inside of the reaction zone. Film thickness homogeneity is now, after integration of the modified coater head, in the specification range.

Experiments were carried out varying the process parameters in a wide range. Optimized process parameters led to an index of refraction of 2.08. The composition of the silicon nitride films was comparable to those of films deposited by low pressure PECVD. First industrial application test series at Centrotherm and Solartec resulted in encouraging passivation properties, but the film homogeneity was still insufficient in this case.

A further series of about 80 wafers was processed into solar cells and the cell parameters were measured. The sample size was large enough to gain statistically significant data. The cell efficiency of the sample cells is good, however not quite as high as for the reference. Summarized, the cells with AP-PECVD-SiN<sub>x</sub> showed encouraging results, however some further need for improving the bulk passivation and the film uniformity is apparent.

Extensive studies of the films were made using both spectro-ellipsometry and FTIR absorption spectroscopy. SEM pictures revealed that the surface of the films is partially highly structured, apparently consisting of powder particles deposited on the growing film.

In first test series SiN coatings were prepared on multi- (mc) and mono-crystalline float zone (FZ) wafers on specialized n-i-n test structures with passivated back side. The results show that the coatings approach the reference material in terms of passivating properties.

### **Summary of results achieved for PV technology development**

The critical issues identified in the work programme could mainly be solved:

- the performance of solar wafers was improved in the case of back surface etching; for silicon nitride deposition a further improvement of the passivation properties is necessary
- homogeneity of the coatings on large volume substrates fulfils the specification ( $\pm 3\%$ ) for 6" wafers
- scalability and operation of coating/etching technologies was proven, long term process stability and reliability was demonstrated for lab-scale conditions.

Against the first intentions, the AP plasma etching of Si wafers appears to be one of the most promising technologies developed in the SOLARPLAS project. Very encouraging results were obtained in several industrial tests for a large

number of potential application fields in the photovoltaic industry of this technology.

### 1.3.3 Generic engineering of power supply

For a stable and reliable operation of the linear extended DC arc plasma source used for the DC arc technology a sophisticated power supply module is necessary. Therefore, a completely new TopCon power supply splitted into 2 modules with each 64 kW DC with improved liquid cooling system and a CANopen control bus architecture was developed. The two modules can be used separately for operation of two DC arc sources. A modulation feature was tested and integrated into the TopCon system firmware. A redesigned ignition unit CIPASS-II for the plasma source was developed and tested. A system for a pre-ignition safety check of the plasma source was included.

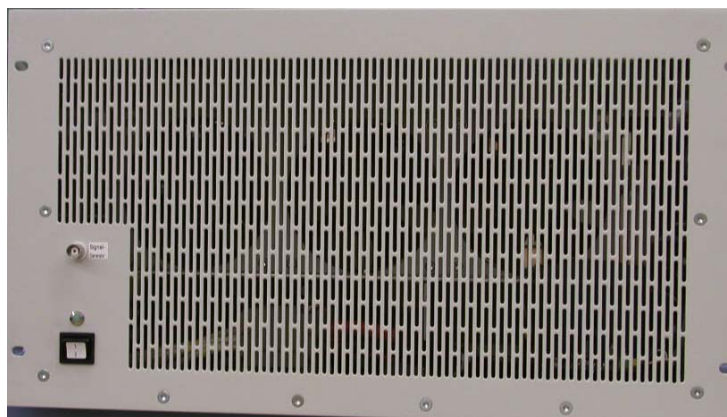


Figure 7:

Power Modulator unit

To track errors in the CIPASS hardware, occurring during the regular operation of the plasma source a current transducer is implemented. On regular operation no current is measured. Once a CIPASS hardware error occurs the arc current flows through the CIPASS partially and the PLC stops operation immediately. Furthermore it is expected that the plasma process can be characterized by examine the arc shape. Therefore a measuring principle was developed to characterize the shape of the arc dynamically and locally resolved. Experiments show that characteristically arc shapes at different gas parameters are obtained.

With this measuring principle arc instabilities and inhomogeneities can be tracked. So, the user can reveal information about the process quality and process stability automatically, non-invasive and in-line during a CVD process which improves the reliability of the LARGE technology.

### 1.3.4 Surface functionalisation of polymers by atmospheric pressure glow dielectric barrier discharge

A further key specific objective of the project was the exploration of a low energy, direct plasma technology based on a glow discharge dielectric barrier discharge (DBD) to demonstrate the feasibility of the deposition of specified functional  $\text{SiN}_x$  layers on mono-crystalline solar wafers. This low cost process has significant advantages for process integration, being scalable to large areas with the potential for continuous air to air processing. Although systems employing filamentary barrier or corona discharges have been used for surface activation and polymerisation, direct plasma systems for the

deposition of high quality inorganic films require the use of a stable, diffuse glow type discharge. This is generally achieved by the use of helium, which facilitates the glow regime via secondary ionization processes, slowing down the breakdown and stabilising the electron concentration, thus avoiding streamer formation. However the cost associated with large volumes of helium has limited the large scale application of such systems. Thus, the development of a system allowing the use of nitrogen or other low cost carrier gases was one of the tasks. The complete objective was assessed as a high risk area.

A further specific objective for a wider exploitation of this AP plasma technology the continuous surface treatment and coating on plastic web has been selected. Potential applications were seen in packaging for food, biotech, medical equipment, printing, adhesives, and flexible electronic circuits, as examples.

A reactor for low oxygen concentration was built up for enhanced control of process conditions (Figure 8).

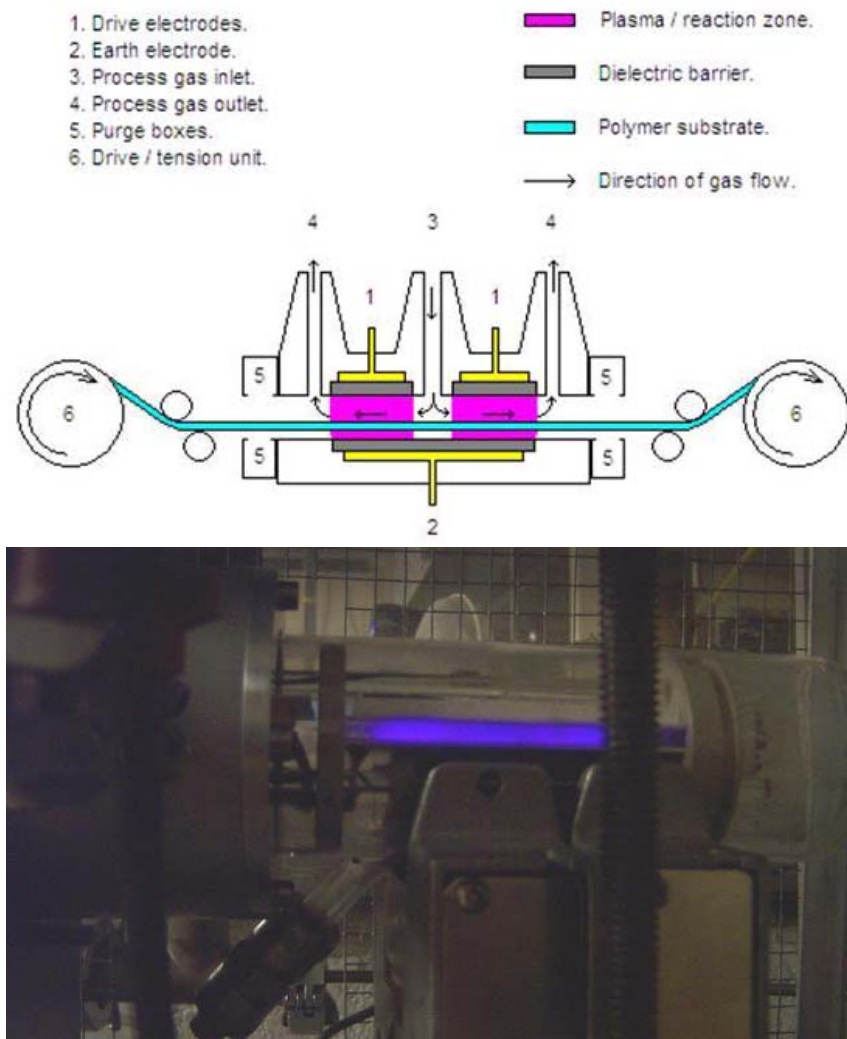


Figure 8: Scheme (top) and image (bottom) of the new low oxygen reactor for non oxide deposition

Furthermore, a new dual flow reactor for continuous reel to reel processing of polymer web was implemented, enabling enhanced dynamic growth rates and high uniformity across the web and providing the potential for scaling-up to an effective concept demonstrator.



In the case of direct plasma systems, the nature of the discharge has a direct bearing on the uniformity of the deposited material, and to some extent the reproducibility of the process. Stable operation at atmospheric pressure is not trivial, depending on multiple factors such as choice of process gas, power supply characteristics, reactor geometry and construction. Each of these interacting parameters had to be investigated in detail. One of the greatest challenges was to reduce projected operating costs by replacing helium with a low cost alternative, with nitrogen being the preferred option. This demanded further power supply investigation and revisions to the reactor system (Figure 9).

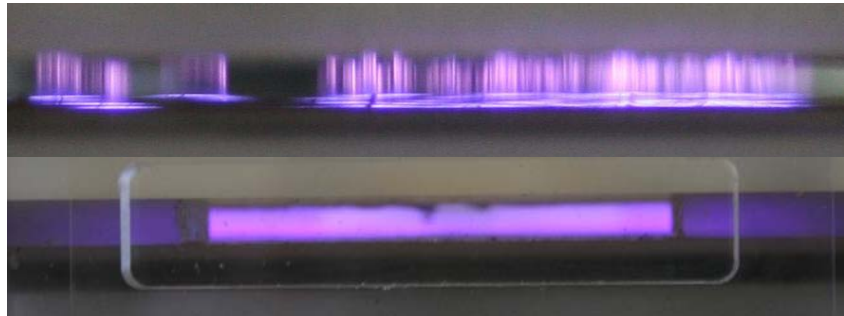


Figure 9: Top: Photograph showing a typical barrier discharge in nitrogen at 11KHz. Note the random localised filaments. Bottom: Photograph showing a diffuse glow-type discharge produced in the dual flow concept demonstrator.

$\text{SiO}_x\text{N}_y\text{C}_z$  films were successfully deposited via a direct glow discharge system operating at atmospheric pressure. However, the following work was focused onto deposition of functional layers (silica) onto plastic substrates which were assessed at mid-term as having more potential for exploitation in the shorter term. Uniform and adherent silica coatings (using helium plasma) were produced on silicon wafers (using the plastic web as a carrier) and on polymer web (PET). The stoichiometric  $\text{SiO}_2$  films appeared dense, smooth and continuous with no signs of particulates (Figure 10).

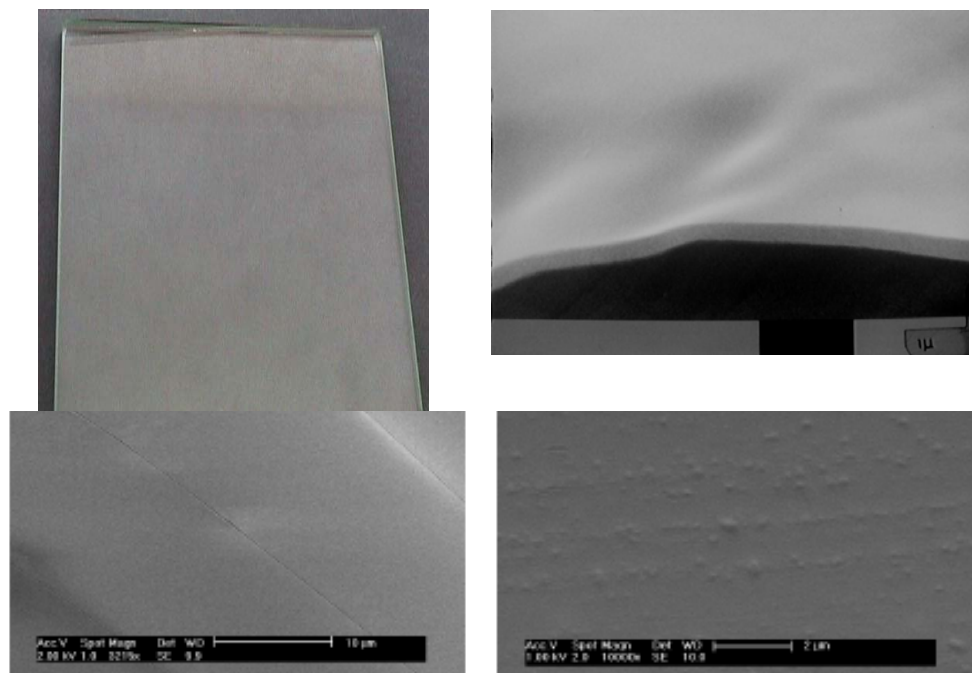




Figure 10: Top left: APGD silica deposited on a 220 mm x 90 mm glass substrate; top right: SEM images of plasma derived silica film on stainless steel; bottom left: 400 nm silica film deposited on PET; bottom right: 50 nm silica film deposited on PET

Potential large area applications have been identified including increased surface energy for processes such as printing and anti-fog layers. Further potential has been identified for the production of novel biocidal as well as TCO coatings.

## 1.4 Impact of the project on its industry or research sector

The two involved R&D performers (FhG/IWS, USAL) have strengthened their worldwide reputation in the area of atmospheric pressure plasma surface processing. The development of AP plasma technologies needs to manage a critical mass of R&D capacity which is normally out of range for SMEs. The SME proposers benefited from the significant scientific and technological expertise which the R&D performers have gained over many years. Closely linked to the R&D performers the SMEs are enabled to introduce on short timescale highly innovative technologies into their portfolio. This gives a significant competitive edge.

Spin-off developments, such as the application of the plasma technology for web coating will offer significant additional prospects. Most of all SMEs, e.g. job coaters, are expected to benefit from the low cost deposition technique solving individual coating problems with reduced development times. The broadening of the application range leads thereby to a market expansion having a positive impact on the job market for qualified personnel in thin film technologies.

## 2 Dissemination and use

### 2.1 Dissemination of knowledge

Table 2: Overview table on dissemination activities by consortium partners

Date	Type	Type of audience	Countries addressed	Size of audience	Partner involved
2006-05	IEEE 4 <sup>th</sup> World Conference on Photovoltaic Energy Conversion	Industry, Research	Europe, USA, Asia		CT
2006-09	21 <sup>st</sup> European Photovoltaic Solar Energy Conference and Exhibition	Industry, Research	Europe, USA, Asia	2700	CT, QC, Solartec, IWS
2006-09	10 <sup>th</sup> International Conference on Plasma Surface Engineering	Research, Industry	Europe, USA, Asia	720	IWS, CT, CTEC

Date	Type	Type of audience	Countries addressed	Size of audience	Partner involved
2006-12	Technological Plasmas Workshop Manchester	Research, Industry	UK		CTEC, USAL, IWS
2007-03	13. Fachtagung Plasmatechnologie	Research, Industry	Germany	300	IWS
2007-04	Workshop „Plasmabehandlung und Plasma-CVD-Beschichtung bei Atmosphärendruck“, Dresden	Research, Industry	Germany	50	IWS
2007-06	XIV. Workshop Plasmatechnik, Ilmenau	Research, Industry	Germany	50	IWS
2007-07	CAPPSA Cold Atmospheric pressure plasmas sources and applications Gent	Research, Industry	Europe, USA	50	IWS
2007-08	18th International Symposium on Plasma Chemistry, Kyoto University, Japan	Research, Industry	Europe, USA, Asia		IWS, CT, ST
2007-11	Symposium „Neue Photovoltaiktechnologien – Innovation durch Synergie“, Wolfen, Germany	Research, Industry	Germany		IWS, QC, ST, CT
2007-09	Conference Innovationscluster 2007	Research, Industry	Germany		IWS, CT, QC, ST
2007-09	22 <sup>st</sup> European Photovoltaic Solar Energy Conference and Exhibition	Industry, Research	Europe, USA, Asia	3000	CT, QC, Solartec, IWS
2007-09	V2007	Industry, Research	Germany, UK	Ca. 300	IWS
2008-04	Hannover Fair	Industry	Europe, USA, Asia		CT, QC, Solartec, IWS
2008 - 09	ELECTRONICA	Research, Industry	Europa	>300	REG
2008-09	23 <sup>st</sup> European Photovoltaic Solar Energy Conference and Exhibition	Industry, Research	Europe, USA, Asia	>3000	CT, QC, Solartec, IWS
2008-09	11 <sup>th</sup> International Conference on Plasma Surface Engineering	Research, Industry	Europe, USA, Asia		IWS, CT, ST, QC, CTEC
2008-04	SVC 2008, Chicago	Research, Industry	Europe, USA, Asia		IWS, CT, CTEC

## 2.2 Publishable results

The following presents exploitable results resulting from the SOLARPLAS project:

1. Surface texturization by plasma etching at atmospheric pressure

A well defined silicon surface structure, resulting from texture etching, leads to an improved light coupling into the solar cell and hence an improved cell efficiency. State of the art technology is wet chemical etching. The substitution of this wet chemical processing step can avoid use of harmful chemicals decreasing environmental impact and increase work safety.

## 2. Rear emitter plasma etching at atmospheric pressure

After phosphorus doping the wafer is completely covered by the emitter like a conductive shell, which leads to a short circuit between front and back of the cell. State of the art are single sided wet chemical etching, laser groove cutting or until recently plasma etching of the edges in a stack of cells. Removal of the emitter from the rear side by atmospheric plasma chemical etching has the additional advantage to form a defined surface on the wafer (structured or polished).

## 3. Plasma chemical etching of PSG at atmospheric pressure

Phosphorus silicate glass (PSG) is formed on the wafer surface during emitter diffusion. Under  $O_2$  atmosphere phosphorus diffuses from the glass into the silicon to form the n-type emitter of the solar cell. Usually, the PSG is removed by wet-chemical etching based on hydrofluoric acid (HF). Since HF is very harmful, the use of this chemical should be avoided.

Plasma etching of PSG represents a very challenging process step, because it has to show a high rate without damaging the underlying emitter layer, (a high etch selectivity).

## 4. PECVD of silicon nitride at atmospheric pressure

Amorphous hydrogenated silicon nitride layers applied on the front surface of solar cells serve as anti-reflecting coating and provide surface and bulk passivation. Nitride films are commonly deposited by low pressure PECVD.

## 5. $SiO_2$ barrier layer on polymer foil

Coatings on polymer web substantially widens out the potential use of these materials. Examples for potential applications comprising a high added value are scratch resistant surfaces, gas or aroma barrier, and anti-fog layers. Technical status for polymer coating is low pressure plasma but costs are too high for applications like food packaging which need barrier and anti-fog layers. A low temperature atmospheric pressure plasma process for roll-to-roll treatment of polymer foils is a solvent free and cost effective solution.

## 6. Electrical equipment for long arc plasma under atmospheric pressure.

For a stable and reliable operation of the linear extended DC arc plasma source used for the ArcJet-technology a sophisticated power supply module is necessary. Therefore, a completely new TopCon power supply system splitted up into 2 moduls 64 kW DC each with improved liquid cooling system and a CANopen control bus architecture was developed. The two modules can be used separately for operation of two LARGE plasma sources.

By using TopCon 'multiload' technology, up to 8 separate power supply systems may operate simultaneously at exactly the same operating point. A modulation feature was tested and integrated into the TopCon

system firmware.

The system is able to drive and maintain stable arc currents even under varying arc load conditions. There are special facilities for the ignition phase as also for handling fault conditions.

The supply section is fully controlled by a CANopen network together with all other system components and provides a 'one-screen' control of the entire plasma system. A 1500 VDC TopCon unit with 10 kW DC power was successfully tested also.

In terms of technical implementation, the system has reached an industrial degree of maturity and is ready to be introduced to an end-user level.

## 2.3 List of conference presentations / publications

Publication	Dani, I., Hopfe, V., Rogler, D., López, E., Mäder, G.: „Plasmachemische Gasphasenabscheidung und Plasmaätzen bei Atmosphärendruck mittels einer linear ausgedehnten DC-Bogenplasmaquelle“, Vakuum in Forschung und Praxis, Volume 18, Issue 4, August 2006
Poster presentation + publication	López, E., Dani, I., Hopfe, V., Heintze, M., Hauser, A., Möller, R., Wanka, H.: “Plasma etching at atmospheric pressure for rear emitter removal in crystalline Si solar cells”, 21 <sup>st</sup> European Photovoltaic Solar Energy Conference and Exhibition, September 4-8, 2006, Dresden, Germany
Poster presentation + publication	López, E., Dani, I., Hopfe, V., Wanka, H., Heintze, M., Möller, R., Hauser, A.: “Plasma enhanced chemical etching at atmospheric pressure for silicon wafer processing”, 21 <sup>st</sup> European Photovoltaic Solar Energy Conference and Exhibition, September 4-8, 2006, Dresden, Germany
Oral presentation	Heintze, M., Hauser, A., Möller, R., Wanka, H., López, E., Dani, I., Hopfe, V., Müller, J.W., Huwe, A.: “In-line plasma etching at atmospheric pressure for edge isolation in crystalline Si solar cells”, IEEE 4 <sup>th</sup> World Conference on Photovoltaic Energy Conversion, May 7-12, 2006, Waikoloa, Hawaii
Oral presentation (invited)	Hopfe, V., Sheel, D.W.: “Atmospheric Pressure Plasmas for Continuous Thin Film Deposition and Etching” 10 <sup>th</sup> International Conference on Plasma Surface Engineering PSE 2006 September, 10-15, 2006, Garmisch-Partenkirchen
Oral presentation	E. López, I. Dani, V. Hopfe, H. Wanka, R. Möller, M. Heintze, A. Hauser: “Atmospheric pressure plasma chemical etching for continuous c-Si solar wafer processing” Marie Curie Conference, April 10-12, 2006, Manchester
Poster presentation	Hopfe, V., Dani, I., López, E., Rosina, M., Mäder, G., Möller, R., Wanka, H., Heintze, M.: “Atmospheric pressure PECVD and atmospheric pressure plasma chemical etching for continuous processing of crystalline silicon wafers”, 21 <sup>st</sup> European Photovoltaic Solar Energy Conference and Exhibition, September 4-8, 2006, Dresden, Germany

Poster presentation + publication	E. López, I. Dani, V. Hopfe, H. Wanka, M. Heintze, R. Möller, A. Hauser: "Plasma enhanced chemical etching at atmospheric pressure for silicon wafer processing" 10 <sup>th</sup> International Conference on Plasma Surface Engineering PSE 2006 September, 10-15, 2006, Garmisch-Partenkirchen
Invited oral presentation	Volkmar Hopfe David W. Sheel: "Atmospheric Pressure Plasmas for Continuous Thin Film Deposition and Etching" Technological Plasmas Workshop Manchester Dec 06
Presentation and Posters, publication	Chr. Rohrer, Markus Müller, Bruno Ammann: "Simulating large power solar cell arrays with TopCon AAP-functionality for development and testing of solar inverters" ELECTRONICA 2008 and 2009
publication	Chr. Rohrer, Hans Loher, Haiyan Tian: " A two-stage DC source concept with increased system dynamics " REGATRON AG CH-9400 Rorschach. REGATRON TECHNICAL PUBLICATION SERVICE 09-2008. <a href="http://www.regatron.ch">www.regatron.ch</a>
Presentation	I. Dani, V. Hopfe: „PECVD und plasmachemisches Ätzen bei Atmosphärendruck für kontinuierliche Prozesse“ 13. Fachtagung Plasmatechnologie, 5.-7.3.2007, Bochum
Presentation	I. Dani: „Plasmagestützte CVD-Verfahren“ Surface Engineering und Nanotechnologie (SENT 2007) Verfahren zur Abscheidung dünner Schichten 27. – 28. März 2007, Dresden
Poster presentation	G. Mäder, E. Lopez, I. Dani, V. Hopfe: „Plasmaätzen von Solarzellen mit linearen Gleichspannungsbogenentladungsplasmaquellen“ Workshop „Plasmabehandlung und Plasma-CVD-Beschichtung bei Atmosphärendruck“, 25.04.2007, Dresden
Presentation	Ines Dani, Sebastian Tschöcke, Liliana Kotte, Gerrit Mäder, Julius Roch, Steffen Krause, Birte Dresler, Volkmar Hopfe: „Kontinuierliche Großflächenbeschichtung durch Mikrowellen-PECVD bei Atmosphärendruck“ Workshop „Plasmabehandlung und Plasma-CVD-Beschichtung bei Atmosphärendruck“, 25.04.2007, Dresden
Presentation	Ines Dani, Volkmar Hopfe: „PECVD und plasmachemisches Ätzen bei Atmosphärendruck für kontinuierliche Prozesse“ XIV. Workshop Plasmatechnik, 21./22. Juni 2007, Ilmenau
Poster presentation	G. MAEDER, J. ROCH, S. KRAUSE, B. DRESLER, S. TSCHOECKE, I. DANİ, V. HOPFE "CONTINUOUS MICROWAVE PLASMA ENHANCED CVD AT ATMOSPHERIC PRESSURE" CAPPSA Cold Atmospheric pressure plasmas sources and applications Gent, July, 11-13, 2007
Poster presentation	Volkmar Hopfe, I. Dani, E. López, M. Heintze: „Atmospheric Pressure PECVD for Crystalline Silicon Solar Wafer Processing“ 18th International Symposium on Plasma Chemistry, August 26 - 31, 2007 Kyoto University, Japan

Presentation+ publication	Volkmar Hopfe, I. Dani, E. López, M. Heintze: „Atmospheric Pressure Plasma Enhanced Chemical Etching for Crystalline Silicon Solar Wafer Processing” 18 <sup>th</sup> International Symposium on Plasma Chemistry, August 26 - 31, 2007 Kyoto University, Japan
Poster presentation+ publication	E. López, I. Dani, V. Hopfe, M. Heintze, R. Möller, H. Wanka, H. Nussbaumer, Poruba, R. Barinka: “New Developments in plasma enhanced chemical etching at atmospheric pressure” 22 <sup>st</sup> European Photovoltaic Solar Energy Conference and Exhibition, September 3-9, 2007, Milan, Italy
Poster presentation+ publication	B. Dresler, I. Dani, V. Hopfe, M. Heintze, R. Möller, H. Wanka, H. Nussbaumer: “ATMOSPHERIC PRESSURE PECVD OF SILICON NITRIDE FOR PASSIVATION OF SILICON SOLAR CELLS” 22 <sup>st</sup> European Photovoltaic Solar Energy Conference and Exhibition, September 3-9, 2007, Milan, Italy
Poster presentation	E. Lopez, B. Dresler, G. Mäder, S. Krause, I. Dani, V. Hopfe, M. Heintze, R. Möller, H. Wanka, M. Kirschmann, J. Frenck, A. Poruba, R. Barinka, R. Dahl, H. Nussbaumer: „Kontinuierliche Prozessierung von kristallinen Si-Solarwafern durch plasmachemisches Ätzen und Beschichten bei Atmosphärendruck” Symposium „Neue Photovoltaiktechnologien – Innovation durch Synergie”, 15.-16. 11. 2007, Wolfen, Germany
2 Papers	D W Sheel, J Hodgkinson, H Yates “Atmos. Pressure Glow Discharge CVD of aluminium oxide” Plasma Processes and Polymer, 2007 vol. 4 issue 5, pg 637-547  J Hodgkinson, D W Sheel, M Pemble, H Yates, “Atmos. Pressure Glow Discharge CVD of metal oxides” Plasma Processes and Polymer, 2006, 3, 597-605
Poster presentation+ publication	Sheel et al.: Technological Plasmas Workshop Belfast, Ireland Dec 07
Poster presentation+ publication	E. Lopez, B. Dresler, G. Mäder, S. Krause, I. Dani, V. Hopfe, M. Heintze, R. Möller, H. Wanka, M. Kirschmann, J. Frenck, A. Poruba, R. Barinka, R. Dahl, H. Nussbaumer: “Plasma enhanced CVD and plasma chemical etching at atmospheric pressure for continuous processing of crystalline silicon solar wafers” SVC 2008, April 2008, Chicago
Oral presentation (invited) + publication	Volkmar Hopfe, David W Sheel, Rainer Moeller: “Atmospheric Pressure Plasmas for Crystalline Silicon Photovoltaic” SVC 2008, April 2008, Chicago