

## PROCESS OPTIMIZATION AND SOLAR CELL RESULTS OF CONCVD EPITAXIAL LAYERS

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**ABSTRACT:** Silicon CVD is required to realise the upcoming “kerfless” c-Si thin-film solar cell concepts, like EpiCell, Lift-off and recrystallized wafer equivalent solar cells. To realise these solar cell concepts, a high throughput reactor with the possibility of continuous deposition is needed. For this reason, the ConCVD is the first epitaxy tool with a continuous wafer transport through the entire system. The requirements for such a machine are very sophisticated. Despite the open construction, the flammable and toxic reactor atmosphere must be separated from the surrounding atmosphere and the other way around, impurities must not get inside the reactor. This work reports on process improvement and solar cell results on layers deposited in the ConCVD at Fraunhofer ISE. The ConCVD (Continuous CVD) is a link between lab type reactors and a production reactor (ProConCVD), also developed at the Fraunhofer ISE. Setup improvements could enhance deposition conditions by providing a particle free environment. Furthermore, processes optimisations in this new setup lead to a solar cell result of 13.8%.

**Keywords:** kerfless, Si-Deposition, Thin-Film, Epitaxy, Chemical Vapor Deposition

### 1 INTRODUCTION

To reduce costs for photovoltaic power conversion it is necessary to develop techniques which are economically profitable and allow producing in an industrial scale. One of the main challenges is that solar grade silicon is rather expensive and most of the materials saving thin film techniques have low efficiencies. A way to realize a thin film solar cell with good crystalline properties and higher efficiencies is the crystalline silicon thin-film (cSiTF). This concept is based on an epitaxy process in which a 10 – 40  $\mu\text{m}$  silicon layer is deposited on a cost-effective substrate. With this technique it is possible to use cheap up-graded metallurgical grade silicon as substrate for a highly pure silicon layer. With the so called epitaxial wafer equivalent efficiencies of up to 17.6% could already be achieved [1].

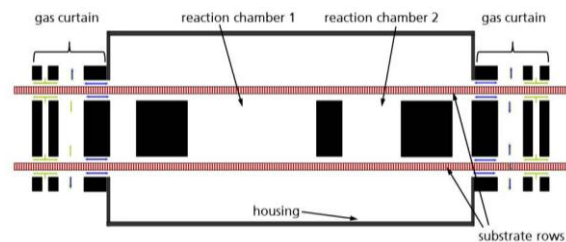
To realise the cSiTF concept in industrial scale, a CVD reactor which allows continuous deposition is needed. Furthermore it has to be cost effective, which leads to compromises between quality and costs. The following conditions have direct consequences on the gas flow in the reaction chamber.

- To be cost effective, the inner setup cannot consist of quartz, it is realized with graphite. This graphite can emit particles, consequently the graphite has to be separated with another material at critical points.
- The reaction chamber needs a purge gas shower at the front and the end to separate the different gas atmospheres. This means, that the gas atmosphere of the reaction chamber is a mixing between purge gas and reaction gas.
- The inlets of the two reaction gas species hydrogen and chlorosilane, must be separated to avoid an overgrowth of the inlets

With these boundary conditions a deposition tool with a complete open setup was realized for the first time, the ConCVD. With the same setup, the ProConCVD has calculated deposition costs of a 20  $\mu\text{m}$  thick epitaxial silicon layer below 20 €/m<sup>2</sup> [2].

### 2 REACTOR SETUP

The basic design of the ConCVD and the ProConCVD has been chosen to follow an in-line approach, featuring an uninterrupted operation with no load locks [3]. The top view of the ConCVD illustrates this possibility for continuous deposition.



**Figure 2:** Top view of the simplified ConCVD setup.

Carriers loaded with wafers, pass different graphite blocks and are moving along tracks through the entire system (red in figure 2). The deposition is initiated by injection of the process gases chlorosilane, hydrogen and dopants into the reaction chambers, while the carriers are continuously sliding during the deposition.

The design requires, that the flammable and toxic reactor atmosphere must be separated from the surrounding atmosphere, and in the opposite direction, impurities must not get inside the reactor. Therefore a gas curtain system relying on pumps, purge gas flows and slits (acting as flow resistors) has been developed and implemented. This system ensures that no gas exchange happens between reactor and laboratory atmosphere. Thus a safe process with a low impurity level is possible, even when the substrates are continuously transported through the reactor.

The current setup of the ConCVD was improved during recent years. The various changes should customize the ConCVD to fulfil the needs of industrial epitaxial quality and allow significant up scaling.

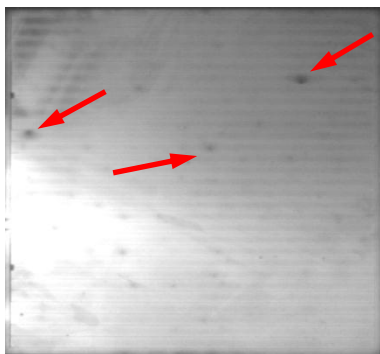
Two reaction chambers with independent gas supply are implemented in the ConCVD. Thus, it is possible to realise a layer stack of two silicon layers of different thickness and doping in one in-line process.

The gas mixture system can provide the process gases  $\text{SiHCl}_3$ ,  $\text{SiCl}_4$ ,  $\text{SiH}_2\text{Cl}_2$ ,  $\text{H}_2$ ,  $\text{HCl}$ ,  $\text{PH}_3$ ,  $\text{B}_2\text{H}_6$  and the purge gases  $\text{N}_2$  and Ar. The great variety of gases allows many different processes, like in-situ emitter and bulk epitaxy, or functional silicon etching with  $\text{HCl}$ . The lower the Cl/H ratio, the higher is the conversion of chlorosilane into solid silicon at a given temperature. Consequently, deposition is carried out at Cl/H ratios lower than approx. 30% (using  $\text{SiCl}_4$ ). Typical deposition parameters used in the ConCVD are:

- 50 slm Hydrogen ( $\text{H}_2$ )
- 1 slm Silicon Tetrachloride ( $\text{STC}/\text{SiCl}_4$ )
- 150 slm Argon (Ar)
- 150 slm Nitrogen ( $\text{N}_2$ )

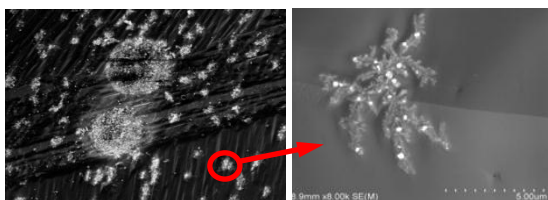
### 3 SETUP IMPROVEMENT

After first improvements concerning system stability and wafer yield, some process optimizations had been done. These optimizations lead to epitaxial layers deposited in the ConCVD on highly doped, and therefore photovoltaically inactive, substrates. These layers had an Etch-Pid-Density of  $6.0\text{e}5 \text{ l}/\text{cm}^2$ . Some of these layers have been produced to solar cells; one of these cells can be seen in figure 3.



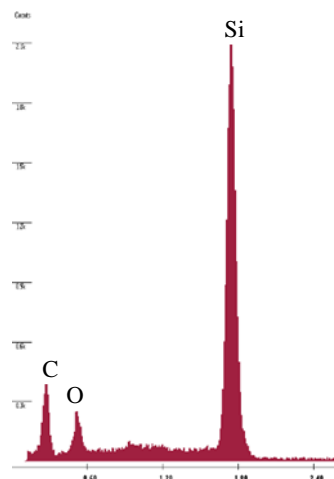
**Figure 3:** Photoluminescence (PL) image of a  $50 \times 50 \text{ mm}^2$  solar cell with dark spots.

The PL-images of the solar cells deposited in the ConCVD show dark areas, which indicate shunts between bulk and emitter. The dark spots were investigated in detail by scanning electron microscopy, as figure 4 shows.



**Figure 4:** SEM-image of the carbon particles.

The dark areas turned out to consist of an accumulation of many dendritic structures. These dendrites are distributed over the whole solar cell, however in lower density than in the dark spots. To identify the chemical composition of the dendrites, energy dispersive X-ray spectroscopy (EDX) was used, to be seen in the following figure.



**Figure 5:** EDX measurement in the center of one dendritic structure.

The EDX measurement in figure 5 shows a very high amount of carbon (left peak) in the centres of the dendrites. This high carbon peak is not detected at other parts of the surface. Therefore, carbon particles cause dendritic growth in the silicon layer. These dendrites have a large surface area where oxygen is attached. Their effects on cell performance are shown in the table I, which compare the solar cell shown in figure 3 with solar cells made in a RTCVD (lab type epitaxy tool with quartz carriers [1]). All solar cells in this paper are deposited on substrates with a p+ doping level, aluminum back side contact, diffused phosphorus emitter, Ti/Pd/Ag front contact and a double-layer anti-reflection coating.

**Table I:** Comparison between the “old” ConCVD setup and the lab type RTCVD

	RTCVD	ConCVD
Substrate	Cz	Cz
Cell dimensions [ $\text{mm}^2$ ]	$20 \times 20$	$50 \times 50$
$V_{OC}$ [mV]	632	569
$J_{SC}$ [ $\text{mA}/\text{cm}^2$ ]	25.2	24.3
FF [%]	82	60
Layer thickness [ $\mu\text{m}$ ]	12	9
$\eta$ [%]	12.8	8.2

The efficiency of the solar cell deposited in the ConCVD is  $4.6\%_{\text{abs}}$  lower than the cell of the RTCVD. According to [4], a thinner layer of  $3 \mu\text{m}$  can explain  $0.5\%$  loss in efficiency, due to a lower  $J_{SC}$ . But the very low fill factor, caused by shunts between bulk and emitter, is the main reason for the low efficiency. These shunts are a consequence of the graphite particle formation in the ConCVD setup. Therefore, a new construction was developed.

### 4 REACTOR AND EPI OPTIMIZATION

The reconstruction of the ConCVD for providing a particle free environment put emphasis on gas velocities, gas stream directions and exchange of materials at critical points. The new setup made it necessary to develop a new process. Because of the open setup of the ConCVD all settings affect each other, for this reason process optimization is tricky. Seven main parameters influence the layer quality of the ConCVD. These seven settings

influence each other, and therefore a general statement about the effect of one setting is not possible. For example, a lower pressure can be good at high temperatures and bad at low temperatures. Due to this extreme wide parameter field, the method of “Design of Experiment” (DoE) [5] was used.

Several runs of DoE lead to a deposition with reasonably good layer properties: 3.8  $\mu\text{sec}$  lifetime (measured with  $\mu\text{w-PCD}$  at 904 nm wavelength and a  $\text{Si}_x\text{N}_y$  passivation) and an Etch-Pid-Density (EPD) of  $4.0\text{e}4$   $1/\text{cm}^2$  have been reached. Therefore, the particle free setup could lower the EPD by an order of magnitude, compared to the old setup. The layers have been deposited in stationary and in continuous transport mode. Out of these layers, solar cells have been produced; table II shows the results of the best solar cells, compared with a layer of the RTCVD.

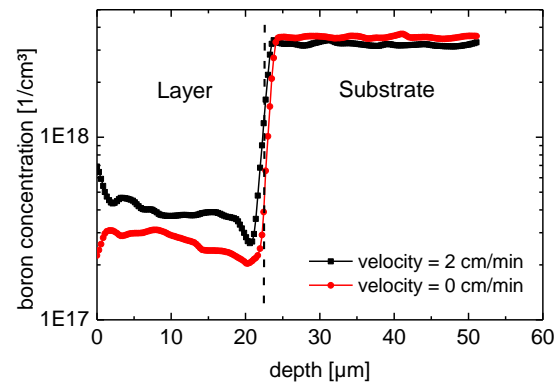
**Table II:** Comparison between the new ConCVD setup and the lab type RTCVD

	RTCVD	ConCVD	ConCVD
Substrate	Cz	Cz	Cz
velocity [cm/min]	0	0	2
Cell dimensions [mm]	20x20	50x50	50x50
$V_{\text{OC}}$ [mV]	640	636	641
$J_{\text{SC}}$ [ $\text{mA}/\text{cm}^2$ ]	30.0	27.4	27.0
FF [%]	80	79	78
Layer thickness [ $\mu\text{m}$ ]	22	17	20
$\eta$ [%]	15.4	13.8	13.5

The difference in efficiency between RTCVD and ConCVD could be decreased to 1.6% in stationary and 1.9% in continuous mode. The RTCVD layer is 22  $\mu\text{m}$  thick and therefore comparable to the layers of the ConCVD. The fill factors of the ConCVD layers are nearly as high as the fill factor of the RTCVD. This underlines that the reaction chamber of the new setup is nearly particle free.

The comparison between the RTCVD and the ConCVD solar cell deposited without transport shows a difference in efficiency of 1.6%<sub>abs</sub>. According to [4], a thinner layer of 5  $\mu\text{m}$  can explain a loss of 0.9% in efficiency. Furthermore the doping level of the ConCVD layers ( $=2.7\text{e}17$   $1/\text{cm}^3$ ) was about 6 times too high, due to false dopant gas flow settings. Without this misfit the efficiency could raise about 0.2% (calculated with PC1D). Therefore, the layer quality has the potential for an efficiency of 14.9%, which is only 0.5% lower than the efficiency of the lab type reactor.

The deposition parameters of the two ConCVD layers have been the same, only the transport velocity varied. The transport influences the temperature profile of the reaction chamber and therefore the doping profile. Figure 5 compares the doping profiles of the ConCVD layers.



**Figure 5:** Doping profile of the ConCVD layers, measured with Spreading-Resistance-Profiling.

Both layers have an increasing boron concentration during deposition. The different initial points can be interpreted by measuring inaccuracy.

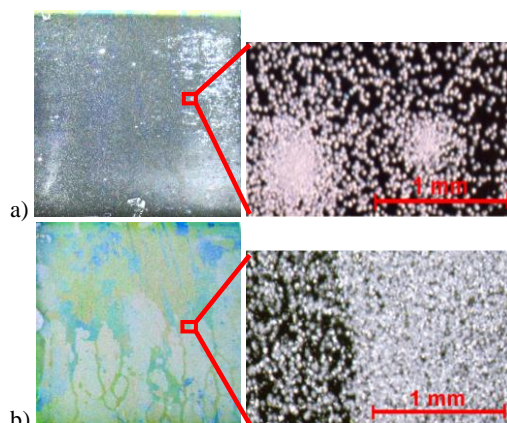
The layer without transport velocity (red line with circle) has a constant position during the deposition; therefore the raise cannot be due to transport effects, but might be explained by lowering of the silicon partial pressure. Another factor could be the temperature profile during deposition time, according to [6] the incorporation of boron into silicon raises with increasing temperature.

The temperature profile of the layer with transport (black curve with rectangle) is steeper; this can be seen in the doping profile. The negative peak represents the start of the deposition while moving into the reaction chamber. After heating the wafer to the final deposition temperature, the doping level is relatively constant. Despite the temperature, the boron incorporation also consists on the practical pressure of the gas species; therefore the boron concentration in the reaction chamber rises at the end of the deposition and lead to a higher doping level towards the surface again. For these reasons, the average doping level of  $3.7\text{e}17$   $1/\text{cm}^3$  is even higher than in the layer without transport. Without this misfit the efficiency could raise to 13.8% (calculated with PC1D).

## 5 POLYCRYSTALLINE SILICON LAYERS

In addition to the homo-epitaxy, polycrystalline silicon on foreign substrates could be used for seed and crystallize solar cell concepts. Modules based on ceramic substrates, for example, would allow integrated solar cells in module size. To apply the cSiTF concept on foreign substrates, a recrystallized seeding layer is needed for crystal information. The depositing of a polycrystalline seeding layer can be done in the ConCVD as described here. The recrystallization can take place in a halogen lamp heated furnace as described in [7].

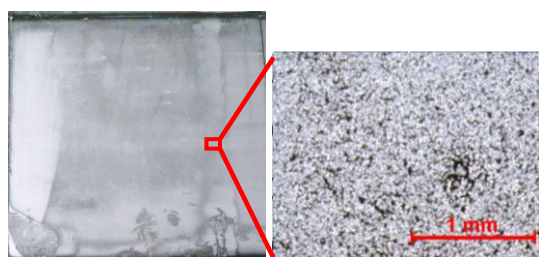
The reference samples for the seeding layer deposition in the ConCVD are silicon wafers which are encapsulated with a 300 nm thick  $\text{SiO}_2$  layer. The  $\text{SiO}_2$  layers are optimized for a low defect surface with few dangling bonds. Therefore, the nucleation of silicon is very ambitious, as shown in figure 6.



**Figure 6:** left) picture right) magnification  
 a) Seeding layer on a normal 156x156 mm<sup>2</sup> substrate.  
 b) Seeding layer on with drying marks

On a normal SiO<sub>2</sub> layer, typical island growth can be observed: the nucleation occurs only at some spots with a higher defect density, and even with longer depositing time, the number of nucleation spots does not raise, only the size of the conglomerates become bigger. This behavior can be seen in figure 6a. On areas with saw damage, drying marks of previous cleaning steps, handling tracks or defect rich grains, the SiO<sub>2</sub> layer cannot passivate all dangling bonds and therefore the number of nucleation spots increases. The result is a layer, which document all previous influences on the surface. An example is figure 6b with drying marks.

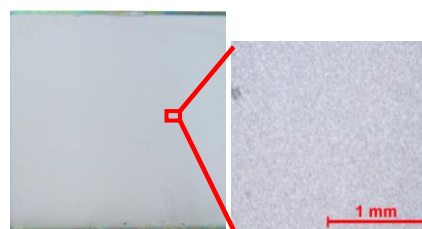
Further experiments as well as calculations indicate that the nucleation on SiO<sub>2</sub> works best, if the deposition conditions show a high supersaturation. A wafer deposited under conditions with maximum supersaturation can be seen in following figure.



**Figure 7:** left) picture right) magnification  
 Seeding layer on a normal 156x156 mm<sup>2</sup> substrate, deposited with maximum supersaturation.

Compared to the layers of figure 6, this layer shows an increased number of nucleation spots. However, even under these conditions with maximum supersaturation the surface is not covered completely with nucleation spots.

The supersaturation cannot be increased in the ConCVD, so the only way to realise a completely covered surface is to increase the number of the dangling bonds on the SiO<sub>2</sub> layer. Therefore, an annealing step in a hydrogen atmosphere was implemented directly before the seeding layer deposition. The SiO<sub>2</sub> layer should be thermally etched by the annealing step and generate dangling bonds. The annealing parameters which had to be adjusted are the time, temperature and partial pressure of H<sub>2</sub>. Figure 8 shows the result of an optimized parameter set.



**Figure 8:** left) picture right) magnification  
 Seeding layer on a 156x156 mm<sup>2</sup> substrate with annealed SiO<sub>2</sub> layer

The seeding layer nucleates pinhole free and uniformly over the whole 156x156 mm wafer. Therefore the annealing step leads to sufficient surface mistakes over the whole wafer.

## 6 ADVANCED REACTOR DESIGN

The standard design of microelectronic CVD reactors is based on a gas system with emphasis on perfect controlled gas streams in order to deposit nearly perfect layers. The main gas flow is parallel to the substrates; therefore the gas transport to the wafers is limited by diffusion of the precursors to the substrate surface. But diffusion depends on temperature and gas composition. Therefore, the disadvantages of such a design are a relatively low gas yield and growth rate. Furthermore, the homogeneity of the layer thickness depends on the temperature profile and little misfits of the gas control. In low cost applications with large dimensions like the ProConCVD an exact temperature and gas stream control would be too expensive to supply or even not possible.

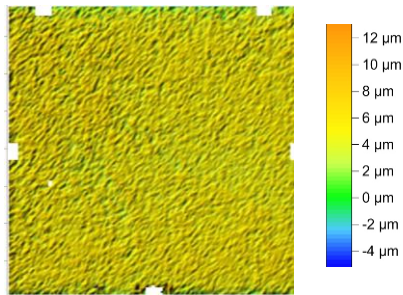
A new setup in the reactor design was realized in the ConCVD to address this problem. With this setup, some important improvements could be achieved, as the following table shows.

**Table IV:** Comparison: “old” and news setup

	old setup	new setup
gas yield [%]	21	44
parasitic deposition [%]	11	14
homogeneity [%]	28	93
growth rate [µm/min]	0.5	0.8

The gas yield of the old setup has a typical value for CVD reactors, whereas the new setup has a more than twice as high yield. Even at the parasitic deposition with a higher absolutely amount, the ratio of gas yield and parasitic deposition is almost twice as large. Therefore the double amount of wafers can be deposited before a cleaning step is necessary. The homogeneity summarizes the areas of the layer which are thicker than 80% of the thickest layer part if the substrate is moving continuously through the reaction chamber. Currently only the new setup, whose layers have a homogeneity of 93%, fulfill the needs of an industrial application. In addition, the overall growth rate of the new setup is higher, whereby a faster transport velocity is possible. All these values are important to be cost effective and the new setup shows better performance in all of them. To point out the performance of the new setup, the following figure shows the thickness homogeneity of a layer deposited in the new reaction chamber.





**Figure 9:** Thickness mapping of a 156x156 mm<sup>2</sup> epitaxial silicon layer, deposited in the new reaction chamber.

The layer thickness of the continuous deposition in the new reaction chamber is nearly perfect, only a narrow strip at the upper and lower edge can be seen. These strips are not caused by the reaction chamber; they are caused by the actual carrier system.

## 7 CONCLUSION

For using thin film techniques without disclaiming the advantages of crystalline silicon, high throughput silicon CVD equipment is needed on an industrial scale. The ConCVD, and as the next step the ProConCVD fit the requirements for such tools. This paper presented the last results of the ConCVD.

One source problem was of particle pollution due to the graphite based setup. It could be eliminated with some new details in the setup. With this optimized setup and several runs of DoE, a sufficient layer quality leads to cell results up to 13.8%.

To cover a wider range of cell concepts, process development for polycrystalline seeding layers has been done. After identifying the problems, homogeneous seeding layers without pinholes could be deposited.

For further improvement of the ConCVD, a new setup of the reaction chamber was developed, which shows good performance in economically important properties like homogeneity, gas yield, growth rate and parasitic deposition.

Bringing together the layer quality of the old setup with the properties of the new setup will be the work of the coming months.

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