

CRYSTALLINE SILICON THIN-FILM SOLAR CELLS FROM THE POROUS SILICON PROCESS APPLYING CONVECTION ASSISTED CHEMICAL VAPOR DEPOSITION

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ABSTRACT: Convection assisted chemical vapor deposition (CoCVD) is applied for the first time to monocrystalline Si thin-film solar cells from the porous silicon (PSI) layer transfer process. The CoCVD reactor allows for Si deposition on large areas of up to $43 \times 43 \text{ cm}^2$. The bulk diffusion length of the epitaxial layer deposited by CoCVD on PSI substrates is $L_{\text{bulk}} = (85 \pm 5) \mu\text{m}$, which is almost three times the cell thickness and is similar to diffusion lengths achieved in commercial CVD reactors used in microelectronics. The simple cell process includes an epitaxially grown back surface field layer and a front surface passivation by a silicon nitride-coated amorphous silicon layer. Despite a planar front surface the cell efficiency is 12.0% ($V_{\text{OC}} = 590 \text{ mV}$, $J_{\text{SC}} = 26.7 \text{ mA/cm}^2$, $FF = 76.4\%$) for a cell size of 4 cm^2 . Thus the CoCVD method is suitable for fabricating efficient PSI solar cells.

Keywords: c-Si, transfer process, epitaxy

1 INTRODUCTION

Layer transfer cells based on epitaxial deposition of the absorber layer on monocrystalline porous silicon substrates, offer the opportunity to combine high cell efficiencies with low material and energy consumption.

The use of monocrystalline Si growth substrates permits lowest defect densities for high-quality absorbers [7], and enables the direct use of trichlorosilane. The small thickness of the epitaxial layer, as well as the re-use of the growth substrate, helps to reduce material and energy consumption.

An industrial exploitation of these properties for solar cell production currently lacks of a cost effective method for the deposition of epitaxially grown Si layers. Up to now the epitaxial layers of solar cells from the PSI (porous silicon) process [1] were deposited in reactors as used in microelectronics. The high electronic quality of the absorber layers is one of the most important prerequisites for manufacturing high efficiency silicon thin-film solar cells. Industrially feasible epitaxy systems therefore need to meet the high quality requirements, but have to provide a more cost effective deposition process.

We investigate the CoCVD (Convection assisted chemical vapor deposition) system with regard to its suitability for high quality epitaxy in particular for the PSI-process. Therefore the bulk diffusion length, the surface recombination achieved with the grown back surface field and the PSI solar cells efficiency are considered.

1.1 PSI process

The PSI process [1] starts with a monocrystalline Si growth substrate. A porous double layer forms by anodic etching on the surface of the substrate. During a bake at 1100°C for 30 min the porous silicon reorganizes leading to a closed surface of the lowly porous layer at the wafer surface and an almost complete dissolution of the underlying highly porous layer. The closed surface is monocrystalline so that the subsequent epitaxy yields a monocrystalline thin-film that is used as active layer of the solar cell. The layer with high porosity serves as

predetermined breaking point for the layer transfer.

The layer transfer allows processing the front side of the PSI solar cell first. Subsequently the Si film is attached to a glass carrier and detached from the substrate by applying mechanical force. In a further step the rear side of the solar cell is finished. The substrate wafer is re-used.

Up to now the PSI solar cells are made from epitaxially grown layers coming from reactors built for microelectronics purposes. Cell efficiencies above 15% on less than $30 \mu\text{m}$ thick epitaxial Si layers have been demonstrated without using photolithography [2].

1.2 Convection assisted chemical vapor deposition system

Alternative Si deposition techniques have been developed in recent years. One promising approach is the CoCVD (convection-assisted chemical vapor deposition) that allows deposition on large rectangular substrates [3]. Figure 1 illustrates the principle of CoCVD epitaxy.

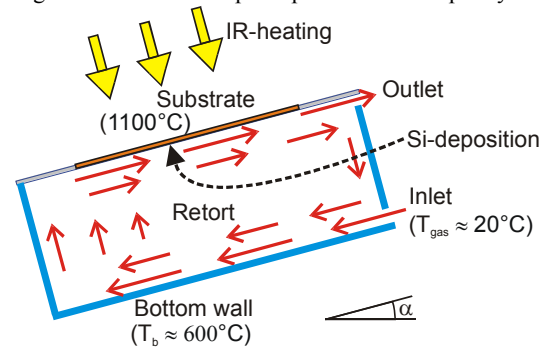


Figure 1: Schematics of the convection-assisted chemical vapor deposition (CoCVD) process.

Cold gas is fed into the reactor and flows along the cold bottom wall that is positioned opposite to the substrate. The gas moves upwards on the substrate side where it is heated, an effect which drives the convection. Some gas leaves the reactor through the outlet while the portion far from the substrate stays in the convection roll

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for another turn. This effect reduces the amount of SiHCl_3 (TCS) that is required to grow a given layer thickness.

Up to now a reactor with a deposition area of $43 \times 43 \text{ cm}^2$ is realized by ZAE Bayern. A variation in thickness of less than $\pm 10\%$ and a difference in doping concentration on the whole area of less than $\pm 15\%$ were demonstrated [4].

2 EXPERIMENTAL

The substrates for the PSI process are highly boron-doped (resistivity $10 \text{ m}\Omega\text{cm}$) monocrystalline silicon wafers of a diameter of 10 cm. The wafers feature a polished front side and are grown by the Czochralski (Cz) method. Both, PSI solar cells and samples for measuring the carrier lifetime are fabricated from the epitaxial layers.

2.1 Porous layer formation

The porous double layer on the highly *p*-type doped monocrystalline Si substrates is formed by anodic etching at different current densities in a two-chamber set up utilizing an aqueous HF-electrolyte. The low porosity layer is about $1 \mu\text{m}$ thick and shows a porosity of about 20% as appropriate for surface closure. The highly porous separation layer is about 200 nm thick and has a porosity of above 50%.

2.2 Annealing and Epitaxy

Annealing and Si layer growth is carried out in the CoCVD system, recently built at ZAE Bayern. The system is operated at atmospheric pressure; the precursor gas consists of a mixture of hydrogen and trichlorosilane (TCS). Further details of the system and deposition processes can be found in References [5, 6]. During annealing the substrate temperature is maintained at 1100°C for 30 min in a pure hydrogen atmosphere. The subsequent growth process is also carried out at 1100°C , with a TCS-concentration in the precursor gas of 2 vol%. For the boron-doping two different recipes are applied:

- Constant gas concentration of BCl_3 resulting in a constant dopant density in the absorber layers of about $2 \times 10^{16} \text{ cm}^{-3}$.
- High initial BCl_3 -concentration for the purpose of back-surface field (BSF) formation. The BCl_3 concentration is decreased after 5 min to achieve a dopant density in the absorber of 1 to $2 \times 10^{16} \text{ cm}^{-3}$.

In both cases the growth rate is $0.9 \mu\text{m}/\text{min}$.

2.3 PSI lifetime sample preparation

Epitaxial layers with BSF are grown on the same porous Si substrates as the PSI solar cells also using recipe b. A getter diffusion identical to the emitter diffusion is carried out whereas the diffused layer is removed before passivating the front side with silicon nitride ($n = 2.4$). The area of the lifetime samples is $2.5 \times 2.5 \text{ cm}^2$. The effective carrier lifetime of the PSI layer is measured twice: First while the layer is still attached to the growth substrate, and second after lift-off.

For a more precise determination of the bulk diffusion length the BSF is removed and substituted by a passivation layer with lower surface recombination velocity. In this case the BSF is chemically etched away

and an amorphous Si layer is deposited.

A $300 \mu\text{m}$ thick *p*-type FZ-Si wafer (resistivity $1.5 \Omega\text{cm}$) is passivated with SiN layers on both sides. It serves as reference sample to assess the quality of the SiN surface passivation. Another FZ-Si wafer is passivated with amorphous silicon on both sides to assess the quality of the a-Si surface passivation.

2.4 PSI solar cell process

PSI solar cells are made from epitaxial Si layers with BSF (recipe b). The thickness of the epitaxially grown Si layer is $(32 \pm 3) \mu\text{m}$ including the BSF layer. The emitter diffusion follows after an RCA cleaning and results in a sheet resistance of about $90 \Omega/\square$. The front surface is then passivated by a 7 nm thick amorphous Si layer prior to the evaporating the Al contact fingers. We thicken the busbar with evaporated Ag. A SiN layer with a refractive index of $n = 1.9$ and a thickness of 60 nm is deposited as an anti-reflective coating. A thin Ag-stripe attached to the Ag-busbar allows contacting after encapsulation using a transparent glue. After the lift-off step evaporation of Al through a shadow mask forms the rear contact. The contacts are annealed at 300°C for 1 to 3 min on a hot plate. No surface texture is applied. The cell size is 3.96 cm^2 .

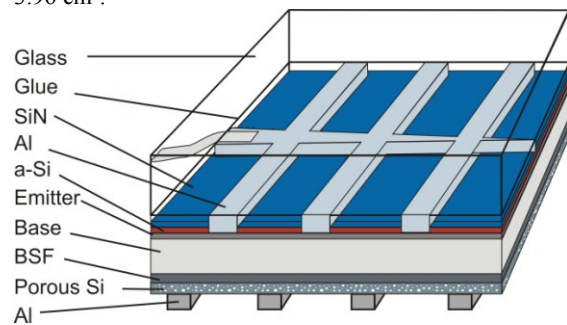


Figure 2: Schematic drawing of the PSI solar cell with local contacts on front and rear.

3 CHARACTERIZATION OF THE EPITAXIAL SI LAYER

3.1 Doping profile

Figure 3 shows the doping profile with an acceptor concentration of $1.2 \times 10^{16} \text{ cm}^{-3}$ in an $(18 \pm 1) \mu\text{m}$ -thick epitaxial layer that is deposited by CoCVD following recipe a.

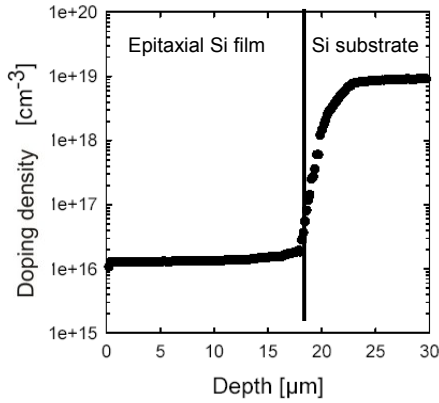


Figure 3: Boron concentration profile determined by ECV measurements of epitaxial Si layers grown on a highly boron-doped substrate. A constant concentration of about $1.2 \times 10^{16} \text{ cm}^{-3}$ is determined.

The thickness of the absorber layers with BSF (recipe b), is $(32 \pm 1) \mu\text{m}$ including the BSF. Their depth-resolved boron concentration is measured by the spreading resistance method [13]. The BSF with a thickness of about $(5 \pm 0.3) \mu\text{m}$ has a constant doping concentration of $5 \times 10^{18} \text{ cm}^{-3}$. Within the deposition of the next $(27 \pm 1) \mu\text{m}$ the doping concentration is reduced to $1.2 \times 10^{16} \text{ cm}^{-3}$. Figure 4 shows a scanning electron microscope (SEM) image of the epitaxially layer with grown BSF.

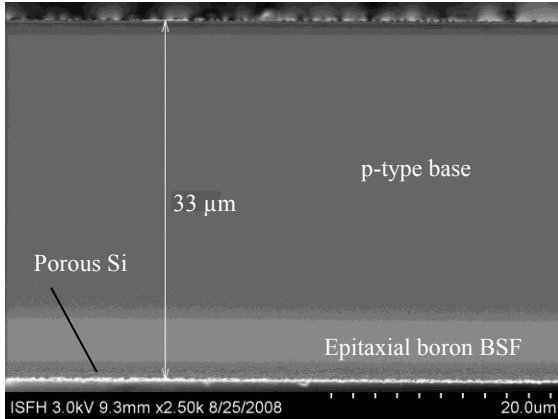


Figure 4: Scanning electron microscope image of the epitaxial Si layer with BSF grown in the CoCVD system.

3.2 Carrier lifetime

Carrier lifetime measurements are conducted applying the microwave photoconductance decay (MWPCD) method [8]. The SiN-passivated FZ-Si reference wafer shows an effective lifetime of $(1030 \pm 100) \mu\text{s}$, which corresponds to a recombination velocity of the SiN-passivated surfaces of $S_{\text{SiN}} = (10 \pm 2) \text{ cm/s}$. The a-Si-passivated reference wafer shows an effective lifetime $\tau_{\text{eff}} = (1000 \pm 200) \mu\text{s}$ corresponding to a surface recombination velocity of $S_{\text{a-Si}} = (10 \pm 5) \text{ cm/s}$.

The harmonic mean of the effective carrier lifetime is $\tau_{\text{eff}} = (3.1 \pm 0.2) \mu\text{s}$ after removing the BSF-layer and

depositing an a-Si:H layer for surface passivation. We assume a rear side recombination velocity of $S_{\text{a-Si}} = (10 \pm 5) \text{ cm/s}$ and a front side recombination velocity of $S_{\text{SiN}} = (10 \pm 2) \text{ cm/s}$ as measured on the FZ samples. With these assumptions a bulk diffusion length $L_{\text{bulk}} = (85 \pm 5) \mu\text{m}$ follows [9,10]. That means the bulk diffusion length is almost three times larger than the thickness of the epitaxially grown Si film. A bulk diffusion length of $85 \mu\text{m}$ is very similar to the diffusion length that was deduced from quantum efficiency data of PSI cell that were grown in commercial CVD reactors [15].

The harmonic mean of the effective lifetime of the PSI sample is $\tau_{\text{eff}} = (1.3 \pm 0.1) \mu\text{s}$ before lift-off, when the layer is still on the growth substrate. As expected the same effective lifetime is measured after lift-off. A rear surface recombination velocity for the BSF of $S_{\text{BSF}} = (1475 \pm 420) \text{ cm/s}$ follows using $S_{\text{SiN}} = (10 \pm 2) \text{ cm/s}$ and $L_{\text{bulk}} = (85 \pm 5) \mu\text{m}$ as derived above. These values of S_{BSF} are in agreement with References [15, 16].

3.3 PSI solar cells

PSI solar cells from epitaxial layers grown by CoCVD are fabricated. The PSI solar cells consist of a nominally $27 \mu\text{m}$ thick base and a $5 \mu\text{m}$ thick BSF layer. The cell area is 3.96 cm^2 . Table 1 summarizes the cell parameters derived from IV-measurements under standard testing conditions.

The efficiency obtained is 12.0% for cell 3-3. The open circuit voltage (V_{OC}) of this cell is 590 mV. A short circuit current density (J_{SC}) of 26.7 mA/cm^2 and a fill factor (FF) of 76.4% are achieved. PSI cell 5-2 shows a slightly higher V_{OC} of 594 mV. A J_{SC} of 25.8 mA/cm^2 and a FF of 76.1% lead to an efficiency of 11.6%.

Table 1: Solar cell parameters derived from IV-measurements under 1 sun illumination. The highest efficiency achieved so far is 12.0% applying a simple solar cell process without front side texture.

Cell no.	V_{OC} [mV]	J_{SC} [mA/cm ²]	FF [%]	η [%]
3-3	590	26.7	76.4	12.0
5-2	594	25.8	76.1	11.6

The $J_{\text{SC}}-V_{\text{OC}}$ curve, dark IV curve, and illuminated IV curve are fitted together by the 2 diode model according to References [12, 14]. High saturation current densities of the first and the second diode are deduced for both cells.

Table 2 lists the extracted parameters. The high level of J_{O2} of about $7 \times 10^{-8} \text{ A/cm}^2$ is caused by the prolonged contact annealing of the COSIMA [11] contacts. The cells mainly differ in their parallel and series resistance.

Table 2: Cell parameters extracted from the dark and illuminated I/V -curve as well as the $J_{SC}-V_{OC}$ curve.

Cell no.	R_{Sh} [Ωcm^2]	R_S [Ωcm^2]	J_{01} [A/cm^2]	J_{02} [A/cm^2]
3-3	820	0.2	2.1×10^{-12}	7×10^{-8}
5-2	8300	0.7	1.7×10^{-12}	6.8×10^{-8}

4 DISCUSSION

The depth-resolved doping profiles of our CoCVD-grown epitaxial layers are comparable to those gained from Si depositions in reactors used in microelectronics. This is also true for the effective lifetime of $(1.3 \pm 0.1) \mu\text{s}$ measured on PSI layers that have one side passivated by an epitaxially grown BSF. From previous experiments we know that such effective lifetimes allow for open circuit voltages well above 600 mV [2, 5].

The open circuit voltage of our CoCVD PSI cells is limited by the large saturation current density $J_{01} = 2 \times 10^{-12} \text{ A}/\text{cm}^2$. However, the bulk lifetime of $(85 \pm 5) \mu\text{m}$ as obtained from the lifetime measurements show that these large recombination losses are not due to the material quality from the CoCVD epitaxy process.

The bulk diffusion length of $(85 \pm 5) \mu\text{m}$ obtained from lifetime measurements is of the same order as that determined for a PSI cell with 15.4% efficiency as shown in Reference [15].

5 CONCLUSION

Epitaxial layers from the CoCVD process have been characterized with regard to their application in the PSI process. A bulk diffusion length of $(85 \pm 5) \mu\text{m}$ is obtained from lifetime measurements. The diffusion length is similar to those measured for epitaxial layers from commercial CVD reactors. The recombination velocity of the BSF layer is also similar to the recombination velocities measured for p/p+-layer systems grown in commercial reactors for microelectronic purposes.

For the first time PSI solar cells have been manufactured applying the CoCVD process. The cell efficiency is 12.0% on an area of 3.96 cm^2 .

Hence the current electronic quality of the Si layers from the CoCVD system is suitable for the application in the PSI solar cell process.

6 REFERENCES

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7 ACKNOWLEDGEMENT

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