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Formation of High Efficiency Epitaxial Emitters by APCVD

T. Rachow, N. Milenkovic, S. Janz, S. Reber

Fraunhofer Institute for Solar Energy Systems, Heidenhofstr. 2, D-79110 Freiburg, Germany

Abstract

Improvements in emitter passivation as well as back contact passivation lead to several high efficiency solar cell concepts. PERC (Passivated Emitter Rear Contact) solar cells on monocrystalline wafers above 21 % [1] have been achieved, but the diffusion processes with POCL₃ and BBr₃ have emerged as one of the limiting factors. The formation of high efficiency emitters by APCVD (Atmospheric Pressure Chemical Vapour Deposition) has several advantages compared to the standard diffusion. Epitaxial emitters can be optimised to match the passivation and metallisation of high efficiency concepts as well as industrial approaches like nickel plating. Simulations by PC1D show the potential of epitaxial emitters by featuring low contact resistance in combination with high shunt resistance, a good blue response and low emitter saturation current (J_{0e}) [2,3]. The emitter profiles can be designed in depth and in doping in the range from 1×10^{17} cm⁻³ up to 1×10^{20} cm⁻³ for p-type and n-type emitters. Simple reference solar cells with J_{0e} = 46 fA/cm² and efficiencies of $\eta = 17.5$ % on float zone (FZ) and $\eta = 16.1$ % on multicrystalline (mc) wafers have been processed. Furthermore an epitaxial selective emitter has been developed. The deposition process itself has been enhanced to improve the emitter profiles as well as material quality.

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1. Introduction

The standard emitter is produced by diffusion of phosphorus with $POCl_3$ or boron using BBr₃ as precursor. The diffusion process takes about 45 and 60 minutes respectively and requires additional steps to produce a deep high efficiency emitter. Epitaxial emitters by APCVD can lift some of those challenging limitations and offer additional advantages:

- The emitter deposition by APCVD takes only a few minutes (deposition rates of 0,25-2.0 µm/min)
- The doping profile can be adjusted and offers new possibilities for the improvement of emitter properties to match high efficiency concepts
- The epitaxial emitter process needs no wet chemical etching after the deposition
- Shunt formation due to firing can be solved by increasing the emitter depth
- The contact resistance can be optimised depending on metallisation scheme and passivation

Furthermore it will be possible to grow cost effective high efficiency emitters as well as epitaxial BSF (<u>Back Surface Field</u>) for industrial applications by APCVD using TCS (Trichlorosilane) in an in-line reactor with very high throughput [4].

2. Formation of epitaxial emitter

The concept of the epitaxial emitter has already been proven on wafer cells by Schmich et al. [5] and as cSiTF (<u>Crystalline Silicon Thin Film</u>) solar cells with voltages of 621 mV and efficiencies of 16.9 % by Van Nieuwenhuysen et al. [6]. The potential of epitaxial emitters has been shown by S. Reber [2] using PC1D simulations. The main task reported in this paper is to transfer improved epitaxial emitters onto wafer substrates, to optimise these emitters for monocrystalline and multicrystalline materials and to design emitter profiles which work perfectly in our existing high efficiency, high throughput concepts.

2.1. Solar cell results

Based on experiments and detailed simulations using PC1D [3] the emitter profiles (see Fig.1a) and the front surface filed (FSF) have been adjusted for different thicknesses and doping concentrations. The following solar cell batch has been done to evaluate the improvement of epitaxial emitters and to have a valid base for the simulation of high efficiency concepts and for further optimisation.

Table 1. Comparison of IV-Characteristics between epitaxial n-type and POCl₃ emitters on mono and mc material

Cell type (20x20mm ²)	V_{oc} [mV]	J_{sc} [mA/cm ²]	FF [%]	η [%]
Epitaxial emitter (FZ; 1 Ω cm) *)	621	35.9	78.3	17.5
Reference with POCl ₃ (FZ; 0,5 Ω cm) ^{*)}	638	35.9	79.8	18.3
Epitaxial emitter (mc; 1 Ω cm) ^{*)}	608	33.1	80.2	16.1
Reference with POCl ₃ (mc; 1 Ω cm) ^{*)}	611	35.3	79.6	17.1

*) Best cell of the batch, internally measured

This simple reference solar cell concept as seen in Fig.1b does not include texturing, back side passivation, local epitaxial BSF or a selective emitter. However this batch shows that epitaxial emitters are able to compete with the standard diffusion. Solar cell results in Table 1. show a similar short circuit current (J_{SC}) and fill factors (FF) for the epitaxial emitter on monocrystalline wafers.

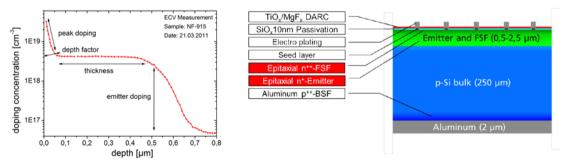


Fig. 1. (a) Profile of an epitaxial emitter processed at standard conditions and measured by ECV. (b) Solar cell concept for the work described in this chapter without texture and rear side passivation and full area aluminium BSF.

Furthermore the dark characteristic curves show that epitaxial emitters have lower saturation currents due to the space charge region (J_{02}) than POCl₃ diffused emitters. On FZ material diffused emitters show a J_{02} of 3.0×10^{-5} mA/cm² and epitaxial emitters only 3.3×10^{-6} mA/cm² (both values are averaged over 10 cells 20x20 mm²). This proves that the stress at the growth interface shown by µRaman measurements [3] has no significant influence on J_{02} because due to high doping concentrations and diffusion the space-charge region is smeared and moved into the bulk material. However further characterisation had to be done because the open circuit voltage of epitaxial emitters in this batch is about 18 mV lower (mainly due to different bulk doping) on FZ material compare to the POCl₃ diffusion.

2.2. Material and solar cell characterisation

As a start, we investigated how the effective lifetime of wafers depends on temperature and process duration. In Fig. 2a the importance of reducing the deposition temperature even for FZ material is shown. The lifetime of 1 Ω cm n-Type FZ material improved from 39 µs to 253 µs by decreasing the deposition temperature about 100 K. A possible reason for this temperature dependence could be thermal stress in the crystal after high temperature treatments. Additional QSSPC measurements show that this effect is even more pronounced for p-type material and multicrystalline substrates.

Table 2. SunsVoc measurements of epitaxial emitters to determine V_{OC} , pseudo FF, and pseudo η

V_{oc} [mV]	pFF [%]	pη [%] ^{2*)}
612,2	81,9	18,06
625,8	81,9	18,46
617,2	81,5	18,11
	612,2 625,8	612,2 81,9 625,8 81,9

^{1*)} Average of two cells ^{2*)} pseudo η for a short circuit current of 36 mA/cm²

The SunsVoc measurements in Table 2 underline the influence of the deposition temperature and the effective lifetime on V_{OC} values for cells with epitaxial emitters. However due to lower layer quality of the emitter does the V_{OC} decrease again for temperatures below 1000 °C. Additional QSSPC, LBIC and MWPCD measurements support these findings. Further process optimisations to find specific deposition temperatures and process conditions for different bulk materials have been done.

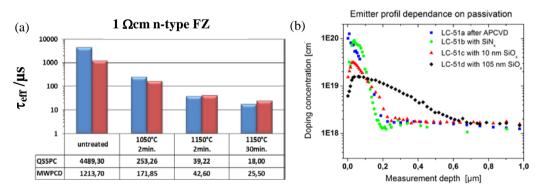


Fig. 2. (a) Effective bulk lifetime determined by QSSPC (Quasi <u>Steady State Photo Conductance</u>) and MWPCD (<u>Microwave Photo</u> <u>Conductance</u> <u>Decay</u>) measurements.; (b) Emitter FSF measured by ECV (<u>Electrochemical</u> <u>Capacitance</u> <u>Voltage</u>) is heavily depending on following high temperature processing steps.

2.3. Process development and optimisation

The APCVD process with TCS currently uses high temperatures of about 1150 °C and deposition rates of up to 2 μ m/min. The reduction of the deposition rate for better control of the emitter profile without reducing the homogeneity can be achieved by adding HCl to the precursor gas mixture (see Table 3.) Furthermore this improvement makes it possible to deposit epitaxial emitters of the same quality at lower temperatures [7]. Depositions with 45% HCl at 1050 °C show a similar average defect density of 9.7x10³ cm⁻² compared to depositions at 1150 °C without HCl. However the change in doping incorporation by reducing the temperature and the deposition rate has to be considered (see Fig.3. left). While the boron incorporation displays a dominant correlation to the deposition temperature does the phosphorous incorporation show an inverse dependence on temperature and deposition rate.

Table 3. Deposition rates for the high conversion efficiency deposition depending on HCl concentration in the gas flow and temperature. Values determined by SRP, ECV, REM and weight. Some values have been determined on a single sample

	Deposition rate [μ m/min] at different deposition temperatures					
% of max. HCl Flow	950°C	975°C	1000°C	1050°C	1150℃	
0%	NE	1,1	1,5	2,4	2,0	
15%	ND	0,5	1,1	ND	1,8	
30%	0,3	0,4	0,8	1,0	1,5	
45%	ND	0,1	0,5	0,8	1	
70%	etching	etching	~ 0	0,6	0,5	
90%	etching	etching	etching	etching	0,1	

(ND = not determined; NE= no epitaxial growth)

When complex emitter profiles are deposited the subsequent process steps have to be taken into account as well. As an example Fig. 2b shows how the FSF (<u>Front Surface Field</u>) of a two layer emitter (deposited at 1150 °C) is changing by the following high temperature passivation. The decreasing deposition rates and diffusion coefficients by reducing the temperature make it possible to deposit sharp emitter profiles with defined shallow FSF in the range of 40-80 nm.

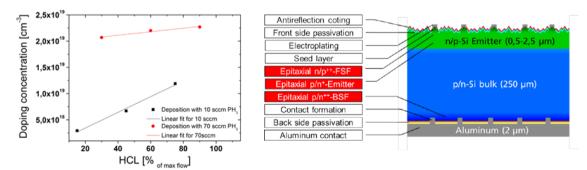


Fig. 3. (left) Increase of the doping incorporation by increasing the HCl flow.; (right) concept for high efficiency p-type solar cells with epitaxial selective emitter by plasma texturing, rear side passivation and local epitaxial BSF.

3. High efficiency solar cell concepts

Based on the presented solar cell result and the improvement in material quality (diffusion length L_{eff} of 840 µm) by reducing the thermal degradation it was reasonable to adapt a high-eta concept including epitaxial emitters. Epitaxial emitters offer unique advantages for the implementation of a selective emitter and texturing. The optimisation of a back side passivation as well as the back contact formation can be improved by using epitaxial BSF. In Fig. 3. (right) the high efficiency front side process using plasma texturing in combination with a simultaneous formation of a selective emitter is shown.

3.1. Optimisation of the epitaxial FSF

For high efficiency concepts it is necessary to improve and adjust the epitaxial FSF depending on passivation and metallisation. A FSF thinner than 10 nm results in lower V_{OC} because of insufficient field effect passivation by the FSF. Above 80 nm the solar cells deteriorate because of auger recombination [8]. However the optimal FSF layer thickness of about 20 nm can only be realised in combination with SiNx by PECVD. The influence of a thermal oxide processed at about 850 °C can be seen in Fig. 2b.

3.2. Standard selective emitter and local BSF formation

The formation of a selective emitter with a potential of 0.5-0.6 %abs [9] can be achieved using various technologies. An overview including advantages and disadvantages is given by Hahn [9]. A standard selective etch back process using 40% KOH at 85 °C has been optimised for epitaxial emitters (see Fig. 4a). The process features etch rates of 900-1300 nm/min and results in emitters with selective FSF (see Fig. 4c). Further improvements can be achieved by developing a local BSF by diffusion, by epitaxial growth or by using doped passivation layer stacks like *PassDop* [10].

3.3. Plasma texturing and selective emitter formation

The plasma texture has certain advantages over the wet chemical texture by KOH [11] and offers interesting possibilities in combination with epitaxial emitter. The plasma texturing can be done after the deposition of an epitaxial emitter including a FSF (see Fig. 4b). An etch rate of 0.2 μ m/min and weighted reflection of about ~ 12 % have been determined. In this case simply by masking the FSF of the epitaxial emitter the plasma texturing includes the formation of a selective emitter (see Fig. 5.).

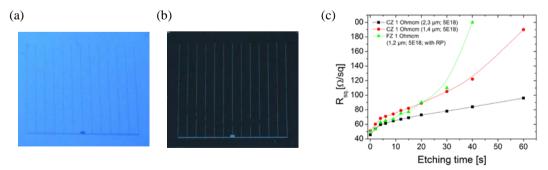


Fig. 4. Solar cells $20x20 \text{ mm}^2$ on FZ 1 Ω cm (a) with SiN_x masking after etching a selective emitter by KOH; (b) after plasma texturing; (c) Four-point probe resistivity measurements on different substrates with varying emitter thicknesses show the behaviour of the epitaxial selective emitter formation by KOH.

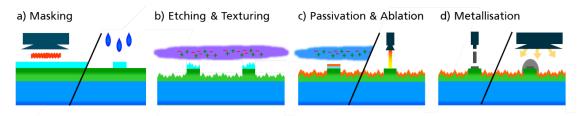


Fig. 5. Process for a) masking of the front side and chemical opening of the etch mask b) plasma texturing and selective removal of the highly doped FSF c) front side passivation and contact opening using laser ablation d) contact formation in this case by seed layer and electroplating

4. Conclusion

This paper shows that epitaxial emitters with efficiencies of $\eta = 17.5$ % are able to compete with standard diffusion and have the potential for high efficiency and industrial application. The deposition process has been improved (L_{eff} =750 µm) by reducing the temperature and introducing the use of HCl. Furthermore technologies for the formation of selective emitters, texturing and the deposition of an epitaxial BSF have been successfully established for epitaxial emitters. Further optimisation, simulations and solar cell batches are ongoing.

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References

[1] Reinwand, et al., "21.1% efficient PERC silicon solar cells on large scale by using inline sputtering for metallization.", Proc. of the 35th IEEE Photovoltaic Specialists Conference, Honolulu, USA (2010).

[2] S. Reber et al., "Epitaxy of emitters for cystalline silicon solar cells", Proc. 17th EU PVSEC, Munich (2001).

[3] N. Milenkovic, T. Rachow et al.,"Simulation and Characterization of epitaxial n- and p-type emitters on silicon wafer solar cells", SiliconPV 2012, SiliconPV 2012, Leuven, Belgium

[4] S. Reber et al., "ConCVD and ProConCVD: Development of high-troughput CVD", Proc. 24th EU PVSEC, Hamburg (2009).

[5] E.Schmich et al., "Epitaxy of emitters on p-type and n-type substartes for crystalline silicon solar cells", Proc. 5th IEEE,USA (2006).

[6] K. Van Nieuwenhuysen et al., "Epitaxially grown emitters for thin film silicon solar cells results in 16% efficiency" Thin Solid Films 518, (2010).

[7] M. Driessen et al.,"Advanced APCVD-Processes for High-Temperature Grown Crystalline Silicon Thin Film Solar Cells", 18th EuroCVD, Kinsale (2010).

[8] K. Van Nieuwenhuysen et al., "Epitaxially grown emitters for thin film crystalline silicon solar" Thin Solid Films 517, (2008).

[9] G.Hahn, "Status of selective emitter tecnology", Proc. 25th EU PVSEC, Valencia (2010)

[10] D.Suwito et al.,"Industrially feasible rear side concept for n-type silicon solar cells approchinmg 700mv of Voc", ", Proc. 25th EU PVSEC, Valencia, Spain (2010).

[11] R. Lüdemann,"Plasmatechnologie für die Photovoltaik", Hartung-Gorre Verlag Konstanz,(1999)