LOW COST MC SILICON SOLAR CELLS WITH SPRAY-/ROLL-ON EMITTER

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ABSTRACT: In this paper we present our work on emitter diffusion in a standard solar cell process. We replaced the industrial used $POCl_3$ diffusion by diffusion in a belt furnace with a commercial available phosphorus spin-on dopant. We present a new approach for the emitter diffusion in respect to the precursor deposition. To be compatible to inline processing the phosphorus containing liquid was either rolled or sprayed it with a spray nozzle on the wafer. The phosphorus glass etch had to be modified as a simple HF dip was not sufficient for a hydrophobic wafer surface. Solar cells were processed on 100 cm^2 mc-Si wafers. Another point of our examination was the difference between single and double sided P-diffusion. We show that the modified process of double sided P-diffusion is comparable to standard $POCl_3$ diffusion process, resulting in a mc-Si solar cell with 15.2 % efficiency.
Keywords: precursor deposition, diffusion, multi-crystalline silicon

1 INTRODUCTION

In industrial solar cell production lines several ways for emitter diffusion are used, such as tube furnace $POCl_3$-diffusion, belt furnace diffusion of screen-printed pastes or spin-on liquid dopants respectively. The processes are either not suited for automation or include time consuming and complicated process steps.

We present new approaches for the emitter diffusion in respect to the precursor deposition. A commercial available phosphorus spin-on dopant was used, but not in the conventional way. To be compatible to inline processing we either rolled the phosphorus containing liquid on the wafer similar to the roller-printing metallization technique[1] or we sprayed it with a spray nozzle on the wafer. We believe that both techniques are well suited for fast inline production and high throughput. In addition it is also easy to upgrade for larger wafer sizes [2].

2 EXPERIMENTAL

In the experiments described below we used a commercial available phosphorus spin-on dopant P845SF from filmtronics[3].

The wafers were a) treated with a roll soaked with the precursor. The roll up was done by hand. Or b) the precursor was sprayed on the wafer using a nozzle. The spray pressure and the amount of liquid sprayed to the wafer could be adjusted. The precursor was brought onto the wafer surface either on one or on both sides.

After drying, the diffusion was carried out in a belt furnace at temperatures between 900°C and 950°C (standard atmosphere) leading to sheet resistances from 30 Ω/sq to 50 Ω/sq.

One major difficulty of the spray/roll-on emitter was the removal of residuals on the surface after diffusion. With the used spin on dopant the surface of the wafer was not hydrophobic after the HF-dip. Several alternatives were tried. We first carried out a HF-NaOH-HF etch sequence. During the short dip into NaOH at room temperature a small layer of the surface is etched of, leading to slightly higher sheet resistance and a hydrophobic wafer surface. However the amount of Si etched of is difficult to control and therefore too much of the emitter could be etched off. The emitter then becomes too shallow, which leads to shunts in the later solar cell processing and therefore a decrease in performance.

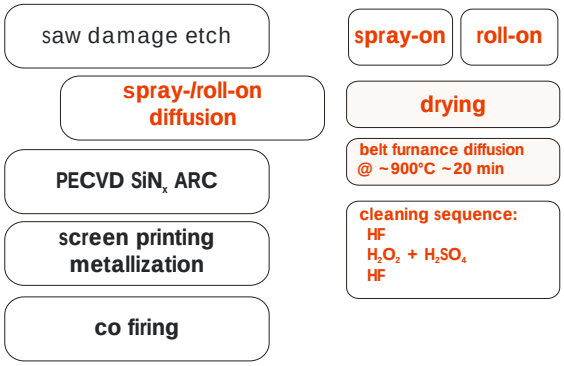

Figure 1: Solar cell process sequence using spray- or roll-on precursor deposition

The easiest and most suitable method for industrial use was found to be a HF-Piranha etch-HF sequence (Figure 1). After the diffusion the phosphorus glass is etched off using HF. To get rid of the residuals on the wafer surface, the wafer is put into H_2O_2 + H_2SO_4 (1:4). During the piranha etch the top layer off the wafer with the residuals is oxidised. The oxidised layer is etched off with the second HF step. The wafers were hydrophobic and ready for further processing.

The spray-/roll-on emitter diffusion was then adapted into our standard solar cell process (saw damage etch, precursor deposition, belt furnace diffusion, phosphorus glass etch, edge isolation, PECVD SiN_x, screen printing metallization and co firing) replacing only the $POCl_3$ emitter diffusion as depicted in Figure 1. Different wafer sizes were processed up to 200×200 mm^2; the results discussed below originate from solar cells processed on 100×100 mm^2 mc Si wafers.

3 RESULTS AND DISCUSSION

Solar cells processed with a roll-on emitter and the HF-NaOH-HF cleaning sequence reached only 13%, as compared to an average value of 15.2% on standard processed solar cells with a $POCl_3$ emitter (see Table I).

Table I: Solar cell results on mc -Si wafers (156 cm2)

	FF [%]	J_{SC} [mA/cm^2]	V_{OC} [mV]	? [%]
$POCl_3$ average	76.7	32.2	616	15.2
roll on average	71.4	30	593	12.7
roll on best cell	73.1	30.4	595	13.1

The overall lower fill factor of the roller printed solar cells is fully dominated by the shunt resistance due to a thinner emitter and therefore the front contact was partly fired through using the standard parameters.

To get more insight on the emitter the carrier concentration profile (Figure 2) of the roll-on emitter was measured by Electrochemical Capacitance-Voltage (ECV) technique and compared to a 50 Ω/sq emitter by $POCl_3$-diffusion. The n-doped region of the roll on emitter only penetrates up to 0.3 µm into the wafer, compared to 0.5 µm at a standard $POCl_3$-diffusion.

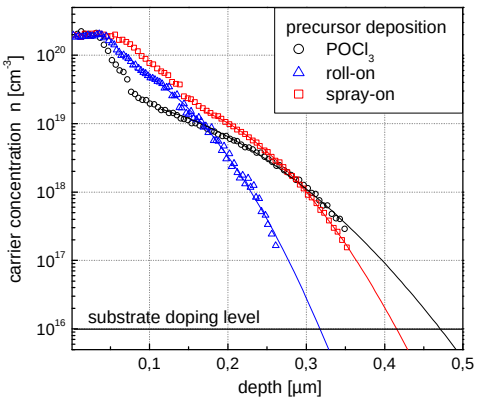

Figure 2: ECV profiles of $POCl_3$-, roll-on and spray-on emitter diffused at~ 900°C

This would explain the formation of shunts during the co firing step and therefor the low fill factors and performances. Further experiments with the HF-NaOH-HF (at room temperature) cleaning sequence lead to even thinner emitters with lower sheet resistance. It turned out that the residuals etch off with NaOH even at room temperature is difficult to control, depended on the temperature and the concentration of the NaOH solution. It adds up that too much of the emitter was also etched off.

In a further approach wafers were processed with the HF-Piranha etch-HF cleaning sequence. Etching off the residuals with H_2O_2 and H_2SO_4 has the advantage thatb only the top layer of the wafer is oxidised. The oxidised Si is then etched away by a 2% HF-solution. We found this cleaning sequence more suitable as the results could be reproduced in different runs. Next the emitter profile was adjusted to that of our $POCl_3$ standard emitter. The diffusion was carried out in a belt furnace. Diffusion time was approx. 20 min, whereas the diffusion temperatures varied between 900°C and 950°C. The diffusion temperature depends also on the wafer size. We only specified the temperatures measures by the furnace not directly on the wafer. Temperatures on the wafer could be less. The ECV measurement of the spray-on emitter is shown in Figure 2. Our spray-on emitter has a deeper plateau at the high doping level and has there for a lower sheet resistance. This could lead to more absorption in the emitter and consequently lower the J_{SC}. Both emitters ($POCl_3$ and spray-on) penetrate deep enough into the wafer to avoid shunts during co firing. Unfortunately we could not apply a drive in step in the belt furnace similar to the one seen in the $POCl_3$ emitter profile, due to the design of the oven.

Table II: Solar cell results on mc-Si wafers (100cm^2)

	FF [%]	J_{SC} [mA/cm^2]	V_{OC} [mV]	? [%]
spray-on average double side	76.5	31.5	619	14.9
spray-on average single side	76.4	30.3	611	14.1

We found that there is also a difference between single sided or double sided diffused wafers. The double sided diffused wafers have a better performance and a higher open circuit voltage (Table II). We claim this to two effects. First phosphor is good for getter the Si during the diffusion process. This effect is also seen on $POCl_3$ diffused wafers, especially on Si material with a lower quality, like mc Si. Secondly the belt furnace where our diffusion was carried out is also used for co firing. Therefore impurities could diffuse into the Si as well. The phosphorus glass on the back side then acts as a protection layer. Both points will lead to a lower L_{eff} and therefore V_{OC} for single sided diffused wafers as we also see in our solar cell results. L_{eff} was calculated from the SR measurements (Figure 3) using the Basore fit on the two best wafers from each group.

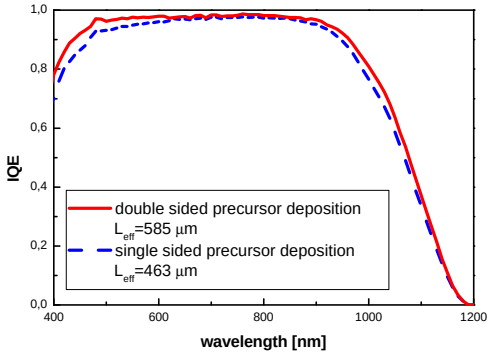

Figure 3: SR measurements on the two best wafers from each group

The results are summarised in the following Tables. Solar cells were processed on 100x100 mm^2 wafers. Each different group exists of five wafers. As a conclusion from the previous paragraph the precursor was brought to both sides of the wafers.

This is similar to $POCl_3$ diffusion where the wafers are also diffused from both sides. In the first line the average results of a reference group is shown with standard $POCl_3$ emitter with 50 Ω/sq. The performances of the solar cells with the spray on emitter (Group B) are a little behind of the reference group (Table III). The lower I_{SC} could be explained by the thicker emitter of 40 Ω/sq. compared to 50 Ω/sq.(Table IV), but cells with a thinner emitter lead to shunts during co firing. The solar cells with the sprayed emitter also have lower V_{OC}, this could be a hint that more impurities diffuse into the wafer in the eventually somewhat contaminated belt furnace (co firing is also done in the same furnace at the moment).

Table III: Solar cell results on mc-Si wafers(100cm^2)

	sheet res. [W/sq.]	**FF [%]**	**J_{SC} [mA/cm^2]**	**V_{OC} [mV]**	**? [%]**
$POCl_3$ mean	~50	78	32	622	15.5
spray-on mean (3) Run B	~40	76.5	31.5	619	14.9
spray-on Best cell Run B	41	78	31.3	622	15.2

The best cell of Run B almost reaches the performance of the reference group. Group A revealed an emitter with ~33 Ω/sq. and a weaker performance but the fill factor was higher, due to a better contact to the stronger diffused emitter (Table IV).

Table IV: Comparison between solar cells with 33 Ω/sq. and 40 Ω/sq. spray on emitter

	sheet res. [W/Sq.]	**FF [%]**	**J_{SC} [mA/cm^2]**	**V_{OC} [mV]**	**? [%]**
spray-on mean Run A	~33	78.8	30	614	14.5
spray-on mean (3) Run B	~40	76.5	31,5	619	14.9

In principle solar cells with roll on emitter should reach the same results as cells with a spray on emitter. For single cells with roll on emitter we get as good results as for cells with spray on emitter (Table V). However with our equipment at the moment the precursor is not applied very homogenously when rolled onto the wafer. The roll is not soaked with the precursor in any place equally. Therefore there is a strong distribution in the solar cell performance of the roll on solar cells. However roller made from more suitable material could be used for further investigations.

Preliminary experiments were carried out on iso-textured mc-Si wafers [4]. It turned out that the diffusion parameters need further adjustment for the textured wafers and the phosphorous glass removal is more challenging. This could be also a matter of the covering of the liquid on the texture. The advantage of the texturisation couldn't be utilised yet.

Table V: Comparison between spray on and roll on cells

	sheet res. [W/sq.]	**FF [%]**	**J_{SC} [mA/cm^2]**	**V_{OC} [mV]**	**? [%]**
spray-on Best cell Run B	41	78	31.3	622	15.2
roll-on Best cell	32	78.4	31	622	15.1

The spray-on emitter process was also used to process 20x20cm^2 wafers. It has proven compatible to the big wafer sizes. The results are presented in [2].

4 CONCLUSION AND OUTLOOK

Roll on or spray on emitter diffusion is a simple process that could replace the $POCl_3$ phosphor diffusion step. Similar solar cells performances were reached. The cleaning of the wafer after diffusion is to be done in a careful way. Further adjustment on the emitter profile could be done with a modified belt furnaces design. With additional oxygen supply a drive in and a oxidation of the phosphorous glass could be achieved in a single step. This may also simplify the residuals etch off.

The transfer of this method for the use with textured wafer has to be done. At the moment we work on the automation of the spray on process compatible to wafer sizes up to 20x20cm^2. We also think of using the spin on dopant to get a selective emitter. Special designed masks that cover part of the wafer could be used with the spray nozzle or roll with a pattern could be used.

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