NOVEL PRECURSOR DEPOSITION METHOD FOR INLINE DIFFUSION

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ABSTRACT: In this paper we present a new method for deposition of precursors, here diluted phosphoric acid, on silicon wafers for the purpose of inline diffusion. The method consists of a surface preparation step to enhance wettability followed by the actual coating step. Coating is carried out by rolling the precursor onto the wafers with a set of sponge rollers. This approach results in homogenous deposition of thin precursor layers without the need for adding surfactants or organic solvents. We demonstrate that the novel precursor deposition method, in conjunction with an appropriate diffusion process, is suitable for preparation of very homogeneous emitters exhibiting depth profiles similar to $POCl_3$ emitters. Cell efficiency of first processed multi-crystalline solar cells was 15.2% in average and 15.6% for the best cell.
Keywords: Diffusion, Doping, Manufacturing and Processing

1 INTRODUCTION

Formation of the pn-junction by phosphorus diffusion is one critical part of the manufacturing process for crystalline silicon solar cells, which affects performance and cost of the product. So far diffusion in tube furnaces with $POCl_3$ is the dominant principle. The process is well understood and has proven performance on industrial scale. However, because it is a batch process, $POCl_3$ diffusion requires complex handling with the risk of wafer breakage and cost of ownership is high. Therefore, there is a demand for alternatives and inline diffusion attracts attention.

Inline diffusion processes consist of two steps: Firstly coating of the wafers with a phosphorus containing dopant and secondly diffusion of the phosphorus from the dopant into the silicon in an inline furnace.

A common approach to coat the wafers is spraying of the dopant. Extensive studies were conducted on that [1, 2]. A drawback of this method is the need for adding surfactants or organic solvents to achieve good wetting and thus homogeneous coating. These additives disturb the diffusion process and increase its complexity and cost.

In this work we employed an alternative coating process. This process, advanced from laboratory scale [3] to industrial feasibility in collaboration with RENA, makes use of sponge rollers to apply the dopant onto the wafers. The aim of our work was a valuation of suitability of this method for processing of homogeneous emitters and for production of solar cells.

2 EXPERIMENTAL SETUP

2.1 Inline / roll-on P-doping

Inline P-doping was carried out by an experimental equipment version of the RENA “InDop” tool. In this tool the wafers are firstly hydrophilised by oxidation in order to achieve good wettability of the wafer surface. Afterwards the substrates are transported through several pairs of sponge rollers as depicted in figure 1. Thus, rear and front side are coated at the same time and it is taken advantage of phosphorus gettering on the cell´s rear side.

The lower rollers are mounted in a dopant filled pan. Accordingly, the sponges are always soaked to saturation allowing for an intrinsically stable quantity of coated precursor without any further regulation or adjustments. The quantity of deposited phosphorus is set by the precursor (phosphoric acid) concentration.

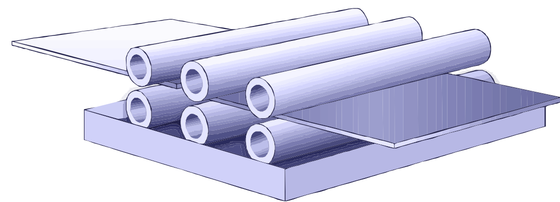

Figure 1: Schematic of roll-on doper.

As a matter of principle the rollers are contacting the wafers during coating. The force exerted, however, is very small and hence no issues regarding wafer breakage were observed. The gentle behaviour of the sponges is illustrated in figure 2: A perturbing material (O-ring with 5 mm diameter) was placed on a wafer and moved through the roller section. As demonstrated in figure 2 the sponges accommodate the foreign body and the wafer does not break. This even holds for very thin wafers of 120 µm thickness.

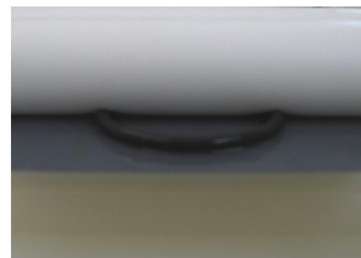

Figure 2: Illustration of behaviour of perturbing materials in the roll-on doper setup.

2.2 Furnace

Diffusion was carried out in a laboratory model TecnoFimes inline-furnace. In this furnace wafers are transported on ceramic rollers. This has the advantage that the wafers are not in contact with metal during diffusion.

It is important to mention, that the length of the heating zones in the lab furnace is only 3 m. Therefore, a significantly slower transport speed had to be chosen compared to an industrial furnace. Hence, also the temperature ramp up was slower and its effect on the process presumably more pronounced.

3 EXPERIMENTS

3.1 Homogeneity of coated dopant quantity

In order to test for the homogeneity of coated dopant quantity, a total number of 70 isotextured multi-crystalline wafers were treated. Figure 3 shows the fluctuations in coated weight from wafer to wafer over a time period of some hours. Intervals between the wafers randomly ranged from a few seconds to a few minutes. The relative standard deviation from the mean coated weight is 1.9%. No significant shift in coated weight over time is observed. The mean coated weight corresponds to a phosphoric acid layer thickness of approximately 6 microns.

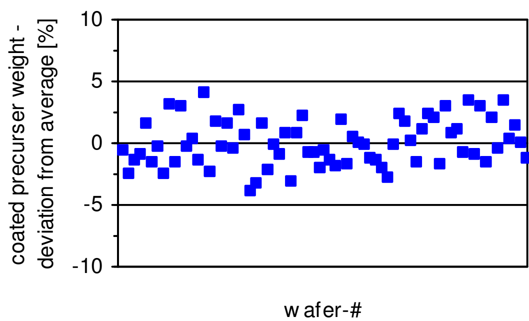

Figure 3: Variation in coated precursor weight over time.

3.2 Homogeneity of PSG

Figure 4 shows an example of a wafer with a light brown phosphosilicate glass (PSG) layer after diffusion. Hardly any variations in colour can be seen. The layer is highly uniform.

Figure 4: Wafer with PSG.

In order to assure the complete coverage of the surface with PSG on microscopic scale and to demonstrate the influence of the surface condition, samples with either hydrophilic or hydrophobic surface were coated, diffused and then analysed by SEM. Multi-crystalline and mono-crystalline wafers with textured surfaces were used. The hydrophobic surface was prepared by dipping the wafers in HF, the hydrophilic surface by oxidation. Figures 5a to 5c depict some SEM images.

It can clearly be seen that the hydrophobic surface results in poor coverage with PSG. In some areas only the tips of the structures are sufficiently decorated while the glass is thinner or even completely absent in recesses (Fig. 5a). Moreover, the adhesion of the PSG appears to be poor since in some places flakes are visible (Fig. 5b). It is evident that this will negatively affect the sheet resistance homogeneity and may result in micro-shunts in areas where emitter formation is not completed.

By contrast the hydrophilic samples are covered with PSG very nicely, indicating that sheet resistance uniformity is good also on microscopic scale (Fig. 5c). This is in accordance with previously published studies [1].

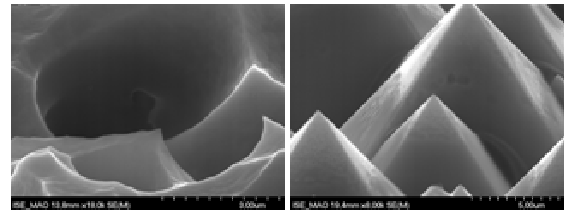

Figure 5a: SEM images of PSG processed on multi- and mono-crystalline wafers with hydrophobic surfaces.

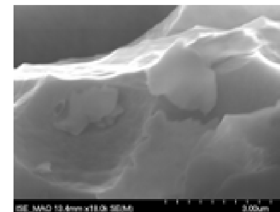

Figure 5b: Poor adhesion of PSG processed on wafers with hydrophobic surfaces.

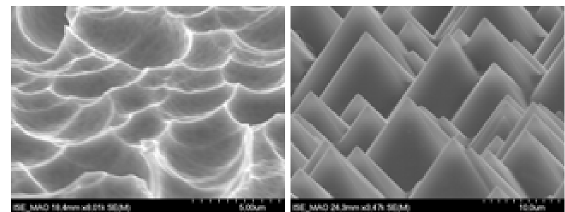

Figure 5c: SEM images of PSG processed on multi- and mono-crystalline wafers with hydrophilic surfaces.

3.3 Homogeneity of sheet resistance

Homogeneity of sheet resistance was determined prior to PSG etch with a four point probe device. 48 multi-crystalline wafers (12.5x12.5 cm²) and 18 mono-crystalline wafers (15.6x15.6 cm²) with a sheet resistance of 60 Ω/□ were analysed. For each wafer sheet resistances were determined on a 5 x 5 reading point matrix. Figure 6 shows the frequency distribution of standard deviation values. The average standard deviation of sheet resistance on multi-crystalline and mono-crystalline wafers was 1.3 Ω/□ and 1.1 Ω/□, respectively. The standard deviation of sheet resistances never exceeded 2 Ω/□.

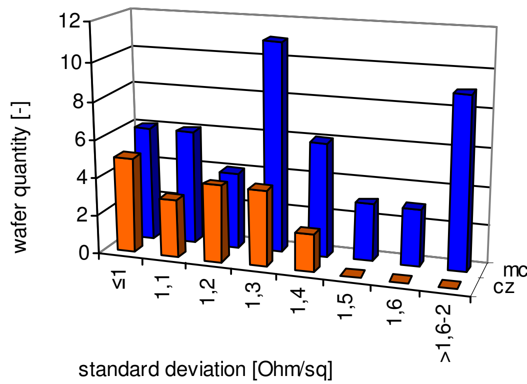

Figure 6: Frequency distribution of standard deviation of sheet resistances on multi-crystalline (mc) and mono-crystalline (cz) wafers.

3.4 Doping profile

Charge carrier concentration profiles were assessed by ECV measurements. For that in general polished wafers are required. Rolling-on of dopants on polished and textured wafers under the same conditions, however, results in completely different emitter sheet resistances. The reason is the difference in amount of coated pre-cursor, which is very low – and also less homogeneous - on a polished compared to a textured wafer.

Challenging problems with ECV measurements are the sealing of the reading point during the measurement against emersion of etching solution and the exact calculation of the enlarged wafer surface. In particular the first issue turned out to be ineffectual in case of isotextured multi-crystalline wafers exhibiting a very rough surface. Therefore, only alkaline textured mono-crystalline wafers could be investigated. Combining the data with a four point probe measurement result and accounting for the surface enhancement we modeled the profile as shown in figure 7. The profile of a 50 Ω/□ emitter produced by inline diffusion was similar to a 55 Ω/□ standard $POCl_3$ emitter.

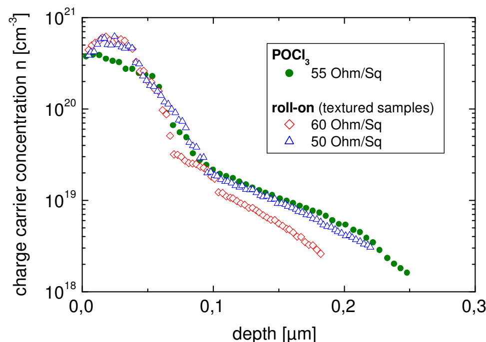

Figure 7: Roll-on emitter profiles (on mono-crystalline wafers) compared to $POCl_3$ emitter profile.

3.5 Cell process

Except for diffusion, the process and the equipment used for processing of solar cells were ISC standard for screen printed solar cells. Multi-crystalline Si substrates with an area of 12.5x12.5 cm^2 were used. The process flow is depicted in figure 8.

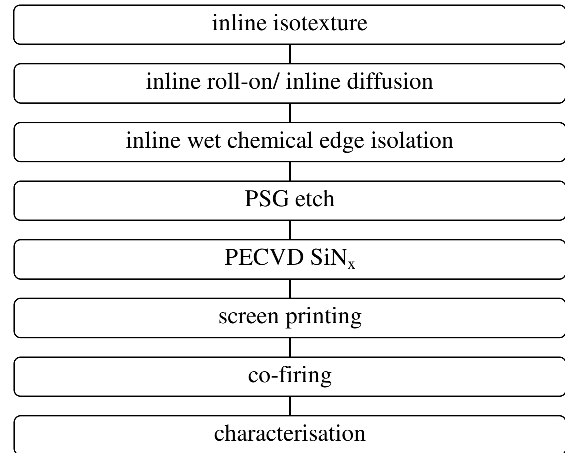

Figure 8: Flowchart of solar cell process.

As mentioned above, the inline roll-on / inline diffusion approach leads to relatively thin layers of phosphoric acid and consequently thin PSG layers, recognisable by their light brown colour. Thin PSG layers correspond to faster diffusion compared to thick (blue) PSG [4]. We hence achieved 50 to 60 Ω/□ emitters in 15 to 20 minutes diffusion time.

Another advantage of thin PSG layers is their un-problematic etching behaviour. A standard HF etching process was sufficient to remove the PSG.

In total 28 cells were processed. The mean and the best cell´s results are summarised in table 1.

Table 1: Results of IV measurements on 28 processed multi-crystalline cells.

	J_{SC} [mA/cm^2]	V_{OC} [mV]	FF [%]	$J_{SC}\cdot V_{OC}$ [mW/cm^2]	η [%]	R_{series} [mΩ]
average	33,7	608	73,9	20,5	15,2	1,36
best cell	34,0	610	75,2	20,7	15,6	1,35

The obtained results are satisfying. All cells show fair values for J_{sc}, V_{oc} and η. Fill factors and series resistances indicate that further improvement may likely be achieved through optimisation of firing parameters.

3.6 IQE

Figure 9 shows IQE curves of in-line diffused samples compared to a single $POCl_3$ reference sample. In previous studies a decrease of IQE at short wavelength relative to $POCl_3$ has been reported due to recombination in the phosphorus dead layer [5, 6]. Remarkably our measurements depict no such decrease. Further investi-gations need to be carried out to confirm that this is a characteristic of our process and the concentration of inactive phosphorus in the top layer is indeed lower than in other approaches.

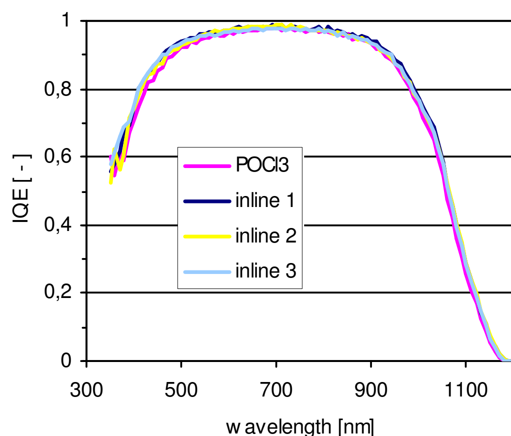

Figure 9: IQE of inline emitters compared to $POCl_3$ emitter.

4 CONCLUSIONS & SUMMARY

The new tested doper approach, utilising sponge rollers to coat the wafers with dilute phosphoric acid, is robust with variation in coating weight from wafer to wafer of only 1.9%. Since the wafer surface is hydrophilised before deposition, homogeneity of coating and consequently PSG is excellent on microscopic and macroscopic scale. Average sheet resistance homogeneities (s.d.) are 1.3Ω/□ on textured multi-crystalline and 1.1Ω/□ on textured mono-crystalline wafers. PSG can be removed with a standard HF etch process. ECV profiling on textured mono-crystalline samples demonstrated that emitter profiles are similar to $POCl_3$ diffusion. Moreover, IQE measurements showed no significant difference in short wavelength response between inline diffusion and $POCl_3$. Cell efficiency on mc material was 15.2% in average and 15.6% for the best cell. Fill factors and series resistances indicate that further improvement may likely be achieved through optimisation of firing parameters.

5 REFERENCES

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