# GOING TO A FINITE SOURCE EMITTER: IMPROVED EMITTER TECHNOLOGY BY REDUCTION OF THE DEAD P-LAYER FOR HIGH-EFFICIENCY CRYSTALLINE SILICON SOLAR CELLS

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ABSTRACT: Standard in industrial in-line emitter processing is to apply an excess phosphorus source on the wafer prior to diffusion. Subsequently, a constant and high phosphorus concentration is present on the surface during the diffusion process. This paper shows that a reduction in the concentration, and thus in the emitter, can give a significant gain in $V_{oc}$ and $J_{sc}$ as the dead P-layer is reduced. Homogeneous reduction over the complete wafer is important to obtain a maximum gain in $J_{sc}$ and $V_{oc}$. Different application methods are tested on homogeneity and the effect on $J_{sc}$ and $V_{oc}$. To optimize the contacting of these emitters, different pastes are tested on their contacting ability.

It is shown that an efficiency increase of 0.1% absolute can be obtained with these emitters for industrial in-line applications, which can be easily and directly implemented in new and existing lines. No additional costs are required and no yield loss is expected, while at the same time the HF usage decreases as the glass is thinner and contains less phosphorus.

Keywords: P-diffusion, cost reduction, multi-crystalline

## 1 INTRODUCTION

Reaching high efficiencies on thin and large solar cells is one of the best ways to reduce the €/Watt-peak costs of multi crystalline silicon solar cells and modules. A general trend to increase the efficiency of a solar cell is to apply shallower, high-ohmic emitters, which will give a higher $J_{sc}$ and $V_{oc}$ [1,2,3]. However, the gain in $V_{oc}$ can be relatively small and the process window becomes smaller as the cells are more difficult to contact (increased series resistance and shunting). In this paper an alternative, easy-to-implement, approach for the standard high-ohmic emitter is presented.

The standard in industrial in-line emitter processing is to apply an excess phosphorus containing source on the surface prior to diffusion in order to have and maintain a constant, high concentration on the surface. Consequently, the emitter profile shows a highly P-doped region near the surface. The surplus of phosphorus, above the solid solubility limit, is known as the dead layer. This layer is distinguished by a high Auger recombination, band gap narrowing and degeneracy [4]. Reduction of the amount of phosphorus applied on the surface will reduce the amount of phosphorus in the highly P-doped. Consequently, the dead layer is reduced, decreasing the high doping effects like the Auger recombination, and thus increasing the $J_{sc}$ and $V_{oc}$. Also a reduced surface P-concentration decreases the surface recombination velocity, thereby increasing $J_{sc}$ and $V_{oc}$. The complete reduction of the dead layer will give a finite source emitter.

By optimizing the phosphorus concentration in the high doped region of the emitter by reducing the P-concentration in the source two different problems occur. The first problem is related to the homogeneity of the emitter. When the amount of P-source is reduced, the gain in $V_{oc}$ and $J_{sc}$ can be expected to be maximal if the emitter is homogeneously low over the whole wafer surface. Microscopic regions containing high concentrations of phosphorus will lower the $V_{oc}$ and $J_{sc}$. Therefore the application method becomes an important parameter. The second problem is related to the contacting ability of the screen print silver paste. Emitters with low P-concentration are more difficult to contact, which results in an increased series resistance and reduced FF.

This paper presents an investigation on the homogeneity of the emitter by examining different application methods relative to the amount of phosphorus on the surface. Also presented is an investigation of the contacting ability of two screen print silver pastes on emitters with a reduced P-concentration in the source.

## 2 EXPERIMENTAL DETAILS

The emitters investigated in this paper are made by reducing the applied amount of phosphorus on the surface prior to diffusion (P-optimized source emitters). The emitter diffusion is done in an industrial in-line belt furnace. Furnace settings (temperature, belt speed) used for the P-optimized emitters are such that they give a 60-65 ohm/sq emitter when an excess P-containing source is used as dopant (P-excess source emitters).

All material used is 210 µm, 156x156 mm$^2$ mc-Si p-type. The wafers within one experiment are from the same section of an ingot. Cells are produced using a standard industrial process; the process flow is given in figure 1.

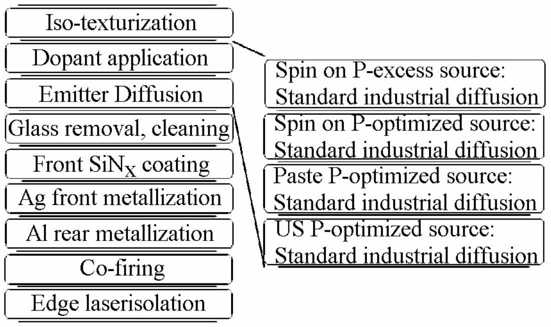

**Figure 1**: Process flow chart

### 2.1 Application methods

Application of the P-containing dopant is tested on three tools: a laboratory spin-on equipment (“spin-on”), screen printer with a P-source paste (“P-paste”) and industrial ultrasonic evaporation tool (“US”). For contacting these emitters a commercial front side silver paste is used.

### 2.2 Front side silver pastes

Two silver pastes are investigated on P-optimized source emitters, paste I and paste II. The P-optimized source emitters are made using the spin-on equipment. The screen printing of each paste is optimized on height, width and conductivity of the fingers. All these parameters are similar for the two pastes. The screen printing is done with an industrial screen printer. Firing is optimized separately for each of these pastes to achieve an optimum FF.

## 3 EXPERIMENTS, RESULTS AND DISCUSSION

### 3.1 Application methods: macro and micro uniformity

The P-optimized source emitters created with the three different application methods are tested on macro uniformity using a 4-point probe instrument, the Sherescan [5], to measure the sheet resistance. The sheet resistance ($R_{sh}$) depends on the active P-concentration in the emitter, the relation is written as [6]

$$R_{sh} = \frac{1}{q\int_{0}^{d_j} \mu_n n(x)\,dx}$$

with $q$ the electron electric charge, $d_j$ the emitter junction depth, $n(x)$ the electron concentration profile and $\mu_n$ the concentration dependent electron mobility. The dead P-layer does not contribute to the sheet resistance and is called in-active.

Lowering the surface P-concentration during diffusion, lowers both the in-active and the active P-concentration in the emitter. Consequently, the sheet resistance increases. The change in in-active P-concentration is much larger than the change in active P-concentration, as shown by Negrini [7]. However, the ratio of these two changes reduces with decreasing P-concentration. Therefore the reduction in in-active phosphorus is highest in the transition from the P-excess diffusion source to a just P-optimized source (the first increase in sheet resistance). In this region the largest gain can be expected in $V_{oc}$ and $J_{sc}$. Reducing the P-concentration will further increase $V_{oc}$ and $J_{sc}$ more, but in increasingly smaller steps.

The change in sheet resistance when reducing the applied P-concentration is of similar behavior for all three application methods and is shown in figure 2 for the spin-on (38 wafers, sheet resistance measured on 49 points per wafer).

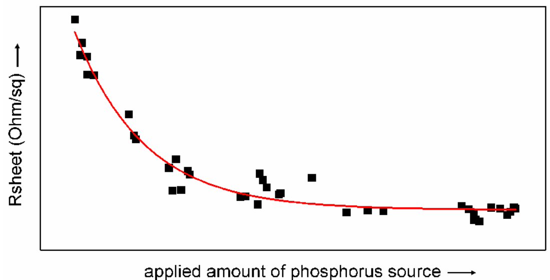

**Figure 2**: Sheet resistance as a function of applied amount of phosphorus source using spin-on method. The line is a guide to the eye.

On the right side of figure 2 a plateau is visible, indicating the region of P-excess source diffusion. The left side of the figure represents emitters with a decreasing dead layer.

In figure 2 it can also be seen that small variations in applied phosphorus do not appear to influence the sheet resistance for a P-excess source emitter, though similar variations for a P-optimized source emitter can influence the sheet resistance significantly. Therefore, when producing P-optimized source emitter a larger variation in sheet resistance from wafer to wafer can be expected.

The variation within a wafer also increases significantly, for the same reason. In figure 3 the standard deviation of the sheet resistance per wafer is given as a function of applied amount of phosphorus.

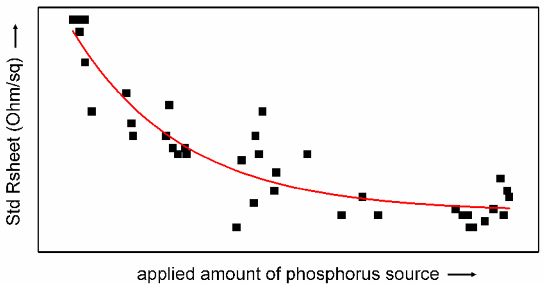

**Figure 3**: Standard deviation of sheet resistance as a function of applied amount of phosphorus source using the spin-on method. The line is a guide to the eye.

The $V_{oc}$ and $J_{sc}$ are influenced by the microscopic homogeneity of the emitter. Regions on the surface which contain high phosphorus concentrations reduce $V_{oc}$ and $J_{sc}$, as the dead P-layer is large in these regions and the surface recombination velocity high. However, contacting (thus FF) will be better. A P-optimized source emitter with a low standard deviation of sheet resistance is likely to have a more homogeneous microscopic uniformity.

A high standard deviation of sheet resistance indicates a non-uniform macroscopic emitter. Homogeneous contacting on such an emitter can become difficult and subsequently the series resistance and FF can decrease. In this case, the in-homogeneity will also negatively influence $V_{oc}$ and $J_{sc}$ and these parameters will decrease as well.

The macroscopic and microscopic uniformity depend on the chosen application method as is depicted in figure 4, where the standard deviation in sheet resistance is given as a function of sheet resistance. For the three different application methods the variation in sheet resistance is solely caused by varying applied amount of P. The sheet resistance is determined using the 4-point probe on 9 points per wafer (spin-on: 127, US: 45, P-paste: 21wafers).

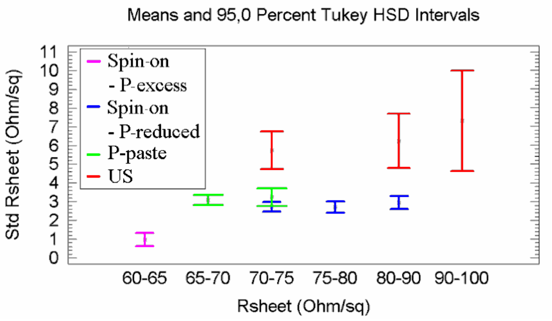

**Figure 4**: Correlation between sheet resistance and standard deviation of sheet resistance of spin-on – P-excess source and the different application methods of the P-optimized source.

For all three P-optimized source application methods it can be seen that the standard deviation increases with increasing sheet resistance, thus reducing the macroscopic uniformity. Also, the variation in sheet resistance from wafer to wafer increases when a P-optimized source is applied, as the data are more scattered as compared to the P-excess source. This corresponds to the result found in figure 2.

The three different application methods show a different slope with increasing sheet resistance. The slope for spin-on is lower than for US and P-paste methods. This indicates that the macroscopic uniformity is better for the spin-on than for the other two methods. This indicates that the micro distribution of phosphorus for the spin-on application method is likely to be more uniform which positively influences the different cell parameters as stated before.

### 3.2. Application methods: HF usage

The P-optimized source emitter is made by applying less phosphorus source on the wafer. Consequently, the glass of the P-optimized source emitter will contain less phosphorus than the glass of a P-excess source emitter. Also, as less $P_2O_5$ is present, less Si can react with it, reducing the amount of $SiO_2$ formed. With similar oxidation, the glass thickness, and thus weight, reduces. In figure 5 the relation between applied amount of phosphorus source and weight of the glass is depicted.

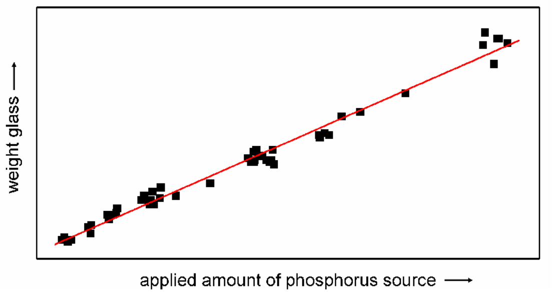

**Figure 5**: Correlation between applied amount of phosphorus source and weight of the glass. The line is a guide to the eye.

A thinner glass with less phosphorus content needs less HF to remove the glass, and also a lower concentration of HF to remove the glass.

### 3.3 Application methods: Cell results

Cells are made with P-optimized source emitters using the spin-on, US and P-paste application methods. In table I the number of wafers is given for the different application methods.

**Table I**: Number of wafers used per application method

| Application methods | Sheet resistance range (Ohm/sq) | number of wafers |
|---|---|---|
| Spin-on – P-excess source | 60-65 | 22 |
| Spin-on – P-optimized source | 70-75 | 27 |
| Spin-on – P-optimized source | 75-80 | 23 |
| Spin-on – P-optimized source | 80-90 | 21 |
| P-Paste | 65-70 | 16 |
| P-Paste | 70-75 | 5 |
| US | 70-75 | 22 |
| US | 80-90 | 12 |
| US | 90-100 | 6 |

In figure 6 and 7 the $J_{sc}$ and $V_{oc}$ are given for the different application methods as a function of the sheet resistance.

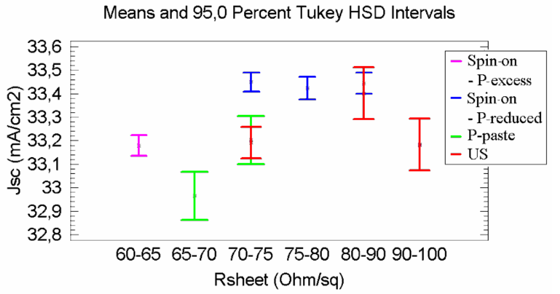

**Figure 6**: $J_{sc}$ as a function of sheet resistance for different application methods.

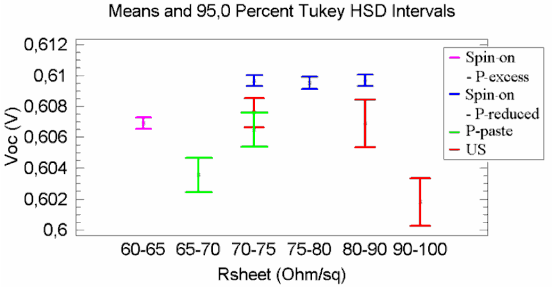

**Figure 7:** $V_{oc}$ as a function of sheet resistance for different application methods.

As stated before, the micro uniformity of the emitter has influence on the obtained $J_{sc}$ and $V_{oc}$. While the spin-on P-optimized source emitter exhibits a clear increase in these cell parameters relative to the spin-on P-excess source emitter, the P-paste shows lower values. Screen printing in itself produces a microscopic inhomogeneous layer, with high concentration agglomerates and regions with little phosphorus.

The micro and macro uniformity obtained with the US application method is not as good as for the spin-on. The increase in $J_{sc}$ and $V_{oc}$ is less than for the spin-on. This indicates that the microscopic uniformity is higher than for the P-paste, though not as good as for the spin-on method.

It should be noted that any change in $J_{sc}$ and $V_{oc}$ can be related to changes *in* the emitter. After glass removal, the additional cleaning also has an influence on the quality of the emitter. This cleaning, the ECN-clean, gives an increase in $J_{sc}$ and $V_{oc}$ of respectively 1% and

0.5% for a P-excess source emitter [8] which is partly in competition with the influence of the phosphor source concentration at the surface. The impact of cleaning is not studied for the results discussed in this paper.

A drop in cell parameters is observed for the spin-on and most clearly for the US group at high sheet resistances. This can be related to the high standard deviation of the emitter sheet resistance, as stated before. The emitter becomes too in-homogeneous to obtain good cell parameters. Additionally, two other factors can also reduce the cell results. The first is that as contacting becomes an increasing problem at higher sheet resistances, the higher contact resistance with the front side metallization can negatively influence the cell parameters. Secondly, the lateral conductivity in the emitter layer is reduced at higher sheet resistances. The front side metal screen was optimized for a 60-65 ohm/sq emitter. An improved pattern could further increase the cell parameters. Contact resistance scans of the cells, using the Corescan [4], (not shown) indicate that the contact resistance between emitter and metal is the main issue.

The influence of the emitter in-homogeneity on $J_{sc}$ can be closer examined by determining the internal quantum efficiency (IQE).

In figure 8 the IQE at 400 nm is given for the different application methods relative to the sheet resistance.

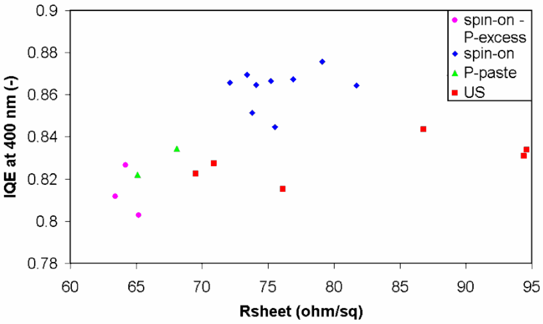

**Figure 8**: IQE at 400 nm as function of sheet resistance for different application methods.

The IQE shows a similar pattern as the $J_{sc}$, as can be expected.

As shown, the micro homogeneity of the emitter is important to obtain maximum $V_{oc}$ and $J_{sc}$. For the tested application sources, the spin-on proved to give the highest results.

### 3.4 Front side silver pastes

To improve the contact resistance and thus FF of the solar cells with a P-optimized source emitter, a second commercially available front side silver paste (paste II) is tested relative to the paste used to compare the different application methods (paste I) [9]. The emitters are made using spin-on. Firing of the pastes is optimized using P-optimized emitters. The fingers and metal coverage of the different pastes is comparable. In figure 9 the FF for the two pastes as a function of the sheet resistance is given. Each group consisted of 25 cells, giving 5 cells per sheet resistance.

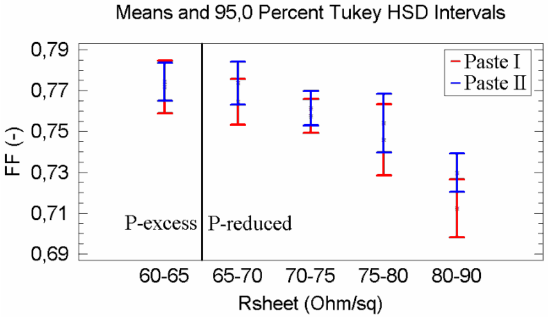

**Figure 9**: FF of the two pastes.

The pastes show similar FF for P-excess source emitters (60-65 ohm/sq), but while the contacting ability of paste I starts to decrease almost directly, paste II has an improved contact with lowly doped emitters.

The improved contact is also evident from the $J_{sc}$ and $V_{oc}$ plots as a function of the sheet resistance. These plots are given in figures 10 and 11.

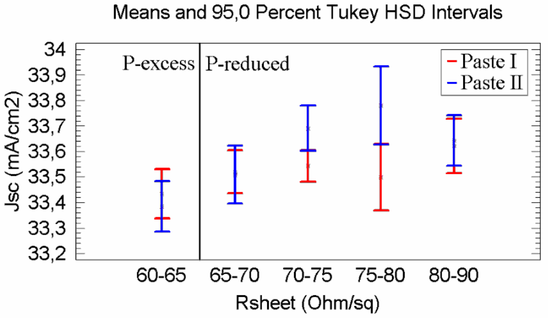

**Figure 10**: $J_{sc}$ of the two pastes.

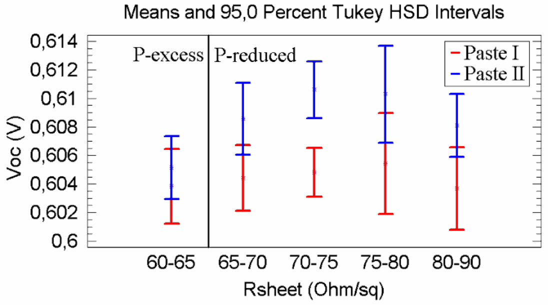

**Figure 11**: $V_{oc}$ of the two pastes.

The improved contact with the emitter gives up to 1% increase in $J_{sc}$ and $V_{oc}$. The FF however, due to increased series resistance, decreases with increasing sheet resistances. The optimum, just behind the transition between the P-excess and P-optimized region, gives a 1% increase in $J_{sc}$, 0,5% in $V_{oc}$, without loss in FF. The efficiency, as a function of sheet resistance, is given in figure 12, and is at the optimum 0,1% absolute higher compared to the P-excess source emitter.

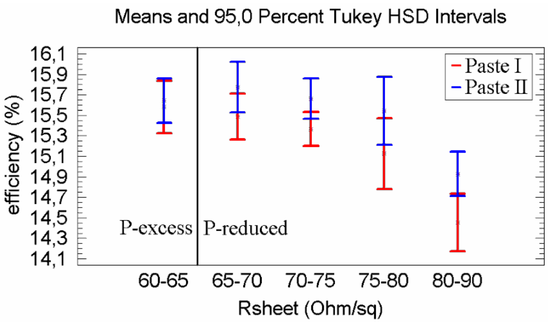

**Figure 12**: Efficiency of the two pastes.

## 4 CONCLUSIONS

In this paper an alternative, easy-to-implement, approach for the standard high-ohmic emitter is presented. By applying a low P-containing dopant on the wafer prior to diffusion, the amount of phosphorus in the highly doped region of the emitter reduces, decreasing the dead P-layer. A significant gain of up to 1% in $V_{oc}$ and 1% in $J_{sc}$ is found for these emitters, depending on the micro homogeneity of the emitter.

It is shown that commercial silver pastes can contact low P-doped emitters. At the optimum FF found, a combined increase of 1% in $J_{sc}$ and 0.5% in $V_{oc}$ has led to a 0.1% absolute increase in efficiency.

The P-optimized emitter can be easily and directly implemented in existing and new industrial in-line systems without any additional costs or yield losses. Additionally, the usage of HF and concentration of HF to remove the glass can be decreased.

## 5 ACKNOWLEDGMENTS

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## 6 REFERENCES

[1] M. M. Hilali et al., IEEE 31st Photovoltaic Specialists Conference, 2005, 1185
[2] M. Bähr et al., 19th EPSEC, 2004, 955
[3] V. Yelundur et al., IEEE 31st Photovoltaic Specialists Conference, 2005, 959
[4] www.Sunlab.nl
[5] P. Kittidachachan, Solar Energy Materials & Solar Cells 91, 2007, 160-166
[6] A. Bentzen, thesis: Phosphorus Diffusion and Gettering in Silicon Solar Cells, Oslo, 2006
[7] P. Negrini, J. Electrochem. Soc, 1975, 1254
[8] C.J.J. Tool, 21st EPSEC, 2006, 1272
[9] P. van Eijk, this conference
[10] M.N. van den Donker, this conference