

SIMULTANEOUS DIFFUSION OF SCREEN PRINTED BORON AND PHOSPHORUS PASTE FOR BIFACIAL SILICON SOLAR CELLS

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ABSTRACT: Most commercial production of silicon solar cells uses phosphorus diffusion step for emitter formation, and Al alloying step for back surface field (BSF) formation. Phosphorus sources used by a majority of manufacturers are from a liquid source that is diffused in silicon using a tube diffusion furnace. This paper shows that new Phosphorus and Boron pastes developed at Ferro can make emitter and BSF formation a simple screen print process. It is possible to achieve high quality n^+ emitter layer on p-type silicon and p^+ emitter on n-type silicon wafers. It is shown that bifacial solar cells can easily be fabricated by using n-type silicon wafers and simultaneous diffusion of Boron and Phosphorus paste in an infrared belt furnace. Effective lifetime using p^+nn^+ , p^+pn^+ and n^+pn^+ structures has been measured by quasi-steady-state photoconductance measurements. Diffusion length in excess of 300 μm are achievable on commercial wafers for solar cell application using screen-printed Phosphorus and Boron pastes. These new high quality diffusion pastes can reduce manufacturing cost and make it possible to use less than 150 μm thick silicon wafers for bifacial solar cell application.

Keywords: Screen Printing, Bifacial.

1 INTRODUCTION

Most one-sun silicon solar cell manufacturers create the p-n junction by means of a non-screen printable Phosphorus diffusion source to create the n^+ emitter, over a p-type silicon substrate. This step requires a semi-batch process and added equipment cost for the phosphorus diffusion step. On the contrary, a screen printable doping paste is compatible with the solar cell manufacturing and can reduce the processing and equipment maintenance time, since the same screen printing (SP) technology for contact printing can be used to create a p-n junction diode. Some manufacturers have already extended the SP technology from metallization to diffusion of the main emitter [1].

For high efficiency structures, Aluminium is often used to create the back surface field (BSF). But as wafer thickness is reduced to below 200 μm , bowing of the wafers becomes a major problem. Also, Al layers are not transparent, and do not allow to use n substrates with a p^+n junction in the front of the cell. On the other hand, a screen printable boron paste can eliminate the wafer bowing, allow the use of n-type substrates and help bifacial solar cell application.

The diffusion times for SP processes maybe quite short; they usually result in very shallow emitters, with high surface concentration and high saturation currents. In addition, when SP techniques are used, the paste composition and the process temperatures often degrade the bulk lifetime and do not allow achieving high quality surface passivation [2].

This paper is focused in the optimization of the screen printing and firing steps of boron and phosphorus doping pastes manufactured by Ferro, in order to manufacture bifacial screen printed solar cells.

2 SP EMITTER CHARACTERIZATION

This work, carried out in close cooperation between Ferro and TiM-UPV/EHU, had as a starting point the previous experience of Ferro in manufacturing and

characterization of phosphorus and boron pastes [3]. TiM has focused not only on obtaining SP deposition and firing procedures, which provide homogeneous emitters in a wide range of resistivities, but also in characterizing:

- recombination in the emitters, characterized by their saturation current, J_{01} ;
- the influence of thermal steps on the volume lifetime, with special attention to gettering capabilities;
- photon emitter collection, which has a direct impact on the photocurrent of the cell.

TiM is also working on obtaining some understanding about the diffusion processes that take place when diffusing from SP doping pastes. The control over the emitter profiles is essential to reach high emitter transparency and very low surface recombination velocities.

2.1 Phosphorus emitter creation

For the creation of n^+ emitters, TiM has used the paste DP99-036 developed by Ferro. The samples used were Cz p-type samples of industrial quality (103x103mm, 1.5 $\Omega\text{-cm}$) and previously NaOH-etched. The paste was deposited with a 180-mesh standard screen with 25 μm of emulsion thickness, and dried for 5 minutes at 300 $^\circ\text{C}$ in a RTC IR belt furnace. The resulting Phosphorus film deposited on the samples was of 8 μm thick.

Figure 1 shows the sheet resistance measured in the emitters, when fired for 4 minutes at temperatures ranging from 825 to 950 $^\circ\text{C}$. Figure 1 also shows the standard deviation of 9 measurements made on each sample, as an indication of the homogeneity of the emitter layer.

These results show that it is viable to create n^+ emitters with a resistivity that ranges from 30 up to over 200 Ω/\square with a thermal step of only 4 minutes by just varying the firing temperature from 950 to 825 $^\circ\text{C}$. In all the cases the homogeneity of the emitters was satisfactory, with deviations smaller than 11% in all the cases and typically around 7%.

QSSPC measurements in n^+pn^+ samples and subsequent analysis with *teffsim* [4] allow to estimate J_{o1} of the emitter. J_{o1} ranged from 0.4 up to 1.3 pA/cm². After the samples were immersed in HF bath, the J_{o1} typically increased by a factor of 2, which indicates that the firing step also creates a thin oxide over the emitter surface, with passivating properties.

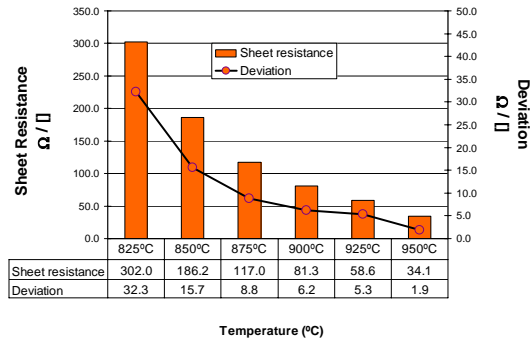


Figure 1: Sheet Resistance and its standard deviation measured in Phosphorus SP emitters created by diffusion at different temperatures during 4 minutes

2.2 Boron emitter creation

For the creation of p^+ emitters, TiM has used the paste FX99-033 manufactured by Ferro. The samples used were Cz n-type samples of industrial quality (105x105mm, 0.8Ω·cm) and previously NaOH-etched. The paste was deposited with a 180-mesh standard screen with 25μm of emulsion thickness, and dried for 5 minutes at 300°C in a RTC IR belt furnace. The quantity of boron film deposited on the samples has been estimated around 1.2mg/cm².

Figure 2 shows the sheet resistance measured in the p^+ emitters, when fired at temperatures ranging from 925 to 1000°C. Two firing times were explored, 8'20" and 12'30". The standard deviation of 9 measurements made in each sample, as an indication of the homogeneity of the emitter layer, is also shown.

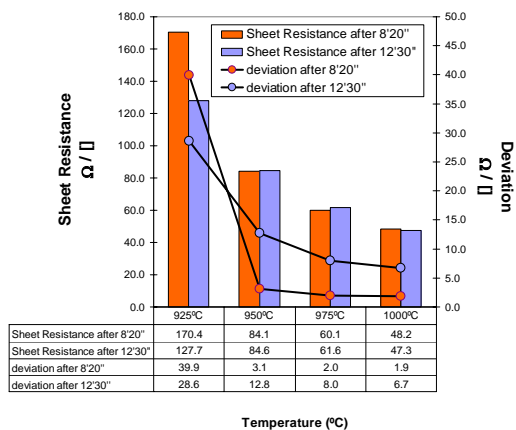


Figure 2: Sheet Resistance and its standard deviation measured in Boron SP emitters created by diffusion at different temperatures during 8'20" and 12'30"

The resulting p^+ emitter resistivities vary from 40 up to 150Ω/□. The average deviation for these boron experiments is again slightly over 10%, but with excellent homogeneity for the emitters created at

temperatures from 950 to 1000°C during 8'20", which show a deviation less than 4%.

QSSPC measurements were also done with p^+np^+ substrates, but the resulting effective lifetime was too low (below 10 μs) to allow J_{oe} estimations. This obliged to use p^+nn^+ and p^+pn^+ structures to evaluate J_{oe} of the emitter. When both Phosphorus and Boron emitters were co-diffused at 950°C for 4' the J_{o1} for both emitters ranged around 0.5 pA/cm².

2.3 Gettering capability of phosphorus SP

Minorities lifetimes in the range of 1 ms have been measured after Phosphorus SP diffusion on Cz-n type 0.8Ω·cm samples with no previous thermal processing [5]. On Cz-p type 1.5 Ω·cm samples, minorities lifetimes after Phosphorus SP diffusion at several temperatures have ranged always over 50μs, and many times over 100μs. SP Phosphorus diffusion also shows gettering capabilities when applied to samples with degraded volume lifetimes. Figure 3 shows the minorities lifetime evolution of 4 Cz-n, 0.8Ω·cm samples with a low initial lifetime (less than 8μs) due to a SP boron diffusion on both sides. After an acid etch removal of p^+ emitters, the samples were SP n^+ diffused and the lifetime was recovered always over 50μs, and in one sample over 140μs.

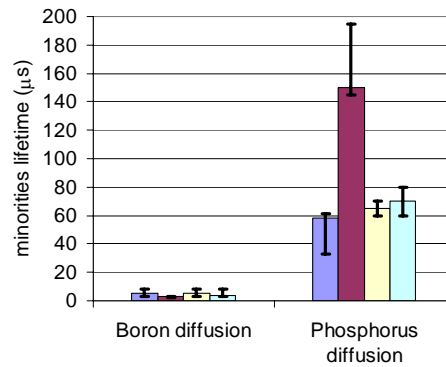


Figure 3: Minorities lifetime evolution in n-type Cz samples, 0.8Ω·cm, after Boron SP diffusion and subsequent Phosphorus SP diffusion

2.4 Thermal processes explored for BSF creation

As expected, Phosphorus and Boron emitter resistivity are mainly dependent on temperature. To obtain a given resistivity in boron p^+ emitters, a higher temperature is required compared to Phosphorus n^+ emitters. If specific control over the profile of each emitter is desired, this obliges to carry out two thermal steps: one for the Boron diffusion and a second one to create the Phosphorus emitter. It is important to perform the Phosphorus diffusion secondly, and so benefiting from the Phosphorus gettering and recovering the lifetime after the degradation after the Boron diffusion. Another possibility consists in performing the co-diffusion in one single step. Both possibilities have been explored in this work, in order to check which one is capable of maintaining high final volume lifetimes. Figure 4 shows the lifetime evolution for several solar cell structures, including n^+pn^+ , n^+pp^+ and n^+np^+ with Boron and Phosphorus emitters of different resistivities and surface concentrations. In order to obtain deeper emitters with lower surface

concentrations, several samples underwent a drive-in step of 15' or 30' after the phosphorus diffusion.

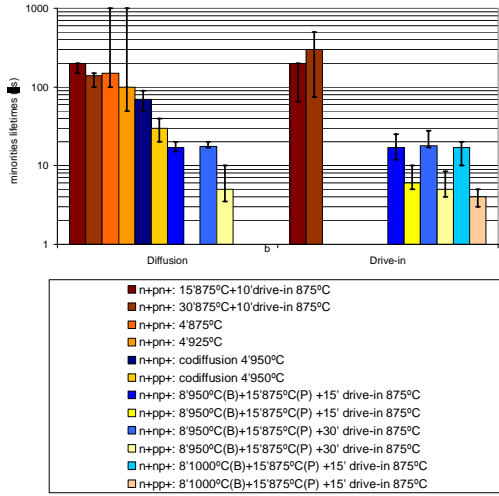


Figure 4: Minorities lifetime evolution in 0.8Ω-cm n- and 1.5Ω-cm p-type Cz samples, after Boron SP diffusion and subsequent Phosphorus SP diffusion

The process which involves only Phosphorus is capable of maintaining lifetimes over 100μs. The samples that underwent first Boron diffusion and secondly Phosphorus diffusion showed low lifetimes: around 17μs for n-type, and below 10μs for p-type. In these cases, the drive-in had a detrimental effect. But the samples co-diffused at 950°C for 4 minutes showed much higher lifetimes: 30μs the p-type sample, and over 70μs the n-type sample. For this last sample, figure 5 shows the fit for the inverse of the effective recombination lifetime derived from QSSPC measurements. The recombination parameters which fit the experimental curve are: J_{01} (Phosphorus)=0.4 pA/cm², J_{01} (Boron)=0.5 pA/cm², J_{02} (Boron)=20 nA/cm², $\tau_m=70\mu s$, $\tau_M=50\mu s$.

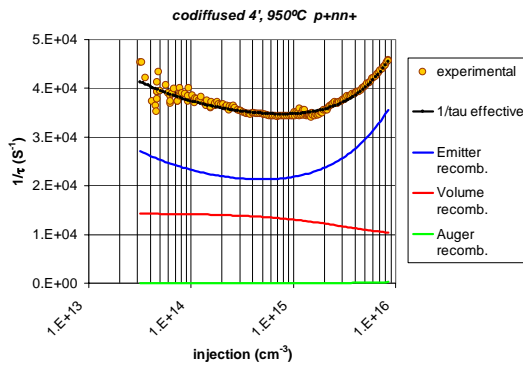


Figure 5: $1/\tau_{\text{effective}}$ from photoconductance measurement for co-diffused 0.8Ω-cm n-type Cz sample, 4' at 950°C, n⁺np⁺ structure before metallization

3 SOLAR CELL RESULTS AND DISCUSSION

Solar cells were finished with the co-diffused structures shown in Figure 4. A TiO_x AR film was deposited over both surfaces. A Ag paste was used for the metallization of the Phosphorus emitter, and a

Ag/Al paste for the metallization of the Boron emitter. This allowed to measure electric characteristics, and External Quantum Efficiency of the emitters. The solar cells do not have surface texturization, which should improve photocurrent values.

3.1 Electric results

Figure 6 and Table I present the I-V curves and cell parameters for the best n⁺pp⁺ and p⁺nn⁺ co-diffused metallized cells.

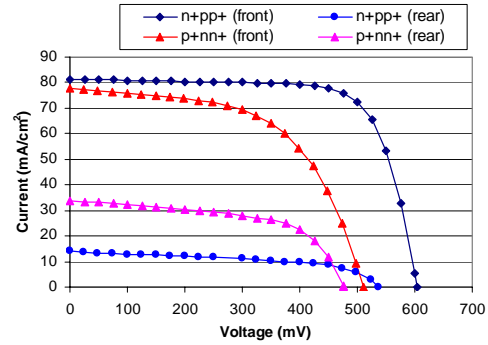


Figure 6: Illumination I-V curves of co-diffused n⁺pp⁺ and p⁺nn⁺ solar cells with SP emitters and SP metallization. Cz-p 1.5Ω-cm, Cz-n 0.8Ω-cm 300μm thick substrates, co-diffusion at 950°C for 4 minutes.

	n ⁺ pp ⁺	p ⁺ nn ⁺
Thickness (μm)	303	280
Resistivity (Ω-cm)	1.5	0.8
η (%)	13.7	8.5
V _{oc} (mV)	604.6	510.3
J _g (mA/cm ²)	30.7	29.4
FF (%)	73.7	56.3
Bifaciality ¹ (%)	18.5	43.4
J ₀₁ (pA/cm ²)	1.55	277
J ₀₂ (nA/cm ²)	2.81	622
R _s (Ω-cm ²)	1.05	1.53
G _{sh} (Ω ⁻¹ /cm ²)	1.27E-4	5.39E-3

Table I. One-sun characteristics and cell parameters of n⁺pp⁺ and p⁺nn⁺ solar cells, co-diffused at 950°C for 4 minutes, with SP emitters and SP metallization.

The n⁺pp⁺ structure presents a high V_{oc} voltage, which can be achieved only with a BSF. 605mV are coherent with the recombination parameters provided by the QSSPC measurements before metallization: τ_m slightly over 30μs, and J₀₁ for both emitters in the range of 0.5pA/cm². The diffusion length² corresponding to this lifetime is in the range of the substrate thickness, 300μm. This implies that the cell is benefiting from the BSF effect. BSF presence is very important for thickness reduction of industrial solar cells [6]. With BSF, the reduction of cell thickness would not imply a reduction of efficiency. However, the bifaciality of this structure is not as high as expected: 18.5%, instead of over 50%. Such bifaciality would correspond to a J₀₁ for the Boron back emitter of 4.5pA/cm². This value is not compatible with a V_{oc} over 600mV. This can be explained by a very inhomogeneous B emitter as a result of the back Ag/Al metallization. The Ag/Al BSF paste has not yet been optimized for contacting Boron emitters. This effect is confirmed by the results

¹ The bifaciality is the ratio between the short-circuit currents under rear and front illumination.

² $L_{\text{Diff}}^2 = \tau_m \cdot D_m$

observed in the p^+nn^+ structure. The n-type substrate, with volume lifetimes over $70\mu s$, shows a strongly reduced V_{oc} of 510mV. J_{02} is responsible for a decrease of 20mV, J_{01} for a decrease of more than 30mV. The shunt losses also present an important increase.

The Aluminium of the metallization paste clearly modifies the Boron emitter characteristics under the contact. This effect is especially important when the Boron emitter is on the front side, also increasing the shunt resistance and the J_{02} , which are phenomena related only to the front side.

The bifaciality shown by this structure, slightly below 50%, is coherent with the volume lifetime estimated before metallization and the J_{01} estimated for the Phosphorus emitter, $0.5pA/cm^2$. Bifaciality should increase over 90% once the thickness of the substrate is reduced down to $100\mu m$.

3.2 EQE of SP Boron and Phosphorus emitters

Figure 7 shows the External Quantum Efficiency of the solar cells with co-diffused Phosphorus and Boron emitters. The EQE of a n^+p cell is also shown as a reference. This cell has an industrial $POCl_3$ diffusion n^+ emitter and a very recombinant surface in the back (no BSF).

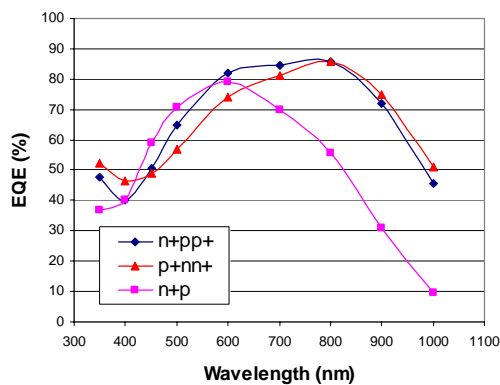


Figure 7: External Quantum Efficiency of codiffused n^+pp^+ and p^+nn^+ solar cells with SP emitters and SP metallization. Cz-p $1.5\Omega\cdot cm$ (blue), Cz-n $0.8\Omega\cdot cm$ (red) $300\mu m$ thick substrates, codiffusion at $950^\circ C$ for 4 minutes.

These measurements are coherent with previous results. The EQE in the shortest wavelengths, directly related to the front emitter collection, is higher in the n substrate (Boron emitter in the front) than in the p substrate (Phosphorus emitter in the front). As both emitters are co-diffused at the same temperature and Phosphorus diffuses more than Boron, the n^+ layer with low photon collection is deeper than in the case of Boron. Besides, both emitters have a higher collection than the highly doped n^+ industrial emitter created by $POCl_3$ diffusion in supersaturation conditions, due to the fact that this last emitter is much deeper.

However, compared to the n^+p structure -without BSF-, the most important improvement in the BSF structures is achieved in longer wavelengths, due to the presence of the BSF. The response to long wavelengths is even better for the n substrate, as the Phosphorus-BSF is more effective than the Boron-BSF.

4 CONCLUSIONS

New Phosphorus and Boron pastes developed at Ferro can make emitter and BSF formation a simple screen print process. It is possible to achieve homogenous n^+ and p^+ emitters with resistivities in the range between 30 and over $150\Omega/\square$ with one firing step in an infrared belt furnace. The simultaneous co-diffusion of Boron and Phosphorus pastes is compatible with diffusion lengths in n-and p-type substrates over $300\mu m$. When metallized with SP metal pastes, these structures provide BSF solar cells. The n^+pp^+ presents a J_{01} of $1.55 pA/cm^2$, which combined with the BSF effect, should allow to obtain efficiency over 15.5% in thin substrates. The p^+nn^+ structure presents higher recombination and losses, due to usage of a non-optimized Ag/Al BSF paste for the metallization of the Boron emitter. The Boron metallization needs further optimization.

The results indicate that a low-cost SP process in combination with co-diffusion can be used to produce bifacial solar cells. This is essential, especially for wafers below $150\mu m$ thickness because of the reduced bowing compared to conventional Al-BSF.

ACKNOWLEDGEMENTS

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