Development and Comparison of Small and Large Area Boron Doped Solar Cells in n-type and p-type Cz-Si

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Abstract — **The first step to introduce an evolutionary approach is the development in the laboratory scale and, then, in pilot plant and mass production. Boron diffusion forms the emitter in n-type substrates and the back surface field (BSF) in p-type silicon wafers. N-type Cz-Si solar cells have been investigated due to the potential to produce high efficiency solar cells and boron BSF may provide a better passivation than aluminum BSF in p-type wafers. The goal of this paper is to present the development and comparison of small and large area solar cells, processed in Czochralski silicon wafers by using spin-on dopant to obtain the boron emitter in n-type Si substrates and the boron BSF in p-type ones. The average efficiency of boron emitter and BSF cells was of around 15.0 % and 13.4 % for small and large area solar cells, independently of the substrate type. The reduction of the efficiency is due to the short-circuit current density that falls of around 5 mA/cm^2 when the area is enlarged. The low fill factor obtained in p$^+$nn$^+$ cells is due to the high resistivity of Ag/Al paste deposited in the boron emitter cells and the soldering of the Ag/Sn/Cu ribbon increased this parameter from 0.70 to 0.75 in large area cells.**

Index Terms — **silicon solar cells, boron-emitter, boron-BSF.**

I. Introduction

An important goal of the PV industry is to reduce the PV electricity cost in order to achieve the grid parity. This objective is influenced by many factors as the introduction of evolutionary technologies in order to increase the efficiency and/or reduce the production cost. The first step to introduce an evolutionary approach is the development in the laboratory, followed by the pilot scale and mass production [1]. In lab. scale, 4 cm^2 silicon solar cells are usually developed and when the area is enlarged technical problems may be overcome.

The industry of silicon solar cells is based on the aluminum back surface field (Al-BSF) formed by the conventional screen printing metallization, using an aluminum paste deposited on Czochralski-grown (Cz-Si) p-type substrate. The average efficiency of industrial solar cells is about 16.5 % [1]. The Al-BSF rear passivation technology limits the efficiency mainly in thin substrates [2]. Moreover, the screen printed Al paste produces bowing of the wafer, despite of the evolution of low-bow pastes. To overcome these challenges, the p$^+$ layer can be produced with boron doping.

In p-type Si substrates, the boron diffusion is used to produce the back surface field (B-BSF) and the challenge is to obtain the surface concentration that fits in well the standard screen printing metallization and without contamination of the silicon substrate during the high temperature diffusion process [2]. Boron BSF silicon solar cells have been developed with dielectric passivation and the efficiency of 20 % was achieved in 4 cm^2 cells and with screen printing metallization [3].

The boron diffusion in n-type silicon material forms the emitter (B-emitter). Beyond of the above mentioned challenges, the Al/Ag pastes currently used on p$^+$ regions present higher resistivity than the Ag paste to form the front metal grid. Nevertheless, since the last decade n-type Cz-Si solar cells are being investigated due to the potential to produce high efficiency solar cells. Substrate doped with phosphorus is more stable and have higher minority carrier lifetimes than p-type silicon [4].

Sun Power developed the interdigitated contact solar cell and the average efficiency in industrial production in float zone substrate (FZ-Si) was above 22 % [1]. With other structure and front boron emitter, Mihailetchi et al [5] developed large area solar cells with efficiency of 17.4%. In multi-crystalline silicon wafers (MC-Si), solar cells with an area of 156.25 cm^2 were processed with boron and phosphorus simultaneous diffusion and the efficiency of 16.4 % was obtained [6]. The influence of the substrate in boron doped emitter cells was experimentally studied and the efficiency of 14.7 %, 15.9 % e 17.1 % was achieved with MC-Si, Cz-Si and FZ-Si, respectively [7]. Solar cells were also processed with boron doped p$^+$ layer using spin-on dopant instead the conventional BBr_3 dopant. In FZ-Si n-type material, the efficiency of 15.9 % was obtained with SiO_2+SiN_x:H passivation.

The aim of this paper is to present the development and comparison of small and large area screen printed silicon solar cells, processed by using spin-on dopant to form the boron emitter in n-type Cz-Si substrates and B-BSF in p-type wafers.

II. Solar Cell Process

The baseline process used to develop the solar cells was the following: texture etching, RCA cleaning, boron spin-on deposition, boron diffusion in a quartz tube furnace, resist deposition and oxide etching, RCA cleaning, phosphorus diffusion, borosilicate glass etching, TiO_2 antireflection coating deposition, screen-printing metallization in both sides and edge isolation. Solar cells were developed in 1 Ω.cm – 20 Ω.cm n-type and p-type solar grade Cz-Si wafers with thickness of 200 μm. The boron dopant was spun onto one

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side of the wafer and the diffusion was carried out in a quartz tube furnace at 1000 °C. The n^+ layer was produced by phosphorus diffusion using $POCl_3$. The oxide to protect the p^+ layer of the phosphorus diffusion was grown in the same thermal step of boron diffusion. A specific passivation was not implemented.

The boron and phosphorus diffusions were independently and experimentally optimized for n-type and p-type material as well as the metal grid firing process. The metal grid was formed with two busbars in large area cell and with only one busbar in small area devices, in order to compare the typical lab. cells with an area of 4 cm^2 with the large area (61.58 cm^2) silicon solar cells.

All solar cells were characterized under standard conditions (100 mW/cm^2, AM1.5G and 25°C) in a solar simulator calibrated with a small (4 cm^2) and a large (61.58 cm^2) area silicon solar cell previously measured at CalLab - FhG-ISE (*Fraunhofer-Institut für Solare Energiesysteme*), Germany.

III. Boron-Emitter Solar Cells

In the p^+nn^+ solar cells, the diffusion processes formed a 43 Ω/□ p^+ emitter and a 25 Ω /□ n^+ layer. The relative standard deviation was about 6 % in both sheet resistances. Table I and Table II present the open circuit voltage (V_{OC}), short-circuit current density (J_{SC}), fill factor (FF) and efficiency (η) of the 4 cm^2 solar cells, processed in the wafer 3 and 7, respectively. The cells were processed in the same batch in order to compare the influence of the different wafers of the same supplier. The average efficiency of 15 % is similar to the cells processed on both wafers, but the V_{OC} is higher for cells of the wafer 3. This result can be attributed to a lower base resistivity or a higher minority carrier lifetime of the wafer 3. The average efficiency is similar, because the reduced value of the FF found in cells of wafer 3 was compensated by the high value of V_{OC}. Open circuit voltage and short-circuit current are limited due to the lack of a high quality passivation.

TABLE I

V_{OC}, J_{SC}, FF and efficiency of the 4 cm^2 B-emitter (p^+nn^+) silicon solar cells processed in the wafer 3.

Cell	V_{OC} (V)	J_{SC} (mA/cm2)	FF	η (%)
3-A	598.4	35.1	0.72	15.1
3-B	586.3	34.7	0.74	15.0
3-C	591.5	35.4	0.73	15.2
3-E	587.5	35.1	0.74	15.2
3-F	597.5	35.9	0.72	15.4
3-G	595.3	35.5	0.70	14.8
3-H	596.9	36.0	0.70	15.1
Aver.	593±5	35.4±0.5	0.72±0.02	15.1±0.2

The average FF was of 0.72 and 0.74. These values are lower than the expected probably due to the resistivity of Ag/Al paste used to form the metal grid on the frontal face. With the same metal grid, but using an Ag paste on the frontal surface, fill factors of 0.78 were obtained in n^+pp^+ solar cells doped with phosphorus and aluminum.

TABLE II

Electrical characteristics of the 4 cm^2 B-emitter (p^+nn^+) silicon solar cells processed in the wafer 7.

Cell	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF	η (%)
7-A	584.2	35.0	0.74	15.2
7-B	576.5	34.6	0.73	14.7
7-C	585.5	35.2	0.74	15.3
7-D	577.7	34.6	0.74	14.8
7-F	577.9	34.7	0.73	14.7
7-G	588.7	35.5	0.74	15.5
7-H	580.2	34.9	0.72	14.5
7-I	589.7	35.2	0.73	15.3
Aver.	582±5	35.0±0.3	0.74±0.08	15.0±0.4

The boron and phosphorus profiles measured by ECV (electrochemical capacitance-voltage) technique are presented in the Fig. 1 and Fig. 2, respectively. The junction depth for p^+ emitter was about 1 μm, similar to the thickness of BSF region doped with phosphorus (~ 1.1 μm). The surface concentration (C_S) of boron was higher than $1x10^{19}$ atoms/cm^3, as Fig. 1 shows. On the other hand, the C_S found with phosphorus profile was of around $5x10^{20}$ atoms/cm^3.

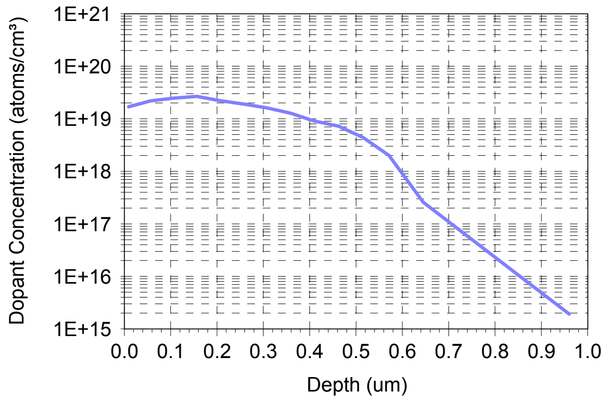

Fig. 1. Boron profile of p^+nn^+ (B-emitter) silicon solar cells measured by ECV technique.

The electrical characteristics of large area solar cells processed in two batches are presented in Table III. The small area devices were fabricated in the same batch of B2-A and B2-B cells. The average efficiency of large cells was (13.4 ± 0.2) %. Comparing the values presented in the Table III and the Table I, we observed that V_{OC} and FF are similar and the main difference occurs in the J_{SC}. The value of J_{SC} is reduced of around 11% when the area of the cells is increased, causing an efficiency reduction of approximately 1.5 % (absolute). This result cannot be explained only by the area of metal grid in the frontal face. In large and small area cells, 9.4 % and 6.0 % of the area is covered by the metal grid, respectively. The p^+nn^+ cells were simulated by using PC-1D device modeling program and the 3.4% higher metal grid coverage in large area cells implied in a J_{SC} reduction of only 3.9%. For instance, it is worth to comment that the difference between J_{SC} of small area and large area cells was also observed in n^+pp^+ cells doped with phosphorus/aluminum, produced in the PUCRS and measured at CalLab - FhG-ISE. In this case, the difference was of around 7%.

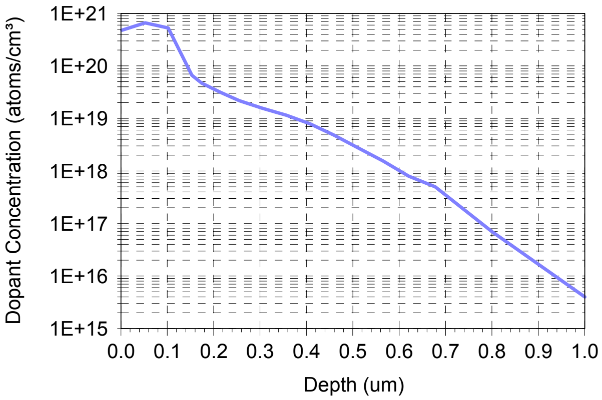

Fig. 2. Phosphorus profile of p^+nn^+ (B-emitter) silicon solar cells.

TABLE III

V_{OC}, J_{SC}, FF AND EFFICIENCY OF THE LARGE AREA B-EMITTER (P^+NN^+) SILICON SOLAR CELLS AND AVERAGE VALUES.

Cell	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	η (%)
B1-A	596.2	31.0	0.73	13.5
B1-B	590.4	31.4	0.73	13.5
B2-A	596.1	31.6	0.70	13.2
B2-B	599.4	31.6	0.71	13.4
Aver.	595.5±1.7	31.4±0.5	0.72±0.4	13.4±0.2

In large area cells, fill factor was also lower than expected. High metal grid resistivity could explain the low FF obtained. To investigate the influence of the Ag/Al paste resistivity, Ag/Sn/Cu ribbons were soldered on the front busbars and cells were measured at standard conditions. Fill factor rose from 0.70 to 0.75 causing an increase of 13.2 % to 14.9 % in the efficiency. PV modules with 36 cells connected in series were fabricated and FF reached values ranging from 0.74 to 0.76.

IV. Boron-BSF Solar Cells

The process was also implemented to obtain n^+pp^+ (B-BSF) cells. The sheet resistivity of the phosphorus emitter and the B-BSF were 30 Ω/□, with the relative standard deviation of 20 % and 9%, respectively. Cells with different areas were processed in the same batch.

The electrical characteristics of 4 cm^2 cells are shown in Table IV and Table V. The small cells were processed in two wafers. The devices produced in wafer 8 presented lower V_{OC} and J_{SC} than that obtained with wafer 14. With wafer 14, the average efficiency of cells was 15.0 %, similar to that achieved in small p^+nn^+ solar cells.

The results obtained with large area cells are presented in Table VI. The average efficiency was 13.3 %, 1.7 % (absolute) lower than the efficiency achieved with 4 cm^2 cells. Again, a worse efficiency of large area cells is due to lower short-circuit current density.

TABLE IV

ELECTRICAL CHARACTERISTICS OF THE 4 CM^2 B-BSF (N^+PP^+) SILICON SOLAR CELLS PROCESSED IN THE WAFER 8.

Cell	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	η (%)
8-F	580.6	33.3	0.74	14.3
8-G	580.5	32.7	0.73	13.8
8-I	580.9	33.6	0.73	14.3
Aver.	580.8±0.3	33.2±0.5	0.73±0.02	14.1±0.8

TABLE V

MEASURED ONE-SUN PARAMETERS OF 4 CM^2 B-BSF (N^+PP^+) SILICON SOLAR CELLS PROCESSED IN THE WAFER 14.

Cell	V_{OC} (mV)	J_{SC} (mA/cm^2)	FF	η (%)
14-A	596.1	36.6	0.71	15.4
14-B	594.8	37.3	0.60	13.4
14-C	591.6	36.4	0.71	15.3
14-D	591.8	35.4	0.73	15.4
14-E	594.5	36.7	0.71	15.4
Aver.	593.7±2.0	36.5±0.7	0,69±0.05	15.0±0.9

TABLE VI

V_{OC}, J_{SC}, FF AND EFFICIENCY OF THE LARGE AREA B-BSF (N^+PP^+) SILICON SOLAR CELLS AND AVERAGE VALUES.

Cell	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	η (%)
A	601.7	30.8	0.72	13.4
B	599.8	30.9	0.69	12.9
C	602.3	31.4	0.72	13.7
Aver.	601.3±1.3	31.0±0.3	0.71±0.02	13.3±0.4

Fig. 3 and Fig. 4 present the boron and phosphorus profiles measured by ECV. Comparing the doping profiles presented in Fig. 1 and Fig. 2 to those presented in Fig. 3 and Fig. 4, we observed that the depth of pn junction or BSF layer thickness are similar for boron doped regions. However, the boron surface concentration is higher in n^+pp^+ solar cells than in p^+nn^+ ones and the C_S for phosphorus doped region is lower. In other words, the surface concentration of the emitter is lower than the C_S of the BSF layer, taking into account the same dopant. The pn junction depth of n^+pp^+ cells was of around 0.6 μm, lower than n^+ layer thickness of the p^+nn^+ devices. This difference in phosphorus doping profiles are due to the nitrogen and oxygen flows used in each process (p^+nn^+ and n^+pp^+) and because in the process to produce p^+nn^+ solar cells there is a drive-in step.

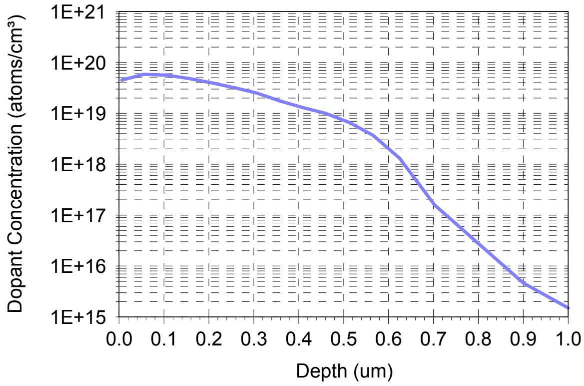

Fig. 3. Boron doping profile of n^+pp^+ (B-BSF) silicon solar cells.

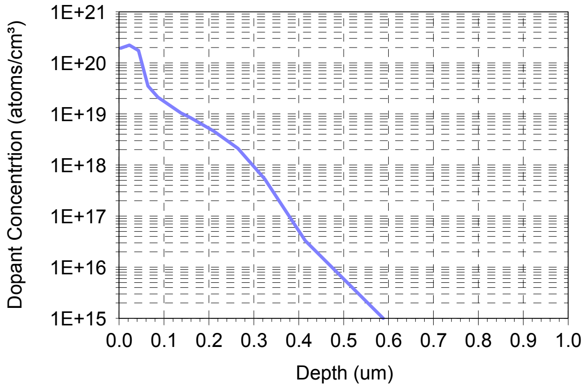

Fig. 4. Phosphorus doping profile of n^+pp^+ (B-BSF) solar cells.

V. Comparison of the Results

Table VII shows the average one-sun parameters concerning to the results of Table I, III, V and VI. The average efficiency of B-emitter and B-BSF cells was of around 15 % and 13.3 % for small and large area solar cells, respectively. This difference is caused by the J_{SC}, which decreases from 35 mA/cm^2 - 36 mA/cm^2 to 31 mA/cm^2 when the area is increased. The average values of V_{OC} and FF are similar to solar cells with both areas and types of substrate.

In Fig. 5 and Fig. 6, the current density as a function of applied voltage (J-V) of the best solar cells is presented. The efficiency achieved with 4 cm^2 cells was of 15.5 % for n-type and p-type Si-Cz. Cells with this efficiency presented the best J_{SC} values. The best efficiency obtained with large area cells was of 13.5 %, similar to the average value.

Comparing the results, we can conclude that the type of substrate did not affect the efficiency of cells, despite of a higher initial minority carrier lifetimes measured in n-type substrates. In this material, the minority carrier lifetime measured in as-cut wafers, after the etching of 10 µm - 20 µm with the CP4 etching, varied from 40 µs to 160 µs. The bulk lifetime found in the p-type substrate was in the range of 25 µs to 50 µs. The cells were simulated by using the PC-1D. Considering a poor surface passivation for p^+ and n^+ regions (a surface recombination velocity of $1x10^6$ cm/s) and fitting the simulated V_{OC} to the experimental ones, base lifetime for p^+nn^+ and n^+pp^+ cells was of 80 µs and of 60 µs, respectively.

TABLE VII
Average values of V_{OC}, J_{SC}, FF and η of B-emitter and B-BSF silicon solar cells with different areas.

	B-emitter small cells	B-emitter large cells	B-BSF small cells	B-BSF large cells
V_{OC} (mV)	593±5	595.5±1.7	593.7±2.0	601.3±1.3
J_{SC} (mA/cm^2)	35.4±0.5	31.4±0.5	36.5±0.7	31.0±0.3
FF	0.72±0.02	0.72±0.4	0.69±0.05	0.71±0.02
η (%)	15.1±0.2	13.4±0.2	15.0±0.9	13.3±0.4

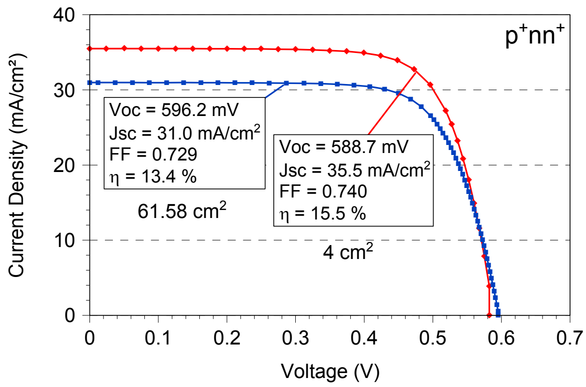

Fig. 5. Current density as a function of applied voltage, measured under standard conditions of the best small and large B-emitter silicon solar cells.

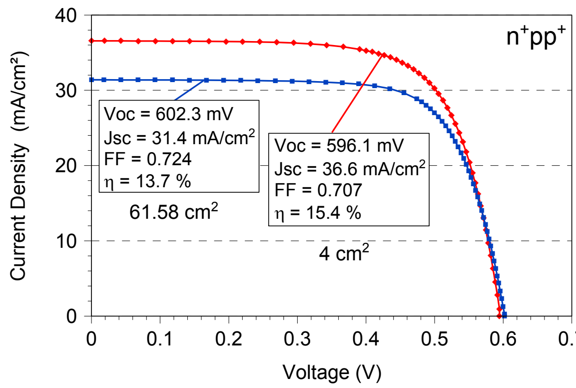

Fig. 6. Current density as a function of applied voltage, measured under standard conditions of the best small and large B-BSF silicon solar cells.

VI. Conclusions

Similar efficiency was found in p^+nn^+ and n^+pp^+ cells, independently of the area. The low fill factor in boron emitter cells was related to the high resistivity of Ag/Al paste and the soldering of the Ag/Sn/Cu ribbon improved this parameter from 0.70 to 0.75 in large area cells. Nevertheless, in large area cells the efficiency falls more than 1.5 % (absolute) due to the J_{SC} reduction.

In summary, the type of substrates does not affect the solar cell efficiency for the processes based on boron deposited by spin-on, followed by the quartz tube diffusion, but the increasing of the area reduces the efficiency. Consequently, from lab. to pilot scale fabrication, efforts have to be made to overcome this undesirable feature.

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