RECORD EFFICIENCIES OF SOLAR CELLS BASED ON N-TYPE MULTICRYSTALLINE SILICON

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ABSTRACT: The current Si supply - consisting also of off-spec and overcapacity silicon from the microelectronics industry - is not sufficient to cover the fast growing Si-demand of solar cell manufacturers. Therefore many silicon producers are currently extending their production capacities for poly-Si (Siemens process) and, at the same time, strong efforts are invested in the improvement of alternative purification techniques for the low cost production of solar grade silicon (SoG-Si, [1, 2]). As n-type (multi- and monocrystalline) Si features – compared to the commonly used p-type Si - a lower sensibility to the most common metallic impurities [3], its use could be a logical consequence of the increasing importance of SoG-Si, which contains more impurities than the high-purity Si produced using the Siemens process. To enable the use of n-type mc-Si as a substrate for solar cells, an appropriate process has to be developed. For this aim, some efforts have been made been made in the last years [4, 5, 6, 7, 8, 9]. This paper reports on our latest results in process development for n-type mc-Si solar cells. Applying a cell process which includes P-diffusion for the back-surface-field (BSF) and B-diffusion for emitter-formation with surface passivation by thermal Si-oxide, an independently confirmed efficiency of 16.1% has been obtained on an untextured 2x2 cm^2 n-type mc-Si substrate. This is the highest independently confirmed solar cell efficiency on n-type mc-Si which has been published up to now.
Keywords: Silicon solar cell, n-type, multicrystalline, boron emitter

1 INTRODUCTION

N-type silicon features higher minority charge carrier diffusion lengths than p-type Si containing the same concentration of most prominent impurities found in Si bulk. This is due to fact, that the capture cross sections of the corresponding defects are much lower for holes than for electrons. This represents an enormous advantage of n-type Si in view of the use of SoG-Si feedstock for the casting of mc-Si ingots. An additional advantage, which is particularly important for Cz-Si, is the lack of light-induced degradation. The concentration of boron in n-type Si is very low leading to a low concentration of B-O-complexes and consequently to stable efficiencies under illumination [10]. Especially with regards to the future use of SoG-Si feedstock, mc-Si is particularly interesting, as the segregation of impurities during the solidification of a mc-Si ingot leads to a further purification of the Si. To exploit these advantageous properties of n-type mc-Si, a simple solar cell process has been developed, applied and optimized for n-type multicrystalline Si. The properties of the used mc-Si, the optimization of process steps and the solar cell results are presented in the following.

2 PROPERTIES OF THE AS GROWN MATERIAL

The n-type mc-Si wafers which have been used for the here presented solar cell process, originate from a 240 kg industrial scale ingot directionally solidified in an Heat Exchange Method (HEM-) furnace at *Deutsche Solar*. Using electronic-grade, Sb-doped Si as feedstock, n-type Si with a resistivity distribution from 0.5 to 2.1 Ωcm has been obtained. To ensure a high minority carrier lifetime, the wafers have been taken from the middle of the ingot (around position 240 out of 440). In that zone, the averaged lifetimes in the as-grown wafers range from 100 to 200 µs. This corresponds to minority charge carrier diffusion lengths of 240 to 480 µm. The specific resistivity of the processed wafers is $\rho \approx 1.3$ Ωcm.

3 SOLAR CELL PROCESS

3.1 Process for BSF solar cells

Considering the high diffusion lengths reported for mc n-type Si (e.g. [11]) and its tolerance to metallic impurities, the development of a dedicated process could possibly lead to solar cells with higher efficiencies than for p-type mc-Si. In this work, our actual progress in the development of a process for n-type mc -Si solar cells with a front-side boron emitter is presented. The key elements of such a process turned out to be the emitter diffusion and its surface passivation. In our case, the emitter has been created by BBr_3-diffusion in an open-tube furnace at moderate temperatures (around 900ºC) – a processes condition under which the carrier lifetime was not deteriorated but even slightly increased [12]. Following earlier studies [13], standard PECVD SiN_x seemed to be not applicable as front surface coating for this cell concept, because a depassivating effect has been observed, resulting in an increase of the surface recombination velocity at the p^+-doped Si surface. In the meantime, a successful surface-passivation of p^+-doped Si surfaces - using laboratory-processes - has been reported by [14] and will be reported for industrial-like processes at this conference [9]. However, our Quasi Steady-State Photoconductance (QSSPC) measurements on symmetrically p^+-diffused test-structures passivated by a thin (10 nm) thermally grown SiO_2 revealed implied open circuit voltages of up to 657mV. So this seems, up to now, to be the method which performs the best on p^+-Si surfaces and has thus been

chosen for emitter-passivation in the present study. Fig. 1 shows the flow chart of the solar cell process, details about the different process-steps are described in [12]. In the following an optimization of this process and the resulting solar cells are presented.

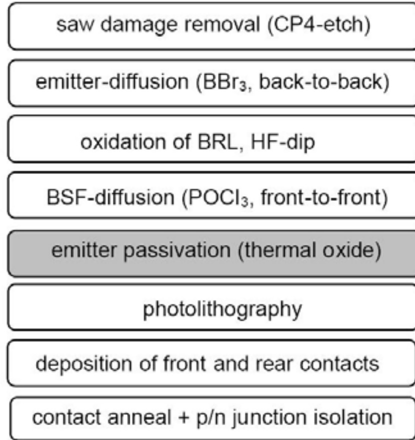

Figure 1: Process for n-type mc-Si solar cells with BSF and oxide-passivated emitter on the front side.

3.2 Process optimization

As (in the process described above) the BSF has been identified to be responsible for the unsatisfactory V_{oc} of the solar cells [12], efforts have been made to attenuate this problem. Hence µW-PCD lifetime measurements have been performed on n-type mc-Si (surface passivation by iodine-ethanol solution) after different process steps - the doped layers being etched off before the measurement. Fig. 2 shows an overview of these experiments.

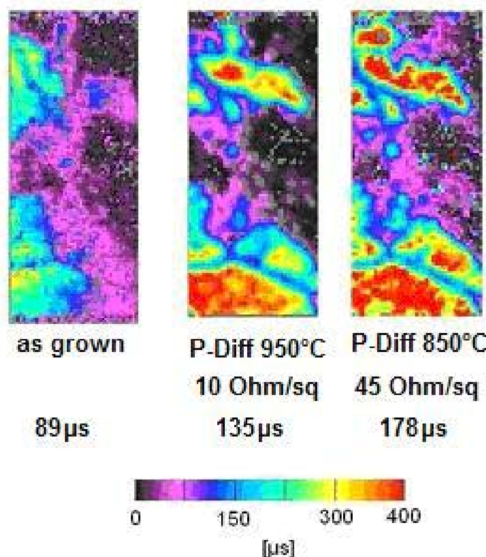

Figure 2: µW-PCD lifetime measurements of 2x5 cm^2 sections from neighbouring n-type mc-Si wafers. The map on the left shows the lifetime in the as grown state (average: 89 µs). The other wafers have been submitted to a 90 Ohm/sq BBr_3-diffusion at 900°C and then respectively to 10 Ohm/sq $POCl_3$ (950°C) and 45 Ohm/sq (850°C). The lifetime after the boron diffusion was 156 µs (lifetime-map not shown) and decreased after P-diffusion at 950°C to 135 µs (map in the middle). In contrast to that, the lifetime after P-diffusion at 850°C increased to 178 µs (on the right).

The results in Fig. 2 show that a 10 Ω/sq diffusion at 950°C causes a degradation of the carrier lifetime, whereas the 45 Ω/sq at 850°C result in an increase due to gettering of impurities. However, as stated above, the depth of the 45 Ω/sq diffusion profile ($d_{45} \approx 0.6$ µm) is not sufficient to provide a good passivation of the rear side and thus, high effective carrier diffusion lengths and a higher V_{oc} in the finished solar cell. Consequently, another recipe for P-diffusion has been conceived and tested. This P-diffusion is performed at 900°C and results in a sheet resistance of 20 Ω/sq. Lifetime measurements of the same type as described above have been performed and the results are shown in Fig.3. It can be seen, that this type of P-diffusion not degrades the material, as the 10 Ω/sq diffusion does (Fig. 2), but results in a significant increase of the carrier lifetime in large parts of the wafer – the average lifetime increases from 50 µs of the as grown wafer to 201 µs after P-diffusion (Fig. 3). In addition it results in a deeper diffusion profile and thus provides a better rear side passivation than the 45 Ω/sq diffusion. Consequently the 20 Ω/sq diffusion at 900°C is well suited for BSF-diffusion of n-type mc-Si solar cells.

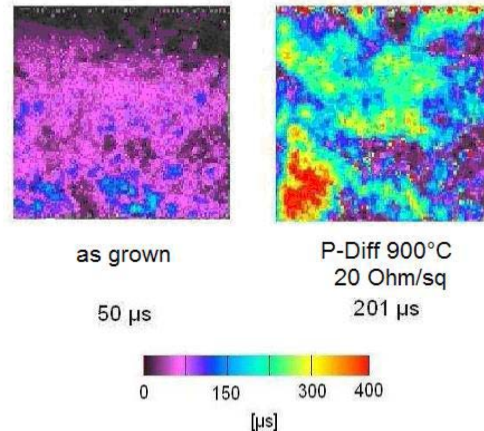

Figure 3: Lifetime maps of two 12.5x12.5 cm^2 wafers before (on the left) and after a 20 Ω/sq at 900°C (on the right). The average values are indicated below the maps.

3.2 Influence of process sequence

Another important point is to verify the influence of the process sequence on the carrier lifetime. To study this effect, neighboring wafers have been processed according to the scheme shown in Fig. 4.

Figure 4: Process sequences applied to neighboring n-type mc-Si wafers used for the lifetime study. For the P-diffusion, the recipe for 20 Ω/sq described above has been applied. The B-diffusion was a 90 Ω/sq emitter diffusion at temperatures of around 900°C.

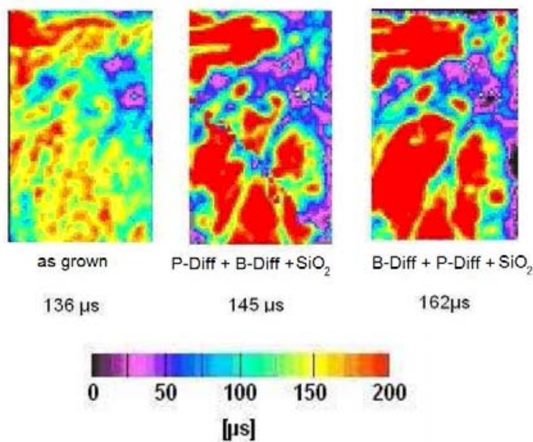

Figure 5: Lifetime measurements of as grown wafer (on the left), of wafer after process depicted in Fig 4.a) (in the middle) and after process shown in Fig. 4 b) (on the right).

The results of the lifetime measurements in Fig 5 show clearly, that performing the P-diffusion after the B-diffusion leads to higher diffusion lengths at the end of the solar cell process (including respectively a final thermal oxidation). This is probably due to the weaker gettering effect of the B-diffusion [15]. In the case of the process sequence from Fig. 4a), where the B-diffusion is not followed by a P-diffusion with its strong gettering effect, impurities that have been outdiffusing from defects or grain-boundaries during B-diffusion will remain in intragrain regions and thus reducing the carrier diffusion length.

4 SOLAR CELL RESULTS

4.1 Processing and cell results

The definitive solar cell process which has been applied to n-type mc-Si wafers originating from the Sb-doped mc-Si ingot described in section 2 corresponds thus to the process depicted in Fig. 1, whereas the optimized recipe for a 20 Ohm/sq $POCl_3$ diffusion has been used for the creation of a homogeneous full BSF. This process resulted in untextured (chemically polished front surface) solar cells with oxide-passivated emitter-surface and a fully metallized rear side. A ZnS/MgF_2 Double Layer AntiReflection Coating (DARC) has been deposited on the front side of the best solar cells by thermal evaporation. In Table I, the results of the I/V-measurements before and after deposition of the DARC are shown for the best mc-Si and the best Cz-Si solar cell. The illuminated I/V-characteristics of the mc- Si solar cell is shown in Fig. 6.

Table I: Paramaters from illuminated IV-characteristics of the best solar cells. For both cells, the values after deposition of the DARC (in the second line respectively) result from calibrated measurements at the EU Joint Research Centre (JRC) at Ispra (Italy).

A=2x2 cm^2	FF [%]	J_{sc}[mA/cm^2]	V_{oc}[mV]	η[%]
cell A: mc-Si	79.3	23.2	603	11.1
	78.6	33.5	609.8	**16.1**
cell B: Cz-Si	78.8	24.1	608	11.5
	77.6	34.8	615.7	16.7

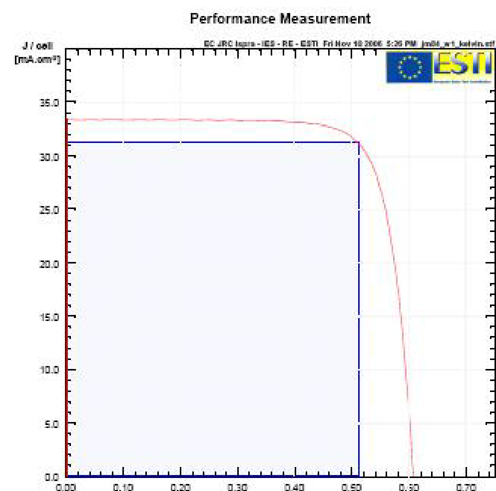

Figure 6: Illuminated I/V-characteristics of the n-type mc-Si solar cell under 1 sun illumination. This calibrated measurement has been performed at the ESTI of the EU JRC at Ispra (Italy).

4.2 Analysis the of n-type mc-Si solar cell

The fill factor (FF) and the short circuit current densities (J_{sc}) of the untextured cells (mc and Cz) are acceptable (Table I). However, considering that a high quality thermal oxide (see 3.1.) has been used to passivate the front surface of the cells, the open circuit voltages (V_{oc}) of both cells are rather poor. To investigate the reasons for the limited V_{oc}, spectral response and Light Beam Induced Current (LBIC) measurements have been carried out. The results of these measurements are shown in Fig. 7. and Fig. 8.

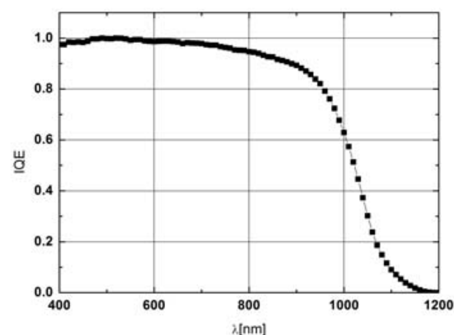

Figure 7: Wavelength dependent IQE of cell A (mc n-type Si).

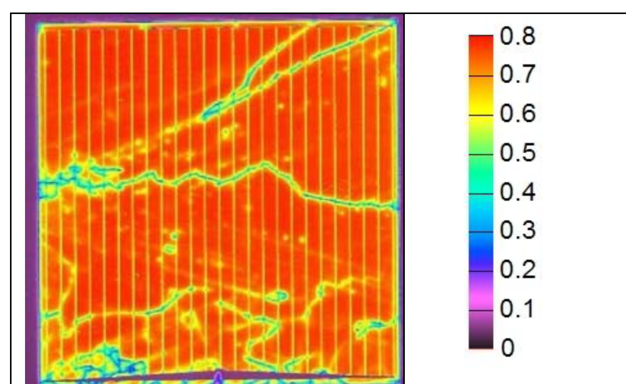

Figure 8: LBIC-measurement of the spatially resolved IQE of the mc-Si cell A at 980 nm.

The fact, that the IQE remains nearly equal 1 going down to short wavelengths of around 400 nm (Fig. 6) confirms the good passivation quality of the SiO_2. To detect an eventual degradation of the bulk lifetime, µW-PCD lifetime measurements have been performed on a neighboring mc-Si wafer (Fig. 8) and on an n-type Cz-Si monitoring wafer and resulted in bulk-lifetimes of 197 µs (mc) and 400 µs (Cz) respectively. These values correspond to bulk-diffusion lengths (480 and 680 µm) that should not limit the V_{oc} of 200 µm thick solar cells to such low voltages.

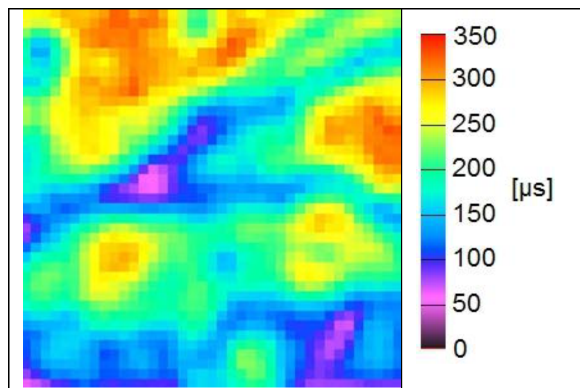

Figure 8: 2x2 cm^2 section (congruent with substrate of cell A) of a µW-PCD lifetime-measurement performed on a neighboring wafer to the wafer used for cell A. This monitoring wafer has been processed together with the solar cells. The average lifetime is 197µs.

Thus, having excluded charge carrier recombination at the front surface and in the bulk, recombination at the rear side of the cell is responsible for the limited V_{oc}. One possibility to reduce recombination at the rear side of the solar cells would be an even deeper BSF-diffusion profile. This could be an option for laboratory cells but as a deeper diffusion profile requires longer diffusion times (higher temperatures degrade the carrier lifetime – see 3.2), it appears not convenient for industrial solar cell production. A more promising solution is the application of a rear side passivation (SiN_x) in combination with local rear contacts (screen printed finger grid), which have already been realized successfully with industrial relevant process steps [7], + [9].

5 CONCLUSIONS AND OUTLOOK

A process for BSF-solar cells on n-type mc-Si has been presented and optimized. The emitter is created by BBr_3-diffusion in an open-tube furnace and passivated by a thin thermal SiO_2. The BSF is obtained by phosphorous diffusion using $POCl_3$. For this purpose, a recipe resulting in an enhancement of the carrier lifetime in the mc-Si bulk and in a deeper BSF-profile has been developed. Performing the P-diffusion after the B-diffusion proved to be the most beneficial with respect to the carrier lifetime at the end of the process.

The optimized process resulted in n-type mc-Si solar cells with an untextured front surface with an efficiency of 16.1% (according to a calibrated measurement at the EU JRC Ispra) after deposition of a DARC. This is the highest independently confirmed value that has been published for n-type mc-Si up to now.

Further improvement is expected from the application of a front-surface texture (e.g. a chemical isotexture for industrial application) – leading usually to an increase in efficiency of 1% absolute - and a rear-side passivation with local rear contacts [7]+[9]. Combining both features, cell efficiencies of 18% should be possible already with the here presented technology.

To enable industrial processing of n-type mc-Si solar cells, the thermal oxidation for the passivation of the boron-emitter should be replaced by low-temperature techniques. The possibility of p^+-Si surface passivation by Plasma-Enhanced Chemical Vapor Deposition (PECVD) of SiC_x [16] and of SiN_x [14], [9] (this conference) is actually being studied and lead to very promising results. This progresses in n-type solar cell process development, together with the higher diffusion lengths in n-type mc-Si could lead to industrial solar cells with the same efficiencies as p-type mc-Si but using substrates with a higher impurity content. Given the growing importance of solar grade silicon this would be an enormous advantage over p-type Si.

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