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N-TYPE MULTICRYSTALLINE SILICON SOLAR CELLS WITH BBr_3-DIFFUSED FRONT JUNCTION

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ABSTRACT

A simplified laboratory process with one photolithographic step for front junction solar cells on n-type multicrystalline (mc) silicon has been developed. The emitter diffusion is done in an open tube furnace with BBr_3 and back-surface-field diffusion using $POCl_3$, loading the wafers front-to-front and back-to-back respectively and thus avoiding additional etching steps. The front surface has been passivated by a 10 nm thermal oxide grown in a tube furnace. With this simple process, efficiencies of 11.0% on n-type mc-Si and 11.5% on n-type Cz-Si have been realized without antireflection coating and without surface texture. Applying a double layer antireflection coating (DARC) on these cells, efficiencies of 16.4% on Cz-Si and 14.7% on mc-Si have been achieved.

INTRODUCTION

There are two main motivations for using n-type mc-Si for solar cell production: the first is the shortage of the p-type Si feedstock which consists primarily of p-type Si scrap material from the electronic industry. As there exists a similar quantity of n-type Si from this source, making n-type Si available for solar cell production would attenuate significantly the shortage. The second reason is that there is growing evidence that mc n-type Si is superior to p-type mc-Si [1], since it is less sensitive to certain metallic impurities [2]. This could result in solar cells with higher efficiencies if a solar cells process is developed and optimised for n-type mc-Si.

EXPERIMENTAL RESULTS

Boron-diffusion is considered to be the main difficulty in processing of n-type mc-Si solar cells. Since the diffusivity of boron is lower than that of phosphorous, higher diffusion temperatures have to be used and, in contrast to phosphorous, there is no strong gettering effect. A degradation of the carrier lifetime may be expected from the combination of these two aspects. Contrary to this, however, we have shown, that boron emitter-diffusion is possible at moderate temperatures (around 900°C) in an open tube furnace using a BBr_3 diffusion source while maintaining the high starting lifetime of the n-type mc-Si material [3].

Different sheet resistances have been obtained by varying the diffusion temperature at a fixed diffusion time of 1 hour. The doping profiles have been measured using the Electrochemical Capacitance Voltage (ECV) method (Fig. 1).

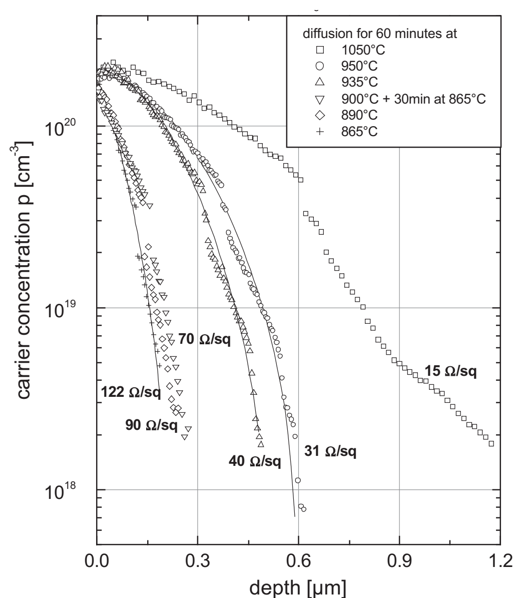

Fig. 1: ECV-profiles of boron-diffused n-type Si substrates.

Small laboratory solar cells (A = 4 cm^2, 270 µm thickness after saw damage removal) have been fabricated using the process depicted in Fig. 2. Before emitter diffusion and before thermal oxidation the wafers were cleaned in hot H_2O_2:H_2SO_4 = 1:4. Emitter diffusion was done as mentioned above with a subsequent thermal oxidation and deglaze step for the removal of the boron-rich layer (BRL) that is created during boron-diffusion. A back-surface-field (BSF) was formed by phosphorous ($POCl_3$) diffusion. One-sided diffusions were obtained in both tube-furnace steps by putting two wafers (125x125 mm^2) back-to-back (for boron diffusion) and front-to-front (for phosphorous-diffusion) respectively in one slot of the quartz-boat.

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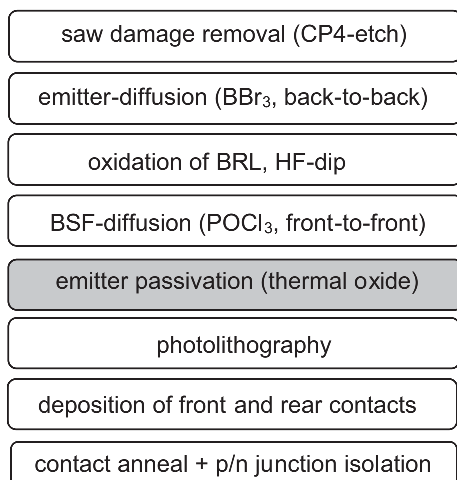

Fig. 2: Solar cell process scheme without antireflection coating

Solar cells with unpassivated front surface

First solar cells have been fabricated without front surface passivation resulting in an efficiency of 10.2% on mc-Si and 10.7% on Cz-Si (Table 1). The front grid was defined by photolithography and after etching of the oxide in the finger-openings and on the rear side, the contacts on both sides were deposited by electron-beam evaporation. The front grid consists of a stack of Al/Ti/Pd/Ag, thickened by Ag-electroplating which resulted in a finger-width of approximately 30 µm. The rear side is completely metalized with Ti/Pd/Ag.
The higher open circuit voltages V_{OC} of the mc cell compared to the Cz cell is due to its lower substrate resistivity. A simulation with PC1D for the V_{OC} of a front junction device using the material parameters and doping profiles of this cell process resulted in a V_{oc} of 592 mV when 5 Ωcm Si is used and 607 mV for 1 Ωcm material, assuming a high front surface recombination velocity (no surface passivation). Since these simulations assume monocrystalline Si, the experimentally obtained V_{oc} of 600 mV shows that the minority carrier lifetime in the bulk of the mc-Si is high enough not to be a limiting factor in the case of an unpassivated front surface.

A=2x2 cm²	**FF [%]**	**J_{SC} [mA/cm^2]**	**V_{OC} [mV]**	**η [%]**
mc cell A (1 Ωcm)	77.3	21.9	600	10.2
Cz-Si (5 Ωcm)	76.2	23.7	595	10.7

Table 1: Solar cell parameters from illuminated IV-characteristics of the best solar cells with unpassivated front surface (no texture, no ARC)

The carrier lifetimes of the mc-cell A were improved by Microwave-Induced Remote Hydrogen Plama (MIRHP)
passivation. This is shown by locally resolved mappings of the internal quantum efficiency (IQE) at different wavelengths. The result of such a measurement on mc-cell A before and after MIRHP-passivation is shown in Figure 3 for incident light of 980 nm wavelength. The comparison of the two LBIC-mappings shows a decrease in recombination activity at most of the grain boundaries – some of them even appear to disappear completely after MIRHP. There is also a slight increase inside some grains. This improved IQE resulted in an increase of the short circuit current density J_{sc} from 21.9 mA/cm^2 to 22.4 mA/cm^2.

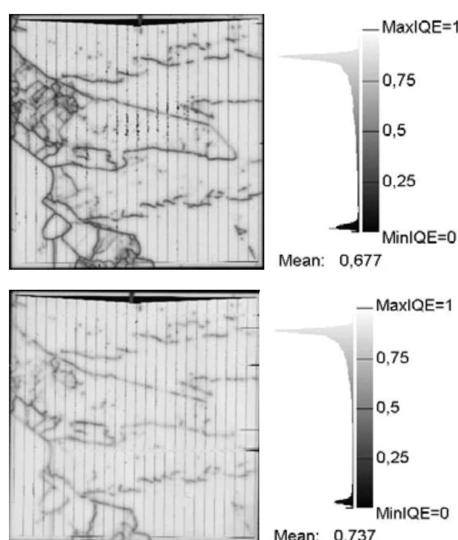

Fig 3: IQE at 980 nm of mc-cell A before (top) and after after MIRHP treatment (bottom)

Solar cells with oxide-passivated front surface

In another experiment, the cells were processed with a 10 nm thick thermal oxide on the front side. The thickness of 10 nm has been chosen as a compromise between surface-passivation and suitability with the Double layer Anti Reflection Coating (DARC: ZnS/MgF_2). The best cell results realised with this process are shown in Table 2.
The emitter saturation current J_{oe} has been determined with the Quasi Steady-State PhotoConductance decay (QSSPC) method to 640 fA/cm² for the unpassivated, and to 67 fA/cm² for the oxide-passivated cells. The improved surface passivation is also visible in the better IQE of cell B in the short wavelength range (Fig. 4), which results in a higher J_{sc} and thus a higher efficiency.

A=2x2 cm²	FF [%]	J_{SC} [mA/cm^2]	V_{OC} [mV]	η [%]
mc cell B (1Ωcm)	78.6	23.3	603	11.0 (16.5)
Cz-Si (2Ωcm)	77.9	24.4	604	11.5 (17)
	mc-cell B with DARC		**Cz-cell with DARC**	
η[%]	**14.7**		**16.4**	

Table 2: Solar cell parameters from illuminated IV-characteristics of the best solar cells with oxide passivated front surface surface (no texture, no ARC). The estimated values, which can be obtained when applying an optimised DARC, are indicated in brackets. Note the changed substrate resitivity of the Cz-Si and the experimentally obtained efficiencies at the bottom.

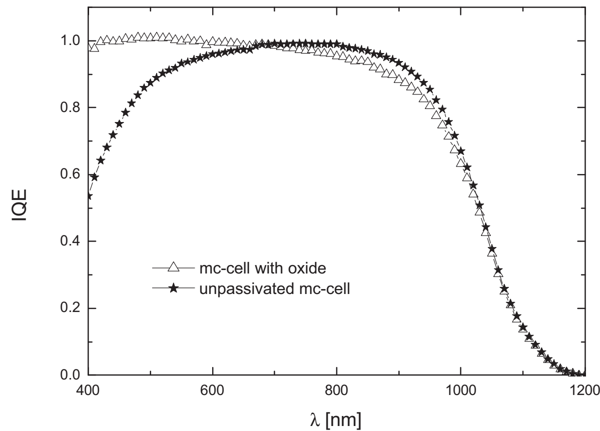

Fig. 4: measured IQE of cell A (unpassivated front surface) and cell B (oxide passivated front surface)

Taking into account the reduction of the bulk resistivity for the Cz-cells (which should result in a substantial increase in V_{oc}) and the passivating effect of the oxide, the increase of the V_{oc} compared to the unpassivated cells is rather moderate.

For the mc cell B, this could partly be explained by the different quality of the wafer-material used for cell A and cell B: cell A was processed on a wafer from position 94 and cell B from position 148 from one column of the same ingot (number 1 being at the bottom of the ingot). For position 94 the minority carrier lifetime of the unprocessed wafer (measured with µW-PCD and Iodine/Ethanol-passivation on a neighbouring wafer) is τ_{bulk}=122 µs and for position 148 τ_{bulk}=100 µs, averaged over 10x10 cm^2 respectively. The increase in V_{oc} for the Cz cell is mainly due to the reduced substrate resistivity (2 Ωcm compared to 5 Ωcm). Since in separate µW-PCD measurements the initial bulk-lifetime of the Cz material (over 400 µs) proved to be unchanged at the end of the process, this is an indication that for the mc and Cz-cells, the effective recombination velocity at the rear side and not the carrier lifetime in the bulk is the limiting factor for V_{oc}. This is understandable considering the light 45 Ω/sq BSF diffusion.

Lifetime monitoring during solar cell process

During processing of mc-cell B the minority charge carrier lifetime in the bulk was monitored (Table 3). Neighbouring wafers were taken out of the process after the respective process steps, the diffused regions were removed by CP4-etching and the lifetime was measured with µW-PCD (surface passivation with I/E-solution). The boron diffusion and the growth of the 10 nm passivating oxide did not degrade the carrier lifetime and the (one-sided) 45 Ω/sq $POCl_3$-diffusion resulted in a slight increase due to the P-gettering effect. The 10 Ω/sq $POCl_3$-diffusion, however, carried out at a higher temperature, resulted in a decrease of the minority charge carrier lifetime.

Bulk lifetime averaged over 5x5 cm^2		
As-grown	**140 µs**	
BBr_3	**147 µs**	
BRL-Oxidation	**143 µs**	
	$POCl_3$-diffusion 10 Ω /sq T > 900°C	**$POCl_3$-diffusion 45 Ω /sq T < 900°C**
P-diffusion	**129 µs**	**158 µs**
Oxide passiv.	**128 µs**	**168 µs**

Table 3: µW-PCD-measurements of the minority charge carrier lifetime in the mc Si-bulk after different high-temperature steps.

Change of the emitter profile due to oxidation

Even if the growth of a 10 nm thermal SiO_2 does not require a very high thermal budget, the doping profile of the boron-emitter is visibly changed (Figure 5). This is due to the higher solubility of boron in SiO_2 compared to its solubility in Si which causes an out-diffusion of the boron from the emitter into the SiO_2-layer. Avoiding this depletion of dopants at the front surface could be favourable for obtaining a higher V_{oc} and increase its long-term stability [6].

A PECVD-process is one possibility to avoid the depletion. In addition it requires a lower thermal budget and is compatible with screen-printed contacts with a firing through process. The passivating capacity of PECVD SiN_x, which is applied on an industrial scale for p-type Si solar cells - has been examined. QSSPC measurements have been performed on a p^+np^+-structure before and after PECVD-deposition of SiN_x, The results did not show a passivating effect – but possibly a slight depassivation. This can be explained assuming a fixed positive charge in the SiN_x that leads to an increase of the electron-

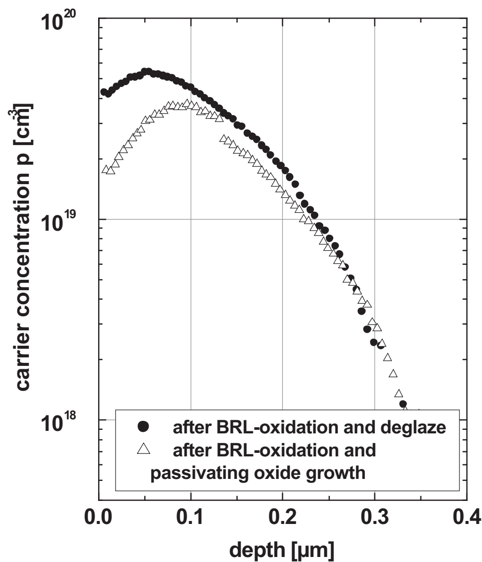

Fig. 5: ECV-profile of the B-emitter before and after growth of a 10 nm thermal SiO_2.

concentration at the surface and consequently to a higher surface recombination [7]. Surface passivation of p^+-doped Si-surfaces by PECVD SiC_x, which proved to provide an excellent surface passivation of 3.3 Ωcm p-Si [5], is currently under investigation.

CONCLUSIONS

We showed that using a BBr_3 diffusion source, emitter diffusion is possible at moderate temperatures – 60 min at 900°C is sufficient to obtain a sheet resistance of 90 Ω/sq (after removal of the boron rich layer) - and that after diffusion at this temperature the high initial lifetime of the n-type mc Si is maintained [3]. This is confirmed by the excellent values for V_{oc} of the solar cells that were obtained with this process: 600 mV on mc-Si without front surface passivation. In addition, for the cells with SiO_2, a monitoring of the lifetime has been performed indicating also the maintained lifetimes after BBr_3 – diffusion, with a slight gettering effect of the one-sided 45 Ω/sq $POCl_3$-diffusion.
Processing of such devices with a 10 nm thermal SiO_2 resulted in a considerable increase of the IQE in the short-wavelength range, and thus in a higher J_{sc} and higher efficiency. The rather moderate increase in V_{oc} is explained by the insufficient BSF-effect of the 45 Ω/sq $POCl_3$-diffusion.
Considering the high reflectance of the polish etched cell surface, simulations show that J_{sc} should improve by 45-50% when a double antireflection coating (ZnS, MgF_2) is applied to these cells. In fact this has been nearly realized by improving the uncoated 11.5% Cz-cell to 16.4% with a DARC. In the case of the mc-cell, the efficiency after coating reached only 14.7% because of processing problems which resulted in an inhomogeneous coating with non-optimal thickness of both layers.

OUTLOOK

In order to improve the V_{oc} of the cells, a deeper and double-sided phosphorous diffusion at lower temperaturees will be performed in the future for a improved BSF and P-gettering [8]. The use of 200 µm thin wafers would also improve V_{oc}, if a suitable BSF is applied. In addition surface passivation by SiC_x of p^+-doped Si-surfaces with different surface concentrations will be examined and adapted for solar cell applications. J_{sc} can be further improved by surface texture, H-passivation and improved rear side reflectance. With these improvements, efficiencies of 17% and more can be realized on n-type mc-Si with a simple process, without using advanced techniques like local rear contacts or a selective emitter.

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