SOLAR CELLS ON SILICON RIBBONS DOPED WITH SPRAYED BORIC ACID AS A DOPING SOURCE

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ABSTRACT: The method for boron bulk doping of silicon ribbons based on the use of sprayed boric acid as a doping source is particularly suitable for producing p-type silicon ribbons that require zone melting recrystallisation (ZMR). This paper reports on a test of the application of this method for the doping of multicrystalline material that was used as the base material for solar cells. The aim was to study the material deterioration due to the spray doping process. Analysis of solar cell performance, lifetime measurements and GDMS contaminants detection, suggest that the doping process with boric acid solution does not produce detectable deterioration of the material quality compared to the control (non-recrystalised) materials.
Keywords: Multicrystalline Silicon, Doping, Zone melting

1 INTRODUCTION

The method for boron bulk doping of silicon ribbons based on the use of sprayed boric acid as a doping source is suitable for producing p-type silicon ribbons in processes that include a zone melting recrystallisation step [1]. The method is compatible with an in-line transport system, reliable, safe and easily controllable, and uses an inexpensive and widely available doping source.

In a previous paper [2], it was shown that one may control the incorporation of boron by changing the initial concentration of boric acid on the surface of the sample, and the mechanism of boron incorporation into the sample was established [3]. In this paper, we report on a test of the application of the sprayed boric acid doping method for the production of solar cells using high resistivity silicon wafers as test substrates.

2 METHODS

2.1 Samples

The original test samples were 30×156 mm^2, cut from 270μm thick, multicrystalline silicon wafers from Deutsche Solar with resistivities between 100–1000Ωcm.

2.2 Doping method

The doping procedure is based on a 2-step process. After cleaning the samples in polishing (15% HF + 75% HNO3 +10% CH3COOH) and HF solutions, the samples are sprayed with a solution of boric acid with a concentration of 0.006 mol/l. In order to guarantee spraying uniformity over the whole area of the sample, a moving sample holder travels underneath a continuously flowing airbrush Badger 250 fed with a fixed pressure of nitrogen, as shown in Fig. 1.

The incorporation of the boron into the samples is achieved during zone melting recrystallisation (ZMR), according to the equation:

$$2\ B_2O_3\ (g) + 6\ Si(s) \rightarrow 6\ SiO\ (g) + 4\ B(s) \qquad (1)$$

The molten zone is achieved by focusing radiation from two 1000 W halogen light bulbs onto a narrow line, 2mm wide. Typical running parameters are: downward sample motion at a velocity of 3 mm/min and argon flow of 3.0 l/min. After recrystallisation, the sample is cleaned with an HF solution to remove residual oxide from the surface.

The boron doped samples were characterised by four point probe sheet resistance mapping and μw-PCD lifetime measurements using a Semilab WT-1000 (since samples showed a low bulk recombination lifetime, no surface passivation treatment was necessary).

The two-step doping process may introduce impurities into the material due to the sprayed solution and the ZMR processing. In order to characterise the incorporation of contaminants during the doping process, a GDSM analysis was performed on: a control sample (standard Silso wafer, as cut), a recrystallised sample (standard Silso wafer recrystallised without any spraying), the original material (high resistivity wafer, as cut) and a sprayed boric acid doped sample. The tested impurities were Cr, Fe, Al and Mo.

The concentrations of impurities were measured by a ThermoFisher Scientific Glow Discharge Mass Spectrometry (GDMS) system [4]. The samples (approximately 30x30 mm^2) surface was pre-sputtered for about 5 min in order to remove surface contamination [5]. The sputtering rate of the GDMS used is approximately 20 nm/s. The analyses were performed at approximately 60 mA, 300ml/min, and 1100V.

Figure 1: Experimental boric acid spraying setup.

2.3 Solar cell process

Solar cells were made on the p-doped recrystallised substrates. These solar cells were used to evaluate the suitability of this doping method for photovoltaic application by testing whether the spray doping process would, via introduction of impurities or other mechanism, induce severe deterioration of the material quality. For this purpose, simple test cells were made: no back surface field, antireflection layer, emitter doping optimization, passivation nor gettering procedures were used. The p-n junction was formed by phosphorous diffusion from a solid source. After mesa etching, aluminium back contacts and a grid of Ti/Pd/Ag front contacts were deposited by evaporation, followed by contact annealing. The solar cells were characterized by spectral response and IV measurements.

3 RESULTS

Experimental results confirmed the uniform incorporation of boron into the silicon substrate, with doping levels of 10^{16} cm^{-3}, without degradation of material quality, as shown in Fig.s 2-4.

3.1 Lifetime measurements

Microwave-photoconductance measurements showed that recombination lifetime decreased significantly with the recrystallisation step applied to high quality wafers, but it was not sensitive to the incorporation of boron from the sprayed film (Fig. 2): the sprayed doped sample featured similar lifetimes to the recrystallised sample (~2μs), lower than ~3μs for the control (non-recrystallised) sample.

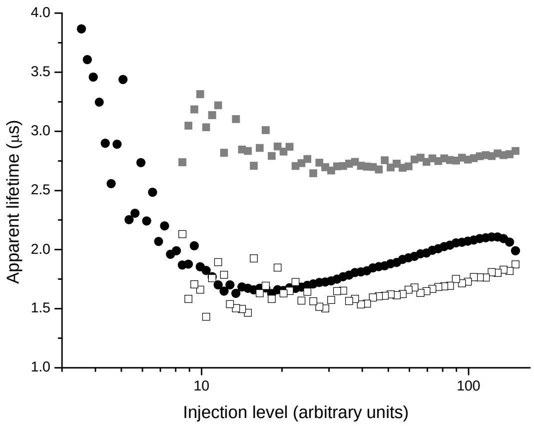

Figure 2: Apparent lifetime measurements as a function of injection level for (●) a typical recrystallised boric acid sprayed silicon sample; (□) a recrystallised control sample; and (■) a control sample of the original material.

Low injection level measurements showed a strong increase in the apparent lifetime suggesting a high density of trapping defects, a feature common to all three samples.

3.2 Contamination

The impurity analysis showed no traces (*i.e.*, below the detection limit, < 10^{12} cm^{-3}) of Mo. The results are shown in Table I.

Table I: Detection of trace elements (ppmw).

	Cr	Fe	Al
Control sample	0.0059	0.0105	0.0084
Recrystallised control	0.0370	0.0410	0.0370
Original sample	0.0084	0.2885	0.0553
Spray-doped sample	0.0030	0.8520	0.0060

The results indicated a high concentration of iron in the original sample (prior and after the doping/ZMR treatment). Comparison with the control sample measurements suggest the variations of Cr and Al as well as the increase of Fe may be attributed to impurity variability in the source material and not on the processing itself.

3.3 Solar cells

Experimental data showed that the incorporation of boron using the sprayed boric acid method does not affect the spectral response of the solar cell nor the V_{oc} or the I_{sc}. Due to the very simple processing used, the solar cells featured relatively poor IV responses (Fig. 3). The high defect density introduced by ZMR resulted in a less than optimum response in the near-infrared (Fig. 4) but there was no significant difference between the sprayed doped sample and the recrystallised control.

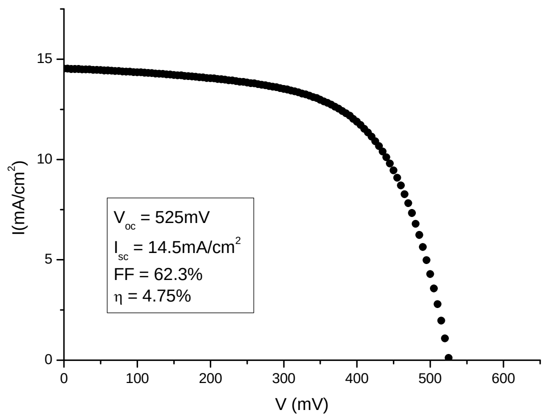

Figure 3: IV-curve for typical recrystallised boric acid sprayed silicon.

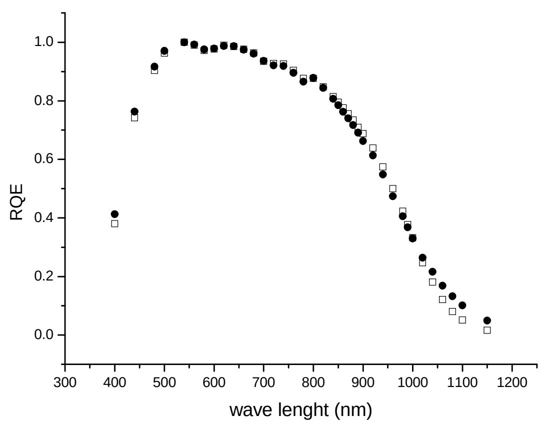

Figure 4: Spectral response level for a typical recrystallised boric acid sprayed silicon sample (●) and a recrystallised control sample (□).

Table II shows that the diffusion length (determined from spectral response measurements) decreases significantly with the recrystallisation step, but does not appear to be sensitive to the spray doping method of incorporation of boron.

Table II: Average solar cell parameters for: (A) Control samples; (B) Recrystallised control samples; and (C) Spray-doped samples.

	A	B	C
Diffusion length	111±68	54±22	53±16
Solar cell efficiency	3.5±0.9	3.5±1.0	3.3±0.8

The recrystallized control samples featured an average diffusion length of 2% longer than the samples under study. The effect on the solar cell efficiency is about 6% relative, which is much smaller than the variation introduced by the solar cell processing itself.

4 CONCLUSIONS

Solar cells were realised on p-type silicon samples bulk doped using sprayed boric acid as a doping source. Material and solar cell characterization has shown that the ZMR step may introduce contaminants into the material and leads to a reduction in the diffusion length, and thus the cell efficiency. However, the solar cell performance seems to be immune to the use of the sprayed boric acid solution.

Since this method was developed for use with silicon ribbons that already require a ZMR step for its growth, we may conclude that the suitability of the use of sprayed boric acid as a doping source for photovoltaic application was demonstrated.

5 ACKNOWLEDGEMENTS

The samples were provided by Deutsche Solar AG. This work has been partially supported by FCT grant SFRH/BD/12763/2003.

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