

## PROGRESS IN THE USE OF SPRAYED BORIC ACID AS A DOPANT SOURCE FOR SILICON RIBBONS

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**ABSTRACT:** This paper reports on an alternative method for boron doping of silicon ribbons based on the use of sprayed boric acid as a dopant source. The sprayed pre-ribbon is subjected to zone melting recrystallization in an argon atmosphere. Boron incorporation occurs via two mechanisms: solid-state diffusion and vapor-phase contamination. In the molten zone the boron is uniformly mixed due to convection in the liquid. It is shown that one may control the incorporation of boron by changing the initial concentration of boric acid on the surface of the sample. It is also established how the incorporation of boron depends on parameters such as the direction of recrystallization and the flux of argon in and out of the furnace.

Keywords: Doping, Ribbon Silicon, Zone melting.

### 1 INTRODUCTION

P-doping of crystalline silicon wafers is usually undertaken by contaminating the feedstock with heavily doped silicon pellets. On the other hand, silicon material grown from silane or chlorosilanes, such as that in amorphous or microcrystalline silicon films, is doped using an atmosphere which includes the dopant, for instance in the form of diborane gas. These techniques, however, are less suited for methods of crystalline sheet silicon growth such as those based on zone melting recrystallization, when the pre-ribbon is best produced undoped [1–4].

In this paper we report on an alternative method for boron doping of silicon ribbons based on the use of sprayed boric acid as a dopant source. The method is compatible with an in-line transport system, is reliable and easily controllable, and uses an inexpensive and widely available dopant source.

The method is based on the spraying of intrinsic silicon pre-ribbons with a solution containing boric acid. This pre-ribbon is then subjected to zone melting recrystallization in an argon atmosphere. As the temperature increases, the boric acid decomposes into boron oxide and water [5], the latter being evaporated from the surface of the sample. For temperatures above 1300K, boron is incorporated into the sample by diffusion across the surface [6]. However, when the sample reaches 1400K, most of the boric oxide has evaporated from the surface of the sample therefore removing the boron source to the diffusion process [7]. The argon-boron atmosphere will then be responsible for further contamination of the silicon with boron. In the molten zone the boron will be uniformly mixed due to convection in the liquid.

The measurement of the incorporation of boron into the silicon samples was undertaken by measuring the sheet resistance of the samples, using the four point probe method. It was assumed that all boron atoms incorporated in the sample are electrically active.

This paper describes the experimental details and preliminary results that demonstrate the feasibility of this doping method. It is shown that one may control the incorporation of boron by changing the initial concentration of boric acid on the surface of the sample. It is also established how the incorporation of boron depends on parameters such as the direction of

recrystallization and the flux of argon in and out of the furnace.

### 2 EXPERIMENTAL PROCEDURE

#### 2.1 Samples

Since the goal of this work was solely to demonstrate the feasibility of the doping process, the samples used were already doped, with carrier concentration of the order of  $10^{16} \text{ cm}^{-3}$ ; uniform doping levels between  $10^{17}$  and  $10^{18} \text{ cm}^{-3}$  were obtained. The pre-ribbons were  $100 \times 30 \times 0.3 \text{ mm}^3$  multicrystalline silicon from Deutsche Solar.

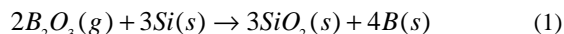
#### 2.2 Boric acid deposition

The doping process begins with the cleaning of the sample with POLISH ( $\text{HF} + \text{HNO}_3 + \text{CH}_3\text{COOH}$ ) and HF solutions. Then, the samples are sprayed with a solution of boric acid with a concentration of 0.1365 mol/l.

The spraying of the boric acid is carried out by using an airbrush Badger 250 fed with a fixed pressure of nitrogen in order to guarantee a reproducible and homogeneous deposition. The airbrush is located 80 cm above the sample. A 22 cm diameter cylindrical enclosure is used to prevent perturbations due to air currents.

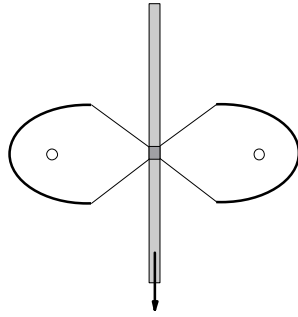
#### 2.3 Recrystallization

The incorporation of the boron into the samples is achieved by zone melting recrystallization, according to the equation



The molten zone is achieved by focusing radiation from two 1000 W halogen light bulbs onto a narrow line, 2mm wide, as shown in Fig. 1. In a typical run, the sample is moved downwards with a 3mm/min velocity and the atmosphere inside the furnace is renewed with a 1.1 l/min argon flux.

After recrystallization, the sample is cleaned with an HF solution that removes the layer of silicon oxide from the surface.



**Figure 1:** Zone melting setup. As the sample is moving downwards, radiation from two halogen lamps is focused onto the sample surface creating a 2 mm wide molten zone.

#### 2.4 Concentration of carriers

The concentration of the charge carriers is estimated from sheet resistance measurements using a standard four point probe system. The thickness is measured with a differential mechanical profilometer developed on our laboratory [8]. From the resistivity  $r$ , the concentration of charge carriers,  $N$ , is calculated using the relationship

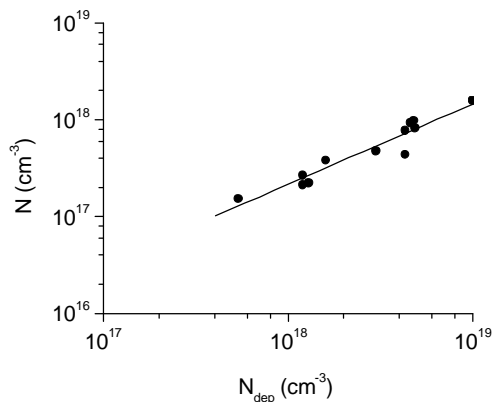
$$r = \frac{1}{qN\bar{m}_p} \quad (2)$$

where  $q$  is the charge of the electron and  $\bar{m}_p$  is the hole mobility. The hole mobility was determined from empirical data for doping dependent hole mobility in silicon at 300 K [9].

### 3 RESULTS

#### 3.1 Boron incorporation rate

It was observed that the mean incorporation of boron into the samples depends linearly on the initial concentration of boric acid. This result is shown in Fig. 2, where the boron concentration in the recrystallized sample is presented as a function of the initial concentration of boric acid for typical run parameters (sample moving downwards at 3mm/min, argon flux 1.1 l/min).



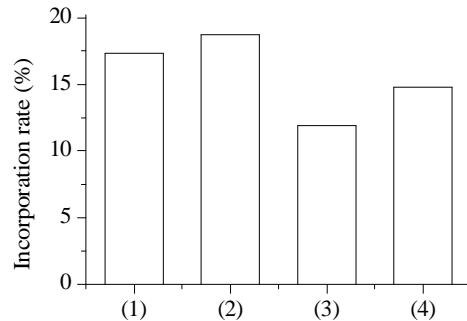
**Figure 2:** Mean boron incorporation as a function of boric acid initial concentration for typical run parameters.  $N$  is the carrier density obtained, and  $N_{\text{dep}}$  is the initial concentration of boric acid.

As mentioned above, as the sample is heated up the boric acid decomposes into boron oxide and water, the latter being evaporated from the surface of the sample. Then, for temperatures above 1300 K, in-diffusion of boron from the surface becomes relevant. Simultaneously, however, part of the boron oxide evaporates and when the sample reaches 1400 K, most of the boron oxide has evaporated, thus removing the boron source to the diffusion process. Part of this evaporated boron oxide will be dragged outside by the argon circulation. The rest will be pushed up by convection currents and either incorporated into the sample, by sticking to the molten zone, or deposited further up on the surface of the sample. The incorporation of boron into the sample is thus achieved through two different mechanisms: solid state diffusion and vapor-phase incorporation.

Considering these mechanisms, we thus expect that the boron incorporation rate will depend crucially on parameters such as the direction of the recrystallization (either upwards or downwards) and the argon flux. Indeed, it was observed that the boron incorporation rate varied between 10 and 20%, depending on these recrystallization parameters.

#### 3.2 Effect of recrystallization direction

The boron incorporation rate is higher when the sample is moving downwards, and therefore the molten zone is moving up the sample ( $17.3 \pm 0.7\%$ ), than when recrystallization is realized in the opposite direction ( $11.9 \pm 0.1\%$ ) (see Fig. 3).



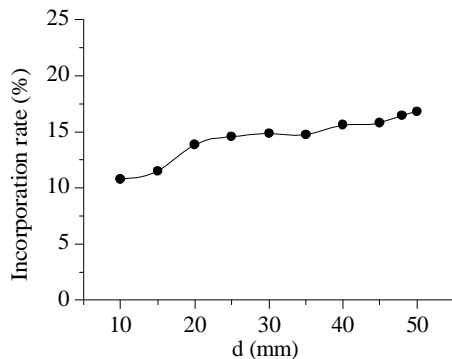
**Figure 3:** Boron incorporation rate for samples recrystallized with (1) molten zone moving upwards; (2) multipass molten zone, first upwards and then downwards; (3) molten zone moving downwards; and (4) multipass molten zone, first downwards and then upwards.

This result may be understood if one notices that, according to the mechanism described in the previous section, part of the evaporated boron oxide is dragged by the upward convection currents and may be either incorporated from the vapor phase or deposited further up on the surface of the sample. If the molten zone is moving downwards, this evaporated boron oxide will either be dragged out by the argon flux or deposited in the surface of the sample, but will not be reheated again and will therefore remain on the surface of the sample (and be removed during the cleaning step after the recrystallization). If the molten zone is moving upwards the evaporated boron oxide has a higher probability of

being incorporated into the sample, by either of the two mechanisms described above.

Fig. 3 also shows mean boron incorporation for multipass molten zone recrystallization experiments. As expected, the highest incorporation rate is achieved for the configuration where in the first pass the molten zone is moving upwards ( $18.7 \pm 1.8\%$ ) and the least favorable configuration is single pass with the molten zone moving downwards. From these results we conclude that, for these experimental conditions, the incorporation of boron due to the solid state diffusion is of the order of 10% of the initial deposited concentration whilst the remaining boron is incorporated from the vapor phase, directly into the molten silicon.

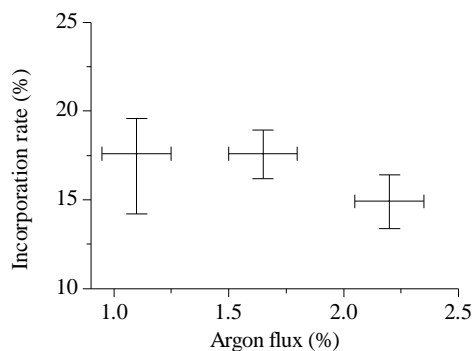
One should also notice that when the molten zone is moving in the same direction as the convection currents, the incorporation of boron will not be constant along the sample: a gradient in the distribution of incorporated boron will be observed. This effect is shown in Fig. 4.



**Figure 4:** Typical distribution of incorporated boron due to evaporated boron oxide incorporation.

### 3.3 Effect of argon flux

The flux of argon will also have an impact on the boron incorporation rate (Fig. 5).



**Figure 5:** Variation of boron incorporation rate with argon flux. The error bars represent the variations of incorporation along the samples.

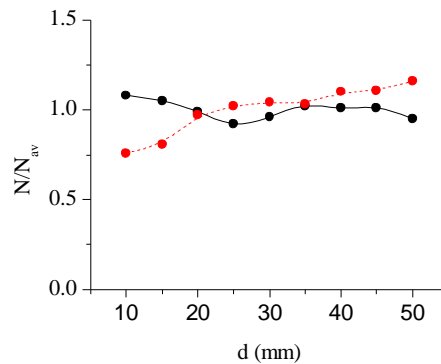
One can see that the doubling of the argon flux (from 1.1 l/min to 2.2 l/min) significantly reduces the rate of incorporation of boron. A larger argon flux drags a higher proportion of boron oxide from the atmosphere to the outside, thus reducing the incorporation of evaporated boron. This may also explain the reduction of

the variation of the amount of boron incorporated along the sample (i.e. a smoother distribution gradient).

### 3.4 Distribution of boron concentration

As we saw previously, the mechanism of evaporation and transport of boron oxide by upward convection currents leads to a gradient in the distribution of the concentration of boron along the sample. This gradient can be more or less pronounced, depending on the argon flux and/or the speed of recrystallization.

This distribution anisotropy may be reduced by using the configuration where the molten zone moves downwards (at the cost of lower boron incorporation rate) or by carefully introducing an opposite gradient in the initial distribution of sprayed boric acid. This approach was shown to be successful in eliminating the gradient in the boron incorporation distribution whilst keeping higher boron incorporation rates (Fig. 6).



**Figure 6:** Boron incorporation along a sample with anisotropic (solid black line) and isotropic (red dashed line) spraying of boric acid,  $N$  is the density of carriers and  $N_{av}$  is the average carrier density on the sample.

## 4. CONCLUSIONS

A new method for boron doping of silicon ribbons based on the use of sprayed boric acid as a dopant source was demonstrated. It was shown that the concentration of charge carriers, deduced from sheet resistance measurements, depends linearly on the amount of deposited boric acid.

It was also observed that the fraction of the deposited boron that is incorporated varies between 10 and 20%, depending on process parameters such as the flux of argon used, the direction of recrystallization, and single pass or multipass recrystallizations.

These results may be understood by considering a dual mechanism of boron incorporation into the silicon ribbon. During heating, boron oxide diffuses across the surface into the sample. On the other hand, as the temperature rises, boron oxide evaporates and will be dragged upwards by convection currents or outwards, by the flux of argon. The argon-boron atmosphere will then be responsible for further contamination of the silicon with boron. In the molten zone the boron will be uniformly mixed due to convection in the liquid.

Finally, resistivity mapping shows a gradient of boron incorporation along the sample which is attributed

to convection of boron in the gas phase. This gradient may be sharpened or smoothed out by changing the direction of the crystallization, the temperature profile and/or the initial distribution of deposited boric acid.

## 5 ACKNOWLEDGEMENTS

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