DISTRIBUTION OF Al, B AND P IN MULTI-CRYSTALLINE Si INGOTS

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ABSTRACT: Mc-silicon ingots were doped with aluminium, boron (p-type) and phosphorous (n-type). The aim of the work was to study the distribution of these dopants along the ingots. A recently developed mathematical model based on the Scheil`s equation was used for evaluating the distribution of aluminium, boron and phosphorous and the values were compared with the experimental results. The mathematical model showed excellent agreement with the experimental results for all ingots.
Keywords: Mc-silicon, Aluminium, Boron, Phosphorous, Doping

1 INTRODUCTION

A large portion of solar cells is presently made from multi-crystalline (mc) silicon. The distribution of dopants and hence impurities during directional solidification of mc-silicon is of importance with regards to material quality and processing methods for making solar cells. Particularly, the study of the effect of dopants and impurities in mc-silicon production is of importance since they may lead to impaired electrical performance. In this work, the mc-silicon ingots were doped with aluminium, boron (p-type) and phosphorous (n-type) and their distribution along the ingots were investigated by using a mathematical model based on the Scheil`s equation [1]. These results were compared with the experimental data.

1.1 MATHEMATICAL MODEL

A detailed description of the mathematical model was previously given [1]. The model is based on the same assumptions of the Scheil`s equation [2, 3], *i.e.*, there is (i) complete mixing in the liquid, (ii) no diffusion in the solid and (iii) no mass flow [2]. Starting from a mass balance, the mathematical model leads to the following equation [1]:

$$\left(\frac{x_l(t)}{x_{l_i}}\right) = \left(1 - \frac{M_c}{M_i}\right)^{[k_{eff}-1]} \qquad (1)$$

where:

$$k_{eff} = k + \rho_{Si}\frac{k_v(A^* - A)}{\dot{M}_c} \qquad (2)$$

k_{eff} is the effective partition coefficient and is given by the partition coefficient k (ratio of solid and liquid concentrations) which for many elements is given in the literature, plus a term which takes into account the evaporation of a certain element from the melt. By fitting the experimental curve to the model it is possible to estimate the effective partition coefficient and the evaporation during the process.

The Scheil`s equation can be written as [3]:

$$\left(\frac{C_l}{C_0}\right) = \left(f_l\right)^{[k-1]} \qquad (3)$$

where:

$$f_l = 1 - f \qquad (4)$$

The similarity between the model (Equation 1) and the Scheil`s equation (Equation 3) is evident. The resistivity of a silicon ingot decreases as the level of dopant increases as shown in Figure 1 [4].

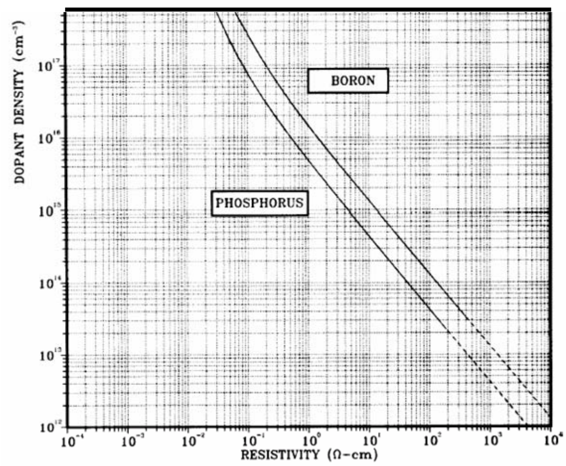


Figure 1: Relation between dopant level and resistivity. ASTM F23-99 [4].

The resistivity is nearly linear in the range 10^{-1}-10^{2} and the relationship may be written as:

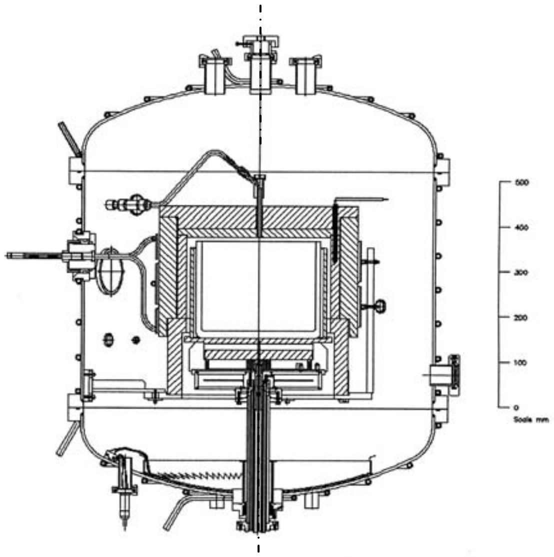
$$\log R \approx -\log C + konst \qquad (5)$$

Inserting into Scheil`s equation the following relationship can be written:

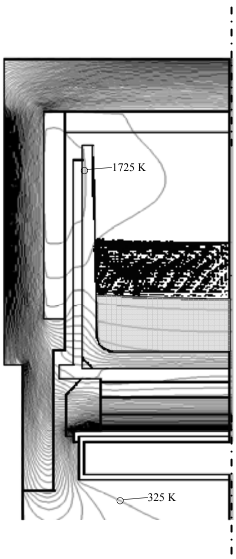
$$\frac{R}{R_0} = (1 - f)^{1-k} \qquad (6)$$

2 EXPERIMENTAL

Mc-silicon ingots were produced in a Crystalox DC250 furnace at SINTEF Materials and Chemistry (Trondheim, Norway). The charge material was approximately 12 kg poly-crystalline (pc) silicon giving an ingot of 250 mm diameter and 100 mm height. Figure 2a is a schematic of the furnace. Figure 2b shows the fluid flow pattern as well as isotherms from CFD modelling [5]. Three ingots were produced and doped with aluminium (p-type), boron (p-type) and phosphorous (n-type), respectively. The initial doping concentrations are indicated in Table I. After solidification and cooling the ingots were cut and samples were prepared for resistivity measurements and chemical analysis. Resistivity measurements were carried out along the axis of the ingot from bottom to top (solidification direction) and were performed with a four-point probe technique [6, 7].



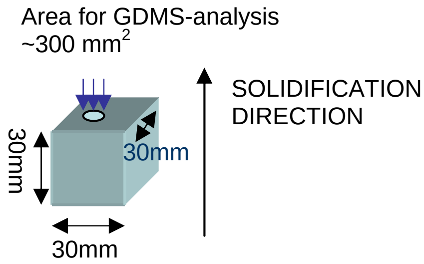
a)



b)

Figure 2: a) Schematic representation of the directional solidification furnace used in the experimental work. b) Fluid flow pattern in molten silicon and isotherms from CFD modelling at fraction solid ~0.5. Maximum velocities are about 2mm/s [5].

a)



b)

Figure 3: a) As cast ingot; b) sample dimension and area for chemical analysis by GDMS.

Table I: Initial doping concentration for each ingot

Ingot	Charge, kg	Initial Dopant Concetration, ppmw
Al-doped	12	8
B-doped	12	0.55
P-doped	12	0.03

A Glow Discharge Mass Spectrometer (GDMS) manufactured by Thermo Electron Corporation (Bremen, Germany) was used to measure the chemical composition. GDMS is a powerful tool which allows to detect trace elements and impurities in concentration less than 1ppm (part per million).

The resistivity measurements were compared with the model prediction (Equation 1) whereas the concentration measurements by GDMS were compared with concentrations given by the Scheil`equation (Equation 3). Figure 3a shows one ingot. Figure 3b shows a schematic drawing of sample dimension and area for chemical analysis by GDMS.

3 RESULTS AND DISCUSSION

Figure 4 shows the resistivity measurements and the model prediction *versus* ingot position (0 refers to the bottom of the ingot). It is also shown the concentration measurements by GDMS and the Scheil`s equation prediction. The model prediction fits well with the resistivity measurements. Resistivity (continuous light-grey line) decreases from the bottom towards the top of the ingot while dopant concentration (continuous black line) increases towards the top of the ingot. Similar considerations are valid for boron- and phosphorous doped ingots. For each ingot the value of the effective partition coefficient (k_{eff} for best fit) is reported. For all the elements investigated, *i.e.*, aluminium, boron and phosphorous, the evaporation from the melt is not significant.

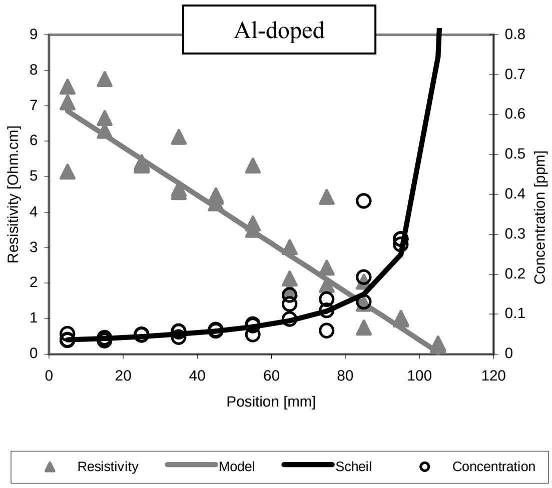


Figure 4: Resistivity and concentration measurements along the Si ingot doped with Al (p-type) using k=0.004 as effective partition coefficient.

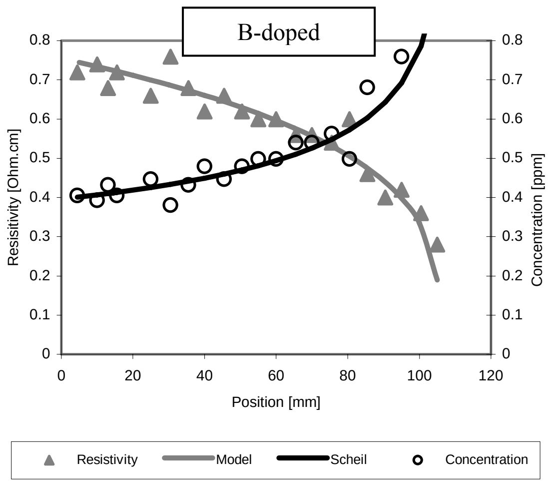


Figure 5: Resistivity and concentration measurements along the Si ingot doped with B (p-type) using k=0.72 as effective partition coefficient.

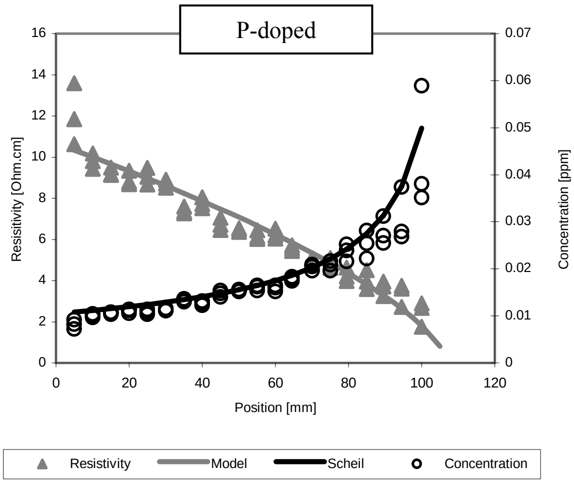


Figure 6: Resistivity and concentration measurements along the Si ingot doped with P (n-type) using k=0.35 as effective partition coefficient.

4 CONCLUSIONS and FUTURE WORK

This study has shown that predictions on distribution of dopants such as aluminium, boron and phosphorous on mc-silicon ingots by the model fit well with the experimental data. Also the chemical analyses by GDMS measurements fit well with the values predicted by the Scheil`s equation. This gives useful information which may help the PV industry to improve their control on doping processing. The application of the model to predict distribution of oxygen and carbon will be the aim in future works.

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LIST OF SYMBOLS

A : ingot surface [m^2]
A* : crucible surface [m^2]
C : dopant concentration [ppm]
C_l : concentration in liquid [wt%]
C_0 : initial concentration [wt%]
k : partition coefficient
k_v : constant of evaporation [m/s]
k_{eff} : effective partition coefficient
f : fraction solid
f_l : fraction liquid
M_c : dopant molecular weight [kg/kmol]

$\dot{M}_c$: molar rate of increase of the ingot [kmol/s]

M_i : initial dopant molecular weight [kg/kmol]

R : resistivity [Ohm cm]

R_0 : intial resistivity [Ohm cm]

x_l : concentration of liquid in mass fraction

x_{l_i} : initial concentration of liquid in mass fraction

ρ_{Si} : silicon density [kg/m^3]

ρ : resistivity [Ohm cm]

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