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Electrical properties of boron, phosphorus and gallium co-doped silicon

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Abstract

A number of ingots were grown from solar grade poly Silicon, to which Boron, Phosphorous and Gallium were added as dopants. The introduction of Gallium as a third dopant allowed for a better control of the resistivity and the doping type during ingot growth. Measured resistivity in this material is shown to be systematically higher than that calculated using Scheil's law for the dopants distribution and Klaassen's model for the majority carrier mobility. This resistivity underestimation is shown to be, at least partially, due to a reduction of the majority carrier mobility in highly compensated Si compared to Klaassen's model. A similar reduction is observed for the minority carrier mobility. We propose a correction term in the mobility calculation, to allow a greater accuracy in the prediction of the resistivity and mobility of compensated solar grade silicon.

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Keywords: Silicon; Doping compensation; Carriers mobility.

1. Introduction

Innovative metallurgical refinement processes [1] for metallurgical grade Silicon have been or are currently under development as alternatives to the standard Siemens purification process, in order to face the increasing demand of silicon feedstock for photovoltaics. Dopants such as boron and phosphorus are the most difficult impurities to remove through metallurgical purification processes. The obtained *upgraded metallurgical grade silicon* (UMG-Si), therefore contains both, p-type and n-type dopants impurities and is thus called *compensated Silicon*. Compensated Si displays specific electrical properties: it may for instance exhibit high minority carrier lifetime for a high compensation level [2], but the carrier mobility may be lower [3,4].

The presence of both B and P in the silicon feedstock usually leads to large resistivity variations along the ingot height, after crystallization. Indeed, since P has a lower segregation coefficient (0.35) than B (0.8), their respective concentrations vary differently throughout the height of the ingot, and the net doping is not uniform. An inversion of Si polarity can even occur within the ingot, leading to a low material yield since the PV industry predominantly requires p-type Silicon for solar cell fabrication. To overcome this problem, Kraiem *et al.* [5] have recently proposed to use doping engineering when using such compensated silicon by adding Gallium as a third p-type dopant during ingot solidification. The low segregation coefficient of Ga (0.008) enables to counterbalance the increasing P concentration throughout the ingot height. It is thus possible to obtain low net doping and p-type resistivity along the full ingot height. We have already validated this method experimentally [6], and we present here a deeper insight of the electronic properties of the B-P-Ga *tri-doped* silicon, especially focusing on the free carrier mobilities.

2. Experiment

2.1. Ingots production

In this study, <100> oriented Cz-Si crystals of around 160 mm in diameter were grown. For each ingot, we used 15 kg of intrinsic solar grade poly-Si, to which known concentrations of B, P and Ga were added (Table 1). The resulting ingots were cut into 125×125 mm² pseudo-square wafers. A multicrystalline ingot (Mc#1) was

grown with the same material and doping concentration as Cz#2, using the crystallization process developed by Cyberstar and Apollon Solar [7].

B and P concentrations (Table 1) used in this work correspond to different cases of partially UMG-Si. The Ga concentrations to be added were calculated using Scheil's segregation law, as presented in [6], in order to obtain a fully p-type ingot and a relatively high resistivity. B and P were introduced using highly doped Si-wafers, and Ga using high purity pellets.

Table 1. Initial concentrations of B, P and Ga added to the melt before crystallization of ingots Cz#1-3 and Mc#1.

Ingot	[B] (cm-3)	[P] (cm-3)	[Ga] (cm-3)
Cz#1	2.7×10^{16}	1.8×10^{17}	5.8×10^{18}
Cz#2	2.1×10^{17}	3.4×10^{17}	3.6×10^{18}
Cz#3	2.1×10^{17}	4.5×10^{17}	6.1×10^{18}
Mc#1	2.1×10^{17}	3.4×10^{17}	3.6×10^{18}

2.2. Characterization

To evaluate the impact of Ga co-doping, we measured the resistivity of samples using four-point probe at various heights along the length of each ingot. SIMS analyses were also carried out to determine the dopant concentration at different ingot heights.

$$\mu = \frac{1}{\rho \times p \times q} \quad (1)$$

Majority carrier mobility was determined with equation 1, using the resistivity ρ measured by four-point probe and the majority carrier density by both Hall effect and free-carrier absorption measurements. The Hall carrier density p_H is known to differ from the true carrier density p_0 by a factor close to unity, called the Hall factor r_H . To determine r_H , we have carried out Hall effect measurements on uncompensated B-doped Cz-Si samples with a resistivity of around $1 \Omega \cdot \text{cm}$. The Hall factor r_H was then calculated as equal to $r_H = p_0 / p_H$, p_0 being calculated from the resistivity using Klaassen's model [8]. We found an average Hall factor of $r_H = 0.73 \pm 0.05$, which is in reasonable agreement with values found in literature [9,10]. By using the same r_H to calculate p_0 in all samples, we assume r_H not to be affected by compensation, as suggested in different studies on carrier mobility in compensated Si [3,4]. We will discuss the validity of this value for our compensated wafers in the results section.

FCA measurements were done using a Fourier transform infrared (FTIR) spectrophotometer, following the method described in [11]. The absorption coefficient component due to free carriers α_{FC} (FCA) is given in p-type Si by:

$$\alpha_{FC}(p_0, \lambda) = c_{FCA} \times q \times \rho \times p_0^2 \times \lambda^2 \quad (2)$$

where λ is the incident wavelength and c_{FCA} a constant. This c_{FCA} constant was determined to be equal to $5.50 \text{ m}^2/\text{V} \cdot \text{s}$ by calibrating our FTIR spectrophotometer with uncompensated B-doped Fz and Cz wafers with a wide range of resistivities (from 3×10^{15} to $1.5 \times 10^{17} \text{ cm}^{-3}$). Absorption measurements were fitted in the middle infrared range ($\lambda = 2$ to $8 \mu\text{m}$) for this analysis. Wafers were mechanically polished on both sides to obtain a mirror-like surface. Undoped ($1 \times 10^4 \Omega \cdot \text{cm}$) Fz-Si was used as reference for that measurement.

Minority carrier mobility was extracted from minority carrier lifetime data, using microwave detected photo-conductance decay measurements. For this application the surface of the sample has to be degraded, to ensure infinite surface recombination velocity. In that case the effective minority carrier lifetime τ is limited by the diffusion of minority carriers to the surfaces of the sample and can be related to the minority carrier diffusion coefficient D_n , and wafer's thickness W , as follows [12]:

$$\frac{1}{\tau} = \frac{1}{\tau_b} + \left(\frac{\pi}{W} \right)^2 D_n \quad (2)$$

where τ_b is the bulk minority carrier lifetime. Using the definition of the diffusion coefficient $D_n = \mu_n kT/q$, the minority carrier mobility μ_n can be extracted from several measurements by varying the wafer thickness W . This was done by thinning the samples using HF/HNO₃ chemical etching between two measurements. To ensure very high surface recombination velocity, without issuing sample breakage, the surface is abraded by a UV pulsed-

laser. We have verified by comparing lifetime values on degraded surfaces before and after chemical polishing, that this entails degradation on few micrometers depth, but preserves the bulk lifetime τ_b .

3. Results and discussion

3.1. Dopant distribution results

The resistivity profiles of the different ingots are shown in Fig. 1, and compared to the theoretical values obtained from the Klaassen's mobility model [8], using the doping concentrations calculated by Scheil's segregation law. The first result is that all ingots are fully p-type with a minimum resistivity of 0.4 $\Omega\cdot\text{cm}$, which can be attributed to the presence of Ga. Indeed, from the initial concentrations of B and P and using Scheil's law, one could expect that ingots Cz#1 would be fully n-type and that ingots Cz#2 and Mc#1 would be only 58% p-type if no Ga had been added.

The measured resistivity is found to be higher than calculated with Scheil's law and Klaassen's model depending on different ingots. Several causes might explain these observed discrepancies:

- The error in the B, P and Ga concentrations used to calculate the net doping ($p_0=[B]+[Ga]-[P]$). Difference between theoretical and effective segregation coefficients of B, P and Ga can lead to such errors. Adjustment of the effective segregation coefficients have been presented based on our first results [6].
- The resistivity is calculated considering that all dopants are fully ionized. This assumption might not be valid in highly compensated Si, as suggested in [13] as well as in Ga-doped Si, Ga having a higher ionization energy than boron (72meV compared to 44meV for B).
- Klaassen's model for calculating the mobility might lead to errors in compensated silicon. A gap between theoretical and experimental mobility was already observed in highly compensated Si [3]. This is discussed in the following section.

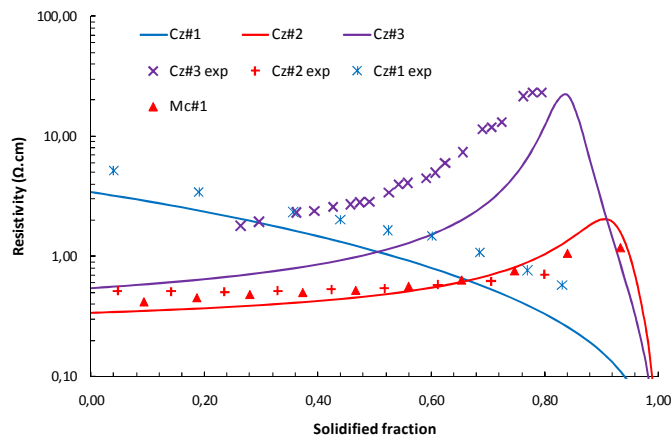


Fig. 1. Comparison between the resistivity calculated using Klaassen's model (lines) and measured on the different ingots (symbol), versus the solidified fraction of each ingot.

3.2. Influence of dopant compensation on carrier mobility

The measured mobilities in samples from Cz#1 are represented in Fig. 2a for majority carriers and on Fig. 2b for minority carriers. Both measured mobilities are in a good agreement with Klaassen's model in the last solidified fraction of the ingot. Since this part of the crystal contains the highest amount of Ga (around $3 \times 10^{17} \text{ cm}^{-3}$) the agreement with Klaassen's model shows that Ga does not impact on the mobility in a significant different manner than B. A large reduction of the mobility, compared to Klaassen's model, is however measured in the first solidified fraction of the ingot. Note that dopant compensation is much more important in that part of the ingot than in the last solidified fraction. To check the influence of compensation on carrier mobility, we have plotted (Fig. 3a) the relative deviation of measured mobility from the calculated mobility using Klaassen's model as a function of the compensation level $Cl = ([B] + [P] + [Ga])/p$. It is clear that the difference between the model and the measurement increases with the compensation level. The same result can be obtained using other mobility models, such as Arora's for instance [14]. The discrepancy between mobility models and experimental values is important, contrary to the results of Rougieux *et al.* [4], who found a good agreement when using samples with

low compensation level (Cl lower than 5). Our results meet the observations of Veirman *et al.* [3], who have used highly compensated Si by thermal donors (Cl up to 140) leading to a drastic reduction of the mobility. In our case the relative difference between data and model can reach up to more than 30% for our highly compensated wafers ($Cl > 20$).

To check that this apparent mobility reduction is not due to a decrease of r_H in highly compensated Si, we have measured the carrier densities by free carrier absorption in the same set of samples and deduced the conductivity mobility from resistivity measurements. Results obtained on samples from Cz#1, are shown on Figure 2.a. As can be seen, FCA and Hall effect are in very good agreement, even in the most compensated part of the ingot. Calculating the r_H using $r_H = p_{FCA}/p_H$ in samples from both Cz#1 and Cz#2 gives an average value of 0.73 ± 0.08 , in perfect agreement with the r_H used for our calculation of p_0 from p_H . This confirms that the observed mobility reduction is to be attributed to a specific compensation effect which is not taken into account in the existing mobility models, rather than to a reduction of r_H .

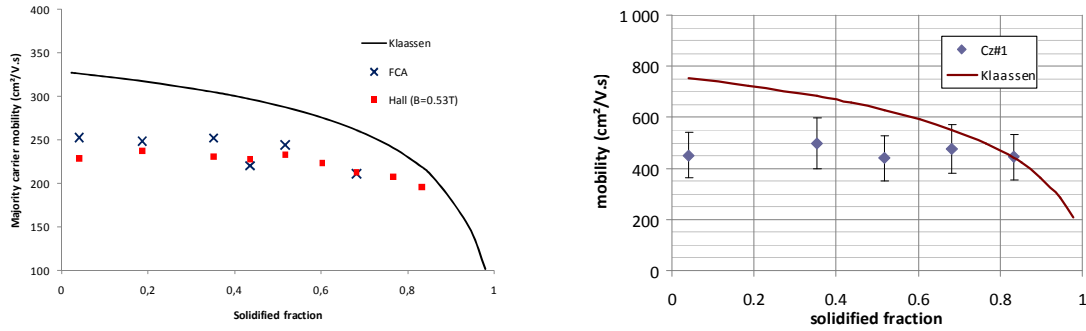


Fig. 2. (a) Majority carrier (holes) mobility measured by Hall effect and free carrier absorption in Cz#1. (b) Minority carrier mobility values on wafer Cz#1, deduced from lifetime measurements, compared to calculated values. Uncertainties are based on the deviation of the linear regression of eq. (2).

We propose therefore to introduce a correction term μ_{cor} depending on the Cl in the mobility calculation, using Matthiessen's rule:

$$\frac{1}{\mu_{conductivity}} = \frac{1}{\mu_{Klaassen}} + \frac{1}{\mu_{cor}} \quad (3)$$

Fig. 3b represents the evolution of this correction term μ_{cor} versus the CL: it can be fitted by a power law: $\mu_{cor} \propto CL^{-3/4}$. Further investigation is needed to explain the physics behind this correction term, but this empirical model should already allow a better prediction of the mobility.

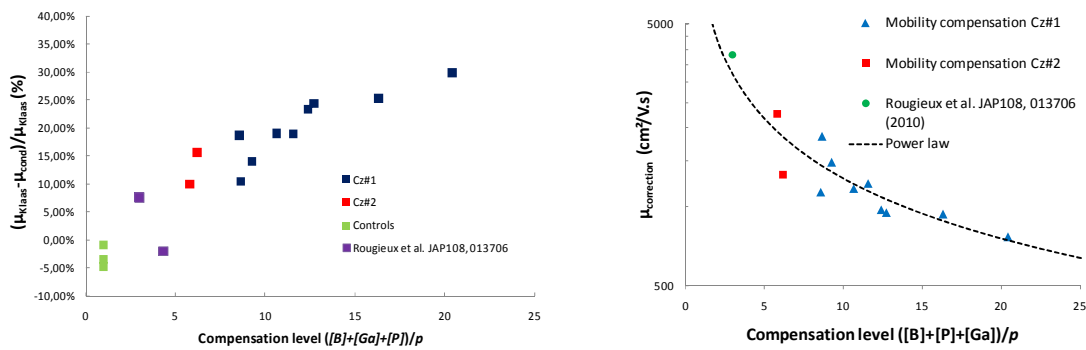


Fig. 3. (a) Relative deviation on the majority carriers mobility depending on the compensation level. Measured data by hall effect are compared to the mobility calculated with the Klaassen's model. (b) Evaluation of the mobility correction term μ_{cor} depending on the compensation level.

4. Conclusion

Gallium addition in boron and phosphorus-doped silicon during ingot crystallization is an efficient way to control the resistivity and the doping type of the resulting ingot, thus increasing the material yield for p-type ingot and wafer production. The mobility measurements in tri-doped silicon showed that the discrepancy between theoretical models and real values increases with the compensation level. An improvement is needed in

the comprehension of the mobility scattering mechanism in highly compensated Si. Nevertheless, we propose an empirical correction factor to the model. This allows to predict with greater accuracy the resistivity in compensated Si.

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