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The accuracy of the standard resistivity–concentration conversion practice estimated by measuring the segregation coefficient of boron and phosphorous in Cz-Si

Armando Giannattasio*, Andrea Giaquinta, and Maria Porrini

MEMC Electronic Materials S.p.a., via Nazionale 59, 39012 Merano, Italy

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* Corresponding author: e-mail agiannattasio@memc.it, Phone: +39 0473 333 222, Fax: +39 0473 333 270

The effective segregation coefficient of boron and phosphorous has been extrapolated from resistivity data collected for a large number of commercial Cz-Si crystals, pulled in similar experimental conditions. A small solidified fraction of the Si melt volume and different initial concentrations of the doping species in the melt have been considered in this study. The dopant concentration in the solid phase has been estimated by converting the resistivity of the Si crystal to the corresponding dopant concentration, according to the standard conversion practice recommended by SEMI. A dependence of the effective segregation coefficient on the initial dopant concentration in the melt has been found experimentally for two specific ranges of concentration. A possible explanation for such dependence, including the effect of the crucible dissolution and the local inaccuracy of the standard resistivity–concentration conversion procedure, is suggested.

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1 Introduction The resistivity of the silicon (Si) crystals normally used in electronics spans over at least six orders of magnitude, ranging from less than 1 mΩ cm (heavily-doped Si) to a few kΩ cm (undoped Si). The concentration of the dopant species incorporated in a Si crystal controls the resistivity of the material. However, the relationship between the dopant concentration and the resistivity is not linear and a standard practice (ASTM, recently re-issued by SEMI [1]) based on some experimental results [2, 3] is normally used in microelectronics to convert the resistivity into concentration of the dopant species and *vice versa*. Czochralski (Cz)-Si wafers are mostly used for VLSI where the resistivity requirements can be very stringent in several applications. The Cz-Si pulling method requires that a certain amount of dopant is normally added to a pure Si charge placed in a quartz crucible. This is heated up above the Si melting temperature and then a seed is dipped into the melt to start a controlled solidification process. In order to attain the expected resistivity in the Cz-Si crystal, the calculation of the correct amount of dopant added to the initial Si charge must be accurate. The laws governing the segregation of the impurities initially present in the liquid phase to the solid phase must be considered in this calculation. In terms of production yield, the acceptable deviation between the actual resistivity measured in a Cz-Si crystal (at a given solidified fraction) and the resistivity initially set as the target value should be as small as possible, ideally not larger than 1%, but in many occasions the discrepancy between the theoretical prediction and the experimental result is much more pronounced. Here we analyze some of the possible causes that produce such discrepancy in boron-doped Si (p-type) and phosphorus-doped Si (n-type). In particular, while studying the effective segregation coefficient of boron and phosphorus in Si in the case of small solidified fractions of the melt volume, we have extrapolated some interesting information on the relationship between resistivity and dopant concentration. In this study we assume that all the boron and phosphorous atoms are isolated and electrically active.

2 Experimental details and methods More than 2000 Cz-Si crystals, p-type, and n-type, have been considered in this work. The crystals were manufactured at MEMC Electronic Materials S.p.a. (Italy) and were (100)-

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oriented, with resistivity ranging from 1 to 300 Ω cm. The crystal pulling conditions were typical of the processes normally used in modern Cz-Si manufacturing and the diameter of the crystals was either 200 or 150 mm. Because of paper length restrictions, most of the details reported here will refer only to boron-doped crystals. However, since a similar study is being carried out on phosphorous-doped crystals, some preliminary results obtained from n-type Si will be also shown in the next session. Each p-type crystal was pulled from a high-purity Si charge opportunely doped by adding a certain amount of boron-doped Si material of well-known resistivity (typically 3.4×10^{-3} to $4.4 \times 10^{-3}\,\Omega\,\text{cm}$). The number of boron atoms initially present in the Si melt was estimated by converting the resistivity of the initial doping material to the corresponding dopant concentration, according to the well-known resistivity–concentration conversion equation for boron in Si [1]. In the case of crystals with a very low resistivity target, pure "metallic" boron (density $= 1.3 \times 10^{23}\,\text{cm}^{-3}$) was used as the doping material instead of boron-doped Si. The experimental data [2, 3] from which the conversion equation is extrapolated, are reported in Fig. 1. The boron concentration in the doping material was larger than $10^{19}\,\text{cm}^{-3}$ according to Fig. 1; assuming that the resistivity–concentration conversion is accurate in this high-concentration range and by knowing the exact amount of doping material added to the pure Si charge, the total number of boron atoms initially present in the melt was easily deduced within a reasonably small error. During the solidification process, the segregation of boron is governed by the normal freezing equation [4]:

$$C = k_{\text{eff}} C_0 (1-g)^{k_{\text{eff}}-1}, \tag{1}$$

where C_0 is the initial concentration of boron in the melt, C is the concentration of boron in the crystal (near the melt–solid interface) after the fraction g of the initial melt volume was solidified, k_{eff} is an effective segregation coefficient for boron which includes the effect of several parameters controlling the crystal growth such as, for example, the pull rate and the rotation speed of the growing crystal. In the experiments described here, we considered for each Si crystal a small solidified fraction, typically between 1 and 2%, depending on the specific growth process, corresponding to the base of the conical part of the crystal (the seed-end) or, equally, the beginning of the cylindrical part forming the rod. The bulk resistivity of a Si wafer taken from the seed-end of each crystal was measured by using standard four-probe techniques. The boron concentration in the solid was then deduced by using the standard resistivity–concentration conversion. Since the parameters C_0, C, and g in Eq. (1) were all known, it was possible to extrapolate the effective segregation coefficient for each crystal directly from Eq. (1) using an iterative method to find k_{eff} numerically. This approach is rather different from that normally used to extrapolate the effective segregation coefficient from a log–log plot of Eq. (1) [5] and the value of k_{eff} as deduced in this study may depend on g. However, for the aim of this work we do not need to consider such dependence on g because the values of k_{eff} extrapolated here were all calculated within a specific range of small solidified fraction (1–2%) for consistency.

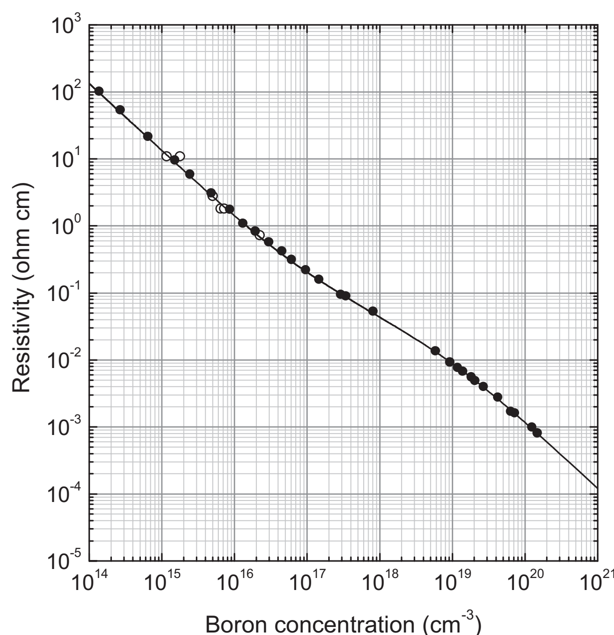

Figure 1 Resistivity–concentration plot for boron in Si. Data points are taken from Ref. [2, 3]: closed circles are related to *C–V* measurements, open circles indicate data from nuclear track experiments. The black line represents the standard fitting function [1].

Equation (1) does not include the effect of impurity atoms that can be released from the crucible in significant concentration due to quartz dissolution. These atoms may play an important role in controlling the resistivity, particularly in Cz-Si crystals for which the expected dopant concentration is small (or, equivalently, the resistivity is high). In the case of small g values, if the contribution of the dissolving crucible to the total boron concentration in the melt (at a given g or at a specific process time) is denoted by C_c, then Eq. (1) can be rewritten as

$$C \approx k_{\text{eff}} (C_0 + C_c)(1-g)^{k_{\text{eff}}-1}. \tag{2}$$

From (1) and (2) we can obtain an expression for the corrected segregation coefficient, k_{corr}, that takes the additive dopant concentration due to the dissolution of the crucible into account. This can be written as

$$k_{\text{corr}} \approx \left(1 + \frac{C_c}{C_0}\right) k_{\text{eff}}. \tag{3}$$

If $C_0 >> C_c$ then $k_{\text{corr}} \approx k_{\text{eff}}$ and the effect of the boron atoms introduced by the crucible dissolution is negligible. The concentration C_c due to the boron content in the crucible can be explicitly written as a function of the crucible dissolution rate γ, the area A of the crucible surface exposed

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to the melt, the volume V initially occupied by the melt, the process duration t, the fraction of boron contained in the quartz crucible f, the boron atomic weight m_B and the Avogadro's number N_0, as in the following equation

$$C_c = \gamma A\, t\, f \frac{N_0}{m_B V}. \tag{4}$$

According to the quartz specifications, the crucibles used to grow the crystals described here had a nominal concentration of boron equal to 0.05 ppmw. This value was considered in Eq. (4) where the other parameters were also estimated to deduce C_c in the experimental conditions described in this work.

3 Results

Figure 2 shows the effective segregation coefficient deduced for each crystal as a function of the resistivity measured in the solid, for a specific solidified fraction (<2%) corresponding to the seed-end. The blue circles in Fig. 2 represent data from crystals doped by adding the correct amount of p-type Si material to the melt. The red circles in Fig. 2 refer to crystals of low resistivity, doped by adding metallic boron to the Si charge. In this low resistivity range (<0.1 Ω cm) the data are all scattered around a typical value and do not show any particular trend.

On the contrary, data indicated by blue circles show an increase of the effective segregation coefficient with increasing resistivity. In particular, for resistivity values larger than approximately 10 Ω cm the observed increase in the segregation coefficient is due to additional boron produced by the dissolved portion of the crucible and it is well predicted by Eq. (3). The black dashed line in Fig. 2 represents a good fit to the experimental data for boron and

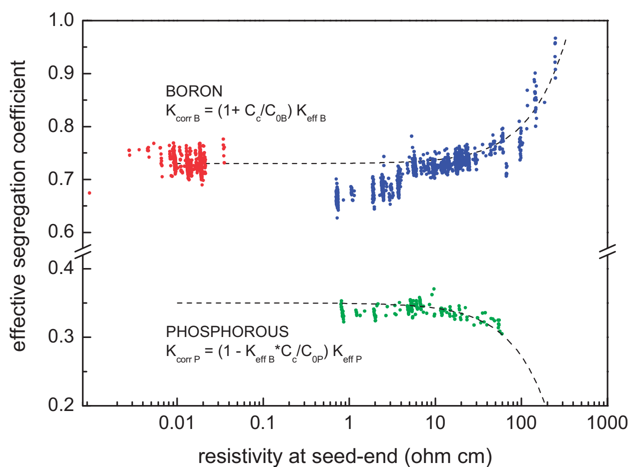

Figure 2 (online color at: www.pss-a.com) Experimental results for the effective segregation coefficient of boron (blue and red) and phosphorous (green) as a function of the resistivity measured at the crystal seed-end. Blue circles refer to crystals doped with suitable p-type Si material of low resistivity. Red circles correspond to crystals doped with pure boron; the average value for these low resistivity data is $k_{eff} = 0.73$. For phosphorous $k_{eff} = 0.35$ was taken for data fit.

was calculated by considering in Eq. (3) different values of C_0, with $C_c = 1.2 \times 10^{13}\,\mathrm{cm}^{-3}$ (the fitting parameter) and $k_{eff} = 0.73$, which was the average value for k_{eff} measured in the low resistivity range (<0.1 Ω cm). This value for k_{eff} is comparable to that measured for resistivity values falling between 5 and 10 Ω cm, where the effect of the crucible dissolution and related impurities is not as pronounced as in the higher resistivity range. Interestingly, at approximately 5 Ω cm we observe a kink in the distribution profile of the data in Fig. 2 and below this value the effective segregation coefficient deviate significantly from $k_{eff} = 0.73$ and from Eq. (3), apparently without a clear explanation for this result. The effective segregation coefficient measured in the middle range 0.7–5 Ω cm is surprisingly smaller than that measured at much lower resistivity values. Figure 2 also shows data for phosphorous-doped Si which seem to follow a modified version of Eq. (3) for this specific case. This includes the compensation effect on the net dopant concentration produced by the incorporation of boron atoms present in the liquid phase in concentration $C_c = 1.2 \times 10^{13}\,\mathrm{cm}^{-3}$. In the case of phosphorous, it is difficult to establish from Fig. 2 if there is a trend similar to that observed for boron in the range 1–5 Ω cm and more data are certainly needed. The value of C_c deduced by fitting the data in Fig. 2 can be used in Eq. (4) to calculate a value for the crucible dissolution rate, which in this case gives $8.5 \times 10^{-7}\,\mathrm{g\,cm^{-2}\,s^{-1}}$, in good agreement with the results published by other authors [6].

4 Discussion

The coefficient k_{eff} depends on several pulling parameters as well as on the dopant concentration in the melt, if this becomes very large. However, for a boron concentration in the melt lower than $10^{20}\,\mathrm{cm}^{-3}$ (as in this work), there is no significant dependence of the segregation coefficient on the dopant concentration [7]. Besides, according to some published data, it seems that even the crystal rotation does not have a strong influence on k_{eff} for values of the rotation speed larger than 7 rpm [5]. Thus, we assume that, under the standard crystal growth conditions considered in this work, k_{eff} can be taken as a constant typical of the chemical species present near the liquid–solid interface. If the growth conditions are effectively unchanged, k_{eff} should not vary significantly with increasing the dopant concentration up to $10^{20}\,\mathrm{cm}^{-3}$. In the present study, the effective segregation coefficient measured in the low resistivity range (<0.1 Ω cm) was not affected by any error due to resistivity–concentration conversion since the atomic concentration of boron in the melt was deduced by considering the density and the weight of metallic boron (the doping material in this case) added to the charge. Unlike the data collected at low resistivity values, the data plotted in Fig. 2 and collected between 0.7 and 300 Ω cm are all affected by an intrinsic error due to the conversion between resistivity and dopant concentration. In this range, the resistivity–concentration conversion was needed to estimate the number of boron atoms initially present in the melt (in this the doping material consisted of boron-doped Si, not pure boron). For resistivity values below 5 Ω cm, where the

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effect of boron from the dissolving crucible on the measured resistivity is negligible, the effective segregation coefficient was not expected to vary significantly. In fact, k_{eff} in this range should be very close to the average value obtained from low resistivity data, that is 0.73 (red circles, Fig. 2). This is actually a reasonable value for the processes and growth conditions considered in the present paper and it is in agreement with previous results achieved in similar experiments [6]. In the specific resistivity range 0.7–5 Ω cm, the deviation of the effective segregation coefficient from the expected trend reported in Fig. 2 has a subtle explanation. This effect is here attributed to the local inaccuracy of the resistivity–concentration conversion practice defined by the SEMI standard and used in this investigation. In fact, by looking at the plot of Fig. 1, the number of experimental data considered in previous studies [2, 3] to work out a fitting equation and a standard resistivity–dopant concentration conversion procedure [1] is perhaps not sufficiently large, given that the resistivity range covers seven orders of magnitude. In particular, there are just a few data points in the resistivity range 0.7–5 Ω cm, which are unlikely to generate a very accurate fitting function. In practice, the extrapolation of a single and accurate conversion equation covering such wide resistivity range is not an easy task. The boron concentration in the solid is regulated by Eq. (1), thus for each crystal the boron concentration at the seed-end can also be deduced from Eq. (1) (with $k_{eff} = 0.73$) rather than converting the resistivity of the material into dopant concentration, as described previously in Section 2. Both the data of the concentration deduced from Eq. (2) and the resistivity measured in each crystal have been plotted in the graph of Fig. 3, which also shows the predicted values calculated according to the standard conversion equation (black line). The experimental data of Fig. 3 reflect what already observed in Fig. 2, that is a sudden deviation of the data points from the predicted values in crystals with resistivity below 5 Ω cm. The deviation is indicated by a red dashed line in Fig. 3. In addition, the data referring to resistivity values larger than 30 Ω cm are also not aligned with the standard resistivity–concentration conversion, but this is the effect due to the extra boron atoms introduced by the crucible dissolution. Such data would result aligned with the standard conversion curve if the correction to the effective segregation coefficient defined by Eq. (3) had been introduced in Eq. (1). A different explanation is needed for the data in the range 0.7–5 Ω cm, which deviate by up to approximately 10% from the values predicted by the SEMI standard (see inset in Fig. 3). We suggest that the explanation in this case is associated with the poor accuracy of the standard resistivity–concentration conversion in that particular range. By fitting the experimental data reported here, a more accurate expression for the resistivity–concentration conversion in the resistivity range 0.7–5 Ω cm, can be the following:

$$N_A = \frac{10^{16.207}}{\rho^{1.101}}, \qquad (5)$$

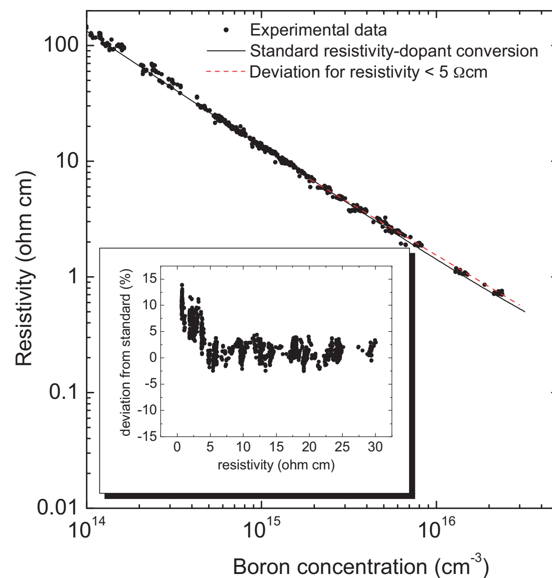

Figure 3 (online color at: www.pss-a.com) Experimental data of the resistivity as a function of the boron concentration. The inset shows the deviation with respect to the standard resistivity–concentration conversion, which can be up to ~10%.

where N_A is the boron concentration and ρ is the resistivity. Below 0.1 Ω cm and above 5 Ω cm the standard conversion equation defined by SEMI should be considered accurate.

5 Conclusions A study of the effective segregation coefficient of boron and phosphorous in Si as a function of the dopant concentration in the liquid has opened up a more general discussion on the accuracy of the standard practice for resistivity–dopant concentration conversion. According to the data for p-type Si, there is a resistivity range (0.7–5 Ω cm) where the error introduced by the conversion can be up to ~10% with respect to the actual boron concentration in the crystal. This discrepancy, which probably does not represent a major concern in most of electronic applications, is rather important in Cz-Si manufacturing where a higher accuracy in targeting the expected value normally translates in a quantifiable improvement in the production yield.

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