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# Transport properties of p-type compensated silicon at room temperature

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## ABSTRACT

Deliberate dopant compensation has proven to be an effective way to control ingot resistivity, although the impact of compensation on carrier recombination and mobilities remains under investigation. This paper summarizes recent findings regarding the carrier transport properties of compensated silicon. The capacity of common mobility models to describe compensated silicon is reviewed and compared to experimental data. The observed reduction of both majority and minority carrier mobility due to dopant compensation is described in terms of the underlying scattering mechanisms. The related problem of conversion between resistivity and dopant density in compensated silicon is discussed, and published values of the Hall Factor in compensated silicon are reviewed. Copyright © 2010 John Wiley & Sons, Ltd.

## 1. INTRODUCTION

To reduce module costs the PV industry aims at using cheaper materials. This can be achieved through less energy intensive purification techniques resulting in less pure silicon, known as Solar Grade Silicon (SoG-Si). Impurities that act as shallow acceptors and donors are difficult to remove using such techniques, meaning that SoG-Si is often compensated. Compensation reduces the net doping ($p_0 = N_A - N_D$ for p-type silicon) and thus increases the resistivity ($\rho = 1/q p_0 \mu_P$). This helps to control carrier recombination. Nevertheless, for a given resistivity, compensated silicon possesses more ionized impurities than non-compensated silicon. An important consequence of the higher impurity concentration is a lower carrier mobility in such material.

This has several consequences concerning the use of compensated silicon for solar cells. Firstly, many measurement techniques rely on mobility models to analyse data under various temperature and injection levels. Those measurement techniques may become less accurate when measuring compensated silicon if the mobility models were not built to take compensation into account. Secondly,

the reduced minority carrier mobility will act to reduce the efficiency of solar cells. Until this minority carrier mobility is well characterized, the impact of compensation on solar cell efficiency remains difficult to predict. The majority carrier mobility reduction will also influence the solar cell efficiency mainly through increased series resistance. Thirdly, the traditional use of resistivity measurements to determine the net doping of a wafer cannot be applied accurately for compensated silicon, due to the majority carrier mobility reduction. The use of Hall measurements to determine the net doping is also uncertain as the Hall Factor could be affected by compensation.

In this work, we analyse the different carrier scattering mechanisms influencing mobilities in compensated silicon, allowing us to identify the best mobility models for compensated silicon. We also review the impact of compensation on the minority carrier mobility and diffusion length. Using several sources from the literature we then review the effect of compensation on the majority carrier mobility. This allows us to validate several ways of converting resistivity into net doping. Finally, we review values for the Hall Factor over a broad range of dopant densities and compensation ratios.

## 2. SCATTERING MECHANISMS

Solar cells are low electric field devices, and the carrier mobility of interest in solar cells is the bulk mobility. Various scattering mechanisms contribute to limit the bulk carrier mobility in silicon. These include defect scattering (crystals defects, impurities), carrier–carrier scattering and lattice scattering (intra and intervalley [1]). Hole–hole ($\mu_{h,h}$) and electron–electron ($\mu_{e,e}$) scattering can not alter the total momentum but can increase the momentum transfer rate [2], as such they only represent a second order effect on the mobility [3,4].

In single crystal silicon at room temperature, crystal defects are almost inexistent and the bulk mobility of electrons and holes has previously been shown to be mainly affected by ionized donor and acceptor impurity scattering ($\mu_{e,D}$, $\mu_{e,A}$, $\mu_{h,D}$, $\mu_{h,A}$), electron–hole scattering ($\mu_{e,h}$, $\mu_{h,e}$) and lattice scattering ($\mu_{e,L}$, $\mu_{h,L}$) [4]. Using Matthiesen's rule, the total mobility is given by the sum of these terms [3,4]:

$$\frac{1}{\mu_e} = \frac{1}{\mu_{e,L}} + \frac{1}{\mu_{e,D}} + \frac{1}{\mu_{e,A}} + \frac{1}{\mu_{e,h}} \qquad (1)$$

$$\frac{1}{\mu_h} = \frac{1}{\mu_{h,L}} + \frac{1}{\mu_{h,D}} + \frac{1}{\mu_{h,A}} + \frac{1}{\mu_{h,e}} \qquad (2)$$

How will compensation affect these various scattering mechanisms? Figures 1 and 2 show the contribution of all these mechanisms in compensated p-type silicon for various compensation ratios ($R_C = (N_A + N_D)/(N_A - N_D)$). From $R_C = 1$ (non-compensated, $N_D = 0\,\mathrm{cm}^{-3}$) to $R_C = 100$ (nearly fully compensated, $N_D = 0.98 \times N_A$) the graphs shows the effect of introducing donors at a fixed acceptor
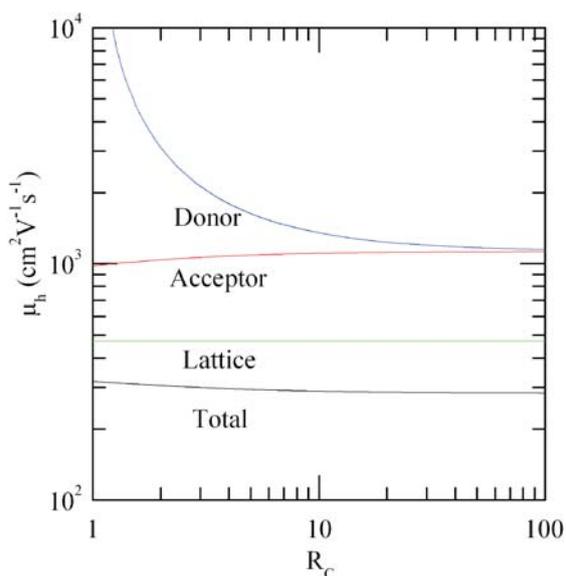


**Figure 1.** Majority hole mobility as a function of compensation ratio for silicon with $N_A = 1 \times 10^{17}\mathrm{cm}^{-3}$, the contributions of the various scattering mechanisms are shown.



**Figure 2.** Minority electron mobility as a function of compensation ratio for silicon with $N_A = 1 \times 10^{17}\mathrm{cm}^{-3}$, the contributions of the various scattering mechanisms are shown.
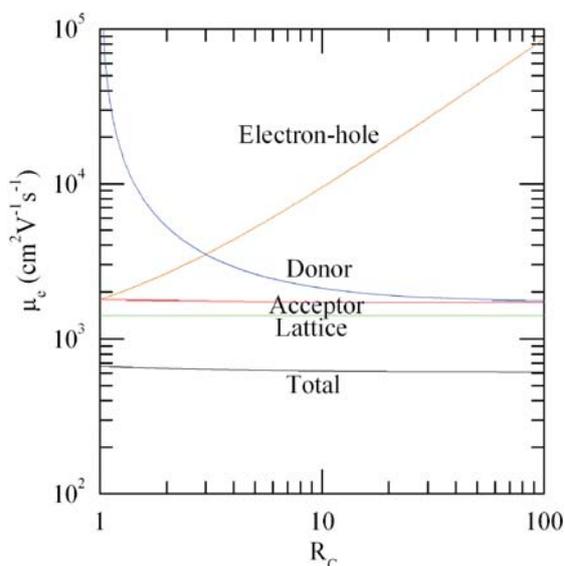
concentration ($N_A = 1 \times 10^{17}\mathrm{cm}^{-3}$). The mobilities are simulated with *Klaassen's* mobility model [3,4]. Figure 1 shows the majority hole mobility. The compensated donors are ionized at room temperature and thus act as additional ionized scattering centres, reducing the mobility. For increasing donor concentration (increasing compensation), the acceptor scattering mechanism becomes slightly less effective. This is due to screening of acceptors by donors. This means that acceptors are more effective scattering centres for very low compensation ratio. Near full compensation ($R_C = 100$), the effect of the acceptor and donor becomes similar. The global result of the three scattering mechanisms shown in Figure 1 is that the majority carrier (hole) mobility is only very slightly reduced by compensation. This is due to the fact that in this example the dominant mechanism is lattice scattering.

Figure 2 corresponds to the minority electron mobility. Because electrons are minority carriers they see many holes, whereas holes virtually see no electrons ($p \times n = n_i^2$). This means that electron–hole scattering is a significant scattering mechanism reducing minority electron mobility in lowly compensated materials ($R_C < 3$ in Figure 2). In compensated silicon the hole concentration is reduced, leading to a strong reduction of the electron–hole scattering. The contribution of the electron–hole scattering on the total minority carrier mobility becomes negligible. Nevertheless, this effect is not sufficient to counteract the additional donor scattering, and so the minority electron mobility still decreases slightly with compensation. The total carrier mobility in Figures 1 and 2, showing only a small dependence on $R_C$, may lead to believe that compensation does not have a significant impact on mobility. This is true in the sense of the addition of donors to a given acceptor concentration not altering the

mobility much. However, the addition of donors produces a tremendous change on the free carrier density and hence on the resistivity. If a comparison was made between silicon of the same resistivity, one compensated and the other not, then the impact of compensation on carrier mobility would seen to be very large. This is the type of comparison most commonly done in practice.

## 3. MOBILITY MODELLING IN COMPENSATED SILICON

Previous measurements using Free Carrier Absorption [5], Capacitance Voltage [6–8], Glow Discharge Mass Spectroscopy [9] or the Hall method [6] [10,11] have shown that the majority carrier mobility in silicon is significantly affected by compensation. However, it is well known that some of those methods are also affected by the presence of grain boundaries in the wafer [12]. To isolate the impact of compensation on mobility we review only mobility data from single crystal silicon. The data of *Macdonald et al.* [5], *Pizzini et al.* [11] and *Libal et al.* [10], in phosphorus compensated single-crystal silicon is used. The experimental acceptor and donor density allows us to determine the theoretical mobility using different models [3,4,13–19]. It is important to note that some of those model uses the net doping ($p_0$) as an input parameters, leading to large errors for compensated silicon (Figure 4). To avoid such error the dopant sum ($N_A + N_D$) instead of the net doping ($N_A - N_D$) is used in our calculations. The calculated mobility is then compared to the experimental mobility. The average error is shown in Table I.

The 20% uncertainty obtained using *Dorkel–Leturcq's* [16] shows that this models is not well suited to describe the effect of compensation on majority carrier mobility. *Klaassen's* [3,4], *Reggiani's* [13] and *Arora's* [15] models lead to uncertainties of approximately 10%, making them better candidates to simulate mobility in compensated silicon.

Figure 3 plots the simulated mobility as a function of the compensation ratio for different acceptor concentrations. The models of *Klaassen* [3,4], *Reggiani* [13], *Arora* [15] and *Dorkel–Leturcq* [16] are used. Even for non-compensated silicon ($R_C = 1$), *Arora's* model and *Dorkel–Leturcq's* model are inaccurate. This partly explains the error due to the use of those two models as displayed in Table I. The variation induced by compensation is also very strong. This is due to the very simple formulation of those models. Indeed they do not take into account the separate influence of acceptor and donor but only the influence of the total impurity concentration ($N_A + N_D$). They also implicitly assume that the free carrier concentration is equal to the total dopant concentration, which is not true in compensated silicon. This applies to other model such as *Caughey–Thomas* [19], *Thurber* [17,18] and *Masetti* [14]. On the other hand, *Klassen's* model and *Reggiani's* model agree well for non-compensated silicon, but *Reggiani's* model seems to be less influenced by compensation.

**Table I.** Error of common mobility model in predicting the majority carrier mobility from acceptor and donor densities.

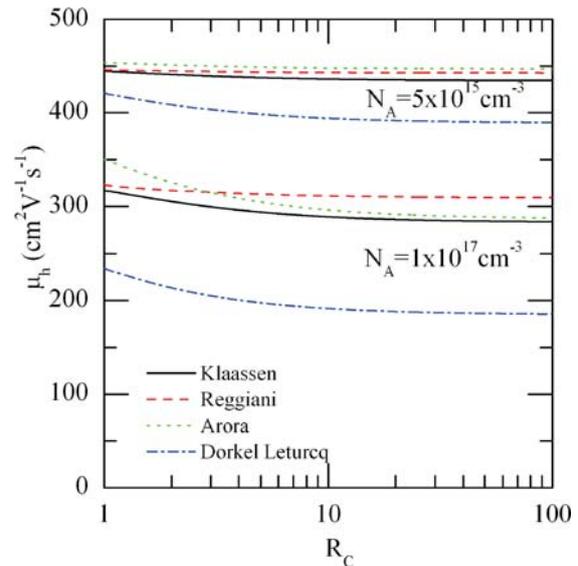| Mobility model | Model parameter | Average error (%) |
|---|---|---|
| Klaassen | $N_A$, $N_D$ | 9.7 |
| Reggiani | $N_A$, $N_D$ | 10.3 |
| Arora | $N_A + N_D$ | 12.4 |
| Dorkel–Leturcq | $N_A + N_D$ | 19.0 |



**Figure 3.** Majority hole mobility as a function of compensation ratio for various mobility models.
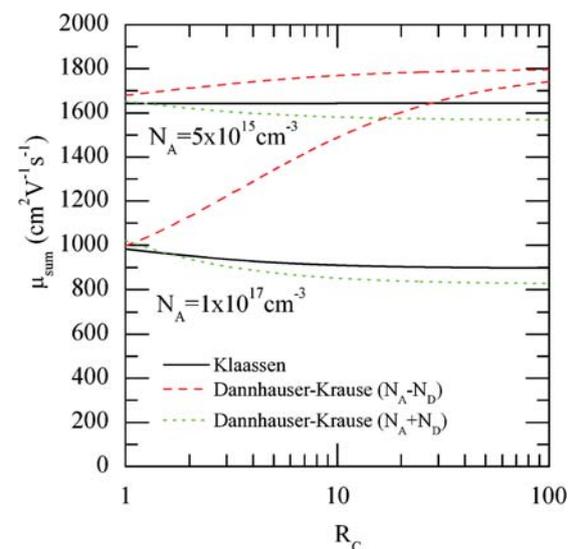


**Figure 4.** Sum of the electron and hole mobility as a function of compensation ratio with Klaassen model and Dannhauser and Krause model.

Both *Klaassen's* model and *Reggiani's* model are based on the empirical model of *Masetti et al.* They introduce a temperature dependence of the doping related parameters and most importantly they take into account the different scattering cross sections of acceptors and donors. *Reggiani's* model fits the experimental data well on non-compensated silicon over a wider range of temperature than *Klaassen's* model [13]. Nevertheless at room temperature *Klaassen's* model has been shown to be more precise for non-compensated silicon [13]. Moreover *Klaassen's* model takes into account electron–hole scattering as well as screening mechanisms. By taking those mechanisms into account *Klaassen's* model is thus, in principle, more suited for mobility modelling in compensated silicon, even if it makes little difference in practice (Table I).

The average errors seen in Table I may be at least partly due to the uncertainty in both the acceptor and donor density measurements, and in the mobility measurements. However, they may also reflect a deficiency of *Klaassen's* model to properly take into account electron–hole scattering and screening effects. Indeed, this model is based upon non-compensated data, where the acceptor concentration and the majority carrier concentration are equal, in which case it is difficult to differentiate between the effect of acceptors and the effect of holes on the electrons. As pointed by *Veirman et al.* [6], several other physical mechanisms specific to compensated silicon, including space charge region scattering and carrier trapping within potential wells, can also alter the mobility [6]. Those mechanisms are not taken into account in these mobility models, and so may also explain the errors seen above.

Another important implication of altered mobilities in compensated silicon is that many common characterization techniques are set up to measure uncompensated samples. What is the impact of compensation on such characterization techniques? In the Quasi-Steady State Photoconductance technique (QSSPC) for example, the net doping is needed as an input parameter [20]. The mobility model of *Dannhauser and Krause* [21,22] is then used to simulate the sum of the electron and hole mobility for different injection levels. Figure 4 shows the model of *Dannhauser and Krause* with the net doping ($N_A - N_D$) and the dopant sum ($N_A + N_D$) as input parameter compared to *Klaassen's* model. Using the net dopant density as the input parameter for this model will inevitably yield an overestimation of the carrier mobility, and an underestimation of the lifetime. It is thus necessary to input the dopant sum, as a basic approximation, instead of the resistivity/net doping, in order to obtain reasonable carrier lifetimes.

# 4. MINORITY ELECTRON MOBILITY REDUCTION

In a solar cell, the short circuit current $J_{sc}$ depends on the minority carrier diffusion length ($L_n = \sqrt{(D_n \times \tau_n)}$). The saturation current density $J_0$ also depends on the minority carrier lifetime ($\tau_n$) as well as on the minority carrier
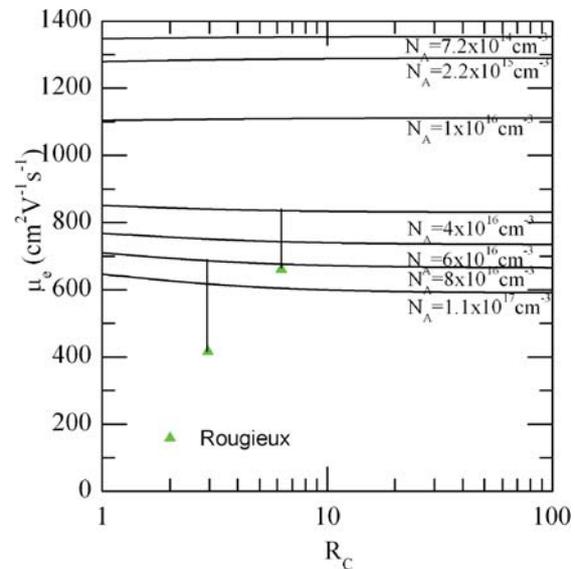


**Figure 5.** Minority electron mobility in compensated p-type silicon as a function of compensation ratio.

diffusivity ($D_n = kT/q^* \mu_n$). Many authors have reported an increase of the diffusion length ($L_n$) with compensation [9,11,23–25]. Direct measurement of the lifetime in p-type mono-crystalline silicon has shown that the presence of phosphorus can increase the lifetime by a factor of three [5], compared to control samples with similar concentrations of boron, due to a reduction of the net doping [9,10]. It is thus of interest to examine how the minority electron lifetime increase and mobility reduction combine to change the diffusion length. Unfortunately, data concerning minority carrier mobilities in compensated silicon are scarce. One study, using surface limited effective carrier lifetime measurements, has reported a 40% decrease of the minority carrier mobility with compensation [26]. Figure 5 shows this data, in comparison to Klaassen's model. It appears that the model underestimates the mobility reduction with doping density. According to the model, the minority electron mobility is not expected to decrease by more than 9% for a fully compensated sample with $N_A = 1 \times 10^{17} cm^{-3}$. This would correspond to less than a 5% reduction in diffusion length, in which case the impact of electron mobility reduction on the cell efficiency would be expected to be minimal. However, the measured decrease of 40% would result in a larger reduction of 22% in the minority carrier diffusion length, which is more significant, but still tolerable.

# 5. MAJORITY HOLE MOBILITY REDUCTION

Figure 6 shows the effect of compensation on the majority carrier mobility. The data of *Macdonald et al.* [5], *Pizzini et al.* [11] and *Libal et al.* [10] in phosphorus compensated single-crystal silicon are shown. The data of *Veirman et al.*
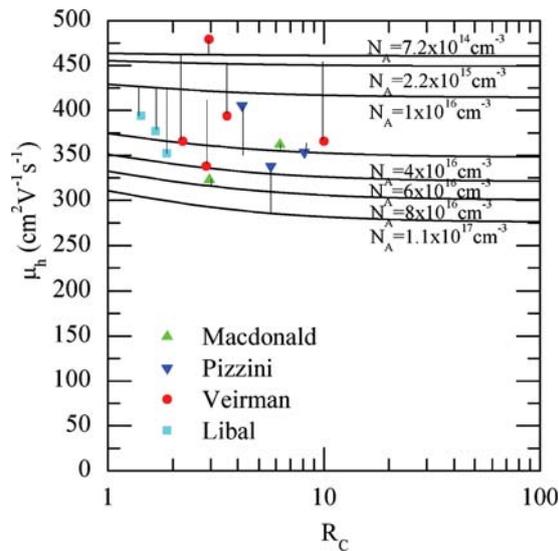
**Figure 6.** Majority hole mobility in compensated p-type silicon as a function of compensation ratio.

[6] in single-crystal silicon compensated with thermal donors are also displayed. Considering that the mobility values from *Pizzini et al.*, *Libal et al.* and *Veirman et al.* were obtained using the Hall method, a Hall Factor of 0.71 is applied to those values to obtain the conductivity mobility [26]. The experimental data fit reasonably well, on average, with *Klaassen's* model. Data from Pizzini are slightly higher than the modelled values, while data from Veirman and Libal are lower. Macdonald's data are in best agreement. As pointed out before, the discrepancy between experimental and simulated values can be partly due to experimental uncertainty in the determination of the mobility (net doping and resistivity), and uncertainty in the determination of the acceptor and donor concentration. The latter leading to inaccurate input parameters in the mobility model. Within experimental uncertainty a general decrease of mobility with increasing compensation ratio is observed with a drop of up to 25% in mobility at similar $N_A$. This is also higher than the simulated 11% reduction in mobility for a fully compensated sample with $N_A = 1 \times 10^{17} \text{cm}^{-3}$.

# 6. Hall FACTOR IN COMPENSATED SILICON

Of the model considered, *Klaassen's* is the most suited to determine the majority hole mobility in compensated p-type silicon. For now, this model is the best choice to convert resistivity into net doping. An easy way to determine the net doping is to use *Klaassen's* model combined with an impurity segregation model to obtain an ingot doping profile using an ingot resistivity profile. Another way to determine the net doping of a wafer is to use a method based on the association time constant of iron–boron pairs [27]. This allows for the determination of

$N_A$ in a wafer. Using a resistivity measurement and the value of $N_A$, one can then iteratively obtain the net doping and $N_D$ using *Klaassen's* model.

The most common way to measure the net doping is to use the Hall method. The Hall method measures the resistivity and the Hall carrier density $p_{0,H}$ in the wafer. The Hall carrier density is different to the net doping or conductivity carrier density by a factor called the Hall Factor ($r_H = p_0/p_{0,H}$). This factor depends on the carrier type, the dominant scattering mechanisms, temperature and the magnitude of the magnetic field. In order to obtain net doping values using the Hall method it is thus fundamental to know the value of the Hall Factor in compensated silicon. The Hall Factor has been found to be larger than 1 in n-type silicon and smaller than 1 in p-type silicon [28,29]. It has been demonstrated that the non-parabolic and anisotropic structure of the valence band causes the Hall Factor to be smaller than one in p-type silicon [29]. The Hall Factor also depends on the scattering mechanisms, and thus partly on the dopant concentration. Nevertheless the effect of dopant scattering on the Hall Factor has previously been shown to be minimal in non-compensated silicon [30,31]. Compensation, being mainly an increase in dopant scattering, is thus not expected to have an important impact on the Hall Factor at room temperature. To confirm this, Hall Factors previously determined in compensated silicon are displayed in Figure 7. The data of *Rougieux et al.* [26] in phosphorus-compensated silicon, *Morin et al.* [31] in low purity compensated silicon and *Veirman et al.* [6] in silicon compensated by thermal donor is used. The Hall Factor is, within uncertainties, quite constant, with an average value
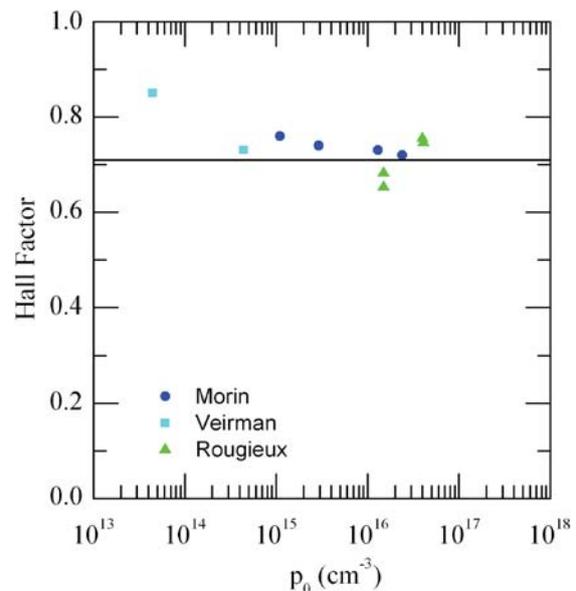


**Figure 7.** Hall Factor in compensated p-type silicon as a function of the net doping.

of 0.71. This value is similar in non-compensated silicon (0.8 [30], 0.75 [31]).

# 7. CONCLUSION

Compensation leads to reduced screening by free carriers, lower electron–hole scattering and greater impurity scattering, leading to an overall reduction in mobilities. Klaassen's model takes into account all those effects, and predicts the resulting reduction in majority carrier mobility in p-type silicon with reasonable accuracy. As such this model is so far the most appropriate to convert resistivity into net doping, provided the acceptor concentration is known or the resistivity can be fitted to an ingot segregation profile. However, those scattering mechanisms can differ in compensated silicon and other physical mechanisms can influence the mobility especially at high compensation. There is thus room for improvement in the modelling of mobility in compensated silicon. Moreover the temperature and injection dependence of the mobility remains unknown in compensated silicon. Using the Hall method one can obtain the net doping with a Hall Factor of 0.71 at room temperature. The model predicts that compensation is not expected to have a large impact on the minority carrier diffusion length with less than 5% reduction in diffusion length due to compensation at doping densities of $N_A = 1 \times 10^{17} \text{cm}^{-3}$. Nevertheless, preliminary experimental data indicate that the impact of compensation on minority carrier mobilities is greater than expected, and may lead to a reduction of the diffusion length in the range of 20%, for a given carrier lifetime.

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