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Majority carrier mobility of compensated silicon: comparison of room temperature measurements and models

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Abstract

In this work the measured majority carrier mobility in compensated silicon is compared to values predicted by two different models: Klaassen's model for conventional silicon and the more recent unified model for compensated silicon by Schindler *et al* (Schindler's model). The purpose of the comparison is to broaden the range of materials included in the newly developed model for compensated materials. As observed previously, the deviation of the prediction by Klaassen's model from the experimental data increases with increasing compensation ratio, R_C. It is observed that above a critical R_C value ($R_C > 5.5$) the deviation from the measured values is lower for Schindler's model. Occasionally high deviations are observed, which are believed to be related to unusually high defect density of the samples, *e.g.* defects related to light elements (oxygen and carbon) or metal impurities. Such impurities may contribute considerably to the ionized impurity concentration. Therefore, it is suggested that knowledge of additional parameters to the doping concentration is needed in order to increase the accuracy of Schindler's model.

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1. Introduction

The presence of ionized impurities in compensated feedstocks not only affects the minority carrier lifetime but can also reduce the majority and minority carrier mobility, potentially leading to higher resistive- and recombination losses. Minority carrier mobility is an important parameter in photovoltaic (PV) application, since it relates to the carrier diffusion length and therefore the efficiency of solar cells [1], while majority carrier mobility is a useful parameter for theoretical cell conversion calculation and lifetime simulation. However, complex scattering mechanisms occur in the PV materials produced from cost-effective silicon (*e.g.* upgraded metallurgical and solar grade silicon), which affect the exact estimation of these carrier mobilities [2,3].

Several models are available for the prediction of carrier mobilities in silicon, of which Klaassen's model is commonly used for conventional silicon.

Model 1: Matthiesen's rule [4] was firstly applied in Klaassen's model [5,6] to estimate the theoretical mobility in silicon. However, recent studies [7,8,9] have shown that Klaassen's model overestimates the majority carrier mobility in compensated silicon, and the discrepancy increases with the compensation ratio. Some authors proposed that such discrepancy may be due to a neglected compensation-specific mechanism.

Model 2: Schindler *et al.* [7] therefore proposed a new experimental correction to Klaassen's model, based on the approach of Klaassen for the description of mobilities in compensated silicon. The authors argue that Klaassen's model does not account for decreased screening with increasing compensation level in the range of dopant concentration typically occurring in compensated PV silicon, since the model is based on an empirical mobility expression for uncompensated silicon. They therefore introduce an additional compensation-dependent term into the Caughey-Thomas mobility. Based on this modified expression, the prediction of Klaassen's model of majority carrier mobilities in compensated p-type silicon is significantly improved in terms of experimental data, while the compensation dependent term disappears for $R_C = 1$.

Recent works [9,10] indicate that other factors, *e.g.* inactive dopants or defects, have an impact on the prediction of mobility. This discrepancy is mainly observed in some cost-effective materials with or without compensation, compared to the values calculated by Klaassen's and Schindler's model, respectively. Further investigations are therefore useful in order to validate this approach for minority carrier mobilities as well as mobilities in n-type Si and different types of compensated silicon – materials that usually have other significant impurities besides dopants.

In this work, we present measurements of majority carrier mobilities by Hall effect in three compensated multi-crystalline silicon ingots and several mono-crystalline Si ingots (Czochralski, Cz) doped with different amounts of boron and phosphorus. The experimental measurements are compared to the prediction based on the two models with the aim to understand the properties of our materials and identify the accuracy of these models for alternative silicon feedstock. In addition, potential scattering mechanisms that may affect the prediction of the mobility will be discussed.

2. Materials and methods

2.1. Materials

The samples used in this work are compensated and non-compensated mono-crystalline (Cz) and multi-crystalline silicon wafers. The sample overview is summarised in Table 1. Interstitial oxygen, $[O_i]$ and substitutional carbon, $[C_s]$ concentrations are measured using Fourier Transform Infrared Spectroscopy (FTIR) at room temperature and quantified using SEMI standards MF1188 and MF1391, respectively. The acceptor density (N_A) and donor density (N_D) were assumed to be equal to the [B] and [P] concentrations measured by glow discharge mass spectrometry (GDMS) and/or inductively coupled plasma mass spectrometry (ICPMS). The compensation ratio (R_C) is calculated according to Equation (1):

$$R_C = \frac{(N_A + N_D)}{|N_A - N_D|} \quad (1)$$

Table 1.Overview of the samples investigated in this work, with acceptor and donor densities as well as the corresponding compensation ratio, and light elements concentration (interstitial oxygen and substitutional carbon).

Sample	**type** #	N_A (cm^{-3})	N_D (cm^{-3})	R_C	O_i (cm^{-3})	C_s (cm^{-3})
1-311	Cz, p	$3.3\cdot10^{17}$	$2.6\cdot10^{17}$	8.5	$\sim10^{18}$	NA
1-458	Cz, n	$4.4\cdot10^{17}$	$6.4\cdot10^{17}$	5.3	$\sim10^{18}$	NA
2-162	Cz, p	$1.6\cdot10^{16}$	NA	1.0	$\sim10^{18}$	$<5\cdot10^{16}$
Cz1-S	Cz, p	$1.9\cdot10^{16}$	$9.7\cdot10^{15}$	3.1	$1.2\cdot10^{18}$	$1.1\cdot10^{17}$
Cz1-T	Cz, p	$2.9\cdot10^{16}$	$1.9\cdot10^{16}$	4.9	$6.2\cdot10^{17}$	$3.7\cdot10^{17}$
Cz2-S	Cz, p	$1.7\cdot10^{16}$	$9.8\cdot10^{15}$	3.7	$1.0\cdot10^{18}$	NA
Cz2-T	Cz, p	$2.4\cdot10^{16}$	$2.0\cdot10^{16}$	9.9	$5.9\cdot10^{17}$	NA
Cz3-S	Cz, p	$1.4\cdot10^{16}$	NA	1.0	$1.3\cdot10^{18}$	$1.1\cdot10^{17}$
Cz3-T	Cz, p	$2.3\cdot10^{16}$	NA	1.0	$7.1\cdot10^{17}$	$5.6\cdot10^{17}$
Cz ref	Cz, p	$7.0\cdot10^{15}$	NA	1.0	$5.5\cdot10^{17}$	NA
A1-022	multi, p	$5.0\cdot10^{16}$	$2.0\cdot10^{16}$	2.3	$3.9\cdot10^{17}$	$2.5\cdot10^{17}$
A1-201	multi, p	$7.1\cdot10^{16}$	$4.4\cdot10^{16}$	4.3	$1.3\cdot10^{17}$	NA
A1-212	multi, p	$8.5\cdot10^{16}$	$7.3\cdot10^{16}$	13.2	$1.3\cdot10^{17}$	NA
A3-071	multi, p	$1.8\cdot10^{16}$	$9.1\cdot10^{15}$	3.0	NA	NA
A3-213	multi, p	$3.1\cdot10^{16}$	$2.4\cdot10^{16}$	7.9	NA	NA
A3-234	multi, p	$3.1\cdot10^{16}$	$2.4\cdot10^{16}$	7.9	NA	NA
R6-111	multi, p	$1.4\cdot10^{16}$	NA	1.0	$2.8\cdot10^{17}$	$1.0\cdot10^{17}$
R6-189	multi, p	$1.4\cdot10^{16}$	NA	1.0	$2.2\cdot10^{17}$	$2.6\cdot10^{17}$

2.2. Hall effect measurements and mobility models

Hall mobilities (μ_{Hall}) and majority carrier concentrations (p_{maj}) of monocrystalline silicon in this work were computed from the resisitivity (ρ) and the Hall coefficient (R_H) measured with an Ecopia HMS 3000 using a van der Pauw configuration [11] according to $\mu_{Hall} = R_H/\rho$, and $p_{Hall} = 1/(q \times R_H)$. Ohmic contacts were formed on each 2×2 cm^2 square sample by mechanically embedding liquid indium-gallium (InGa) at the corners of the sample before the Hall effect measurements. The multi-crystalline silicon samples were selected by following the principle of single grain for Hall effect to avoid the influence of grain boundaries [12]. Since all measurements were carried out under low magnetic field conditions ($B \ll 10^4 \mathrm{Tcm}^2/\mathrm{Vs}$), the Hall mobilities and carrier concentrations differ from their true values according to $p_h = p_{Hall} \times r_H$ and $\mu_h = \mu_{Hall}/r_H$, where r_H is reasonably assumed as an independent value on finite compensation level samples at room temperature. The multi-crystalline samples were analysed with r_H = 0.71as an acceptable average for the relevant dopant range, according to Rougieux *et al.* [13], whereas the mono-crystalline samples were analysed with r_H = 0.77 [14]. The experimental values are compared to the calculated values obtained from the models by Klaassen and Schindler *et al.* The calculation and basic parameters are described in Equations **(2-5)** [5,6,7]. The comparisons are reported in the following as the ratio between the experimental value and the calculated value, and are labelled Hall/Klaassen (H/Klaassen) and Hall/Schindler (H/Schindler), respectively. N_A^- and N_D^+ values used in the calculations are reported in Table 1.The drift mobility $\mu_{h,\ Model}$ as calculated with Klaassen's and Schindler's models, using the dopant concentrations (B and P) (see Table 1), is calculated as follows:

$$\frac{1}{\mu_{h,Klaassen}} = \frac{1}{\mu_{Lattice}} + \frac{1}{\mu_{Impurity}} \tag{2}$$

$$\frac{1}{\mu_{h,schindler}} = \frac{1}{\mu_{Klaassen}} + \frac{1}{\mu_{cor}} = \frac{1}{\mu_{Lattice}} + \frac{1}{\mu_{Impurity}} + \frac{1}{\mu_{cor}} \tag{3}$$

$$\mu_{Impurity} = \mu_N \left(\frac{N_{ref}}{N_{A/D}}\right)^{\alpha} + \mu_c \left(\frac{p}{N_{A/D}}\right) \tag{4}$$

$$\mu_{cor} = \mu_N(\frac{N_{ref}}{N_{A/D}})^{\alpha} - \mu_N[\left(\frac{N_{A/D}}{N_{ref}}\right)^{\alpha} + \left(\frac{R_C - 1}{R_{C,ref}}\right)^{\beta}]^{-1} \quad (5)$$

where $\mu_{Lattice}$, $\mu_{Impurity}$ are the lattice and impurity mobility, p is the net doping level; μ_N, μ_C are the fitting parameters; $N_{A/D}$ is the acceptor/donor concentration; and $R_{C,ref}$ and β are fitting parameter for the screening effect.

3. Results and discussion

3.1. Compensation level

The samples presented in this work are cut from different ingots with interstitial oxygen concentrations ranging from $5.9 \cdot 10^{17}$ cm^{-3} to $1.3 \cdot 10^{18}$ cm^{-3} and from $8.0 \cdot 10^{16}$ cm^{-3} to $5.5 \cdot 10^{17}$ cm^{-3} for mono- and multi-crystalline materials, respectively. The possible presence of electrically active oxygen-related defects is not included in the calculation in both models and it could impact the accuracy of the comparison. The different O_i concentrations in materials are used to investigate the accuracy of the two models under the effect of impurity levels besides dopants. The comparisons between the experimental data and the calculated values of majority carrier mobility along the compensation level and total dopant concentrations are reported in Fig. 1 (a) and (b), respectively.

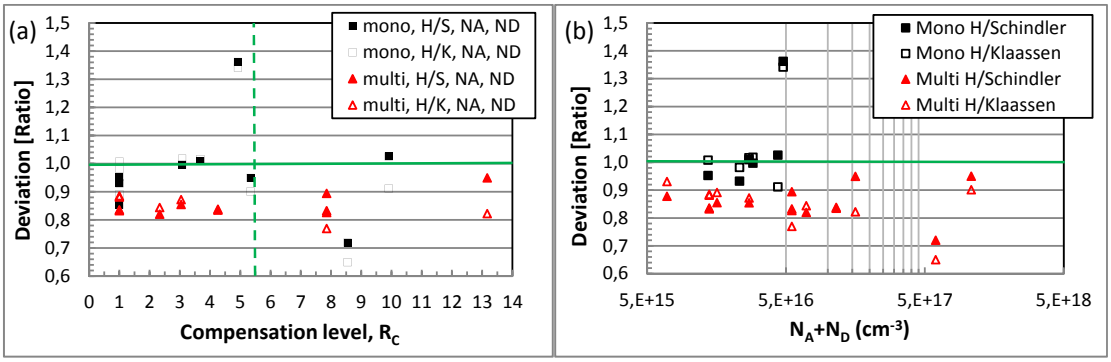

Fig. 1. Comparison of majority carrier mobility as measured by Hall effect and as modelled, plotted against R_C (a) and total dopant concentration (N_A+N_D) (b), respectively. Deviation (ratio) is the experimental value over the calculated value. The dashed line represents R_C = 5.5.

There is no clear linear relationship in either figure. Nevertheless, it is still possible to see that the deviation is more dependent on the compensation ratio than the total doping level, even though the deviations show stable values over the whole range of R_C studied here. Especially above R_C = 5.5, the deviation between the calculation from the two models becomes clearer and the accuracy of the model by Schindler *et al.* seems to become higher, both for the mono- and multi-crystalline samples. This can be explained based on Equation 5 for μ_{cor}, indicating that the compensation effect has considerable influence on the basic scattering mechanism compared to the non-compensation materials, *e.g.* decreased screening effect. This observation therefore indicates that Schindler's model is providing a better fit for increasing compensation levels, especially for R_C > 5.5.

The multi-crystalline samples show a relatively larger but more homogeneous deviation over the whole R_C range compared to the mono-crystalline samples generally with higher O_i and C_s concentration, as shown in Fig. 1 (a). The high deviation at R_C = 4.9 is for a sample from the tail of a p-type Cz ingot, with high concentration of light elements, *i.e.* substitutional carbon ($C_s = 3.6 \cdot 10^{17}$ cm^{-3}) and interstitial oxygen ($O_i = 1.2 \cdot 10^{18}$ cm^{-3}), compared to the other Cz materials. It has been suggested that the significant presence of C_s is affecting the agglomeration of impurities (O_i and metallics) in the material [15,16], *e.g.* leading to a lower density of N_D-like scattering centres by inhibiting the formation of thermal donors. Moreover, our previous work shows that C_s introduces higher vacancy

concentrations, which can cluster with phosphorus and thus decrease the scattering effect of compensation dopants [17]. Furthermore, the possible presence of these defects in the non-compensated samples ($R_C = 1$) accounts for the deviation from the models. For example, Cz-Ref has one of the highest O_i concentration among the materials presented here, and a possible addition of $5 \cdot 10^{15}$ cm^{-3} [18] to the N_D density will enhance the deviation between the experimental and calculated values (from 0.88 to 0.98), *i.e.* light elements contribution to scattering mechanism may not be negligible.

3.2. Incomplete ionization of dopants

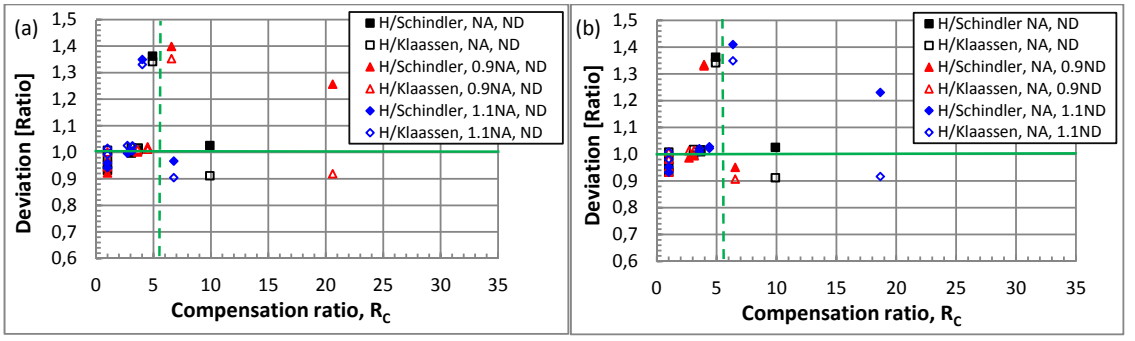

Fig. 2. Effect of potential incompletely ionized boron (a) and phosphorus (b) on the deviation of calculated values using Schindler's and Klaassen's models, respectively.

It has been shown that incomplete ionization is of greater importance in highly doped compensated Si than in uncompensated Si of the same net doping [9]. Given the accuracy and resolution of the dopant measurement techniques (GDMS and ICPMS) and the potential presence of thermal donors, a difference of ±10% concentration of [B] and [P] is used to further estimate the accuracy of the calculations based on the models, as shown in Fig. 2 (a) and (b). The uncertainties in B and P concentrations influence primarily the compensation ratio, and secondarily it enhances the deviation between the models. It is clear that the deviation increases greatly for the material with larger initial compensation ratio, *i.e.* Cz2-T (see Table 1), in good agreement with what observed in Fig. 1(a). A precise prediction of mobility is based therefore on accurately measured doping levels.

The deviation at $R_C = 4.9$ seems not to be well explained only by the uncertainty in measured doping levels. Firstly, the variations in doping levels in Fig. 2 (a) do not introduce significant deviation. Secondly, both Schindler's and Klaassen's models lead to similarly underestimated mobility values, contrary to the observations at higher R_C. Therefore, it is reasonable to believe that there might be another scattering mechanism besides that of compensation level in our samples, which could be combined in both models to further improve the accuracy of mobility prediction.

4. Conclusion

The comparison between the measured majority carrier mobility in compensated silicon and the values calculated by two different models shows that the accuracies of both models are rather stable along the R_C range of this work (*i.e.* $R_C \leq 14$) for different types of materials (multi- or mono-crystalline) and other parameters (e.g. total doping levels). As observed previously, the deviation of the prediction by Klaassen's model from the experimental data increases slightly with increasing R_C. This is mainly noticeable above a critical R_C value, *i.e.* for $R_C > 5.5$ the values calculated using Klaassen's model deviate from the measured values slightly more than unified Schindler's model. Hence, Schindler's model provides a better fit for the samples presented in this work. However, the prediction by

the two models has a visible fluctuation when a reasonable error of dopant measurement is considered. It indicates the importance of the presence of incompletely ionized dopants and their related status.

For some samples, large deviations between measurements and calculated mobility values are observed. These differences are attributed to the presence of unusually high defect densities in the samples. Light elements (O_i and C_s) and metallic impurities, which may contribute significantly to the ionized impurities concentration, are believed to be the cause of the deviation. Multi-crystalline silicon shows a more stable prediction on the majority carrier mobility than mono-silicon, most likely due to lower O_i levels. Inclusion of a term describing ionized impurities in the parameterisation of the model for compensated silicon could improve its accuracy.

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