Incomplete Ionization and Carrier Mobility in Compensated p -Type and n-Type Silicon

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Incomplete ionization and carrier mobility in compensated *p*-type and *n*-type silicon

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Abstract — **In this paper, we show through both calculations and Hall effect measurements that incomplete ionization of dopants has a greater influence on the majority-carrier density in *p*-type and *n*-type compensated Si than in uncompensated Si with the same net doping. The factors influencing incomplete ionization at room-temperature are shown to be the majority-dopant concentration, its ionization energy and type and the compensation level. We show that both the majority- and the minority-carrier mobilities are lower in compensated Si than expected by Klaassen's model and that the discrepancy increases with the compensation level at room-*T*. The study of the *T*-dependence of the majority-carrier mobility shows that there is no compensation-specific mechanism and that the reduction of the screening in compensated Si cannot explain alone the observed gap between experimental and theoretical mobility.**

Index Terms — **compensated silicon, boron, phosphorus, gallium, ionization of dopant, carrier mobility, scattering.**

I. INTRODUCTION

Both the majority-carrier density (p_0 in *p*-type or n_0 in *n*-type) and the mobility of majority- and minority-carrier (respectively μ_{maj} and μ_{min}) have a critical influence on the electrical properties of crystalline silicon (Si) and on the performance of solar cells. For modeling, characterization or to understand the physics of silicon material, it is often required to know theses quantities. In commonly used uncompensated Si, they can usually be deduced directly from the dopant concentration. In compensated upgraded metallurgical grade (UMG)-Si, the prediction of these quantities is, however, not as straightforward. For example, it is common practice when dealing with compensated Si to consider the majority-carrier density as equal to the net doping (N_A-N_D in *p*-type and N_D-N_A in *n*-type) which is equivalent to consider all dopants to be ionized. In a recent paper [1], we used numerical resolution of the Poisson equation and Hall experimental data to demonstrate that neglecting incomplete ionization (*i.i.*) can lead to significant errors in compensated *p*-type Si, depending on the concentration of acceptors and on the compensation level. In this work, we apply same kind of calculation and experiment to compensated *n*-type Si and draw the general factors that influence the importance of *i.i.* in Si.

The majority- as well as the minority-carrier mobilities have been experimentally shown to be lower [2-11] than expected by common mobility models such as Klaassen's [12, 13]. In this work, we confirm these previous findings by measuring μ_{maj} and μ_{min} on a set of samples with a wide range of dopants concentrations. We finally discuss the possible reason for that discrepancy by analyzing the *T*-dependence of the majority-carrier mobility.

II. EXPERIMENTAL METHODS

A. Material preparation

All the samples studied in this work originate from a batch of <100>-oriented Si ingots of about 160mm in diameter, which were crystallized using the Czochralski pulling technique. They were grown using electronic-grade (EG)-Si to which were added various concentrations of B, P and Ga. Because of its low segregation coefficient, Ga was used to compensate the increase of P along the ingot height and hence enable a better control of the net doping profile in those compensated ingots. The B concentrations were chosen in the range that can be found in different grades of UMG-Si while the added concentrations of P and Ga were calculated to obtain the desired net doping profile along the ingots. A detailed description of the technique of compensation engineering, by Ga co-doping can be found in previous papers [14-17].

All the ingots were then shaped into 125×125mm^2 pseudo-square bricks and wire sawed into 200μm thick wafers.

B. Characterization

Samples of 2×2cm^2 in dimension were cut into wafers selected from different heights of each ingot. All samples were subjected to a 1h annealing at 600°C under nitrogen ambient to dissolve oxygen-related thermal donors that might have formed during ingot cooling. Temperature (*T*)-dependent Hall-

effect measurements were then carried out using an Ecopia HMS-5000 device equipped with a T control system cooled with liquid nitrogen. The resistivity (ρ) and the Hall carrier density (n_H) were measured on a Van Der Pauw configuration between 80K and 350K. The conductivity majority-carrier density p_0 or n_0 was deduced from n_H using for the Hall factor r_H the values given at each T by Szmulowicz [18] for p-type Si and Ohta and Sakata [19] for n-type Si. μ_{maj} was then deduced from the measured ρ and majority-carrier density.

μ_{min} was also measured on samples taken from neighboring wafers in the ingot, using a version of the technique developed by Sproul *et al.* [20, 21] in which the surface is damaged by laser ablation. More details on this measurement are given in [16].

III. RESULTS AND DISCUSSION
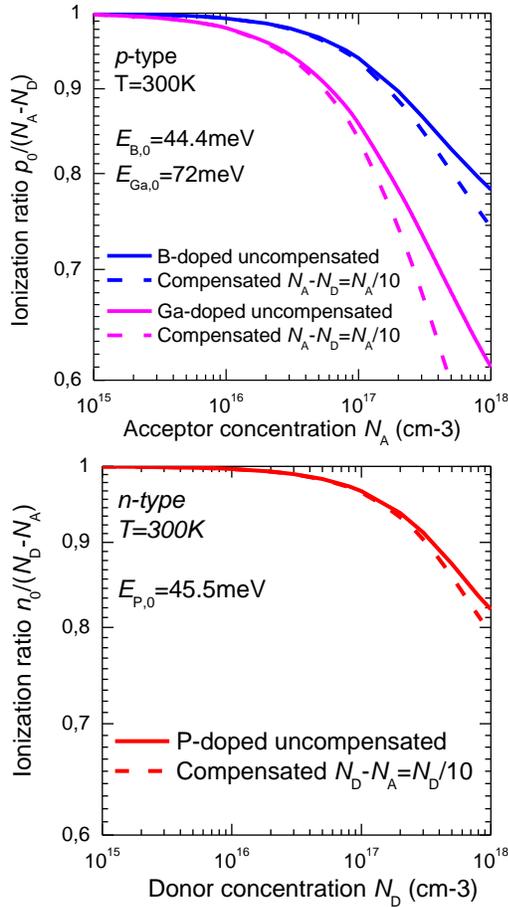
A. Majority-carrier density

Fig. 1. Incomplete ionization ratio calculated as a function of the majority-dopant concentration in p-type (a) and n-type (b) Si for different dopants and compensation levels. The 4 factors influencing incomplete ionization are highlighted in these two graphs, i.e. the majority-dopant concentration, its ionization energy, its type (p- or n-type) and the compensation level.

To calculate the importance of incomplete ionization, we determine the only possible Fermi energy level (E_F) which satisfies the Poisson equation, for a given set of T and dopant concentrations. Once the position of the Fermi level is known, the concentrations of ionized dopants and the carrier densities, relevant to the study of *i.i.*, can be calculated using respectively the Fermi-Dirac and the Boltzmann statistics. This section presents results obtained using this procedure for the calculation of p_0, n_0, N_A^-, N_D^+ with N_A, N_D and T as input parameters. More details on this calculation are given in [1].

The impact of incomplete ionization on the majority-carrier density is assessed using the ratio of the majority-carrier density to the net doping ($p_0/(N_A$-$N_D)$ in p-type and $n_0/(N_D$-$N_A)$ in n-type). This ratio, called incomplete ionization ratio in the rest of the paper, brings to light the error that is made when considering dopants to be completely ionized, i.e. when assuming that the majority-carrier density p_0 (resp. n_0) equals the net doping N_A-N_D (resp. N_D-N_A).

Fig.1 shows the evolution of the incomplete ionization ratio as a function of the majority dopant concentration, calculated at 300K respectively for p-type (a) and n-type (b) silicon. These two plots highlight the main factors influencing incomplete ionization in Si: they are (1) the majority-dopant concentration, (2) its ionization energy, (3) the type of majority-dopant and (4) the compensation level.

1) In the 10^{15}-10^{18}cm^{-3} doping range, i.e. for concentrations below the Mott transition, the impact of *i.i.* on the carrier density increases with the concentration of majority-dopant.

2) The higher the ionization energy of the majority dopant is and the stronger the majority-carrier density will be affected by *i.i.*. This is revealed by the lower incomplete ionization ratio in the case of Ga ($E_{Ga,0}$=72meV) doping compared to B ($E_{B,0}$=44.4meV) doping.

3) *i.i.* is calculated to be stronger in B-doped Si than in P-doped, despite the slightly lower ionization energy for B ($E_{B,0}$=44.4meV) than for P ($E_{P,0}$=45.5meV) [22]. This is due to the fact that acceptors are fourfold degenerate (each acceptor level is able to accept one hole of either spin together with the fact that there are two degenerate valence bands) in contrast with donors that are only twofold degenerate (each donor level can accept one electron of either spin). For a given ionization energy and majority-dopant concentration, incomplete *i.i.* is therefore stronger in p-type than in n-type Si.

4) Last, one can see that the *i.i.* ratio is, in highly-doped compensated Si, lower than in uncompensated Si, showing that compensation enhances the importance of *i.i.*. This is so because as compensation increases, the net doping is reduced compared to the majority dopant concentration. As a consequence, a given fraction of non ionized majority dopants leads to a stronger relative impact on the carrier density [1].

One general rule that can be deduced from the way these four factors influence *i.i.* is that for a given net doping, the

carrier density will be more strongly affected in compensated than in uncompensated Si.

From Fig.1 (a) and (b), one can infer if a Si sample with a given doping will be affected by *i.i.* or not. As the range of dopant concentrations found in compensated UMG-Si is as broad as 10^{16}-$5\times10^{17}\mathrm{cm}^{-3}$ (Figure 1), the influence of *i.i.* on the carrier density might be negligible (<1% in *p*-type Si with N_A=[B]=$1\times10^{16}\mathrm{cm}^{-3}$) or on the contrary very important (40% for *p*-type Si with [Ga]= $5\times10^{17}\mathrm{cm}^{-3}$), depending on the quality of the material. In general, *i.i.* becomes important (>3%) in *p*-type Si containing more than $5\times10^{16}\mathrm{cm}^{-3}$ of B or $2\times10^{16}\mathrm{cm}^{-3}$ of Ga or in *n*-type Si containing more than $1\times10^{17}\mathrm{cm}^{-3}$ of P.
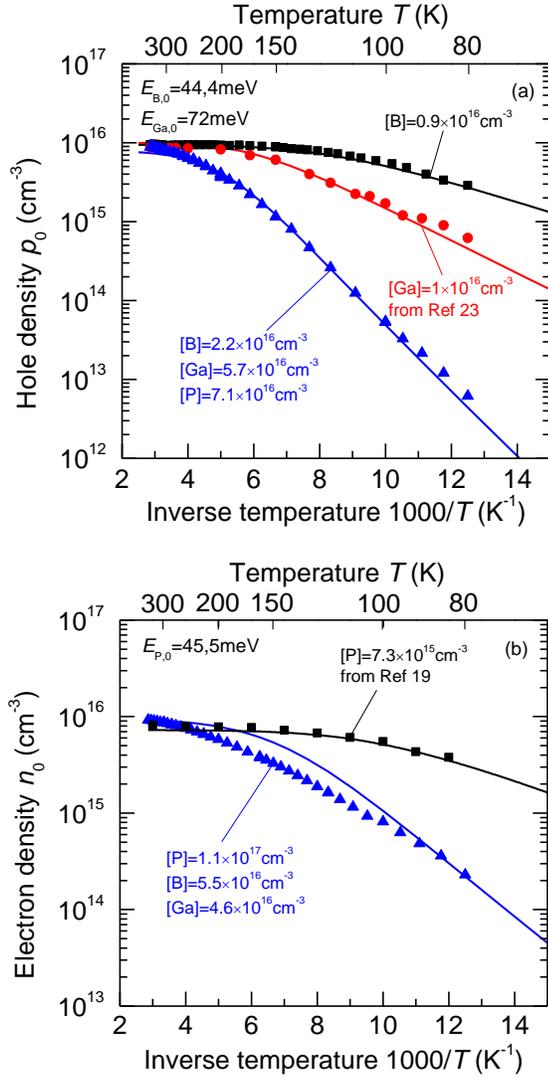

Fig. 2. *T*-dependence of the measured carrier density in uncompensated and compensated p-type (a) and n-type (b) Si samples. The Hall data in Ga-doped Si and in P-doped Si are respectively taken from [23] and [19]. Solid lines are obtained from calculations.

Fig.2 shows p_0 and n_0, deduced from Hall effect measurements, as a function of *T* in one uncompensated B-doped Si sample and both in *p*-type and *n*-type Si samples co-doped with B, P and Ga. Samples were chosen to have a similar net doping in the range $(8\text{-}9)\times10^{15}\mathrm{cm}^{-3}$. For comparison, we have added to the plot published Hall data on uncompensated P-doped [19] and Ga-doped Si [23] with similar net doping (respectively $7.3\times10^{15}\mathrm{cm}^{-3}$ and $10\times10^{15}\mathrm{cm}^{-3}$). One can see that, due to *i.i.*, the majority-carrier density decreases with *T* in all samples. In the compensated samples shown here, it decreases by about 2 or 3 orders of magnitude between 350K and 80K while it only does by a factor of 5, 20 or 2 in respectively uncompensated B-, Ga- or P-doped Si. This illustrate the general stronger importance of incomplete ionization in compensated than in uncompensated Si. A closer look at the variation of the carrier density around room-*T* also reveals that in uncompensated B-, Ga- or P-doped Si, the carrier density is stable between 300K and 350K, indicating that in these samples, the saturation range is already reached at 300K i.e. there is virtually no *i.i.* at room-*T*. In compensated samples, however, the carrier density keeps up increasing between 300K and 350K by about 15% in the *p*-type sample (Fig.2 (a)) and 7% in the *n*-type sample which shows that there is significant *i.i.* at room-*T*. This confirms our previous theoretical finding that room-*T i.i.* is stronger in compensated Si than in uncompensated Si with equivalent net doping.

As can be seen on Fig. 2 (a), the experimental p_0 agrees very well with the calculated one (see [1] for details on the calculation), including in compensated Si, over the entire studied *T* range. This good agreement gives confidence regarding the validity of the procedure we used to evaluate the position of the Fermi level in *p*-type Si. In contrast, there is a noticeable discrepancy between the experimental and the calculated n_0 in the *n*-type compensated sample (Fig.2 (b)). The weaker slope of the measured carrier density dependence with $1000/T$ in the lower *T* range indicates that the ionization energy of P (E_P) might be lower than what we used in our calculation. Note that the parameterization that we chose to account for the variation of E_P [24] with P concentration was established for uncompensated Si. Photoluminescence analyses have previously shown that E_P could be affected by compensation for dopant concentrations close to the Mott transition [25]. A recent study of the donor-acceptor pair luminescence [26] in B and P compensated Si with [B] and [P] lower than $1\times10^{17}\mathrm{cm}^{-3}$, however, indicates that there is no change of the E_P and E_B compared to the commonly accepted values. The scarcity of the data found in literature for compensated Si in the 10^{17}-$10^{18}\mathrm{cm}^{-3}$ doping range leaves us with no other option than to use the available parameterization given by Altermatt *et al.* for uncompensated Si [24]. Note that a better fit could not be achieved by adjusting E_P. Another possible source of error might arise from the Hall factor r_H that was used to convert n_H into n_0. Again, r_H was determined for mildly compensated Si and might not be valid for the higher compensation levels encountered in our samples. Further work is needed to assess the *T*-dependence of r_H in compensated Si, for example by confronting Hall effect measurements to

carrier density data collected with alternative techniques such as capacitance-voltage measurements. It is worth noting that although there is a visible discrepancy between the experimental and the calculated n_0, the relative error on the ionized P concentration is very small. Indeed, the maximum difference between the measured and the calculated n_0 is of 2.3×10^{15}cm^{-3} at 160K which represents only 2% of the expected ionized P concentration (1.07×10^{17}cm^{-3}) at that T. Hence, the calculated ionized dopant concentrations can still be considered as correct to use as input parameters in Klaassen's model, when calculating μ_{maj}.

Because the only E_F solution to the Poisson equation systematically lies in the lower half of the band gap in p-type Si and in the upper half in n-type Si, compensating dopants (shallow donors in p-type Si and shallow acceptors in n-type Si) remain always completely ionized, independently of T. As a result, the concentration of ionized majority dopants cannot decrease below the total concentration of compensating dopants but can only get closer to it as T decreases. In that respect, reducing T is equivalent to tuning the compensation level (C_l see (1)), since it effectively closes the gap between the concentrations of ionized majority and compensating dopants.

$$C_l = \frac{N_A^- + N_D^+}{\left| N_A^- - N_D^+ \right|} \tag{1}$$

Calculation shows that, in the co-doped sample shown in Fig.2 (a) C_l increases from 21 at 300K up to 3×10^4 at 80K (Fig.3). This increase of C_l, due to $i.i.$ of majority-dopants at low T will enable us, in the next section, to rule out the existence of a compensation-specific scattering mechanism.

B. Carrier mobility

The relative reduction of μ_{maj} and μ_{min} measured at 300K compared to Klaassen's model [12], is plotted as a function of C_l in Fig.4. It appears that Klaassen's model describes accurately the experimental data in uncompensated Si but overestimates the mobility in compensated Si. Note that the deviation from Klaassen's seems to be the same in p- and n-type Si and that μ_{min} is in general more strongly affected than μ_{maj}. Similar discrepancy between theoretical and experimental mobility was independently observed by different authors [2-11, 15, 16] and is similar if using other available mobility models [27, 28]. This section discusses the possible reasons for this observed discrepancy.
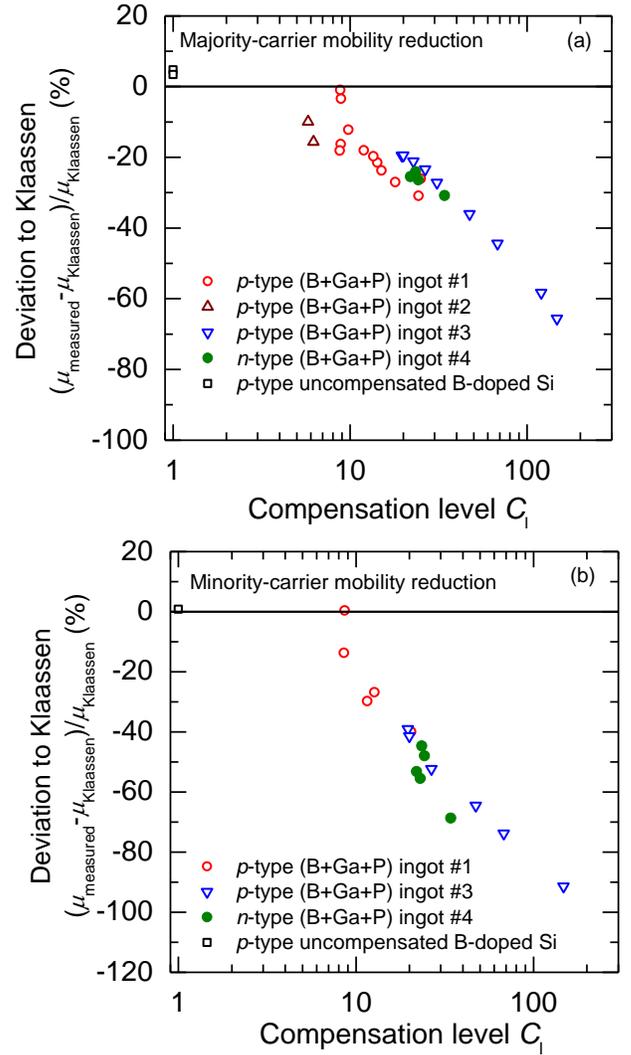
Fig. 4. Reduction of the measured majority-carrier mobility (a) and minority-carrier mobility (b) compared to Klaassen's model at 300K. The deviation unambiguously increases with the compensation level for both majority and minority carriers.
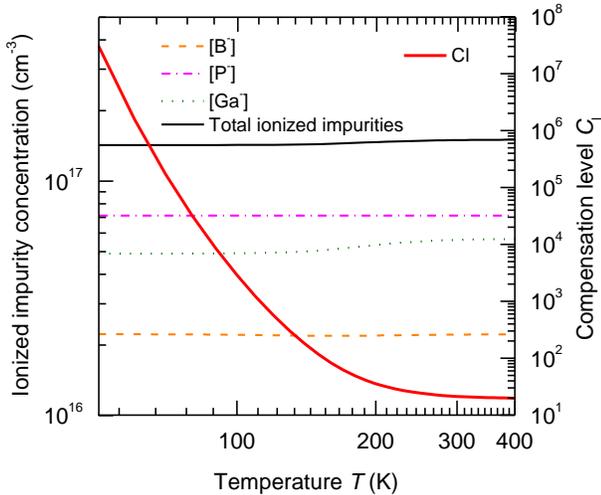

Fig. 3. T-dependence of the calculated ionized dopant concentrations and of the compensation level. The total ionized dopant concentration remain almost constant with decreasing T leading to a strong increase of the compensation level.

Klaassen's model takes into account 3 different scattering mechanisms that are relevant to the study of compensated Si: lattice scattering, ionized impurity scattering and electron-hole scattering. In addition, it incorporates the screening of scattering centers by free-carriers and differentiates the collision cross-sections of scattering centers with attractive or repulsive potential. There are two possibilities to explain why Klaasen's model fails to match the measured mobility in compensated Si. The first one involves the existence of an additional scattering mechanism in compensated Si which Klaassen's would not account for, i.e. a compensation-specific scattering mechanism [3, 16]. The fact that the difference between theoretical and experimental mobility increases with C_1 at room-T supports this explanation. However, a quick look at the T-dependence of the measured μ_{maj} in compensated Si disqualifies this proposition, since there is no drop at low T at which compensation was shown to be extreme [1]. Another explanation could be that one or several of the above-mentioned scattering mechanisms are not correctly described by Klaassen's model or that the relative weight given to each of them is inaccurate. For example, it was put forward that the mobility reduction in compensated Si could be due to a reduction of the screening, because of the lower carrier density, that Klaassen's model considers inconsequential in this doping range. This suggestion was, however, not backed by any experimental or theoretical supportive elements.

A way to assess the nature of the scattering mechanisms that are not well described by Klaassen's model in compensated Si is to use Mathiessen's rule (3) to isolate the mobility component $\mu_{comp.}$ responsible for the discrepancy.

$$\frac{1}{\mu_{comp}} = \frac{1}{\mu_{measured}} - \frac{1}{\mu_{Klaassen}}, \qquad (2)$$

This mobility component, plotted for different samples in Fig.5 appears not to have, in general, a monotonic dependence on T. In most samples, $\mu_{comp.}$ increases with T at low T and decreases with T in the higher T range. This suggests that the deviation from Klaassen's model is not due to the underestimation of a single scattering mechanism or mobility component. For example, the underestimation by Klaassen's model of the reduction of the screening of ionized impurities by free carriers with increasing compensation should lead to a monotonic decrease of $\mu_{comp.}$ with T, due to the decrease of the collision cross-section of ionized impurities with increasing T. In contrast, a monotonic increase of $\mu_{comp.}$ with T should be observed if the only miscalculated mobility component was lattice scattering. The non-monotonic T-dependence of $\mu_{comp.}$ therefore seems to indicate that the error made by Klaassen's model concerns more than one scattering mechanism. It should be noted here that Klaassen's model lays on a substantial amount of fitting of calculated and experimental data, in particular to derive the screening, the collision cross-section ratio of repulsive to attractive scattering centers, and the

collision cross-section ratio of mobile to immobile scattering centers. Fitting of experimental data was also done to define the constants used for the variation of the mobility with T. Since all these fittings were achieved on uncompensated Si, it is not utterly surprising that Klaassen's model fails to describe μ in compensated Si in which the different sources of scattering are present in different proportions. The discrepancy between experimental and theoretical μ in compensated Si highlights the non-physical character of Klaassen's model rather than an actual mobility reduction due to compensation. A complete re-assessment of all the fitting parameters is needed to establish a model that would successfully reproduce the mobility in compensated Si as well as in uncompensated Si.
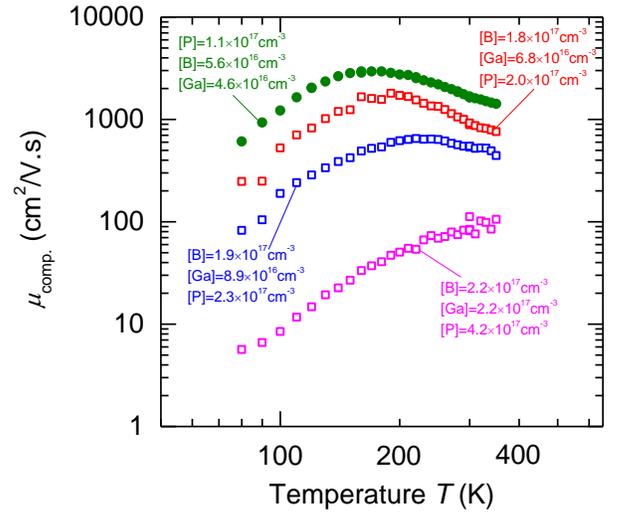

Fig. 5. *T*-dependence of the calculated mobility component responsible for the discrepancy between Klaassen's model and the measured mobility in compensated Si.

IV. CONCLUSION

In summary, both calculations and Hall-effect measurements show that *i.i.* has a stronger influence on the majority-carrier density in compensated Si than in uncompensated Si with the same net doping. This is despite the fact that the total concentration of ionized dopants is in compensated Si almost unaffected by *i.i.*, even at low T. In general, room-temperature *i.i.* impacts on the carrier density in *p*-type Si when [B] is higher than $5 \times 10^{16} \text{cm}^{-3}$ or [Ga] higher than $2 \times 10^{16} \text{cm}^{-3}$, and in *n*-type Si when [P] is higher than $1 \times 10^{17} \text{cm}^{-3}$. The previously reported discrepancy between theoretical and experimental μ was confirmed on a wide range of samples. The *T*-dependence of μ_{maj} shows that the reduction of screening is not alone sufficient to explain the observed deviation.

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