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Compensation Engineering for Silicon Solar Cells

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Abstract

This paper discusses the role of compensation engineering as a means to allow higher concentrations of dopants in silicon than would otherwise be acceptable for solar cell fabrication. Special attention is given to tri-doping, a technique consisting on the addition of gallium to boron and phosphorus doped UMG-Si (upgraded metallurgical grade silicon) feedstock to better control the net dopant density. Firstly, we review the current understanding of compensated silicon, focusing on the fundamental electronic properties of charge carriers: their density, mobility and lifetime. Based on those parameters, we then model solar cell efficiency in order to identify the advantages and limitations of compensation engineering. Given the current uncertainty of the majority and minority carrier mobilities, we study the possible impact of different levels of mobility reduction on solar cell efficiency. This modelling indicates that it is possible to achieve reasonable solar cell efficiencies, around 18%, even in cases of strong dopant compensation and mobility reduction. Lastly, the alternative of using n-type compensated silicon is briefly discussed, taking into account recent evidence that such material can degrade significantly upon illumination.

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1. Introduction

Fabrication methods based on upgrading the purity of metallurgical silicon can lead to drastic reductions in the energy consumed to produce PV silicon and facilitate ramping up of production capacity, thanks to the use of relatively simple equipment and techniques. A distinctive characteristic of UMG-Si is that it contains both acceptor (boron and aluminium) and donor (phosphorus) atoms in

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relatively large amounts [1-3]. The presence of these dopants may be regarded as an inevitable curse, but deliberate compensation doping also presents opportunities to manipulate the properties of the material.

Thanks to compensation, it is possible to tolerate high concentrations of phosphorus and boron, which are frequently difficult to remove completely by means of metallurgical refining methods. In principle it is possible to use silicon materials to make solar cells that have very high concentrations of both dopant types, but controlling these concentrations precisely can be challenging in practice. For example, a 10% precision could allow to use dopant densities of $N_A = 10^{17} \text{ cm}^{-3}$ and $N_D = 9 \times 10^{16} \text{ cm}^{-3}$ to obtain a popular value for the net dopant density. But, even such good precision would stumble against another practical problem that arises during the crystallisation of Si into an ingot. The different segregation coefficients of B and P would then result in a very broad distribution of net dopant densities, hence of resistivities, along the ingot, part of which would become n-type.

We discuss here a creative approach based on triple doping, which is based on the deliberate addition of controlled amounts of gallium to B and P. This method offers a surprisingly good, in theory, control of the net dopant density and the resistivity along the whole ingot. Preliminary experiments [4] have already lent support to the idea. Nevertheless, tri-doping is subject to practical limitations related to the precision with which a fine compensation between the three dopants can be implemented. The B and P concentrations pre-existing in the Si feedstock must be known or measured accurately in order to calculate the optimum addition of Ga. Problems may arise if three-dimensional gradients in temperature occur within the crystallisation furnace. These issues will probably limit the level of total dopant concentration that can be manageable in practice.

More fundamentally, the presence of relatively high densities of acceptors and donors can affect the electronic properties of charge carriers in the material: their lifetime and mobility. In this paper we review the current understanding of such impact in order to predict, via modelling, the potential performance of highly compensated silicon for solar cells.

2. Considerations for making compensated silicon

Perhaps the main consideration when growing a silicon crystal is to obtain a target resistivity that is regarded as optimal for the intended application. Nowadays the common target resistivity for p-type mc-Si solar cells is around 1-1.5 Ωcm , which can be achieved by adding boron to the Si melt so that its final concentration in the crystal is in the vicinity of $1 \times 10^{16} \text{ cm}^{-3}$. The general agreement that this is a suitable doping level is based on experience, particularly in the context of industrial solar cells, which have non optimal n⁺ phosphorus doped and p⁺ aluminium doped regions at the front and back surfaces, respectively. This is a resistivity that turns out to yield reasonable carrier lifetimes and diffusion lengths for defect and contaminant rich multicrystalline Si, whereas for oxygen rich CZ material a slightly higher value of 2-3 Ωcm is usually preferred. Needless to say, the optimisation of the wafer resistivity is, in a general sense, affected by the design of the solar cell device structure, the recombination quality of its two surfaces, the ability to control contamination during its fabrication, and other factors.

The common emphasis on resistivity is due to its easy measurability, but the physical parameter of real interest is the majority carrier density p_o . This density is approximately equal to the net dopant concentration, and it is frequently estimated from the measured resistivity by using published models for the majority carrier mobility μ_p . The reason why p_o should be the primary goal of PV material design is

that it is one of the best tools to control the minority carrier lifetime, which is the main material parameter for achieving a good carrier collection and a high output current.

While most silicon material experts are used to the fact that the carrier lifetime can vary by orders of magnitude, it is commonly surmised that the minority carrier mobility μ_n cannot be engineered at will and is predetermined by nature, as described by reliable empirical models [5, 6]. Indeed, the mobility of electrons in p-type silicon does not change much over a broad range of dopant densities, and is higher than $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ up to about $N_A = 2.5 \times 10^{16} \text{ cm}^{-3}$. Conveniently, it has been experimentally found that it takes very similar values to the electron mobility in n-type silicon, within the same range of dopant densities. One of the worrying aspects of compensated silicon is that recent experimental evidence points towards a significant reduction of both the majority and minority carrier mobility in highly compensated silicon. This is a new factor that may alter the way in which compensated silicon is optimised.

Let us consider first the main factors that need to be considered when applying compensation techniques to control the majority carrier density during the crystallisation of silicon ingots: a) the degree of incomplete dopant ionisation; b) the possible mix of dopants with complementary segregation properties; c) the mobility of holes as majority carriers. Before launching into the modelling of solar cell performance we will also consider: d) the mobility of electrons as minority carriers and e) their lifetime, particularly when boron and oxygen are present in the material.

2.1. Incomplete ionisation of dopants

When the dopant concentration reaches the 10^{17} to 10^{18} cm^{-3} range, not all dopant atoms are ionised at room temperature. Although it can usually be ignored in silicon materials within the typical doping range used for solar cells ($N_A = (0.5-2) \times 10^{16} \text{ cm}^{-3}$), incomplete ionisation of boron and gallium can have a significant impact on the modelling and characterisation of p-type compensated silicon. As the acceptor concentration increases, the Fermi energy approaches the valence band, hence also the energy level of substitutional boron in silicon. The probability of occupation (by an electron) of this boron energy level is thus reduced slightly, which means that a fraction of boron atoms is not ionised (that is they do not release a hole to the valence band). For perspective, the percentage of non-ionised dopants can reach 25% at boron concentrations in the range of $N_A \cong 2 \times 10^{18} \text{ cm}^{-3}$ [7]. Therefore, it is important to include this effect when designing the growth of a compensated Si ingot, or when interpreting measurements of its resistivity once it has been grown. As an example, the impact of incomplete ionisation of boron and gallium (it is slightly greater for Ga) on the determination of the carrier density in ingot B described below is noticeable, but relatively small. When incomplete ionisation is accounted for, the average carrier density along the ingot is $p_o \cong 5.1 \times 10^{16} \text{ cm}^{-3}$, which is 14% lower than the net dopant density $N_A - N_D \cong 6.2 \times 10^{16} \text{ cm}^{-3}$. Proper regard to incomplete ionisation can also be important when evaluating compensated silicon in its feedstock form via resistivity measurements. Note that incomplete ionisation does not affect donor atoms in p-type compensated Si.

2.2. Compensation by a third dopant

Assuming that Si feedstock initially contains only B and P and that the concentrations of these two dopants are well known, we can determine the amount of a third p-type dopant, such as Ga or Al, that gives the best possible uniformity of the net dopant density along the ingot. As an illustrative example, let us consider a certain silicon feedstock that contains 4 ppmw of phosphorus and 1 ppmw of boron. These concentrations are significantly higher than those achievable through UMG methods, but may, if tolerable

from the performance point of view, lead to process simplifications and cost reductions. If used directly in a crystallisation furnace, such feedstock would result in an ingot that would be p-type only up to 70% of its height, the rest being n-type, according to Scheil's equation with segregation coefficients of 0.8 for B and 0.35 for P. There are two options to improve ingot yield: a) add more boron, or b) add gallium. Let us explore these two options, first in terms of resistivity control along the height of the ingot and then in terms of achievable solar cell efficiency.

In the first scenario, one can determine that it is necessary to add to the feedstock 1 ppmw of boron, thus bringing the total boron concentration to 2 ppmw (alternatively, one could manipulate the purification process so that it would result in this same amount of boron). Figure 1(a) shows that it is then possible to achieve 90% ingot utilisation, that is, the cross-over point between phosphorus and boron concentrations is now shifted to relative position 0.9 along the ingot.

In the second scenario, one can determine that, by adding 120 ppmw of gallium (segregation coefficient 0.008) together with the initial 1 ppmw B and 4 ppmw P, it is possible to avoid type inversion altogether and achieve a good control of the resistivity (see Fig. 1(b)). Note that the acceptor concentration is lower than in the first case, courtesy of the low segregation coefficient of Ga, which means that the concentration of Ga is high only where it is needed to compensate the phosphorus, towards the top of the ingot. As a result the net doping, represented in Fig. 1 via the majority carrier density p_o , is almost constant along the ingot, $p_o \cong 5.1 \times 10^{16} \text{ cm}^{-3}$ and the average resistivity of ingot B is $0.48 \text{ } \Omega\text{cm}$. In comparison, ingot A has a higher and less uniform carrier density, $p_o \cong 1 \times 10^{17} \text{ cm}^{-3}$, and a lower resistivity of $0.26 \text{ } \Omega\text{cm}$. We will see that this difference in majority carrier concentration results in a significantly different solar cell performance.

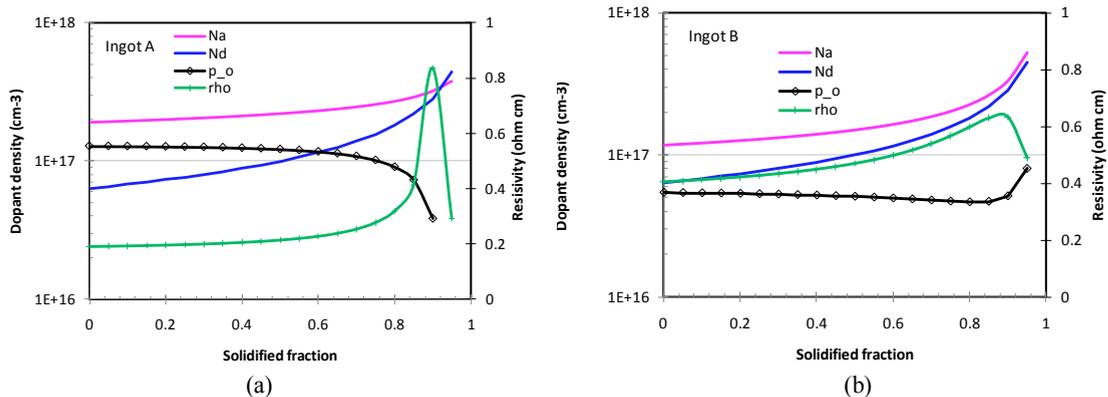


Fig. 1. (a) Dopant density and resistivity profiles for a silicon ingot grown from feedstock containing 2 ppmw B and 4 ppmw P; (b) Profiles corresponding to 1 ppmw B, 4 ppmw P and 120 ppmw Ga.

In the calculations shown in Fig. 1 we have accounted for incomplete ionisation of both B and Ga even if, as mentioned above, the impact is relatively small for these two ingots (about 14%). A higher impact can come from the majority carrier mobility used to calculate the resistivity. We have assumed the model proposed by Klaassen *et al.* [6], but if the actual majority carrier mobility turned out to be lower, as discussed below, then higher resistivities would be measured. This is of interest to the characterisation of Si ingots but does not affect much the performance of solar cells which is mainly determined by the minority carrier mobility and lifetime and by the density of majority carriers, as we shall see in the next

section. The majority carrier mobility in the wafer is, nevertheless, important for advanced device designs with local contacts or junctions.

2.3. Majority carrier mobility

Some of the available experimental evidence [8, 9] indicates that the model of Klaassen *et al.* [5, 6] describes well the dependence of the hole mobility in p-type Si as a function of the sum of all dopant species present in the material. In fact, by using the sum N_A+N_D as the total dopant density, other majority carrier mobility models [10] also give similar results. Nevertheless, recent measurements on highly compensated silicon [11-14] have yielded mobility values that are significantly lower than those predicted by Klaassen's model. These and other [15-18] experimental data are plotted in Fig. 2 as a percentage deviation from Klaassen's model. Although the dopant species should not have a strong influence, it is worth noting that data from Ref. [13] were obtained on B-doped Si compensated with oxygen-related thermal donors while data from Ref. [14] correspond to Si co-doped with B, P and Ga. We have excluded data for wafers with almost full compensation, for which extremely low values of the mobility [13] have been measured. It is possible that some of these measurements are affected by strong non-uniformities and disorder of the net dopant density [19]. To convert Hall mobility measurements into conductivity mobility, we have used a Hall factor of 0.75 [12]. When analysed one by one, the groups of data reported by every author seem to follow a trend towards a lower mobility with increasing compensation ratio, defined as $f_c = (N_A+N_D)/p_o$, with $p_o = N_A - N_D$. The general scatter of the data is partly attributable to the fact that the total dopant concentrations can be different, even if the compensation ratio may be similar.

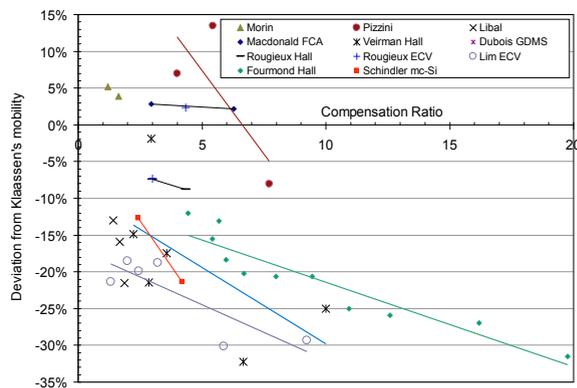


Fig. 2. Hole (majority carrier) mobility in p-type compensated silicon reported by different authors and expressed as a deviation from Klaassen's model as a function of the compensation ratio.

2.4. Minority carrier mobility

The minority carrier mobility in compensated silicon has been characterised via measurements of the effective lifetime of wafers with a high surface recombination, which is dominated by the diffusion of carriers towards those surfaces. The still scarce available experimental evidence indicates that the minority carrier mobility is affected by dopant compensation more strongly than the majority carrier one. Figure 3 presents data from four recent papers [9, 11, 14, 20] indicating that the electron mobility in p-type compensated silicon is about 20-40% lower than that predicted with Klaassen's model. Similarly to the trend observed for the majority carrier mobility, the data in Fig. 3 seem to indicate that the reduction

of the minority carrier mobility may be correlated to the degree of compensation. The different sets of data do not overlap, partly because the total dopant density is much lower for the CZ samples used by Lim *et al.* [11] than for those used by Fourmond *et al.* [14] and the multicrystalline silicon samples also used by Lim *et al.* [20]. The uncertainty of these measurements has been estimated at 20% [11].

More experimental evidence and theoretical work are clearly needed to gain a deeper understanding of the mechanisms behind mobility reduction in compensated silicon. In the interim we will treat the mobility as a variable parameter in our study, with a possible range from the values predicted by Klaassen's model down to one tenth of them. In the modelling we apply the same percentage reduction to both the majority and minority carrier mobilities.

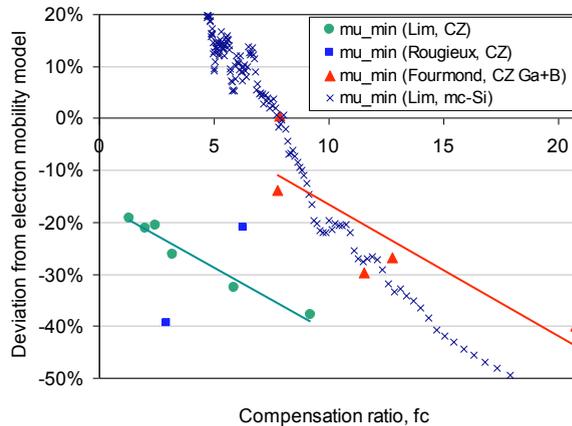


Fig. 3. Electron (minority carrier) mobility in p-type compensated silicon reported by different authors and expressed as a deviation from Klaassen's model as a function of the compensation ratio.

2.5. Minority carrier lifetime

The ultimate goal of PV material design and fabrication is to achieve a high minority carrier lifetime. As mentioned before, this can be done to a large extent by controlling the majority carrier density p_o , as discussed in a recent paper [21]. Nevertheless, carrier recombination is a complex matter, and there are a multitude of perils that need to be overcome. One of them is posed by oxygen, which is usually present in both CZ and mc-Si. In the modelling presented in the next section we assume that the compensated material has a concentration of interstitial oxygen of $[O_i] = 3 \times 10^{17} \text{cm}^{-3}$, lower than what is typical in CZ silicon but not uncommon in mc-Si ingots. This interstitial oxygen is known to produce a significant reduction of the minority carrier lifetime through the boron-oxygen related defect, which we model using the empirical expression proposed by Bothe *et al.* [22], with the precaution of using the majority carrier density p_o , rather than the boron concentration [23]. Although not all mc-Si will contain this amount of oxygen and even though methods to annihilate the BO defect are being developed, we use this defect as a way of representing the fact that most Si wafers, CZ or mc-Si, have carrier lifetimes well below the intrinsic limit. A relatively low lifetime will help us show the incidence of different assumptions for the mobility.

For a given surface recombination quality, p_o is also determinant of the level of recombination losses that occur at the surfaces. Even more directly, the majority carrier density p_o is one of the main drivers for

achieving a high output voltage, the other being the excess minority carrier density, which is governed by the lifetime, hence also by p_o . The problem is that those two roles of p_o are in opposite directions: a low p_o is desirable to increase the lifetime, a high p_o is usually (but not always!) desirable to increase the voltage. Hence, a compromise is needed and an optimisation that takes into account all the above factors is required.

3. Modelling solar cells made with compensated silicon

To evaluate the performance of solar cells made with wafers cut from the two ingots described in the previous section we use a simple computer model [24], with reasonable assumptions for the recombination at the front and rear surface regions, $J_{o(front)} = J_{o(back)} = 1 \times 10^{-13} \text{ Acm}^{-2}$, which allow us to focus on the base region. The AM1.5G spectrum and a temperature of 27°C were assumed (the latter being customary for mobility data), together with a 75 nm thick silicon nitride antireflection coating on the front planar surface, and a wafer thickness of 200 μm . With these optical and surface conditions, the maximum achievable efficiency (no grid shading or resistive losses) would be 19.5%. Texturing would bring the upper limit to approximately 21.5%.

Figure 4 shows modelling results for the two ingots described in the previous section. The efficiency for cells from ingot B, averaged over 90% of the ingot height, is 17.7%, nearly two absolute points below the upper limit imposed by the surfaces and the optics. On average, the conversion efficiency for ingot A is 0.5% (absolute) lower than for ingot B, which has a lower net doping p_o thanks to Ga compensation. The main reason for this difference is the minority carrier lifetime, which is approximately two times higher for ingot B (20 μs on average, in low injection) than for ingot A (11 μs on average), the latter being more affected by the BO defect, proportional to p_o . At the top of the ingot there is an improvement for ingot A when the net doping decreases near the type switch point. This is due to a reduced SRH recombination as net doping decreases. The opposite behaviour can be observed for ingot B, due to the fact that the net doping increases slightly towards the top of the ingot. It is also interesting to consider what would be the efficiency of material that would have identical majority carrier density and recombination properties but without compensating dopants.

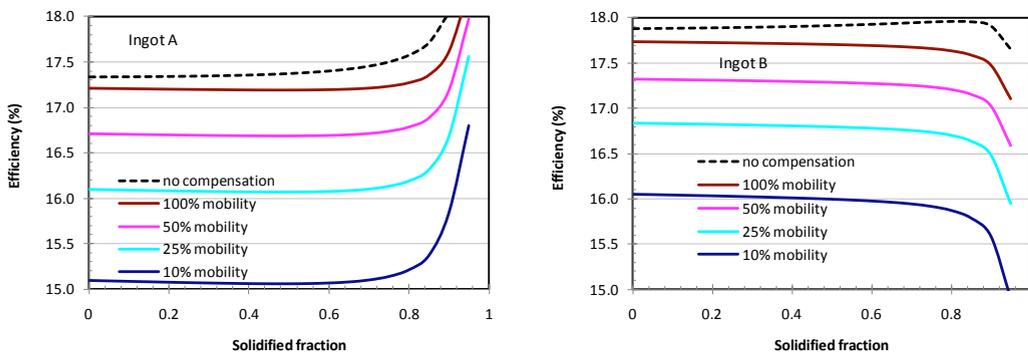


Fig. 4. Modelled conversion efficiency for silicon wafers from ingots A (2 ppmw B, 4 ppmw P) (left), and B (1 ppmw B, 4 ppmw P, 120 ppmw Ga) (right). The different curves correspond to different assumptions for the carrier mobilities, from the values given by Klaassen's model down to a factor of 10 lower. The dashed line indicates the efficiency corresponding to material with the same majority carrier density but no compensation.

The dashed lines in Fig. 4 indicate that the efficiency would be slightly higher, but not much, just 0.2 absolute points on average. Therefore the impact of mobility reduction for compensated silicon according to Klaassen's model translates into an efficiency loss of about 0.2 points in the examples considered here.

If the mobility is assumed to be 50% lower than the "Klaassen mobility" then the efficiency drops by approximately 0.5% (absolute), for both ingots. This means that a 50% reduction of the mobility is not catastrophic. The mobility would need to drop to one fourth of Klaassen's values for the reduction in efficiency to reach about one efficiency point. If the reduction in mobility is as drastic as a factor of ten, which has been reported [20, 25] for nearly fully compensated material, then the efficiency would drop by more than two points in case A and about 1.7 points for case B. This second case, Ga compensated, would still maintain a device conversion efficiency close to 16%, which gives some comfort in the event that such extremely low carrier mobilities are confirmed. Note that his theoretical exercise applies to mobility reductions of any kind, including those that may result from crystallographic defects or grain boundaries.

The example given here is for relatively low carrier lifetimes consequence of the BO defect. A low carrier lifetime exacerbates the impact of reduced carrier mobilities. Obviously, higher conversion efficiencies may be achievable with compensated material that is oxygen free and has a better lifetime. In such case the differences between the two ingots A and B would be much lower, but Ga compensation would still be superior in terms of uniformity along the ingot and avoidance of type inversion.

4. The case for n-type compensated silicon

We commenced this exercise of compensation engineering on the premise that it is harder to reduce the concentration of phosphorus than that of boron via UMG purification methods. Why not then accept this as a fact of life and grow silicon ingots that are n-type instead of p-type? Keeping the same starting material, with 4 ppmw P, it only takes to reduce the concentration of boron to 0.3 ppmw, which is achievable by current UMG methods, to achieve a fully n-type ingot. In fact the conversion to n-type would already happen at 0.6 ppmw B, but a further reduction to 0.3 ppmw allows us to use the triple doping method by adding 115 ppmw Ga and thus obtain a flatter profile for the majority carrier density n_o . Figure 5 shows the dopant and carrier density profiles for this case, together with the resistivity calculated using Klaassen's model. Both the resistivity and n_o vary more than in the p-type ingot B discussed above, but still much less than the variability that would occur in the absence of Ga. The average values for this n-type ingot C are $n_o \cong 2.8 \times 10^{16} \text{ cm}^{-3}$ (lower than for ingot B) and 0.4 Ωcm (nearly the same as ingot B).

We maintain the same oxygen concentration as in the previous cases. In non-compensated n-type Si this oxygen would not degrade the carrier lifetime in a significant manner. Unfortunately, it has recently been found that compensated n-type silicon containing both boron and oxygen is also victim to a light-induced degradation effect [11, 26]. Research of this problem is still in its early stages; the physical mechanism and its dependence on boron, phosphorus and oxygen concentrations are not well characterised yet. The degradation is slow and can take many days, which makes comparison among different authors difficult. In a recent experiment, Rougieux *et al.* [27] have measured that the final, degraded lifetime of several n-type Si wafers having different dopant and compensation levels was in the vicinity of 100 μs . This is for CZ Si, with a higher oxygen concentration than we have assumed here. In the modelling we use this lifetime value, assumed to be constant for all dopant densities, as representative of n-type compensated silicon after light induced degradation.

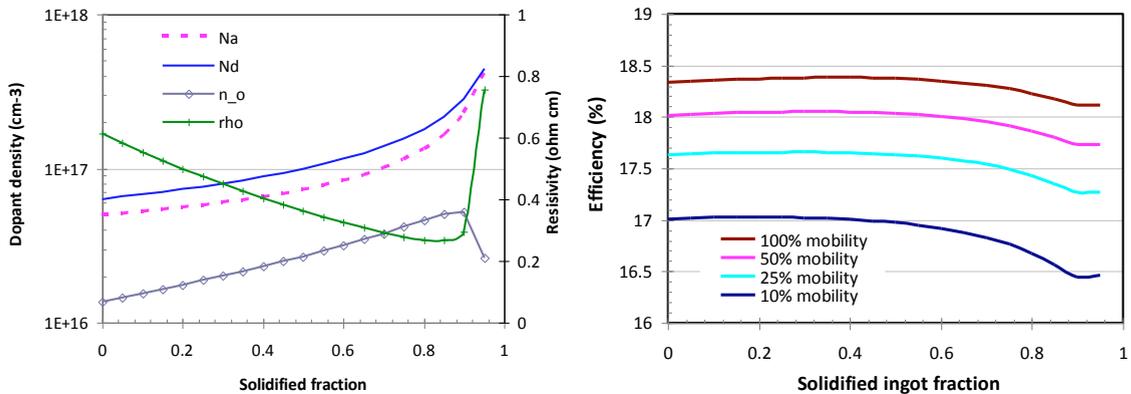


Fig. 5. (Left) Dopant density, majority carrier concentration and resistivity profiles for an n-type silicon ingot grown from feedstock containing 0.3 ppmw B, 4 ppmw P and 115 ppmw Ga. (Right) Modelled conversion efficiency for silicon solar cells from the n-type Si ingot. The various curves correspond to different assumptions for the carrier mobilities, from the values given by Klaassen's model down to a factor of 10 lower.

Figure 5 (right) shows the modelled conversion efficiency for ingot C if used to make $p^{+}nn^{+}$ solar cells with symmetrical surface regions, as in the previous case. The conversion efficiency is approximately 18.3%, nearly independent of ingot position, if the minority (hole) carrier mobility follows Klaassen's model. It drops to 18.0%, on average, for a mobility reduction of 50%, 17.6% for a 75% reduction, and 16.9% for a 90% reduction. These values are slightly higher than those determined for the p-type ingot B, mainly due to the difference in lifetime (five times higher for the n-type ingot). The calculations indicate that the efficiency is reduced less than 10% relative even if the mobility drops by 90%.

Is there any other alternative? May be yes, go back to p-type Si and reduce the concentrations of both boron and phosphorus. For example a feedstock containing 0.3 ppmw B, 1 ppmw P and 27 ppmw Ga would give a very uniform resistivity of $0.9 \Omega\text{cm}$, $p_o \cong 2 \times 10^{16} \text{cm}^{-3}$ and a conversion efficiency of 18.2% in the degraded state. So this approach would push the p-type case to the same efficiency levels as the n-type case. Nevertheless, the efficiency gain obtained with such dopant reductions is not large, compared to the 17.7% that was predicted for 1 ppmw B, 4 ppmw P and 120 ppmw Ga.

5. Conclusions

Boron and phosphorus doped compensated UMG silicon is already an industrial reality, particularly as multicrystalline Si. The addition of gallium as a third dopant offers significant advantages for controlling the net dopant density, particularly in terms of a better ingot yield and uniformity. In principle, high phosphorus concentrations may be tolerable; in this paper we have modelled a case with 4 ppmw of P (about 4 times higher than industry standard) and determined that conversion efficiencies close to 18% (no texturing, no grid shading or resistive losses) are achievable if the feedstock material is compensated with 1 ppmw B and 120 ppmw Ga. This was meant to be an extreme case to show the limitations of compensation engineering. Very high dopant concentrations, finely compensated with each other, may offer technological and economic advantages, but they face an unforeseen challenge: a strong reduction of the minority carrier mobility.

A corollary of our modelling studies is that the impact of carrier mobility on conversion efficiency is, per se, not very drastic, although it can become quite significant in conjunction with a low lifetime. That

led us to investigate n-type compensated Si as a possible way towards high carrier lifetimes, but this avenue is hampered by recent evidence that boron and oxygen containing n-type Si degrades when exposed to light. It seems, therefore, that oxygen needs to be avoided in both p-type and n-type compensated silicon in order to achieve stable, high carrier lifetimes. Nevertheless, oxygen is not the only threat to the carrier lifetime; in practice other impurities and defects can have a more decisive role on the different performance that may be achieved with n-Si and p-Si. Lastly, this paper has remained in the theoretical realm, oblivious of the fact that dopant engineering requires a tight control of the concentration of the different dopant species. This control will place practical limits to extreme compensation.

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