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Possible reduction of recombination lifetime due to compensated dopants.

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Abstract

Dopant compensation is a convenient way to use all available solar grade silicon, and still arrive at the required wafer resistivity by mixing differently doped pieces of silicon. We review the possibility that compensated dopants can be a significant source of recombination in silicon solar cells, based on a variety of results in literature. The capture cross section of the ionised dopants for minority carriers is large, and not limiting recombination. Rather, the capture cross section of the neutral dopants for majority carriers is the rate-limiting parameter. There is very large variation in literature data of this neutral dopant capture cross section, between about 10^{-15} and 10^{-22} cm^2. If the higher values are correct this would mean that compensated dopants can be a very significant recombination channel in solar cells. A value below, but not much below, 10^{-17} cm^2 is most likely based on literature results, which would mean the effect would be noticeable in strongly compensated material, but not very important.

Introduction

Compensation occurs in wafers from solar grade silicon due to the mixing of differently doped sources of silicon. In particular, to reduce costs, new solar grade silicon production techniques [1] will generally be less effective in removing dopants than the conventional Siemens route to high-purity polysilicon for the semiconductor industry. Therefore, there may be a mix of p- and n-type dopants present in wafers produced from such silicon. Furthermore, generally as much of the available silicon is used for PV production as is possible. This means that n-type doped waste silicon is recycled and mixed with p-type silicon or compensated by adding p-type dopants, in order to produce ingots of roughly standard resistivity.

Compensation will increase the number of scattering centers for charge carriers and thus may reduce the mobility and diffusion length. Dopants could possibly also form complexes or defects with other impurities or crystal defects, and thus change the charge transport and recombination in the silicon wafer. The topic discussed in this paper is whether compensated dopants as such (without considering any interaction with other defects or impurities) can have a significant impact as recombination centers.

Little attention seems to have been paid in published PV literature to effects of compensation. The seminal impurity studies by Westinghouse [2] have investigated the topic in monocrystalline Cz ingots. Their results show a slight suppression of cell efficiency for a phosphorous density larger than 2.5×10^{17} cm^{-3} in p-type ingots of resistivity 4 Ωcm. However, as the baseline cell efficiency and effective diffusion length in the Westinghouse cell process was quite low (for example, no BSF was used), it is possible that currently a more significant effect could be expected.

Acciarri et al. have studied intentionally compensated Eurosolare ingots [3]. They focussed on effects on mobility, but also solar cells were made. Probably due to variability of mc-Si properties (especially variation of crystal defect density), in studying two ingots of the same resistivity the compensated one showed the higher mobility and a cell efficiency 1.3% higher than the uncompensated one. Modelling showed that effects of compensation on mobility should actually be negligible at room temperature.

To our knowledge, apart from the above references, there have been few, if any, explicit results of the effects of compensation reported in open PV literature. In this paper, we will therefore also use literature results outside the PV field to assess the possibility that compensated dopants cause significant recombination. It will turn out that this is a possibility based on some results, but also that there is a lot of variation in published values of the relevant defect parameter (the majority capture cross section). Therefore, experiments to determine recombination lifetime in controlled bulk samples would be useful as a sensitive test for this phenomenon. Such experiments are in preparation.

Compensated dopants as recombination centers

A compensated dopant in silicon is a shallow impurity near the minority-carrier band-edge. Generally, shallow impurities are expected to be not very effective as recombination centers, because the occupation probabilities of the two charge states of the center are very asymmetric. For example, in the case of phosphorous in p-type silicon (alternating between P^+ and P^0) the occupation of the neutral state is very low, hole capture is therefore very unlikely, and the recombination rate might be expected to be low. Rather, shallow levels are often expected to act as traps (capturing and releasing minority carriers).

However, for the typical resistivity of PV wafers, and a significant compensation fraction, the density of the shallow defect levels can be much higher than typical metal impurity levels. This high defect density could potentially offset the low level occupation, and result in a significant recombination rate.

In this paper we will apply the Shockley-Read-Hall (SRH) model to evaluate quantitatively the recombination rate in compensated silicon. One could worry that the SRH model would not be valid for this purpose, since in its commonly used form it is only applicable when the density of recombination centers is 'small'. This arises from the assumption that the non-equilibrium carrier densities Δn and Δp must remain almost equal, which does not hold if the recombination centers 'trap' a significant fraction of carriers. Macdonald and Cuevas [4] investigated the range of validity of the SRH model. They found that the SRH model is valid if the recombination center density N_t is at least one order of magnitude lower than a critical level N_{crit}. For the very shallow levels near the band edges that are considered in this paper, N_{crit} is very high, above 10^{18}. So, perhaps surprisingly, it is therefore valid to use the SRH model from this perspective. This reflects the fact that, although the shallow compensated dopants will indeed trap carriers, they will re-emit them quickly enough to avoid trapping problems.

Applying the usual SRH equation then,

$$\tau_{SRH} = \frac{\tau_{no}(p_o + p_1 + \Delta n) + \tau_{po}(n_o + n_1 + \Delta n)}{n_o + p_o + \Delta n}$$

$$n_1 = N_C e^{(E_t - E_c)/kT}; \quad p_1 = N_V e^{(E_t - E_g - E_c)/kT};$$

$$\tau_{po} = \frac{1}{N_t v_{th} \sigma_p}; \quad \tau_{no} = \frac{1}{N_t v_{th} \sigma_n}$$

In the case of shallow levels (E_c-E_t≈0.045 eV), for net p-type doping, n_1≈5x10^{18} cm^{-3} and p_1 is negligible. Therefore, in p-type material (n-type is similar):

$$\tau_{SRH} = \tau_{no} + \tau_{po} \frac{n_1}{p_o + \Delta n}$$

Hence, the majority carrier capture time constant (τ_{po} in p-type) limits the recombination lifetime, being multiplied by e.g. a factor 500 if the net doping density is 10^{16} cm^{-3}. The calculations in Fig. 1 illustrate that SRH recombination at compensated dopants could be of relevance in standard mc-Si solar cells, depending on the neutral dopant capture cross section (σ_p in p-type).

Incidentally, this dominance of majority capture time constant differs from the situation for deep levels where the minority capture time constant is usually limiting [5]. Thus, the fact that the minority carrier capture cross section will be very high (due to Coulombic attraction) is hardly relevant.

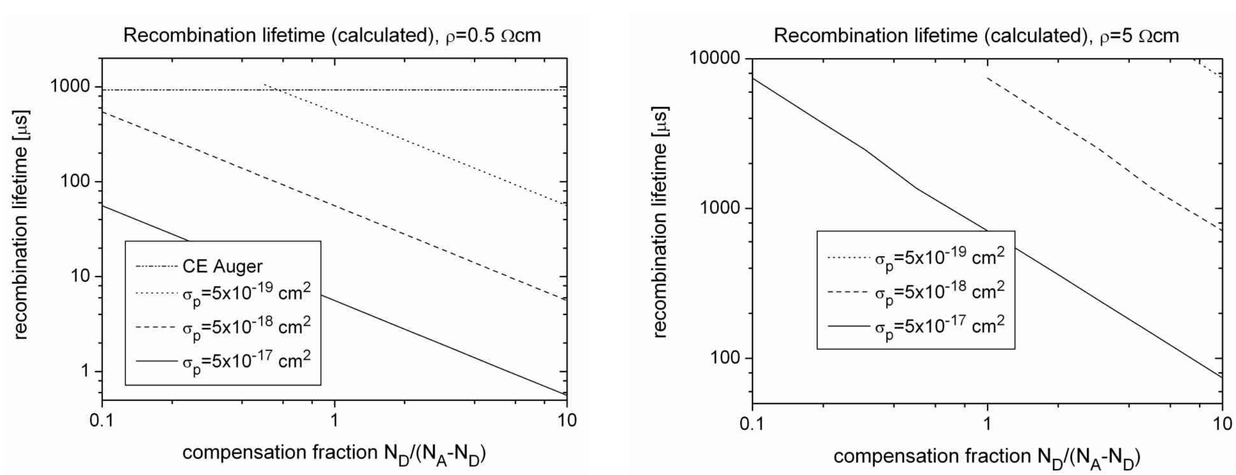

Figure 1.Bulk recombination lifetimes calculated for various capture cross sections of neutral donors. Left: 0.5 Ωcm resistivity, right: 5 Ωcm resistivity. Injection level 10^{14} cm^{-3}, p-type silicon, donor level Ec-Et=0.045 eV. In the calculation of the compensation fraction, the carrier mobilities are assumed to be unchanged by the compensation. In reality the lines would probably not be straight due to dopant-dopant-interaction.

Published results about capture cross sections

Most information in literature about capture rates or capture cross sections of dopant impurities in silicon is from photoluminescence (PL) experiments, almost exclusively at low temperature. Some data is available from investigations of bipolar transistors.

Concerning the minority carrier capture (i.e., capture by ionised dopants), it is generally accepted that the capture cross section is very large [6]. In ref [7] the capture rate of electrons by P^+ at T=3K corresponds to a cross section of $6x10^{-11}$ cm^2.

Concerning the more important majority carrier capture, there is much more spread in results. The capture rate of neutral In for electrons corresponds to a cross section of $2x10^{-22}$ cm^2 at T=80K according to [8]. In [9] the cross section is given as function of T, and extrapolation to room temperature results in about 10^{-21} to 10^{-22} cm^2, too small to be of importance. Other experiments [10] yielded values of 10^{-16} to 10^{-18} cm^2, the high side of this range would be of importance in PV materials. In [11] from fits of the beta of IC transistors, the capture cross section of neutral acceptors as well as donors is even found to be as high as $1.3x10^{-15}$ cm^2. In strongly compensated (N_t=$10^{16}cm^{-3}$) 1 Ωcm material this latter result would yield a recombination lifetime of 3 μs!

Discussion

The variation in literature for the capture cross section of neutral dopants is too large to give a somewhat reliable prediction of the effect of compensation on recombination lifetime. According to the previous section, literature values would result in lifetimes between a few μs and infinity. Nevertheless, some further estimates are possible based on other results as described below.

A special situation where compensation could be important is the emitter of solar cells. For the highest value of the capture cross section reported ($1.3x10^{-15}$ cm^2) the recombination lifetime in the emitter would be orders of magnitude lower than due to Auger recombination. Since generally no large discrepancies seem to be observed between experimental emitter recombination currents and modelling based on Auger recombination[12], the upper bound on the capture cross section should be of order 10^{-17} cm^2. In turn, this would give a lower bound on the recombination lifetime in strongly compensated (N_t=$10^{16}cm^{-3}$) 1 Ωcm material of order 300 μs.

Looking in detail at the Westinghouse results [2] for compensation, the largest observed reduction of cell parameters is just a few percent. In two cases the net doping of test and reference ingots are closely similar: one ingot (W092) with ρ≈4Ωcm and N_D=$2.8x10^{16}$ cm^{-3} showed no reduction of cell I_{sc} or V_{oc}, or carrier lifetime; the other (W116) with ρ≈0.47Ωcm and N_D=$1.0x10^{17}$ cm^{-3} showed 2% reduction in I_{sc}, but no significant reduction in carrier lifetime measured by open circuit voltage decay (1.4 μs in test and reference ingot). According to the model by Westinghouse, the recombination due to compensation in ingot W116 would be approx. 20 μs, which corresponds to σ_p≈$4x10^{-18}$ cm^2. Obviously there is large uncertainty in this number. Moreover, the I_{sc}-reduction could probably be also due to reduced mobility.

Conclusions

As new sources of silicon feedstock are used in silicon PV, and at the same time efforts towards high cell efficiency are increasing, it is becoming more and more important to understand whether recombination via compensated dopants can be a significant issue in solar cells. From Shockley-Read-Hall theory it is likely that capture of majority carriers by neutral dopants is the rate-limiting step. Reported values for the capture cross section vary enormously. Results obtained on bipolar transistors suggest that compensated dopants would be a very significant recombination channel in solar cells, whereas some photoluminescence results suggest an insignificantly small carrier capture cross section. From other results a value below, but not much below, 10^{-17} cm^2 is most likely, which would mean the effect would be noticeable in strongly compensated material, but not very important. Given the large uncertainties further investigation will be useful.

Acknowledgments

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