

# Origins of carrier traps in p-type multicrystalline silicon

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Carrier trapping effects in multicrystalline silicon wafers are investigated by measuring the dependence of their photoconductance on carrier injection level and by fitting a theoretical model to the data. The main information thus obtained is the density of trapping centres, which may be a useful indicator of the quality of the material. We have found that the trap density can vary significantly for different cast multicrystalline silicon ingots. Typically, the concentration of traps also changes for wafers from different positions within an ingot, and we have found a correlation between the concentrations of trapping centers and dislocations in the mc-Si wafers. Additional experiments based on cross-contaminating ultra pure single-crystal silicon wafers with multicrystalline silicon specimens revealed that some of the traps are mobile and probably due to transition metal contaminants. The density of trapping centers in p-type float zone wafers of varying resistivities was found to be linearly proportional to the background boron concentration, suggesting that the trapping effects are caused by boron-impurity pairs. Two possible physical origins for the trapping centers in multicrystalline silicon have been identified: crystallographic defects (dislocations) and mobile impurities.

## 1. Introduction

The measurement of the minority carrier lifetime of multicrystalline silicon (mc-Si) has been disconcerting for some time: anomalously high photoconductance values (implying very high apparent lifetimes) are frequently observed, particularly at low carrier densities (see Fig.1). Finding a satisfactory conceptual explanation for this anomalous photoconductance was an important step forward in the understanding of mc-Si. A physical model for carrier trapping effects developed in the mid 50's<sup>1,2</sup> proved to be capable of explaining very well the experimental photoconductance of mc-Si at low injection levels<sup>3</sup>; the puzzle was solved, at least conceptually. The next step is to investigate what are the physical origins of the trapping centers and their practical implications on device performance

We present here the results of several experiments aimed at improving the understanding of trapping

centers and learning about their physical origin. A group of experiments use phosphorus gettered multicrystalline wafers, where the consequences of crystallographic defects should be revealed more clearly. The second type of experiments involve the transferring to crystallographically perfect FZ wafers of the mobile contaminants present in un-gettered mc-Si to elucidate whether they also produce trapping or not.

All lifetime measurements presented in this paper were performed using the quasi-steady-state photoconductance (QSSPC) technique<sup>4</sup>. However, any photoconductance based method, such as transient photoconductance decay (PCD), would be subject to the same trapping phenomena explored here<sup>5</sup>. The QSSPC data analysis was performed with both steady-state and transient terms in the determination of lifetimes, allowing a large range of lifetimes to be measured<sup>6</sup>.

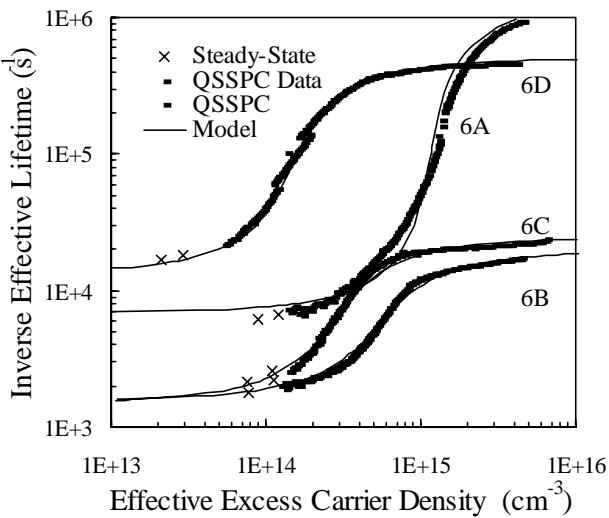


Figure 1. Quasi steady-state photoconductance measurements of wafers from the top (6A), near top (6B), centre (6C) and bottom (6D) of the same mc-Si ingot. The continuous lines represent the theoretical model.

## 2. Trapping in gettered multicrystalline silicon

Figure 1 shows QSSPC data from four mc-Si wafers from different parts of a p-type multicrystalline solar grade silicon ingot grown by directional solidification at Eurosolare, SpA. Wafers labelled 6A, 6B, 6C and 6D come from the top, near top, centre and bottom of the ingot respectively. The samples were phosphorus gettered, etched, and then given a light phosphorus diffusion and oxidation to passivate the surfaces. The apparent rapid increase in lifetime at lower injection levels is due to minority carrier trapping.

The theoretical model originally developed by Hornbeck and Haynes<sup>1</sup> is, as Figure 1 shows, capable of describing the behaviour of a variety of mc-Si wafers with very different recombination lifetimes and trap densities over a broad range of carrier density levels. By fitting the model to the experimental data, the trap density  $N_t$  can be determined. For example, for wafer 6A the trap density is  $N_t = 3 \times 10^{15} \text{ cm}^{-3}$  and the true minority carrier recombination lifetime is  $0.7 \mu\text{s}$ . The results in Figure 1 show that the top of the ingot has the largest trap density and the bottom the lowest.

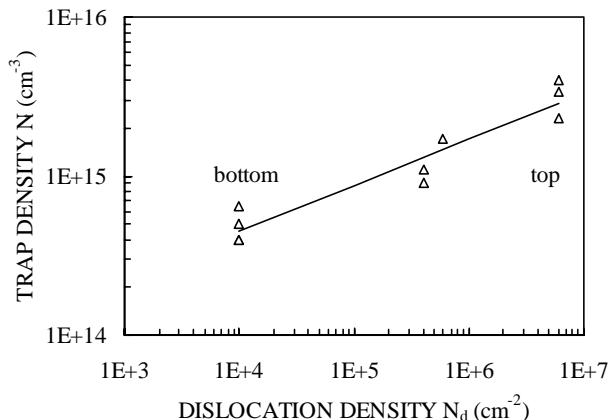


Figure 2. Dislocation density  $N_d$  versus trap density  $N_t$  for phosphorus gettered wafers from different regions of the same mc-Si ingot. The line of best fit takes the form  $N_t = 3.1 \times 10^{13} (N_d)^{0.29}$ .

As an additional characterization of the material, we measured the density of dislocations by counting etch pits under an electron microscope. The dislocation density was found to be highest at the top of the ingot, probably due to high thermal stresses resulting from rapid cooling at the end of the casting process. Figure 2 shows a plot of trap density against dislocation density for the samples in Figure 1, plus data from five additional samples from the same ingot. Figure 2 reveals that a correlation exists between the densities of trapping centres and dislocations for this particular mc-Si ingot.

## 3. Transferring the traps to single crystal silicon

Mobile impurities in mc-Si can be transferred to nearby high quality, single crystal, float zone (FZ) wafers by effusion at high temperature<sup>7</sup>. Such cross-contamination produces a reduction in the lifetimes of the FZ wafers that is proportional to the initial contamination level of the mc-Si wafers. We have recently noticed that these contaminated FZ wafers also exhibit considerable trapping effects, which is a clear indication that mobile impurities can also be responsible for the creation of trapping centers.

An important advantage of the cross-contamination experiments is that they allow the study of trapping and recombination centers in a material that is practically free of crystallographic defects. They also provide a way of examining the possible correlation between the background doping and the trapping effects by contaminating FZ wafers of different resistivities. This may not be possible with the mc-Si wafers, which come only in a narrow dopant density range, and in which a similar crystal quality cannot be guaranteed.

Cross-contamination of p-type FZ Si wafers was achieved by an  $840^\circ\text{C}$  light phosphorus diffusion followed by a thin thermal oxide growth at  $900^\circ\text{C}$ , for a total of 60 minutes. The high temperature allows the effusion of impurities from the mc-Si to the FZ Si (separated by about 5mm), whilst the diffusion and oxidation passivate the surfaces for lifetime measurements. After cross-contamination, the trap density  $N_t$  in the FZ wafers was found to be around 100 times less than in the mc-Si wafers. Consequently we used mc-Si samples with a high trap density to ensure measurable trapping effects in the FZ wafers. The mc-

Si samples used in this study were adjacent wafers taken from the top of a 1 Ωcm p-type cast mc-Si solar grade ingot. These mc-Si wafers were similar to sample 6A of Figure 1, although they had not been gettered and presented a slightly greater trap density of around  $7 \times 10^{15} \text{ cm}^{-3}$ .

Figure 3 shows lifetime measurements of two such cross-contaminated FZ samples of 0.3 and 8 Ωcm resistivity. At higher injection levels the effective lifetimes reflect the bulk lifetimes, however at around  $1 \times 10^{14} \text{ cm}^{-3}$  and  $2 \times 10^{12} \text{ cm}^{-3}$  for the 0.3 and 8 Ωcm samples respectively, trapping effects begin to dominate. The contaminating species are most likely transition metals such as Fe and Cr (known to exist in significant amounts in these mc-Si wafers). Their presence in the FZ material has two effects on lifetime – firstly the introduction of trapping centers and the associated apparent increase in lifetime at low injection level; secondly, the introduction of recombination centres and the resulting Shockley Read Hall (SRH) dependence of lifetime on injection level<sup>8,2</sup>. The presence of the emitter caused by the phosphorus diffusion in these samples also impacts on the lifetime at the highest injection levels<sup>9</sup>.

As well as experimental data, Fig 3 also shows fit lines for the trapping model. However, the fitting procedure is more complex than that used in Fig 1, where the recombination lifetime  $\tau_r$  was assumed constant. The curves in Fig 3 clearly show an injection level dependence at carrier densities higher than the region where traps dominate. This dependence is caused by the SRH behaviour of the impurities, and also by the emitter as mentioned above. As a result, for p-type Si,  $\tau_r$  must be modeled by<sup>2,8</sup>:

$$\frac{1}{\tau_r} = \frac{1}{\tau_{SRH}} + \frac{1}{\tau_{emit.}}$$

where

$$\frac{1}{\tau_{SRH}} = \frac{N_A + \Delta n}{\tau_{p0}(n_1 + \Delta n) + \tau_{n0}(N_A + p_1 + \Delta n)}$$

$$\frac{1}{\tau_{emit.}} = \frac{2J_0(N_A + \Delta n)}{qn_i^2 W}.$$

Here,  $\Delta n$  is the excess carrier density,  $N_A$  the dopant density,  $n_1$  and  $p_1$  the equilibrium densities of electrons and holes respectively when the Fermi energy coincides with the flaw energy, and  $\tau_{n0}$  and  $\tau_{p0}$  the capture time constants for electrons and holes<sup>2</sup>.  $J_0$  is the emitter saturation current, which characterises recombination in the diffused regions ( $\approx 5 \times 10^{-14} \text{ A cm}^{-2}$

$\text{cm}^2$ ), and  $n_i$  and  $W$  the intrinsic carrier concentration and sample thickness respectively.

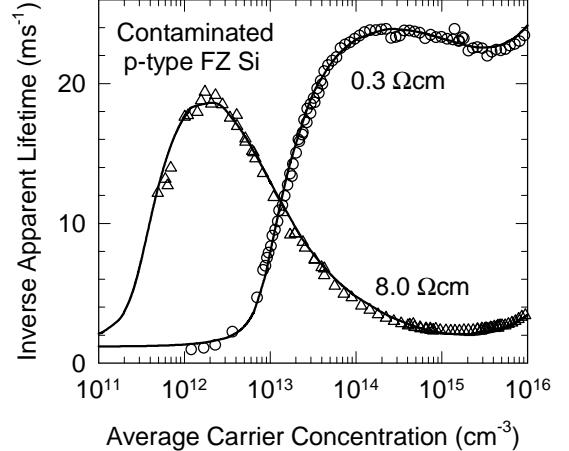


Figure 3: Inverse apparent lifetime versus average carrier concentration for 0.3 and 8.0 Ωcm cross-contaminated FZ Si wafers. The open symbols are experimental data. The solid lines represent the trapping model fitted with the recombination lifetime  $\tau_r$  modelled by two SRH centers and an emitter term. Both curves show the emitter term dominating at high injection, SRH behaviour at moderate to low injection, and trapping at the lowest injection levels.

To obtain an accurate fit to the experimental data in Fig 3, it was necessary to model  $\tau_r$  with two SRH centers. Having two centers means that there are six fit parameters for the SRH contribution to  $\tau_r$ , resulting in a large number of possible sets of parameters that provide reasonable agreement with the experimental data. As a consequence, it is not possible to uniquely determine  $\tau_{n0}$  and  $\tau_{p0}$  or the energy level of the recombination centers. However, for any set of parameters that provide a good fit, the corresponding trap density  $N_t$  is restricted to a narrow range. Hence we are in a position to accurately specify  $N_t$ , even if we can infer little about the detailed properties of the SRH centers.

#### 4. Dependence of the density of traps on boron concentration

The bulk trap density was determined for a range of contaminated FZ wafers of resistivity from 0.3 to 1000 Ωcm. For the 1000 Ωcm case the trap density was so small ( $< 1 \times 10^{11} \text{ cm}^{-3}$ ) as to be unmeasurable. The results for the other wafers are shown in Fig 4 as a function of boron concentration in the FZ substrate. There is a clear linear relationship between these variables, implying that the traps are related to a boron-impurity pair. The impurity, or impurities have clearly come from the mc-Si wafers, and hence must

be highly mobile in silicon at high temperatures in order to effuse out of them and diffuse into the bulk of the FZ wafers.

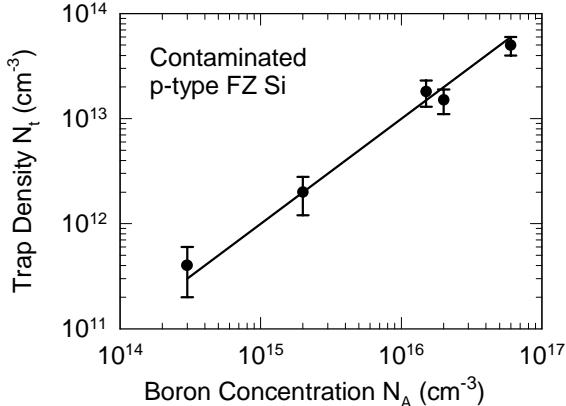


Figure 4: Boron concentration  $N_A$  versus trap density  $N_t$  for cross-contaminated B-doped p-type FZ wafers of different resistivities. The solid line represents the linear fit  $N_t = 0.001N_A$ .

## 5. Conclusions

Cross-contamination of FZ wafers with impurities from mc-Si wafers reveals that some trapping centers in mc-Si wafers are mobile and can effuse from them and penetrate the bulk of the FZ wafers. This leads to associate those trapping centers with highly mobile impurities such as transition metals. Moreover, the density of such traps is linearly related to the boron concentration in the contaminated p-type FZ wafers, implicating the formation of boron-impurity pairs. A similar correlation is to be expected for mc-Si wafers with various boron doping levels.

There are two pieces of evidence, on one hand the trap density in *gettered* mc-Si wafers is related to the dislocation density in the material; on the other hand, it is also correlated to boron-impurity pairs in *un-gettered* mc-Si wafers. The overall effect of trapping in common, un-gettered mc-Si is logically attributable to a combination of both causes, although their specific contributions can vary from sample to sample and can not be discerned yet. It is also reasonable to expect that trapping centers related to dislocations (and possibly other crystallographic defects) dominate the trapping behaviour of gettered mc-Si. Nevertheless, the possible role of residual metal contaminants cannot be completely ruled out, since they may be precipitated at dislocation sites and be impervious to the gettering treatment. In this latter scenario, even if the dislocations may not be the direct cause of trapping they would still be correlated to it as vehicles for

the anchorage of the impurities.

In conclusion, two possible physical origins for the trapping centers in multicrystalline silicon have been identified: crystallographic defects (dislocations) and boron-impurity pairs produced by mobile contaminants. Experimental evidence indicates that the trapping effects per se do not affect detrimentally solar cell steady-state operation<sup>10</sup>. It remains to be seen whether they can be useful for material diagnostic and optimization of mc-Si growth and processing techniques.

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## 6. References

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## APPENDIX.

The application of Hornbeck-Haynes model to steady-state photoconductance measurements can be summarized in the following expressions.

Charge neutrality demands that  $\Delta p = \Delta n + n_t$ , where  $n_t$  is the trapped electron concentration. The excess conductivity  $\Delta\sigma$  (due to untrapped carriers) is:

$$\Delta\sigma = q\Delta n(\mu_n + \mu_p) + qn_t\mu_p$$

$$\Delta n = g_e\tau_r$$

$$n_t = \frac{N_t\Delta n}{\Delta n + N_t\tau_t/\tau_g}.$$

where  $\mu_n$  and  $\mu_p$  are the electron and hole mobilities,  $g_e$  is the photo-generation rate,  $N_t$ , the density of trapping centers and  $\tau_t$  and  $\tau_g$ , the trapping and escape times. In the common interpretation of steady or quasi steady-state photoconductance measurements, the effective carrier lifetime  $\tau_{eff}$  is calculated from the excess conductivity and the photo-generation rate as:

$$\tau_{eff} = \frac{\Delta\sigma}{g_e (\mu_n + \mu_p)}.$$

Note that, for a given photogeneration rate, the density of free electrons  $\Delta n$  remains equal to that expected when no traps are present. The main consequence of trapping is an increased number of excess holes, resulting in an enhanced photoconductance.