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Understanding carrier trapping in multicrystalline silicon

Daniel Macdonald*, Andrés Cuevas

Centre for Sustainable Energy Systems, FEIT, Department of Engineering, Australian National University, Canberra ACT 0200, Australia

Abstract

The physical origin of minority carrier trapping centers in multicrystalline silicon is explored in both gettered and non-gettered material. The experimental evidence suggests that there are two types of trap present. One species can be removed by gettering and is related to the presence of boron–impurity pairs or complexes. The other type is impervious to gettering and is correlated to the dislocation density. Annealing experiments reveal that the trapping centers caused by boron–impurity complexes can be dissociated, and that these trapping centers do not contribute to recombination. The effect of trapping centers on open-circuit voltage is shown to be negligible when the trap density is less than the dopant density. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Minority carrier 'traps' are often present in significant quantities in solar grade multicrystalline silicon (mc-Si), as well as in polycrystalline silicon thin films and cadmium telluride [1]. In the context of this paper, the term 'traps' refers to states in the band gap which temporarily hold minority carriers, but may not act as recombination centers. Such trapping centers cause a drastic increase in photoconductivity at carrier injection levels equal to and below the trap density [2,3]. An important consequence of such behavior is that any photoconductance-based lifetime technique

* Corresponding author..
E-mail address: daniel@faceng.anu.edu.au (D. Macdonald).

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cannot be relied upon to provide reasonable lifetime measurements at these injection levels, which are often of great interest in solar cell applications. Such considerations provide a strong incentive for gaining a greater understanding of these centers.

In this paper we present work which attempts to determine the physical origin of trapping centers in mc-Si. Evidence of two different types of trapping center is presented, one type being related to dislocations and the other to boron–impurity complexes. The effect of the trapping centers on solar cell open-circuit voltage (V_{OC}) is also examined. In accordance with expectations from theoretical considerations, the impact of traps on cell voltage is negligible when the density of trapping centers is significantly less than the dopant density. However, the presence of traps does affect our ability to *predict* V_{OC} using photoconductance data measured on cell precursors.

2. Experimental methods

Apparent minority carrier lifetimes were measured using the quasi-steady-state photoconductance technique (QSSPC), which is well suited for taking 'averaged' measurements on highly inhomogeneous material like mc-Si [4]. The instrument is sufficiently sensitive to allow a very large range of injection levels to be examined, from 1×10^{12} to $1\times10^{17}\,cm^{-3}$. The QSSPC data analysis is performed according to a recently modified approach which permits the measurement of lifetimes from less than 1 μs to several milliseconds [5].

The mc-Si wafers used in these experiments were grown by directional solidification at Eurosolare SpA (Italy). The wafers come from standard solar grade ingots that are typical of those processed commercially into cells. To allow bulk lifetime measurements, the surfaces of the samples were passivated with a light phosphorus diffusion and a thin dry oxide. Such a passivation scheme, when applied to single-crystal floating-zone (FZ) silicon, is sufficient to allow lifetime measurements about an order of magnitude larger than any measured on the multicrystalline wafers. Hence, we are able to interpret all lifetime measurements on the mc-Si samples as relating to bulk properties.

Gettering was performed by a heavy phosphorus diffusion at 900°C for 3 h. The gettering layer was subsequently etched away before re-passivation as above. Infrared illumination was used when measuring lifetimes of samples which had diffusion lengths significantly lower than the wafer width, in order to ensure uniform carrier profiles.

3. Trapping model

During the 1950s, trapping phenomena were common in single-crystal silicon due to the relatively poor quality of the material [6,7]. Haynes and Hornbeck [6] developed a simple trapping model that explained the effect of trapping on drift mobility measurements, and also on steady-state and transient photoconductance decay (PCD) lifetime measurements. Their model was centered on the concept of

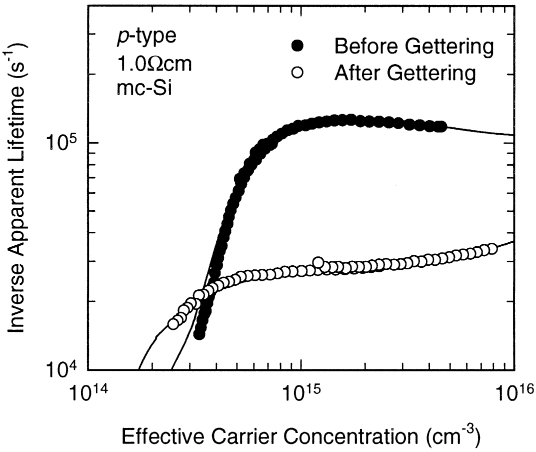

Fig. 1. Inverse apparent lifetime versus effective carrier concentration for a typical mc-Si sample before and after gettering. The solid lines represent the trapping model fitted to the data.

states in the energy gap which temporarily hold minority carriers, but do not act as recombination centers. Such states result in a certain proportion of minority carriers being removed from the recombination channels, resulting in an increase in the concentration of majority carriers, in turn causing a larger photoconductance and hence a larger apparent lifetime. Such lifetimes do not however reflect *minority* carrier lifetimes [2,3].

Modern FZ silicon is no longer plagued by trapping effects, but mc-Si very often is. Fig. 1 illustrates the effect of traps on a typical mc-Si sample. As the carrier density decreases below about $1\times10^{15}\,\mathrm{cm}^{-3}$, the apparent lifetime increases rapidly due to the relative build-up of majority carriers caused by the traps. Such dramatic injection level dependence is diagnostic of trapping effects, since other sources of injection level dependence, such as Shockley–Read–Hall recombination, are very unlikely to produce such behavior. Fig. 1 also shows the Haynes and Hornbeck model fitted to the data, which allows determination of the trap density. The adaptation of the model for the QSSPC method, including details of the fitting procedure, is reported elsewhere [8,9].

4. Results

Fig. 1 shows inverse 'apparent' lifetime versus injection level data for a typical mc-Si wafer, both before and after gettering. We refer to the results as 'apparent' lifetimes because only at carrier concentrations above the trap density can we associate the measured values with recombination lifetimes. Note that the presence of trapping centers makes measurement of the recombination lifetime below about $1\times10^{15}\,\mathrm{cm}^{-3}$ in the non-gettered wafer impossible. This is significant for solar cell applications, since at maximum power under 1 sun illumination, a cell made from this sample would be operating at carrier densities well below $1\times10^{15}\,cm^{-3}$.

The gettering treatment has had a two-fold effect, namely to reduce the trap density (from 2×10^{15} to $7\times10^{14}\,cm^{-3}$), and also to increase the recombination lifetime (from around 10 to 30 μs). Phosphorus gettering has been known for many years to remove mobile impurities from the bulk of silicon wafers, resulting in the observed increase in lifetime. Clearly, the gettering treatment has also removed some of the centers responsible for the trapping effects. However, there still remains a significant quantity of trapping centers after gettering. Hence, we broadly classify the trapping centers into two categories: those which can be removed by gettering, and those which cannot. We next describe experiments which help to elucidate the physical source of these two types of trapping centers.

4.1. Traps in gettered mc-Si

For the sample in Fig. 1, the trap density decreased after gettering, but then remained constant despite subsequent extra gettering steps. These remaining traps must therefore be related to non-getterable defects or impurity complexes. In some early single-crystal wafers which exhibited trapping, dislocations were found to be the culprits [10]. Since multicrystalline wafers also contain significant quantities of dislocations, we looked for a correlation between dislocation density and trap density.

Fig. 2(a) illustrates that such a correlation exists for this mc-Si material. Two possible interpretations of this result suggest themselves: firstly, dislocations may be directly responsible for the trapping centers. Alternatively, dislocations may act as precipitation sites for other impurities which cause traps, rendering the complexes impervious to gettering [11].

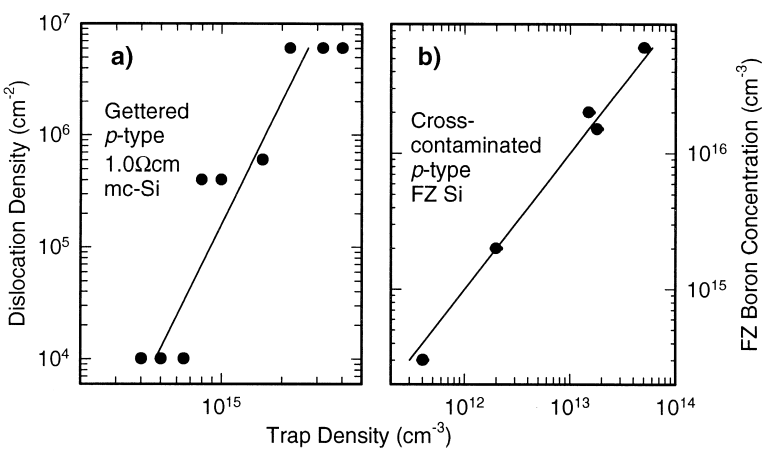

Fig. 2. (a) Trap density versus dislocation density in gettered mc-Si samples, and (b) trap density versus boron doping concentration in cross-contaminated FZ samples of varying resistivities. The solid lines provide guides to the eye.

4.2. Traps in non-gettered mc-Si

The fact that some traps in non-gettered material are removed by gettering implies that they are caused by mobile impurities. To investigate further the exact nature of these mobile trapping states, we performed a series of cross-contamination experiments [12,9], in which impurities from mc-Si wafers are effused, at high temperature, into closely packed single-crystal FZ silicon wafers. The full details of this experiment can be found elsewhere [9], but the important result is that trapping centers are evident in these cross-contaminated wafers, indicating that trap-causing impurities have effused into the FZ wafers from the mc-Si. Furthermore, as revealed by different resistivity FZ wafers, the density of these trapping centers is linearly related to the background boron concentration in the FZ samples, as shown in Fig. 2(b). Clearly then the density of trapping centers in the FZ material depends on both the boron concentration and the presence of impurities from the mc-Si samples. The natural conclusion is that these traps are caused by impurity–boron pairs or complexes.

Further weight is lent to this hypothesis by the mc-Si wafers themselves. Fig. 3 illustrates results for a standard mc-Si wafer before and after gettering. However, before the gettering treatment, the wafer was subjected to a 10 min 200°C anneal, and the lifetimes re-measured. The annealing had no impact on the recombination lifetime, but did result in a decrease in the trap density from 2.7×10^{15} to $1.3\times10^{15}\,cm^{-3}$. The wafer was re-measured again after one week, and the trap density was found to have increased again to $1.9\times10^{15}\,cm^{-3}$. These results are consistent with the suggestion that in non-gettered wafers, some traps are caused by

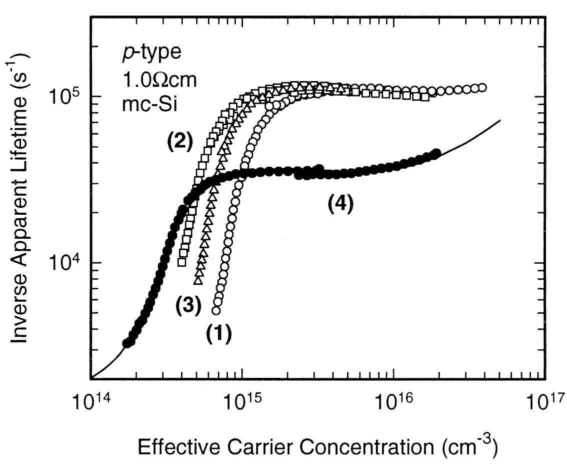

Fig. 3. Inverse apparent lifetime versus effective carrier concentration for a mc-Si sample as measured (1) six months after any thermal treatment; (2) directly after thermal annealing at 200°C for 10 min; (3) 7 days after thermal annealing and (4) after gettering. The results for thermal annealing of the sample after gettering are not shown as they lie on top of curve (4). The solid line through curve (4) represents the trapping model fitted to the data.

impurity-boron complexes. These complexes can be dissociated through annealing, after which they slowly re-associate at room temperature, in a similar way to Fe–B pairs in silicon. Note however, that we can rule out Fe–B pairs as the cause of the traps, because if they were present in such high concentrations, the recombination lifetime would necessarily be much lower.

A further interesting result of this study is that these centers act only as traps, i.e. they do not also act as recombination centers. This is in-keeping with one of the main assumptions of the trapping model.

As a final piece of evidence, Fig. 3 also shows the same sample after gettering. As is usual, the recombination lifetime has increased, and the trap density decreased (to $9.5\times10^{14}\,\mathrm{cm}^{-3}$), indicating that the trap-causing impurity–boron complexes have been dissociated and removed by the gettering. The sample was then annealed at 200°C again. Both the recombination lifetime and trap density remained unchanged, confirming that the remaining traps are not boron–impurity related.

5. Effect of traps on open-circuit voltage

From a theoretical standpoint, minority carrier traps result only in a relative increase in majority carrier concentration. The density of free (un-trapped) minority carriers remains exactly as would be the case if the traps were absent. Hence, if the trap density is significantly less than the dopant density (always true in our samples), the excess majority carriers will not significantly change the total majority carrier population. Consequently, we would not expect the presence of traps to noticeably affect device voltage.

A useful feature of the QSSPC technique is that it allows an implied V_{OC} to be calculated for a given sample, since the concentration of excess carriers is known at each illumination level [13]. The implied V_{OC} is measured after all high-temperature cell fabrication steps, and immediately prior to metallization. These values are then compared with the measured V_{OC} after metallization.

Such a comparison is presented in Fig. 4 for two different wafers. The mc-Si sample in Fig. 4(a) had a relatively low trap density ($2\times10^{13}\,\mathrm{cm}^{-3}$), in fact low enough to be insignificant at 1 sun illumination levels. Consequently, the value of the implied V_{OC} agrees well with the measured V_{OC} (612 and 616 mV) at 1 sun. However, the implied V_{OC} curve is affected by trapping at illumination levels below about 0.2 suns, due to the erroneously large excess carrier density measured by the QSSPC technique. In contrast, the measured V_{OC} values do not reflect any such effects. These results confirm that trapping centers do not affect cell voltage significantly.

A more typical mc-Si solar cell is shown in Fig. 4(b). In this case, the trap density is high ($1\times10^{16}\,\mathrm{cm}^{-3}$), and causes a drastic over-prediction of V_{OC} at 1 sun (by about 100 mV). This example serves to illustrate how trapping causes difficulty in process monitoring in standard mc-Si. The solid line in the figure represents an extrapolation of the recombination lifetime as measured above $1\times10^{16}\,\mathrm{cm}^{-3}$, to lower injection regions. Such an extrapolation predicts a V_{OC} at 1 sun of 602 mV, as compared with the measured V_{OC} of 585 mV. Clearly, such a procedure is still insufficient for

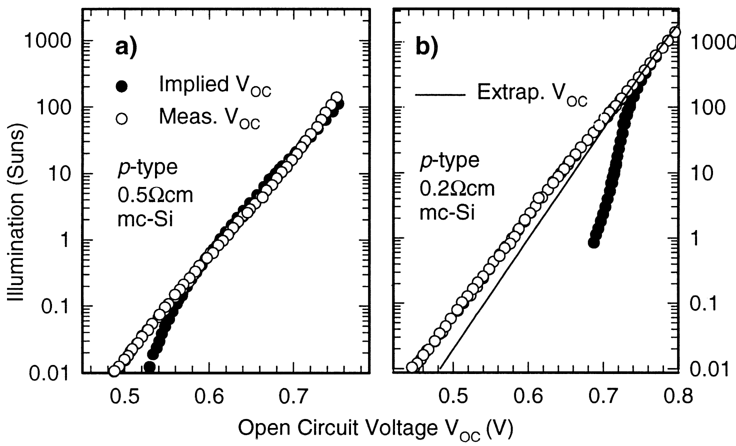

Fig. 4. Comparison of implied and measured open-circuit voltage V_{OC} versus illumination in suns for mc-Si substrates with (a) a low trap density, and (b) a high trap density. The solid line in (b) represents an extrapolation of the recombination lifetime as measured at high illumination levels to lower illumination levels.

predicting cell V_{OC}, due to the masking of the injection level dependence of the recombination lifetime at lower injection levels by the trapping centers.

6. Conclusions

Two types of trapping centers appear to occur in mc-Si, one related to dislocations and another to boron–impurity complexes. The boron–impurity traps can be removed by gettering, and can also be dissociated by thermal annealing. The presence of traps distorts photoconductance measurements, and hence minority carrier lifetimes calculated from such measurements, but does not impact directly on cell voltage.

Acknowledgements

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References

[1] R. Ahrenkiel, B. Keyes, D. Levi, Proceedings of the 13th European Photovoltaic Solar Energy Conference, H.S. Stephens and Associates, Felmersham, 1996, pp. 914–917.
[2] J.S. Blakemore, Semiconductor Statistics, Pergamon Press, Oxford, 1962.
[3] R.A. Smith, Semiconductors, Cambridge University Press, Cambridge, 1959.

[4] R. Sinton, A. Cuevas, Appl. Phys. Lett. 69 (1996) 2510.
[5] H. Nagel, C. Berge, A. Aberle, Generalized analysis of quasi-steady-state and quasi-transient measurements of carrier lifetimes in semiconductors, J. Appl. Phys. 86 (1999) 6218.
[6] J.A. Hornbeck, J.R. Haynes, Phys. Rev. 97 (1955) 311.
[7] H.Y. Fan, Phys. Rev. 92 (1953) 1424.
[8] D. Macdonald, A. Cuevas, Appl. Phys. Lett. 74 (1999) 1710.
[9] D. Macdonald, A. Cuevas, Appl. Phys. Lett. 75 (1999) 1571.
[10] K. Glinchuk, N. Litovchenko, V. Novikova, Sov. Phys. Solid State 8 (1966) 777.
[11] S. McHugo, A. Thompson, I. Perichaud, S. Martinuzzi, Appl. Phys. Lett. 72 (1998) 3482.
[12] D. Macdonald, A. Cuevas, Proceedings of Second World Conference on Photovoltaic Solar Energy Conversion, Vienna, European Commision, Luxembourg, 1998, 2418–2421.
[13] A. Cuevas, R. Sinton, Prog. Photovoltaics 5 (1997) 75.