Recombination and Trapping in Multicrystalline Silicon Solar Cells

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Declaration

I certify that this thesis does not incorporate without acknowledgement any material previously submitted for a degree or diploma in any university, and that, to the best of my knowledge, it does not contain any material previously published or written by another person except where due reference is made in the text. The work in this thesis is my own, except for the contributions made by others as described in the Acknowledgements.

Daniel Macdonald

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Abstract

In broad terms, this thesis is concerned with the measurement and interpretation of carrier lifetimes in multicrystalline silicon. An understanding of these lifetimes in turn leads to a clearer picture of the limiting mechanisms in solar cells made with this promising material, and points to possible paths for improvement. The work falls into three broad categories: gettering, trapping and recombination. A further section discusses a powerful new technique for characterising impurities in semiconductors in general, and provides an example of its application.

Gettering of recombination centres in multicrystalline silicon wafers improves the bulk lifetime, often considerably. Although not employed deliberately in most commercial cell processes, gettering nevertheless occurs to some extent during emitter formation, and so may have an important impact on cell performance. However, the response of different wafers to gettering is quite variable, and in some cases is non-existent. Work in this thesis shows that the response to gettering is best when the dislocation density is low and the density of mobile impurities is high. For Eurosolare material these conditions prevail at the bottom and to a lesser extent in the middle of an ingot. However, these conclusions can not always be applied to multicrystalline silicon produced by other manufacturers. Low resistivity multicrystalline silicon suffers from a concurrent thermally induced degradation of the lifetime. This had previously been attributed to the dissolution of precipitated metals, although we note that the crystallographic quality also appears to deteriorate. The thermal degradation effect results in an optimum gettering time for low resistivity material. Edge-defined Film-fed Growth (EFG) ribbon silicon was also found to respond to gettering, and even more so to bulk hydrogenation. Evidence for Cu contamination in the as-grown EFG wafers is presented.

Multicrystalline silicon is often plagued by trapping effects, which can make lifetime measurement in the injection-level range of interest very difficult, and sometimes impossible. An old model based on centres that trap and release minority carriers, but do not interact with majority carriers, was found to provide a good explanation for these effects. These trapping states were linked with the presence of dislocations and also with boron-impurity complexes. Their annealing behaviour and lack of impact on device parameters can be explained in terms of the models developed. The trapping model allowed a recently proposed method for correcting trap-affected data to be tested using typical values of the trapping parameters. The correction method was found to extend the range of useable data to approximately an order of magnitude lower in terms of carrier density than would be available otherwise, an improvement that could prove useful in many practical cases.

High efficiency PERL and PERC cells made on gettered multicrystalline silicon resulted in devices with open circuit voltages in the 640mV range that were almost entirely limited by

bulk recombination. Furthermore, the injection-level dependence of the bulk lifetime resulted in decreased fill factors. Modelling showed that these effects are even more pronounced for cells dominated by interstitial iron recombination centres. Analysis of a commercial multicrystalline cell fabrication process revealed that recombination in the emitter created the most stringent limit on the open circuit voltage, followed by the bulk and the rear surface. The fill factors of these commercial cells were mostly affected by series resistance, although some reduction due to injection-level dependent lifetimes seems likely also. Secondary Ion Mass Spectroscopy on gettered layers of multicrystalline silicon revealed the presence of Cr and Fe in considerable quantities. Further evidence strongly implied that they resided almost exclusively as precipitates.

More generally, injection-level dependent lifetime measurements offer the prospect of powerful contamination-monitoring tools, provided that the impurities are well characterised in terms of their energy levels and capture cross-sections. Conversely, lifetime measurements can assist with this process of characterising impurities, since they are extremely sensitive to their presence. This possibility is explored in this thesis, and a new technique, dubbed Injection-level Dependent Lifetime Spectroscopy (IDLS) is developed. To test its potential, the method was applied to the well-known case of FeB pairs in boron-doped silicon. The results indicate that the technique can offer much greater accuracy than more conventional DLTS methods, and may find applications in microelectronics as well as photovoltaics.

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Introduction

Crystalline silicon remains the material of choice for large-scale commercial production of photovoltaic modules. It has the natural advantages of being an abundant element with a well-suited band-gap for photovoltaic conversion, and is non-toxic. Also, due to its dominance in the microelectronics industries, it has become by far the most studied of all the semiconductors, and many specialised processes involving its use have been developed and refined over several decades. Some of these processes and much of the accumulated knowledge have been directly transferred to photovoltaic applications with great benefit.

However, crystalline silicon is not guaranteed to maintain its dominant position in photovoltaics in the medium to long term, at least not in the form of wafers sawn from bulk ingots. Reduced processing costs and improved cell fabrication techniques will ultimately lead to the underlying cost of the wafers themselves placing a limit on how cheaply such cells can be produced[1]. The need for further cost reductions is expected to lead eventually to the dominance of thin-film technologies, possibly still based on crystalline silicon. However, it is fair to say that thin-film cells, sometimes referred to as second generation photovoltaics, have been slower to oust bulk silicon from market dominance than many observers originally expected. It seems unlikely that any current thin-film technique will be in a position to do this within the next few years at least.

Taking an even longer-term view, such thin-film technologies as they are being developed today may still not represent full maturity of the photovoltaic industry. The underlying material costs of these devices are anticipated to continue to impose a significant lower limit on final product price, though much reduced compared to bulk silicon. The best path to further reductions then is to dramatically improve efficiency without a corresponding price increase. Such improvements can only be achieved by employing completely new device structures that avoid the fundamental efficiency limits of current single band-gap structures. These technologies are only now beginning to be seriously considered, and are collectively termed third generation photovoltaics[1]. It is expected to be many years, perhaps twenty, before such novel devices are in a position to dominate the marketplace.

As such there will very likely be a fairly long period in which bulk silicon still plays a major role in the photovoltaics industry. This is reflected by the fact that in the year 2000, bulk silicon accounted for 86.4% of world production, up from 84.4% in 1999[2]. The work presented in this thesis is firmly rooted in such first generation technology, and is devoted to exploring ways of improving the performance of silicon solar cells manufactured using widely available techniques. In particular, it focuses on the use of cast multicrystalline silicon (mc-Si), a material that has become increasingly important in the commercial sphere. This material is somewhat cheaper to produce than single-crystal Czochralski-grown (Cz) wafers, but also results in less efficient cells, although this gap is narrowing. This trade-off between cost and efficiency had resulted in mc-Si and single-crystal Cz cells being approximately comparable in price per watt terms. However, it seems that this balance has recently shifted in favour of mc-Si, which accounted for 48.1% of world production in 2000 compared with 42% in 1999[2]. Over the same period, the market share of single-crystal silicon cells dropped from 42% to 37.3%. Judging from planned capacity expansions over the next few years it appears that this gap will widen further. It seems then that mc-Si will enjoy at least several years of market dominance, and, depending on the success of thin-film development, possibly many more.

In broad terms, this thesis is intended to contribute to the existing body of knowledge concerning mc-Si cells and how their performance may be improved. To provide a context for the work, a brief overview of the main efficiency loss mechanisms in silicon cells in general is presented next. In particular, a comparison between high-efficiency single-crystal Float Zone (FZ) cells and standard commercially produced mc-Si cells, reveals the important points which provide the motivation for the ensuing work.

Loss mechanisms in crystalline silicon solar cells

For a single band-gap solar cell, there are a number of fundamental and hence unavoidable loss mechanisms. Two of the most important of these are illustrated in Figure 1. Photons with energy higher than the band-gap are easily absorbed, producing an electron-hole pair in the process. However, the extra energy of the photon causes the photogenerated carriers to be excited into states of higher energy than the band-edges. These ‘hot’ carriers then rapidly lose energy until they reach the band-edges, a process called thermalisation. This energy loss occurs through successive emission of phonons, and is generally complete within a nanosecond, making it effectively instantaneous in comparison to other important carrier processes such as diffusion and recombination. By using AM1.5G spectrum data[3,4] and assuming a silicon band-gap of 1.124eV and no reflection, these thermalisation losses alone result in a loss of approximately 28% of the available incident energy. This type of loss can be reduced by tandem cell approaches, and possibly also by ‘hot carrier’ cells which extract carriers before they can thermalise. For standard single-junction devices such as mc-Si cells, however, this loss is unavoidable.

Photons of energy less than the band-gap represent another loss, as they are not absorbed by silicon, as shown again in Figure 1. This transmission of infrared light represents an

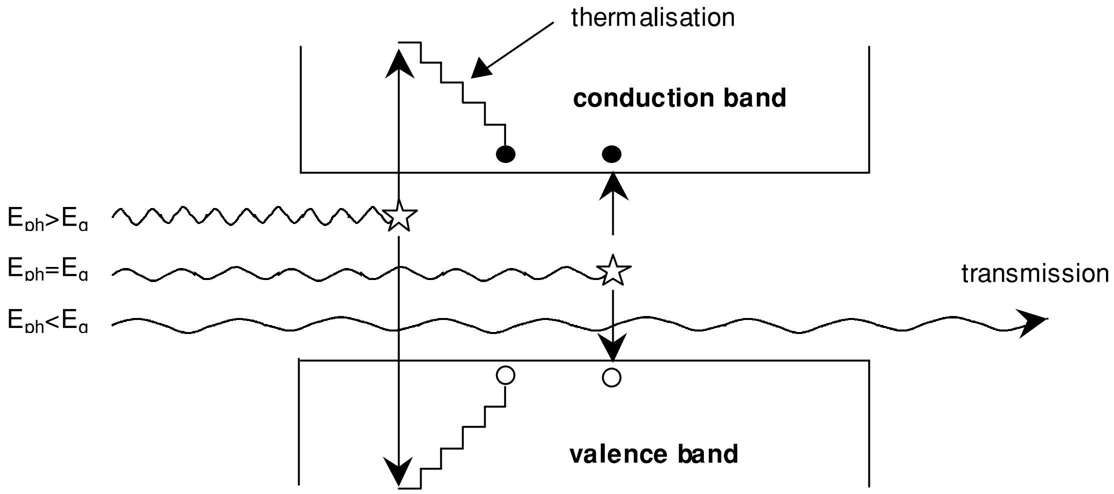

Figure 1. Thermalisation and transmission loss mechanisms in a single band-gap solar cell.

approximate loss of another 27% under AM1.5G conditions, assuming there is no sub-band-gap absorption due to phonon-assisted processes. Together, these fundamental mechanisms of thermalisation and infrared transmission reduce the maximum achievable efficiency for single-junction silicon cells to around 45%.

There are, however, additional fundamental processes that further reduce this figure. For a 1-sun cell (i.e. no concentration), radiative recombination brings this limit down to 31.7% when using the measured optical absorption spectrum of silicon, with the effects of free carrier absorption included[5]. Auger recombination causes a further reduction in the limit to around 29.8%[5,6]. Slightly higher values can be produced by including phonon- or impurity-assisted sub-band-gap generation, or by multiple electron-hole pair creation by very high energy photons[3,7]. However, the limits mentioned above are sufficient for our current purposes. All of these calculations still assume perfect light trapping and no external reflection, idealisations that are in practice unachievable. Other loss mechanisms that must be present to some extent in any real cell are recombination through defects in the bulk and at the surfaces, and resistive effects.

The best 1-sun single-crystal FZ silicon cell made to date was a 24.7% efficient Passivated Emitter and Rear Locally diffused (PERL) device[8], which, considering the potential for other losses, is remarkably close to the Auger limit above. To illustrate their relative importance, the impact of these other avoidable loss mechanisms in a typical high-efficiency PERL cell are shown in Figure 2. The values in the chart are based on those published by Aberle *et al.*[7] for a PERL cell with a slightly lower efficiency of 22.9%. The fundamental mechanisms of Auger, radiative, thermalisation and infrared loss discussed above have been excluded to allow better presentation of those that can be reduced through improved

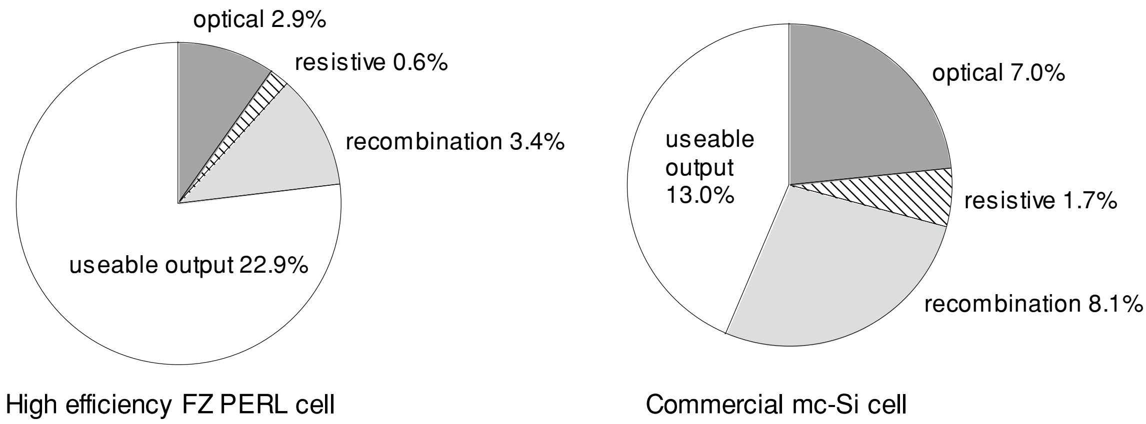

Figure 2. Relative impact of optical, resistive and recombination losses in high-efficiency PERL cells and standard commercial mc-Si cells at maximum power. In both cases only avoidable losses are depicted, hence the sum of the percentages in each chart is only 29.8%, the Auger efficiency limit.

processing and design. Therefore, the entire pie chart only represents 29.8% of the incident energy, consistent with the Auger limit quoted above.

The losses in the chart are broken into three broad categories, namely optical, resistive and recombination losses. In principle, these losses can be reduced indefinitely. Note that the optical section includes front surface reflection (from metal fingers and the anti-reflection coating (ARC)), absorption by the ARC and the rear reflecting surface, and escape of long wavelength light through the front surface (imperfect light-trapping). The resistive component includes bulk, emitter, contact and metal resistive losses. Finally, the recombination section also has a number of contributors, the significant ones being recombination in the bulk, the emitter, and at the front and rear surfaces. The results show that for this PERL cell resistive losses are minimal, while recombination and optical losses have approximately equal impact. No attempt has been made here to break these three major components into their respective parts, although that was partially done by Aberle *et al*. They showed that, at maximum power, approximately half of the recombination losses occurred in the base. The other recombination losses were split between the rear and front surfaces, with the rear probably having the greater impact of the two. Recombination in the emitter region was negligible in this cell. The chart for the PERL cell in Figure 2 serves as a useful ‘baseline’ for comparison with less efficient devices.

Figure 2 also shows a corresponding chart for a standard mc-Si cell produced commercially using screen-printed contacts on a heavily doped, homogeneous emitter with a TiO_x ARC and aluminium back-surface-field (BSF). The values are based on measurements of BPSolar cells, which are described in more detail in Chapter 4. The efficiency of 13% is typical for such cells[9]. Essentially, the optical losses can be easily modelled in PC-1D[10] using the known ARC properties and metal finger dimensions. The resistive losses are estimated from the typical fill factor values, and the recombination losses assumed to make up the difference. As such the results are not exact, but they do serve as a useful comparison with the PERL cell. Also, it should be noted that it is not possible to simply state that by removing optical losses, the mc-Si cell efficiency would improve by 7% absolute, since the recombination and resistive dynamics would be altered also. Similarly, altering the recombination properties will induce changes in the resistive losses.

The results indicate that all three broad categories have increased their relative impact in the mc-Si cell in comparison to the PERL cell. The high optical losses are mostly a reflection of the fact that texturing is difficult to achieve on these substrates due to their random grain orientations. It is not surprising then that texturing of mc-Si has become a major focus of many researchers, with diverse approaches such as mechanical grooving[11], wet acidic etching[12,13], and reactive ion etching[14,15] currently being explored. The optical losses are further increased by absorption of long wavelength light at the rear Al-BSF, and by reflection from the screen-printed metal fingers, which typically cover about 10% of the front surface. By contrast, the PERL cell has inverted pyramid texturing on the front, better rear reflection, and a much lower front metal coverage due to the photolithographically defined and electroplated fingers. The relatively poor electrical performance of the screen-printed contacts also results in greater resistive losses in the mc-Si cells.

However, the major source of loss in these mc-Si cells is recombination, which produces a slightly more severe restriction on performance than optical losses. In fact, by completely eliminating recombination in such cells, the efficiency would improve to near 20%, although, as mentioned, resistive losses would then have more impact. Of course, it is impossible to achieve *zero* recombination in practice, especially considering that it may occur in many parts of the cell such as the bulk, at the surfaces, or within the heavily-doped emitter. Also, to maintain low costs it is necessary to use simple processes, which often lead to greater recombination. Nevertheless, it is clear from the chart that a better understanding of these recombination losses would be of great benefit in developing strategies to reduce their impact while maintaining process simplicity. It is in fact this analysis of recombination in mc-Si cells that forms the basic motivation and unifying theme for the work in this thesis. Optical and resistive losses are not considered in detail in this work, although, as mentioned, they are also important.

In a more general sense, this thesis also aims to develop and demonstrate techniques for studying recombination in semiconductors that can be applied to other types of solar cell, and even more broadly in microelectronics. Since the most relevant parameter for characterising recombination is the carrier lifetime, it is natural that such lifetime measurements and their interpretation play a central role in this thesis. Specifically, the Quasi-Steady-State Photoconductance (QSSPC) technique, a relatively recent and very versatile method for lifetime measurement, is used extensively. This technique is described in detail in Chapter 1, along with other important concepts and tools that are heavily relied upon. Chapters 2 to 4 contain the core of the work regarding mc-Si, dealing with the areas of gettering, trapping and recombination respectively. Chapter 5 is more broadly focused in that it presents a new technique for characterising recombination centres in semiconductors, a development which arose out of the extensive use of lifetime measurements in the preceding chapters. The following section provides a brief outline of each of the five chapters.

Thesis outline

Chapter 1 is concerned with introducing the key techniques and concepts that are used in many places in the following chapters. In particular, the various recombination mechanisms that may be important in silicon solar cells are discussed from a physical point of view, including Auger, radiative and recombination through defects. Expressions for the injection-level dependence of the carrier lifetimes produced by each of these processes are introduced. These expressions are critical in later analysis of measured lifetimes. There are a number of ways in which these fundamental recombination mechanisms may be manifest in a cell, and these are discussed next, particularly defect recombination at surfaces and Auger recombination in heavily-doped regions. The way in which these mechanisms contribute together to produce an *effective* lifetime is also considered. In order to justify the almost exclusive focus on lifetimes, a brief account of their critical impact on cell performance is given, including the effect on open circuit voltage, short circuit current and fill factor. Following that, various lifetime measuring methods are discussed, with special attention paid to the QSSPC technique. The relative advantages of this and other commonly used methods are considered in some detail. Finally, some useful surface passivation recipes are presented.

Chapter 2 examines the effect of phosphorus gettering on the bulk lifetime of mc-Si. Cast mc-Si was found to respond best when the dislocation density was low, and the concentration of mobile impurities high. However, low resistivity wafers were found to suffer from a concurrent thermal degradation of the bulk lifetime during high temperature steps. It has previously been suggested that precipitate dissolution may be responsible for this reduction, but specifically designed gettering experiments indicated that this might not be true. Some circumstantial evidence for a decrease in the crystallographic quality provides an alternative explanation for the thermal degradation. Edge-defined Film-fed Growth (EFG) mc-Si was found to respond to phosphorus gettering to a small extent, while the remaining recombination centres could be passivated by atomic hydrogen, consistent with previous studies. Secondary Ion Mass Spectroscopy (SIMS) revealed that Cu might be responsible for the low initial lifetimes.

Chapter 3 focuses on trapping in mc-Si. This effect distorts recombination lifetime measurements, and as such is somewhat of a nuisance. Nevertheless, it appears to be very common in this type of material, and so is important to understand in order to try to make sense out of such lifetime measurements. A minority carrier trapping model developed in the 1950's is shown to provide a good explanation for the unusual injection-level dependence caused by the effect. The lack of impact that trapping has on device performance can also be explained in terms of this model. The physical origin of the trapping centres is examined, with evidence pointing to both dislocations and boron-impurity complexes. Finally, a recently proposed method for correcting trap-affected lifetime data is tested and found to provide a useful extension of the range of usable data.

Chapter 4 is in some ways the culmination of the previous chapters, bringing the conclusions and techniques together to allow an in depth analysis of the recombination mechanisms in mc-Si cells. High efficiency 1.5Ωcm mc-Si PERL cells fabricated at ANU produced reasonable efficiencies, but were almost entirely dominated by bulk recombination. This was also true for Passivated Emitter and Rear Cells (PERC) cells made on 0.2Ωcm mc-Si. The PERL cells were found to have reduced fill factors due to the injection-level dependence of the bulk lifetime, an effect which is shown to be even more pronounced if a cell is dominated by interstitial Fe. SIMS results on cast mc-Si revealed both Cr and Fe, but further evidence suggests that these are present almost exclusively as precipitates, not interstitially. Lifetime techniques were applied to the commercial mc-Si process used by BPSolar, indicating that the emitter is the source of the greatest recombination loss in these cells, followed by the bulk and the rear Al BSF.

Chapter 5, while still based firmly on recombination and lifetime measurements, is not focused on mc-Si. This chapter introduces a new technique for determining the capture cross-sections of impurities in semiconductors in general. In the previous chapters, it was recognised that accurate knowledge of these cross-sections allows powerful diagnostic tools to be developed. In general however, these cross-sections are not well known. Injection-level dependent lifetime measurements, being extremely sensitive to impurities, offer an excellent possibility for determining these cross-sections if samples with controlled impurity doses are used. Chapter 5 applies this new technique, dubbed Injection-level Dependent Lifetime Spectroscopy (IDLS), to the acceptor level of FeB pairs. The results are more accurate than comparable results from the widely used Deep Level Transient Spectroscopy (DLTS) technique. Other future applications of IDLS are discussed.