

**Surface, Emitter and Bulk
Recombination in Silicon and
Development of Silicon Nitride
Passivated 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.

Mark Kerr

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Abstract

Recombination within the bulk and at the surfaces of crystalline silicon has been investigated in this thesis. Special attention has been paid to the surface passivation achievable with plasma enhanced chemical vapour deposited (PECVD) silicon nitride (SiN) films due to their potential for widespread use in silicon solar cells. The passivation obtained with thermally grown silicon oxide (SiO₂) layers has also been extensively investigated for comparison.

Injection-level dependent lifetime measurements have been used throughout this thesis to quantify the different recombination rates in silicon. New techniques for interpreting the effective lifetime in terms of device characteristics have been introduced, based on the physical concept of a net photogeneration rate. The converse relationships for determining the effective lifetime from measurements of the open-circuit voltage (V_{oc}) under arbitrary illumination have also been introduced, thus establishing the equivalency of the photoconductance and voltage techniques, both quasi-static and transient, by allowing similar possibilities for all of them.

The rate of intrinsic recombination in silicon is of fundamental importance. It has been investigated as a function of injection level for both *n*-type and *p*-type silicon, for dopant densities up to $\sim 5 \times 10^{16} \text{cm}^{-3}$. Record high effective lifetimes, up to 32ms for high resistivity silicon, have been measured. Importantly, the wafers were commercially sourced and had undergone significant high temperature processing. A new, general parameterisation has been proposed for the rate of band-to-band Auger recombination in crystalline silicon, which accurately fits the experimental lifetime data for arbitrary injection level and arbitrary dopant density. The limiting efficiency of crystalline silicon solar cells has been re-evaluated using this new parameterisation, with the effects of photon recycling included.

Surface recombination processes in silicon solar cells are becoming progressively more important as industry drives towards thinner substrates and higher cell efficiencies. The surface recombination properties of well-passivating SiN films on *p*-type and *n*-type silicon have been comprehensively studied, with S_{eff} values as low as 1cm/s being unambiguously determined. The well-passivating SiN films optimised in this thesis are unique in that they are stoichiometric in composition, rather than being silicon rich, a property which is attributed to the use of dilute silane as a process gas. A simple physical model, based on recombination at the Si/SiN interface being determined by a high fixed charge density within the SiN film (even under illumination), has been proposed to explain the injection-level dependent S_{eff} for a variety of differently doped wafers. The passivation obtained with the optimised SiN films has been compared to that obtained with high temperature thermal oxides (FGA and annealed) and the limits imposed by surface recombination on the efficiency of SiN passivated solar cells investigated. It is shown that the optimised SiN films show little absorption of UV photons from the solar spectrum and can be easily patterned by photolithography and wet chemical etching.

The recombination properties of n^+ and p^+ emitters passivated with optimised SiN films and thermal SiO₂ have been extensively studied over a large range of emitter sheet resistances. Both planar and random pyramid textured surfaces were studied for n^+ emitters, where the optimised SiN films were again found to be stoichiometric in composition. The optimised SiN films provided good passivation of the heavily doped n^+ -Si/SiN interface, with the surface recombination velocity increasing from 1400cm/s to 25000cm/s as the surface concentration of electrically active phosphorus atoms increased from $7.5 \times 10^{18} \text{cm}^{-3}$ to $1.8 \times 10^{20} \text{cm}^{-3}$. The optimised SiN films also provided reasonable passivation of industrial n^+ emitters formed in a belt-line furnace. It was found that the surface recombination properties of SiN passivated p^+ emitters was poor and was worst for sheet resistances of $\sim 150 \Omega/\square$. The hypothesis that recombination at the Si/SiN interface is determined by a high fixed charge density within the SiN films was extended to explain this dependence on sheet resistance. The efficiency potential of SiN passivated n^+p cells has been investigated, with a sheet resistance of $80\text{-}100 \Omega/\square$ and a base resistivity of $1\text{-}2 \Omega\text{cm}$ found to be optimal. Open-circuit voltages of $670\text{-}680\text{mV}$ and efficiencies up to $\sim 20\%$ and $\sim 23\%$ appear possible for SiN passivated planar and textured cells respectively. The recombination properties measured for emitters passivated with SiO₂, both n^+ and p^+ , were consistent with other studies and found to be superior to those obtained with SiN passivation.

Stoichiometric SiN films were used to passivate the front and rear surfaces of various solar cell structures. Simplified PERC cells fabricated on $0.3 \Omega\text{cm}$ p -type silicon, with either a planar or random pyramid textured front surface, produced high V_{oc} 's of $665\text{-}670\text{mV}$ and conversion efficiencies up to 19.7% , which are amongst the highest obtained for SiN passivated solar cells. Bifacial solar cells fabricated on planar, high resistivity n -type substrates ($20 \Omega\text{cm}$) demonstrated V_{oc} 's up to 675mV , the highest ever reported for an all-SiN passivated cell, and excellent bifaciality factors. Planar PERC cells fabricated on gettered $0.2 \Omega\text{cm}$ multicrystalline silicon have also demonstrated very high V_{oc} 's of $655\text{-}659\text{mV}$ and conversion efficiencies up to 17.3% using a single layer anti-reflection coating. Short-wavelength internal quantum efficiency measurements confirmed the excellent passivation achieved with the optimised stoichiometric SiN films on n^+ emitters, while long-wavelength measurements show that there is a loss of short-circuit current at the rear surface of SiN passivated p -type cells. The latter loss is attributed to parasitic shunting, which arises from an inversion layer at the rear surface due to the high fixed charge (positive) density in the SiN layers. It has been demonstrated that a simple way to reduce the impact of the parasitic shunt is to etch away some of the silicon from the rear contact dots. An alternative is to have locally diffused p^+ regions under the rear contacts, and a novel method to form a rear structure consisting of a local Al-BSF with SiN passivation elsewhere, without using photolithography, has been demonstrated.

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CHAPTER 1

Introduction

Solar cells convert sunlight directly into electricity using the *photovoltaic effect*. They are a promising technology for satisfying current and future energy demands in a sustainable and environmentally friendly way. The first commercial use of solar cells was in space applications for powering satellites in the late 1950's. Today, the terrestrial market for solar cells greatly exceeds that for space applications, with a variety of end uses including grid connected systems, consumer products and for remote area power supply. This rapidly expanding market calls for advanced technologies and devices capable of yielding a higher performance at lower cost.

1.1 Market Overview

The market for solar cells has benefited significantly from government based subsidy programs over recent years. Figure 1.1 shows the annual worldwide shipments of photovoltaic (PV) modules over the last 25 years [1, 2]. Worldwide production at the end of 2000 was 288 MW of which 287.3 MW was for terrestrial applications. In the period from 1977-1983 the market was operating from a very small base and grew at a very high rate. The following decade was characterised by a relatively constant growth rate of around 12%pa. In the last four years,

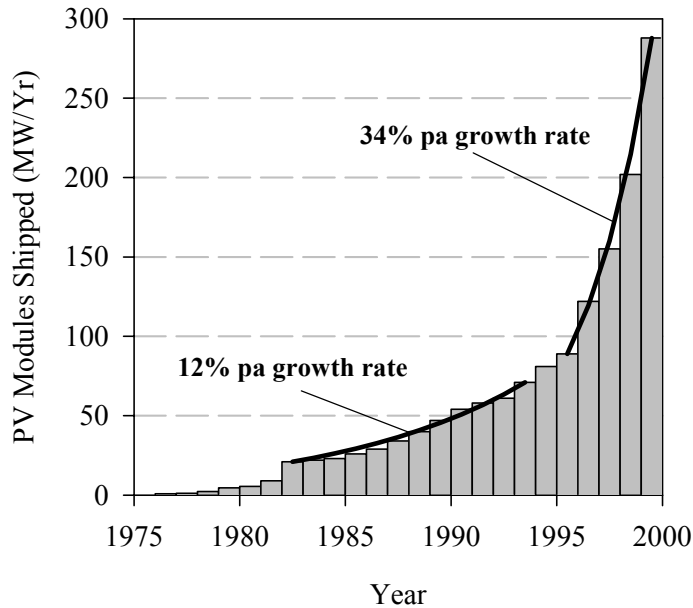


Figure 1.1: Worldwide shipments of PV modules over the last 25 years.

the market for PV modules has undergone tremendous growth at an annual rate of 34%. The resulting average growth rate since 1983 is then 16.6%pa.

Based on the above growth rates, projections of the future market size for PV modules are given in Figure 1.2 for the period up to 2010. A growth rate of 25%pa is included, as it has been used historically, although some experts are now considering it to be a conservative estimate for growth over the next two decades [3]. It can be seen that the landmark achievement of a market size exceeding 1GW/Yr is expected to occur during the period 2005-2008, if not sooner [4]. Indeed, market growth is expected to be at the higher rates over at least the next few years on the basis of capacity expansions already announced [5, 6].

A major determinant of increased market growth will be reduced costs. The cost of industrial solar cell modules is presently US\$3.5-6/W_p [7], resulting in an energy cost of US\$0.4-0.6/kWh depending of the available solar insolation for a grid-connected system [8]. The ability to achieve continued cost reductions depends largely on three interrelated factors:

- Mass manufacturing of solar cells in large facilities resulting in economies of scale - The European study of Bruton *et al.* [9], based essentially on established technologies with some conservative extrapolations, has concluded that module costs could be reduced to around 1Euro/W_p (≈US\$1/W_p) for a range of technologies. Materials would be approximately two-thirds of the total cost/W_p for a large plant.
- Improved cell efficiency – A large proportion of the costs of installed PV systems are area dependent. Therefore if cell efficiency can be increased without increasing the manufacturing cost, significant reductions in energy cost can be achieved. A high efficiency approach is all the more important to make the best use of the high material cost. High efficiency approaches now

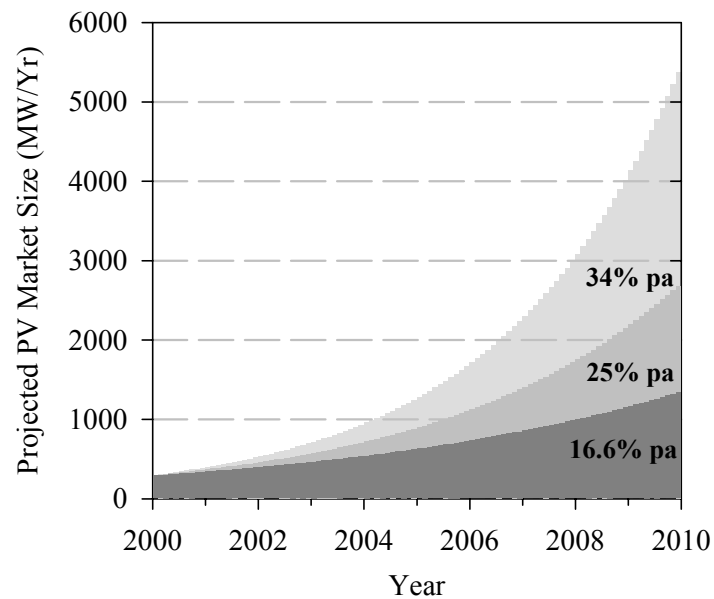


Figure 1.2: Projected market size for PV modules using a variety of growth rates for the period up to 2010.

at the industrial scale include the laser grooved buried grid (LGBG) cells produced by BPSolar under the Saturn™ name, HIT™ cells from Sanyo and OECO cells from ASE.

- Reduced material costs – Green has argued that as a cell technology matures, the constituent materials dominate the costs [10]. This is particularly true for silicon wafer based technologies where the cost of the starting wafer is currently about one half of the final module cost. Thin film and silicon based ribbon technologies (sometimes referred to as second generation technologies) avoid the cost of the silicon ingot and associated wafering and therefore offer potential savings. Indeed, the study of Bruton *et al.* [9] found that a ribbon based process would offer the lowest cost/ W_p for this reason. Extrapolating, the cost assessment of Bruton *et al.* for modules based on thin ribbon substrates (<100 μ m) suggests that module costs close to US\$0.50/ W_p are feasible.

A transition in the PV market from silicon wafer based technologies to thin film approaches has been predicted since the mid 1980's [11]. Thin film technologies currently at the pilot plant or industrial scale include cadmium telluride (CdTe), copper indium diselenide (CIS), amorphous silicon (a-Si), thin-film polycrystalline silicon (eg Pacific Power [11]), thin-film crystalline silicon (eg Astropower [12]), and silicon based ribbon technologies such as the edge-defined film-fed growth (EFG) and dendritic web. It would appear however that bulk crystalline silicon (single-crystal and multicrystalline) has actually increased its market share during the last decade. Figure 1.3 shows the market share by technology for both 1990 [13] and 2000 [2]. Over this period the total market size increased by a factor of more than six. Significantly, the market share for bulk crystalline silicon has actually increased from 67.9% to 85.4%, contrary to the perceived thin film revolution. While shipments of a-Si cells have grown

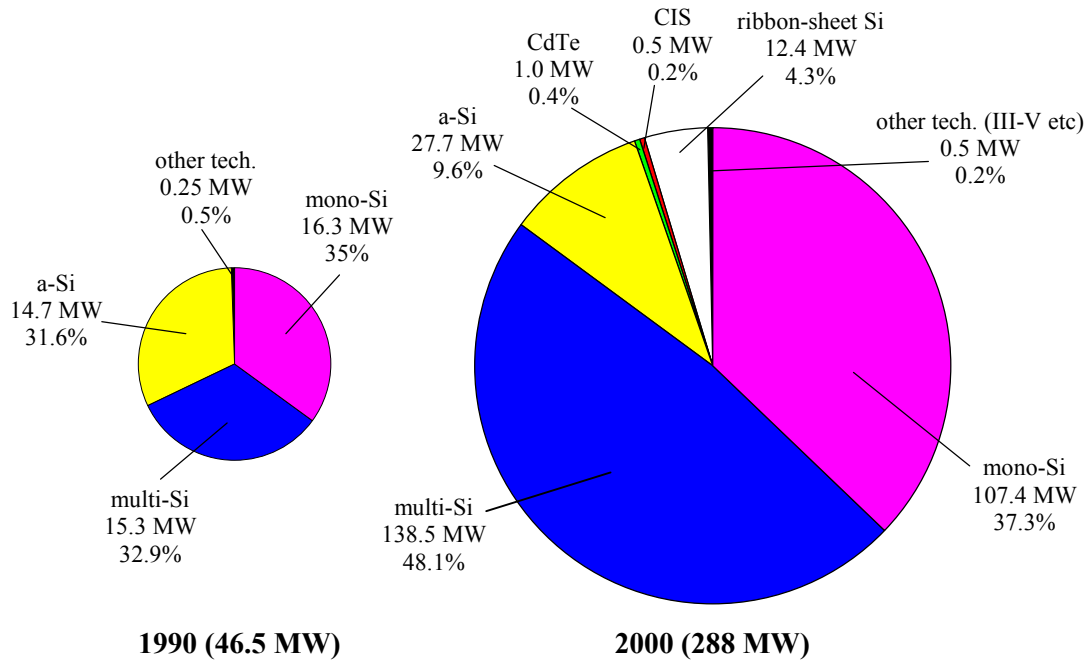


Figure 1.3: Market share of PV modules by technology type.

in absolute terms, the relative market share has reduced from 31.6% to 9.6%. The major benefactor of the reduced market share for a-Si has been multicrystalline silicon, which is now the dominant technology with a share of 48.1%. Ribbon and/or sheet silicon technologies have developed a reasonable market share of 4.3%. Thin film CdTe and CIS cells also now have a small market share (<0.5%). However, doubts are rising over the potential for these non-silicon based technologies to significantly displace silicon in large volumes due to toxicity (mainly for cadmium) and resource depletion issues (telluride and indium are relatively rare elements), problems that are not associated with silicon [14].

It appears there has been expanding diversity in cell fabrication technologies over recent years. Even for cells made from single crystal Czochralski (CZ) silicon wafers there are a number of approaches from simple screen-printed cells to more complicated LGBG and HIT cells. What does seem clear is that bulk crystalline silicon technologies are strongly placed to dominate the industry for at least the next decade and quite possible longer. Reductions in cost will require that progressively thinner wafers of higher bulk quality be used in combination with higher efficiency cell structures.

In the longer-term thin film cells are likely to dominate. Exactly what the nature of the thin film technology will be is unclear, particularly if a large scale PV industry based on silicon wafers with large amounts of invested capital becomes established, as would seem likely. There is a natural transition from thin wafer based silicon substrates to the various ribbon and sheet based technologies, or possibly other processes currently at the laboratory scale, such as the

epitaxial growth of thin crystalline silicon films [15, 16]. There are thus significant prospects for crystalline silicon to remain dominant, even in a thin film era.

A third generation of high efficiency, thin film PV technology is now being proposed [10]. This approach aims to overcome the fundamental efficiency limits associated with crystalline silicon solar cells due to thermalisation, transmission and intrinsic recombination, which account for more than 70% of the energy incident on a cell. Through band-gap engineering, it aims to achieve energy efficiencies much greater than the 15-20% currently obtained. Third generation PV is based on novel device structures such as tandem cells, hot carrier cells and multi-band cells, many of which are still at an embryonic stage of development [10].

1.2 Thesis Motivation

From the above overview, the short to medium term future for industrial solar cells appears to be based on single crystal (CZ) and multicrystalline silicon wafers. For costs reasons the substrates will have to be progressively thinner over time while simultaneously maintaining, but preferably increasing cell efficiency. Surface recombination losses thus become more significant and can indeed be the dominant mode of recombination losses for a high quality substrate, where the whole cell volume is electronically active. The minimisation of surface recombination losses, known as *surface passivation*, is a core topic of this thesis.

The current state of the art method for the surface passivation of silicon is thermal oxidation at *high temperature* (900°C-1100°C), and as such, silicon dioxide (SiO₂) passivation layers have been used for reference throughout this work. An emerging technology that offers high quality passivation layers at *low temperature* is plasma enhanced chemical vapour deposited (PECVD) silicon nitride (SiN) films, and these form the main theme investigated in this thesis. PECVD SiN films were transferred to the PV field by Hezel and co-workers in the early 1980's [17]. Due to the high hydrogen content of the films, they also offer the potential for *bulk passivation*, which is of special interest for lower quality starting material such as multicrystalline and ribbon silicon. Furthermore, their optical properties make them nearly ideal as a single layer anti-reflection coating for encapsulated solar cells. Therefore, SiN films offer great potential for increasing the efficiency of industrial crystalline silicon solar cells without increasing the fabrication cost, as they can simultaneously passivate the surfaces and the bulk as well as reduce surface reflection.

The surfaces of solar cells can be physically quite diverse. The surface may simply be the doped silicon wafer, or it may be diffused to form an emitter region. It can be planar or textured, and may or may not be contacted with metal. The degree of surface passivation provided by SiN and SiO₂ films has been investigated in this thesis for a variety of these different surface conditions. Importantly, accurate studies of surface recombination processes rely on accurate knowledge of the bulk recombination rate and on having simple, yet versatile techniques for quantifying the recombination rate. Therefore, the limits imposed on bulk recombination due to intrinsic processes (Auger recombination and radiative recombination) have also been studied, and new techniques for interpreting the recombination lifetime in terms of device characteristics have been introduced. Finally, it is important to demonstrate that the separate constituents can be put together to produce advanced solar cells. Consequently, the SiN films developed in this thesis were used to fabricate solar cells with high open-circuit voltages and high conversion efficiencies, thus demonstrating their excellent passivation properties in real devices. From a broader perspective, the data provided in this thesis for surface, emitter and bulk recombination in silicon, while useful for modeling silicon solar cells, is also of general interest for silicon semiconductor device modeling and analysis.

1.3 Thesis Outline

This thesis starts with the development of novel tools to investigate recombination losses in silicon and goes through to a detailed study of recombination in the two major regions that constitute a solar cell, the base and the emitter. Special attention is paid to their respective surfaces and an emphasis is placed on the passivation achieved using PECVD SiN technologies. Finally, the separately optimised elements are brought together to fabricate advanced solar cell devices based on the application of PECVD SiN.

Chapter 2 discusses the basic recombination mechanisms that occur within crystalline silicon. The recombination components within specific test structures of interest for this thesis are analysed and the photoconductance based methods used throughout this thesis for measuring the carrier lifetimes are described. New techniques for interpreting the effective lifetime in terms of device characteristics are introduced. Methods for determining the effective lifetime by measuring the open-circuit voltage of a device under arbitrary illumination are also described, and the equivalency of the photoconductance and voltage techniques, both quasi-static and transient, demonstrated.

Chapter 3 investigates the limits imposed on the bulk lifetime of crystalline silicon due to intrinsic recombination processes. The injection-level dependence and doping dependence is investigated for both n -type and p -type silicon of various doping densities, allowing a new general parameterisation for the intrinsic recombination rate in silicon of arbitrary injection level and dopant density to be developed. This new parameterisation is then used to re-evaluate the limiting efficiency of crystalline silicon solar cells as a function of cell thickness, dopant density and dopant type.

Chapter 4 presents a systematic study of the surface recombination properties of PECVD SiN films, fabricated using dilute silane gas, and thermal SiO₂ layers (FGA and annealed) on n -type and p -type silicon wafers. The effects of the PECVD deposition parameters on the surface recombination velocity are investigated, and it is found that the SiN films optimised in this thesis are unique because they are *stoichiometric* in composition, where it was previously thought that well-passivating SiN films had to be silicon rich. The surface recombination velocity at the Si/SiN interface and at the Si/SiO₂ interface is reported as a function of injection level and dopant density. The limits imposed on the efficiency of SiN passivated solar cells due to surface recombination process is then determined. Finally, a characterisation of relevant non-electrical properties of the optimised stoichiometric SiN film is presented, where it is demonstrated that apart from their excellent surface passivation, they also show no absorption in the UV portion of the solar spectrum and that they can be easily patterned using photolithography and wet chemical etching

Chapter 5 investigates the recombination of n^+ and p^+ emitters passivated with optimised SiN films and thermal SiO₂ layers over a large range of sheet resistances. The role of the PECVD deposition parameters is investigated for passivating n^+ emitters, and again, the optimised SiN films are shown to be stoichiometric in composition. Device simulation is used to determine the surface recombination velocity as a function of the surface phosphorus concentration at the heavily doped n^+ -Si surface when passivated with SiN or SiO₂. It is shown that the recombination properties of SiN passivated p^+ emitters is relatively poor compared to SiO₂ passivation and is worst for sheet resistances of $\sim 150\Omega/\square$. The efficiency potential of SiN passivated n^+p solar cells is also investigated.

Chapter 6 reports on the performance of experimental silicon solar cells passivated with stoichiometric SiN films. A variety of cell designs have been investigated, incorporating n -type and p -type float-zone silicon and p -type multicrystalline silicon. High open-circuit voltages are demonstrated for the different substrate types (up to 675mV for float-zone cells and up to 659mV for multicrystalline cells). The performance of large area cells, where the n^+ emitter was

formed in an industrial belt-line furnace, is also discussed. Finally, the research of this thesis is briefly summarized in **Chapter 7** and areas for future work are outlined.