The Impact of Atomic Hydrogen on the Properties of the Silicon/Silicon Dioxide Interface

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October 2010

A thesis submitted for the degree of Doctor of Philosophy of The Australian National University
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.

Chun Zhang
Acknowledgment

I would like to express my deepest gratitude to my primary supervisor, Associate Prof. Klaus Weber, for his enormous support and earnest teachings. Without his consistent and illuminating instruction, positive encouragement, and generous financial support, this thesis would certainly not have reached its present form. His enthusiastic approach to research, patient instructions and meticulous scholarship benefited me a great deal.

I would also like to thank Dr. Keith McIntosh for forming part of my supervisor panel, for a wealth of insightful and helpful discussions. I am also grateful to Prof. Andres Cuevas as a member of my supervisory panel and his warm encouragement. I would also like to thank Prof. Andrew Blakers for giving me the ANU Miscellaneous Scholarship.

I am very appreciative of Dr. Jin Hao for his energetic assistance in the laboratories, especially in the first year of my study, and for his help with lifetime, CV and EPR measurements. I would like to thank Dr. Wendy Jellett for explaining techniques of Boron diffusion and Kelvin Probe measurements. I would also like to thank Dr Paul Smith, from the department of Chemistry, ANU, for his great help with EPR measurements.

I am also grateful to Dr. Daniel Macdonald for cheerful help with the PECVD system. Thanks to Dr. Jason Tan for wise and friendly help with the PECVD and the RTA system.

I would like to thank the people in the CSES at ANU for making it such a great place to work. In particular, I would like to thank Sonita Singh and Nina de Caritat who trained me with the necessary skills to prepare my samples safely in the clean room. I am especially thankful to Chris Samundsett for his patient tutelage in the intricacies of photolithography work. I also would like to thank Neil Kaines and Bruce Condon for generosity of their time and skills whenever I had a technical problem. Thanks to James Cotsell for help with flash tester operation and John Musladin for constructing the jigs for electroplating.

For many other forms of assistance throughout my time as a student at ANU, I am very grateful to the following people: Soe Zin Ngwe (thanks for the fabrication of solar cell), Andrew Li (thanks for the PECVD system), Sieu-Pheng Phang (thanks for proofreading help), Dr. Andrew Thomson (thanks for calculation of the activation
energy), Dr. Bijaya Paudal (thanks for the TIDLS operation), Fiona Beck (thanks for the EPR references), Simeon Baker-finch (thanks for proofreading chapter 6), Yongling Ren (thanks for compute issues), Natalita Nursam, Nicholas Grant, Kean Chern Fong, Fiacre Rougieux, Erin Davies for many interesting discussions. I would like to express my gratitude to all those who helped me during the writing of this thesis.

Finally, my thanks would go to my beloved parents, my sister, my wife, my son and my niece for their loving considerations and great confidence in me all through these years.
Abstract

In this thesis, the influence of atomic hydrogen on the surface passivation of Si-SiO$_2$ interface was mainly investigated. The effect of corona charging, humidity, UV exposure and mineral acid on Si-SiO$_2$ interface was compared to the effect of atomic hydrogen. The electrical properties of thin (~20nm), low temperature (750-900°C) oxides, and in particular the degree of surface passivation achievable with such oxides, was also investigated and compared with the properties of oxides grown at higher temperatures (1000°C). Both wet and dry oxidations were used.

Inductively coupled photoconductivity decay and Capacitance-voltage (CV) techniques were used to characterize the electronic properties of Si-SiO$_2$ interface. A Plasma enhanced chemical vapour deposition (PECVD) system was used for atomic hydrogen exposure. This system is equipped with both a radio frequency (RF) and the microwave (MW) power source, both of which can be used to create a hydrogen plasma. The effect of atomic hydrogen plasma exposure parameters, such as power, pressure, and time, on the Si-SiO$_2$ interface in both cases was investigated. The effect of atomic hydrogen exposure and the post-atomic hydrogen exposure thermal anneal on the Si-SiO$_2$ interface has been studied.

It was found that generally, higher oxidation temperatures resulted in better surface passivation, as expected. A significant increase in emitter saturation current density ($J_{0e}$) and interface defect density ($D_{it}$) was observed when the oxidation temperature was decreased below 850°C.

Surface orientation had a large effect on achievable surface passivation. (111) surfaces displayed high recombination rates even at an oxidation temperature of 850°C and following an FGA.

The diffusion of phosphorous into the oxide resulted in a significant improvement in surface passivation. However, this improvement appeared to be related to a slight increase in positive charge density in the oxide rather than to a decrease in the unpassivated interface defect density.

Atomic H exposure at room temperature was observed to result in the generation of additional defects at the Si-SiO$_2$ interface. These defects were efficient carrier recombination centres, were thermally unstable and could be effectively removed by a short RTA anneal at 300°C or above. The annealing of this thermally unstable defect was not characterized by a single activation energy but rather by a spread of activations energies.
Following sufficiently long atomic H exposure times, the fraction of unpassivated P
\text{bx} centres reached a steady-state value which was independent of the initial passivation
state of the interface. The degree of steady-state passivation showed no discernible
dependence on temperature in the range 25-600°C during atomic H plasma exposure. In
particular, at all sample temperatures in the range 25-600°C, the efficiency of defect
passivation by H was lower than that afforded by H\text{2}. A similar behaviour was observed
between phosphorous diffused and undiffused samples and also for (100) planar, (111)
planar and (100) textured samples.

For oxide/nitride stacks in particular, there is no conclusive evidence that atomic
hydrogen is actually diffusing through nitride film.

A sufficiently high electric field created by corona charging resulted in the
introduction of additional defects to the Si-SiO\text{2} interface and these defects could be
subsequently removed by an RTA treatment, which were consistent with effects of
atomic hydrogen on the Si-SiO\text{2} interface. Following identical low temperature
annealing, both corona charging and atomic hydrogen exposed samples showed similar
but not identical improvement behaviour. This suggested that, while the underlying
cause of the degradation was likely to be the same in both cases (atomic H), there were
some differences in the generated defects, perhaps as a result of different H fluxes or
other factors.

Humidity and UV exposure resulted in the degradation of Si-SiO\text{2} stack. For
humidity exposed samples, the general trend of the interface modification, both after
humidity exposure and subsequent thermal anneal, was largely consistent with the effect
of atomic hydrogen on the Si-SiO\text{2} interface. For UV exposed samples, the general trend
of the interface modification was largely consistent with the hydrogen redistribution
model in which the atomic H in the oxide film is mainly responsible for the change of
the Si-SiO\text{2} interface.

Immersion of oxidised silicon samples in mineral acids resulted in a modification to
the Si-SiO\text{2} interface properties. Care therefore needed to be taken when such treatments
were employed for the preparation of samples for characterisation. However, acid
immersion could also provide a very cheap, alternative means of surface passivation due
to hydrogen or a hydrogen complex diffusing into the oxide layer and affecting the
interface properties.
<table>
<thead>
<tr>
<th>Acronyms</th>
<th>Description</th>
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<tbody>
<tr>
<td>ALNEAL</td>
<td>Aluminium Anneal</td>
</tr>
<tr>
<td>APC</td>
<td>Anomalous Positive Charge</td>
</tr>
<tr>
<td>ARC</td>
<td>Antireflection coating</td>
</tr>
<tr>
<td>CV</td>
<td>Capacitance Voltage</td>
</tr>
<tr>
<td>CZ</td>
<td>Czochralski growth method for crystalline silicon</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron Paramagnetic Resonance</td>
</tr>
<tr>
<td>FGA</td>
<td>Forming Gas (5%H2 in 95% Ar) Anneal</td>
</tr>
<tr>
<td>FZ</td>
<td>Float-zone</td>
</tr>
<tr>
<td>HFCV</td>
<td>High Frequency Capacitance Voltage</td>
</tr>
<tr>
<td>IPA</td>
<td>Isopropanol</td>
</tr>
<tr>
<td>LPCVD</td>
<td>Low Pressure Chemical Vapor Deposition</td>
</tr>
<tr>
<td>MIS</td>
<td>Metal Insulator Semiconductor</td>
</tr>
<tr>
<td>MOS</td>
<td>Metal Oxide Semiconductor</td>
</tr>
<tr>
<td>MOSFET</td>
<td>Metal Oxide Semiconductor Field Effect Transistor</td>
</tr>
<tr>
<td>MW</td>
<td>Microwave</td>
</tr>
<tr>
<td>PCD</td>
<td>Photo Conductance Decay</td>
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<tr>
<td>PECVD</td>
<td>Plasma Enhanced Chemical Vapour Deposition</td>
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<tr>
<td>QSCV</td>
<td>Quasi Static Capacitance Voltage</td>
</tr>
<tr>
<td>QSSPC</td>
<td>Quasi Steady State Photo conductance</td>
</tr>
<tr>
<td>RTA</td>
<td>Rapid Thermal Anneal</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>SCCM</td>
<td>Standard Cubic Centimeters per Minutesute</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectroscopy</td>
</tr>
<tr>
<td>SRH</td>
<td>Shockley-Read-Hall</td>
</tr>
<tr>
<td>SRV</td>
<td>Surface Recombination Velocity</td>
</tr>
<tr>
<td>TCA</td>
<td>Trichloroethane</td>
</tr>
<tr>
<td>TIDLS</td>
<td>Temperature and injection dependent lifetime spectroscopy system</td>
</tr>
<tr>
<td>TMAH</td>
<td>Tetramethyl Ammonium Hydroxide</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<th>Symbols</th>
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<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>$C_{hf}$</td>
<td>High (Low) frequency capacitance</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Capacitance of insulator(semiconductor)</td>
</tr>
<tr>
<td>$D_{it}$</td>
<td>Interface (midgap) state density</td>
</tr>
<tr>
<td>$E_F$</td>
<td>Fermi level energy</td>
</tr>
<tr>
<td>$E_i$</td>
<td>Intrinsic Fermi level energy</td>
</tr>
<tr>
<td>$J_0e$</td>
<td>Emitter saturation current density</td>
</tr>
<tr>
<td>$q$</td>
<td>Magnitude of the elementary charge</td>
</tr>
<tr>
<td>$Q_f$</td>
<td>Fixed charge</td>
</tr>
<tr>
<td>$Q_m$</td>
<td>Mobile charge</td>
</tr>
<tr>
<td>$Q_o$</td>
<td>Oxide charge</td>
</tr>
<tr>
<td>$Q_{ot}$</td>
<td>Oxide trapped charge</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Sheet resistance</td>
</tr>
<tr>
<td>$S$</td>
<td>Surface recombination velocity</td>
</tr>
<tr>
<td>$U_s$</td>
<td>Net recombination rate via surface states</td>
</tr>
<tr>
<td>$V_{fb}$</td>
<td>Flat Band voltage</td>
</tr>
<tr>
<td>$V_g$</td>
<td>Gate voltage</td>
</tr>
<tr>
<td>$\Phi_{ms}$</td>
<td>Work function difference between metal and semiconductor</td>
</tr>
<tr>
<td>$\psi_s$</td>
<td>Surface potential</td>
</tr>
<tr>
<td>$\tau_b$</td>
<td>Bulk lifetime</td>
</tr>
<tr>
<td>$\tau_{eff}$</td>
<td>Effective lifetime</td>
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CHAPTER 1

Introduction

Photovoltaics, the direct conversion of sunlight into electricity using solar cells, is recognized as one of the most promising options for a sustainable energy. Today, single- or multi-crystalline silicon wafers dominate the present photovoltaic market and this market dominance is likely to continue at least until the next decade. The solar industry needs to reduce production costs of solar modules while, at the same time, improving the energy conversion efficiency of the solar cell. For silicon wafer-based solar modules, large cost savings can come from reducing silicon wafer thickness, since silicon feedstock, crystallization, and wafering make up 33% of the direct manufacturing costs. As cell thickness is reduced and efficiency increases, the surfaces of the solar cell become increasingly important. The challenge is then to obtain thin, high efficiency silicon solar cells with very well passivated surfaces.

The surface recombination velocity \( S \) at the semiconductor surface measured in units of \( \text{cm/s} \) can be defined as [1]

\[
U_s \equiv S \cdot \Delta n_s \tag{1-1}
\]
where $\Delta n_s$ is the excess minority-carrier concentration at the surface, $U_s$ the net recombination rate via surface states, which is determined by carriers concentrations, capture cross sections for carriers and the surface state density.

Based on equation (1-1), surface recombination velocity depends on the density of interface defects, their properties (capture cross sections, to a less extent energy levels) and the concentration of carriers at the surface.

Since 1960s, the Si-SiO$_2$ structure has been one of the most intensively studied systems in the realms of materials and condensed matter physics. The main driver for this intense effort is the critical role of the structure in the metal-oxide-semiconductor field effect transistor (MOSFET), which dominates contemporary integrated circuit (IC) technology [2]. During the past decades, the Si-SiO$_2$ interface has become the most intensively investigated semiconductor-insulator system. In the photovoltaic community, the standard method for the passivation of Si surfaces—both diffused and non-diffused—is the thermal oxidation at high temperature (~1000$^\circ$C) [3]. For non-diffused Si surfaces, thermal SiO$_2$ provides excellent surface passivation on high-resistivity (>100$\Omega$.cm) n- and p-type Si wafers, as demonstrated by effective surface recombination velocity $S_{\text{eff}}$ values below 10cm/s. For low substrate resistivity (~1$\Omega$.cm) the passivation quality depends on the doping type. Thermal SiO$_2$ is also very effective in passivating diffused Si surfaces. Furthermore, due to the large surface doping level ($N_s \geq 5 \times 10^{18}$ cm$^{-3}$), the band bending at the surface is virtually independent of the operating condition of the sample and hence the surface recombination velocity at diffused Si surfaces can be treated as being independent of the bulk injection level $\Delta n$.

Although thermally grown SiO$_2$ films provide very good surface passivation on silicon wafers, with regards to fabrication of solar cells they feature two severe drawbacks [4]: (i) they do not provide efficient reduction of reflection losses because of their small refractive index of 1.46 and (ii) their fabrication requires high processing temperatures and relatively long processing times which will bring numerous problems such as cost and throughput considerations, degradation of bulk lifetime especially for multi crystalline silicon and etc. In order to eliminate the above problems associated with the high temperatures during the thermal oxidation of silicon, significant effort has been devoted in the past to the development of low-temperature surface passivation schemes. The most successful of these approaches has turned out to be the formation of SiN films by means of the low-temperature Plasma Enhanced Chemical Vapor Deposition (PECVD). PECVD SiN combines a number of desirable features for the
achievement of high-performance solar cell [5]: (i) high interface charge density leading to high concentration of carriers at the semiconductor surface, (ii) long-term stability of these charges at elevated temperatures, (iii) relatively low interface defect density of electrically active defects, (iv) good antireflection (AR) coating properties with the refractive index in the range of 1.7-2. The SiN film properties can be varied widely depending on deposition parameters such as deposition temperature, pressure, plasma power, gas flow rate and gas ratio. All deposition parameters strongly affect the surface recombination velocity as well as the stability of the SiN film against the UV exposure, therefore there is significant room to optimise the properties for a given application. It should be emphasized that plasma SiN films are of an amorphous structure and contain large amounts of atomic hydrogen which can passivate bulk and interface defects. However, as discussed above, when PECVD SiN is deposited directly on silicon, a very thin interfacial SiO$_x$ film (<2nm), which grows on the silicon surface prior or in the initial stages of nitride deposition, is converted into an oxynitride film. This oxynitride film is not a mixture of SiO$_2$ and Si$_3$N$_4$ clusters, but of Si-O and Si-N bonds blended on an atomic scale, and is believed to be inferior in terms of its electronic properties to the Si-SiO$_2$ interface [4].

The Si-SiO$_2$ interface is still very important in crystalline silicon solar cell devices. In addition to the excellent surface passivation it affords, the research of the properties of Si-SiO$_2$ interface is also driven by a few factors. Firstly, oxide/PECVD silicon nitride stacks are under active investigation within photovoltaic community and a low surface recombination velocity of nearly 10cm/s on 1.25Ω·cm p-type (100) silicon surface has been reported [6]. Secondly, even when PECVD nitride is used, interface is an oxynitride converted from a very thin SiO$_x$ film. Hence, it can be expected that the actual interfacial region on silicon wafers covered by a PECVD SiN$_x$ film is rather similar to the one found at the thermally grown Si-SiO$_2$ interface [7]. Thirdly, it has been known that excellent surface passivation can be obtained by thin Al$_2$O$_3$ films prepared by plasma-assisted atomic technique and it was verified that an interfacial oxide layer of about 1.5nm is present between the silicon and Al$_2$O$_3$ as a result of the deposition process [8]. Last but not least, rear surface passivation is becoming increasingly important in crystalline silicon solar cell technology and thermally grown silicon dioxide layers meet all major requirements to be suitable for it: good surface passivation, good rear reflectance, and thermal stability in solar cell production processes. Only the process throughput and cost and the possible degradation of the
solar cell precursors seem to be the major and crucial problems [9]. Therefore, the properties of the Si-SiO\(_2\) interface continue to be of great interest for solar cells applications.

From the above overview, it is natural to expect that PECVD SiN\(_x\)/SiO\(_2\)/Si stacks will display lower surface recombination rates and better thermal stability than PECVD SiN\(_x\)/Si structures. That is because, on the one hand, the thin layers of thermally grown SiO\(_2\) is known to be the best technique for passivating the Si surface and Si-SiO\(_2\) interface containing a lot of recombination centres caused by the dangling bonds can be effectively passivated by atomic hydrogen. In the above applications, usually the thin SiO\(_2\) layer is grown at lower temperatures (900°C or below) for short time to get about 10nm thickness [10]. On the other hand, PECVD SiN\(_x\) films contain high density of hydrogen (20-25% depending on deposition conditions [11, 12]). This hydrogen will release (in atomic and/or molecular form, depending on the SiN\(_x\) film properties) during the following high temperature solar cell processing step and then diffuse into the silicon bulk, where it can passivate both deep and shallow level defects, including dopant atoms [13-15]. Actually, a novel SiO\(_2\)/SiN double-layer antireflection coating, which greatly improves the efficiency and performance of solar cell, has been developed [16]. Furthermore, it is found that SiO\(_2\)/SiN stack passivation quality, following either low or high temperatures annealing, is superior to the counterpart individual films [17].

It is well known that hydrogen readily attaches to broken chemical bonds in semiconductors, thereby repairing damage and eliminating detrimental electronic states from the energy bandgap. Technological interest in the study of hydrogen in the semiconductors arises from two diametrically opposed motivations. Firstly hydrogen can be unintentionally introduced into the material during any phase of semiconductor processing, such as crystal growth, deposition or growth of over-layers, wet or dry chemical processing, and even device operation. On the other hand, hydrogenation can also be incorporated as a deliberate processing step in the fabrication of semiconductor devices for the purpose of passivating dopants and defects. In either case, a fundamental understanding of the properties of hydrogen in semiconductors will provide the most vigorous basis for addressing the technological implications and realizing the technological opportunities of hydrogen in semiconductors [18].

The role of molecular hydrogen at the Si-SiO\(_2\) interface is relatively well understood, especially through the studies by Stesmans et al [19-23]. However, the reaction of atomic hydrogen with the Si-SiO\(_2\) interface has not been investigated in as
much detail, despite its important role in surface passivation. An example is the so-called alneal (aluminium anneal), resulting in excellent surface passivation (superior to that obtained by a forming gas anneal) for Si-SiO$_2$ structures. This is often attributed to the generation of atomic H during the alneal [24]. However, this view is not supported by the work by Stesmans and Cartier [19, 25], as well as Jin et al [26].

The aim of the thesis is to explore the properties of lower temperature oxides in comparison with high temperature oxides, to improve the understanding of the interaction of hydrogen, especially atomic hydrogen, with the Si-SiO$_2$ interface, and to determine to what extent atomic hydrogen may be responsible for commonly observed degradation of Si-SiO$_2$ interface following the application of high electric fields, humidity exposure, UV exposure and mineral acid immersion.

**Thesis outline**

In chapter 2, a review of the properties and effects of hydrogen, including molecular and atomic on Si-SiO$_2$ interface is presented. The basic characterization techniques used in this thesis are described in chapter 3, and then the details of processing equipments and general sample processing are demonstrated in chapter 4. In chapter 5, effect of wet oxidation, and with oxide/LPCVD nitride stacks on Si-SiO$_2$ interface is discussed. In chapter 6, results for applying atomic hydrogen to Si-SiO$_2$ interface and following different thermal treatments are presented and discussed. Finally, effects of corona charging, humidity, Ultraviolet (UV) exposure and mineral acid solutions on Si-SiO$_2$ interface are investigated in chapter 7. These experiments cover both planar and textured (111) and (100) surfaces.
CHAPTER 2

The role of hydrogen in the Si-SiO$_2$ interface

It has long been known or suspected that hydrogen plays a major role in numerous useful and harmful phenomena in the Si-SiO$_2$ system. Although certain specific situations have been fairly well studied, many have not.

The incorporation of atomic hydrogen into crystalline, polycrystalline or amorphous semiconductors causes significant changes in both the electrical and optical properties of these materials. The principal interest in hydrogen in crystalline semiconductors occurs because of its ability to passivate (render electrically inactive) dangling bonds or defects. Hydrogen can be introduced into semiconductors during crystal growth, by direct implantation, by exposure to hydrogen-containing plasma, or by chemical reaction at the surface [27]. In many cases its incorporation into crystalline semiconductors is unintentional, and can cause changes in the electrically active dopant profile in the near-surface region.

Due to its ability to deactivate both shallow and deep impurities in one of the most technologically important semiconductors, silicon, the role of hydrogen in silicon has attracted wide interest. Hydrogen will also passivate many deep defects in other elemental and compound semiconductors [28], as well as surface dangling bonds in
both amorphous and single crystal silicon [29] and trivalent Si defects at Si-SiO$_2$ interfaces [30].

### 2.1 Configurations of Hydrogen in Silicon

At the present time there is a consistent picture of the states of hydrogen within the lattice for Si. In this section knowledge of these different forms of hydrogen will be detailed, which is based primarily on a series of calculations from the Albany group [31-33], in which they think there are three states of hydrogen in Si at low temperatures [13]:

1. Bound to a dangling bond at a defect site. These give rise to the multiplicity of Si-H stretching modes observed by infrared absorption in the frequency range 1800-2300 cm$^{-1}$. This site has the lowest potential energy for any of the states of hydrogen.

2. Molecular hydrogen (H$_2$) which is the stable configuration in the absence of defect sites to which the hydrogen can bond. Molecular hydrogen is electrically and optically inactive, and essentially immobile at low temperatures ($<500^\circ$C). The extra stability of the molecular form over atomic hydrogen at low temperatures translates to a total dominance in the relative concentrations in defect-free Si.

3. Atomic hydrogen (H) occupies the lowest energy site for unbound hydrogen. The diffusivity of atomic hydrogen is high even at room temperature as it migrates through the lattice at the cost of a small energy barrier (0.3 eV) [34, 35]. It is the state responsible for the passivation of dangling bond electrical activity. The reason why little direct observation of the electrical activity has been made for atomic hydrogen is that it tends to either bond at a defect site, or coalesce into molecules [32].

These three forms of hydrogen are in equilibrium amongst themselves. At low temperatures, for example, the bonded forms (Si-H and H$_2$) predominate, and hence hydrogen is relatively immobile. At high temperatures the atomic form dominates as the bound forms break up, and then the effective diffusivity is high. A summary of the properties of the three states of hydrogen in Si is given in Table 2.1 [32].
Table 2.1 Calculated properties of three states of hydrogen in c-Si [32]

<table>
<thead>
<tr>
<th></th>
<th>Si-H</th>
<th>H₂</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential energy [eV]</td>
<td>-14--15.8</td>
<td>-26.6</td>
<td>-12.5</td>
</tr>
<tr>
<td>Heat of solution [eV]</td>
<td>-</td>
<td>1.7</td>
<td>1.65 (exp.1.87)</td>
</tr>
<tr>
<td>Activation energy for diffusion [eV]</td>
<td>-</td>
<td>2.7</td>
<td>0.32 (exp.0.5~1.2)</td>
</tr>
<tr>
<td>Dissociation energy [eV]</td>
<td>1.5~3.3</td>
<td>1.6</td>
<td>-</td>
</tr>
</tbody>
</table>

2.2 Effect of molecular hydrogen on the Si-SiO₂ interface

It has long been recognized that, following thermal oxidation, the crystalline silicon atoms at the Si-SiO₂ interface bond to oxygen atoms of the SiO₂. Nevertheless, up to approximately 0.5% of the crystalline interfacial atoms are not bonded to oxygen atoms and give rise to a specific dangling bond type of defects, Si₃≡Si·, called the Pb center. In this notation, the three horizontal lines represent the three bonds to bulk silicon atoms (the Si₃), and the · represents the fourth, unpaired valence electron of the silicon atom (the so called dangling bonds). In the neutral charge state, this interface defect is observable with electron paramagnetic resonance (EPR). The paramagnetism of this defect arises from an unpaired electron located in a sp³[111]-like hybrid orbital localized on the defect silicon atom [36]. In general, there is only one type of paramagnetic defect, namely Pₖ centre is observed on (111) Si interface, while two distinct paramagnetic defects called Pₖ₁ and Pₖ₀ are observed on (100) Si interface. The Pₖ₀ (100) is reasonably attributed to Si₃≡Si· on the (100) face while Pb₁ (100) tentatively consistent with Si₂O≡Si· centres [36]. The disposition of Pb centres on the three principal Si faces in shown in figure 2.1[2].
These $P_b$ defects are believed to be the dominant interfacial charge traps that make this as-grown Si-SiO$_2$ system less than ideal in device applications. In order to minimize the effects of charge trapping at such defects, much research has been done during last decades. In most experiments the Si-SiO$_2$ stacks are exposed to molecular hydrogen to passivate, or annealed in vacuum to depassivate samples, the idea being that the hydrogen will chemically bind to and passivate these defects. Brower [36, 37] researched the kinetics of $H_2$ of $P_b$ centres and the dissociation kinetics of hydrogen-passivated $P_b$ defects on the (111) Si-SiO$_2$ interface. The mechanism is simply summarised in the following reactions:

\[ P_b + H_2 \rightarrow P_bH + H \]  \hspace{1cm} (2.1)
\[ P_bH \rightarrow P_b + H \]  \hspace{1cm} (2.2)
\[ H_2 \rightarrow H + H \]  \hspace{1cm} (2.3)
\[ P_bH + H \rightarrow P_b + H_2 \]  \hspace{1cm} (2.4)
\[ P_b + H \rightarrow P_bH \]  \hspace{1cm} (2.5)
Where $P_b H$ represents a passivated $P_b$ centre. Brower’s results indicated that the molecular hydrogen chemistry of $P_b$ centres is dominated by three thermochemical effects. The first is that $P_b$ centres appear to be stable under vacuum annealing to temperatures of at least 850°C. The second is that $P_b$ centres can be passivated with molecular hydrogen to form $P_b H$ centres. The third is that passivated $P_b H$ centres dissociate in vacuum for temperatures in excess of 550°C.

Stesmans et al. conducted further detailed experiments to obtain a better understanding of the $P_b$ centre at the Si-SiO$_2$ interface [38]. At first, they accurately determined the density of interfacial (111) $P_b$ centres (Si$_3$$\equiv$Si- defects, passivated or not) to be $(11.4\pm0.6)\times10^{12}$ cm$^{-2}$ on all (111) Si-SiO$_2$ interfaces prepared by oxidation in dry $O_2$ at 920-1000°C. The $P_b$ centres were found to account for all electrically active fast interface states. Stesmans et al. then extended and revised Brower’s work by using more accurate and correct EPR practice [19-21] for (111) and (100) samples respectively. The results indicate that passivation with molecular $H_2$ of all $P_{bx}$ interface defects in either thermal (111) or (100) Si-SiO$_2$ over extended temperature and time ranges show a non-exponential decay of the unpassivated $P_b$ centre density with time. The results were explained by postulating a Gaussian spread in the activation energy $E_f$ for the passivation of $P_b$ centres. The mean activation energy for all $P_{bx}$ centres are similar and in the range of 1.51 to 1.57 eV and the Gaussian spread $\sigma_{E_f}$ is in the range of 0.06 to 0.15 eV for all $P_{bx}$ centres.

Stesmans [23] also analysed the simultaneous action of passivation and dissociation during thermochemical interaction of $P_b$ defects with molecular hydrogen at the (111) Si-SiO$_2$ interface. A unified description is attained through solution of the simultaneous set of the first-order rate equations describing passivation and dissociation, under the restriction that the $H_2$ concentrations at the interface and in the ambient are continuously equal and inclusion of the spreads $\sigma_{E_f}$ and $\sigma_{E_d}$ in activation energies. Focusing on the passivation in 1 atm $H_2$, Stesmans found that optimum passivation can be achieved in the range of 400-430°C for 10-60 minutes. Stesmans also pointed out that the combined chemical reactions 2.1 and 2.2 make the $P_b$ defect a catalyst for $H_2$ dissociation, in which both the passivation and depassivation process lead to the emission of atomic hydrogen.

When optimally passivated, the density of unpassivated $P_b$-type defects can become very low, with a density in the range $(2-10)\times10^9$ cm$^{-2}$ of residual interface traps detected electrically in state-of-the-art passivated Si-SiO$_2$. 
2.3 Oxides grown at different temperatures

It has been presented in previous chapter that oxide/PECVD silicon nitride stacks are under active investigation within photovoltaic community and usually the thin tunnel oxide is thermally grown at lower temperatures (900°C or below). Aberle et al. [4] found that there is an enormous increase in the effective lifetime by increasing the oxidation temperatures during the range of 500-800°C. Schmidt et al. [39] investigated the thin thermal SiO$_2$/PECVD SiN$_x$ stacks. The oxides were grown in an oxygen/trichloroethylene ambient using a conventional quartz furnace at 900°C with thickness range of 5-25nm. The results showed that there was an enormous increase in lifetime from 5-8µs to 1-2ms after the deposition of 60nm SiN$_x$ layers on top of the SiO$_2$. Rohatgi et al. [10] investigated the thin rapid thermal oxide (RTO)/PECVD SiN$_x$ stacks. This rapid thermal oxidation at 900°C for 150 seconds resulted in an oxide with thickness of about 8-10nm on diffused surface and 6nm on undiffused surface. The results showed the optimum passivation scheme consisting of a thin RTO with PECVD SiN$_x$ layer followed by a very short 730°C anneal can significantly reduce the emitter saturation current density and the back surface recombination velocity. Furthermore, this double-layer RTO+SiN$_x$ passivation is relatively independent of the deposition conditions (direct or remote) of the SiN film and is more stable under heat treatment than SiN$_x$ or RTO alone.

2.4 Effect of atomic hydrogen on the Si-SiO$_2$ interface

The role of molecular hydrogen at the Si-SiO$_2$ interface is relatively well understood, especially through the studies by Stesmans and co-workers [19-23]. However, the reaction of atomic hydrogen with the Si-SiO$_2$ interface has not been investigated in as much detail, despite its important role in surface passivation. Very often it is atomic H that interacts directly with the Si-SiO$_2$ interface, rather than molecular H$_2$. For example, it is atomic H rather than H$_2$ that is usually released from PECVD nitride films during high temperature thermal treatments, such a contact firing. Another example is the alneal, resulting in excellent surface passivation for Si-SiO$_2$ structures. This is often attributed to the generation of atomic H during the alneal [24]. Therefore it is important to understand the interaction of atomic hydrogen with Si-SiO$_2$ as well.
2.4.1 Passivation and depassivation of existing \( P_b \) centres

Cartier et al. carried out numerous investigations into the effect of atomic hydrogen, produced by remote PECVD reactor, at the Si-SiO\(_2\) interface at room temperature [25]. In their experiments, samples were oxidised in dry oxygen at 900\(^\circ\)C and exposed to atomic hydrogen by using remote microwave hydrogen-plasma system. The EPR technique was used to investigate the \( P_b \) centre density at Si-SiO\(_2\) interface. These experiments showed that atomic hydrogen at the (111) Si-SiO\(_2\) interface both depassivates and passivates silicon dangling bonds simultaneously at room temperature according to the reactions (2.4) and (2.5). This was indicated by an increase in the EPR signal for paramagnetic \( P_b \) centres for as-grown, hydrogenated Si-SiO\(_2\) sample and a decrease in the signal for paramagnetic \( P_b \) centres for initially dehydrogenated samples following atomic hydrogen exposure. The fact that the EPR signal from \( P_b \) centre was reduced on initially depassivated samples shows that atomic H can passivate \( P_b \) centres. On the other hand, the fact that the signal increases on initially passivated sample shows that atomic H can depassivate and that the passivation of atomic H is not as effective as that of molecular H\(_2\). (Note that, in their experiments, the samples did not receive a forming gas anneal or other anneal in molecular hydrogen following oxidation. Such an anneal, had it been carried out, would not have changed the experimental results since no EPR signal was detected after oxidation, and a forming gas anneal would, if anything result in a further lowering of the unpassivated \( P_b \) centre density, based on the work of Stesmans et al. Furthermore, in order to prove that the low saturation \( P_b \) density value of \( 3.0\pm0.5\times10^{11}\text{cm}^{-2} \) is actually the result of simultaneous passivation and depassivation of silicon dangling bonds, a sample with high \( P_b \) density \( (2.4\times10^{12}\text{cm}^{-2}) \) following high temperature \( (700-800\text{\,\degree C}) \) vacuum annealing received a long atomic hydrogen exposure for about 120 minutes. After that, the \( P_b \) density in this kind of depassivated sample decreased to a value of \( 4.5\pm0.5\times10^{11}\text{cm}^{-2} \), which is very close to that measured after atomic hydrogen exposure of the thermal as-grown passivated sample.

The important result, therefore, is that the final unpassivated \( P_b \) density following atomic hydrogen exposure reaches a steady state value that is, to a first order, independent of initial passivation state of the \( P_b \) centres.

In addition to (111) samples, Cartier et al. also investigated the reaction of atomic hydrogen with defects at the (100) Si-SiO\(_2\) interface by EPR [40]. The experiment conditions are identical as above (111) samples. Their results showed that the two paramagnetic defects at the (100) interface, \( P_{b0} \) and \( P_{b1} \), respond in a similar way to
atomic hydrogen as the P$_b$ centre at the (111) interface. However, the two kinds of P$_b$ defects display quantitative difference in behaviour. It is found the P$_{b0}^{100}$ centre is produced more readily than P$_{b1}^{100}$ and is also much harder to passivate by atomic hydrogen. This means that the P$_{b0}^{100}$ is the dominant defect at the (100) Si-SiO$_2$ interface and it is chemically not equivalent to P$_b^{111}$. On the other hand, there is strong evidence to suggest that P$_b^{111}$ and P$_{b1}^{100}$ are similar to each other (ie have the same backbonding arrangement) and different from P$_{b0}^{100}$.

### 2.4.2 Generation of new defects

Cartier et al. also discovered that atomic H can generate new interface defects [25]. The C-V technique was used to compare the interface state density ($D_{it}$) at midgap with the paramagnetic P$_b$ density (from EPR) at the (111) Si-SiO$_2$ interface. Samples received dry oxidation followed by atomic H exposure for different times. They found that mid-gap interface state density ($D_{itm}$) of the as-grown sample increased linearly with atomic hydrogen dose at least up to a density of $1 \times 10^{13} \text{eV}^{-1}\text{cm}^{-2}$ with no indication of saturation. However, the P$_b$ density increased at a roughly ten times smaller rate than the density of electrically active defects and saturated at a value of about $3 \times 10^{11}\text{cm}^{-2}$. The authors rule out the possibility that the difference is due to the difference in substrate resistivity or oxide thickness by measuring the $D_{itm}$ values on samples with different oxide thickness and resistivity but getting close $D_{itm}$ values. This kind of phenomenon was also observed at (100) Si. Similar to the (111) interface in which the P$_b^{111}$ centre could account for only a fraction of the atomic hydrogen-generated interface states, paramagnetic defects (P$_{b0}$ and P$_{b1}$) likewise could not account for all of the electrically active defects at the (100) interface. The above results suggest that atomic hydrogen introduces defects at the Si-SiO$_2$ interface which are not EPR-active.

In subsequent more detailed studies, Cartier et al. studied the generation of interface states in atomic hydrogen plasma exposure over a wide range of oxide thickness grown on various p- and n-type substrates using the C-V technique [41]. The results indicated that, firstly, $D_{it}$ increased linearly with the atomic H-dose up to values of $1 \times 10^{13} \text{eV}^{-1}\text{cm}^{-2}$ for both (111) and (100) interface. Also, the results showed that the (111)-interface degrades approximately 2.5 times faster than (100)-interface, independent of the oxide thickness. The reason behind this is possibly due to a higher precursor density at the (111) interfaces. Secondly, the authors found that the generation rates on p-type substrate are systematically higher compared to n-type samples. This might be related to
a dependence of the interface-state generation rate on the Fermi level at the Si-SiO$_2$ interface. Thirdly, from $D_n$ distributions across the band-gap with different atomic hydrogen dose (both n- and p-type samples), the authors again found these distributions are strongly asymmetric respect to mid-gap of the band-gap and are not compatible with those reported $P_b$ dangling bonds. Again, the results provide evidence that the majority of the electrically detected defects are not related to the well known EPR signal for $P_b$ Si dangling bonds.

Cartier et al. also studied interface defect formation caused by introducing atomic hydrogen into the gate oxide of MOSFETs and compared the results to introducing it into a gate-free thermal oxide [42]. MOSFETs with the edges of the gate oxide at the source and drain exposed to the ambient were placed downstream of atomic hydrogen plasma. Baffles prevented UV rays from the plasma from reaching the device. Interface traps in the MOSFETs were measured by charge pumping and interface defect formation was examined by high-low C-V measurements performed with a mercury probe. They observed that both types of samples exhibit the same energy distribution of interface traps from the C-V results. While atomic hydrogen produces the same defects in both the MOSFETs and bare thermal oxides, the diffusion pattern of the atomic hydrogen through the two types of samples is very different. For the bare thermal oxide, the interface trap generation rate decreases with oxide thickness, $t_{ox}$, as approximately $t_{ox}^{-0.5}$ for an oxide thickness in the range 5 to 200nm. Figure 2.2 [42] shows the typical distribution of interface states across the bandgap caused by atomic H exposure at the n-type, (100) silicon wafer. The distribution is characterized by an evolution of a broad peak above midgap that increases with atomic H exposure. The same analysis performed on p-type capacitors shows that the $D_n$ build up below midgap is small. These distribution are similar to those observed after hot-electron stress or irradiation and differ from those reported for $P_b$ Si dangling bonds.
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2.4.3 Formation of anomalous positive charge

Besides producing the interface defects, Cartier et al. also found atomic hydrogen exposure can lead to the formation of anomalous positive charge (APC) near the Si-SiO$_2$ interface at room temperature by analysing interface defects and oxide charge through C-V measurements [43]. After thermal oxidation (with oxide thickness of about 100nm) and forming gas anneal (FGA), the sample received a few minutes room temperature atomic hydrogen exposure. A simultaneous increase of the high-frequency C-V stretch-out and hysteresis caused by atomic hydrogen exposure can be observed, with the hysteresis of the high frequency curve increasing from less than 20mV to several volts. It is possible that the defect responsible for the APC is similar in structure to the interface defect that can be measured from the C-V curves, but with much longer charging/discharging times (typically in the order of seconds to hours). The charge state of the defect can be cycled between positive and neutral by the gate voltage.

2.4.4 Effect of hot electrons on Si-SiO$_2$ interface

Hot-electron effects are known to degrade the performance of Si-SiO$_2$-based electronic devices. It is known that hot-electron stress liberates atomic hydrogen from within the oxide (or from the oxide/gate-metal interface), and some of this atomic
hydrogen will diffuse to the Si-SiO\(_2\) interface to react with interface defects. Cartier et al. observed that the hot electron degradation shows similar processing dependences as the atomic H-induced degradation at both (111) and (100) Si-SiO\(_2\) [25, 40].

Generally, there are two main degradation modes that are observed to be responsible for the degradation. These two mechanisms are the phenomena of “trap creation” and “impact ionization” produced by electrons with energy exceeding about 2eV [44] and 9eV [45], respectively. For the trap creation process, electrons with energy greater than 2eV release hydrogen from defect sites near the anode interface (metal or gate-SiO\(_2\) interface). This mobile species can then move to the cathode-oxide interface (Si-SiO\(_2\)) where it produces interface states and a distribution of oxide electron traps near this interface. This process is thermally activated, has a weak oxide thickness dependence (for films over 10nm), and is observed in an electric field as low as 1.5MV/cm. For impact ionization process, mobile holes produced in the oxide bulk near the anode move under the applied field to the Si-SiO\(_2\) interface where some are trapped in oxygen vacancies. Some of the injected electrons from the Si recombine with these trapped holes producing interface states and traps near the Si. This process is weakly dependent on lattice temperature, has a strong oxide thickness dependence up to about 50nm, occurs only at fields exceeding 7MV/cm, and is measurable at injected fluencies as low as 1x10\(^{-6}\)C/cm\(^2\).

Similar to the remote hydrogen plasma experiments in which reactions (2.4) and (2.5) can occur simultaneously and reaction (2.5) is more efficient at room temperature, Cartier et al. showed that these same reactions may also occur during hot electron stress in MOS capacitors [46]. In their experiments, silicon dioxide films (20nm) were thermally grown at 850°C on n- and p-type (111) oriented silicon (40-60Ω.cm). Dehydrogenation was realised by using vacuum annealing at 700°C for 2 hours. Quasistatic and high frequency C-V measurements were done on dehydrogenated MOS stacks. Their results indicated that, during hot electron stress at certain electron fluence, pre-existing unpassivated P\(_b\) centres are passivated, indicated by the significant reduction of two capacitance peaks position nearly symmetrically about mid-gap in the D\(_it\) distributions, in which the area under each peak agrees well with the P\(_b\) density measured by EPR. However, there is a clear increase of D\(_it\) distribution under the same processing conditions at the same time. Following a 180°C anneal, the interface defects density decreases again and almost recovers to the level of dehydrogenated control sample. Secondly, by analysing the dependence of [P\(_b\)] and mid-gap D\(_it\) on electron fluence, their results indicated that, with increasing electron fluence, there was a gradual
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decrease in unpassivated \(P_b\) until a stable-state density was reached, but a linear increase with no indication of saturation during the whole range of electron fluence for mid-gap \(D_n\), showing the simultaneous \(P_b\) passivation and the generation of new interface defects during hot electron stressing. Combined with earlier experiments on the \(P_b\) generation due to hot electrons [47, 48], these results demonstrate a strong analogy between the degradation during hot electron stress and the degradation in a remote hydrogen plasma, providing a firm basis for the hot-electron-induced hydrogen-release model for interface degradation.

DiMaria et al. [44] found that hot electrons in SiO\(_2\) can cause the generation of small capture cross-section traps (\(\leq 1\times 10^{-18}\text{cm}^2\)) in oxide layers at injected charge fluences \(\geq 1\text{C/cm}^2\) and fields \(\geq 1.5\text{MV/cm}\). In their experiments, poly-silicon gated n-channel MOSFETs on p-type (100) silicon samples were used. The gate oxides were grown at 1000\(^\circ\)C in O\(_2\) with 4.5\% HCl. Optically induced hot electron injection from the Si substrate was used on the sample. Their results show that, at first, if the electric field magnitude is more than 1.5MV/cm, bulk oxide electron traps are proportional to the injected charge and the electric field applied on the SiO\(_2\) layer by considering voltage shifts deduced from I-V characteristics. Moreover, the high frequency C-V characteristics indicated that both the density of positive charge and interface states at the Si-SiO\(_2\) interface show a similar trend to that of the bulk oxide electron traps. The generation of these sites was attributed to the liberation of some forms of hydrogen which pile up near the Si-SiO\(_2\) interface and lead to both the bulk negative trapped charges, interface positive charges, and the interface states observed. For both thin and thick oxides, there is a threshold for trap creation of about 2.3eV by the hot electrons in the oxide conduction band.

2.4.5 Effect of Ultraviolet light on Si-SiO\(_2\) interface

In 1985, Blumenstock and Hezel [49] reported a surface state creation by UV radiation. They found that interface states at the Si-SiO\(_2\) interface are generated by UV irradiation after plasma silicon nitride deposition onto the thermal silicon oxide. The generation occurs at photon energies greater than 4.3\(\pm\)0.2eV even at nearly zero oxide fields.

Gruenbaum et al. [50] discussed the degradation of single crystal silicon point-contact solar cells after UV exposure. Carrier lifetime and density of interface traps were measured by a contactless inductance coil and high-low frequency C-V
measurement respectively. UV exposures were done with either concentrated sunlight, mercury lamp or a xenon arc lamp. The experiment results show that there is an efficiency loss for the point contact solar cells with increasing UV exposure time. These cells had a textured front surface with a Trichloroethane (TCA) oxide as surface passivation. The efficiency dropped quickly in the first three hours and then the degradation slowed during the total eight hours exposure time. Moreover, some MOS capacitors were made to directly measure the density of interface traps. These devices were exposed to either the mercury lamp or to 50W/cm$^2$ of concentrated sunlight (5-hour exposure to sunlight at 50W/cm$^2$ had a similar effect to a 30-minute exposure under the mercury lamp). The effects of the two types of exposure were very similar: there was a rise in surface states, and the surface charge became significantly more negative after the UV exposure. Meanwhile, the $D_{it}$ distribution curves for these two devices were identical within the error of the measurement, and the charge density was also approximately the same. These results suggested that the interface damage caused by concentrated sunlight is of a similar kind to that caused by 254nm UV light. In addition, the effects of processing variables were also investigated by the authors. FZ, (100), high resistivity, n-type wafers were used for lifetime measurements. Parameters including two different silicon surface (polished and texturized), three different oxidations (with TCA, without TCA, and without TCA but with a HF treatment), and two different anneals (forming gas anneal and aluminium anneals) were investigated. The results showed that texturization, TCA oxidations, and aluminum anneals all contribute to the instability of the Si-SiO$_2$ interface. The HF treatment makes no difference for the polished wafers, but may make texturized wafers somewhat less stable. Lastly, they attempted a different processing technique to make more stable passivations and prevent UV degradation by using phosphorous diffusions. Reasonably good resistance to ultraviolet can be created by putting a phosphorous diffusion at the surface, and can be improved further by stripping off the deposited oxide after the diffusion and regrowing a dry thermal oxide.

Zhong et al. [51] also reported similar results by using gate-free Si-SiO$_2$ stacks. It was found that the effective lifetime in silicon substrate with thermal oxide decreases dramatically after 4.9eV UV irradiation but remains almost unchanged after exposure to 4.2eV photons. The lifetime degradation is correlated with the generation of interface traps, and explained by the authors with the hot electron induced hydrogen redistribution model, in which an electron in the oxide conduction band needs an extra energy of 2eV to release hydrogen atoms trapped in the oxide. Since the samples used
are gate-free, it is suggested that the oxide itself can be at least a part of the hydrogen source.

Lee et al. [52] also reported the effect of UV irradiation on the minority carrier recombination lifetime using a laser-microwave photo-conductance method for wafers oxidized at 700, 900, and 1000°C respectively and for different oxidation times at these temperatures. A UV chamber with three 8W UV lamps at the top and bottom of the chamber was used to illuminate the wafer from both sides with UV wavelength 253.7nm. For wafers oxidized at 1000°C (oxide thickness>10nm), the lifetime was found to decrease with UV irradiation and then saturate. The saturation values increased with the thickness of oxide, which indicates that for thicker oxide, the interfacial layers are more resistant to photogeneration of surface trapping centres by UV irradiation. For wafers oxidized at 700°C (oxide thickness<10nm) and 900°C (oxide thickness between 6.5 and 42.5nm), the lifetimes could continually increase or decrease or initially decrease and then increase with UV irradiation, depending on the oxide thickness. It was suggested that, all the effective lifetime changes with UV irradiation could be attributed to surface trap generation and annihilation activities. However, a change in the oxide charge due to the UV irradiation could also produce changes in lifetime. Meanwhile, they also proposed a mathematical model which describes the effect of UV irradiation on the effective lifetime and surface potential of silicon wafers [53]. Five variable parameters including total trap density and charge density (oxide and interface) and maximum O$_2^-$ charge density on the oxide surface etc are used in the model. This simple model assumes the presence of two species of interface traps, which interchange their densities. By comparing the simulations and experimental data for either lifetime or surface potential to UV illumination time, the simulations using the model are in good agreement with the experimental data.

McIntosh et al. [54] investigated the effect of surface charge on defect generation at the Si-SiO$_2$ interface by ultraviolet radiation. It was found that the presence of positive charge on the surface of oxidised silicon significantly reduced the photon energy required for both electron injection and defect generation at the Si-SiO$_2$ interface under UV irradiation. Defect generation was found to occur with photons of considerably less energy than previously reported, with evidence that photons with energy below 3.66eV were capable of defect generation in the presence of charge. They attributed this effect to the reduction of the effective interface potential barrier for electron injection due to the field generated by the charge. Contrary to results for MOS structures, it was found that the majority of defect generation occurred for oxide fields less than ~1MV/cm. A
possible explanation for these results was discussed in terms of the hydrogen redistribution model of defect generation, in which defect generation resulted from the release of atomic hydrogen in the oxide by injected electrons (under UV illumination) and its subsequent diffusion to the Si-SiO₂ interface.

2.5 Effect of post-oxidation thermal annealing on Si-SiO₂ interface

Stesmans et al. investigated the interface degradation induced in thermal (111) Si-SiO₂ by post-oxidation annealing (POA) in the range of 480-1135°C in vacuum for 62 minutes [55]. Firstly, they found there is an exponential increase of P_b density in the range of 480-640°C, which is due to the dissociation of initially passivated P_bH centres. For an anneal temperature lower than 480°C, the P_b density was not significantly affected by the following thermal annealing. Secondly, they found a monotonic increase of P_b density in the range of 640-1135°C, due to the creation of new P_b centres. These new P_b centres were thought to be due to the release of SiO(g) as a result of the reaction between Si and SiO₂. Once created, the newly formed P_b centres are stable and exhibit similar H passivation-depassivation kinetics as the ‘original’ centres, naturally introduced during oxidation. The same effects have also been observed in nitrogen ambient. A similar but less dramatic trend was found for the (100) Si-SiO₂ interface, with the P_b1 density increasing monotonically but the P_b0 density tends decreasing slightly [56]. Finally, they found that the vacuum POA-induced interface degradation in (111) Si-SiO₂ is strongly enhanced when performed in H₂. The molecular H₂ anneal atmosphere was found to increase P_b centre generated by nearly a factor of 6 compared to vacuum [22].

2.6 Simple model for atomic hydrogen

Figure 2.3 illustrates a simple model that will be used to discuss and explain the experimental results. In the illustration in fig 2.3, an initially de-hydrogenated interface is assumed, indicated by (electrically active) P_bx centers. Following atomic H exposure at low temperatures for a sufficient period of time t_pass, the majority of the P_bx centers are passivated with hydrogen and a steady state fraction of passivated P_bx centers is
reached. At the same time, additional, thermally unstable defects (denoted D in fig 2.3) are also introduced. Again, after a sufficient period of time $t_{\text{gen}}$, the density of these additional defects reaches a steady state. In general it may be expected that $t_{\text{pass}} > t_{\text{gen}}$ and that the two time constants display different temperature dependencies. Apart from temperature, the time constants would be expected to depend on the flux of atomic hydrogen and the interface orientation. If the interface is initially hydrogenated (following an FGA), then the initial diagram will be different - most of the $P_{bx}$ centres would be hydrogenated - but subsequent diagrams (following atomic H exposure and annealing) may be the same. In other words, the final degree of passivation of $P_{bx}$ centres following hydrogen plasma exposure should be independent of the initial degree of hydrogenation. Following an anneal at sufficiently high temperatures and for sufficient times, the unstable defects are removed.

Figure 2.3. Illustration of the model to explain experimental results. The blue balls represent Si atoms; red balls represent H atoms (labelled H); lines represent defects (labelled $P_{bx}$ and D).

According to the model, atomic H exposure does not result in permanent interface damage. After atomic H exposure, both the $P_{bx}$ defects passivation and thermally unstable defect generation will reach steady state at some point, but not necessarily at the same point in time.

An interesting question is whether the passivation afforded by atomic hydrogen (once the unstable defects are removed) is superior or inferior to that provided by an
The results of EPR studies, which measure the electrically active P$_{bx}$ density following various treatments, strongly suggest that the passivation provided by atomic H is inferior [25, 40]. Meanwhile, Jin et al. [26] work indicates that the atomic hydrogen induced defects are thermally unstable. In their experiments, H was introduced to Si-SiO$_2$ interface by exposing Si-SiO$_2$ stack into ammonia plasma at room temperature. After ammonia plasma exposure, there is a dramatic increase in the interface defects which act as the effective surface recombination centres. After a RTA or FGA at 400°C, the majority of additional defects introduced by atomic hydrogen can be annealed out, indicated by both of D$_{it}$ and J$_{0e}$ returning to values similar to those prior to ammonia plasma exposure. Therefore, if one is interested in comparing the degree of P$_{bx}$ passivation by atomic H and by molecular H$_2$ (in terms of the surface recombination rate) then this may be able to be done by removing all the thermally unstable defects, but this needs to be achieved without removing any H from the P$_{bx}$-H centres. The question is whether this can be done.

2.7 Summary

In this chapter, the configurations of hydrogen in silicon have been summarized. Furthermore, effect of molecular on Si-SiO$_2$ interface has been reviewed, and then the oxides grown at low temperature and its application for oxide/PECVD SiN$_x$ has been briefly discussed. Moreover, effects of atomic hydrogen on Si-SiO$_2$ interface have been described. After that, the effect of post-oxidation thermal annealing on Si-SiO$_2$ has been presented. Lastly, a simple model used to explain the experimental results has been illustrated. Most of the above experiments provided direct insight into the hydrogen chemistry at Si-SiO$_2$ stacks. The remote plasma experiments show that silicon dangling bonds, as detected by EPR measurements, account only for a small fraction of the electrically detected interface-states, reopening the quest for the microscopic nature of the defects responsible for interface degradation in Si-based electronic devices. Meanwhile, hot electron and UV experiments showed quite clearly that atomic hydrogen, if released by hot electrons, will generate interface states (including anomalous positive charges) and will cause low-field leakage currents in thin gate oxides, likely because atomic hydrogen also produces distributed electron traps.

From all these results, the following conclusion can be drawn. At ambient temperatures, atomic hydrogen supplied from a remote plasma, and likely atomic
hydrogen released by hot-carrier stress or by radiation during device operation, will produce only small amounts of silicon dangling bonds at either (111) or (100) Si-SiO$_2$ interface. The majority of the electrically active defects are of unknown microscopic structure. In addition, the (111) Si-SiO$_2$ interface has only one type paramagnetic defect, namely the $P_b$ centre, whereas two distinct paramagnetic defects, namely the $P_{b0}$ and $P_{b1}$ centres, are associated with the (100) interface, in which the $P_{b0}$ is the dominant defect at the (100) interface and it is chemically not equivalent to $P_b$.

The results of Cartier et al., while conclusive, were limited to room-temperature and microwave power excited atomic H exposures and to the measurement of $P_b$ centres. For solar cell applications, it is the rate of the recombination of excess carriers, mediated by interface defects, that is of interest. This requires measurement of the surface recombination rate. Moreover, further work is necessary to understand the properties of the majority of the unknown electrically active defects introduced by atomic hydrogen exposure.
CHAPTER 3

Quantifying and measuring of Si surface electrical properties

This chapter briefly describes the main measurement techniques and the theory behind them used in this dissertation for Si electronic properties. The quality of a surface passivation can be assessed by measuring the surface recombination velocity (SRV) as it is related to the fundamental properties of the surface defects. The Si surface recombination velocity is affected by multiple factors, according to the “extended Shockley–Read–Hall (SRH) formalism” established by Aberle et al. [57]. The calculations of SRH-recombination rates at the Si-SiO$_2$ interface are based on the theory of a surface space charge layer under non-equilibrium conditions and take into account the impact of illumination level, gate metal work function, fixed oxide charge density, and the energy dependence of capture cross sections and interface state density. In this thesis, the effective minority-carrier lifetime of Si samples is determined by means of Photo-conductance decay (PCD) tool in transient or generalized mode. The emitter saturation current density($J_{0e}$), which is an indicator of degree of surface passivation, can in many cases be deduced from these lifetime measurements. Determination of $J_{0e}$, in turn, allows calculation of the surface recombination velocity.
Meanwhile, a combination of high frequency and quasi static capacitance voltage (C-V) measurements is used to determine the defect distribution within the Si forbidden bandgap and charge density in SiO$_2$ near the Si-SiO$_2$ interface. Electron paramagnetic resonance (EPR) measurements are used to observe specific, paramagnetic defects at the Si-SiO$_2$ interface.

### 3.1 Measurement of minority carrier lifetime

As the name indicates, lifetime spectroscopy uses the recombination lifetime for defect characterization. The carrier recombination lifetime is the central parameter to the device design, production, and process control for silicon solar cells. The longer an excess carrier lives in the excited state, the better the solar cell that will be made from this wafer, all other things being equal.

In semiconductors, generation refers to the process by which electron-hole pairs are created. The energy for the excitation of an electron from the valence to the conduction band can come from thermal process or through absorption of photons. While on the other hand, recombination refers to the inverse process whereby electron-hole pairs are lost due to a spontaneous transition of an excited electron from the conduction band to an unoccupied state (hole) in the valence band. The excess energy and the change in momentum are either released as either photons or phonons or transferred to other carriers. To semiconductor materials, simply speaking, the minority carrier lifetime is the mean lifetime of the minority carriers either electrons or holes. Experimentally, it is the recombination lifetime that is measured. The recombination rate [58], $U$, has the following relationship with the recombination lifetime, $\tau$:

$$\tau \equiv \frac{\Delta n}{U}$$

where $\Delta n$ is the excess carrier concentration, $\Delta n=n-n_0$, $n$ the carrier concentration, and $n_0$ the carrier concentration in thermal equilibrium. This relationship is valid for both electrons and holes.

#### 3.1.1 Recombination mechanics

A common classification of the different recombination mechanisms distinguishes intrinsic and extrinsic mechanisms. For intrinsic recombination mechanisms, there are
two fundamental distinguished processes: radiative band-band recombination, if the excess energy is released as a photon, and Auger band-band recombination, if the excess energy is transferred to a third carrier, the transition thus non-radiative. In the case of extrinsic recombination mechanisms, the decay of an electron-hole pair occurs stepwise by electron transition via defect centre with an intermediate energy level in the band gap. This process is commonly known as Shockley–Read–Hall (SRH) recombination. SRH recombination can occur either through bulk defects, induced by impurities or lattice defects (bulk SRH recombination), or as a result of surface states (surface SRH recombination) [58].

3.1.1.1 Bulk recombination

As mentioned above, there are three fundamental recombination processes in semiconductors: radiative recombination, band-to-band Auger recombination and recombination via defects. The total net recombination rate $U$ in a semiconductor is the sum of these three different recombination processes. Since these recombination processes proceed independently from each other, the resulting total bulk carrier lifetime $\tau_b$ can be calculated from the individual carrier lifetimes according to

$$\frac{1}{\tau_b} = \frac{1}{\tau_{\text{radiative}}} + \frac{1}{\tau_{\text{auger}}} + \frac{1}{\tau_{\text{defect}}}$$

(3-2)

Radiative recombination is the inverse process to optical generation in a semiconductor and involves two charge carriers. It is the dominant recombination process in direct-bandgap semiconductors such as GaAs. However, radiative recombination produces negligible recombination rates compared to Auger recombination and recombination via defects and it has little significance in crystalline silicon because silicon is indirect-bandgap semiconductor.

Auger recombination is traditionally viewed as a three-particle injection where the energy released by the recombination of an electron-hole pair is transferred to a third free carrier. The third, excited carrier returns to its initial energy state by emitting phonons to the crystal. Auger recombination will become the dominant recombination mechanism at high injection levels, or in heavy doped silicon.

The process of recombination via defects, which is due to impurities, dislocations etc., is of paramount importance for indirect-bandgap semiconductors such as silicon. Although this defect-mediated recombination process may in principle be removed by producing an ideal crystal of perfect purity, under real conditions it is very often the
dominant process, as any imperfection of the ideal crystal structure induces defects levels, which may act as recombination centres if located within the band gap \[58\]. The whole process involves a two-step recombination process in which, at first, an electron makes a transition from the conduction band into the defect level and then from there into the valence band where it recombines with a hole. Usually, the excess energy is released in form of phonons. For a single defect level, the recombination rate, \( U_{SRH} \) is given by,

\[
\frac{np - n_i^2}{\tau_{n0}(n + n_i) + \tau_{p0}(p + p_i)} \tag{3-3}
\]

where \( n_i \) is the intrinsic carrier concentration. \( \tau_{p0} \) and \( \tau_{n0} \) are capture time constants of electrons and holes, \( n_1 \) and \( p_1 \) are the so-called SRH densities, which are statistical factors and depend on the defect’s energy level and defined as:

\[
n_i = n_i \exp \left( \frac{E_t - E_i}{kT} \right) \quad \text{and} \quad p_i = n_i \exp \left( \frac{E_t - E_i}{kT} \right) \tag{3-4}
\]

where \( E_t \) is the defect (trap) energy level, \( E_i \) the intrinsic Fermi energy, \( k \) Boltzmann constant, and \( T \) temperature. \( \tau_{p0} \) and \( \tau_{n0} \) are given by:

\[
\tau_{p0} = \frac{1}{N_i \sigma_p V_{th}} \quad \text{and} \quad \tau_{n0} = \frac{1}{N_i \sigma_n V_{th}} \tag{3-5}
\]

where \( V_{th} \) is the thermal velocity of charge carriers, \( N_i \) the density of defects in the semiconductor bulk, and \( \sigma_p \) and \( \sigma_n \) the hole and electron capture cross sections \[59\].

### 3.1.1.2 Surface recombination

Surface recombination \[58\] is a special case of SRH recombination in which the localised states occur at the surface. On the one hand, a large density of surface defects existing within the whole bandgap results from Si dangling bonds. On the other hand, additional processing-related surface states come from chemical residues and metallic depositions on the surface or from dislocations. Actually, interface states do not normally occupy a single energy level, but are continuously distributed throughout the band gap. Thus, the over surface recombination rate \( U_s \) is given by the equation (3-6) over the entire bandgap.
where $n_s$, $p_s$ are the electron and hole concentrations at the Si surface, $v_{th}$ the thermal velocity of minority carrier, $n_1$ and $p_1$ statistical factors depending on the defect energy level, $\sigma_p(E)$ and $\sigma_n(E)$ the energy dependent capture cross sections for holes and electrons, and $D_{it}(E)$ the density of interface states at a given energy. In contrast to the bulk recombination rate, the surface recombination rate is a rate per unit area instead of per unit volume. This is why the definition of a surface lifetime to equation (3-1) makes no sense. Alternatively, a new quantity called surface recombination velocity $S$ (SRV) has to be defined:

$$S \equiv \frac{U_s}{\Delta n_s}$$

where $\Delta n_s$ is the excess minority carrier concentration at the surface.

As the SRV is related to the fundamental properties of the surface defects, it is a direct measure of the recombination activity of the semiconductor surface and thus allows the quality of a surface passivation to be assessed [60].

### 3.1.2 Emitter recombination

In silicon solar cells, another important source of carrier loss, which is recombination within the heavily doped emitter region, must be considered. Such effects are difficult to model from a fundamental approach for a number of reasons because of the heavily doped emitter regions. However, two simplifications can often be applied. Firstly, the minority carrier concentration in the emitter region normally remains low and secondly, Auger recombination is likely to be the dominant bulk recombination mechanism. As a result the recombination lifetime in the emitter region is constant with injection level, and the recombination current into the emitter, $J_{rec}$, can be expressed as [61, 62]:

$$J_{rec} = J_{0e} \frac{np}{n_i^2}$$

where $J_{0e}$ is defined to be the emitter saturation current density, and $n$ and $p$ refer to the electron and hole concentrations on the base side of the space-charge region. $J_{0e}$ is an
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indicator of the degree of surface passivation and a parameter of direct technological importance for photovoltaics. Measurement of $J_{0e}$, rather than the effective surface recombination velocity, has the advantage that it allows the unambiguous separation of surface and bulk recombination [63]. On the other hand, recombination within the emitter depends strongly on the dopant distribution within the emitter [64]. The emitter saturation current density includes contributions from recombination at the emitter surface as well as the emitter bulk [65]. Today, the majority of commercial Si solar cells are still made by screen-printed contacts on 35–60Ω/sq emitters, instead of on higher sheet resistance of 100Ω/sq shallow emitters, to avoid high contact resistance and junction shunting. Unfortunately, heavy doping itself causes reduced short wavelength response and higher emitter saturation current density, which reduces cell performance [66]. Several cell designs in commercial production or in the research phase have emitters significantly lighter than this [67].

The recombination rate for the emitter, can be referred to the entire volume of the wafer in order to compare it with other bulk processes

$$U_{emitter} = J_{0e} \frac{np}{qWn_i^2}$$

(3-9)

where $q$ is the elementary charge of an electron, and $W$ the width of the wafer.

Therefore, the emitter recombination lifetime $\tau_{emit}$ could be expressed as:

$$\tau_{emit} = \frac{qn_i^2W}{J_{0e}(N_A + \Delta n)}$$

(3-10)

where $N_A$ is the dopant density of the Si bulk and $\Delta n$ is the excess carrier concentration in the Si bulk. When the bulk is in low level injection ($\Delta n \ll N_A$), the emitter recombination lifetime is independent of injection level. In high level injection, $\tau_{emit}$ decreases with increasing injection level, as shown in equation 3-11. This provides the basis for measuring $J_{0e}$ [62, 64].

$$\tau_{emit} = \frac{qn_i^2W}{J_{0e}\Delta n}$$

(3-11)

Emitter recombination, as determined by measurement of $J_{0e}$, includes recombination from the emitter bulk and the surface. If the emitter region is defined as the effective surface region, the effective surface recombination velocity, $S_{eff}$, can be expressed as [68]:
\( S_{\text{eff}} = J_{0e}(N_A + \Delta n)/q n_i^2 \) \hspace{1cm} (3-12)

which is also known as the quasi-static emitter approximation.

Emitter recombination can be viewed as a special case of surface recombination. In this condition, \( U_s \) can be defined as:

\[ U_s = J_{0e} \frac{np}{q n_i^2} \] \hspace{1cm} (3-13)

Combining Eq. (3-6) and Eq. (3-13), a relationship between \( D_{it} \) and \( J_{0e} \) is established.

Recombination in emitter regions becomes even more important as the carrier density becomes higher than one-tenth of the wafer doping, approximately. The determination of \( J_{0e} \) is facilitated by use of high-lifetime, high resistivity wafers to ensure that the measured effective lifetime is clearly dominated by the emitter regions.

### 3.1.3 Effective lifetime

In general, the recombination processes can be considered to occur independently and simultaneously in the Si bulk and at the surface. Meanwhile, in most practical cases two or more of the recombination mechanisms mentioned above might be critical in a given sample at a given injection level. For independent process the overall recombination rate is just the sum of the individual recombination rates, resulting in an effective recombination rate, \( U_{\text{effective}} \) given by

\[ U_{\text{effective}} = U_{\text{bulk}} + U_{\text{surface}} + U_{\text{emitter}} \] \hspace{1cm} (3-14)

where \( U_{\text{bulk}} = U_{\text{rad}} + U_{\text{Auger}} + U_{\text{SRH}} \) \hspace{1cm} (3-15)

Following from Eq.(3-1), the effective lifetime is given by

\[ \frac{1}{\tau_{\text{effective}}} = \frac{1}{\tau_{\text{back}}} + \frac{1}{\tau_{\text{surface}}} + \frac{1}{\tau_{\text{emitter}}} \] \hspace{1cm} (3-16)

For the specific test structures which have been passivated on both sides with an identical dielectric film, the effective lifetime can be expressed as:

\[ \frac{1}{\tau_{\text{effective}}} = \frac{1}{\tau_{\text{back}}} + \frac{2S_{\text{eff}}}{W} \] \hspace{1cm} (3-17)

On the other hand, for the specific test structures which is of a symmetrical n\(^+\)pn\(^+\) or p\(^+\)np\(^+\) test structure, the effective lifetime can be expressed as:

\[ \frac{1}{\tau_{\text{effective}}} = \frac{1}{\tau_{\text{back}}} + \frac{2J_{0e} (N_A + \Delta n)}{q W n_i^2} \] \hspace{1cm} (3-18)
Typically, the different injection-level dependence of these mechanisms results in the effective lifetime having segments that are dominated by different processes. This is illustrated in Figure 3.1 [69] for a substrate with $N_A = 1 \times 10^{14}$ cm$^{-3}$, an emitter characterised by a saturation current density of 20fAcm$^{-2}$ and a deep SRH centre with $\tau_{n0} = 1$ms and $\tau_{p0} = 1$s. In low-injection, the sample is dominated by SRH recombination, while at intermediate to high-injection, emitter recombination takes over. It is this region which can be used to determine the value of $J_{0e}$ using the method described above. At the highest injection-levels, Auger recombination is the most important process [69].

![Figure 3.1. Lifetime curves for SRH recombination, radiative recombination and Auger recombination [69].](image)

### 3.1.4 Lifetime measurement techniques

The recombination lifetime in the wafer is one of the most important input parameters for any device model of design optimization and efficiency prediction. Due to its importance, the photovoltaic community has developed several techniques to report this parameter in order to be able to determine bulk lifetime and surface recombination parameters with good accuracy. There have been many techniques developed over the decades with the objective of measuring lifetime [70]. The measurement of carrier lifetime in a wafer can be accomplished by monitoring the carrier-density balance as a function of the photo-generation of excess carriers. This carrier density can be monitored under constant illumination (the steady-state between
excess carriers and photo-generation), after illumination (the excess carrier density transient decay), or during a time of varying light intensity, the “Quasi-Steady-State”, or “Generalized” case [71]. In this section, two techniques in particular, namely photo-conductance decay and quasi-steady-state method (QSSPC), are discussed in detail, due to their widespread use and special suitability to solar cell applications. The different techniques may be classified in terms of the time dependence of the illumination and the technique used to measure the excess carrier density.

3.1.4.1 Photo-conductance decay

Characterization of the minority carrier lifetime in semiconductor materials and devices is often achieved using some form of transient measurement technique [70]. The traditional transient technique, used especially to measure high carrier lifetimes, involves a sharp pulse of illumination that is rapidly turned off and a subsequent determination of the excess carrier density without illumination. The effective lifetime quantifies the rate of recombination occurring within a solar cell, and therefore strongly impacts its performance. A schematic of the experimental apparatus used in this thesis for PCD measurements is given in Figure 3.2 [72].

![Figure 3.2. PCD setup used to measure injection-dependent carrier lifetimes. Left: Schematic diagram of the inductively-coupled photo-conductance apparatus. Right: WCT 100 apparatus from Sinton Consulting used in this thesis [72].](image)

The experimental sample is inductively combined by a coil to an rf-bridge circuit which senses changes in the sample’s permeability and therefore its conductance. A change in the sample conductivity (as a result of the photo-generation of excess carriers,
for example) results in a change in the inductance of the coil, and a change in the output voltage from the circuit. Calibration of the apparatus is achieved by measuring the voltage output for different wafers with a range of known conductance.

For a silicon wafer with steady state or transient light incident on the sample, solving the continuity equation gives the effective lifetime [71]

\[
\tau_{eff} = \frac{\Delta n_{av}}{G - \frac{d\Delta n_{av}}{dt}}
\]  

(3-19)

where \(\Delta n_{av}\) is the time-dependent average excess carrier density and \(G\) the photo-generation rate for electron-hole pairs

In the transient photo-conductance decay method, the photo-generation is abruptly terminated, then after the light is fully off, the only reason for the electron concentration to change is the recombination rate and the effective lifetime is then calculated via (3-20), a negative value of the derivative indicates that the electron concentration is decreasing.

\[
\tau = -\frac{\Delta n_{av}}{\frac{d\Delta n_{av}}{dt}}
\]  

(3-20)

Meanwhile, the resulting decay of carriers back to their equilibrium concentrations is monitored via the photo-conductance, and the effective recombination lifetime calculated. In the absence of significant trapping, the excess carrier densities are equal, and the net excess conductance \(\Delta \sigma\) will be given by:

\[
\Delta \sigma = q \Delta n_{av} (\mu_n + \mu_p) W
\]  

(3-21)

where \(\mu_n\) and \(\mu_p\) are the electron and hole mobility and \(W\) the sample thickness.

The advantage of the PCD method is the optical factors (i.e. light intensity, pulse shape and optics) are irrelevant in the PCD analysis. The only purpose of the light sensor is to indicate when the flash has finished, and the date analysis can begin. The disadvantages are the lifetime must be significantly longer than the flash turn-off time and relying on the derivative can lead to noisy data in some cases. It should be noted that the temperature, uniformity of diffusion layer and calibration will all contribute the measurement errors.

Figure 3.3 shows a typical inductively-coupled PCD trace with the corresponding lifetime versus excess carrier density curve. The particular apparatus at the Australian National University (produced by Sinton Consulting) is excellent for samples with long lifetimes (>100\(\mu s\)) when used in PCD mode, but is less accurate for lower lifetimes due
to the poor cut-off time of the flash-lamp. Such samples are best measured with the 
quasi-steady-state photo-conductance (QSSPC) technique described in the next section.

Figure 3.3. A typical inductively-coupled photo-conductance decay (PCD) trace for a 
100Ω.cm FZ wafer showing the sharp illumination peak and the ensuing carrier decay.

3.1.4.2 Quasi Steady State photo-conductance

Sinton and Cuevas first proposed the inductively-coupled QSSPC technique in 
1996 [73]. In the QSSPC technique the incident light is slowly reduced to zero over 
several milliseconds. If the effective lifetime of the sample is significantly less than the 
rate of decay of the light, then the sample can be considered to be in steady state at any 
one point in time, and the effective lifetime can be determined from knowledge of the 
rate of carrier generation and the excess carrier density within the sample. In this way 
the effective lifetime can be determined over a large range of injection levels. We can 
use the expression for the balance between generation and recombination to calculate 
the effective lifetime:

$$\tau = \frac{\Delta n_{av}}{G_L}$$  \hspace{1cm} (3-22)$$

where $G_L$ is the generation rate produced by incident light and the average excess 
carrier density $\Delta n_{av}$ also can be calculated from Eq.(3-20). $G_L$ can be determined 
accurately by using a calibrated photo-detector, for example, a calibrated solar cell. 
Because of its finite thickness and reflectivity, the silicon wafer will absorb only a 
fraction of these photons. If we assume the illumination is one sun, the generation rate 
per unit volume can be evaluated as:
\[ G_k = \frac{N_{ph} f_{\text{abs}}}{W} \]  

(3-23)

where \(N_{ph}\) is the total photon flux incident on the surface of the wafer per unit area. \(f_{\text{abs}}\) is the coefficient which must be estimated or experimentally determined for each sample to be measured.

A common feature of both techniques is that they are non-contacting, which make them ideally suited for lifetime spectroscopic purposes, as partially finished devices that are free of metal contacts can be investigated, even including the starting material itself.

### 3.2 Measurement of Si interface properties by the Capacitance-Voltage method

Since it is well known that the characteristics of solar cells are critically dependent on the surface condition of the semiconductor material, the properties of semiconductor surfaces have been the subject of many investigations. A method in which the capacitance of the semiconductor surface is studied as a function of the applied normal electric field is provided by using a Metal-Insulator-Semiconductor (MIS) structure. This technique is particularly easy to use in a study of oxide covered surface, since a simple metal-oxide-semiconductor sandwich provides convenient capacitor. Soon after the MIS structure was proposed as voltage-dependent capacitor, it was widely employed in studies of the oxide-silicon interface [74].

#### 3.2.1 Structure and theory of ideal Metal Insulator Semiconductor

The MIS structure was first proposed as a voltage-variable capacitor in 1959 by Moll [75] and by Pfann and Garrett [76]. Its characteristics were then analysed by Frankl [77] and Lindner [78]. The MIS structure was first employed in the study of a thermally oxidized silicon surface by Ligenza and Spitzer in 1960 [79]. A comprehensive and in-depth treatment of the Si-SiO\(_2\) MOS structure can be found in MOS Physics and Technology by Nicollian and Brews [80]. Figure 3.4 is the schematic
diagram of the metal-insulator-semiconductor structure, where d is the thickness of insulator and V is the applied voltage on the metal field plate [81].

![Figure 3.4. Metal-Insulator-Semiconductor structure.](image)

An ideal MIS structure is defined as follows [86]:

1. at zero applied bias, the work function difference is zero:
   
   \[
   \phi_{ms} = \phi_m - \left( \chi + \frac{E_g}{2q} - \psi_B \right) = 0 \quad \text{for n type} \quad (3-24)
   \]
   
   \[
   \phi_{ms} = \phi_m - \left( \chi + \frac{E_g}{2q} + \psi_B \right) = 0 \quad \text{for p type} \quad (3-25)
   \]

   where \( \phi_{ms} \) is the work function difference between metal and semiconductor, \( \phi_m \) the metal work function, \( \chi \) the semiconductor electron affinity, \( E_g \) the bandgap, \( \psi_B \) the potential difference between the Fermi level \( E_F \) and the intrinsic Fermi level \( E_i \).

2. a negligible interface state density \( D_{it} \)

3. a negligible interface charge density \( Q_f \)

The ideal MIS structure is to be considered as a foundation for understanding practical MIS structures and exploring the physics of semiconductor surfaces. When an ideal MIS capacitor is based with positive or negative voltages, basically three cases may exist at the semiconductor surface. The energy band diagram of an ideal MIS structure for \( V \neq 0 \) is shown in figure 3.5 [81].
Chapter 3: Quantifying and measuring Si surface electrical properties

Although the MIS structure based on a p-type semiconductor, the results can be readily extended to an n-type semiconductor. The polarity of the voltage, however, should be changed for the n-type semiconductor. When a negative voltage is applied to the metal plate, the top of the valence band bends upward (because the product of potential energy–qv is positive) and is closer to the Fermi level. For an ideal structure, no currents flows in the structure, therefore the Fermi level remains constant in the semiconductor. Since the carry density depends exponentially on the energy difference (E_F-E_V), this band bending causes an accumulation of majority carriers (holes) near the semiconductor surface. This is the “accumulation” case. When a small positive voltage is applied, the bands bend downwards, and the majority carriers are depleted. This is the
“depletion” case. When a large positive voltage is applied, the bands bend even more downward so that the intrinsic level $E_i$ at the surface cross over the Fermi level $E_F$. At this point the number of electrons (minority carriers) at the surface is larger than that of the holes, the surface is thus inverted, and this is the inversion case [81]. Note that if the C-V curve is made from the accumulation side, non-equilibrium depletion characteristics prevent the measurement of the interface state. Thus C-V curves must be made from inversion to accumulation. For this plot direction the sweep rate has not been found to affect the interface states measurement [82].

### 3.2.2 Calculation of the overall electrical characteristics of silicon surfaces

The essence of the MIS technique lies in a comparison between an idealised theory and experimental observations; conclusions regarding the nature of the interface are based upon interpretation of the deviations between the two. Many detailed properties of the oxide-silicon interface, such as the surface state density, the fixed surface charge density, and the dependence between the surface band bending and the applied gate voltage and so on, can be obtained from C-V technique.

Terman [83] developed and used the high frequency method for determining interface trap capacitance. In the high frequency capacitance method, capacitance is measured as a function of gate bias with frequency fixed at a high enough value so that interface traps do not respond and contribute no capacitance to the high frequency C-V curve. However, these interface traps will cause stretch-out or distortion on the high frequency curve along the gate bias axis compared to an ideal C-V curve. On the other hand, oxide fixed charge and work function difference will produce a parallel shift of the C-V curve along the gate bias axis compared to an ideal C-V curve. At high frequency, capacitance is given by:

$$ C = \frac{1}{C_i} + \frac{1}{C_s} \quad (3-26) $$

where $C_i$ is insulator capacitance, $C_s$ the semiconductor capacitance.

Berglund [84] developed and was first to use the low frequency C-V method. Again, a C-V curve is measured at a constant frequency, but now at a frequency so low that interface trap response is immediate. Because interface traps immediately respond to the ac gate voltage, they will contribute an additional capacitance to the measured low frequency C-V curve. In addition, interface traps follow changes in gate bias so that
the measured low frequency C-V curve will stretched out along the gate bias like the high frequency C-V curve. At low frequency, capacitance is given by:

\[ C = \frac{1}{C_i} + \frac{1}{C_s + C_u} \]  

(3-27)

where \( C_u \) is the interface trap capacitance.

Castagne and Vapaille [85] were the first to combine high and low frequency C-V curves to obtain a measured semiconductor capacitance. In our C-V measurements, the quasi-static C-V technique was used. This method is based on the proportionality that exists between MOS capacitance and the charging current in the structure when it is subjected a linear voltage ramp. As a result of this proportionality, a low frequency thermal-equilibrium capacitance-voltage curve can be obtained. The quasi-static and high-frequency curves are then used to extract the interface-states density distribution in the band gap.

C-V curves at high frequency and under quasi static conditions for Si-SiO₂ structures are shown in figure 3.6 (a) passivated sample and (b) depassivated sample. A (100), p type, 1-10Ω.cm, single side polished Si wafer was used. A 50nm thick oxide layer was thermally grown on Si followed by an in-situ anneal in N₂ at the oxidation temperature and FGA at 400°C for 30 minutes for passivated sample and followed by a RTA 700°C for 3 minutes for depassivated sample.

![Figure 3.6. High frequency and Quasi static CV curves for p-type Si-SiO₂ structures (a) passivated (b) depassivated.](image-url)
From these curves, important information like insulator thickness, Si substrate doping level, flat band voltage, surface potential and interface defect distribution within the Si forbidden bandgap, can be extracted.

3.2.2.1 Calculation of insulator thickness

Insulator thickness can be obtained from high frequency curve. In the accumulation region, the measured capacitance $C$ is close to the insulator capacitance, $C_i$, since this condition minimizes the spacing between the charges in the semiconductor and the polarized insulator, the semiconductor capacitance $C_s$ is very large so the total measured capacitance approaches $C_i$ (see Eq. 3-26). The insulator thickness $d$ is calculated via:

$$d = \frac{A \varepsilon_i \varepsilon_0}{C_i}$$

where $A$ is the area of capacitor plates, $\varepsilon_i$ is the dielectric constant for the insulator, $\varepsilon_0$ is the permittivity of vacuum.

3.2.2.2 Calculation of doping level

The doping level can also be obtained from high frequency CV curve. In the strong inversion region, the measured capacitance $C_{min}$ from the high frequency CV curve has the following relationship with the maximum depletion width, $W_m$, [81]:

$$C_{min} = \frac{\varepsilon_i}{d + \frac{\varepsilon_i}{\varepsilon_s} W_m}$$

where $\varepsilon_s$ is the dielectric constant for the semiconductor.

Meanwhile, $W_m$ has the following relationship with doping level, $N_A$ under strong inversion condition which begins at a surface potential $\psi_s \approx 2\psi_B$ (Fermi potential with respect to midgap) [81],

$$W_m \approx \sqrt{\frac{4\varepsilon_s kTm(N_A/n_i)}{q^2 N_A}}$$

where $k$ is Boltzmann’s constant. Therefore, the doping level can be calculated from $C_{min}$.

3.2.2.3 Calculation of flat band voltage
Referring to MIS devices, flat band voltage is the voltage at which the surface potential is zero, therefore, no voltage drop across the semiconductor; in band diagram the energy bands of the semiconductor are horizontal (flat). The flat band voltage of real MOS structures is further affected by the presence of charge in the oxide or at the oxide-semiconductor interface and can be calculated from the high frequency C-V curve.

At flat band conditions, the semiconductor capacitance is given by [81]:

\[ C_s = \frac{\varepsilon_s}{L_D} \]  

(3-31)

where \( L_D \) is the Debye length which is a measure of the distance over which a charge imbalance is neutralized by majority carriers under steady-state or equilibrium conditions, and is given by:

\[ L_D = \sqrt{\frac{\varepsilon_s kT}{q^2 N_A}} \]  

(3-32)

The flat band capacitance can be calculated from a combination of equations (3-26), (3-31) and (3-32) and obtained from corresponding capacitance value in CV curve.

### 3.2.2.4 Calculation of fixed oxide charge density

Oxide charges \( Q_o \) include the oxide fixed charge \( Q_f \), the oxide trapped charge \( Q_{ot} \), and the mobile ionic charge \( Q_m \).

\[ Q_o = Q_f + Q_{ot} + Q_m \]  

(3-33)

The fixed oxide charge \( Q_f \) has the following properties: it is fixed and cannot be charged or discharged over a wide variation of \( \psi_f \); it is located in the oxide layer less than 25Å from the Si-SiO\(_2\) interface; its density is not greatly affected by the thickness or by the type or concentration of impurities in the silicon; it is generally positive and depends on oxidation and annealing conditions, and on silicon orientation. It has been suggested that the silicon dangling bonds or the loss of an electron from excess oxygen centres near the Si-SiO\(_2\) interface is the origin of fixed oxide charge. In electrical measurements, \( Q_f \) can be regarded as a charge sheet located at the Si-SiO\(_2\) interface [86, 87].

For a practical CV experiment, the value of work function difference \( \Phi_{ms} \) is not zero and the oxide charge exist, so if we assume negligible interface traps, the experimental Capacitance-voltage curve will be shifted from the ideal curve by an amount
If mobile ions and oxide trapped charges are negligible, Eq. (3-34) reduces to

$$V_{FB} = \Phi_{ms} - \frac{Q_m}{C_i} = \Phi_{ms} - \frac{Q_f + Q_m + Q_{st}}{C_i}$$  \hspace{1cm} (3-35)$$

For a certain MIS structure, $\Phi_{ms}$ is a constant, therefore, the fixed oxide charge density can be calculated from $V_{FB}$ and $C_i$.

According to the analysis above, fixed oxide charge density cannot be determined unambiguously in the presence of moderate densities of interface trapped charge, it is only measured after a low-temperature (minus 450°C) hydrogen treatment to minimise trap density [88].

### 3.2.2.5 Calculation of interface defect density and surface potential

By comparing the Metal Insulator Semiconductor (MIS) capacitance at high and low frequency, Castagne [85] pointed out the areal interface defect density, $D_{it}$, has the following relationship with capacitance

$$D_{it}(V_g) = \frac{1}{qA} \left( \frac{C_i C_{lf}}{C_i - C_{lf}} \frac{C_i C_{hf}}{C_i - C_{hf}} \right)$$  \hspace{1cm} (3-36)$$

where $A$ is the surface area, $C_{lf}$ is the low frequency capacitance and $C_{hf}$ is the high frequency capacitance. The dependence between the gate voltage $V_g$ and surface potential $\psi_s$ is determined by Berglund’s [84] formula

$$\psi_s(V_g) = \int_{V_{FB}}^{V_g} \left(1 - C_{lf}(V_g)/C_i \right) dV_g$$  \hspace{1cm} (3-37)$$

Combining equation (3-28) to (3-37), a computer program written in Matlab was used to analyse the $D_{it}$ distribution within the Si forbidden bandgap. It should be noted that because equation (3-36) takes the difference between the quasi static and high frequency CV curves to calculate $D_{it}$, it is not valid for gate biases at accumulation where the capacitance is too small or in or near inversion where minority carriers do not follow the high frequency gate voltage. Such a determination is valid only in a limited interval of the forbidden gap. In practice, the range extends flatband condition to the onset of strong inversion; this means from $E_i\Delta$ to $-E_i+\Delta/2$, where $E_i\Delta = E_{fb}$ (i.e. flatband, this is for p type). In principle, the extraction of $D_{it}$ from the measurements is most
accurate for energies spanning the range from flatband conditions to the onset of strong inversion at the surface (~Ev+0.26eV to Ev+0.86eV). It should be noted that, considering the parameters (including metal area, insulator thickness and insulator permittivity) used in the analysing software, there is a measurement error for $D_{it}$ to about ±10%.

Figure 3.7 shows the $D_{it}$ distribution for a (100), p-type, 1-10Ω.cm, single side polished, oxidised and passivated Si wafer.

![Graph showing $D_{it}$ distribution with bandgap energy (eV) on the x-axis and $D_{it}$ (eV^-1 cm^-2) on the y-axis.]

Figure 3.7. $D_{it}$ distribution in the Si forbidden bandgap for p-type, passivated sample.

### 3.3 Measurement of paramagnetic interface defects by Electron Paramagnetic Resonance

#### 3.3.1 Paramagnetic point defects at the Si-SiO$_2$ interface

Electron paramagnetic resonance is perhaps the only spectroscopic tool which responds exclusively to detect atomic states in Si-SiO$_2$ system. Of all the EPR signals reported in Si-SiO$_2$ system, $P_b$ appears to be most pertinent to the inherent defect structure of the interface, whereas $P_c$ is due to iron contamination, and $P_a$ resembles the signal from donor or conduction electrons [88, 89]. In the last decades, the very important dangling orbital or paramagnetic centres have been the object of extensive
research in all forms of silica, crystalline [90], vitreous [91], and thermal thin film [92, 93]. Most of the paramagnetic defects which have been observed in thermal silica are shown in figure 3.8 [2].

![Figure 3.8](image)

Figure 3.8. Paramagnetic point defects observed in Si-SiO$_2$ structures by electron paramagnetic resonance [2].

Actually, the early results from EPR were rather lightly dismissed by the MIS device community, due to unconvincing interpretations [88, 94]. However, they were later superseded by solid and correct identifications [89]. These included the critical P$_b$ centre, deduced to be an ·Si≡Si$_3$ structure occurring precisely at the Si-SiO$_2$ interface. The P$_b$ centre is by far the most important defect identified at the interface, and its observation and correct assignment have touched off numerous research activities on the interface.

### 3.3.2 EPR operation and calculation of P$_b$-type defect density

EPR measurements of the Si interface defect (P$_b$) centres were undertaken using a Bruker 300E spectrometer operating at X Band (9.44 GHz), fitted with an Oxford ES-9 liquid helium cryostat with temperature control via an Oxford ITC-4 controller. Measurements were done using a modulation frequency of 100kHz, modulation amplitude ($M_A$) of 1.011G and a microwave power of 20µW at a temperature of around
6.5K. The low temperature is realized by immersing the tubes containing the samples into liquid helium. The defect spin at the Si interface saturates when a high microwave power is applied. 20µW was observed to be non-saturating. Samples were placed in 3 mm ID quartz EPR tubes, which were flushed with pure argon to remove oxygen. The sample tubes were sealed with rubber septa and the sample end frozen to 77K. The angle between the sample surface and the magnetic field is less than 3°.

A Cu(NO$_3$)$_2$ solution of known molarity is used for instrument calibration. The spectrum shown in figure 3.9 was obtained at a temperature of around 6.5K, $M_A$ of 10.115G and microwave power of 0.1mW. The conditions used for obtaining the Cu$^{2+}$ spin signal are similar to those used for measuring Pb centres in order to allow a direct and accurate comparison between the two signals.

![Figure 3.9. EPR spectrum from Cu(NO$_3$)$_2$ solution.](image)

The total spin number is calculated from the following equation:

$$S_{\text{spin}} = \frac{DI \times T \times \left( \frac{\text{SW}_G}{\# \text{pts}} \right)^2}{K \times \#S_{\text{can}} \times M_A \times G_N \times \sqrt{\text{MWP}}}$$

(3-38)

where K is a constant determined by calibration with the Cu(NO$_3$)$_2$ solution, DI is the absolute value of the signal obtained by double integrating the spin signal, SW$_G$ is the field sweep width, #pts is the resolution, #S$_{\text{can}}$ is the number of scan, G$_N$ is the receiver gain level, MWP (W) is the microwave power in the unit of watt, and T (K) is the...
temperature in Kelvin. From the solution signal, K is determined to be $9.68 \times 10^{11}$. All spin density calculations in this work are obtained with this K value.

The $P_b$ defects density, $[P_b]$, can be obtained from the following equation:

$$[P_b] = \frac{S_{pin}}{A} \tag{3-39}$$

where $A$ is the sample’s area, in this work the EPR sample’s size is $25\text{mm} \times 2.5\text{mm}$.

EPR measurements of $P_b$-type defects on the (111) rather than the (100) Si-SiO$_2$ interface are preferred two reasons [37]. First, the signal-to-noise ratio is greater in the case of (111) interface because of its greater interface state density. Second, the (111) Si-SiO$_2$ interface has only one type of paramagnetic defect, namely the $P_b$ centre, whereas two distinct paramagnetic defects, namely, $P_{b1}$ and $P_{b0}$ centres, are associated with (100) Si-SiO$_2$ interface. These two defects give rise to only two partially overlapping resonances providing the applied magnetic field is perpendicular to the (100) interface [95]. This complications make it very difficult to measure the intensity of the individual defect spectra associated with the (100) interface. Actually, for standard oxidation temperatures (800-950°C), areal densities of physical defect sites (including both ESR active and inactivated ones) of $[P_b] \sim 5 \times 10^{12}\text{cm}^{-2}$ and $[P_{b0}]$, $[P_{b1}] \sim 1 \times 10^{12}\text{cm}^{-2}$ are naturally incorporated [23]. Thus, the EPR experiments in this thesis are limited to the (111) interface.

### 3.4 Summary

This chapter briefly describes the main measurement techniques and the theory behind them used in this dissertation for Si electronic properties. A combination of lifetime and Capacitance-Voltage is mainly used to analyse the properties of Si-SiO$_2$ interface. The fundamental recombination mechanisms in silicon have been discussed. Photo-conductance based methods are used for determining the effective lifetime and emitter saturation current density, which are parameters widely used in the photovoltaic community for developing, optimizing and maintain process control for surface passivation.

C-V technique, in which the capacitance of the semiconductor surface is studied as a function of the applied normal electric field, is particularly easy to use in a study of MOS stack as it provides a convenient capacitor. C-V technique determines the
effective interface charge density and the density of interface states within the forbidden bandgap of silicon, which represent two critical parameters related to the electrical properties of the Si-SiO$_2$ interface.

Electronic Paramagnetic Resonance measurements allow the determination of the density of a specific interface defect, conclusively identified as three-fold coordinated interfacial silicon, which is EPR active when neutral and is known to be a detrimental electrically active interface defects. The thermochemical characters of this kind defect appear dominated by interaction with hydrogen.
CHAPTER 4

Experimental

Collected in this chapter are descriptions of three main processing equipments used in this thesis and general and standard lifetime and C-V samples processing conditions. The three main equipments are PECVD reactor, Rapid thermal annealing (RTA) reactor and Temperature and injection dependent lifetime spectroscopy (TIDLS) system. Details specific to experiments are described in the relevant chapters.

4.1 Hydrogenation Systems

For the routine injection of atomic hydrogen controlled methods are required. There are two common methods for achieving this objective: exposure to a low power density H₂ plasma; or implantation of very low energy H⁺ ions from a broad beam source. In this thesis, a remote PECVD system was used to produce hydrogen plasma.
4.2 Hydrogenation Plasma Exposure

Usually, the hydrogenation systems used by most researchers are relatively simple and generally consist of a quartz tube through which molecular hydrogen is pumped at a reduced pressure. The plasma is excited by capacitively or inductively coupling low-frequency (~30kHz) or radio-frequency (13.56MHz) power via a high frequency oscillator or a copper coil encircling the quartz tube [96]. It is, of course, possible to use commercially available plasma-assisted deposition reactors in which the electrodes are inside the chamber. Hydrogen is introduced at reduced pressure into the system and ionized by a dc voltage.

Normally, the plasma is a combination of positive and negative ions, molecules, neutral atoms and free radicals, which is neutral overall [97]. The hydrogen gas also shows emission from its vibrational levels, causing to the familiar light purple colour of the discharge. The electron energy in these plasmas is typically 1-10eV with an electron density of $10^9$-$10^{12}$ cm$^{-3}$ [98]. The sample therefore is subjected to ion and electron bombardment and a high level of UV and visible light exposure unless optical baffles are used, and the plasma is contained upstream from the sample. Several experiments have demonstrated the incorporation of atomic hydrogen into Si [99, 100], using a simple two-electrode electrochemical cell, by which atomic hydrogen is introduced to crystalline silicon to passivate deep bulk defects. Under these circumstances, there is no bombardment but defect passivation results similar to plasma hydrogenation are obtained in this method of hydrogen insertion. Pure bombardment-related effects can be examined using He plasmas in place of active hydrogen. Under high-power density conditions, or when using very pure samples (doping density $<10^{14}$ cm$^{-3}$), damage related levels can be observed in the near-surface region after direct exposure to a hydrogen plasma [101].

Whatever method of hydrogen insertion is used, one needs to be aware of the possible pitfalls of that particular technique. For example, high leakage current in hydrogenated diode structures for C-V measurements is an indication of the presence of plasma-induced surface damage or a contaminating layer deposited during the exposure.

In our hydrogen plasma exposure experiments, the samples were exposed to atomic H in a remote plasma system by using a commercially available plasma-assisted deposition reactor, Roth&Rau AK400 PECVD system. Figure 4.1 shows schematic of PECVD reactor, dashed line means the RF power generator can not be seen from this section view. In this plasma system, in addition to the two quartz glass tubes the plasma
source includes a shield on the quartz glass side facing away from the substrate and a multi-pole magnetic field (permanent magnets) which purpose is to improve plasma stability. The plasma source is powered by two magnetron heads (2.46GHz, 2000W) with circulator and 3-rod tuner. The microwave generators are supplied with power from two units of 2000W, 3.5kV in the rack cabinet.

The substrate holder is made of high-grade special steel, ceramics and graphite. It may be heated up to 800°C. The substrate carrier plate is heated using two graphite heating elements shaped in wave patterns. This rear side radiation heater is necessary because the substrate carrier plate lies on RF potential. Temperature is measured using a type K thermocouple at a reference measuring location just below the substrate carrier plate. An RF generator, 13.56MHz, arranged in the rack cabinet of the system provides the substrate holder with RF power source. All testing samples are put on a four inch substrate wafer, which was coated on both sides with 100nm SiO₂ and 100nm LPCVD Si₃N₄, to act as an impurity diffusion barrier.

The hydrogen plasma is generated by microwave (MW) or radio frequency (RF) respectively. The MW power used in this thesis is within the limits of 200 to 1200W, and the RF power is in the range of 50 to 300W.

The main disadvantage in our PECVD system is that we can not monitor the accurate atomic hydrogen concentration and it is difficult to compare the hydrogen flux during the hydrogen plasma exposure experiments.

Figure 4.1. Schematic illustration of the remote PECVD reactor using microwave or radio frequency excitation.
4.3 Rapid thermal annealing

Rapid thermal anneals (RTA) are frequently used in photovoltaic research and manufacturing [102-105]. They provide a means to fire metal contacts, to densify dielectric films, to remove hydrogen from interfaces, and to drive hydrogen from silicon nitride films into underlying silicon.

In our experiments, RTA is mainly utilised to accomplish the dehydrogenation of Si-SiO$_2$ stacks as well as the post-hydrogen plasma exposure thermal annealing. Dehydrogenation can be achieved by RTA under conditions of 700°C, 3 minutes in N$_2$ ambient. In this case, the dissociation reaction of pre-existing P$_b$H centres will dominate the Si-SiO$_2$ interface and meanwhile little additional P$_b$ defects will be generated. The post-hydrogen plasma exposure thermal annealing can be achieved by RTA under conditions of below 400°C, 3 minutes in N$_2$ ambient. Because the Si-SiO$_2$ interface can be affected by even small amounts of moisture in the atmosphere, making results difficult to interpret, therefore a dry (moisture and H free) atmosphere was needed to ensure a purely thermal treatment. The RTA had been previously tested and found to provide this [106] (when N$_2$ is used) while other furnaces do not. However, when applying RTA treatment, there are some disadvantages, such as the illumination effect during RTA; the difference between the actual temperature and target temperature due to the contact problem between the thermocouple and the test sample; and the possibility of sample contamination. These limitations sometimes lead to inconsistent results following RTA treatments.

In this thesis, the RTA annealing treatments were carried out in a Unitemp 1100 oven. High-intensity lamps shown in figure 4.2 are used to rapidly heat the wafer to the desired annealing temperature in a very short time. Extremely rapid temperature ramp-up and ramp-down rates are achieved. Samples, which received atomic hydrogen plasma exposure, were loaded into the RCA cleaned chamber. A thermocouple was attached to the back of one testing samples to monitor its temperature during the run, which was assumed equal to the testing samples temperature. A typical RTA at 400°C was carried out as follows. After loading samples, the chamber was purged in N$_2$ for 1 minute before the temperature was ramped for ~40 seconds to 400°C with a gradually decreased rate. The samples were maintained for 3 minutes in N$_2$ and then cooled rapidly by turning off the IR lamps and flushing the chamber with a high flow of N$_2$. It should be noted that illumination under the conditions used in this thesis does not
produce any defects. Figure 4.3 plots the temperature profile of standard RTA annealing program.

Figure 4.2. Schematic illustration of the rapid thermal annealing (RTA) apparatus.

Figure 4.3. Temperature profile of 400°C RTA annealing.
4.4 Temperature and injection dependent lifetime spectroscopy system

As described in the third chapter, the inductive-coil photo-conductance decay (PCD) lifetime measurement has the advantages of being contactless and capable of measuring lifetimes over a wide range of injection levels in a few seconds. Meanwhile, Temperature and injection dependent lifetime spectroscopy (TIDLS) is a defect characterisation technique based on such lifetime measurement and is considered to provide relatively unambiguous characterisation of defect parameters in comparison to injection-dependent lifetime spectroscopy alone [107]. The TIDLS apparatus consisted of the WCT-100 from Sinton Consulting Inc., which was combined with a modified heating and cooling stage (HCS302) supplied by INSTEC, as shown in Figure 4.4 [108]. The inner (sample) chamber of the HCS302 is either heated with resistive elements using switching PID control or cooled by circulating liquid nitrogen inside the same system. The external components of the HCS302 are kept close to the room temperature by circulating water through ducts within the outer chamber.

The samples were put in the chamber in air or N\textsubscript{2} at temperatures in the range of 120-240°C for different times. Lifetime values were measured automatically at a set time interval for at least 20 hours. Two measurements per point were done to obtain an average. For C-V samples, following each anneal in N\textsubscript{2}, the samples were cooled down

![Figure 4.4. Experimental setup of PCD-based TIDLS system][108].
to room temperature and C-V measurements were carried out on the same dot. The sample were then returned to the anneal chamber for additional processing, and then retested.

### 4.5 General sample processing

Most samples used for lifetime measurements were FZ, p-type, 100-1000Ω.cm, (100), 550µm thick silicon wafers. Samples for C-V measurements were CZ, p-type, 1-10Ω.cm, (100), single side polished silicon wafers. Treatments applied to these samples are listed in table 4.1 and table 4.2.

| Table 4.1 Experimental processes for lifetime sample preparation |
|---|---|---|---|
| Step | Description | Chemical | Details |
| 1 | Saw damage etch | Tetramethyl ammonium hydroxide (TMAH) solution | Remove saw damage from Si surface and edges by etching in TMAH solution at 85°C for 20 minutes |
| 2 | Saw damage etch | HF:HNO₃ solution | Remove saw damage from Si surface and edges by etching in HF:HNO₃ solution for 2 minutes |
| 3 | Cleaving | | (100) wafers were cleaved into quarters and labelled |
| 4 | RCA clean 1 | 5:1:1 H₂O:NH₄OH:H₂O₂ solution | For 10 minutes in warm solution (~80°C) |
| 5 | RCA clean 2 | 5:1:1 H₂O: HCl: H₂O₂ solution | For 10 minutes in warm solution (~80°C) |
| 6 | HF dip | Clean 10% HF solution | Until hydrophobic to remove native oxide |
| 7 | Light phosphorous diffusion | POCl₃ and O₂ | In TCA cleaned furnace at 764°C for 20 minutes followed by an in situ drive in process in N₂ for 10 minutes on selected samples. |
| 8 | HF dip | Clean 10% HF solution | Until hydrophobic to remove phosphorous glass |
| 9 | Oxidation | O₂ | In TCA cleaned furnace at 1000°C to |
Chapter 4: Experimental

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
<th>Chemical Details</th>
<th>Details</th>
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<tbody>
<tr>
<td>1</td>
<td>Saw damage etch</td>
<td>HF:HNO₃ solution</td>
<td>Remove saw damage from Si surface and edges by etching in HF:HNO₃ solution for 2 minutes.</td>
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<tr>
<td>2</td>
<td>Cleaving</td>
<td></td>
<td>(100) wafers were cleaved into quarters and labelled.</td>
</tr>
<tr>
<td>3</td>
<td>RCA clean 1</td>
<td>5:1:1 H₂O:NH₄OH:H₂O₂ solution</td>
<td>For 10 minutes in warm solution (~80°C).</td>
</tr>
<tr>
<td>4</td>
<td>RCA clean 2</td>
<td>5:1:1 H₂O: HCl: H₂O₂ solution</td>
<td>For 10 minutes in warm solution (~80°C).</td>
</tr>
<tr>
<td>5</td>
<td>HF dip</td>
<td>Clean 10% HF solution</td>
<td>Until hydrophobic to remove native oxide.</td>
</tr>
<tr>
<td>6</td>
<td>Oxidation</td>
<td>O₂</td>
<td>In TCA cleaned tube at 1000°C to grow ~50nm oxide layers, followed by an in situ anneal in N₂ for 30 minutes on selected samples.</td>
</tr>
<tr>
<td>7</td>
<td>Forming gas anneal (FGA)</td>
<td>Forming gas (5% H₂ in 95% Ar)</td>
<td>All samples receive FGA at 400°C for 30 minutes to hydrogenate the Si-SiO₂ interface.</td>
</tr>
<tr>
<td>8</td>
<td>HF fume</td>
<td>HF bottle concentration solution</td>
<td>One side of oxide was removed by HF fume.</td>
</tr>
<tr>
<td>9</td>
<td>Al deposition</td>
<td>Al</td>
<td>At high vacuum (&lt;3×10⁻⁶ torr),</td>
</tr>
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</table>

Table 4.2 Experimental processes for CV sample preparation
~80nm thick Al was deposited on oxide layer through a shadow mask with area of $4.7 \times 10^{-3}$ cm$^2$

<table>
<thead>
<tr>
<th>10</th>
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<th>Ga-In</th>
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<tr>
<td></td>
<td>Ohmic contact by Ga-In paste on oxide free Si side</td>
<td></td>
</tr>
</tbody>
</table>

### 4.6 Summary

Three major experimental equipments used in this thesis as well as the general and standard lifetime and C-V sample processing conditions are described in this chapter.

The hydrogen plasma exposure experiments were carried out by using a commercially available plasma-assisted PECVD deposition reactor. The plasma source is powered by either microwave or radio frequency. The main disadvantage in our PECVD system is that it is difficult to monitor the accurate atomic hydrogen concentration.

Rapid thermal annealing has replaced the tube furnace in many applications to perform solar cell processing steps for dehydrogenation or defect annealing. Although a precise control of thermal profile can be achieved during RTA processing, the impact of illumination and/or contact problem between the thermocouple and testing sample should be considered sometimes.

Temperature and injection dependent lifetime spectroscopy (TIDLS) is a relatively simple defect characterisation technique to provide relatively unambiguous characterisation of defect parameters in comparison to injection-dependent lifetime spectroscopy alone, which can be applied to a large temperature range. Because this technique is based on the inductive coil photo-conductance lifetime measurement, the disadvantage of being affected by such as depletion-region modulation for diffused samples is always unavoidable.
In this chapter the passivation achieved with relatively low temperature, thin thermal oxides which are grown in the temperature range 750-900°C in wet oxidation (with steam) conditions, and with oxide/LPCVD nitride stacks is investigated. Dry and wet oxidations at different temperatures are compared and the surface recombination velocities of (100), (111) and textured Si surfaces are studied. The thermal stability of thin oxide and oxide/LPCVD nitride stacks are also studied. The influence of phosphorous diffusion on Si surface passivation is discussed.
Chapter 5: Passivation effect of wet oxidation, and with oxide/LPCVD nitride stacks on the Si-SiO$_2$ interface

5.1 Introduction

High oxidation temperatures (1100-1200$^\circ$C) achieve the lowest density of interface states within the forbidden gap of silicon at the Si-SiO$_2$ interface. This translates to lower recombination losses at the silicon surfaces. Very thin SiO$_2$ (-100Å) layers are routinely used in high-efficiency silicon solar cells, MOSFET, and advanced bipolar devices to reduce surface recombination or to provide high-quality insulating layers. Generally, the thin oxide is formed by high temperature (850-1050$^\circ$C) oxidation because low-temperature processing generally produces low-quality oxides with high recombination velocity at the Si-SiO$_2$ interface [109].

However, high process temperatures are generally undesirable for solar cell fabrication for a number of reasons, including a higher risk of contamination of the wafer bulk, and the fact that the effective lifetime of multi-crystalline silicon in particular often degrades following high temperature treatments [110]. In addition, higher temperature processing requires more energy to run, and thus resulting in higher manufacturing cost. Therefore, high temperature dry oxidation is not readily applicable as an industrial process and surface passivation processes at lower temperatures have become very important in silicon solar cell fabrication, particularly for thin silicon wafers. Among a large number of developed passivation layers for crystalline silicon surfaces, low temperature oxides are desirable for greater flexibility in the process sequence and preservation of minority carrier lifetime in high performance silicon devices [111]. Ideally the oxide should be grown rapidly, at low temperatures and low cost. It should also be thin enough not to increase substantially the reflectance of the surface. There are several other possible methods for oxide preparation in addition to thermally grown SiO$_2$, such as low temperature PECVD oxides which generally have $D_{it}$ values that are slightly higher but nearly comparable to thermally grown oxides at high temperatures [110], and intrinsic hydrogenated amorphous silicon oxide (a-SiO$_X$:H) prepared by very high frequency plasma-enhanced chemical vapour deposition(VHF-PECVD) at a very low substrate temperature (170$^\circ$C) with maximum effective lifetime of 400$\mu$s measured for 1-10$\Omega$.cm, 380$\mu$m, p-type silicon wafer [110].

Wet oxidations using water vapour can give about the same $D_{it}$ values as oxidations performed with dry oxygen, but result in higher positive oxide charges [80]. This offers interesting possibilities with regard to the field-effect passivation method.
The work in this chapter is aimed at thin oxide and thin oxide/LPCVD nitride stacks, with the thin oxide having the purpose of providing good surface passivation. Given that low process temperatures are generally desirable, it is of interest to determine how oxide passivation quality varies with oxidation temperature. Wet oxidations at temperatures in the range 750-900°C were carried out, and the $J_{0e}$ values obtained from these oxides compared with the $J_{0e}$ value from a high temperature, dry oxide. In general, there is a clear trend of increasing surface recombination with decreasing oxidation temperature, with a particularly significant increase between 800 and 850°C. However, very good surface passivation was achieved when a low temperature (750°C) oxidation was followed by a phosphorous diffusion into the oxide.

5.2 Effect of low temperature oxides on the passivation of Si-SiO$_2$ interface

In this section, work is focused on the properties of low temperature thermally grown oxides, and in particular on the effect of oxidation temperature.

5.2.1 Experimental details

A detailed description of lifetime and C-V measurements is given in previous chapters. Lifetime samples received a standard phosphorous diffusion and oxidation. The oxide was then stripped by 10% HF solution and another oxide with different processing conditions was grown. This was done to ensure nearly identical phosphorous diffusion profiles for samples with different oxides, since the oxidation temperature for the second oxidation was lower than that of the first oxidation. The oxidation conditions were chosen to give approximately the same oxide thickness in each case of ~30nm. The actual oxide thicknesses were measured using a Filmetrics F20-UV film measurement system. Table 5.1 summarizes the second oxidation conditions and the oxide thicknesses.

Following the second oxidation, the samples received a number of additional treatments for different experiments.
Table 5.1. Second oxidation conditions and oxide thickness for different oxidation processes

<table>
<thead>
<tr>
<th>second oxidation conditions</th>
<th>Process #1</th>
<th>Process #2</th>
<th>Process #3</th>
<th>Process #4</th>
<th>Process #5</th>
</tr>
</thead>
<tbody>
<tr>
<td>dry/wet</td>
<td>dry</td>
<td>wet</td>
<td>wet</td>
<td>wet</td>
<td>wet</td>
</tr>
<tr>
<td>temperature (°C)</td>
<td>1000</td>
<td>750</td>
<td>800</td>
<td>850</td>
<td>900</td>
</tr>
<tr>
<td>time (minute)</td>
<td>21</td>
<td>120</td>
<td>35</td>
<td>15</td>
<td>5.5</td>
</tr>
<tr>
<td>oxide thickness (nm)</td>
<td>38</td>
<td>31</td>
<td>31</td>
<td>38</td>
<td>30</td>
</tr>
</tbody>
</table>

5.2.2 Effect of oxidation temperature on the passivation of Si-SiO₂ interface

It is well known that oxidation temperature is very important in determining interface properties as \(D_{it}\) and \(Q_f\) reduce with increasing oxidation temperature [85, 112].

After the second oxidation, all samples received an in situ anneal in \(N_2\) for 30 minutes. This was followed by a forming gas anneal at 400°C for 30 minutes. Two samples were prepared with each processing condition and every value is the average of measurements on two samples. Figure 5.1 summarises the \(J_{0e}\) results. Figure 5.2 shows HFCV and QSCV curves of samples with thin oxides grown at different temperatures. Figure 5.3 shows the corresponding \(D_{it}\) distribution.

![Figure 5.1. \(J_{0e}\) values for samples with different oxides.](chart.png)
Figure 5.2. CV curves of samples with thin oxides grown at different temperatures: (a) 750°C: wet oxidation 2 hours+15 minutes dry oxidation+30 minutes N₂; (b) 800°C: wet oxidation 28 minutes+15 minutes dry oxidation+30 minutes N₂; (c) 850°C: wet oxidation 15 minutes+15 minutes dry oxidation+30 minutes N₂; (d) 1000°C: dry oxidation 21 minutes +30 minutes N₂.
The results in fig 5.1-5.3 show a gradual change in $J_{0e}$ and $D_{it}$, although the rate of change is particularly high in the range 800-850$^\circ$C, suggesting that there exists to be a critical temperature between 800 and 850$^\circ$C where the passivation quality changes substantially. Furthermore, there are different changes in $J_{0e}$ and $D_{it}$ between dry and wet oxides. For example, the $D_{it}$ for dry oxide is nearly one order of magnitude lower than for 850$^\circ$C wet across almost the entire bandgap, yet $J_{0e}$ differs by less than a factor of two. Yet comparing different wet oxides, the $D_{it}$ trend is more consistent with the $J_{0e}$ trend. This may suggest that the nature of the interface defects (especially capture cross sections) is different for wet oxides than for dry.

5.2.3 The influence of exact processing conditions on the passivation quality of 750$^\circ$C oxide

The above results show that for the wet oxides used in this work, the passivation quality changes substantially between 800 and 850$^\circ$C. However, it is not clear whether subsequent thermal treatments can improve the passivation quality of lower temperature oxides. In this section, a low temperature oxidation (750$^\circ$C) is investigated in more detail.
The wet low temperature oxidation was followed by various other thermal treatments to determine the effect of such treatments. Two general classes of treatment were investigated: further treatments at 750°C, and further, short treatments at 1000°C. Two samples were prepared for each treatment and every value is the average of measurements on two samples. All samples received a 400°C forming gas anneal as the final treatment. The oxidation and thermal anneal conditions are summarized in table 5.2. The effective lifetime and $J_{0e}$ results are displayed in figure 5.4. All treatments were carried out in-situ except the process#6 sample.

Table 5.2. Oxidation and proceeding thermal anneal conditions for different oxidation.

<table>
<thead>
<tr>
<th>oxidation conditions</th>
<th>Process #1</th>
<th>Process #2</th>
<th>Process #3</th>
<th>Process #4</th>
<th>Process #5</th>
<th>Process #6</th>
</tr>
</thead>
<tbody>
<tr>
<td>temperature (°C)</td>
<td>750</td>
<td>750</td>
<td>750</td>
<td>750</td>
<td>750</td>
<td>750</td>
</tr>
<tr>
<td>wet+dry</td>
<td>wet only</td>
<td>wet only</td>
<td>wet+dry</td>
<td>wet+dry</td>
<td>wet only</td>
<td>wet only</td>
</tr>
<tr>
<td>time (minute)</td>
<td>120</td>
<td>120</td>
<td>120+15</td>
<td>120+15</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>thermal anneal</td>
<td>no</td>
<td>in situ</td>
<td>no</td>
<td>in situ</td>
<td>in situ 5 min</td>
<td>1000°C</td>
</tr>
<tr>
<td>conditions</td>
<td>30 min N₂</td>
<td>30 min N₂</td>
<td>30 min N₂</td>
<td>N₂ ramping</td>
<td>up to 1000°C</td>
<td>few seconds</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>in N₂</td>
<td>seconds</td>
</tr>
</tbody>
</table>

Figure 5.4. (a) Effective lifetime values and (b) $J_{0e}$ values for samples with various processing.
It can be seen from figure 5.4 that following a 750°C wet oxidation with a N₂ anneal at the same temperature results in some improvement of the interface – this is consistent with findings on high temperature oxides. However, the passivation quality is substantially worse than what can be achieved with a high temperature oxide. Short thermal treatments at a high temperature are not sufficient to improve the interface. It appears that treatments at higher temperatures need to be in the order of at least a few minutes (such as during the ramp up to 1000°C) to give a benefit.

5.3 Effect of a phosphorous diffusion on the passivation quality of the oxide

Work in this section is focused on further exploring the properties of thin oxides grown at low temperature, especially at 750°C, and in particular, on better understanding the effect of a phosphorous diffusion into the oxide.

5.3.1 Experimental details

A detailed description of effective lifetime and C-V measurements is given previously. Samples used for the lifetime experiments received a standard light phosphorous diffusion and oxidation. The oxide was then stripped by HF solution and another wet oxide or dry oxide was grown at different temperatures. Following the second oxidation, samples received a number of additional treatments for different experiments.

5.3.2 Effect of a phosphorous diffusion into the thin oxide on surface recombination

5.3.2.1 Effect on planar sample

After the first oxide layers were stripped using HF solution, second oxidations were prepared as follows to get similar oxide thickness of about 30 nm:
w2: 2 hours wet oxidation + 15 minutes dry oxidation + 30 minutes N₂ all at 750°C
w4: 35 minutes wet oxidation + 15 minutes dry oxidation + 30 minutes N₂ all at 850°C
w6: 21 minutes dry oxidation + 30 minutes N\textsubscript{2} all at 1000°C

Following second oxidation, wafers received an FGA and the J\textsubscript{0e} values were measured. Wafers were then subjected to another deep phosphorous diffusion (at 800°C for 1 hour) and given another FGA, and J\textsubscript{0e} values were re-measured. Results are summarised in table 5.3 below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>After First FGA</th>
<th>After Deep P Diffusion + FGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>w2 (750°C)</td>
<td>67</td>
<td>15</td>
</tr>
<tr>
<td>w4 (850°C)</td>
<td>22</td>
<td>14</td>
</tr>
<tr>
<td>w6 (1000°C)</td>
<td>16</td>
<td>18</td>
</tr>
</tbody>
</table>

It can be seen from table 5.3 that the phosphorous diffusion into the oxide reduced surface recombination to a very low level, for low temperature oxides. The reduction is unlikely to be simply due to the thermal treatment and seems to be linked to the diffusion itself. It may be that the improvement is linked to changed oxide properties (e.g. lower reflow temperature) due to the introduction of phosphorous.

In order to develop a better understanding of the effect of phosphorous diffusion on surface recombination, several experiments were carried out with different oxide thicknesses. The oxidation conditions and oxide thicknesses were:

1. 750°C: 1 hr wet oxidation + 15 min dry oxidation + 30 min N\textsubscript{2}, thickness ~10nm
2. 750°C: 3.5 hr wet oxidation + 15 min dry oxidation + 30 min N\textsubscript{2}, thickness ~52nm
3. 800°C: 28 min wet oxidation + 15 min dry oxidation + 30 min N\textsubscript{2}, thickness ~21nm

Following oxidation, an identical phosphorous diffusion was carried out into the oxide of the wafers, and the wafers then received an FGA treatment. In addition, sheet resistance (R\textsubscript{s}) measurements were carried out before and after the phosphorous diffusion into the oxide by using a linear four-point probe. The J\textsubscript{0e} and R\textsubscript{s} results are summarized in table 5.4 below.
Table 5.4. $J_{0e}$ (fA/cm$^2$), Sheet resistance $R_s$ (Ω/□) values before and after a phosphorous diffusion into the oxide.

<table>
<thead>
<tr>
<th>Sample thickness</th>
<th>$J_{0e}$ before P diffusion</th>
<th>$J_{0e}$ after P diffusion</th>
<th>$R_s$ before P diffusion</th>
<th>$R_s$ after P diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. ~10nm</td>
<td>61</td>
<td>510</td>
<td>400</td>
<td>200</td>
</tr>
<tr>
<td>2. ~52nm</td>
<td>59</td>
<td>42</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>3. ~21nm</td>
<td>59</td>
<td>120</td>
<td>1100</td>
<td>400</td>
</tr>
</tbody>
</table>

These results suggest that, once the phosphorous diffusion reaches the Si-SiO$_2$ interface, indicated by a decrease of $R_s$ after deep phosphorous diffusion, a dramatic deterioration in interface passivation occurs resulting in an increase in recombination.

To complement the lifetime results, C-V measurements were carried out. Figure 5.5 shows an example of a HFCV curve following deep phosphorous diffusion into the oxide, for the case where the phosphorous diffusion has gone through the oxide. Figure 5.6 compares the high frequency C-V curves for samples with a thin oxide (grown at 750°C wet oxidation for 2 hour followed by in situ 15 minutes dry oxidation and 30 minutes N$_2$ anneal) with and without a phosphorous diffusion into the oxide (all samples received an FGA prior to measurement). In this case, the oxide was chosen to be thick enough that the phosphorous did not diffuse to the Si-SiO$_2$ interface.

Figure 5.5. HFCV curve of thin oxide sample (800°C: wet oxidation 28 minutes+15 minutes dry oxidation+30 minutes N$_2$) followed by phosphorous diffusion and FGA.
Figure 5.6. Comparison of HFCV curves of samples before and after deep phosphorous diffusion into the oxide.

It is worth to note that, following phosphorous diffusion into the oxide, it was not possible to obtain QSCV curves because the oxide was too leaky. Comparison with the no deep phosphorous diffused curve [fig 5.2(b)], the fig 5.5 shows significant degradation of the interface, evidenced by the ‘stretch-out’ of the curve (ie the transition from high to low capacitance is not as rapid).

It can be seen from figure 5.6 that the two curves are almost identical except for a voltage shift of ~0.5V. This confirms that the phosphorous did not diffuse to the interface. There is no indication that the phosphorous diffusion resulted in a reduction in interface defect density, although a comparison of the HFCV curves above gives somewhat limited sensitivity.

The major effect of the phosphorous diffusion therefore appears to be the incorporation of more positive charge in the oxide. The increase in the effective charge density (ie assuming that all of the charge is located near the Si-SiO₂ interface) is estimated to be ~4x10¹¹ cm⁻².

From the above results we can make a conclusion that a phosphorous diffusion into a thin oxide results in significant degradation to the Si-SiO₂ interface, and an increase in recombination, if the phosphorous reaches the interface. If the phosphorous does not diffuse all the way to the interface, then the phosphorous diffusion can result in a significant reduction in interface recombination. This reduction seems to be linked to a
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A slight increase in the positive charge density in the oxide. The phosphorous diffusion does not appear to lead to a change in the interface defect density.

### 5.3.2.2 Effect on textured sample

Work in this section is focused on the investigation of the effect of deep phosphorous diffusion on textured samples. Random pyramid textured samples were used to investigate the passivation of surfaces with a thin oxide and light phosphorous diffusion.

Figures 5.7 (a) effective lifetime and (b) $J_{0e}$ summarise the results of the comparison between planar and textured samples. Samples first received standard light phosphorous diffusion and oxidation. The oxide was then stripped and another oxide was grown at 750°C (2 hours wet oxidation +15 minutes dry oxidation +30 minutes N$_2$ all at 750°C; thickness ~30nm). Following the second oxidation, wafers received an FGA and $\tau_{\text{eff}}$ and $J_{0e}$ were measured. Wafers were then subjected to another deep phosphorous diffusion (at 800°C for 1 hour) and given another FGA treatment, and $\tau_{\text{eff}}$ and $J_{0e}$ was re-measured. Two samples were prepared with each process and every value is the average of measurements on two samples.
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Oxidation and FGA Deep P diffusion

Figure 5.7. (a) Effective lifetime \(\tau\) and (b) \(J_{0e}\) of planar and textured samples following various processing steps.

The above results show that textured samples show the same trend as planar samples: a deep phosphorous diffusion into the oxide, which is not sufficient to reach the Si-SiO\(_2\) interface, results in a moderate improvement to the interface (reduced \(J_{0e}\), increased \(\tau_{\text{eff}}\)). However, interface recombination for the textured samples is much higher (by \(\sim\)factor of 10) than for the planar ones.

5.4 Comparison of passivation effect of low temperature wet oxidation on (100) and (111) Si-SiO\(_2\) interface

Work reported in the previous section shows that textured surfaces display much greater interface recombination than identically processed planar equivalents. An important question is whether this degradation is related to the particular crystal orientation (ie near (111) orientation for random texture) or to the presence of corners and edges on textured surfaces, which may result in high localized stresses and defects. In this section, we compared (100) and (111) oriented, planar samples oxidized at 750 or 850°C. The results show that the (111) crystal orientation is to a large extent
responsible for the much worse passivation of random textured surfaces. It is therefore possible that textures which largely avoid exposing (111) planes may be able to achieve much better passivation.

### 5.4.1 Experimental details

Samples used for lifetime experiments received a standard light phosphorous diffusion and oxidation first. The oxide was then stripped and another oxide was grown. The second oxide was prepared at 750°C (80 minutes wet oxidation +30 minutes N₂ all at 750°C; thickness ~20nm) or 850°C (10 minutes wet oxidation + 30 minutes N₂ all at 850°C; thickness ~30nm). The (100) samples were FZ, p-type, ~100Ω. cm and (111) samples were FZ, n-type, (~60Ω.cm)

Following oxidation, wafers received an FGA, and \( \tau_{\text{eff}} \) and \( J_0e \) were measured. The results are shown in figure 5.8.

### 5.4.2 Effect of surface orientation and oxidation temperature

The results in figure 5.8 are in broad agreement with those previously obtained for similarly processed samples (see for example results in figure 5.1 for planar samples with a 750°C oxide). \( J_0e \) values for (100) samples with 850°C oxide are somewhat higher than previously measured.

![Diagram showing the effective lifetime (\( \tau_{\text{eff}} \)) and recombination current density (\( J_0e \)) for different processing steps and temperatures.](attachment:image.png)
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5.4.3 Thermal stability of low temperature wet oxidation (100) and (111) Si-SiO\(_2\) stack

Work on the samples from last section is extended. The re-measurement of lifetime and \(J_{0e}\) of samples following 1 month of storage seems to indicate that the interface passivation is not stable for samples with oxide. On the other hand, the passivation is stable following short term, 5 minutes anneals at 500-800\(^\circ\)C.

5.4.3.1 Experimental details
Samples previously prepared and measured, as described in the last section, were used for experiments. No further treatment had been carried out on these samples. Other samples received RTA in a N\textsubscript{2} atmosphere for 3 minutes at temperatures between 500 and 800°C, in order to determine the thermal stability of the passivation.

It should be noted that the RTA treatments are quite different in their effect from the N\textsubscript{2} anneals following oxidation. This is because the RTA treatments are carried out in sealed systems in which no moisture can enter. In contrast, the oxidations and subsequent anneals are done in a tube furnace which is not completely sealed. There is thus the possibility that moisture from the air will enter the furnace and influence the results. Reliable results are therefore best obtained by first passivating samples with an FGA and then, if required, carrying out depassivating treatments in an RTA system.

5.4.3.2 Stability of lifetime and $J_{0e}$ of samples following FGA

Figure 5.9 shows the lifetime and $J_{0e}$ values of the control samples. It can be seen that the surface passivation of some of the samples does not appear stable. This is particularly the case for the (100) samples with a 750°C oxide.
Figure 5.9. (a) Effective lifetime and (b) $J_{0e}$ results for samples after various processing steps. 1) Wet oxidation and N$_2$ anneal; 2) subsequent FGA; 3) repeat of measurement 3 days later; 4) repeat of measurement 40 days storage in N$_2$.

5.4.3.3 Stability of lifetime and $J_{0e}$ of samples following RTA

Figure 5.10 shows the change in effective lifetime and $J_{0e}$ with subsequent RTA treatments.
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5.5 Passivation effect of oxide/nitride stacks on Si-SiO$_2$ interface

5.5.1 Effect of LPCVD nitride deposition temperature on surface passivation of Si-SiO$_2$ stack

Previous work [113] has shown that a thin SiO$_2$ layer should be grown before LPCVD Si$_3$N$_4$ deposition to prevent irreversible bulk damage caused by stress from the nitride layer. Such LPCVD Si$_3$N$_4$/SiO$_2$/Si stacks can act as effective antireflection...
coatings and simultaneously allow good surface passivation to be achieved. Of particular interest for potential photovoltaic applications is the recombination rate of minority carriers at the interface. In our work, we have found that the deposition temperature has a tremendous impact on surface passivation, with high temperatures leading to much higher values of the emitter saturation current $J_{0e}$.

Samples used for the experiments received a standard light phosphorous diffusion, followed by an oxidation at $1000\degree C$ for 1 hour, 30 minutes in situ $N_2$ anneal and FGA successively with oxide thickness about 50nm. ~50nm of LPCVD $Si_3N_4$ was then deposited at 775 or 825$\degree C$. The LPCVD nitride layer (but not the oxide) was then stripped in hot phosphoric acid at 170$\degree C$, and the samples were given another FGA treatment. Table 5.5 summarizes the results following different processing steps.

Table 5.5. Effective lifetime($\mu s$) and $J_{0e}$(fA/cm$^2$) values following various process steps. 1. oxidized and FGA, 2. LPCVD deposition, 3. strip nitride, 4. FGA again.

<table>
<thead>
<tr>
<th>Step</th>
<th>$\tau$ (µs)</th>
<th>$J_{0e}$ (fA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>825$\degree$C LPCVD $Si_3N_4$</td>
<td>5100</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>1700</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>4000</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>775$\degree$C LPCVD $Si_3N_4$</td>
<td>4800</td>
</tr>
<tr>
<td></td>
<td>4100</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>460</td>
<td>400</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>20</td>
</tr>
</tbody>
</table>

The results of the effective lifetimes at the beginning and end of the process (steps 1 and 4) show that there has been some degradation to the Si bulk. The degradation is clearly in the bulk, and not at the surfaces (as can be seen from the $J_{0e}$ values). There are two possible degradation mechanisms – 1) contamination and 2) introduction of defects due to the presence of the nitride film. Previous experiments have shown that the presence of a nitride layer does cause irreversible bulk damage, and that at least some of this damage is almost certainly due to defect generation resulting from the presence of a nitride layer [114]. The extent of the bulk degradation was observed to depend on...
interfacial oxide thickness, with even a relatively thin (~25nm) oxide reducing the bulk degradation to very low levels.

The degradation observed here is more likely to be due to contamination, since the oxide was relatively thick and the degradation is quite severe. Nevertheless, effective lifetimes at the end of the process are still high enough that the results relating to surface passivation can be interpreted without difficulty.

The J<sub>0e</sub> results in table 5.5 indicate that J<sub>0e</sub> depends sensitively on deposition temperature (compare J<sub>0e</sub> values in tables at step 2). Nitride deposition has two effects on the Si-SiO<sub>2</sub> interface: 1) it leads to the generation of some additional defects; and 2) it causes the de-passivation of previously passivated defects. The fact that the final J<sub>0e</sub> values (step 4, following re-hydrogenation of interface defects) are comparable to the initial values (step 1) for both deposition temperatures suggests that effect (1) is dominant. Note that the error in J<sub>0e</sub> measurements is typically +/- 10%. A higher furnace temperature will lead to a greater loss of hydrogen from the interface prior (and probably also during) nitride layer deposition. Hence, the nitride deposition temperature is a critical parameter.

5.5.2 Effect of LPCVD nitride deposition on surface passivation of Si-SiO<sub>2</sub> stack

In this section, the effect of LPCVD nitride deposition on surface recombination was examined for various oxides. Lifetime/J<sub>0e</sub> values were measured at various stages during the process sequence. Oxidation conditions for the different samples were as follows to achieve nearly identical oxide thickness about 30 nm:

w1: 2 hours wet oxidation + 15 minutes dry oxidation +30 minutes N<sub>2</sub> all at 750°C
w3: 35 minutes wet oxidation + 15 minutes dry oxidation +30 minutes N<sub>2</sub> all at 850°C
w5: 21 minutes dry oxidation +30 minutes N<sub>2</sub> all at 1000°C

Table 5.6 summarises J<sub>0e</sub> results following various processing steps. J<sub>0e</sub> was measured after forming gas anneal; after LPCVD nitride deposition at 775°C; and after a subsequent N<sub>2</sub> anneal at 900°C for 30 minutes (to simulate possible subsequent high temperature steps).
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<table>
<thead>
<tr>
<th>Sample</th>
<th>after FGA</th>
<th>after LPCVD</th>
<th>after N$_2$ 900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>w1 (750°C)</td>
<td>73</td>
<td>110</td>
<td>330</td>
</tr>
<tr>
<td>w3 (850°C)</td>
<td>19</td>
<td>54</td>
<td>690</td>
</tr>
<tr>
<td>w5 (1000°C)</td>
<td>13</td>
<td>29</td>
<td>590</td>
</tr>
</tbody>
</table>

A higher $J_{0e}$ after oxidation translates into a higher $J_{0e}$ following LPCVD nitride deposition, underlining the need to achieve the best possible passivation prior to nitride deposition.

### 5.5.3 Effect of subsequent LPCVD nitride deposition treatments on surface passivation of (100) and (111) samples

Figure 5.11 shows the change in $J_{0e}$ and effective lifetime with subsequent LPCVD nitride deposition. The nitride deposition process causes much less degradation of surface passivation than the thermal treatments (RTA), despite the fact that it is carried out at a high temperature. This is attributed to the liberation of hydrogen during nitride deposition, which helps to re-passivate interface defects.

The results also show that it is very difficult to achieve good surface passivation on (111) oriented surfaces. It is therefore important to avoid this orientation as much as possible for textured surfaces. Despite the fact that the thermal stability of passivation (100) surface is relatively poor, well passivated oxide/LPCVD nitride stacks can be fabricated on (100) oriented surfaces.
In order to better understand the difference between (100) and (111) Si-SiO$_2$ stack for LPCVD Si$_3$N$_4$ deposition, LPCVD Si$_3$N$_4$ was deposited on some previously depassivated samples using RTAs at various temperatures (figure 5.10). Figure 5.12 and
5.13 compares effective lifetime and $J_{0e}$ values before and after LPCVD Si$_3$N$_4$ deposition for 750°C and 850°C wet oxidation respectively.

Figure 5.12. (a) Effective lifetime $\tau$ and (b) $J_{0e}$ before and after LPCVD nitride deposition on (100) and (111) 750°C wet oxide.
Chapter 5: Passivation effect of wet oxidation, and with oxide/LPCVD nitride stacks on the Si-SiO\textsubscript{2} interface

Figure 5.13. (a) Effective lifetime $\tau$ and (b) $J_{0e}$ before and after LPCVD nitride deposition on (100) and (111) 850°C wet oxide.

It can be seen from figure 5.12 and 5.13 that, following nitride deposition on either 750°C wet oxide or 850°C wet oxide, the (100) samples have improved substantially, while the (111) samples have not.

The above results suggest that, for the samples investigated, the (111) surface does not display inherently worse recombination if all the defects are unpassivated. Instead, the major difference is the ability to passivate interface defects with hydrogen. While
the (100) interface defects can be passivated reasonably well using either an FGA or with hydrogen from another source (such as from a H containing film), a large fraction of the (111) defects are not able to be passivated in this way. This behaviour is similar as the behaviour observed for higher temperature oxides.

5.5.4 Thermal stability of samples with oxide/LPCVD nitride stacks

Samples which previously had LPCVD nitride deposited were re-measured in order to determine if there was any degradation after 40 days storage at room temperature. The results are shown in figure 5.14. The trend is similar to that in figure 5.9, with apparently significant degradation in surface passivation for the (100) samples but no significant degradation for the (111) samples. However, there is significant variation in the response of identically prepared samples, especially in the $J_{0e}$ for (100) samples with 750°C oxide.
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Figure 5.14. Evolution of (a) effective lifetime and (b) \(J_{0e}\) with process treatments: (1) oxidation and anneal; (2) subsequent FGA; (3) subsequent LPCVD nitride deposition (4) repeat measurements 40 days later.

Following the lifetime/\(J_{0e}\) re-measurement, the samples received anneals at temperatures in the range 500-800°C. The results are shown in figure 5.15 plotting the ratio of the lifetime at 850 and 750°C for (100) and (111) samples. It is clear that the response of the samples to anneals is quite different to the response of oxide only samples. Note that slightly different treatments were used in the two cases (RTA for 3 minutes in the case of the oxide only samples and \(\text{N}_2\) anneals in conventional furnace for 5 minutes in the case of the oxide/nitride stack). However, the differences between these treatments are not expected to have a significant impact on the results. In both cases, the treatments were designed to ensure no influence from atmospheric gases. For oxide only samples, moisture in the atmosphere can have a significant effect and must be excluded (this is the case in the RTA) while for oxide/nitride stacks, moisture has no impact for the range of temperatures investigated.

The relative stability of the samples during the high temperature steps indicates that re-passivation of defects with hydrogen supplied by the SiN is able to counter the effect of H loss.
Figure 5.15. Evolution of (a) effective lifetime ratio and (b) $J_{0e}$ ratio with process treatments. (1) oxidation and anneal and LPCVD (50nm); (2)-(5) subsequent N$_2$ anneal treatments at 500, 600, 700 and 800°C for 5 minutes, respectively. Treatments are cumulative.

The results indicate that good, stable surface passivation using low temperature thermal oxides is difficult to achieve. Surfaces with a (111) orientation can not be well
passivated even following a forming gas anneal. Surfaces with a (100) orientation can be relatively well passivated, particularly if the oxidation temperature is 850°C (or above). However, even at this temperature, the passivation does not appear to be completely stable when the sample is stored in the dark at room temperature in N₂ atmosphere. This result also holds for oxide/nitride stacks. In addition, the (100) samples appear to not be stable at room temperature, but actually show reasonable stability during anneals at moderate temperatures. This suggests that the main problem is that some interface defects depassivated over time even at room temperature. At elevated temperatures, the reasonable stability is likely the result of the release of atomic hydrogen from the LPCVD layer which re-passivated defects.

The thermal stability of (100) oxide only samples is much poorer than of samples with a high temperature nitride, indicating a rapid loss of hydrogen from the interface at temperatures of 500°C and above. However, the degradation resulting from the deposition of an LPCVD nitride layer, and from subsequent high temperature treatments for moderate periods of time, is small due to the simultaneous re-passivation with atomic hydrogen from the nitride film.

5.6 Summary

The work in this section has investigated the passivation that can be achieved with relatively low temperature, thin thermal oxides (grown in the temperature range 750-900°C), and with oxide/LPCVD nitride stacks. The results can be summarized as follows:

For thin oxides, firstly, higher oxidation temperature results in better surface passivation. A reasonable compromise may be a temperature of ~850°C. The lower the temperature, the poorer the surface passivation and the stability of the surface passivation will be. Secondly, surface orientation has a large effect on achievable surface passivation. (111) surfaces display high recombination rates even at an oxidation temperature of 850°C and following an FGA. Surfaces with (111) orientation are therefore undesirable, and surface textures which avoid this orientation are likely to offer better passivation. Thirdly, the diffusion of phosphorous into the oxide results in a significant improvement in surface passivation. However, this improvement appears to be related to a slight increase in positive charge density in the oxide rather than to a decrease in the unpassivated interface defect density. Since surface passivation
deteriorates markedly if the diffusion reaches the interface, this is unlikely to be a practical process.

On the other hand, for oxide/nitride stacks, firstly, the nitride deposition temperature should be kept as low as possible in order to retain good surface passivation following nitride deposition. A practical temperature may be in the range 750-775°C. In this temperature range, the degradation in surface passivation is small. Secondly, the thermal stability of the surface passivation is much better than for samples with an oxide only, due to the presence of hydrogen in the nitride which re-passivates interface defects. Thirdly, even for oxide/nitride stacks, the passivation does not seem to be stable. Further experiments would be required to definitively establish that the measured changes in effective lifetime and \( J_{0e} \), at room temperature, are due to interface degradation.
Chapter 5: Passivation effect of wet oxidation, and with oxide/LPCVD nitride stacks on the Si-SiO$_2$ interface
CHAPTER 6

Influence of atomic hydrogen exposure on the Si-SiO₂ interface

In this chapter, the influence of atomic hydrogen on the surface passivation of the Si-SiO₂ interface is investigated. Atomic hydrogen is mainly produced in a remote PECVD system using RF or MW power. Inductively coupled photoconductivity decay measurements indicate an increase in carrier recombination at the surfaces following atomic hydrogen exposure, as measured by an increase in the emitter saturation current density. These defects are not thermally stable and are removed by subsequent thermal treatments above 240°C in N₂. In addition, atomic hydrogen results in the passivation of a certain fraction of thermally stable interface defects. However, the fraction of defects passivated is always lower than can be achieved by exposure to molecular hydrogen. Variation of sample temperature during atomic H exposure in the range 25-600°C does not have a significant impact on the passivation efficiency.
Chapter 6: Influence of atomic hydrogen exposure on the Si-SiO\textsubscript{2} interface

6.1 Experimental details

Lifetime and C-V samples received standard processing steps. Annealing in forming gas at 400\textdegree C was performed to hydrogenate the Si-SiO\textsubscript{2} interface of some samples, while others samples were dehydrogenated by a rapid RTA at 700\textdegree C for 3 minutes in N\textsubscript{2}.

The samples were exposed to atomic H in the PECVD reactor. For some samples, a 2.45GHz microwave plasma was used for atomic hydrogen generation while for others a 13.56MHz RF source was used. For both sources, the source frequency is sufficiently high that no ion bombardment of the substrate is expected. The penetration of hydrogen to the Si-SiO\textsubscript{2} interface is therefore by diffusion rather than by ion bombardment [115]. The standard plasma conditions used in this chapter for MW power are: MW power 200W, pressure 0.2mbar, time 5 minutes/side, room temperature and H\textsubscript{2} flow rate 150 Standard Cubic Centimeters per Minute (sccm) whereas the plasma conditions for RF plasma power are: RF power 300W, pressure 0.05mbar, time 5 minutes/side, room temperature and H\textsubscript{2} flow rate 150sccm. For the symmetrical photo-conductance samples, both sides were exposed, while in the case of CV samples, just the polished side was exposed.

After plasma exposure, an RTA was carried out at temperatures in the range 25-400\textdegree C for up to 3 minutes in N\textsubscript{2} to remove plasma-induced defects. Subsequently, an FGA treatment was carried out at 400\textdegree C for 30 minutes, which has the effect of re-hydrogenating the interface and thus rendering the majority of residual defects electrically inactive. In addition, an alternative thermal anneal technique by using a TIDLS lifetime tester was also applied to investigate the properties of Si-SiO\textsubscript{2} interface at temperatures in the range 120-240\textdegree C in air or N\textsubscript{2} atmosphere.

Lifetime measurements were carried out using the inductively coupled photoconductivity measurement technique [59, 116]. The value of the emitter saturation current density \( J_{0e} \) was extracted from measurements of the effective carrier lifetime in high injection, as described in detail in chapter 3.

Prior to C-V measurements, about 80nm Aluminium was deposited with an area of around \( 4.7 \times 10^{-3} \text{cm}^2 \) through a shadow mask on the oxide to form a MOS structure. This is done in a vacuum chamber at pressure lower than \( 3 \times 10^{-6} \text{torr} \) and the thickness of metal is accurately controlled. High-Frequency C-V (HFCV) measurements were carried out at 1 MHz, and Quasi-Static C-V (QSCV) measurements were carried out at 0.01Hz, with a sweep rate of 50mV/s. The charge density in the oxide layers is deduced from the flat-band voltage of curves (HFCV) at 1MHz. The Si-SiO\textsubscript{2} interface defect
density is calculated by joint HFCV and QSCV measurements using the method of Castagne and Vapaille [85].

The use of different substrates was dictated by the requirements of the characterization techniques. For C-V measurements, moderately doped wafers are required for accurate results, while the unambiguous extraction of the emitter saturation current $J_{0e}$ requires the use of lightly doped material as well as diffused surfaces, because extraction of $J_{0e}$ requires measurement with the wafer bulk in high-level injection but the surfaces in low-level injection.

### 6.2 Background tests

#### 6.2.1 Effect of molecular H$_2$ on the Si-SiO$_2$ interface

Figure 6.1 shows the C-V curves of (a) depassivated and (b) passivated samples after molecular hydrogen exposure in the PECVD reactor chamber at pressure 0.05mbar, gas flow rate 150sccm and time 5 minutes/side at room temperature and 400°C, respectively. For comparison, the corresponding curves for depassivated and passivated samples without H$_2$ exposure are also shown in figure 6.1 (a) and (b), respectively. Methods of hydrogenation and dehydrogenation to the Si-SiO$_2$ stacks are described above. Figure 6.2 shows the corresponding $D_{it}$ distributions for the samples in fig 6.1 (a), extracted using the curves from fig. 6.1 (a). Table 6.1 summarizes the $J_{0e}$ results of an initially passivated sample after molecular hydrogen exposure at the pressure 0.2mbar, gas flow rate 150sccm and time 5 minutes at 400°C in the PECVD reactor chamber. The samples were then rinsed in an isopropanol (IPA) solution and water to remove the surface charges. After that, another FGA treatment was performed.
Figure 6.1. C-V curves for (a) depassivated samples and (b) passivated samples, before \( \text{H}_2 \) exposure, after room temperature 5 minutes \( \text{H}_2 \) exposure, and after 400\(^\circ\)C, 5 minutes \( \text{H}_2 \) exposure respectively.
It can be seen from figure 6.1, either for depassivated or passivated samples, the HFCV or QSCV curves overlap almost completely, which means neither the interface charge density nor the interface defect density has been changed under our experiment conditions, in other words, the effect of molecular hydrogen may be neglected during the analysis of the effect of atomic hydrogen plasma exposure.

It is well established that the surface charges can be easily removed by rinsing the wafer in water or alcohol [117]. The results in table 6.1 suggest that, under experimental conditions used, no additional surface charges have been introduced to the Si-SiO$_2$ stack, indicated by the stable $J_{0e}$ values measured before and after IPA rinse. Meanwhile, there is no additional interface defects generated after molecular hydrogen exposure, which is consistent with the CV results. The reduction in $J_{0e}$ after the H$_2$ exposure perhaps is due to some degradation of the oxide following the first FGA and prior to measurement. It was observed that oxidised samples often degraded gradually (over a period of days or weeks) when stored in air.
6.2.2 Effect of illumination during RTA

Following H plasma exposure, selected samples were annealed in an RTA furnace. The RTA chamber heats the samples by irradiating them with intense light overing a broad spectrum of wavelengths. The RTA process is therefore not a purely thermal process; the high energy photons produced may also result in changes at the Si-SiO$_2$ interface. Since anneals were generally carried out at low temperatures (in the range 100-400°C) the lamps generate far lower fluxes of high energy photons than at higher energies, and therefore the effect of illumination during RTA treatments is likely to be negligible. To confirm this, samples that had been exposed to a H plasma (introducing thermally unstable defects) were annealed in the RTA furnace. One sample was sandwiched between two Si wafers (thus eliminating any effect due to illumination) while another sample was not. Samples were heated to 200°C for times ranging from 5 to 180 seconds (cumulative). The low temperature was chosen to allow the annealing behaviour to be observed. After that, the same samples received a 400°C, 10 second RTA treatment. Figure 6.3 shows the results following 200°C RTA, the $J_{0e}$ values at zero annealing time come from samples that just received hydrogen plasma exposure.

![Graph showing $J_{0e}$ values](image)

Figure 6.3. $J_{0e}$ values of MW hydrogen plasma exposed samples after RTA in N$_2$ at 200°C with time range from 5 to 180 seconds.

It can be seen from fig 6.3 that both samples show a similar trend. After the 200°C RTA treatment, the $J_{0e}$ values for sandwiched and bare samples are 58fA/cm$^2$ and
52fA/cm² respectively. Following a 400°C RTA for 10 seconds, the $J_{0e}$ values for both sandwiched and bare samples decreased to about 35fA/cm². From these results, it appears that the illumination during RTA at low temperatures does not have any impact on the annealing of the thermally unstable interface defects. All RTA treatments in this thesis were carried out for samples without sandwich structure.

### 6.3 Effect of RTA on the Si-SiO₂ interface following atomic hydrogen plasma exposure

In this section, the effect of RTA treatments following hydrogen plasma exposure on the Si-SiO₂ interface properties is discussed. RTAs in dry nitrogen gas were carried out at different temperatures from 100°C to 400°C for up to 180 seconds. The difference of the effect of RTA at 300°C and 400°C was compared. Samples just after RF or MW hydrogen plasma exposure under standard conditions were investigated respectively. Initially hydrogenated and dehydrogenated samples were used for plasma exposure treatments and subsequent RTA treatments.

#### 6.3.1 RF power

Figure 6.4 shows the dependence of (a) effective lifetime $\tau$ and (b) corresponding $J_{0e}$ on RTA time and temperature for RF hydrogen plasma exposed samples. Four passivated samples, with initial $J_{0e}$ values between 58 to 72fA/cm², were used for the RTA curves following a RF hydrogen plasma exposure under the standard conditions. The bottom straight dashed line in fig 6.4 (b) represents the average initial $J_{0e}$ values before RF hydrogen plasma exposure. The values at time zero are from just after hydrogen plasma exposure. Figure 6.5 illustrates the effects of atomic H plasma exposure and subsequent RTA on the CV characteristics, measured on p-type MOS stacks (note that in all cases, the metal to form the MOS structure was evaporated just prior to measurement). Figure 6.6 shows the corresponding $D_{\text{it}}$ distribution. Three passivated samples were used. Figure 6.7 shows the C-V results for initially depassivated, p-type MOS stacks subjected to otherwise identical processing treatments as the samples fig 6.5. Figure 6.8 shows the corresponding $D_{\text{it}}$ distribution. Three depassivated samples were used. RF hydrogen plasma exposure conditions are standard and RTA at 400°C in N₂ for 3 minutes. For comparison, the corresponding curves for an
as oxidized and forming gas annealed MOS stack as well as an as oxidized and RTA 700°C de-hydrogenated MOS stack are also shown in fig 6.5 and 6.7 respectively.

![Figure 6.4.](image-url) (a) Effective lifetime $\tau$ and (b) Emitter saturation current density $J_{0e}$ for initially RF atomic hydrogen exposed samples as a function of RTA annealing temperature and time.

It can be seen from figure 6.4 that the majority of the H-generated defects appears to be rapidly removed by anneals at a temperature of 300°C and above (these anneals do not influence the $P_{ox}$ defects that always exist at a thermally grown Si-SiO$_2$ interface [55, 118]. Further, the $J_{0e}$ values do not return to their initial values which indicates that
either some H-generated defects have not been removed, or that atomic H has resulted in some de-passivation of initially passivated P_{bx} centres (in other words, atomic H results in a new, lower steady state fraction of passivated P_{bx} centers compared to an FGA). In addition, a 400°C anneal for prolonged times causes an increase in J_0e, probably due to some de-passivation of P_{bx} defects.

![Graph showing CV curves](image)

**Figure 6.5.** CV curves (a) HFCV, (b) QSCV for p type MOS stacks prepared just after an FGA; after FGA and 25°C RF hydrogen plasma; after FGA, 25°C RF hydrogen plasma and 400°C RTA in N₂ 3 minutes.
Chapter 6: Influence of atomic hydrogen exposure on the Si-SiO$_2$ interface

The C-V results in figures 6.5 and 6.6 are consistent with the lifetime and $J_{0e}$ results. The interface defect densities have dramatically decreased after an RTA at 400$^\circ$C for 3 minutes, but remain higher than that of the passivated control sample, indicated by the drop in the minimum quasi static capacitance in fig 6.5 (b) and the $D_{it}$ distribution in fig 6.6. Meanwhile, the interface charge density increases markedly after hydrogen plasma exposure and is almost completely restored to the initial value of the passivated control sample after a 400$^\circ$C RTA. Before hydrogen plasma exposure, the interface charge density and defect density are $1.0 \times 10^{11}$cm$^{-2}$ and $3.3 \times 10^9$eV$^{-1}$cm$^{-2}$ respectively. After H plasma exposure, the interface charge density and defect density are $4.2 \times 10^{12}$cm$^{-2}$ and $4.6 \times 10^{12}$eV$^{-1}$cm$^{-2}$ respectively, and after RTA 400$^\circ$C, 3 minutes annealing, they are $1.1 \times 10^{11}$cm$^{-2}$ and $6.0 \times 10^{10}$eV$^{-1}$cm$^{-2}$ respectively. The increase of interface defects after RTA 400$^\circ$C anneal, compared to passivated control sample, is almost certainly at least partly due to P$_b$H dissociation.
Fig 6.7. CV curves (a) HFCV, (b) QSCV for p type MOS stacks prepared just after an RTA 700°C; after RTA 700°C, 25°C RF hydrogen plasma; after RTA 700°C, 25°C RF hydrogen plasma and 400°C RTA in N₂ 3 minutes.
It can be seen from figure 6.7 and 6.8 that depassivated samples respond to hydrogen treatments in similar ways as passivated ones. Before hydrogen plasma exposure, the interface charge density and defect density are $1.1 \times 10^{12} \text{cm}^{-2}$ and $1.7 \times 10^{12} \text{eV}^{-1}\text{cm}^{-2}$ respectively. After H plasma exposure, the interface charge density and defect density are $3.2 \times 10^{12} \text{cm}^{-2}$ and $5.5 \times 10^{12} \text{eV}^{-1}\text{cm}^{-2}$ respectively, and after RTA 400°C, 3 minutes annealing, they are $5.2 \times 10^{11} \text{cm}^{-2}$ and $6.9 \times 10^{11} \text{eV}^{-1}\text{cm}^{-2}$ respectively. The decrease of interface defects after RTA 400°C anneal, compared to depassivated control sample, should be principally attributed to the passivation effect of atomic hydrogen.

Although the changes of C-V curves following H plasma exposure are similar to the work by Cartier et al.[119], the $D_{it}$ distribution, both of passivated and depassivated samples, is not similar to those Cartier’s which are strongly asymmetric with respect to midgap and showing only one peak above midgap [40]. However, no peak and strong asymmetry are observed in above results. The reason for this might be related to different H plasma exposure conditions.

It is worth noting that there is an appreciable decrease in doping level following atomic hydrogen plasma exposure for both passivated and depassivated samples, indicated by the decrease of the minimum capacitance in fig 6.5 (a) and 6.7 (a). This
phenomenon is also observed by Cartier et al [119]. This can be explained by the deactivation of boron acceptors by atomic hydrogen [14, 15].

### 6.3.2 MW power

Figure 6.9 shows the dependence of (a) effective lifetime and (b) $J_{0e}$ on RTA time and temperature for MW hydrogen plasma exposed samples. Four passivated samples, with nearly identical initial $J_{0e}$ values of about 30fA/cm$^2$, were used for the RTA curves following MW hydrogen plasma exposure. The bottom straight dashed line in 6.9 (b) represents the average initial $J_{0e}$ values before MW hydrogen plasma exposure. Figure 6.10 (a) HFCV and (b) QSCV, illustrate the effects of atomic H plasma exposure and subsequent RTA anneal in p-type MOS stacks. Figure 6.11 shows the corresponding $D_\alpha$ distribution. Three depassivated samples were used. MW hydrogen plasma exposure conditions are standard. For comparison, the corresponding curve for an as oxidized and RTA 700°C de-hydrogenated MOS stack is also shown.
Figure 6.9. (a) Effective lifetime $\tau$ and (b) Emitter saturation current density $J_{0e}$ for initially MW atomic hydrogen exposed samples as a function of RTA annealing temperature and time.
Figure 6.10. CV curves (a) HFCV, (b) QSCV for p type MOS stacks prepared just after an RTA 700°C; after RTA 700°C, 25°C MW hydrogen plasma; after RTA 700°C, 25°C MW hydrogen plasma and 400°C RTA in N₂ 3 minutes.
It can be seen from figures 6.9-6.11 that MW plasma exposed samples show a similar trend to the RF plasma exposed samples following RTA annealing. Again, the majority of the H-generated defects are rapidly removed by anneals at a temperature of 300°C and above. The $J_{0e}$ values do not restore to their initial values and 400°C anneal for prolonged times causes increase in $J_{0e}$. There is a decrease in doping level following atomic H plasma exposure. The C-V curves show similar changes after H plasma exposure. However, there are some differences between RF and MW hydrogen plasma exposure. Firstly, the use of RF power introduces a higher interface charge density compared to MW power, indicated by a larger parallel left shift of the C-V curves. Secondly, the shape of the $D_{it}$ distribution following MW plasma exposure is somewhat different to that following RF plasma exposure. The $D_{it}$ distribution exhibits a pronounced peak at ~0.68eV, which is similar to the peak position of sample exposed to atomic hydrogen in 5 arbitrary units. Samples show similar manner reported by Cartier et al. [42] in which the typical distribution of interface states across the bandgap caused by atomic hydrogen exposure is strongly asymmetric with respect to midgap and showing only one peak above midgap. Because this characteristic is dependent on the atomic hydrogen dose [40], the difference in $D_{it}$ distribution is dependent more on the dose of atomic hydrogen and little on the source of plasma power. But this is not always observed in this thesis’s experiments even under identical plasma hydrogen exposure conditions.
6.3.3 Comparison of RTA results at 300°C and 400°C

The results of RTA treatments presented in figs 6.4 and 6.9, for both RF and MW hydrogen exposed samples, suggest that a 300°C RTA treatment for a short time (less than 30 seconds) is most effective at removing the thermally unstable defects and without leading to a loss of hydrogen from H passivated defects (P\textsubscript{b}H centres). In comparison, a 400°C RTA treatment results in slightly increased surface recombination, suggesting a loss of hydrogen from passivated defects. However, this was inconsistent with the findings of Stesmans, who did not observe a significant increase in [P\textsubscript{b}] until 480°C by using conventional tube furnace. This was investigated further.

Figure 6.12 shows the (a) HFCV and (b) QSCV curves for p type MOS stacks measured after MW hydrogen plasma exposure under standard conditions, and following an RTA in N\textsubscript{2} for 3 minutes at 300°C and 400°C successively. Figure 6.13 shows the corresponding D\textsubscript{it} distribution. Three depassivated samples were used. For comparison, an as oxidized and RTA 700°C de-hydrogenated MOS stack is also shown. Figure 6.14 shows the J\textsubscript{0e} values for two oxidised depassivated (100) p-type samples after different processing steps. The MW plasma conditions are standard. After H plasma exposure, samples received RTA 300°C 3 minutes in N\textsubscript{2} and 400°C 3 minutes in N\textsubscript{2} successively. During RTA, samples were touched directly by thermocouple. The figure shows the average and error of the two values.
Figure 6.12. (a) HFCV and (b) QSCV curves following different processing steps: after RTA 700°C 3 minutes; after RTA 700°C 3 minutes and H plasma; after RTA 700°C 3 minutes, H plasma and RTA 300°C, N\textsubscript{2}, 3 minutes; after RTA 700°C 3 minutes, H plasma, RTA 300°C, N\textsubscript{2}, 3 minutes and RTA 400°C 3 minutes.
Figure 6.13. Interface defect density ($D_{it}$) distribution across the energy gap at the Si-SiO$_2$ interface subjected to identical situations as those in fig 6.12.

It can be seen from fig 6.12 (a) that after RTA 300°C annealing, the interface charge density returns to the initial level (about $1.6 \times 10^{11}$ cm$^{-2}$), while a subsequent 400°C RTA leads to a further slight decrease to about $1.3 \times 10^{11}$ cm$^{-2}$. On the other hand, from fig 6.12 (b) and 6.13, it can be seen that there is also a decrease in $D_{it}$ distribution after a 400°C RTA annealing, and the midgap $D_{it}$ value decreases from $2.1 \times 10^{11}$ eV$^{-1}$cm$^{-2}$ to $1.3 \times 10^{11}$ eV$^{-1}$cm$^{-2}$ for 300 and 400°C RTA treatments respectively.
Figure 6.14. $J_{0e}$ values for samples following various processing steps. step 1: FGA; step 2: RTA 700°C in N$_2$ 3 minutes; step 3: H plasma exposure; step 4: H plasma exposure and RTA 300°C in N$_2$ 3 minutes; step 5: H plasma exposure, RTA 300°C in N$_2$ 3 minutes and successive RTA 400°C in N$_2$ 3 minutes.

It can be seen from fig 6.14 that, after H plasma, the $J_{0e}$ values is about 400fA/cm$^2$ and decreases to about 130fA/cm$^2$ after 300°C RTA, then further decreases to around 50fA/cm$^2$ after the 400°C RTA. The lifetime results are consistent to the CV results in this section; that is, the 400°C RTA results in a further improvement in surface passivation compared to the 300°C RTA.

It is clear that the results in this section are not consistent with those in fig 6.4 and 6.9, in which the 400°C RTA leads to a slight degradation compared to a 300°C RTA. The major difference between the two sets of results is the way in which the RTA treatment was carried out. For the results of the previous section (fig 6.4 and 6.9), a five inch silicon base plate was used as a substrate to contact the thermocouple rather than a smaller quarter, in order to minimise the risk of contamination. It appears that this method resulted in the sample temperature increasing significantly above the measured temperature. The RTA was done in this section and subsequent experiments in a way in which the thermocouple directly touched the bottom of the test sample.
6.4 Effect of atomic hydrogen plasma exposure parameters on the Si-SiO$_2$ interface

In this section, hydrogenated and de-hydrogenated p-type silicon samples were exposed to RF or MW plasma atomic hydrogen produced by a PECVD reactor, followed by RTA and FGA treatments. The effects of atomic H plasma power, pressure and time on Si-SiO$_2$ interface passivation were studied.

6.4.1 Influence of hydrogen plasma exposure power on Si-SiO$_2$ interface defect distribution

6.4.1.1 RF power

The section aims to investigate the effect of RF power on the Si-SiO$_2$ interface properties following H exposure. A higher power level of the excitation source will lead to a higher degree of dissociation of the process gases. For PECVD film depositions, this usually results in a better uniformity of the deposited layers and an increase in deposition rate. On the other hand, a higher power level will also produce a greater density of energetic ions which can produce damage at the wafer surface and thus, a degradation of the surface properties [120].

Figure 6.15 exhibits (a) C-V curves and (b) corresponding $D_{it}$ distribution for initially passivated Si-SiO$_2$ stacks after RF hydrogen plasma exposure with RF power ranging from 50 to 300W and under otherwise standard conditions. Table 6.2 summarizes the flat band voltage, interface charge density, and midgap interface defect density for these samples. For comparison, the corresponding curve for an as oxidized and forming gas annealed MOS stack is also shown.
Figure 6.15. (a) C-V curves and (b) corresponding $D_{it}$ distribution for initially passivated Si-SiO$_2$ stacks after RF hydrogen plasma exposure at an RF power ranging from 150 to 300W and otherwise standard conditions.
Table 6.2. Flatband voltage(V), interface charge density( x 10^{11} \text{cm}^{-2} ), and midgap surface defect density( x 10^{10} \text{eV}^{-1}\text{cm}^{-2} ) after various RF power H plasma exposure.

<table>
<thead>
<tr>
<th></th>
<th>$V_{fb}$</th>
<th>Q</th>
<th>$D_{itm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF 300W</td>
<td>-18</td>
<td>66</td>
<td>680</td>
</tr>
<tr>
<td>RF 150W</td>
<td>-15</td>
<td>52</td>
<td>520</td>
</tr>
<tr>
<td>Passivated control</td>
<td>-1</td>
<td>0.66</td>
<td>0.39</td>
</tr>
</tbody>
</table>

As can be seen from fig 6.15 (a), there is a big shift along the voltage axis and a rise of the minimum quasistatic capacitance for 150W and 300W samples, which means, with increasing RF exposure power, there is a corresponding significant increase in interface charge and defect density to the Si-SiO\textsubscript{2} interface. Fig 6.15 (b) also presents the evidence that a plasma power as low as 150W can generate a high density of interface defects. Again, an appreciable decrease in doping level following atomic hydrogen plasma exposure can be observed in fig 6.15 (a). For an exposure power between 150-300W there does not seem to be a significant difference in Si-SiO\textsubscript{2} interface passivation, although a slightly higher charge and defect density is produced at 300W.

6.4.1.2 MW power

Figure 6.16 shows $J_{0e}$ values for initially passivated Si-SiO\textsubscript{2} stacks after H plasma exposure at a MW power ranging from 200 to 1200W under otherwise standard conditions, as well as the $J_{0e}$ values for the same samples after a subsequent RTA at 400°C for 3 minutes in N\textsubscript{2} and an FGA at 400°C for 30 minutes. Figure 6.17 shows the results for depassivated samples subjected to identical H plasma exposure and thermal anneal treatments. The $J_{0e}$ values at the first step come from samples that did not receive any plasma exposure. Figure 6.18 shows (a) HFCV and (b) QSCV curves for initially passivated p type MOS stacks measured after different processing steps. Samples were subjected to MW hydrogen plasma exposure at 1200W and under otherwise standard conditions. Figure 6.19 shows corresponding $D_{it}$ distribution, four passivated samples were used.
Figure 6.16. $J_{oe}$ values for passivated samples following different treatments. Step 1: FGA; step 2: H plasma exposure; step 3: RTA 400°C 3 minutes in N$_2$; step 4: FGA 400°C 30 minutes.

Figure 6.17. $J_{oe}$ values for depassivated samples following different treatments. Step 1: FGA; step 2: RTA 700°C 3 minutes in N$_2$; step 3: H plasma exposure; step 4: RTA 400°C 3 minutes in N$_2$; step 5: FGA 400°C 30 minutes.
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Figure 6.18. CV curves (a) HFCV, (b) QSCV for p type MOS stacks prepared just after an FGA; after FGA and 1200W hydrogen plasma exposure; after FGA, 1200W hydrogen plasma exposure and 400°C RTA 3 minutes; after FGA, 1200W hydrogen plasma exposure, 400°C RTA 3 minutes and FGA.
It can be seen from fig 6.16 and 6.17 that there is a permanent degradation of the interface with increasing MW power, especially for the 1200W exposed samples. Although the subsequent 400°C RTA and FGA treatments can significantly improve the surface passivation, the final $J_{0e}$ values (after second FGA) are much higher than initial values, indicating that a high plasma power generates defects which are not removed by subsequent anneals at 400°C. These defects are presumed to have a different origin to the atomic hydrogen induced defects, although their exact origin is not clear. At a power level of 200-400W, the $J_{0e}$ values come back to the initial level (before plasma) after a 400°C FGA, indicating that the additional defects created during H plasma exposure in this power range can be removed at low temperatures (≤400°C). At intermediate power levels between 400 and 1200W, additional defects may also be generated, as can be seen from the results for 800W MW power. The chief conclusion is that even a remote, high frequency plasma source can result in the introduction of plasma-generated interface defects, and that great care must be taken in the choice of the operating parameters.

It can be seen from figs 6.18 and 6.19 that the RTA treatment has resulted in only a small reduction in interface defect density; this reduction is much smaller than is usually
observed for samples exposed at lower plasma powers. However, following an FGA the interface defect density is almost the same as the initial defect density prior to plasma exposure. Given the fact that $J_{0e}$ following an FGA is still significantly higher than the initial $J_{0e}$, this may indicate that defects in the emitter (that is, in the near-surface region of the silicon) are perhaps the most likely explanation for this. It is also can be seen in fig 6.18 (a) that the voltage shift, indicating positive charge density, is much smaller compared with RF hydrogen plasma exposed sample. This means there seems to be a significant difference in the effect of the two different plasmas, and the high positive charge density observed for RF plasmas (and also by Cartier et al.) [119] may not be a fundamental property of the atomic hydrogen exposure. Again, there is a reduction in minimum capacitance after MW hydrogen plasma exposure and the explanation for fig 6.5 (a) for RF plasma can be applied here. It should be noted that although high plasma power will introduce defects in the emitter near the surface region of the silicon, the $D_{it}$ level is not much higher than that following lower power exposure. This may be due to experimental error - slightly different exposure conditions every time a sample is exposed in the chamber (i.e. the different H plasma density and uniformity). Further work is worth to confirm this.

6.4.2 Influence of hydrogen plasma exposure time on Si-SiO$_2$ interface defect distribution

Usually, the atomic hydrogen dose during plasma exposure is proportional to exposure time. In this section, the effect of hydrogen exposure time on passivation of Si-SiO$_2$ defects has been investigated.

6.4.2.1 RF power plasma hydrogen exposure

Figure 6.20 shows the (a) HFCV and (b) QSCV curves for two oxidised passivated samples following RF hydrogen plasma exposure for 5 and 20 minutes, respectively, with otherwise standard process parameters. Figure 6.21 shows the corresponding $D_{it}$ distribution. Table 6.3 summarizes the flat band voltage ($V_{fb}$), interface charge density ($V$), and defect density at mid gap ($D_{itm}$) following the same process steps. Figure 6.22 shows (a) the effective lifetime and (b) the corresponding $J_{0e}$ values for oxidised passivated samples following different processing steps. Figure 6.23 shows the
hysteresis effect observed on HFCV curves of Si-SiO$_2$ stacks just after RF hydrogen plasma exposure at room temperature for 5 and 20 minutes, respectively. Table 6.4 summarizes the flat band voltages values.

Figure 6.20. C-V results for 5 and 20 minutes RF hydrogen plasma exposure under standard conditions.
Figure 6.21. $D_{it}$ distribution for 5 and 20 minutes RF hydrogen plasma exposure under standard conditions.

Table 6.3. Flatband voltage $V_{fb}$(V), interface charge density $Q(\times 10^{11} \text{cm}^{-2})$, and midgap surface defect density $D_{itm}(\times 10^{11} \text{eV}^{-1}\text{cm}^{-2})$ for samples following various processing treatments.

<table>
<thead>
<tr>
<th></th>
<th>$V_{fb}$</th>
<th>$Q$</th>
<th>$D_{itm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 minutes H plasma</td>
<td>-12.4</td>
<td>42</td>
<td>44</td>
</tr>
<tr>
<td>20 minutes H plasma</td>
<td>-13.3</td>
<td>43</td>
<td>62</td>
</tr>
<tr>
<td>5 minutes H plasma and RTA</td>
<td>-1.1</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>20 minutes H plasma and RTA</td>
<td>-1.0</td>
<td>1.0</td>
<td>1.7</td>
</tr>
</tbody>
</table>
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Figure 6.22. (a) Effective lifetime (b) $J_{0e}$ values for 5 and 20 minutes RF hydrogen exposure samples following various processing steps. Step 1: after FGA, Step 2: after RF H plasma exposure, Step 3: after RTA $400^\circ$C in N$_2$ 3 minutes, Step 4: after FGA.

Figure 6.23. HFCV curves for 5 and 20 minutes RF hydrogen plasma exposure under standard conditions.
It can be seen from figures 6.20 and 6.21 that 5 and 20 minutes RF hydrogen plasma exposure result in approximately the same effect on the Si-SiO₂ interface, although the 20 minutes sample shows a slightly higher interface defects density. After RTA treatments, the interface defect density is higher for the sample with 20 minutes exposure than for the sample following 5 minutes exposure, indicating some thermally stable defects have been generated.

The lifetime results in particular show that the 20 minutes exposure (and probably also the 5 minutes exposure) has resulted in permanent defects - particularly visible from the J₀ₑ results, which are very high after the final FGA. Therefore the key message is that the use of RF power leads to plasma damage following prolonged exposure, and probably even following short (5 minutes) exposure. Comparing the Dᵢₜ and J₀ₑ data highlights to some extent the limited usefulness of CV measurements - The CV results do not show this anywhere as clearly as the lifetime results.

The hysteresis effect observed on HFCV curves of Si-SiO₂ stacks in fig 6.23 is just after hydrogen plasma exposure. This type of behaviour is also observed in SiNx films [5] where it has been attributed to the charging and discharging of bulk and interface traps. The presence of “slow” interface traps is likely to be the reason of hysteresis observed here. There appears to be no significant change in the density of slow interface traps with longer plasma exposure time.

### 6.4.2.2 MW power plasma hydrogen exposure

Figure 6.24 shows (a) HFCV and (b) QSCV curves for p type MOS stacks measured after MW hydrogen plasma exposure for 5 and 20 minutes respectively, under otherwise standard conditions and followed by an RTA at 400°C in N₂ 3 minutes. Figure 6.25 shows the corresponding Dᵢₜ distribution. Two depassivated samples were used. Table 6.5 summarizes the flat band voltage (Vᵢᵣ), interface charge density (V), and defect density at mid gap (Dᵢₜₘ) following the same process steps. Figure 6.26 shows the
results of two depassivated lifetime samples subjected to MW hydrogen plasma for 5 and 20 minutes respectively, under otherwise standard conditions and followed by an RTA at 400°C in N\textsubscript{2} 3 minutes.

Figure 6.24. (a) HFCV and (b) QSCV curves after H plasma exposure and RTA 400°C for 5 and 20 minutes H exposure respectively.
Figure 6.25. $D_{it}$ distribution across the energy gap for initially depassivated samples for 5 and 20 minutes H exposure respectively.

Table 6.5. Flatband voltage $V_{fb}$ (V), interface charge density $Q(\times 10^{11}\text{cm}^{-2})$, and midgap surface defect density $D_{itm}(\times 10^{11}\text{eV}^{-1}\text{cm}^{-2})$ for samples following various processing treatments.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>$V_{fb}$</th>
<th>$Q$</th>
<th>$D_{itm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 minutes H plasma</td>
<td>-2.6</td>
<td>5.6</td>
<td>17</td>
</tr>
<tr>
<td>20 minutes H plasma</td>
<td>-2.2</td>
<td>4.3</td>
<td>17</td>
</tr>
<tr>
<td>5 minutes H plasma and RTA</td>
<td>-1.2</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>20 minutes H plasma and RTA</td>
<td>-1.2</td>
<td>1.5</td>
<td>2.0</td>
</tr>
</tbody>
</table>
In contrast to the last section, depassivated samples were used in this section. CV results show that, after 5 and 20 minutes H plasma exposure, the midgap $D_{it}$ values are nearly identical for the two samples, suggesting that there is little additional defects generation. However there appears to be a higher defect density above midgap energy level for 20 minutes sample. Following subsequent RTA, $D_{it}$ value is higher for 20 minute sample, suggesting that there is some thermally stable defects generation. In comparison to the samples following RF exposure in the previous subsection, the $D_{it}$ value is slightly higher following RTA.

$J_{0e}$ results are similar to CV results. The results following the RTA suggest that long time exposure can still result in some permanent interface damage, since $J_{0e}$ value following 20 minutes exposure is higher than that after 5 min exposure. This can clearly not be due to $P_b$H passivation-depassivation.

### 6.4.3 Influence of hydrogen plasma exposure pressure on Si-SiO$_2$ interface defect distribution
Figure 6.27 shows $J_{0e}$ values for initially (a) depassivated and (b) passivated Si-SiO$_2$ stacks after 5 minutes H plasma exposure at room temperature, at a MW power ranging from 200 to 400W and a pressure 0.2 and 0.67mbar respectively. This was followed by an RTA at 400°C for 3 minutes in N$_2$. $J_{0e}$ at zero exposure time come from samples that did not receive any plasma exposure.

![Comparison of plasma power and $J_{0e}$ values](image.png)

Figure 6.27. Comparison $J_{0e}$ values at 0.2 and 0.67 mbar for H plasma exposed and subsequent RTA 400°C N$_2$ 3 minutes for (a) depassivated and (b) passivated samples.
It can be seen from figure 6.27 that more interface damage occurs with higher pressure at a MW power in the range 200 to 400W. After a 400°C RTA (removing thermally unstable defects), no significant difference is observed between the 0.2mbar and 0.67mbar exposure. This trend was observed for both passivated and depassivated samples. The results indicate that higher pressure has the effect of accelerating the rate of generation of defects at lower pressure. In other words, the density of atomic hydrogen in the plasma is a function of both the pressure and the MW power. For sufficiently high plasma power (400W), for an exposure time of 5 minutes saturation in \( J_{0e} \) (and presumably \( D_{it} \)) is observed for both pressures. In addition, the passivation of thermally stable interface defects appears to have reached steady state after 5 minutes at 0.2mbar, while the density of unstable defects has not yet reached steady state.

### 6.4.4 Optimization of the atomic hydrogen plasma exposure parameters

The section aims to achieve plasma operating conditions which, on the one hand, can avoid plasma damage (i.e. introduction of defects which do not appear to be due to the action of atomic H itself but more likely the result of the bombardment of the surface with energetic particles), and on the other hand ideally, result in a sufficient H flux to result in steady state passivation of existing interface defects (\( P_b \)) and saturation of atomic H induced defects.

Results in previous sections suggest that both RF and MW can result in damage if exposure time is too long or power is too high. \( J_{0e} \) results in particular indicate that RF power results in more damage than MW power. Even 5 minutes exposure can result in introduction of permanent defects.

Overall conclusion is that it is best to use MW plasma with low power(200W), and minimise exposure time(5 minutes). Plasma conditions are a compromise - from the results of the section on influence of process pressure it is apparent that 5 minutes at 0.2mbar is not enough to result in saturation of thermally unstable defects.

### 6.5 Effect of MW hydrogen plasma exposure and following thermal anneal on the Si-SiO\(_2\) interface
In our PECVD system, the MW hydrogen plasma is produced by using the so-called remote PECVD method, in which the Si wafers are located outside the plasma region, allowing the hydrogen plasma exposure with virtually no surface damage of the samples [121]. The effect of atomic hydrogen on the Si-SiO₂ interface by using this technique is to be discussed below.

### 6.5.1 Effect of MW hydrogen plasma exposure and following thermal anneal on the Si-SiO₂ interface

This section summarises the results of atomic H exposure on the (100) thermally oxidised Si-SiO₂ interface, using the conditions that have been determined to be optimal from the experimental results presented in previous sections.

Figure 6.28 shows the CV curves for p type MOS stacks measured before and after MW hydrogen plasma exposure under standard conditions. Figure 6.29 shows the corresponding Dᵋit distribution. Two passivated samples were used. Figures 6.30 and 6.31 show the results of depassivated samples received MW H plasma exposure under identical conditions.

![Figure 6.28. C-V curves before and after MW hydrogen plasma exposure under standard conditions for initially passivated samples.](image-url)
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Figure 6.29. $D_{it}$ distribution across the energy gap at the Si-SiO$_2$ interface for samples displayed in fig 6.28.

Figure 6.30. C-V curves before and after MW hydrogen plasma exposure under standard condition for initially depassivated samples.
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It is evident that, first and foremost, MW hydrogen plasma exposure causes a significant increase in interface defect density for passivated samples, consistent with the results of Cartier et al [25, 119]. It can be seen from the fig 6.28 and 6.29 that there is a notable increase in $D_{it}$ distribution after MW hydrogen plasma exposure under standard conditions. The mid-gap $D_{it}$ increased from $3.4 \times 10^9$ eV$^{-1}$cm$^{-2}$ to $4.5 \times 10^{12}$ eV$^{-1}$cm$^{-2}$ after hydrogen plasma exposure. Furthermore, a high density of positive charge introduced by MW hydrogen plasma exposure, indicated by a substantial shift along the voltage axis of the HFCV curves in fig 6.28, is also consistent to the results of Cartier et al. [119]. The interface charge densities before and after H plasma samples are estimated at $7.5 \times 10^{10}$ cm$^{-2}$ and $1.5 \times 10^{12}$ cm$^{-2}$, respectively.

The results of depassivated samples in fig 6.30 and 6.31 are similar to passivated samples. The mid-gap $D_{it}$ increased from $2.1 \times 10^{11}$ eV$^{-1}$cm$^{-2}$ to $5.7 \times 10^{12}$ eV$^{-1}$cm$^{-2}$ after atomic hydrogen plasma exposure. Meanwhile, the interface charge densities before and after H plasma samples are estimated at $1.5 \times 10^{11}$ cm$^{-2}$ and $1.6 \times 10^{12}$ cm$^{-2}$, respectively. Both depassivated and passivated samples respond to MW hydrogen plasma exposure in similar ways. Meanwhile, both midgap $D_{it}$ and interface charge get very similar values after H plasma exposure, indicating nearly saturated $D_{it}$ distribution has been reached after H plasma exposure.
To further determine the effect of atomic hydrogen produced by MW on interface recombination, two initially passivated samples for lifetime measurements were exposed to a H plasma under standard conditions. $J_{0e}$ values of these samples increased from $28\,\text{fA/cm}^2$ to $260\pm20\,\text{fA/cm}^2$ following plasma exposure. It should be noted that $J_{0e}$ is influenced by interface charge as well as by changes in the interface defect density. The increase in positive charge following H plasma exposure would, in the absence of changes to the interface defect density or properties, be expected to result in a small decrease in $J_{0e}$, based on the calculated decrease in the surface minority carrier concentration by this amount. The $J_{0e}$ results are in good qualitative agreement with the C-V results: a large increase in the interface defect density causes a large increase in surface recombination, indicating that the additional defects introduced by atomic H act as efficient carrier recombination centres. However, the increase in $D_n$ is substantially larger than the increase in $J_{0e}$. This is probably the result of different capture cross sections of the H-introduced defects compared to the existing interface defects ($P_{bx}$ centres).

Following H plasma exposure, selected samples received RTA and FGA annealing successively. Figure 6.32 shows (a) HFCV and (b) QSCV curves for p type MOS stacks measured following various processing steps. Atomic hydrogen plasma exposure was under standard conditions. Figure 6.33 shows the corresponding $D_n$ distribution. Four depassivated samples were used. For comparison, an as oxidized and RTA 700°C dehydrogenated MOS stack is also shown. Figure 6.34 shows the effective lifetime values for oxidised, passivated and undiffused sample following different processing steps. MW hydrogen plasma conditions are standard.
Figure 6.32. (a) HFCV and (b) QSCV curves following different processing steps: after RTA 700°C 3 minutes; after RTA 700°C 3 minutes and H plasma; after RTA 700°C 3 minutes, H plasma, and RTA 400°C, N₂, 3 minutes; after RTA 700°C 3 minutes, H plasma and RTA 400°C, N₂, 3 minutes and FGA.
Figure 6.33. Interface defect density ($D_{it}$) distribution across the energy gap at the Si-SiO$_2$ interface following the identical processing steps in fig 6.32.

Figure 6.34. Effective lifetime values for undiffused samples following various processing steps. Step 1: FGA; step 2: H plasma exposure; step 3: RTA 400°C 3 minutes in N$_2$; step 4: FGA.
The CV results show that firstly, the mid-gap $D_\text{it}$ values are $4.5 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$ to $1.6 \times 10^{12}$ eV$^{-1}$ cm$^{-2}$ before and after H plasma exposure. Secondly, H plasma exposure can also improve the passivation of Si-SiO$_2$ interface, indicated by a decrease of minimum capacitance in quasi static CV curves in fig 6.32 (b) and a decrease of $D_\text{it}$ distribution in fig 6.33 for the curves after H plasma and RTA 400$^\circ$C compared to control sample. Actually, the mid-gap $D_\text{it}$ values are $1.6 \times 10^{12}$ eV$^{-1}$ cm$^{-2}$ to $1.6 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$ before and after RTA 400$^\circ$C annealing. Thirdly, after FGA treatment, the mid-gap $D_\text{it}$ decreases to $1.8 \times 10^{10}$ eV$^{-1}$ cm$^{-2}$, indicating molecular H$_2$ is more efficient at passivating interface defects than atomic hydrogen.

It can be seen from fig 6.34 that undiffused sample displays a similar trend to diffused sample as well. A substantial decrease in effective lifetime can be observed following H plasma exposure, and with a significant increase following a 400$^\circ$C RTA and a further increase following FGA 400$^\circ$C treatment. It should be noted that the recovery extent following thermal annealing, either RTA or FGA, is lower than those diffused samples since undiffused samples are more sensitive to surface passivation. In a nutshell, diffused and undiffused surfaces respond to atomic hydrogen treatments in similar ways.

The above results, firstly, indicate that atomic hydrogen can result in good Si surface passivation, indicating a re-introduction of atomic hydrogen to the Si-SiO$_2$ interface. Furthermore, after FGA the mid-gap $D_\text{it}$ value is low and close to passivated level, suggesting little or no introduction of additional defects during hydrogen plasma exposure. It should be noted that the increase in $D_\text{it}$ (and red -o- line in fig 6.33) after atomic hydrogen plasma exposure for depassivated sample should be a competition result of introduction of thermally unstable defects and passivation effect of $P_{\text{bx}}$ centres, and the former is more stronger in that case. Secondly, it is clear from the results in fig 6.34 that undiffused sample responds to atomic hydrogen exposure in a similar way to diffused sample.

### 6.5.2 Influence of hydrogen plasma exposure temperature on Si-SiO$_2$ interface passivation

Figure 6.35 shows the effect of sample temperature during MW hydrogen plasma exposure under standard conditions. Seven passivated samples were used.
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Figure 6.35. Variation of $J_{0e}$ for initially passivated samples following various processing steps, for different sample temperatures during H plasma exposure. step 1: FGA; step 2: H plasma exposure; step 3: RTA 400$^\circ$C 3 minutes; step 4: FGA.

As can be seen from the results in fig 6.35, sample temperature during plasma exposure results in significant differences in $J_{0e}$ just after H exposure, due to the fact that defect generation and annealing occur simultaneously, with the rate of annealing increasing with increasing temperature. However, temperature has no discernible effect on $J_{0e}$ results after RTA or FGA. In particular, at all sample temperatures in the range 25-600$^\circ$C, the degree of surface passivation following H plasma treatment (and after subsequent thermal treatments) is equal to or slightly worse than that following passivation by H$_2$ using an FGA. This suggests that the hydrogenation of P$_b$ centres with atomic H is no more efficient (and probably somewhat less efficient) than the hydrogenation with H$_2$ at the optimal temperature.

The very weak temperature dependence of P$_{bx}$ defect passivation observed in our experiments was predicted by Cartier et al [40]. Atomic hydrogen plasma exposure of the Si-SiO$_2$ interface results in competition reactions between passivation and depassivation of P$_{bx}$ centres. Both of these reactions occur with essentially no energy barrier, so that the fraction of P$_{bx}$ centres is determined by the reaction cross sections $\sigma_1$ and $\sigma_2$ of passivation and depassivation reactions:
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\[
\frac{[P_{bx}]^\prime}{[P_{bx}]^{\text{max}} - [P_{bx}]^\prime} = \frac{\sigma_2}{\sigma_1}
\]  

(6-1)

independent of the initial (unpassivated) $P_b$ centre density $P_{bx}$, and only weakly dependent on temperature. Here, $[P_{bx}]^\prime$ is the steady-state value of the unpassivated $P_{bx}$ centre density and $[P_{bx}]^{\text{max}}$ is the total $P_{bx}$ centre density.

The different $P_b$ centres that have been identified ($P_b$ at the (111) Si-SiO$_2$ interface, $P_{b0}$ and $P_{b1}$ at the (100) interface) appear to have quite different reaction cross sections [39, 40], leading to different degrees of steady-state passivation.

This situation can be contrasted with the accepted theory concerning the action of molecular hydrogen, which can also passivate and depassivate $P_{bx}$ centre simultaneously. In contrast to atomic hydrogen exposure, both these processes have a significant energy barrier, resulting in a strong temperature dependence of the passivation. Note that the reaction of H$_2$ with $P_{bx}$ centres creates atomic hydrogen, so that in principle, atomic hydrogen reactions will take place as well. However, these reactions are usually neglected and are assumed not to play a significant role due to the much lower densities of atomic compared to molecular hydrogen; an assumption for which there is some experimental support [23].

6.6 Effect of hydrogen plasma exposure and subsequent thermal anneal treatments on the Si-SiO$_2$ interface of planar (111) and textured (100) samples

6.6.1 Effect of hydrogen plasma exposure and subsequent thermal anneal treatments on Si-SiO$_2$ interface of planar (111) Si interface properties

Figure 6.36 shows the $J_{0e}$ values for oxidised, passivated (111) planar samples after different processing steps. (111) samples are n-type, 2K-4K$\Omega$.cm, single side polished, FZ silicon wafers. Table 6.6 summarizes the $J_{0e}$ values for two oxidised, passivated (111) samples after different process steps. The MW hydrogen plasma conditions are at room temperature and 400°C respectively, under otherwise standard conditions. RTA conditions are at 400°C in N$_2$ atmosphere for 3 minutes. The purpose of the second
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RTA (step 5 in table 6.6) is to determine whether RTA annealing at 400\textdegree C in N\textsubscript{2} ambient will result in some dehydrogenation of the Si-SiO\textsubscript{2} interface or not.

![Graph showing J\textsubscript{0e} values for (111) samples following various processing steps: step 1: FGA, step 2: H plasma 25\textdegree C and 400\textdegree C respectively, step 3: RTA 400\textdegree C, N\textsubscript{2}, 3 minutes, step 4: FGA.]

Figure 6.36. J\textsubscript{0e} values for (111) samples following various processing steps: step 1: FGA, step 2: H plasma 25\textdegree C and 400\textdegree C respectively, step 3: RTA 400\textdegree C, N\textsubscript{2}, 3 minutes, step 4: FGA.

Table 6.6. J\textsubscript{0e}(fA/cm\textsuperscript{2}) values for planar (111) samples following different processing steps (\(\Delta_1\)=step3-step1 and \(\Delta_2\)=step5-step4).

<table>
<thead>
<tr>
<th>Processing steps</th>
<th>Step 1 After FGA</th>
<th>Step 2 After H plasma</th>
<th>Step 3 After RTA</th>
<th>Step 4 After FGA</th>
<th>Step 5 RTA again</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT H plasma</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J\textsubscript{0e}</td>
<td>50</td>
<td>440</td>
<td>71</td>
<td>44</td>
<td>55</td>
</tr>
<tr>
<td>(\Delta J_{0e})</td>
<td>(\Delta_1=21)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>400\textdegree C H plasma</td>
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<tr>
<td>J\textsubscript{0e}</td>
<td>46</td>
<td>270</td>
<td>58</td>
<td>44</td>
<td>51</td>
</tr>
<tr>
<td>(\Delta J_{0e})</td>
<td>(\Delta_1=12)</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

These results, either for room temperature H plasma exposure or for 400\textdegree C exposure, show similar trend to planar (100) wafers, indicating the response to atomic hydrogen is qualitatively similar regardless of crystal orientation.
It is worth to note in table 6.6 that the RTA has clearly resulted in some depassivation (dehydrogenation) of the Si-SiO₂ interface, indicated by the increase in $J_{0e}$ ($\Delta_2$) after second RTA. Therefore the larger $J_{0e}$ following the first RTA, compared to the initial $J_{0e}$, is partly due to this, providing the thermally unstable defects introduced by atomic hydrogen have completely been removed. However, the fact that $\Delta_1$ is larger than $\Delta_2$ suggests that the degree of hydrogenation of interface thermally stable defects ($P_{bx}$ centres) following atomic hydrogen exposure was less than after the FGA. In other words, the results provide some (tentative) support to the results of Cartier that atomic hydrogen results in some depassivation of $P_B$ from an initially well passivated interface.

6.6.2 Effect of hydrogen plasma exposure and subsequent thermal anneal treatments on Si-SiO₂ interface of textured (100) Si interface properties

Figure 6.37 exhibits the $J_{0e}$ values for oxidised, passivated (100) textured samples after different process steps. Samples used for TMAH texturing are p-type, $\geq 100$ohm.cm, (100), ~500µm thick, FZ silicon wafers. Samples were textured using an isopropanol/TMAH etch solution to give a random pyramid texture with faces of near (111) orientation. In the case of a (100) wafer, the (100) and (110) planes are etched, leaving random four-sided pyramids whose faces are (111) orientation. The texturing takes around 60 minutes and the temperature is about between 85-90°C. MW hydrogen plasma conditions are standard. Table 6.7 summarizes the $J_{0e}$ values after different processing steps.
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Figure 6.37. $J_{0e}$ values for (100) textured sample following various processing steps: step 1: FGA, step 2: that after H plasma exposure in step 1, step 3: that after RTA 400°C in step 2, step 4: that after FGA in step 3.

Table 6.7. $J_{0e}$(fA/cm$^2$) values for textured (100) samples following different process steps ($\Delta_1$=step3-step1 and $\Delta_2$=step5-step4).

<table>
<thead>
<tr>
<th>Step 1</th>
<th>Step 2</th>
<th>Step 3</th>
<th>Step 4</th>
<th>Step 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>After FGA</td>
<td>After H plasma</td>
<td>After RTA</td>
<td>After FGA</td>
<td>After RTA again</td>
</tr>
<tr>
<td>$J_{0e}$</td>
<td>83</td>
<td>630</td>
<td>220</td>
<td>110</td>
</tr>
<tr>
<td>$\Delta J_{0e}$</td>
<td></td>
<td></td>
<td>$\Delta_1$=137</td>
<td></td>
</tr>
</tbody>
</table>

It can be seen from table 6.7 that, after step 3, there is an increment $\Delta_1$ of 137fA/cm$^2$, and after step 5, there is a de-hydrogenation effect, indicated by an increase of 50fA/cm$^2$ in $J_{0e}$ value. Basically, the textured surface is (111) crystal plane plus additional edges and corners. There are a few reasons of the higher $J_{0e}$ values for textured sample. The first is a larger surface area. The second is a higher fraction of dangling bonds. The third is possibly additional defects induced by film stress [122]. Again, the explanation for table 6.6 for (111) wafers can be applied here.
6.7 Effect of atomic hydrogen and subsequent thermal annealing treatments on LPCVD Si$_3$N$_4$/SiO$_2$/Si stacks

LPCVD is a reliable batch production method which provides a nearly stoichiometric (Si$_3$N$_4$) film. LPCVD Si$_3$N$_4$ has a range of properties which make it interesting for photovoltaic applications. It is an excellent diffusion mask and is resistant to chemical attack by alkaline or acidic silicon etchants. In a finished cell, Si$_3$N$_4$ provides an excellent antireflection coating. Further, LPCVD Si$_3$N$_4$ deposition is highly conformal, allowing even obscure surfaces to be coated uniformly. This is important for some cell structures such as the Sliver® cells [123].

Although LPCVD Si$_3$N$_4$ layers do not provide good surface passivation and the deposition of LPCVD Si$_3$N$_4$ directly on Si can lead to irreversible Si bulk damage, a thin layer of SiO$_2$ usually thermally grown prior to nitride deposition can be used to resolve this problem. The Si-SiO$_2$ interface properties of post-Si$_3$N$_4$-deposition are therefore of great importance, as these properties will determine the recombination properties of the silicon surface in the finished device [124]. Previous work by Jin et al. [125], using ammonia as atomic hydrogen resource, has shown that atomic H can be rapidly introduced and diffused through LPCVD Si$_3$N$_4$ films, and also demonstrated the passivation of the Si-SiO$_2$ interface of LPCVD SiN/SiO$_2$/Si stacks at a temperature of 400°C. Furthermore, an anneal in N$_2$ gas at 500°C following the ammonia plasma treatment further improved the surface passivation. In this section, some experiments were carried out to examine the effect of atomic hydrogen and subsequent thermal anneals on LPCVD Si$_3$N$_4$/SiO$_2$/Si stacks by using H$_2$ as gas source to avoid the complicating effect due to nitridation when ammonia was used.

Figure 6.38 shows the $J_{0e}$ values for nine LPCVD Si$_3$N$_4$/SiO$_2$/Si stack samples – (a) five passivated and (b) four depassivated - after different processing steps. Following standard processing, about 50nm LPCVD Si$_3$N$_4$ film was deposited on the top of the oxide. LPCVD deposition parameters were as follows: pressure: 0.5torr, ammonium, Dichlorosilane (DCS) flow rates: 120sccm, 40sccm, temperature: 775°C, time: 10 minutes. After LPCVD Si$_3$N$_4$ deposition, selected samples were dehydrogenated by N$_2$ annealing at 900°C for 30 minutes. MW hydrogen plasma conditions are an exposure power ranging from 200W to 400W for 10 minutes each side, and otherwise standard conditions. After H plasma exposure, all samples are annealed in N$_2$ at 500°C with 10 minutes, in which this annealing can minimize the loss of hydrogen bonded to interface
defects and maximize the annealing of interface defects [126]. Figure 6.39 shows the comparison of $J_{0e}$ values following different processing steps between two depassivated samples for 25 and 400°C respectively, under otherwise standard conditions and followed by an N$_2$ anneal at 500°C in N$_2$ 10 minutes.

Figure 6.38. (a) $J_{0e}$ values for passivated samples following various processing steps. step 1: FGA; step 2: LPCVD Si$_3$N$_4$ deposition; step 3: H plasma exposure; step 4: N$_2$ 500°C 10 minutes; (b) $J_{0e}$ values for depassivated samples following various processing steps. step 1: FGA; step 2: LPCVD Si$_3$N$_4$ deposition; step 3: N$_2$ 900°C 30 minutes; step 4: H plasma exposure; step 5: N$_2$ 500°C 10 minutes.
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Figure 6.39. Comparison of \(J_{0e}\) for depassivated Si\(_3\)N\(_4\)/SiO\(_2\)/Si stacks following different processing steps under H plasma temperature at 25\(^\circ\)C and 400\(^\circ\)C respectively. Step 1: FGA; step 2: LPCVD Si\(_3\)N\(_4\) deposition; step 3: N\(_2\) 900\(^\circ\)C 30 minutes, step 4: H plasma exposure; step 5: N\(_2\) 500\(^\circ\)C 10 minutes.

It can be seen from Fig 6.38 that, for passivated samples, there is a slight but not significant increase in \(J_{0e}\) after H plasma exposure, which is contrast to previous (100) planar sample results. After 500\(^\circ\)C N\(_2\) 10 minutes anneal, the \(J_{0e}\) values drop again. The reason for the decrease in \(J_{0e}\) following 500\(^\circ\)C N\(_2\) anneal is likely to be due to the hydrogen in the nitride layer, in the form of N-H and Si-H bonds which dissociate and diffuse toward the Si-SiO\(_2\) interface during thermal annealing [125]. For depassivated samples, there is greater increase in \(J_{0e}\) values after H plasma exposure. However, after 500\(^\circ\)C N\(_2\) annealing, although the \(J_{0e}\) values declined slightly, they were still higher than those following 900\(^\circ\)C N\(_2\) dehydrogenation treatment, which is contrast to Jin’s results. Meanwhile, it can be seen from fig 6.39 that the LPCVD Si\(_3\)N\(_4\)/SiO\(_2\)/Si stacks respond to atomic hydrogen plasma exposure in a similar way at both room temperature and 400\(^\circ\)C. After a 500\(^\circ\)C N\(_2\) anneal, there is little or no decrease in \(J_{0e}\), indicating no atomic hydrogen has reached the Si-SiO\(_2\) interface. In conclusion, there is no conclusive evidence, based on these results, that atomic hydrogen is actually diffusing through nitride film, which is contrast to Jin’s results [125]. The difference might be due to the different type of plasma used in Jin’s experiment, where a direct RF plasma was applied,
and it may be that H atoms had sufficient energy to be implanted deep in the nitride film. Some of the SIMS results give some support for this [125].

6.8 Effect of low temperature thermal annealing on Si-SiO\textsubscript{2} stack following MW hydrogen plasma exposure

The work in this section is focused on investigating the thermal annealing behavior of Si-SiO\textsubscript{2} interface defects introduced by atomic hydrogen using carrier lifetime and capacitance-voltage measurements. Because RTA cannot be used to give detailed annealing characteristics; in an attempt to determine these characteristics, anneals will be carried out at lower temperature and lifetime/J\textsubscript{0e} measurements carried out periodically during the anneal. Previous work [125-127] has shown that the defects are thermally unstable, however detailed properties of the defects have not been investigated.

Samples following H plasma exposure were put into the TIDLS chamber in air or N\textsubscript{2} atmosphere. The wafer can reach the target temperature within about 120 seconds. Lifetime measurements were carried out automatically at regular time intervals during the anneal process. The time interval between measurements can be varied according to requirements and 2 measurements were taken for each time interval to obtain an average.

Figure 6.40 shows the J\textsubscript{0e} dependence on annealing time and temperature for H plasma exposed samples. Five initially oxidised and passivated samples were used. After plasma exposure, a thermal anneal was carried out at temperatures in the range of 120-240\degree C for up to 20 hours in air to remove plasma-induced defects. H plasma conditions are standard with MW power 300W. The starting points at zero were just after H plasma exposure and the first annealing points were measured after 3 minutes stabilization at set temperature in TIDLS chamber. Fig 6.40 was arrived at as follows: Firstly, the J\textsubscript{0e} values measured at elevated temperatures were converted to room temperature J\textsubscript{0e} values, using the pair of J\textsubscript{0e} values (one at elevated and one at room temperature) for each sample at the end of the anneal process. After that, the initial J\textsubscript{0e} (measured prior to atomic H exposure) was subtracted, since this represents the contribution to J\textsubscript{0e} from thermally stable, unpassivated defects which will not be significantly affected by the atomic H exposure. Finally, J\textsubscript{0e} for each curve was
normalised by dividing all values by the adjusted value of $J_{0e}$ immediately following atomic H exposure ($J_{0ei}$). Table 6.8 summarizes the $J_{0e}$ results before and after thermal annealing.

Figure 6.40. $J_{0e}$ for initially hydrogen plasma exposed samples as a function of annealing temperature and time.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>After FGA</th>
<th>After H plasma</th>
<th>After 3min stabilization</th>
<th>After 20hr anneal</th>
</tr>
</thead>
<tbody>
<tr>
<td>120°C</td>
<td>30</td>
<td>690</td>
<td>570</td>
<td>510</td>
</tr>
<tr>
<td>150°C</td>
<td>32</td>
<td>690</td>
<td>410</td>
<td>330</td>
</tr>
<tr>
<td>180°C</td>
<td>31</td>
<td>680</td>
<td>250</td>
<td>130</td>
</tr>
<tr>
<td>210°C</td>
<td>30</td>
<td>700</td>
<td>150</td>
<td>74</td>
</tr>
<tr>
<td>240°C</td>
<td>34</td>
<td>660</td>
<td>100</td>
<td>60</td>
</tr>
</tbody>
</table>

The results of fig 6.40 indicate a strongly non-exponential decay of $J_{0e}$, which suggests that the annealing of the H – induced defects is not characterised by a single activation energy but by a spread of activation energies about a mean.

Figure 6.41 compares the $J_{0e}$ values following 150 and 180°C annealing. One initially oxidised and passivated sample was used. After atomic hydrogen exposure, the sample received a 150°C, 24 hours annealing. After two weeks, it was subjected to
another 150°C, 24 hours annealing and a subsequent 180°C, 22 hours annealing were carried out successively.

![Graph showing J_0e values for a H plasma exposed sample followed by successive 150°C (x2) and 180°C anneals. H plasma conditions are standard with MW 300W.](image)

Fig. 6.41. Comparison J_0e values for a H plasma exposed sample followed by successive 150°C (x2) and 180°C anneals. H plasma conditions are standard with MW 300W.

The discontinuity in the J_0e values (in fig 6.41) between the first and second 150°C anneals is most likely the result of some degradation of the oxide in this period of time. However, the rate of decrease of J_0e at the beginning of the second 150°C anneal is approximately the same as at the end of the first 150°C anneal, as would be expected. When the anneal temperature is increased to 180°C, there is a sudden and large decrease in J_0e, suggesting the removal (annealing) of some defects which were only removed very slowly at 150°C. This provides further evidence for a spread in activation energies for the removal of the thermally unstable defects.

Figure 6.42 compares the J_0e values between measuring values (fig 6.40) and calculated values from equation 6.2. More sophisticated models, which assume various distributions of activation energies, can be applied in attempt to fit the experimental data. One possibility is a Gaussian distribution of activation energies about a mean value, see equation (6.2) [23].
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\[
\frac{N(t)}{N_0} = \frac{1}{\sqrt{2\pi}\sigma_{E_a}} \int_0^\infty e^{-\left(Ea - E\right)^2 / 2\sigma_{E_a}^2} \times e^{-[\Delta H]k_0\exp(-qE/kT)} dE
\]

where \( N \) is the total density of H induced defects at time \( t \), \( N_0 \) is the density of H induced defects just after H plasma exposure, \( E_a \) is the mean activation energy for the defects, \( E \) is the activation energy, \( \sigma_{E_a} \) is the parameter determining the Gaussian spread of the activation energies, \( t \) is the anneal time, \( k_0 \) is the pre-exponential factor, \( q \) is the electron charge, \( k \) Boltzmann’s constant, and \( T \) is the anneal temperature. The parameters used for the modelling are \( E_a=1.5\text{eV}, \sigma_{E_a}=0.02 \text{ eV}, k_0=1.5\times10^{15}, T=293\text{K}. \)

![Figure 6.42. Comparison \( J_{0e} \) for initially hydrogen plasma exposed samples as a function of annealing temperature and time between test samples and a model. \( J_{0e} \) for test samples and model from fig 6.41 and equation 6.2 respectively.](image_url)

It can be seen from fig 6.42, the fit is not very good between testing and modelling results. The application of eq. (6.2) to the \( J_{0e} \) data assumes that the density of atomic H induced defects at any point in time is proportional to the \( J_{0e} \) increase. This is only a good approximation if atomic H induced defects with different annealing activation energies have nearly the same electrical properties (in particular, hole capture cross sections). In addition, more accurate measurement may contribute a better fit.
To complement the lifetime results, C-V measurements were carried out. CV samples received identical H plasma exposure processing as those lifetime samples in fig 6.40. After H plasma exposure, samples were annealed in the TIDLS chamber under a N₂ atmosphere in an analogous fashion to the lifetime samples. Samples were initially heated to 180°C for different times. This was followed by a 240°C 24 hour anneal. Figure 6.43 shows the high-frequency curve and figure 6.44 shows the corresponding Dₙ distribution of an initially passivated sample. C-V measurements were carried out after the sample had cooled down to room temperature. The same metal dot was measured every time. Figures 6.45 and 6.46 show the corresponding results for an initially depassivated sample that received otherwise identical treatment. For comparison, two as oxidized and hydrogenated (after stand FGA) or dehydrogenated (after an RTA 700°C in N₂) MOS stacks are also shown in fig 6.43 and 6.45 respectively. Figure 6.47 shows the dependence of (a) the midgap Dₙ and (b) interface charge density on the annealing time at 180°C for passivated and depassivated H plasma exposed samples. Table 6.9 summarizes the influence of annealing time and temperature on p-type Si-SiO₂ interface properties.

![HFCV curves for hydrogen plasma exposed passivated sample following annealing at 180°C for different times and a successive 240°C 24 hours in N₂.](image-url)

Fig 6.43. HFCV curves for hydrogen plasma exposed passivated sample following annealing at 180°C for different times and a successive 240°C 24 hours in N₂.
Figure 6.44. $D_{it}$ distribution for hydrogen plasma exposed passivated sample subject to identical processing in fig 6.43.

Fig 6.45. HFCV curves for hydrogen plasma exposed depassivated sample following annealing at 180°C for different times and a successive 240°C 24 hours in N₂.
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Figure 6.46. $D_{it}$ distribution for hydrogen plasma exposed depassivated sample subject to identical processing in fig 6.45.

Figure 6.47. (a) Mid gap $D_{it}$ distribution and (b) interface charge density for initially passivated and depassivated samples following H exposure and 180°C anneal.
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Table 6.9. The interface charge density \(Q(\times10^{11}\text{cm}^{-2})\) and Midgap interface defect density \(D_{itm}(\times10^{11}\text{eV}^{-1}\text{cm}^{-2})\) before and after H plasma and following annealing at 180\(^\circ\)C and 240\(^\circ\)C in a succession.

<table>
<thead>
<tr>
<th></th>
<th>passivated</th>
<th>After FGA</th>
<th>After 400(^\circ)C</th>
<th>After 180(^\circ)C</th>
<th>After 180(^\circ)C</th>
<th>After 240(^\circ)C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>plasma</td>
<td>3mins</td>
<td>10mins</td>
<td>25mins</td>
<td>60mins</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180(^\circ)C</td>
<td>180(^\circ)C</td>
<td>180(^\circ)C</td>
<td>180(^\circ)C</td>
<td>240(^\circ)C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(D_{itm})</td>
<td>0.02</td>
<td>58</td>
<td>7.7</td>
<td>4.4</td>
<td>3.0</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>22</td>
<td>3.4</td>
<td>2.1</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>(Q)</td>
<td>0.045</td>
<td>0.055</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>depassivated</th>
<th>After RTA</th>
<th>After 700(^\circ)C</th>
<th>After 180(^\circ)C</th>
<th>After 180(^\circ)C</th>
<th>After 240(^\circ)C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>plasma</td>
<td>3mins</td>
<td>10mins</td>
<td>25mins</td>
<td>60mins</td>
</tr>
<tr>
<td></td>
<td></td>
<td>180(^\circ)C</td>
<td>180(^\circ)C</td>
<td>180(^\circ)C</td>
<td>180(^\circ)C</td>
<td>240(^\circ)C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(D_{itm})</td>
<td>3.2</td>
<td>43</td>
<td>6.1</td>
<td>3.9</td>
<td>2.9</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>19</td>
<td>3.2</td>
<td>2.3</td>
<td>1.8</td>
<td>1.4</td>
</tr>
<tr>
<td>(Q)</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Several conclusions can be drawn from above results. Firstly, both initially passivated and depassivated samples show a rapid decrease in charge density following short anneals at 180\(^\circ\)C. The decay of the charge follows a similar curve to the decrease of midgap \(D_{itm}\), suggesting that the same kind of defect is responsible for both. It is worth to note that there is a significant increase in interface charge after hydrogen plasma exposure compared to previous results. This may be due to experimental error as before -slightly different exposure conditions every time resulting in different H plasma density and uniformity. Secondly, the distribution of \(D_{itm}\) is relatively uniform over the entire band-gap energy range; defects closer to the valence band edge appear to be removed slightly faster than others. Thirdly, the annealing behaviour of initially passivated and depassivated samples is very similar. Finally, the decay of \(D_{itm}\) and \(Q\) shows the same general behaviour as the decrease in \(J_{be}\) following annealing, exhibiting strongly non-exponential behaviour which implies a spread of activation energies.

6.9 Summary

The results show that, consistent with earlier observations, atomic H exposure results in the generation of additional defects at the Si-SiO\textsubscript{2} interface. These defects are efficient carrier recombination centres, are thermally unstable and can be effectively
removed by a short RTA anneal at 300°C or above. Furthermore, TIDLS anneal results show that even at lower temperature (240°C) in air or N₂, most thermally unstable defects can also be removed by longer annealing time. The annealing of this thermally unstable defect is not characterized by a single activation energy but rather by a spread of activation energies. In addition, it looks like higher plasma exposure pressure accelerates the reaction but higher exposure power (above 400W) will introduce some permanent damage which can not be removed completely by subsequent thermal treatments.

Atomic H exposure does not appear to have a significant effect on the density of thermally stable Pₜₓ centres. Following sufficiently long atomic H exposure times, the fraction of unpassivated Pₜₓ centres reaches a steady-state value which is independent of the initial passivation state of the interface. The degree of steady-state passivation shows no discernible dependence on temperature in the range 25-600°C during atomic H plasma exposure, in agreement with previous predictions [40]. In particular, at all sample temperatures in the range 25-600°C, the efficiency of defect passivation by H is lower than that afforded by H₂. The similar behaviour is observed between phosphorous diffused and undiffused samples and also between (100) planar samples and (111) planar and (100) textured samples, indicating that the presence of a phosphorous diffusion layer does not fundamentally alter the physics of interface passivation and the response to atomic hydrogen is insensitive to crystal orientation.

This result has significant implications for silicon solar cells. The front surfaces of most crystalline silicon solar cells feature a layer of silicon nitride (SiNₓ) deposited by plasma-enhanced chemical vapour deposition, which acts as an antireflection coating, a surface passivation layer and a source of hydrogen for bulk passivation. At elevated temperatures, atomic hydrogen is released from the nitride film and driven into the bulk, where it passivates defects. The interface region of such cells consists of an oxynitride layer. In addition, stacks consisting of a thin layer of SiO₂ and a thicker film of SiNₓ are also under active consideration since such stacks can, in principle, combine the advantages of the Si-SiO₂ interface (low Dₐ) with the benefits of SiNₓ. Recently, excellent surface passivation has also been demonstrated by thin Al₂O₃ films prepared by atomic layer deposition and it was verified that an interfacial oxide layer of about 1.5nm is present between the silicon and Al₂O₃ as a result of the deposition process [128]. It is noted that, while it is difficult to compare the total hydrogen flux released during silicon nitride layer deposition and subsequent thermal treatments, and the hydrogen flux during the experiments described here, possible differences in the total
flux are unlikely to have a significant impact on the results because the fraction of passivated interface defects reaches a steady state value.

The results suggest that, for oxide/nitride stacks in particular, there is no conclusive evidence that atomic hydrogen is actually diffusing through nitride film, which is contrast to previous results.
CHAPTER 7

Effect of corona charging, humidity, UV exposure and mineral acid on the Si-SiO$_2$ interface

In this chapter, the effect of corona charging, humidity, UV exposure and mineral acid on the Si-SiO$_2$ has been investigated. Especially, the purpose of the work in this chapter is to see to what extent of the annealing behaviour of the resulting defects (as measured by $J_{0e}$ and $D_{it}$) is similar to that of the defects introduced by atomic hydrogen from a plasma, as was done in the previous chapter.
Chapter 7: Effect of corona charging, humidity, UV exposure and mineral acid on the Si-SiO₂ interface

7.1 Effect of corona charging and following thermal anneal on Si-SiO₂ stacks

Corona charging, as an effective means of introducing external charges to the surface region, has been widely used for research purposes in photovoltaics due to the field-effect passivation it provides. It has been shown in the literature that corona charging can affect the Si band bending and surface recombination velocity of the Si-SiO₂ structure dramatically [129]. Surface recombination velocities lower than 1cm/s can be achieved with corona charging [130]. However, degradation can occur when the electric field is high (typically ~6MV/cm, i.e. sufficiently large to result in an appreciable tunnelling current). The damage resulting from corona charging with high electric fields is often attributed to hot electrons leading to H liberation, either in the oxide or at the oxide surface. The atomic hydrogen is then believed to diffuse to the Si-SiO₂ interface where it creates interface defects [46].

In this section, we experimentally investigate the influence of corona charging and subsequent thermal anneals on the surface passivation of the Si-SiO₂ interface in more detail. The corona charges were generated by applying a voltage of 10kV to a steel needle about 5cm above the samples. On samples for lifetime measurements, corona charging was carried out on both sides, sequentially, for equal amounts of time. On samples for C-V measurements, corona charging was carried out only on the oxidized surface on which the measurement was performed.

Samples used for lifetime measurements were p-type, 100Ω.cm, (100), FZ wafers. After standard processing, samples received corona charging and IPA rinse. CZ, p-type, (100), 8-12Ω.cm samples were used for C-V measurements. C-V samples were processed together with the lifetime samples except for the phosphorous treatment.

7.1.1 Effect of corona charging and post corona RTA on the Si-SiO₂ surface passivation

Table 7.1 shows the variation of the effective lifetime and $J_{0e}$ with processing steps for negative corona charged Si-SiO₂ stacks. A negative 10kV voltage was applied without grid between sample and needle. Five oxidised and corona charged samples were used and average values are shown. Figure 7.1 shows the variation of (a) the effective lifetime and (b) $J_{0e}$ with RTA time and temperatures for negative corona
charged samples. Prior to RTA treatments, the samples had received the treatments
detailed in table 7.1. Five oxidised and corona charged samples were used - one for each
Corresponding RTA annealing temperature. Figure 7.2 shows the dependence of midgap
\( D_{it} \) on RTA temperature for a sample that received 5 minutes positive corona charging
and a control sample (no corona charging). The samples had initially been de-
hydrogenated with a 700°C RTA for 3 minutes.

Table 7.1. Processing steps and corresponding effective lifetime(\( \mu s \)) and Emitter
saturation current density \( J_{0e} \) (fA/cm\(^2\))

<table>
<thead>
<tr>
<th>Processing steps</th>
<th>Description</th>
<th>Average effective lifetime</th>
<th>Emitter saturation current density ( J_{0e} ) (fA/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step1</td>
<td>Standard processing</td>
<td>5500</td>
<td>17</td>
</tr>
<tr>
<td>Step2</td>
<td>RTA 700°C, 3minutes</td>
<td>430</td>
<td>380</td>
</tr>
<tr>
<td>Step3</td>
<td>negative corona charging 5 minutes/side</td>
<td>850</td>
<td>160</td>
</tr>
<tr>
<td>Step4</td>
<td>Removing charges by IPA and RCA</td>
<td>160</td>
<td>440</td>
</tr>
</tbody>
</table>
Figure 7.1. (a) Effective lifetime of samples following processing steps in table 7.1 and subsequent RTA in N$_2$ for 30 to 300 seconds at temperatures ranging from 200°C to 500°C. Starting points corresponding to those of step 4 in table 7.1, (b) corresponding $J_{0e}$.

Figure 7.2. Midgap $D_{it}$ vs RTA temperatures for positive corona charged and no corona charged control samples.
Chapter 7: Effect of corona charging, humidity, UV exposure and mineral acid on the Si-SiO\(_2\) interface

It can be seen from table 7.1 that, after an RTA at 700°C, the lifetime decreases and \(J_{0e}\) increases dramatically due to the loss of hydrogen from the Si-SiO\(_2\) interface. Corona charging then causes an increase of the effective lifetime and decrease of \(J_{0e}\), which is attributed to the field passivation effect resulting from the high density of negative charge resulting from corona charging: the deposited corona charges create an electric field across Si-SiO\(_2\) interface, which reduces the surface concentration of minority carriers so that the surface recombination velocity decreased and effective lifetime is increased [129, 130]. After removing the charges by IPA and an RCA clean, the lifetime declines and \(J_{0e}\) rises again (step 4). After step 4, the lifetime is lower and \(J_{0e}\) is higher than those after step 2. It is therefore clear that the corona charging process has resulted in damage to the Si-SiO\(_2\) interface.

It is clear from fig 7.1 that the passivation quality improves with increasing RTA temperature up to 400°C. This indicates a removal of the unstable interface defects introduced by the corona charging process, consistent with that observed for atomic hydrogen [26]. Above 400°C, the lifetime decreases and the values of \(J_{0e}\) increase because anneals above 400°C can result in the loss of hydrogen from the Si-SiO\(_2\) interface, but do not modify the interface in other ways. The results strongly suggest that the corona charging introduced additional hydrogen to passivate a fraction of the (stable) interface defects, because the effective lifetime is higher, and \(J_{0e}\) is lower, following a suitable RTA treatment after corona charging, than for the sample in the de-hydrogenated state (step 2 in table 7.1).

It can be seen from fig 7.2 that, compared with the control sample, a substantial decrease in midgap \(D_{it}\) is observed for the corona charged sample between RTA annealing temperatures 200°C and 450°C for 3 minutes, and an increase at 500°C can also be observed. The C-V results from positive corona charging are consistent with the lifetime results from negative charging. The very high \(D_{it}\) values measured after positive corona charging are chiefly the result of non-paramagnetic defects, since the majority of the defects are removed by a short RTA treatment. The results therefore support the conclusion that the corona damage is mainly due to atomic hydrogen.

The results confirm that corona charging results in the introduction of additional defects to the Si-SiO\(_2\) interface, and show that these defects can be subsequently removed by an RTA treatment, which are consistent with previous results [26]. Further, both lifetime and C-V measurements strongly suggest that hydrogen has been introduced to the interface [131]. The damage observed following corona charging and
the removal of this damage following subsequent RTA treatments, are all consistent with the effects of hydrogen on the Si-SiO$_2$ interface [40]. The application of a large electric field - as was created here - leads to tunnelling of carriers across the oxide. In the case of negative corona charging, the likely mechanism is the tunnelling of electrons from the SiO$_2$ to the Si; in the case of positive corona charging electrons tunnel from the Si to the SiO$_2$. In either case, it appears that the energetic electrons liberate atomic hydrogen in the SiO$_2$, which causes the observed changes in D$_n$ and surface passivation.

### 7.1.2 Detailed investigation of annealing behaviour of defects introduced by corona charging

In this section, the thermal stability of Si-SiO$_2$ interface defects by corona charging is investigated in more detail. Figure 7.3 shows the dependence of J$_{0e}$ on annealing time and temperature for samples following corona charging. Four initially oxidised passivated samples are used. Corona charging was used to create a very high electric field across the oxide (>6MV/cm) to cause tunnelling of electrons from the silicon substrate across the oxide. The starting points at time zero in fig 7.3 are just after corona charging and before thermal annealing. The J$_{0e}$ values were normalized using the procedure employed for the results in fig 6.41. J$_{0ei}$ is the adjusted value of J$_{0e}$ immediately following corona charging. Table 7.2 summarizes the J$_{0e}$ results before and after thermal annealing.

![Figure 7.3. J$_{0e}$ dependence of annealing time and temperature after Corona charging.](image-url)
Table 7.2. $J_{0e}$ (fA/cm$^2$) values before and after corona charging and annealing.

<table>
<thead>
<tr>
<th>Annealing temperature</th>
<th>After FGA</th>
<th>After corona and IPA</th>
<th>After anneal</th>
</tr>
</thead>
<tbody>
<tr>
<td>120°C</td>
<td>30</td>
<td>200</td>
<td>86</td>
</tr>
<tr>
<td>150°C</td>
<td>32</td>
<td>220</td>
<td>61</td>
</tr>
<tr>
<td>180°C</td>
<td>31</td>
<td>250</td>
<td>49</td>
</tr>
<tr>
<td>210°C</td>
<td>30</td>
<td>170</td>
<td>37</td>
</tr>
</tbody>
</table>

It can be seen from fig 7.3 that the $J_{0e}$ values of corona charged samples reduce quickly during the first a few minutes of annealing and then enter a regime where it is only weakly affected by the longer annealing time. This result is in agreement with those in fig 6.41 in which it has been shown that H plasma exposure caused thermally unstable defects on Si-SiO$_2$ stack can be effectively removed by low temperature annealing. Similarly, with increasing annealing temperatures, the $J_{0e}$ values can recover to a level that is closer to the initial value (prior to charging). For a specific annealing temperature, annealing times longer than ~200-400 minutes do not result in a significant further decrease of $J_{0e}$. In general, the annealing behaviour of the samples following corona charging is qualitatively similar to that of samples exposed to atomic H (fig 6.41). However, there are significant differences in the shapes of the decay curves.

To illustrate this, figure 7.4 compares the $J_{0e}$ dependence on annealing time for corona charged and PECVD hydrogen plasma exposed samples after annealing at 180 and 210°C respectively, using the data from figs 6.41 and fig 7.3.
Figure 7.4. Comparison Emitter saturation current density $J_{0e}$ for initially hydrogen plasma exposed and positive corona charged samples following annealing at 180°C and 210°C respectively.

It can be seen from fig 7.4, on the one hand, PECVD atomic H plasma exposure can generate much more additional thermal unstable defects than corona charged sample under our experimental conditions, indicated by the much higher initial values from zero time. Further, after low temperature annealing under identical conditions (temperature and time), the saturation values of corona charged samples are lower than those of H plasma exposed samples at both 180 and 210°C temperature. Also, the decay curve is clearly different in shape, suggesting a different spread of activation energies for the defect annealing reaction in the two cases. Comparison of the annealing of corona-induced defects and defects introduced directly by atomic H reveals similar but not identical behavior, suggesting some differences in the nature of the defects introduced. This suggests that, while the underlying cause of the degradation is likely to be the same in both cases (atomic H), there are some differences in the generated defects, perhaps as a result of different H fluxes or other factors.
7.2 Effect of humidity on the properties of the Si-SiO$_2$ interface

Ensuring long term solar cell reliability to environmental exposure is a critical factor for photovoltaic applications. It is well known that moisture can reduce solar cell module reliability in a number of ways [132]. Lancellotti et al. [133] studied the effect of humidity on Si solar cells. In their experiments, FZ, p-type, (100), 0.3Ω.cm samples were used to fabricate the solar cell devices, which were exposed to an oven at 95°C with 100% humidity. The results show that following 60 hours exposure, the short circuit current decreased about 2%, and the integrated External Quantum Efficiency decreased 1% after 15 hours and a further 1% after 59 hours. In this section, some experiments were carried out to examine the effect of moisture on the Si-SiO$_2$ interface and the following thermal anneal results were compared to those of atomic hydrogen exposure and corona charging.

The Samples used for lifetime are FZ, p-type, (100), 100-1000Ω.cm, passivated, and FZ, n-type, (111), 91-109Ω.cm, depassivated. After standard phosphorous diffusion processing, samples received an oxidation at 1000°C for 1 hour or 30 minutes for (100) and (111) samples respectively followed by 30 minutes in situ N$_2$ anneal. Hydrogenation was realized by FGA 400°C 30 minutes and de-hydrogenation was realized by RTA 700°C 3 minutes in N$_2$. Both passivated and depassivated samples were put in a saturated humidity cabinet. Humidity conditions were: temperature 80°C, humidity concentration 100 per cent, time a week. After humidity exposure, passivated sample received an annealing at 180°C for 24 hours and followed by a 240°C for 5 hours, while depassivated samples received a RTA annealing at 300°C in N$_2$ for 1 minute.

Table 7.3 summarizes the $J_{0e}$ values of passivated and depassivated samples before and after humidity exposure and annealing. Figure 7.5 shows the $J_{0e}$ dependence on annealing time and temperature for passivated samples after humidity exposure, and figure 7.6 compares the $J_{0e}$ dependence of annealing time at 180°C for passivated samples after humidity exposure, corona charging and atomic hydrogen exposure respectively.
Table 7.3. $J_{0e}$ (fA/cm$^2$) values of passivated and depassivated samples before and after humidity exposure and annealing

<table>
<thead>
<tr>
<th></th>
<th>After FGA</th>
<th>After RTA 800°C 3mins</th>
<th>After a week humidity</th>
<th>After 24 hours 180°C</th>
<th>After RTA 300°C 1mins and IPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>passivated</td>
<td>34</td>
<td>55</td>
<td>44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>depassivated</td>
<td>77</td>
<td>670</td>
<td>600</td>
<td></td>
<td>420</td>
</tr>
</tbody>
</table>

Figure 7.5. $J_{0e}$ dependence on annealing time and temperature for passivated sample after humidity exposure.
Figure 7.6. Comparison the $J_{0e}$ dependence of annealing time for passivated samples after humidity exposure, corona charging and atomic hydrogen plasma exposure respectively and following 180°C annealing.

It can be seen from table 7.3, after the humidity exposure under our experimental conditions, the general trend of the interface modification – for passivated samples, there is degradation and for depassivated sample, there is an improvement after exposure and thermal treatments, is largely consistent with the effect of atomic hydrogen on the Si-SiO$_2$ interface. Meanwhile, it can be seen in fig 7.5 that the $J_{0e}$ values do not decline further following higher annealing temperature and the $J_{0e}$ values remain at almost the same level at 180 and 240°C, which is inconsistent to atomic H exposed and corona charged samples. Finally, it is clear from fig 7.6 that, by comparing humidity exposure, corona charging and atomic H plasma exposed samples after 180°C annealing, there is a clear difference in the $J_{0e}$ dependence of annealing time between hydrogen plasma exposure and corona charging and humidity exposure. Although the reasons for this difference are not clearly understood at present, several plausible factors are responsible for this difference such as the dose of atomic hydrogen, the stress applied on the Si-SiO$_2$ interface and some other H related species introduced into the Si-SiO$_2$ stack.
7.3 Effect of UV illumination on the Si-SiO$_2$ surface passivation

Many works have discussed how ultraviolet light can excite electrons from silicon into silicon dioxide, and how this can lead to the creation of interface states. Most of these experiments have been done on MOS capacitors in which a field drives the electrons into the oxide during UV exposure and a current through the oxide is measured.

In addition to experiments involving MOS capacitors, much of the work in this section uses diffused, oxidised wafers with voltage applied by corona charging across the oxide during UV exposure. Evidence that damage is caused by UV illumination is presented and the effects of oxidation variables on the stability of the Si-SiO$_2$ interface were examined. UV exposures were done with either sunlight or a Halogen lamp.

Figure 7.7 shows the variation of the effective lifetime and $J_{0e}$ with sunshine illumination time for positive corona charged Si-SiO$_2$ samples. Lifetime samples received standard phosphorous diffusion and followed by two different oxidations (dry oxidation and TCA oxidation) to get nearly identical oxide thickness (about 50 nm). After that, two samples—one dry oxidised and one TCA oxidised, received FGA treatment. Finally, all samples received positive corona charging and followed by sunshine exposure on both sides for identical time. Corona charge conditions are positive 8kV, 5 minutes, a steel grid was put between needle and sample to prevent charging damage and make uniform charge distribution. Starting points are from those following corona charging. Four oxidised and corona charged samples are used.
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![Graphs showing effective lifetime and J$_{0e}$ as a function of sunshine illumination time.]

Figure 7.7. (a) Effective lifetime and (b) J$_{0e}$ for initially corona charged samples as a function of sunshine illumination time.

It can be seen from fig 7.7 that, on the one hand, the degree of degradation during UV exposure is much higher for TCA oxidised samples than those dry oxidised samples. On the other hand, for TCA oxidised samples, the FGA treatment can further result in degradation. The results indicate that hydrogen content in SiO$_2$ film plays a crucial role in the degradation of Si-SiO$_2$ stack during UV exposure. One reasonable mechanism behind this phenomenon is that energetic electrons are injected from Si substrate into
the oxide and release the atomic hydrogen in it, which subsequently diffuse to the Si-
SiO₂ interface and generate defects.

Figure 7.8 shows the variation of $J_{0e}$ with halogen lamp illumination time for
positive corona charged Si-SiO₂ samples. Lifetime samples received standard
phosphorous diffusion and followed by 1000°C TCA oxidation 34 minutes, N₂ in situ
30 minutes and FGA successively. Two 300W halogen lamps used as UV sources are
set on the top of samples and distance between sample and lamp is about 20cm. Starting
points are following immediately corona charging. The straight dashed line in fig 7.8
represents the initial value before corona charging.

![Graph showing variation of $J_{0e}$ with halogen lamp illumination time.]

Figure 7.8. Emitter saturation current density $J_{0e}$ for initially corona charged samples as
a function of halogen lamp illumination time.

Compared with the line of TCA oxidation and FGA in fig 7.7, the increment of $J_{0e}$
is similar, which suggests that the damage caused by sunlight is similar to that caused
by UV light in halogen lamp.

An interesting question is whether the hydrogen source is from the dielectric film or
from the interface of dielectric and air. To further elucidate this, a SiN-SiO₂-Si stack
was designed to research the hydrogen source. Figure 7.9 shows the variation of the
effective lifetime and $J_{0e}$ with sunshine illumination time for positive corona charged Si-
SiO₂-LPCVD Si₃N₄ samples. Lifetime samples received standard phosphorous diffusion and followed by 1000°C TCA oxidation 34 minutes, N₂ in situ 30 minutes and FGA successively. Finally, 50nm LPCVD Si₃N₄ was deposited on the top of SiO₂, the LPCVD Si₃N₄ can impede the hydrogen in atmospheric moisture from diffusing into SiO₂ film. Starting points are from those following corona charging. The straight dashed line in fig 7.9 represents the initial value before corona charging.

Figure 7.9. (a) Effective lifetime and (b) Emitter saturation current density J₀ₑ for initially corona charged samples as a function of sunshine illumination time.
It can be seen results from the figure 7.9 that, even with the LPCVD Si\textsubscript{3}N\textsubscript{4} film impeding the invasion of moisture in the air into the SiO\textsubscript{2} film, degradation is still occurring in the Si-SiO\textsubscript{2} interface. And this degradation is believed mainly due to the hydrogen species existing in the TCA oxidised SiO\textsubscript{2} film.

Figure 7.10 shows the variation of $J_{0e}$ with halogen lamp illumination time for positive corona charged Si-SiO\textsubscript{2}-PECVD SiN samples. Before corona charging, lifetime samples received standard phosphorous diffusion and followed by 1000\degree C TCA oxidation 34 minutes and dry oxidation 60 minutes respectively to get nearly identical oxide thickness. After that, samples received N\textsubscript{2} in situ 30 minutes and FGA successively. Finally, 30nm PECVD SiN was deposited on the top of SiO\textsubscript{2} and followed by 400\degree C N\textsubscript{2} 30 minutes anneal. Starting points are from those following corona charging.

By comparing with two different stacks, although the starting points are different, there is a bigger increment for the TCA oxide stack. After halogen lamp illumination, the increment is 23fA/cm\textsuperscript{2} and 8fA/cm\textsuperscript{2} for TCA oxide stack and dry oxide stack.
respectively. The results in fig 7.9 and 7.10 give evidence that the hydrogen sources which lead to the UV degradation are mainly from the existing hydrogen in SiO$_2$ film.

### 7.4 Effect of mineral acid solution on the Si-SiO$_2$ surface passivation

Experimental investigations of the surface passivation of solar cell structures often require wet sample cleaning and etching steps, such as RCA cleaning and dielectric etching in hydrofluoric, phosphoric or other acids. It is usually assumed that such treatments do not affect the surface or interface properties of the samples. In this section, we investigate whether these assumptions may be invalid under certain conditions.

In this section, the effect of immersion of oxidised silicon samples in hydrochloric acid (HCl) and phosphoric acid (H$_3$PO$_4$) solutions is investigated. A combination of minority lifetime decay, C-V and EPR measurements is used to study the Si-SiO$_2$ interface defect properties and recombination velocity.

#### 7.4.1 Experimental details

Lifetime and C-V samples received standard processing measurements described in chapter 4. Samples used for EPR measurements were n-type, 3000~5500Ω.cm, (111) CZ silicon wafers. Samples were cut with a diamond saw into 25mm×2.5mm pieces. They were subsequently etched to remove saw damage from the surfaces. A ~50nm oxide was thermally grown at 1000°C in dry oxygen, followed by RTA at 700°C for 3 minutes in N$_2$, in order to dehydrogenate the Pb centres, and thus render them paramagnetic [40].

Selected samples for lifetime, C-V and EPR measurements were immersed in bottle strength (85%) H$_3$PO$_4$ solution at 170°C for 40 minutes, while other samples were immersed in bottle strength (37%) HCl solution at 60°C for 16 hours. The temperatures were well controlled.

#### 7.4.2 Effect of hydrogen introduction by acid solution on Si-SiO$_2$ interface
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Figure 7.11 shows $J_{0e}$ values for several lifetime samples. Samples 1 received an FGA after oxidation while samples 2 received a 700°C RTA. Samples 3 and 4 received a 700°C RTA and subsequent acid immersion. In addition, samples 4 received an RTA at 400°C in N₂ for 3 minutes after the acid immersion. Figure 7.12 shows the $D_{it}$ distribution within the forbidden gap following various treatments. Samples labelled ‘control 1’ and ‘control 2’ received a 700°C RTA and an FGA, respectively. Samples labelled ‘HCl’ and ‘H₃PO₄’ were immersed in acid following a 700°C RTA. All samples received a 400°C RTA prior to measurement. Figure 7.13 shows the EPR spectra for a dehydrogenated control sample and samples following dehydrogenation and acid immersion. All samples received a 400°C RTA prior to measurement. The spectra were taken with the magnetic field perpendicular to the (111) surface orientation. Table 7.4 displays values for midgap $D_{it}$ and the $P_b$ spin density. The spin density for the hydrogenated samples was below the sensitivity threshold (~$10^{12}$cm⁻²) and could not be determined. Figure 7.14 shows the C-V curves for p-type MOS stacks measured before H₃PO₄ immersion, after H₃PO₄ immersion and followed by a RTA at 400°C for 3 minutes in N₂. Immersion conditions are identical with those used above. Three depassivated samples were used. For comparison, a passivated without H₃PO₄ immersed control sample also displayed in fig 7.14. Figure 7.15 shows the corresponding $D_{it}$ distribution.

![Figure 7.11. Comparison $J_{0e}$ values for different processing samples.](image-url)
Chapter 7: Effect of corona charging, humidity, UV exposure and mineral acid on the Si-SiO₂ interface

Figure 7.12. Comparison of the $D_{\text{it}}$ distribution for control samples (control 1: dehydrogenated sample and control 2: hydrogenated sample) and samples following dehydrogenation and acid immersion.

Figure 7.13. Comparison of EPR spectra for (a) a dehydrogenated control sample, and (b), (c) samples following dehydrogenation and acid immersion. All samples received a 400°C RTA in N₂ prior to the measurements.
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Table 7.4. Comparison of midgap $D_{it} (10^{10} \text{eV}^{-1} \text{cm}^{-2})$ and spin density ($10^{12} \text{cm}^{-2}$) of HCl and H₃PO₄ immersed samples, and control samples (control 1: dehydrogenated sample and control 2: hydrogenated sample)

<table>
<thead>
<tr>
<th></th>
<th>Control 1</th>
<th>Control 2</th>
<th>HCl</th>
<th>H₃PO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{itm}$</td>
<td>5.2</td>
<td>0.78</td>
<td>2.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Spin concentration</td>
<td>24.5</td>
<td>&lt;1</td>
<td>12.3</td>
<td>4.5</td>
</tr>
</tbody>
</table>

Figure 7.14. CV curves for p type MOS stacks before H₃PO₄ immersion, after H₃PO₄ immersion, and following an RTA in N₂ for 3 minutes at 400°C, a passivated control sample also displayed.
Chapter 7: Effect of corona charging, humidity, UV exposure and mineral acid on the Si-SiO$_2$ interface

![Graph showing $D_{it}$ distribution for $\text{H}_3\text{PO}_4$ immersed depassivated sample subject to identical processing in fig 7.14.](image)

It can be seen from fig 7.11 that, following acid immersion, there is a slight increase in $J_0e$ compared to those after 700$^\circ$C RTA. However, after the 400$^\circ$C RTA, the $J_0e$ values improve dramatically, especially for the sample immersed in phosphoric acid.

It can be seen from fig 7.12 that the $D_{it}$ curves for the samples immersed in acid show a degree of passivation that is between the hydrogenated and dehydrogenated control samples, in agreement with the lifetime results.

It can be seen from fig 7.13 that the control sample has a strong and clear Pb signal, which diminishes after acid immersion.

The results in figures 7.14 and 7.15 show very similar trend as those discussed during atomic hydrogen plasma exposure. Both of the interface charge density and defect density have dramatically decreased after RTA treatment but still higher than that of passivated control sample. Clearly, such distributions are compatible with those reported following atomic hydrogen plasma exposure.

### 7.4.3 Effect of temperature and time of acid immersion on Si-SiO$_2$ interface
In this section, the effect of immersion temperature and time on the passivation of Si-SiO$_2$ interface is investigated. After acid immersion under different conditions, samples received cumulatively RTA anneal until 4 minutes. Figure 7.16 and 7.17 show H$_3$PO$_4$ and HCL immersed depassivated samples respectively. For comparison, a depassivated control sample without any acid immersion also displayed in figure 7.16 and 7.17.

Figure 7.16. (a) Effective lifetime $\tau$ and (b) $J_0e$ for samples of initially H$_3$PO$_4$ immersed at different times and temperatures as a function of RTA annealing time.
It can be seen from figures 7.16 and 7.17, it is the acid temperature rather than the immersion time that plays a critical role in the passivation effect of mineral acids on the Si-SiO₂ interface. Even 5 minutes 170°C H₃PO₄ immersion can reach nearly equivalent passivation effect to that received 40 minutes immersion sample.
The results for the different measurements clearly show that hydrogen or a hydrogen complex is diffusing into the oxide layer during acid immersion of the samples, and affecting the interface properties.

One possible explanation could be that the acid immersions result in the creation of atomic hydrogen which then diffuses into the oxide. It has been shown that exposure of the interface to atomic hydrogen results in the (incomplete) re-hydrogenation of existing Si interface defects, but also in the generation additional, thermally unstable defects, as has been observed previously for Si-SiO\textsubscript{2} interfaces exposed to atomic hydrogen [25, 26, 39]. The slight increase in $J_{0e}$ following acid immersion could be the result of the additional, thermally unstable but recombination active defects, which offset the effect of the partial passivation of existing, thermally stable defects (chiefly $P_{bx}$ centres). The subsequent 400°C RTA is sufficient to remove these additional defects without a significant loss of hydrogen from the interface, resulting in the observed $D_{it}$ and $P_b$ centre density. However, the density of unpassivated defects reduction of $J_{0e}$, as well as the reduction in both passivated interface defects is not reduced to the level achieved by the introduction of molecular hydrogen, through a forming gas anneal. Previous work has shown that atomic hydrogen exposure is not as effective at defect passivation as molecular hydrogen.

The fact that H\textsubscript{3}PO\textsubscript{4} immersion results in more efficient re-hydrogenation than HCl is probably a result of the higher temperature of the former, which leads to a faster diffusion and may also result in the availability of a higher concentration of atomic hydrogen in the solution. Differences in solution concentration and the chemical properties of the acid may also play a role. In particular, the (slow) etching of the oxide in H\textsubscript{3}PO\textsubscript{4} (estimated reduction in oxide thickness after etching ~5nm) may play an important role in the generation of atomic hydrogen.

### 7.5 Summary

The results show, on the one hand, corona charging is not necessarily a non-invasive technique and there are some difference in the nature of defects introduced between corona charging and atomic H exposure, and on the other hand, corona charging could perhaps be used as a low cost means of atomic hydrogen generation. However, it is necessary to continue to explore and find the optimum corona charging condition.
In addition, the results show that humidity and UV exposure will result in the degradation of Si-SiO$_2$ stack. The mechanism behind this is mainly due to the atomic hydrogen existed in the oxide film. For humidity exposed samples, the general trend of the interface modification, both after humidity exposure and subsequent thermal annealing, was largely consistent with the effect of atomic hydrogen on the Si-SiO$_2$ interface. For UV exposed samples, the general trend of the interface modification was largely consistent with the hydrogen redistribution model in which the atomic H in the oxide film released by hot electrons is mainly responsible for the change of the Si-SiO$_2$ interface.

Finally, the results show that the immersion of oxidised silicon samples in mineral acids can result in a modification to the Si-SiO$_2$ interface properties. Care therefore needs to be taken when such treatments are employed for the preparation of samples for characterisation. However, acid immersion could also provide a very cheap, alternative means of surface passivation due to hydrogen or a hydrogen complex diffusing into the oxide layer and affecting the interface properties.
Chapter 7: Effect of corona charging, humidity, UV exposure and mineral acid on the Si-SiO₂ interface
Summary and further work

In summary, the work of this thesis has mainly focused on the effect of atomic hydrogen on the Si-SiO\textsubscript{2} interface. Firstly, the passivation effect of thin thermal oxides grown at relatively low temperature (750-900°C), and of oxide/LPCVD nitride stacks with a low temperature oxide was investigated. Secondly, the influence of plasma atomic hydrogen on the surface passivation of the Si-SiO\textsubscript{2} interface was investigated. Finally, the degree of similarity of corona charging, humidity, UV exposure and mineral acid, in terms of their effect on the Si-SiO\textsubscript{2} interface properties compared to the effect of atomic hydrogen, was studied. The main results can be summarized as follows:

For low temperature wet oxidations, firstly, a higher oxidation temperature results in better surface passivation. A reasonable compromise may be a temperature of ~850°C. Secondly, surface orientation has a large effect on achievable surface passivation. (111) surfaces display high recombination rates even at an oxidation temperature of 850°C and following an FGA. Thirdly, the diffusion of phosphorous into the oxide results in a significant improvement in surface passivation due to a slight increase in positive charge density. However, the surface passivation deteriorates markedly if the diffusion reaches the interface.

On the other hand, for oxide/nitride stacks, firstly, a practical temperature for the LPCVD nitride deposition may be in the range 750-775°C. Secondly, the thermal stability of the surface passivation is much better than for samples with an oxide only, due to the presence of hydrogen in the nitride which re-passivates interface defects. Thirdly, even for oxide/nitride stacks, the passivation does not seem to be stable.

For the effect of atomic hydrogen on the Si-SiO\textsubscript{2} interface, the atomic H exposure results in the generation of additional defects at the Si-SiO\textsubscript{2} interface. These defects are efficient carrier recombination centres, are thermally unstable and can be effectively removed by a short RTA anneal at 300°C or above. Even at lower temperature (240°C) in air or N\textsubscript{2}, most thermally unstable defects can be removed for a sufficiently long annealing time. The annealing of this thermally unstable defect is not characterized by a single activation energy but rather by a spread of activations energies.

It is best to use MW plasma with low power and minimise exposure time to avoid plasma damage and achieve a steady state. The degree of steady-state passivation shows no discernible dependence on temperature in the range 25-600°C during atomic H plasma exposure. In particular, at all sample temperatures in the range 25-600°C, the
efficiency of defect passivation by H is lower than that afforded by H₂. The presence of a phosphorous diffusion layer does not fundamentally alter the physics of interface passivation and the response to atomic hydrogen is insensitive to crystal orientation.

A sufficiently high electric field created by corona charging results in the introduction of additional defects to the Si-SiO₂ interface and these defects can be subsequently removed by an RTA treatment, which are consistent with effects of atomic hydrogen on the Si-SiO₂ interface. Following identical low temperature anneal, both corona charging and atomic hydrogen exposed samples show similar but not identical improvement behaviour. This suggests that, while the underlying cause of the degradation is likely to be the same in both cases (atomic H), there are some differences in the generated defects, perhaps as a result of different H fluxes or other factors.

Humidity and UV exposure will result in the degradation of Si-SiO₂ stack and there is an improvement following thermal annealing. The general trend of the interface modification is largely consistent with the effect of atomic hydrogen on the Si-SiO₂ interface. The mechanism behind this is mainly due to the atomic hydrogen existing in the oxide film.

Finally, our results show that immersion of oxidised silicon samples in mineral acids can result in a modification to the Si-SiO₂ interface properties. Care therefore needs to be taken when such treatments are employed for the preparation of samples for characterisation. However, acid immersion could also provide a very cheap, alternative means of surface passivation due to hydrogen or a hydrogen complex diffusing into the oxide layer and affecting the interface properties.

From the work of this thesis, some of further work is suggested as follows:

**Determining the mean activation energy of atomic hydrogen induced defects**

In this thesis, the thermal annealing behaviour of defects introduced by atomic hydrogen at the Si-SiO₂ interface has been investigated. However, the experimental data could so far not be fitted to models describing the annealing behaviour, and hence the important parameters describing the annealing behaviour (activation energy and spread) have not been determined. Modelling the results is complicated by the fact that $J_0e$ is not only related to the defect density, but also to the charge density and the properties of the interface defects. It seems warranted to achieve more accurate post-atomic hydrogen exposure annealing results to calculate the mean activation energy of atomic hydrogen.
induced defects. This could be realized by measuring low temperature annealed samples at ‘real’ room temperature (ensuring to accurately convert all $J_{0e}$ measurements to room temperature equivalents) after sufficiently long time cooling TIDLS system (i.e. more than 2 hours). Meanwhile, a ‘control’ lifetime sample could be used in measurements. This ‘control’ sample should be a diffused sample with a good $J_{0e}$ and ideally with silicon nitride on top, thus it is not susceptible to degradation due to humidity. $J_{0e}$ measurements of this sample using TIDLS could be done every time when other annealed samples are measured at room temperature. An accurate activation energy value can direct our thermal annealing with an effective and economical measure.

UV stability of Si-SiO$_2$ stacks and Si-SiO$_2$-PECVD SiN stacks

The results presented in this thesis suggest that the source of hydrogen which leads to the UV degradation under an applied electric field is mainly the existing hydrogen in the SiO$_2$ film. More work on understanding the source of the hydrogen, and the impact that the oxide growth conditions (dry/wet, with/without TCA) have on the rate and magnitude of the degradation would be appropriate. Currently there is no clear picture on these issues from the literature. Detailed investigation of stack structures, in particular SiO$_2$/PECVD SiN$_x$ stacks could be performed, since these are of greatest practical interest. Therefore it is appropriate to investigate the influence of oxide thickness (and oxide growth conditions) on both the rate and total extent of any observed degradation. Silicon nitride layers usually contain a positive charge. The results of Black and McIntosh [54] have shown that the presence of positive charge on the surface of an oxide plays a key role in promoting degradation, and that this surface charge is neutralised by electrons injected into and across the oxide. It would be worth investigating whether a similar effect can be observed with respect to the positive nitride charge.

Comparison of passivation effect on Si-SiO$_2$-PECVD SiN stacks between H and H$_2$ following high temperature thermal anneal

The passivation effect on Si-SiO$_2$ stacks between H and H$_2$ has been investigated. However, it is the Si-SiO$_2$-PECVD SiN$_x$ stacks that attract more attention in photovoltaic community. It would be worth to investigate the difference in passivation
effectiveness on this kind of stacks between H and H₂. This could be done by measuring the appropriate quantities (D₀/J₀/J/S) at various stages of sample processing – after thermal oxidation and FGA; after PECVD SiNₓ deposition; after a subsequent high temperature treatment to release atomic H; and again after stripping the nitride layer and re-hydrogenating the oxide with an FGA.
List of Publications

Publications arising from the work in this thesis

Refereed Journal papers


Refereed conference publications:


[38]. A. Stesmans and G. V. Gorp, “Maximum density of P\textsubscript{b} centres at the (111) Si-SiO\textsubscript{2} interface after vacuum anneal,” Applied Physics Letters, 57(25), 2663, (1990).


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[56]. A. Stesmans and V. V. Afanas’ev, “Thermally induced interface degradation in (100) and (111) Si/SiO$_2$ analyzed by electron spin resonance,” Journal of Vacuum Science and Technology B, 16(6), 3108, (1998).


