Hydrogenated Amorphous Silicon Carbide Prepared using DC Saddle Field PECVD for Photovoltaic Applications

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Graduate Department of Electrical and Computer Engineering
University of Toronto

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2011

Abstract

Hydrogenated amorphous silicon carbide (a-SiC:H) can provide exceptional surface passivation essential for high-efficiency crystalline silicon solar cells. This thesis reports on the fundamental study of a-SiC:H films deposited using a novel deposition technique, DC saddle field PECVD, in contrast to the conventional industrial use of RF-PECVD. The growth conditions were optimized and correlated with passivating, structural, and optical characteristics. The lifetime has a strong dependency on deposition temperature and improves by over two orders of magnitude as the temperature increases; the maximum lifetime achieved in this work reached 0.5 ms. In addition, the Tauc optical gap can be increased from 1.7 eV to 2.3 eV by varying the precursor gas mixture ratio. Post-deposition annealing experiments demonstrate thermal stability of the samples deposited at 250 °C and in some instances shows improvement in passivation quality by a factor of two with a one-step annealing treatment at 300 °C for 15 minutes.
Acknowledgments

Firstly, I would like to acknowledge and thank my supervisor, Professor Nazir Kherani, for his support, as well as for providing the opportunity to partake in research studies in the APD Lab.

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Finally, I would like to thank Mom, Dad, and Tony for believing in me.
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List of Symbols and Acronyms

\( \alpha \) absorption coefficient

AC alternate-current

a-Si:H hydrogenated amorphous silicon

a-SiC\(_x\):H hydrogenated amorphous silicon carbide

a-SiC:H hydrogenated amorphous silicon carbide

a-SiN\(_x\):H hydrogenated amorphous silicon nitride

at. % atomic %

B\(_2\)H\(_6\) diborane

c speed of light

CH\(_4\) methane

c-Si crystalline silicon

\( \Delta E_c \) conduction band offset

\( \Delta E_v \) valence band offset

\( \Delta n_b \) bulk excess carrier density

\( \Delta n_s \) injection level

\( \Delta n_s \) surface excess carrier density

\( \Delta n \) excess carrier density of electrons

\( \Delta n \) excess carrier concentrations of electrons

\( \Delta p \) excess carrier density of holes

\( \Delta p \) excess carrier concentrations of holes

\( \Delta \sigma \) change in conductance

D\(^-\) doubly occupied defect state
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>D^+</td>
<td>unoccupied defect state</td>
</tr>
<tr>
<td>D^0</td>
<td>singly occupied defect state</td>
</tr>
<tr>
<td>D_n</td>
<td>diffusion coefficient of electrons</td>
</tr>
<tr>
<td>D_p</td>
<td>diffusion coefficient of holes</td>
</tr>
<tr>
<td>DC</td>
<td>direct-current</td>
</tr>
<tr>
<td>DCSF</td>
<td>DC saddle field</td>
</tr>
<tr>
<td>E_{binding}</td>
<td>binding energy</td>
</tr>
<tr>
<td>E_i</td>
<td>intrinsic Fermi energy</td>
</tr>
<tr>
<td>E_{kinetic}</td>
<td>kinetic energy</td>
</tr>
<tr>
<td>E_{tauc}</td>
<td>Tauc gap</td>
</tr>
<tr>
<td>E_T</td>
<td>trap energy level near the middle of the band gap</td>
</tr>
<tr>
<td>(\varepsilon_0)</td>
<td>permittivity of free space</td>
</tr>
<tr>
<td>(\varepsilon_{Si})</td>
<td>relative dielectric constant for silicon</td>
</tr>
<tr>
<td>ECD</td>
<td>excess carrier density</td>
</tr>
<tr>
<td>eV</td>
<td>electron volt</td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>G</td>
<td>generation rate</td>
</tr>
<tr>
<td>Gen 1</td>
<td>generation 1 DC saddle field system</td>
</tr>
<tr>
<td>(\eta)</td>
<td>solar cell efficiency</td>
</tr>
<tr>
<td>h</td>
<td>Plank’s constant</td>
</tr>
<tr>
<td>HF</td>
<td>hydrofluoric acid</td>
</tr>
<tr>
<td>HSM</td>
<td>high-stretching mode</td>
</tr>
<tr>
<td>InGaAs</td>
<td>indium gallium arsenide</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>short-circuit current</td>
</tr>
<tr>
<td>$K$</td>
<td>Boltzmann’s constant</td>
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<tr>
<td>$k$</td>
<td>extinction coefficient</td>
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<tr>
<td>KOH</td>
<td>potassium hydroxide</td>
</tr>
<tr>
<td>LED</td>
<td>light emitting diode</td>
</tr>
<tr>
<td>LMS</td>
<td>least mean square</td>
</tr>
<tr>
<td>LSM</td>
<td>low-stretching mode</td>
</tr>
<tr>
<td>$\mu_n$</td>
<td>electron mobility</td>
</tr>
<tr>
<td>$\mu_p$</td>
<td>hole mobility</td>
</tr>
<tr>
<td>$\mu$-PCD</td>
<td>microwave-detected photoconductance decay</td>
</tr>
<tr>
<td>MEMS</td>
<td>micro-electro-mechanical system</td>
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<tr>
<td>$N_s$</td>
<td>interface defect density</td>
</tr>
<tr>
<td>$N_s$</td>
<td>density of defects at the surface per unit area</td>
</tr>
<tr>
<td>$N_{st}$</td>
<td>density of surface states</td>
</tr>
<tr>
<td>$n_i$</td>
<td>intrinsic carrier density</td>
</tr>
<tr>
<td>$n_o$</td>
<td>thermal equilibrium concentration of electrons</td>
</tr>
<tr>
<td>$n_s$</td>
<td>surface electron carrier concentration</td>
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<td>near infrared</td>
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<tr>
<td>$\phi_n$</td>
<td>quasi-Fermi levels of electrons at the edge of the space charge region</td>
</tr>
<tr>
<td>$\phi_p$</td>
<td>quasi-Fermi levels of holes at the edge of the space charge region</td>
</tr>
<tr>
<td>$p_o$</td>
<td>thermal equilibrium concentration of holes</td>
</tr>
<tr>
<td>$p_s$</td>
<td>surface hole carrier concentration</td>
</tr>
<tr>
<td>PECVD</td>
<td>plasma-enhanced chemical vapour deposition</td>
</tr>
</tbody>
</table>
PH$_3$  phosphine

$\varphi_{\text{spectrometer}}$  work function of the XPS spectrometer

$\psi_s$  surface potential

$q$  elementary charge

$Q_s$  interface charge density

QSS-PC  quasi steady-state photoconductance

$R$  microstructure factor or absorption strength ratio

$R^2$  statistical measure of how well a regression line approximates real data points

RF  radio-frequency

$\sigma$  standard deviation

$\sigma_n$  capture cross sections of electrons

$\sigma_n^+$  capture cross-sections of the charged state of electrons

$\sigma_n^0$  capture cross-sections of the neutral state of electrons

$\sigma_p$  capture cross sections of holes

$\sigma_p^-$  capture cross-sections of the charged state of holes

$\sigma_p^0$  capture cross-sections of the neutral state of holes

$S_{\text{back}}$  back surface recombination velocity

$S_{\text{eff}}$  effective surface recombination velocity

$S_{\text{front}}$  front surface recombination velocity

$S_{n0}$  fundamental recombination velocity for electrons

$S_{p0}$  fundamental recombination velocity for holes

SE  spectroscopic ellipsometry

SiH$_4$  silane
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
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<tr>
<td>SiO₂</td>
<td>silicon dioxide</td>
</tr>
<tr>
<td>SRH</td>
<td>Shockley-Read-Hall</td>
</tr>
<tr>
<td>SRV</td>
<td>surface recombination velocity</td>
</tr>
<tr>
<td>( \tau )</td>
<td>carrier recombination lifetime</td>
</tr>
<tr>
<td>( \tau_{Auger} )</td>
<td>Auger lifetime</td>
</tr>
<tr>
<td>( \tau_{bulk} )</td>
<td>bulk lifetime</td>
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<tr>
<td>( \tau_{eff} )</td>
<td>effective lifetime</td>
</tr>
<tr>
<td>( \tau_{peak} )</td>
<td>peak effective lifetime</td>
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<tr>
<td>( \tau_{rad} )</td>
<td>radiative lifetime</td>
</tr>
<tr>
<td>( \tau_{SRH} )</td>
<td>Shockley-Reed-Hall lifetime</td>
</tr>
<tr>
<td>( T )</td>
<td>temperature</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>( U )</td>
<td>recombination rate</td>
</tr>
<tr>
<td>( U_b )</td>
<td>bulk recombination rate</td>
</tr>
<tr>
<td>( U_{DB} )</td>
<td>recombination rate through dangling bonds</td>
</tr>
<tr>
<td>( U_s )</td>
<td>surface recombination rate</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra high vacuum</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>VIS</td>
<td>visible spectrum</td>
</tr>
<tr>
<td>( V_{oc} )</td>
<td>open-voltage circuit</td>
</tr>
<tr>
<td>( \nu_{th} )</td>
<td>thermal velocity</td>
</tr>
<tr>
<td>( W )</td>
<td>wafer thickness</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
1 Introduction

For economic mass production of photovoltaic cells, new and improved technological processes that serve to decrease the cost per watt of solar electricity are desirable. The use of crystalline silicon (c-Si) for commercial high efficiency solar cells has a major drawback: the high cost of high quality crystalline substrates. Thus, a key drive in the silicon photovoltaic industry is to decrease the cost per watt of solar electricity produced by diminishing material cost. This is carried out by the reduction of silicon wafer thickness while maintaining or even increasing the conversion efficiency of silicon photovoltaics. The consequence of decreasing the wafer thickness is that it significantly amplifies the effect of surface recombination on the cell efficiency, and therefore surface passivation becomes a critical aspect of high efficiency thin silicon photovoltaic research.

Surface recombination refers to recombination processes arising from defect states due to the abrupt termination of semiconductor crystals at the surface which consists of dangling bonds, strained bonds, and missing atoms. Various materials have been utilized for the purpose of surface passivation such as silicon dioxide (SiO$_2$), hydrogenated amorphous silicon (a-Si:H), hydrogenated amorphous silicon nitride (a-SiN$_x$:H), and most recently, hydrogenated amorphous silicon carbide (a-SiC$_x$:H), hereafter referred to as amorphous silicon carbide (a-SiC:H). As seen above, the most common surface passivation technique is to directly reduce the density of surface defect states by depositing a thin hydrogenated passivating layer on the surface which saturates the surface dangling bonds with atomic hydrogen.

High quality thermal oxides require high process temperature and long growth time which are not suitable for industrial manufacturing, while amorphous silicon has poor thermal stability, unable to withstand high processing temperatures required for certain solar cell manufacturing steps. Recent studies have focused on investigating the passivating qualities of hydrogenated amorphous silicon carbide due to its widely tunable band gap, dopability ($n$ or $p$), high hydrogen content, and thermal and mechanical stability. This amorphous alloy of silicon and carbon adds an extra degree of freedom in controlling optical, electrical and thermal properties by varying the carbon-silicon ratio. Recently, literature reports using a-SiC:H grown by RF plasma-enhanced chemical vapour deposition (PECVD) method have resulted in state of the art passivation
yielding effective carrier lifetime of over 1 ms and at the photovoltaic cell level reaching 20.2% conversion efficiency [1]. An alternative deposition method with potentially significant advantages is the DC saddle field (DCSF) PECVD technique; key advantages include its scalability for uniform, large area depositions making it amenable for mass production, and its ability to separate the plasma regime from the growth regime thereby providing fine control over the growth conditions and thus high quality interfaces, films and devices.

The objective of this research is to study for the first time the potential of DCSF PECVD in the preparation of a-SiC:H. Accordingly, the goals of this thesis are to undertake a systematic investigation and optimization of the deposition of intrinsic hydrogenated amorphous silicon carbide films using the novel DC saddle field PECVD method, characterize their passivating, structural and optical properties and analyze its feasibility as a potential surface passivation candidate. The experiment research focuses on two key aspects: i) investigating the effects of varying deposition parameters (temperature, gas ratio, time) on film characteristics, and ii) examining post-deposition annealing effects on the thermal stability of a-SiC:H films. Minority carrier lifetime measurements are used to determine the quality of surface passivation, while optical characterization includes measurements of thickness, optical band gap, and absorption coefficient. Moreover, structural measurements provide information regarding carbon and hydrogen concentration in the film. The properties of these films are to be investigated as a function of the deposition conditions which include varying deposition temperature, pressure, gas flow rate, bias voltage, along with different film thicknesses. In addition, annealing experiments at various temperatures and annealing times are carried out to monitor changes in passivating characteristics, as well as hydrogen concentration to identify potential causes for changes. Furthermore, the results of DCSF PECVD films are compared with RF PECVD literature results to assess apparent advantages and disadvantages of the saddle field system.

The organization of this thesis document is as follows: Chapter 2 explains the fundamental theory of carrier recombination processes and provides background information on the properties of amorphous silicon carbide. This chapter also includes an overview of interfacial defect models which forms the basis of some of the analysis of the experimental results. Chapter 3 details the experimental apparatus of DC saddle field system and various characterization techniques. Chapter 4 presents the experimental results and analyzes the feasibility of amorphous silicon
carbide as a surface passivation material. In particular, experimental minority carrier lifetime measurements are analyzed in light of interfacial defect models to gain insight on the relative role of chemical passivation and field passivation. Finally, Chapter 5 summarizes the overall thesis achievements and limitations, and describes potential future directions for further research.
2 Background

2.1 Overview of Recombination

2.1.1 Recombination Processes

In semiconductors, carrier generation and recombination are processes that create and eliminate electron-hole pairs. Recombination of electrons and holes occurs when electrons occupy the empty states related to the holes though one or more steps; this results in both carriers annihilating each other and in the process, releasing the excess energy from the energy difference between the initial and final state of the electron. The three fundamental recombination processes in the bulk of the wafer are i) radiative recombination, ii) Auger recombination, and iii) Shockley-Read-Hall (SRH) recombination via defects and impurities. Under constant illumination, a steady-state condition is held with an equal generation rate \( G \) and recombination rate \( U \). With the assumption of equal excess carrier concentrations of electrons and holes \( \Delta n = \Delta p \), an excess carrier recombination lifetime \( \tau \) can be defined as:

\[
\tau \equiv \frac{\Delta n}{U}
\]  

(2.1)

where \( \Delta n \) is the excess carrier concentration and \( U \) is the recombination rate. The associated bulk recombination lifetimes of the three processes, \( \tau_{rad} \), \( \tau_{Auger} \), and \( \tau_{SRH} \) can be grouped together to be expressed as one single term, \( \tau_{bulk} \), the bulk lifetime as shown in Equation (2.2) [2]. From this equation, it can be seen that the recombination process associated with the smallest lifetime has the most dominant effect on the bulk lifetime.

\[
\frac{1}{\tau_{bulk}} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{Auger}} + \frac{1}{\tau_{SRH}}
\]  

(2.2)

The impact of each recombination process can vary depending on the injection level and hence the excess carrier concentration. Therefore, it is possible to extract the various parameters from different recombination processes at different excess carrier densities. For instance, Auger
recombination dominates at high injection levels where the excess carrier density is much greater than the wafer doping concentration.

2.1.1.1 Radiative Recombination

Radiative recombination, also known as band-to-band recombination or thermal recombination, involves an electron in a high energy state in the conduction band returning to a non-occupied, lower energy state in the valence band, known as a hole [2]. The direct annihilation of electrons and holes is referred to as a recombination process. Band-to-band recombination is a radiative process where the excess energy is released as a photon as the electron-hole pair recombines as illustrated in Figure 2.1. Radiative recombination is the exact reverse of absorption where an electron-hole pair is generated upon absorption of a photon [3]. The radiative lifetime, $\tau_{\text{rad}}$, characterizes radiative recombination and is dependent on the type of doping and concentration in the wafer, as well as the excess carrier concentration. However, radiative lifetime is almost always longer than the Auger lifetime and hence plays a secondary role as it does not greatly influence the lifetime of charge carriers [4].

![Figure 2.1: Band-to-band recombination of conduction band electron and valence band hole results in the release of a photon.](image)

In addition, the recombination process is slightly different for direct and indirect semiconductors as there is a large change in crystal momentum for indirect semiconductors. In addition to the emission of a photon, a phonon must be emitted to conserve momentum as shown in Figure 2.2 (b).
Figure 2.2: The Energy-Momentum plot of (a) direct and (b) indirect semiconductors illustrates band-to-band recombination. In direct semiconductors, only photons are released, whereas in indirect semiconductors, both photons and phonons are released to conserve energy and momentum.

2.1.1.2 Auger Recombination

Auger recombination involves the same type of band-to-band recombination of conduction band electron and valence band hole, but the energy released is transferred to another carrier in either the conduction or valence band instead of emitting a photon. Hence, the Auger process involves three charge carriers. The excited carrier then loses the excess energy through thermalization, in small steps as it collides with the lattice, and eventually returns to its original energy state [3]. Auger recombination is characterized by the Auger lifetime, $\tau_{Auger}$, and is dependent on the wafer doping type and doping concentration, as well as the excess carrier concentration. The Auger effect is especially dominant in high-quality silicon wafers at high excess carrier concentrations greater than the wafer doping concentration. In Figure 2.3, Auger recombination processes in the conduction band and valence band are shown in (a) and (b), respectively.
2.1.1.3 Recombination via defects and impurities

Recombination due to defects and impurities is referred to as Shockley-Read-Hall (SRH) recombination. Impurity atoms and crystal defects in the wafer introduce allowed energy levels in the mid-bandgap region and these energy trap levels, $E_T$, act as intermediaries in the recombination process for electrons and holes (Figure 2.4). These midgap transitions are known as center recombination processes.

Figure 2.4: SRH center recombination processes through defects and impurities in the mid-bandgap region of a semiconductor with the excess energy being released as phonons [5].
In the figure above, electron-hole pairs can be annihilated by recombining by two methods: i) an electron from conduction band and a hole from valence band can both be captured at the same trap site in the midgap region, and ii) a carrier can initially be captured at the trap site, then makes another transition to the opposite carrier band where it undergoes recombination [5]. SRH recombination, also known as indirect thermal recombination, is typically non-radiative as it releases the excess energy as thermal heat through phonons (lattice vibrations). Figure 2.5 below illustrates the various energy levels for different impurity elements in silicon.

![Defect energy levels of various elements in silicon](image)

**Figure 2.5:** Defect energy levels of various elements in silicon [3].

In SRH theory, the four fundamental processes involved in recombination via defect levels are as follows: a) an electron is captured by an unoccupied trap, b) an electron is emitted from the trap into the conduction band, c) a hole is captured by a trap occupied with an electron, and d) a hole is emitted from the trap to the valence band. These processes are shown in Figure 2.6, with the arrows indicating the transition of an electron. SRH recombination is characterized by the SRH lifetime, $\tau_{SRH}$, and is dependent on the impurity and defect concentration, the defect energy level, and the doping and excess carrier concentration.
Figure 2.6: The four fundamental recombination processes via defects: a) an electron is captured by an unoccupied trap, b) an electron is emitted from the trap into the conduction band, c) a hole is captured by a trap occupied with an electron, and d) a hole is emitted from the trap to the valence band. The arrows indicate the transition of an electron [6].

Additionally, donor and acceptor sites can act as intermediaries providing recombination via shallow levels. The electronic transitions of carriers are similar to those in center recombination processes, except that at room temperature, electrons captured at donor sites and holes at acceptor sites can be re-emitted to the conduction and valence bands, respectively. This occurs due to the small energy gap between the donor level and the conduction band, and similarly the acceptor level and the valence band. At room temperature, there is enough thermal energy to allow carriers to be re-emitted to the original bands before they complete the next transition to recombine. Hence, recombination via shallow levels is more observable at lower temperatures as the probability of recombination occurring increases with decreasing wafer temperature.

Figure 2.7: Recombination via shallow donor and acceptor levels occurs similarly
Moreover, recombination can occur via defects and impurities at the surface of a wafer. Instead of being characterized in terms of lifetime, surface recombination is quantified using the term surface recombination velocity, $S$ [cm/s]. The combination of bulk and surface recombination processes can be expressed collectively using the term effective lifetime, $\tau_{eff}$, given by:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{S_{front}}{W} + \frac{S_{back}}{W}$$

(2.3)

where $W$ is the wafer thickness and $S_{front}$ and $S_{back}$ are the surface recombination velocities related to the surface recombination on the front and back sides of the wafer, respectively [4].

In Figure 2.8, recombination is shown, in the context of an illuminated silicon solar cell, to occur at three main sites: i) blue light photogenerated carriers recombine at the front surface, ii) intermediate-wavelength light photogenerated carriers recombine in the bulk of the wafer, and iii) red light photogenerated carriers recombine at the back surface or deep in the wafer [7]. The theory of surface recombination is explained in more details in the following section.

**Figure 2.8:** Potential recombination sites at the front and back surface and the bulk of a wafer [7].
2.1.2 Surface Recombination Fundamentals

Due to the abrupt termination of semiconductor crystals, surfaces and interfaces usually have a large density of recombination centers, that is, electronic states within the bandgap. In addition, impurities on the surface arising from various processing steps contribute to recombination via impurity defect states. Surface recombination occurs when a conduction band electron recombines with a valence band hole via a surface state defect located within the bandgap. From the Shockley-Read Hall (SRH) theory [8], the recombination process at the surface can be mathematically described by Equation (2.4) given below. The recombination rate $U_s$ through a surface state at a single trap energy level $E_t$ is given by:

$$U_s = \frac{n_s p_s - n_i^2}{S_{p0} + \frac{p_s + p_1}{S_{n0}}} \left[ cm^{-2}s^{-1} \right]$$  \hspace{1cm} (2.4)

where $S_{n0} = \sigma_n v_{th} N_s$, $S_{p0} = \sigma_p v_{th} N_s$, $n_1 = n_i \exp \left( \frac{E_t - E_i}{kT} \right)$, $p_1 = \frac{n_i^2}{n_s}$ where $S_{n0}$ and $S_{p0}$ are fundamental recombination velocities, $n_s$ and $p_s$ are surface electron and hole carrier concentrations, respectively, $\sigma_n$ and $\sigma_p$ are capture cross sections of electrons and holes, respectively. $N_s$ is the density of defects at the surface per unit area, $n_i$ is the intrinsic carrier density, $E_i$ is the intrinsic Fermi energy, $v_{th}$ is the thermal velocity, $k$ is Boltzmann’s constant, and $T$ is the temperature.

Using an analogy to the bulk expression, $U_b \equiv \Delta n_b / \tau_b$, where $\Delta n_b$ is the bulk excess carrier density and $\tau_b$ is the bulk carrier lifetime, the surface recombination velocity (SRV), $S$, can be defined as $U_s \equiv S \Delta n_s$, where $\Delta n_s$ is the surface excess carrier density. Under flat band conditions at the surface, the excess carrier density of electrons and holes are equal ($\Delta n_s = \Delta p_s$) [8]. In this particular case, the SRV can be expressed as Equation (2.5) below by substituting $n_s = n_o + \Delta n_s$ and $p_s = p_o + \Delta p_s$, where $n_o$ and $p_o$ are the thermal equilibrium concentration of electrons and holes.

$$S(\Delta n_s) = \frac{(n_o + \Delta n_s)(p_o + \Delta n_s) - n_i^2}{n_o + \Delta n_s + n_i + \frac{p_o + \Delta n_s + p_1}{S_{n0}}}$$  \hspace{1cm} (2.5)
This equation shows that the surface recombination velocity depends on a number of parameters including the properties of surface states (trap energy level), the injection level $\Delta n_s$, and the doping density ($n_o, p_o$). In addition, Equation (2.5) assumes that the excess carrier concentration of electrons and holes are equal. However, in practical devices, $\Delta n_s \neq \Delta p_s$ due to surface band bending as a consequence of field-effect passivation and accordingly the SRV must be calculated from Equation (2.4). Therefore, it is useful to establish a virtual surface within the wafer at the edge of the space charge region and define an effective surface recombination velocity, $S_{\text{eff}}$, shown below:

$$U_s = S_{\text{eff}} \Delta n(x = d)$$  \hspace{1cm} (2.6)

where $\Delta n$ is the minority carrier density. At $x = d$, the limit of the surface space charge region, the photogenerated excess carrier densities in the bulk crystalline silicon are equal, $\Delta n(x = d) = \Delta p(x = d)$.

Based on Equation (2.4) which relates recombination rate and surface state properties, there are two ways to minimize surface recombination: i) reducing the density of surface states ($N_s$) by appropriately passivating the defect states on the surface, and ii) reducing the surface concentration of one type of free carriers ($n_s$ or $p_s$) by forming a built-in field to repel charges. These surface passivation techniques are reviewed in the next section. Moreover, the quality of surface passivation can be evaluated using a measurable parameter: the effective lifetime, $\tau_{\text{eff}}$. The effective lifetime is an averaged carrier lifetime representing an effective sum of all the recombination processes, bulk and surface; $\tau_{\text{eff}}$ is related to the effective surface recombination velocity by Equation (2.7) below [9]:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{2S_{\text{eff}}}{W}$$  \hspace{1cm} (2.7)

For a high purity float-zone wafer, the bulk lifetime, $\tau_{\text{bulk}}$, can be assumed to be very large and hence does not have a big influence on the effective lifetime. It is then possible to calculate $S_{\text{eff}}$ from the measured $\tau_{\text{eff}}$ and the wafer thickness, $W$. The best quality of surface passivation is resembled by a minimum $S_{\text{eff}}$ value.
2.1.3 Impact of Lifetime on Efficiency

The lifetime of the excess carriers in the wafer can have a large influence on the overall solar cell efficiency. If the lifetime is shorter than the transit time it takes for a carrier to move across the wafer thickness, then the carrier will recombine before it can be collected as usable current. Therefore, it is necessary for the lifetime to be higher than the transit time in order to generate solar power. Furthermore, as the lifetime in the wafer increases, the current can be collected at even higher voltages, and hence produce more solar power [10]. For standard solar cells, the efficiency is dependent on the lifetime up to a certain degree; then other types of losses will nullify any further efficiency gains from additional lifetime increases. On the other hand, high-efficiency solar cells are exceedingly dependent on the excess carrier lifetime as recombination losses are the most crucial parameter. Solar cells with higher lifetimes usually result in higher efficiencies, keeping all other solar cell designs and parameters the same. Hence, it is essential to improve the lifetime by reducing recombination, specifically, the most critical aspect of thin wafer solar cells: the surface recombination velocity.

2.1.4 Surface Passivation Techniques

The two main methods of surface passivation are the saturation of defects (dangling bonds) and field effect passivation. Field effect passivation involves band bending at the surface which creates an internal electric field, and thus repelling and reducing the surface concentration of one type of charge carriers. This effectively reduces the recombination rate since both types of carriers (electrons and holes) are needed for the process. If the carrier concentrations of electrons and holes are equal, then the probability of recombination processes taking place is maximized; conversely, an unbalanced proportion of charge carriers results in the reduction of $S_{eff}$. The electric field can be formed by a number of methods including creating a high-low junction ($p^+\cdot p$ or $n^+\cdot n$) or a p-n junction, inducing a charge on the surface by depositing a charged film and applying a gate voltage.

The saturation of defects at the surface results in a direct reduction of the density of surface states ($N_S$), which in turn diminishes the $S_{eff}$. This is achieved by depositing a thin passivating layer on the silicon surface and atomically saturating the surface dangling bonds; for example, atomic hydrogen serves to effectively saturate/passivate silicon dangling bonds [9]. Since the
presence of surface impurity defects contributes to recombination, it is important to effectively clean the silicon surface using standard RCA cleaning techniques. Additionally, it is important to chemically passivate the silicon surface prior to undertaking the deposition of passivating layers, thereby ensuring that the surface is not chemically active and hence resistant to impurities. A standard chemical passivation technique involves dipping silicon wafers in hydrofluoric acid (HF) which strips any native oxide and terminates the surface with atomic hydrogen [3]. Furthermore, deposition of a passivation layer can serve both functions of chemically passivating the dangling bonds through a reduction in the surface defect density, and field passivation through a trapped-charge induced electric field; an example of this is a dielectric layer of thermal SiO₂ on crystalline silicon [11].

A number of surface passivation materials have been investigated prepared using a variety of film growth techniques. Additionally, it is important to consider the application of the surface passivation layer. For example, front surface passivation ideally requires transparency and antireflective properties while the back surface requires a high refractive index to reflect light back into the cell. Moreover, additional passivation methods include forming a high-low junction at the rear (back surface field) and creating p-n junction using doped emitters [8].

Thermally grown silicon dioxide (SiO₂) has been the optimum choice for passivating crystalline surface due to its excellent passivating performance in reducing surface state density, as well as introducing field-effect passivation due to fixed positive oxide charges [12]. However, in order to increase the throughput, and to mitigate degradation of crystalline silicon and decrease the thermal budget due to high temperature processing (900-1100°C), alternative materials have been grown by low temperature plasma-enhanced chemical vapour deposition (PECVD) such as hydrogenated amorphous silicon (a-Si:H), hydrogenated amorphous silicon nitride (a-SiNx:H), and hydrogenated amorphous silicon carbide (a-SiC:H). PECVD is a glow-discharge plasma technique in which precursor gases are transformed into radicals and ions which impinge on a given substrate and thus lead to the growth of a film. The plasma is generated by an electric field, where vapour-phase chemical reactions occur due to excitation and decomposition of precursor gases. The power source of the electric field can either be DC or AC (commonly, radio frequency of 13.56 MHz is used). These PECVD amorphous silicon-based compounds can offer lower manufacturing costs and potential for large area scalability for industrial production while maintaining excellent passivating qualities. Hydrogenated amorphous silicon passivates the
crystalline surface by direct reduction of surface state density through defect saturation. Hydrogenated amorphous silicon nitride is presently the state of the art material for crystalline silicon passivation due to its antireflective properties in addition to its relatively excellent surface passivation qualities. It mainly passivates through field effect passivation given the high fixed charge density in the film. Recent studies are focusing on investigating the passivating qualities of hydrogenated amorphous silicon carbide due to its widely tunable band gap, dopability (n or p), high hydrogen content, and thermal and mechanical stability [12].

In summary, it is worthy to note that passivation layers need to meet certain key conditions in order to qualify as industrially viable application materials. First, the film must have excellent passivating qualities with minimal $S_{eff}$ and corresponding high effective lifetime. Second, the deposition process must be fast to lower the cost and increase throughput. Third, the layer must maintain its passivating characteristics throughout the solar cell fabrication process [13].

2.2 Hydrogenated Amorphous Silicon Carbide

2.2.1 Properties and Motivations

Hydrogenated amorphous silicon carbide (a-SiC$_x$:H) has a number of advantages that can be beneficial to crystalline silicon surface passivation. It is widely deposited by RF plasma enhanced vapour deposition (PEVCD) technique through the decomposition of silane (SiH$_4$) and methane (CH$_4$) gases and can be doped by phosphorous or boron using phosphine (PH$_3$) or diborane (B$_2$H$_6$) gases, respectively. The main motivations for using a-SiC$_x$:H as a passivating layer are: i) excellent passivation quality on crystalline silicon due to high hydrogen content which promotes saturation of dangling bonds, ii) tunable wide band gap making it amenable as an optical window layer, iii) thermally stability, where it can withstand medium to high temperature processing, and iv) n- and p- dopability to implement emitter layers in heterojunction cells. This amorphous alloy of silicon and carbon adds an extra degree of freedom in controlling optical, electrical and thermal properties by varying the carbon-silicon ratio. Typically, the band gap of a-SiC$_x$:H ranges from 1.8-3.85 eV depending on carbon content; this high band gap leads to lower parasitic light absorption which is desirable for its usage as an emitter layer [14]. The band gap widens as the carbon concentration increases, but the trade off
entails degrading electronic properties due to an increased disorder in the atomic network [15]. The band gap values for various passivating films are listed in Table 2.1.

**Table 2.1:** Band gap values for various films [14], [16].

<table>
<thead>
<tr>
<th>Film</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal SiO$_2$</td>
<td>8.9</td>
</tr>
<tr>
<td>a-Si:H</td>
<td>1.7</td>
</tr>
<tr>
<td>a-SiN$_x$:H</td>
<td>2-4</td>
</tr>
<tr>
<td>a-SiC$_x$:H</td>
<td>1.8-3.85</td>
</tr>
</tbody>
</table>

2.2.2 Applications

Hydrogenated amorphous silicon carbide has potential to be used in a number of applications in various types of solar cells as listed below:

1. Homo junction crystalline silicon solar cells
   - Front and rear surface passivation layer
2. Amorphous – crystalline silicon heterojunction solar cells
   - Front and rear surface passivation layer
   - Passivating emitter layer
3. PIN amorphous silicon solar cells
   - P-window layer

Furthermore, this material has been explored in biomedical, optoelectronic, and IC fields for various applications. For example, a-SiC:H films has been investigated as hermetic encapsulation materials for neural interface devices due to its biocompatibility in implantable devices [17]. However, the thickness of the films, ranging from 0.55 to 2.4 µm, is much larger than the thickness typically used for surface passivation of solar cells. Additionally, amorphous silicon carbide has been explored in the application of X-ray mask lithography due to its physical and optical properties, including hardness, high Young’s modulus, and optical transparency [18].
Other applications include the use of a-SiC:H photodiodes in optical communications [19], optical sensors [20], LEDs [21], and MEMS [22].

2.2.3 State of the art

As previously mentioned, excellent surface passivation is attributed to a minimum $S_{\text{eff}}$ value and this parameter can be used to compare between different samples. The lowest $S_{\text{eff}}$ for hydrogenated amorphous silicon carbide achieved are 5 cm/s and 22 cm/s for p-type and n-type wafers, respectively [23]. With the basis of effective surface passivation, significant device performance can be realized. For example, the state of the art for a-SiC$_x$:H rear surface passivation for a full solar cell structure (p-type wafer) resulted in best efficiency of 20.2% and $V_{oc}$ of 665 mV [1], while application as an emitter layer in a heterojunction solar cell (p-type wafer) resulted in efficiency of 18.2% and $V_{oc}$ of 689 mV [14]. The rear passivation results are shown in Table 2.2. Furthermore, the effective lifetime and open-circuit voltage improved significantly with post-deposition thermal annealing steps, with lifetime improvement by a factor of 2.2 [23] and $V_{oc}$ increase of 100 mV [14].

**Table 2.2:** State of the art solar cell results with a-SiC$_x$:H rear passivation [1].

<table>
<thead>
<tr>
<th>Area (cm$^2$)</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>$\eta$ Efficiency (%)</th>
<th>$\tau_{\text{eff}}$ (ms)</th>
<th>$S_{\text{eff}}$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>665</td>
<td>37.5</td>
<td>80.3</td>
<td>20.2</td>
<td>2.0</td>
<td>6.25</td>
</tr>
</tbody>
</table>

2.2.4 Band Diagram

The band diagram of the heterostructure of a-SiC:H and c-Si is displayed in Figure 2.9 below; it does not include the presence of surface states. The work function of a-SiC:H is calculated to be approximately 4.04 eV assuming the Fermi level is at mid-gap, while the electron affinity is around 2.76 eV [24]. Since the amorphous silicon carbide electron affinity is smaller than that of crystalline silicon (4.05 eV), an accumulation of electrons at the c-Si surface occurs as shown in the figure. The difference in the band gaps between the two materials causes discontinuities in the conduction band and valence band at the metallurgical junction at thermal equilibrium which
results in uniform Fermi level across the two materials. The conduction and valence band offsets are $\Delta E_c = 1.27 \text{ eV}$ and $\Delta E_v = 0.15 \text{ eV}$, respectively. The sum of the valence band and conduction band offsets is equal to the difference in the band gaps of the two materials as shown in Equation (2.8).

$$\Delta E_g = \Delta E_c + \Delta E_v$$

Figure 2.9: The energy band diagram of intrinsic a-SiC:H and n-type c-Si heterojunction under zero bias (not to scale). The band gap of this a-SiC:H film is 2.52 eV [24].

2.3 Surface Recombination Fitting Models

The surface recombination occurring at the crystalline silicon to amorphous silicon carbide interface can be modeled to determine interface properties. By fitting the effective surface recombination velocity ($S_{\text{eff}}$) parameter, it is possible to extract the interface defect density, $N_s$, and interface charge density, $Q_s$, which can reveal the effects of chemical and field effect
passivation. $S_{\text{eff}}$ can be determined as a function of excess carrier density by rearranging the effective lifetime equation:

$$S_{\text{eff}} = \left( \frac{1}{\tau_{\text{eff}}} - \frac{1}{\tau_{\text{bulk}}} \right) \frac{W}{2} \quad (2.9)$$

The widely used SRH model describes surface recombination using interface traps as recombination centres. Each discrete trap has two possible charged states and it is assumed that all traps occupy the same energy level, $E_T$ [25]. Simplifying Equation (2.4), the recombination rate, $U_{\text{SRH}}$, is given by:

$$U_{\text{SRH}} = \frac{n_s p_s}{n_s/\sigma_p + p_s/\sigma_n} v_{th} N_s \quad (2.10)$$

where $N_s$ is the surface defect density, $v_{th}$ is the thermal velocity, $n_s$ and $p_s$ are surface electron and hole carrier concentrations, respectively, $\sigma_n$ and $\sigma_p$ are capture cross sections of electrons and holes, respectively. The surface recombination rate can be related to the experimentally determined $S_{\text{eff}}$ values by:

$$S_{\text{eff}} = U_{\text{SRH}} / \Delta n \quad (2.11)$$

where $\Delta n$ is the excess carrier concentration. However, the bare crystalline silicon surface features dangling bonds (DB), which have three charged states. Olibet et al. proposed to model the interface recombination taking into account for such amphoteric defects (dangling bonds) [26]. Each dangling bond state can be occupied by zero, one, or two electrons, and hence leading to three different charge states of the trivalent bonded silicon sites, $\text{Si}_3$ [27]. The three states are i) $D^+$: positively charged when the DB is not occupied by any electrons forming $\text{Si}_3^+$, ii) $D^0$: neutral charged with one electron occupation forming $\text{Si}_3^0$, and iii) $D^-$: negatively charged when occupied by two electrons forming $\text{Si}_3^-$. With these three possible states, two parallel recombination paths can occur with each path consisting of two successive capture events:

1) (a) $D^0 + \text{hole} \rightarrow D^+ \text{ (hole capture cross-section } \sigma_p^0) \)
   
   (b) $D^+ + \text{electron} \rightarrow D^0 \text{ (electron capture cross-section } \sigma_n^+)$
2) (a) \(D^0 + \text{electron} \rightarrow D^-\) (electron capture cross-section \(\sigma_{n}^0\))

(b) \(D^- + \text{hole} \rightarrow D^0\) (hole capture cross-section \(\sigma_{p}^-\))

These two recombination paths are illustrated in Figure 2.10 below.

**Figure 2.10:** Two dangling bond recombination paths exist simultaneously each consisting of two successive capture events through \(D^0\). \(n_f\) and \(p_f\) are the free-carrier densities, \(D^+, D^0,\) and \(D^-\) are the positively, neutral, and negatively charged states, and \(r_p^0, r_n^+, r_n^0,\) and \(r_p^-\) are the respective capture rates [26].

Using the model of recombination via dangling bonds with three charge state conditions, the recombination rate, \(U_{DB}\), is given as:

\[
U_s = U_{DB} = \frac{n_s \sigma_{n}^0 + p_s \sigma_{p}^0}{p_s \frac{\sigma_{p}^0}{n_s \sigma_{n}^0} + 1 + \frac{n_s \sigma_{n}^0}{p_s \sigma_{p}^0}} v_{th} N_s
\]  

(2.12)

where \(N_s\) is the surface defect density, \(v_{th}\) is the thermal velocity, \(n_s\) and \(p_s\) are surface electron and hole carrier concentrations, respectively, \(\sigma_{n}^0\) and \(\sigma_{p}^0\) are capture cross-sections of the neutral states and \(\sigma_{n}^+\) and \(\sigma_{p}^-\) are capture cross-sections of the charged states.
Furthermore, the surface charge, $Q_s$, induces surface band bending and results in a surface potential, $\psi_s$. Thus the surface carrier densities $n_s$ and $p_s$ are different from the bulk carrier densities, and are then given by Equations (2.13) and (2.14):

$$n_s = (n_0 + \Delta n) \exp \left( \frac{q \psi_s}{kT} \right)$$  \hspace{1cm} (2.13)

$$p_s = (p_0 + \Delta n) \exp \left( - \frac{q \psi_s}{kT} \right)$$  \hspace{1cm} (2.14)

The surface potential, $\psi_s$, is has to be numerically determined as it is given by the nonlinear equation below:

$$Q_{Si} = \pm \sqrt{\frac{2kTn_1\varepsilon_0\varepsilon_{Si}}{q^2}} \left[ e^{q(\phi_p-\psi_s)/kT} - e^{q\phi_p/kT} + e^{q(\psi_s-\phi_n)/kT} - e^{-q\phi_n/kT} + \frac{q\psi_s(p_0 + n_0)}{kTn_i} \right]$$  \hspace{1cm} (2.15)

where $Q_{Si}$ is the total charge density induced in the c-Si by $Q_s$, $\phi_n$ and $\phi_p$ are the quasi-Fermi levels of electrons and holes at the edge of the space charge region, $n_0$ and $p_0$ are the equilibrium electron and hole densities, respectively, $T$, $k$, $\varepsilon_0$, $\varepsilon_{Si}$, $n_i$, and $q$ are the temperature, Boltzmann constant, permittivity of free space, and relative dielectric constant for silicon, intrinsic carrier density, and the elementary charge, respectively. $\phi_n$ and $\phi_p$ are given by the equations $\phi_n = -(kT/q) \ln[(n_0 + \Delta n)/n_i]$ and $\phi_p = +(kT/q) \ln[(p_0 + \Delta n)/n_i]$.

Using Equations (2.12) - (2.14), measured surface recombination velocity data as a function of excess carrier density can be fitted with the Olibet model described above, and extract the parameters of interface defect density and the interface charge density. In this thesis, the following were assumed: $v_{th} = 2 \times 10^7 \text{cm/s}$, $\sigma_n^+ / \sigma_n^0 = 50$, and $\sigma_p^- / \sigma_p^0 = 0.25$ [28].

An example of the fit is shown in Figure 2.11, demonstrating a fit with a least mean square value of 0.001372.
Figure 2.11: An example of a $S_{\text{eff}}$ fit using the Olibet Thermal model.
3 Experimental Apparatus and Characterization Techniques

3.1 DC Saddle Field System

While most of the research on a-SiC$_x$:H has been with the use of radio frequency plasma-enhanced chemical vapour deposition (RF-PECVD) systems, this thesis is focused on using the novel DC saddle-field (DCSF) technique. The DCSF system uses DC power rather than the commonly used AC radio frequency (RF) power to generate the plasma, and also differs from traditional DC systems which consist of a simple dual-electrode diode setup. DCSF utilizes a simple DC power source and does not require the complex matching network in RF powered PECVD. The complete DCSF PECVD system layout including the gas delivery and vacuum system is shown below in Figure 3.1.

![Figure 3.1: A schematic layout of the complete DCSF PECVD system [29].](image-url)
The saddle-field deposition technique is based on the idea of extending the mean free path of electrons by oscillating them in a symmetric DC electric field along the axis of the plasma chamber [30]. Thus, the probability of ionizing collisions between the electrons is greatly increased. The DC electric field, and hence the plasma, is created between a positively biased central anode and each of the two grounded cathodes symmetrically or asymmetrically placed on either sides of the anode as shown in Figure 3.2. Semi-transparent wire grids are used for the anode and cathodes to allow electrons to oscillate through the anode and also allow activated gas species to pass through the cathode towards the substrate placed beyond the cathodes. The impinging activated gas species adsorb on the substrate positioned outside of the plasma region, leading to the growth of the desired thin film. Due to this configuration of the electrodes, the density of electrons increases significantly compared to the conventional DC system, and results in a higher probability of impact ionization which contributes to the activation of precursor gas species [31]. This technique not only affords the ability to separate the plasma from the growth regime, but is also easily scalable to allow large area depositions thus making it amenable for industrial application. In addition, DCSF system operates at lower pressures than RF system (less than 200 mTorr) and permits independent biasing of the substrate.

**Figure 3.2:** DC saddle-field PECVD system (Gen 1) [31].
A variety of saddle field configurations can be arranged by appropriately choosing the relative placement of the electrodes and the number of electrodes. Additionally, the distance between the electrodes and the transparency of the grids can be altered to provide different conditions for DCSF plasma. In this thesis, tetrode configuration, sometimes referred to as the shielded triode configuration, was used to establish a remote plasma that is farthest removed from the substrate, as shown in Figure 3.3. The remote plasma is generated about the semi-transparent anode with the semi-transparent cathode on the substrate side and the solid cathode on the other side. The ions and radicals created in the plasma traverse through the semi-transparent cathode towards the substrate; the ions are driven by the electric field due to the sheath at the cathode while the radicals are driven by diffusion. This arrangement provides growth of the film over a large area albeit the growth rate is low.

Figure 3.3: A schematic of the tetrode configuration of the DC Saddle Field PECVD system which provides low ion energy film growth environment owing to the remote plasma. The tetrode configuration was operated such that the cathode grid was held at ground potential and the substrate was connected to ground via a 1 ohm resistor, the latter permitting measurement of the current impinging on the substrate.

Every effort was made to ensure that each experiment was carried out under identical chamber conditions. Specifically, a clean stainless steel shield was placed on the inside diameter/wall of
the chamber, clean anode and cathode grids were installed, and the samples were placed on a cleaned substrate holder. After each deposition, the stainless shield and the grids were cleaned by soaking them in a hot KOH bath which served to etch off the deposited amorphous silicon carbide film. These were subsequently rinsed with deionized water and then dried in an oven prior to being placed in the chamber for another deposition. The stainless steel grids and the DC saddle field system are pictured in Figure 3.4 and Figure 3.5 below.

**Figure 3.4:** The substrate holder and chamber grids after a deposition.

**Figure 3.5:** DC Saddle Field system used in this thesis.
3.2 Sample Preparation

The lifetime samples require the use of low resistivity wafers with the following parameters:

- 100 mm diameter
- n-doped float-zone wafer
- 260-300 µm thickness
- 1-5 Ω cm resistivity
- <100> orientation, double side polished

Transmission measurements using FTIR require high resistivity wafers with the following parameters:

- 100 mm diameter
- n-doped float-zone wafer
- 498-524 µm thickness
- > 30 Ω cm resistivity
- <100> orientation, double side polished

The wafers were purchased pre-cleaned using RCA-1 and RCA-2 procedures to remove any organic and metal residues. Over time, the silicon is oxidized resulting in a thin layer of native oxide on the surface of the wafer. Therefore, before each deposition, the wafer was dipped in 5% hydrofluoric (HF) acid for 30 seconds to etch away the oxide. After the HF dip, the wafer was spun dry and immediately transported to the deposition system to be placed in the substrate holder. Although the HF cleaning process takes place inside the nitrogen glove box to minimize oxidation, samples are still exposed to air for a short period of time (5 minutes) before being loaded in the vacuum system.

3.3 Sinton Lifetime Tester

The effective lifetime is a good measure of the quality of surface passivation and can be measured using two different instruments: the Sinton WCT-120 lifetime tester and the Semilab μ-PCD (microwave-detected photoconductance decay) tester. The Sinton apparatus performs
effective lifetime ($\tau_{\text{eff}}$) measurement as a function of excess carrier density (ECD) using the quasi steady-state photoconductance (QSS-PC) technique. This method allows for contactless measurement of wafers by generating excess carriers in the bulk using flash lamp illumination and detecting conductance changes in the sample. The intensity of illumination is slowly reduced over a few milliseconds to keep the recombination processes in steady state while preventing the sample to heat up [32]. The Sinton tester employs the Eddy-current method, where a coil circuit under the sample holder detects the increase in sample conductance as the illumination generates excess carriers in the wafer. The conductance ($\Delta \sigma$) data is first converted to excess carrier density ($\Delta n$) using the relationship in Equation (3.1) [33], where $q$ is the elementary charge, and $\mu_n$ and $\mu_p$ are the electron and hole mobilities, respectively. Then, the carrier lifetime can be determined using the ambipolar transport equation as shown in Equation (3.2), where $D_n$ is the diffusion coefficient, $G$ is the excess carrier generation rate, $\tau_n$ is the minority carrier lifetime, and $\Delta n$ is the excess minority carrier concentration. This equation describes the diffusion, drift, generation, and recombination of minority carriers as a function of time and space. The lifetime analysis assumes a uniform distribution of excess carriers ($D_n \frac{\partial^2 (\Delta n)}{\partial x^2} = 0$) and a zero electric field ($\mu_n E \frac{\partial (\Delta n)}{\partial x} = 0$).

$$\frac{1}{\Delta \sigma} = \frac{1}{q \Delta n (\mu_n + \mu_p)} \quad (3.1)$$

$$D_n \frac{\partial^2 (\Delta n)}{\partial x^2} + \mu_n E \frac{\partial (\Delta n)}{\partial x} + G - \frac{\Delta n}{\tau_n} = \frac{\partial (\Delta n)}{\partial t} \quad (3.2)$$

The lifetime can be analyzed using three different methods: i) quasi steady-state (QSS) photogeneration, ii) transient decay, and iii) generalized analysis. For the quasi-steady-state measurement, the longest available time constant of the flash lamp is selected to measure the photoconductance during a long, slow varying light pulse compared to the effective lifetime of the wafer (at least 10 times slower) [34], [35]. This assumes near steady-state conditions with the generation and recombination in balance, which means that the concentration of excess carriers does not change with time ($\frac{\partial (\Delta n)}{\partial t} = 0$), and hence simplifies the ambipolar equation to Equation (3.3).
The flash used in this mode has a decay constant of 2 ms, and hence is suitable for lifetimes of 200 µs or less [4].

\[ \tau_{\text{eff.steady}}(\Delta n) = \frac{\Delta n}{G} \]  

(3.3)

Conversely, the transient decay method uses a short, light pulse with a small time constant (10-20 µs) to measure the photoconductance after the illumination. Therefore, the photogeneration is abruptly terminated \((G = 0)\) and the excess carrier concentration is no longer in steady-state as it decays exponentially with time. The lifetime then can be defined as the characteristic decay time using Equation (3.4) below.

\[ \tau_{\text{eff_transient}}(\Delta n) = \frac{\Delta n}{\partial \Delta n / \partial t} \]  

(3.4)

The QSS and transient method represent two extremes of the generalized analysis where both generation and non-steady state conditions may be valid. The lifetime can be presented as Equation (3.5) below, where the expression simplifies to the quasi steady-state expression when \(\frac{\partial (\Delta n)}{\partial t} = 0\) and to the transient equation when \(G = 0\) [36]. This analysis is valid for any carrier lifetime and any time constant of the lamp illumination in principle. However, the effective lifetimes reported under each of the three analysis methods may differ depending on the quality of surface passivation. The differences are likely to be small if the sample has a large value of lifetime, but if the lifetime is significantly limited by surface recombination, then there may be large inconsistencies between the various analysis methods. For example, in transient measurements, the excess carriers that recombine at the surface are not replenished \((G = 0)\), and therefore the lifetime is weighted towards the carriers in the centre of the wafer. The difference in carrier profiles through the wafer thickness can result in variations in the value of lifetimes reported.

\[ \tau_{\text{eff.generalized}}(\Delta n) = \frac{\Delta n(t)}{G(t) - \partial \Delta n(t) / \partial t} \]  

(3.5)
There are several advantages and disadvantages for the QSS and transient methods. Firstly, the quasi steady-state technique is under almost true steady-state conditions, and represents similar results to a solar cell under constant illumination. In addition, the value of lifetime shown in Equation (3.3) depends on absolute values of measured data as opposed to the derivatives. Hence, the measured lifetimes are less susceptible to noise. Contrarily, the fraction of incident light that is absorbed in the sample, known as the optical constant or the effective transmission coefficient, must be determined to calculate the generation rate. The uncertainty of the optical constant is estimated to within 5% and contributes to 5% error in the resulting lifetime. A value of 0.7 has been used as the optical constant for all QSS measurements. A wafer with surface texturing and antireflection coatings could increase the optical constant.

The advantages of the transient technique are that it does not require the optical constant and the intensity of the light since it assumes a generation rate of zero. The estimate of the optical constant value used in QSS is a source of error for the measurement. On the other hand, based on Equation (3.4), the effective lifetime relies on derivatives of the excess carrier concentration with respect to time which introduces noise in the plot. Therefore, the transient technique is only valid for lifetimes above 100 µs to minimize the error.

Since the Sinton instrument reports effective lifetime as a function of excess carrier density, it is desirable to convey one effective lifetime value to compare between different samples. The ECD of $10^{15}$ cm$^{-3}$ is a commonly used value for reported data in publications, and has many benefits including the following: i) it has good signal-to-noise ratio for the apparatus, ii) it is measureable for most lifetime samples, and iii) it relates to solar cell efficiencies as high efficiency solar cells operate in the range of $10^{15}$ to $10^{16}$ cm$^{-3}$ [37]. An example of measured lifetime data is plotted in Figure 3.6. The Sinton tester can measure lifetimes from 0.1 µs to 20 ms for sample sizes of 4 cm in diameter to samples as small as 1 cm$^2$. A bare, unpassivated silicon wafer with native oxide has a measured lifetime of as low as 2-3 µs, while a sample with excellent surface passivation can reach well over 1 ms in lifetime [38].
Figure 3.6: A sample output of Sinton lifetime tester displays the effective lifetime as a function of excess carrier density (ECD). For a single-point value, it is possible to report the lifetime at a specific ECD (2.0E14 in this example). [37]

The Sinton instrument uses a Xenon flash with Schott glass filters. The light passes through a thick black infrared (IR) pass filter with a 700 nm edge (the spectrum shown in Figure 3.7). The use of the IR filter is due to the variation of surface and bulk recombination in silicon with the wavelength of light. Specifically, based on the absorption coefficient of silicon, visible light is most absorbed at the surface within the top 10 µm, whereas IR light is absorbed deeply in the wafer. This means that excess carriers generated by visible light is exceptionally sensitive to surface recombination, while IR light tends to have more uniform generation of excess carriers that are less susceptible to surface recombination [38]. The Sinton instrument is pictured in Figure 3.8.
Figure 3.7: The IR pass filter in Sinton WCT-120 lifetime tester allows uniform generation of excess carriers in the wafer through the absorption of IR light with wavelengths greater than 700 nm.

Figure 3.8: The Sinton lifetime tester.
3.4 Microwave Photoconductivity Decay Lifetime Tester

The microwave PCD (µ-PCD) method is a transient technique that determines minority carrier lifetime following a high injection light pulse. It detects photoconductance decay with the reflection of microwaves at 10.377 GHz from the sample and generates high-resolution images to illustrate spatial variations of lifetimes on the wafer [39]. It uses an InGaAs laser with a wavelength of 904 ± 10 nm, and a pulse width of 200 ns as a light source to generate excess carriers in the wafer [40]. The structure of the microwave photoconductivity decay system is shown in Figure 3.9.

![Figure 3.9: The structure of the integrated light source and sensor of µPCD instrument [40].](image)

Similar to the Sinton instrument, the µ-PCD lifetime tester monitors the change in conductivity of the sample after illumination. Instead, the conductivity is measured differently by detecting the change in reflected microwave power as a function of time. Since the reflected microwave power is proportional to the conductivity, and hence the carrier concentration, the data can be
fitted directly with an exponential curve to extract the time constant and hence effective lifetime. The lifetime is recorded for every position of measurement and then used to generate a map. High-resolution images can be obtained by decreasing the spacing between each measurement, but this increases the time of measurement. A resolution of 500 µm raster was selected to minimize measurement time, while maintaining enough clarity of the image for analysis. An example of the colour-coded lifetime map is shown in Figure 3.10 below. The µ-PCD measurements were used mainly for picturing spatial variations and uniformity of lifetime across the wafer, whereas the Sinton lifetime values were used to calculate the surface recombination velocity and to compare between various samples. All µ-PCD measurements were performed on the Semilab Model WT-2000 instrument shown in Figure 3.11.

Figure 3.10: Colour-coded µ-PCD lifetime map with 500 µm raster selected.
3.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is used to quantitatively identify the elemental composition within a material. This technique provides data regarding the carbon content in the film and can be used to examine the effect of varied carbon content on optical and passivation characteristics. In addition, detailed XPS scans can reveal information regarding the chemical bonding in the material which is useful in alloy compositions such as hydrogenated amorphous silicon carbide.

The physics behind XPS is the principle of the photoelectric effect, which describes the emission of photoelectrons due to the absorption of short-wavelength electromagnetic radiation. XPS uses X-rays to bombard the surface of the sample and induce photoelectron emission, which is then captured by an electron detector and analyzer. It simultaneously measures the kinetic energy and the number of the photoelectrons which then generates the XPS spectrum. Since the photoelectrons have energy characteristics of the sample atoms, the measured energies can be analyzed to determine the elemental and chemical compositions. Using Equation (3.6) below, the electron binding energy of the photoelectrons can be calculated from the measured kinetic
energy ($E_{kinetic}$), and known values of the X-ray wavelength and the work function of the spectrometer ($\phi_{spectrometer}$). The sample holder and the spectrometer are contacted electrically to prevent surface charging and the thermal-equilibrium band diagram is shown in Figure 3.12. Equation (3.6) can be derived directly from the band diagram.

$$E_{binding} = h\nu - (E_{kinetic} + \phi_{spectrometer})$$  \hspace{1cm} (3.6)

Figure 3.12: The thermal equilibrium band diagram shows the shift in the vacuum level for an equalized Fermi level. The kinetic energy refers to the energy detected by the spectrometer with reference to the vacuum level [41].

Each element is characterized by its own specific binding energy, and hence the measured binding energies can be used for identification. Furthermore, the intensity of the binding energy allows for quantification of each elemental component. A sample XPS survey scan is shown in Figure 3.13. The peaks in the XPS spectra correspond to the electron configuration of the core electrons (1s, 2s, 2p, etc.), which are correlated with elements of the same binding energy.
Figure 3.13: XPS survey scan identifies elements based on the binding energy of each element. The photoelectron count rate is plotted against binding energy to create the XPS spectrum.

In addition, the chemical bond configurations can be determined from XPS since the different types of bonds result in varying magnitude of shifts in the binding energy [42]. A list of the binding energies of different bonds is listed in Table 3.1 below. Different bonding configurations with other elements cause the detected binding energy to shift from the main peak. This is due to Coulombic interactions of the core electrons between the two elements, which cause a shift in binding energy between approximately 0.1 to 10 eV. For example, Si electrons from Si-C bonds (100.5 eV) have a slightly different binding energy than electrons from pure Si atoms (99.2 eV) [43]. The measured XPS spectrum is a superposition of peaks from the various types of bonds, and therefore it is possible to deconvolve the overall spectrum to determine the chemical bond...
configurations present in the sample. Also, the Shirley background was applied to cancel any asymmetry offsets due to background noise from recorded data [44]. An example of deconvolution of the C1s peak is shown in Figure 3.14.

Table 3.1: Binding energy variation of different bonds used in XPS element identification [45]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy peak (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si–Si/Si–H</td>
<td>99.2 ± 0.1</td>
</tr>
<tr>
<td>Si–C</td>
<td>100.5 ± 0.1</td>
</tr>
<tr>
<td>O–Si–C</td>
<td>101.8 ± 0.2</td>
</tr>
<tr>
<td>Si–O&lt;sub&gt;x&lt;/sub&gt;</td>
<td>103.2 ± 0.3</td>
</tr>
<tr>
<td>C–Si</td>
<td>283.2</td>
</tr>
<tr>
<td>C–C/C–H</td>
<td>284.6 ± 0.1</td>
</tr>
<tr>
<td>C–O–H</td>
<td>286.4</td>
</tr>
<tr>
<td>C==O</td>
<td>288.4 ± 0.4</td>
</tr>
</tbody>
</table>
Figure 3.14: Deconvolution of the C1s peak measured using XPS. The ratio of the different bonding configurations can be determined by comparing the area under each Gaussian peak.

All XPS measurements were performed using the Thermo Scientific K-Alpha instrument (Figure 3.16) which uses a monochromatic aluminum K-α X-ray source, with a variable spot size of 30 – 400 µm. The sample stage setup, shown in Figure 3.17, can hold numerous samples for multiple XPS measurements. The XPS technique is a non-destructive measurement of the surface chemistry that detects the top 1-10 nm of the material being analyzed. The main XPS limitations are as follows: i) XPS requires ultra high vacuum (UHV) environment to minimize the error in photoelectron counts at each energy level, and ii) XPS cannot detect hydrogen or helium due to their small orbital diameters which reduces the photoelectron catch probability to nearly zero. The detector is able to identify all other elements with atomic numbers higher than two.
If contamination occurs on the surface of the sample that is being analyzed, it is possible to perform sputtering to clean off surface contamination. The K-Alpha instrument is equipped with an Argon ion gun that uses an ion beam to etch the surface. The etch depth can be varied by controlling the energy level of the ion beam and the time of sputtering. In addition, a depth profile of the thin film can be obtained by taking XPS measurements in between sputtering runs until the entire film has been completely etched off.

**Figure 3.15:** The basic XPS setup uses a X-ray source to cause photoelectron emission which is detected by the electron detector and analyzer [41].
Figure 3.16: Thermo Scientific K-Alpha XPS instrument [46].

Figure 3.17: Sample stage setup as captured by internal cameras [46].
3.6 Spectroscopic Ellipsometry

The principle of spectroscopic ellipsometry (SE) is to measure the change in polarization upon the reflection of polarized light from the sample surface. This is a useful optical technique that can determine the dielectric properties of thin films such as refractive index, extinction coefficient, thickness, absorption coefficient, optical band gap, and optical constants. It can be used to determine the properties of either single or multi-layer models. The widely accepted Tauc-Lorenz model was applied to fit the measured data of amorphous silicon carbide films against the theoretical values of the assumed model. An initial guess of the model including thickness and the complex refractive index is required for regression fitting. In this thesis, a model with three layers was used: i) roughness layer representing thin native oxide film as the uppermost layer, ii) amorphous silicon carbide film as the next layer, and iii) the crystalline silicon substrate. First-order approximation of film thicknesses from profilometry measurements were used for initial parameters in the fitting routine.

Upon completion of a good graphical fit with low fitting error ($R^2 > 0.99$), the thickness of each layer is reported, along with various optical constants. It is also possible to extract the refractive index and extinction coefficient as a function of energy and hence wavelength. This allows for the extrapolation of the Tauc gap (optical gap) based on the following equations [47]:

\[
(aE)^{1/2} = A'(E - E_{\text{tauc}})
\]  
\[\alpha = \frac{4\pi k}{\lambda}\]  
\[
\lambda = \frac{hc}{E}
\]  
\[
\left(\frac{4\pi k}{hc^2 E^2}\right)^{1/2} = A'(E - E_{\text{tauc}})
\]

In Equation (3.7), the relationship between the absorption coefficient, $\alpha$, and the Tauc gap ($E_{\text{tauc}}$) is displayed as a function of energy ($E$), where $A'$ is a constant. The absorption coefficient
equation is displayed in Equation (3.8) as a function of wavelength \((\lambda)\) and extinction coefficient, \(k\), and the wavelength can be converted to energy through Equation (3.9) using the Planck’s constant \((h)\) and the speed of light, \(c\). Through substitution of the equations above, Equation (3.10) is in the form of \(y = a + bx\), where a linear fit can be performed on the Tauc plot to determine the Tauc gap from the X-intercept. This is shown in Figure 3.18 below. The Tauc gap is finally calculated by dividing the Y-intercept by the slope \((4.13384 \times 10^{-21} / 1.94725 \times 10^{-21})\), resulting in a Tauc gap of 2.12 eV.

Figure 3.18: A Tauc plot is displayed with a linear fit to extrapolate the Tauc gap.

The Sopra UV-VIS-NIR Spectroscopic Ellipsometer (Figure 3.19) was used to carry out all SE measurements. The range of photon energy used is between 1.55 eV and 5.5 eV, which corresponds to the wavelength range of 225 to 800 nm.
3.7 Profilometry

Profilometry is a first-order method that determines the thickness of thin film materials by measuring the profile of the film surface. The thickness measurements from Tencor Alphastep 200 Automatic Step Profiler were compared with the results from spectroscopic ellipsometry in order to verify the accuracy of the ellipsometry structure model. The instrument is shown in Figure 3.20 below.

The step profiler uses a 12.5 micron tipped stylus that can move along the vertical and horizontal axes. It first moves vertically to make contact with the sample surface, and then moves laterally across the sample. The profiler is able to detect small vertical features ranging from 10 nm to 1 mm with a vertical resolution of 5 Å and a horizontal resolution of 400 Å. The vertical

**Figure 3.19:** The Sopra Spectroscopic Ellipsometer equipment is used for determining the thickness of thin films, and various optical constants.
displacement of the stylus generates an analog signal that is converted into a digital signal to be
analyzed and displayed on screen. Since the profiler is able to detect vertical displacements, the
thickness of films can be measured across a step between the bare wafer and the film. This
requires the sample to be prepared using a mask to create a step by preventing any film growth in
a selected area.

While the profilometry measurements are independent of optical properties of the sample, they
are sensitive to the mechanical properties of the film, such as surface roughness and hardness. In
addition, the procedure may damage the sample surface in contrast to contactless methods.
Accurate thin film thickness measurements can also be determined from cross-sectional
transmission electron microscopy (TEM), but the sample preparation involves a complex
procedure. In contrast, profilometry is a fast and straightforward method that provides a first
order approximation of thickness. The tradeoff of loss in accuracy can be justified by the
simplicity and quickness of profilometry measurements.

Figure 3.20: The Tencor Alphastep 200
Automatic Step Profiler instrument.
3.8 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared (FTIR) spectroscopy is a technique that can determine the bonding structure and the relative hydrogen concentration in the sample by observing the characteristic absorption of different molecular vibrational groups. Since every molecule has its own natural frequency that the bond vibrates at, it can absorb radiation at the resonant frequency which is characteristic of its bond structure. Therefore, the existence of certain molecular species or bonds can be verified by measuring and detecting the peaks in the absorption spectra. The vibrational groups usually detected in a-SiC$_x$:H layers are listed in Table 3.2. In addition, the peak intensities of hydrogen bonds, such as CH$_x$ and SiH$_x$, can reveal the relative hydrogen concentration in the sample.

Table 3.2: Vibrational frequencies of different molecular groups [23].

<table>
<thead>
<tr>
<th>Wavenumber [cm$^{-1}$]</th>
<th>600-650</th>
<th>760-770</th>
<th>900, 860</th>
<th>970</th>
<th>950-1110</th>
<th>1250</th>
<th>1340</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group</td>
<td>Si-H</td>
<td>C-H</td>
<td>Si-H</td>
<td>Si-O-Si</td>
<td>C-H</td>
<td>C-H</td>
<td>C-H</td>
</tr>
<tr>
<td>1400</td>
<td>2000</td>
<td>2080</td>
<td>2880</td>
<td>2950</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H</td>
<td>Si-H</td>
<td>Si-H$_n$</td>
<td>C-H</td>
<td>C-H</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The spectral range of the Perkin Elmer 2000 FTIR equipment (Figure 3.21) is 400 cm$^{-1}$ to 5200 cm$^{-1}$ with a resolution of 1 cm$^{-1}$. The instrument uses a broadband light source, containing the full spectrum of wavelengths, and a Michelson interferometer which allows certain wavelengths of light to pass through while blocking others. Data acquisition involves measuring the transmission intensity of the selected wavelengths through the sample. Multiple data points are taken for each set of wavelengths, and post computer processing using Fourier transform converts the raw data into transmission as a function of wavenumber.

Transmission measurements using FTIR require the amorphous silicon carbide films to be deposited on one side of high resistivity wafers. Since lifetime samples were deposited on both sides of low resistivity wafers (1-5 Ω cm), FTIR samples using 30 Ω cm n-type wafers were made under the same deposition conditions. Additionally, samples must be purged with desiccated air in the sample holder before each measurement since the water vapour and carbon dioxide in air can affect the transmission measurement results. An example of normalized
transmission spectrum from FTIR measurement is shown in Figure 3.22. The background is removed using a linear fit and then converted to an absorption spectrum as shown in Figure 3.23.

Figure 3.21: The Perkin Elmer 2000 FTIR equipment has a spectral range of 400 cm\(^{-1}\) to 5200 cm\(^{-1}\) with a resolution of 1 cm\(^{-1}\).

Figure 3.22: Normalized transmission spectrum of an a-SiC:H sample measured using FTIR.
Furthermore, the microstructure factor or absorption strength ratio, $R$, shown in Equation (3.11), can be determined from analyzing the Si-H peaks at around 2000 cm$^{-1}$. This factor is the ratio between the low-stretching mode (LSM) and high-stretching mode (HSM) absorption bands centered at 2000 cm$^{-1}$ and 2080 cm$^{-1}$, respectively [48]. The LSM absorption peak is related to monohydrides (SiH), whereas the HSM peak is attributed to the microvoid-related dihydrides (SiH$_2$). Atomic hydrogen is known to desorb and form molecular hydrogen in these interconnected microvoids, creating a path for hydrogen to effuse out of the film [49]. Since the saturation of dangling bonds require high hydrogen content, it is desirable to minimize the microstructure factor in a-SiC:H films.

$$R = \frac{\int I_{2080}(v)dv}{\int I_{2000}(v)dv + \int I_{2080}(v)dv}$$

(3.11)

Figure 3.23: The deconvolution of the Si-H$_x$ absorption coefficient peak for SiH and SiH$_2$. 
3.9 Hot Plate

A hot plate, shown in Figure 3.24, was used to carry out post-deposition annealing experiments with a maximum rating of 550 °C. The hot plate was placed inside a nitrogen-filled glove box to prevent any oxidation reactions in the samples. The annealing samples were placed on a dummy wafer to provide a flat and clean surface. A calibration of the surface temperature of a typical sample was carried out prior to proceeding with the annealing experiments. Multiple annealing recipes were tested to optimize the annealing procedure, which are detailed further in Chapter 4.

**Figure 3.24:** Hot plate used for annealing samples with a maximum rating of 550 °C
4 Results and Analysis

This chapter presents the experiment sample space, the various characterization results, and the appropriate analysis. It aims to correlate the passivation quality and film characteristics with deposition parameters and compares the outcome of the film properties grown using DCSF PECVD with literature results on films grown using RF PECVD.

4.1 Overview of Experiments

4.1.1 Objectives

As mentioned in Chapter 1, the goals of this thesis are to investigate and optimize the deposition of intrinsic hydrogenated amorphous silicon carbide films using DC saddle field PECVD method, characterize their passivating, structural and optical qualities and analyze their feasibility as potential surface passivation candidates. The experiments are separated into two main components: i) investigating the effects of varying deposition parameters (temperature, gas ratio, time) on film characteristics, and ii) examining post-deposition annealing results to analyze the thermal stability of a-SiC:H films.

4.1.2 Sample set space

The initial deposition temperature (400° C), gas mixture ratio ([CH₄] / ([CH₄] + [SiH₄]) : 0.5 [32]) and film thickness (20-40 nm [11]) were selected on the basis of the optimal conditions reported in the literature. With respect to chamber pressure (160 mTorr), flow rate (30 sccm), and anode current (17.5 mA), these were selected on the basis of prior experience in the group [31]. All the experiments were carried out using the shielded triode configuration.

From results reported in the literature, temperature was seen to have the most impact on effective lifetime [50]. Therefore, the order of experiments commenced with a variation of the deposition temperature, followed by a scan of different gas ratios, and then film thickness. For completeness, a gas ratio scan in the low temperature range was also performed.
Furthermore, the annealing experiments entailed scanning a temperature range of 150 to 400° C and time steps spanning 15 to 240 minutes so as to identify the trends in passivating quality with respect to these parameters. With each experiment sample set, various characterization techniques are applied to extract parameters such as effective lifetime, effective surface recombination velocity, thickness, optical band gap, and carbon content. All deposited films showed good adhesion and no exfoliation was observed. A summary of the sample sets is shown in Table 4.1 below.

**Table 4.1: Summary of experimental sample sets.**

<table>
<thead>
<tr>
<th>#</th>
<th>Sample Set</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Temperature Scan</td>
<td>The deposition temperature was varied from 250 °C to 500 °C, while keeping the gas mixture ratio at 0.5 and deposition time at 30 minutes.</td>
</tr>
<tr>
<td>2</td>
<td>High Temperature Gas Ratio Scan</td>
<td>The methane to silane gas ratio, ([\text{CH}_4]/([\text{CH}_4] + [\text{SiH}_4])), was varied from 0.1 to 0.7, while keeping deposition temperature at 500 °C and deposition time at 30 minutes.</td>
</tr>
<tr>
<td>3</td>
<td>Thickness Scan</td>
<td>With the optimal temperature of 500 °C and gas ratio of 0.5, the thickness of the film was varied by varying the deposition time from 5 to 40 minutes.</td>
</tr>
<tr>
<td>4</td>
<td>Low Temperature Gas Ratio Scan</td>
<td>The gas ratio scan (set 2 above) was repeated at a lower deposition temperature of 250 °C for completeness.</td>
</tr>
<tr>
<td>5</td>
<td>Repeatability</td>
<td>This set of samples was made using identical deposition parameters to investigate the repeatability of Gen 1 system in the tetrode configuration.</td>
</tr>
<tr>
<td>6</td>
<td>Annealing Study</td>
<td>All samples were subjected to annealing treatments using a hot plate. The various annealing experiments are detailed in the Annealing section.</td>
</tr>
<tr>
<td>7</td>
<td>FTIR</td>
<td>Samples for FTIR analysis were deposited on high resistivity wafers (&gt; 30 Ω cm). The deposition parameters from the temperature scan samples were repeated and films were only grown on one side of the wafer.</td>
</tr>
</tbody>
</table>
4.2 Temperature Scan

In this sample set, the deposition temperature is varied from 250 °C to 500 °C, while keeping the chamber pressure, gas ratio, flow rate, anode current, and deposition time constant at 160 mTorr, 0.5 ratio, 30 sccm, 17.5 mA, and 30 minutes, respectively. The passivation quality is investigated as a function of the deposition temperature, and the effective surface recombination velocity data are fitted to the Olibet model described in Chapter 2 to extract the interface defect density and the charge density. Furthermore, the hydrogen content of the films was determined from FTIR measurements. Additional information such as the growth rate, elemental composition, and Tauc gap are also inferred experimentally.

4.2.1 Passivation Quality

The effective lifetime measured by the Sinton lifetime tester is plotted against the excess minority carrier density for deposition temperatures from 250 °C to 500 °C in Figure 4.1 below. The value of effective lifetime is recorded at the excess carrier density of 1E15 cm⁻³ by convention for each sample (Table 4.2) and it can be seen that the lifetime increases as the deposition temperature rises. The effect of Auger recombination on effective lifetime is most prominent at high excess carrier densities and is most pronounced on the 500 °C sample data [51], [52]. For the 250 °C curve, the low lifetime suggests a poor quality of surface passivation, leading to high recombination rates that limit the excess carrier density to a maximum of 5E15 cm⁻³.

Table 4.2 below summarizes the lifetime and associated $S_{eff}$ values for the various samples. Due to the temperature limits of the heater in the deposition system, 500° C was the highest temperature achievable in the Gen 1 vacuum system. Significant effort was devoted to increasing the deposition temperature by designing and building a lamp heater. The new lamp heater system was found to be superior to the existing heating system, however, the new heater required additional design improvements and commissioning which would have been beyond the available time and accordingly the study proceeded with the existing heating system.
Table 4.2: The lifetime values taken at 1E15 cm\(^{-3}\) and the associated effective surface recombination velocities for the deposition temperature scan.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Deposition Temperature (°C)</th>
<th>Effective Lifetime (µs)</th>
<th>(S_{\text{eff}}) (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY35A</td>
<td>250</td>
<td>22.5</td>
<td>621</td>
</tr>
<tr>
<td>JY13A</td>
<td>400</td>
<td>52.8</td>
<td>265</td>
</tr>
<tr>
<td>JY12A</td>
<td>450</td>
<td>78.0</td>
<td>179</td>
</tr>
<tr>
<td>JY11A</td>
<td>500</td>
<td>112.0</td>
<td>124</td>
</tr>
</tbody>
</table>

Figure 4.1: The effective lifetime as a function of excess carrier density increases as the deposition temperature rises from 250 °C to 500 °C. The value of effective lifetime is recorded at the excess carrier density of 1E15 cm\(^{-3}\) by convention for each sample.

The surface passivation improves with increasing deposition temperature as shown by the \(S_{\text{eff}}\) values, reaching 124 cm/s for films prepared at 500 °C. In comparison, the bare crystalline
wafer has an effective lifetime of less than 5 µs, which correlates to a $S_{\text{eff}}$ value of more than 3000 cm/s. State of the art surface passivation by amorphous silicon carbide has shown to have $S_{\text{eff}}$ values of less than 15 cm/s [1]. Furthermore, since the lifetime samples involve two-sided depositions, the lifetime can be measured for both sides. Assuming identical depositions were performed on both sides, the surface passivation quality should be similar for both a-SiC:H films. However, sample side A (first side of deposition) consistently shows better passivation than side B (second side of deposition) as illustrated in Figure 4.2 where a lower $S_{\text{eff}}$ represents better passivation.

**Figure 4.2:** Side A (first deposition) and side B (second deposition) $S_{\text{eff}}$ data of the temperature scan samples. Side B consistently has worse passivation qualities than side A.

The lifetime difference between the two sides may be due to a combination of annealing and charging effects arising during the second deposition. Specifically, during the second deposition, the a-SiC:H film from the first deposition is in direct contact with the heated substrate and
accordingly undergoes a thermal treatment which could have contributed to relaxing the amorphous network and thus improving the interface properties leading to a higher lifetime. Also, the undoped film from the first deposition may serve as a low loss insulator, preventing the wafer from being completely grounded or discharged through the substrate holder. This could have lead to charge build-up on the growth surface and hence alter the energy of the ions on the growth surface and thus result in a relatively lower passivation quality. The side B lifetimes and effective surface recombination velocities are shown in Table 4.3 below. Since the trends of side A and B film characteristics are similar for both sides, only side A data is presented for the remainder of this thesis document.

**Table 4.3:** Side B (second deposition) data of the temperature scan samples.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Deposition Temperature (°C)</th>
<th>Effective Lifetime (µs)</th>
<th>$S_{\text{eff}}$ (cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY35B</td>
<td>250</td>
<td>15.0</td>
<td>918</td>
</tr>
<tr>
<td>JY13B</td>
<td>400</td>
<td>31.6</td>
<td>442</td>
</tr>
<tr>
<td>JY12B</td>
<td>450</td>
<td>55.3</td>
<td>253</td>
</tr>
<tr>
<td>JY11B</td>
<td>500</td>
<td>92.0</td>
<td>152</td>
</tr>
</tbody>
</table>

### 4.2.2 Recombination Model Fitting

The interface defect density, $N_s$, and the interface fixed charge density, $Q_s$, are inferred from fitting the $S_{\text{eff}}$ vs. ECD data to the Olibet model presented in Chapter 2 and are listed in Table 4.4 below. These two parameters can assist in explaining the potential causes of lifetime improvement as deposition temperature increases.

**Table 4.4:** Extracted values of interface defect density, $N_s$, and the interface fixed charge density, $Q_s$, from fitting the $S_{\text{eff}}$ vs. ECD data to the Olibet model.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Deposition Temperature (°C)</th>
<th>$S_{\text{eff}}$ (cm/s)</th>
<th>Interface Fixed Charge Density $\times 10^{11}$ (cm$^{-2}$)</th>
<th>Interface Defect Density $\times 10^{10}$ (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY35A</td>
<td>250</td>
<td>621</td>
<td>1.3</td>
<td>7.93</td>
</tr>
<tr>
<td>JY13A</td>
<td>400</td>
<td>265</td>
<td>2.0</td>
<td>7.04</td>
</tr>
<tr>
<td>JY12A</td>
<td>450</td>
<td>179</td>
<td>2.0</td>
<td>6.78</td>
</tr>
<tr>
<td>JY11A</td>
<td>500</td>
<td>124</td>
<td>2.0</td>
<td>3.37</td>
</tr>
</tbody>
</table>
Firstly, the positive charge of $Q_s$ implies that the interface is under an accumulation state for the n-type wafer where the surface potential, $\psi_s$, is also positive. The accumulation of electrons near the surface of the wafer causes the valence band to bend downwards and preventing holes to gather at the interface. This effectively creates field effect passivation which repels one type of charge carrier and minimizes the probability of surface recombination processes, hence reducing the surface recombination rate. However, the fixed charge density remained constant at the same order of magnitude for the temperature scan samples, which implies that field effect passivation is not the predominant cause of improvement in surface passivation. The fixed charge density for DCSF a-SiC:H is similar to RF-deposited films reported in literature of $0.5$ to $1.1\times10^{11}$ cm$^{-2}$ [53].

Next, the interface defect density is plotted as a function of deposition temperature in Figure 4.3 below. The inferred defect density is slowly dropping with temperature with a sharp drop as the temperature is raised to $500$ °C. This overall trend of this figure corresponds to the $S_{eff}$ plot and indicates that the lowered interface defect density is due to the saturation of silicon dangling bonds by atomic hydrogen. Lower deposition temperatures result in a high $N_d$ while increasing the deposition temperature reduces the interfacial defect density significantly which is likely due to hydrogen redistribution within the film and in particular at the interface where the dangling bonds are passivated [52]. For higher temperatures beyond $500$ °C, the defect density is expected to reach a minimum, then increase rapidly as samples at high temperature causes hydrogen effusion; the amorphous films would have low hydrogen content which reduces the amount of chemical passivation occurring at the interface [54].
Figure 4.3: The interface defect density is plotted as a function of deposition temperature. A sharp decrease is observed at 500 °C.

4.2.3 Hydrogen Content

Since hydrogen atoms cannot be detected by XPS measurements, FTIR transmission samples were prepared to determine the hydrogen content. The FTIR data was analyzed and fitted as described in Chapter 3. Higher substrate temperature lead to a higher hydrogen effusion rate [55], while a lower process temperature resulted in a reduced diffusivity of hydrogen atoms [27]. This trend is shown in Figure 4.4 where hydrogen content decreases rapidly as the deposition temperature is raised. For amorphous silicon (a-Si:H) films, hydrogen effuses out rapidly at 250-300 °C and very low hydrogen remains at 500 °C [56]. For a-SiC:H films, the hydrogen content
is expected to drop rapidly as deposition temperature increases past 500 °C and eventually leading to degradation in passivation quality due to reduced bonded hydrogen at the interface and thus higher interface defect densities [27].

Table 4.5: Hydrogen content determined from FTIR measurements.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Deposition Temperature (°C)</th>
<th>Hydrogen Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY37</td>
<td>250</td>
<td>22.67</td>
</tr>
<tr>
<td>JY31</td>
<td>400</td>
<td>20.38</td>
</tr>
<tr>
<td>JY30</td>
<td>450</td>
<td>17.63</td>
</tr>
<tr>
<td>JY29</td>
<td>500</td>
<td>15.68</td>
</tr>
</tbody>
</table>

Figure 4.4: Hydrogen content is plotted as a function of deposition temperature. The hydrogen content decreases as the temperature is increased due to the effusion of hydrogen from the samples with increasing temperature.
4.2.4 Elemental Composition

For the temperature scan samples, the elemental composition of each sample remained relatively stable as shown in Table 4.6 and Figure 4.5 below. This indicates that temperature does not have a dominant effect on the elemental composition of a-SiC:H films including the silicon, carbon, oxygen, and fluorine content; only the hydrogen content of the film (not detectable by XPS) was shown to vary with temperature.

![Elemental Composition Graph](image)

**Figure 4.5:** Elemental composition of a-SiC:H films from XPS measurements remained constant with changes in deposition temperature.

**Table 4.6:** The elemental composition of a-SiC:H films as determined from XPS measurements.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Deposition Temperature (°C)</th>
<th>Silicon (At. %)</th>
<th>Carbon (At. %)</th>
<th>Oxygen (At. %)</th>
<th>Fluorine (At. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY35</td>
<td>250</td>
<td>82.09</td>
<td>15.26</td>
<td>2.48</td>
<td>0.17</td>
</tr>
<tr>
<td>JY13</td>
<td>400</td>
<td>81.61</td>
<td>15.99</td>
<td>2.24</td>
<td>0.15</td>
</tr>
<tr>
<td>JY12</td>
<td>450</td>
<td>81.90</td>
<td>15.47</td>
<td>2.51</td>
<td>0.12</td>
</tr>
<tr>
<td>JY11</td>
<td>500</td>
<td>82.27</td>
<td>15.34</td>
<td>2.27</td>
<td>0.12</td>
</tr>
</tbody>
</table>
4.2.5 Tauc Gap

The Tauc gap was also determined for the temperature scan samples using SE absorption data. The values of the Tauc gap remained constant (within 2%) with the variation in deposition temperature (see Table 4.7). This correlates with the elemental composition data since the carbon content did not change significantly for the samples. An increase in carbon content is known to have a widening effect on the Tauc gap. This is illustrated in the gas ratio scan experiments in the next section.

**Table 4.7:** Tauc gap values remained constant with the variation in deposition temperature.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Deposition Temperature (°C)</th>
<th>Tauc Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY35</td>
<td>250</td>
<td>2.09</td>
</tr>
<tr>
<td>JY13</td>
<td>400</td>
<td>2.05</td>
</tr>
<tr>
<td>JY12</td>
<td>450</td>
<td>2.07</td>
</tr>
<tr>
<td>JY11</td>
<td>500</td>
<td>2.06</td>
</tr>
</tbody>
</table>

4.2.6 Growth rate

The thicknesses of the a-SiC: H films are determined from spectroscopic ellipsometry modeling. Since all temperature scan experiments had a constant deposition time of 30 minutes, it is possible to express the data in terms of growth rate. The growth rate is plotted in Figure 4.6 in the units of nanometers per minute. For increasing deposition temperatures from 250 °C to 500 °C, the growth rate increased roughly 7.5% which correlates to thickness increase from 48.3 nm to 52.0 nm.

The growth rate increase with deposition temperature correlates with that of amorphous silicon [57]. There are several effects of higher deposition temperature on the growth rate of the film. Firstly, an increase in temperature raises the surface mobility of molecules, and enhances the rate of chemical reactions on the surface of the substrate. Moreover, the gas temperature is also raised beyond room temperature, resulting in additional energy to plasma molecules to dissociate. Thirdly, higher temperature results in an elevated hydrogen effusion rate. The atomic hydrogen from Si-H bonds at the surface desorbs and leaves behind a more reactive surface for impinging
radicals and ions. This allows other molecules to attach and bind, forming layers of a-SiC:H film.

Figure 4.6: The growth rate is plotted as a function of deposition temperature; it increases approximately 7.5% as the deposition temperature rises from 250 °C to 500 °C.

The growth rate in DCSF PECVD Gen 1 system is much less than reported growth rates in literature using RF-PECVD systems due to their use of higher power to operate the plasma discharges. The RF systems can reach deposition rates from 8 nm/min [58] to as high as 18 nm/minute [59].
4.3 Gas Ratio Scan

In this set of experiments, the gas ratio was varied while using the optimum deposition temperature of 500 °C determined from the temperature scan experiments. In addition, a gas ratio scan at a lower temperature of 250 °C is carried out to compare and contrast the properties of films at the two ends of the temperature spectrum. The gas ratio, defined as \( \frac{[\text{CH}_4]}{([\text{CH}_4] + [\text{SiH}_4])} \), was scanned from 0.1 to 0.7. A gas ratio of 0 would deposit amorphous silicon using only silane gas, while a gas ratio of 1 would deposit amorphous carbon using only methane gas.

4.3.1 Passivation Quality and Model Fit

The passivation quality of the two gas scans are shown in the \( S_{\text{eff}} \) plot below in Figure 4.7. The \( S_{\text{eff}} \) values for the 250 °C is consistently higher than 500 °C which reinforces the hypothesis that high temperature grown films are passivated better as illustrated in the temperature scan section.

![Graph of S_eff vs Gas Ratio for 250 °C and 500 °C](image)

**Figure 4.7**: The \( S_{\text{eff}} \) data are plotted for the gas ratio scans at 250 °C and 500 °C. Both curves display a local minimum in gas ratio scan.
In addition, both curves show a sharp local minimum at 0.3 and 0.5 gas ratios with $S_{\text{eff}}$ of 536 cm/s and 124 cm/s for 250 °C and 500 °C, respectively. This dependence of $S_{\text{eff}}$ on the gas ratio is similarly observed for RF PECVD deposited a-SiC:H films with a minimum at just under 0.5 ratio [60]. This suggests that both DCSF and RF PECVD surface passivation films are based on similar physical mechanisms. The surface recombination velocity data of both gas ratio scans were also fitted to the Olibet model to extract the interface defect density and fixed charge density. The summary of surface passivation data are shown in Table 4.8 and Table 4.9 for 250 °C and 500 °C, respectively.

**Table 4.8:** Surface passivation data for gas ratio scan deposited at 250 °C.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Gas Ratio</th>
<th>Effective Lifetime (µs)</th>
<th>$S_{\text{eff}}$ (cm/s)</th>
<th>Interface Fixed Charge Density x 10^{11} (cm^{-2})</th>
<th>Interface Defect Density x 10^{10} (cm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY33</td>
<td>0.1</td>
<td>10.24</td>
<td>1371</td>
<td>1.5</td>
<td>8.96</td>
</tr>
<tr>
<td>JY34</td>
<td>0.3</td>
<td>25.76</td>
<td>536</td>
<td>1.3</td>
<td>6.80</td>
</tr>
<tr>
<td>JY35</td>
<td>0.5</td>
<td>14.99</td>
<td>918</td>
<td>1.3</td>
<td>7.93</td>
</tr>
<tr>
<td>JY36</td>
<td>0.7</td>
<td>8.88</td>
<td>1572</td>
<td>1.3</td>
<td>12.17</td>
</tr>
</tbody>
</table>

**Table 4.9:** Surface passivation data for gas ratio scan deposited at 500 °C.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Gas Ratio</th>
<th>Effective Lifetime (µs)</th>
<th>$S_{\text{eff}}$ (cm/s)</th>
<th>Interface Fixed Charge Density x 10^{11} (cm^{-2})</th>
<th>Interface Defect Density x 10^{10} (cm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY18</td>
<td>0.1</td>
<td>33.4</td>
<td>420</td>
<td>2.0</td>
<td>10.60</td>
</tr>
<tr>
<td>JY17</td>
<td>0.2</td>
<td>35.2</td>
<td>399</td>
<td>2.0</td>
<td>9.64</td>
</tr>
<tr>
<td>JY16</td>
<td>0.3</td>
<td>42.0</td>
<td>334</td>
<td>2.0</td>
<td>8.55</td>
</tr>
<tr>
<td>JY15</td>
<td>0.4</td>
<td>53.1</td>
<td>263</td>
<td>1.6</td>
<td>7.12</td>
</tr>
<tr>
<td>JY11</td>
<td>0.5</td>
<td>112.0</td>
<td>124</td>
<td>2.0</td>
<td>3.37</td>
</tr>
<tr>
<td>JY19</td>
<td>0.6</td>
<td>38.4</td>
<td>365</td>
<td>2.0</td>
<td>9.10</td>
</tr>
<tr>
<td>JY20</td>
<td>0.7</td>
<td>40.0</td>
<td>350</td>
<td>2.0</td>
<td>8.63</td>
</tr>
</tbody>
</table>

The interface fixed charge density, $Q_s$, remained constant for each of the gas ratio scans with higher values for the high temperature depositions. This indicates that changes to surface passivation quality shown in Figure 4.7 are not directly related to the fixed charge density. On the other hand, the variation of $S_{\text{eff}}$ can be represented by the change in surface configuration as shown in the plot of interface defect density in Figure 4.8 below.
**Figure 4.8:** The inferred interface defect density is plotted for the gas ratio scans deposited at 250 °C and 500 °C. The $S_{\text{eff}}$ minimum correlates to the minimum seen in the interface defect density.

The plot above shows that the minimum in $S_{\text{eff}}$ correlates to the minimum observed in the interface defect density, supporting the premise that low values of $S_{\text{eff}}$ is due to better interface characteristics [61]. Both the high and low temperature curves show the decrease of defect density to a minimum as gas ratio increases, then an increase as the feed gas contains higher concentration of methane. This can be linked to the rise of hydrogen content with increasing carbon content [62]. However, at a certain point, the hydrogen content saturates and remains constant, even with further increases in carbon content. The incorporation of more carbon atoms in the alloy film prevents the diffusion of passivating hydrogen towards the interface and leads to the increase in the defect density [55]. Furthermore, the $N_s$ values of both 250 °C and 500 °C are of the same order of magnitude even though the $S_{\text{eff}}$ plot shows that the 250 °C samples have
worse passivation quality. This may be due to the influence of the fixed charge density as the values of $Q_s$ are higher for the 500 °C, and hence could provide field effect passivation in addition to the chemical passivation of hydrogen saturation of dangling bonds. Therefore, passivation with the amorphous silicon carbide layer includes both field effect and chemical passivation. From the results displayed above, it appears that a gas ratio between 0.3 to 0.5 is optimum for a-SiC:H film yielding the lowest interface defect density, leading to the best passivation quality.

### 4.3.2 Elemental Composition

The elemental composition of the gas ratio scan films were determined from XPS measurements. Specifically, the variation of carbon content with changes in the feed gas ratio is of particular interest. The XPS data presented in this section are obtained after a sputtering procedure that removes surface contamination. The comparison between as-is data and sputtered results is presented in Section 4.8: XPS Analysis. The elemental composition data for 250 °C and 500 °C are plotted in Figure 4.9 and Figure 4.10 below, respectively. The raw data values are provided in the appendix for reference.

The fluorine content that could have remained from the HF acid dip is negligible in the overall composition with less than 0.3 atomic %. Traces of oxygen atoms were found in the film even after the sputtering process that removes the surface oxides. For all gas ratios at both deposition temperatures, the oxygen content remained constant at less than 3 atomic %. As expected, an increase in carbon content was observed as more methane is added to the overall feed gas and consequently results in a drop in silicon content. At 0.5 gas ratio with equal silane and methane gas pressures, the carbon content for both deposition temperatures is only around 15 at. %. The incorporation of carbon is much less efficient than silicon due to the high activation energy necessary for methane dissociation [63], as well as for bonding carbon species within the film [64]. The ionization and dissociation energies for methane are 12.6 eV and 10 eV [65], [66], while for silane they are 11 eV and 8 eV, respectively [67], [68]. Both the ionization and dissociation energies are lower than those of methane; this is in keeping with the observed silicon incorporation which is much higher than carbon, even at high gas ratios of 0.7 where the carbon content is only around 25 at. %.
Figure 4.9: Elemental composition for 250 °C gas ratio scan; an increase in carbon content is observed with increasing gas ratio.

Figure 4.10: Elemental composition for 500 °C gas ratio scan. The results indicate an increase in carbon content with higher gas ratios.
Figure 4.11 presents a closer look at the comparison between the carbon content for the two deposition temperatures. The carbon content appears to be higher for 250 °C than 500 °C. This may be due to increased silicon incorporation at higher temperatures. The silane dissociation rate may increase slightly above the methane dissociation rate with higher temperature, hence providing more plasma energy for breaking down silane into silicon molecules. Additionally, the hydrogen effusion rate also increases dramatically at higher temperature [55], creating a more reactive surface for silicon molecules to bond. Since the difference of carbon content between the two curves is less than 2 at. %, the amount of carbon incorporation can be assumed to be similar for the two temperatures.

Figure 4.11: The carbon content is shown for gas ratio scan samples deposited at 250 °C and 500 °C. The carbon concentration is slightly higher for 500 °C samples than that of 250 °C under the same gas ratios.
4.3.3 Tauc Gap

The Tauc gap values of the gas ratio samples were extracted from the SE absorption data and are plotted in Figure 4.12 below. A clear widening effect on the Tauc gap is observed for both 250 °C and 500 °C samples with increasing methane concentration in the feed gas. The Tauc gap ranges from 1.83 eV to 2.26 eV for the low temperature gas scan, while the high temperature gas scan has a slightly lower range of 1.70 eV to 2.23 eV.

![Figure 4.12](image_url)

**Figure 4.12:** The Tauc gap is plotted as a function of the gas ratio for samples deposited at 250 °C and 500 °C. The Tauc gap nearly increases linearly with gas ratio with 0.99 R² fits.

The range of the DCSF PECVD optical gap correlates well with RF PECVD gap values of 1.7-2.1 eV for the same gas ratio range reported in literature [69]. Both sets of Tauc gap data were fitted with linear equations, obtaining excellent fits with R² of 0.99. The slopes of the linear fits indicate a rise of 0.070 eV and 0.087 eV per 0.1 fractional increase of methane in the precursor
gas for 250 °C and 500 °C samples, respectively. Additionally, the Y-intercepts values, meaning pure silane feed gas, are reported to be 1.76 eV and 1.61 eV for the low and high temperatures, respectively. The Tauc gap for pure silane depositions at the lower temperature, and hence amorphous silicon films, has been reported to be around 1.80 eV [70]; in contrast, a value of 1.83 eV is observed for a methane gas fraction of 0.1 in the above described experiments. The small change of Tauc gap from 0 to 0.1 gas ratio correlates with the small incorporation of carbon at 3 at. % corresponding to a gas ratio of 0.1. Also, the difference in Tauc gaps between the two temperatures can be attributed to higher carbon incorporation in the low temperature samples as shown in Figure 4.13.

![Graph showing Tauc gap vs carbon content for 250 °C and 500 °C samples.]

**Figure 4.13:** The Tauc gap is plotted as a function of carbon content. The higher gap values at 250 °C are due to higher carbon content in the films.

As more carbon gets incorporated into the film, the Tauc gap increases as Si-Si bonds are replaced by stronger Si-C bonds. When the carbon content increases beyond 50 at. %, the Tauc
gap is expected to widen even more rapidly as the Si-C bonds are replaced by even stronger C-C bonds [63]. At such high carbon content in the films the gap can increase to values ranging from 3-4 eV [71]. However, beyond 65 at. % carbon content, the Tauc gap begins to narrow due to the onset of significant sp² bonding of carbon [72]. Furthermore, Brown, et al. found that the valence band offset, $\Delta E_v$, varies from 0.44-1 eV for 0-50 at. % carbon content [73]. The valence band’s downward shift accounts for most of the Tauc gap changes observed as the carbon concentration increases, while the conduction band remains relatively constant. Detailed Tauc gap data is presented in the appendix.

4.3.4 Chemical Bond Content

The chemical bond content can be determined from peak analysis of XPS scans. In Figure 4.14, the C1s peak in films grown at 500 °C at different methane gas ratios are overlaid to illustrate the increase in normalized counts of C-Si content with methane gas fraction. This confirms the hypothesis of increasing Tauc gap due to the formation of stronger C-Si bonds.
Figure 4.14: The C1s peaks for the a-SiC:H films grown at 500 °C with methane gas fraction ranging from 0.1 to 0.7 are overlaid as a function of binding energy; Specifically, the C-Si peak is highlighted for the four samples. The increasing peak height with increasing methane gas fraction is clearly evident.

Normalized peak heights for various chemical species for films prepared at 250 °C and 500 °C are plotted in Figure 4.15 and Figure 4.16, respectively; detailed XPS data values can be found in the appendix.
**Figure 4.15:** The chemical bond content of four bonded species is plotted for films grown at 250 °C with methane gas fraction ranging from 0.1 to 0.7. An increase of C-Si bond content is observed as the gas ratio is raised.

**Figure 4.16:** The chemical bond content of four bonded species is plotted for films grown at 500 °C with methane gas fraction ranging from 0.1 to 0.7. The C-Si content also increases rapidly.
In the plots above, the C-C and C-H content are combined as it is not possible to accurately differentiate between these peaks owing to the fact that the binding energies of the two peaks have a small difference of the order of 0.1 eV [74].

For both 250 °C and 500 °C samples, the C-C/C-H content is initially greater than C-Si content at the lowest gas ratio, which correlates with the measured carbon content of less than 3 at. % indicating that there is very little carbon available to bond with silicon. Also, the dissociation of methane (CH₄) produces many CHₓ molecules that are incorporated in the film, contributing to the C-H peak. As the gas ratio increases, a rapid increase of C-Si bonds is observed accounting for more than 50% of carbon bonds. This increase is directly related to the Tauc gap increase due to the higher bond dissociation energy of C-Si (435 kJ/mol) than that of Si-Si (327 kJ/mol) [75]. As the carbon content goes beyond 25 at. % which is observed at a gas ratio of 0.7, the C-C content is expected to increase replacing the C-Si bonds; there is a corresponding widening of the Tauc gap which is attributed to presence of even stronger C-C bonds (607 kJ/mol) [75]. The plots presented above are of sputtered samples which removed the surface oxide, thus showing low concentrations of C-O-H and C=O bonds. The differences in chemical bond content of as-is and sputtered samples are compared in more detail in Section 4.8.

4.4 Thickness Scan

This set of experiments investigates the effect of deposition time, hence the thickness of the film, on the passivation quality. Using the optimum deposition and gas ratio from the previous sample sets, the deposition time is varied from 5 minutes to 40 minutes. Profilometry measurements were taken to give an initial estimate for ellipsometry modeling to determine the thickness.

4.4.1 Profilometry Measurements

The profilometry result of sample JY11 of 30 minute deposition time is presented in Figure 4.17. The height difference in the figure represents the thickness of the film where the scan spans over a step extending from an area on bare silicon to an area with a-SiC:H film. The profilometer obtained a value of 41 nm compared to SE modeling value of 52 nm, yielding an error of 21%. This error arises from the resolution of the equipment’s stylus tip and its sensitivity to the mechanical properties of the film such as the surface roughness and hardness. However the
trade-off between the quickness and simplicity of profilometry measurements and the accuracy of results still gives a sufficiently accurate first-order estimate of thickness.

Figure 4.17: Profilometry measurement of sample JY11 obtained a value of 41 nm, which was used as a first-order estimate for ellipsometry modeling. The SE regression fitting obtained a thickness value of 52 nm (error of 21%).

4.4.2 Thickness Analysis

The thickness of the a-SiC:H films deposited at 500 °C and 0.5 gas ratio is plotted as a function of deposition time (minutes) in Figure 4.18 below. A linear fit was performed obtaining an $R^2$ value of 0.997 and a slope of 1.68 nm/minute. This is the average growth rate that can be expected within the 5-40 minutes time regime. Thus, the DSCF PECVD a-SiC:H film growth is considered uniform over a thickness range of 10 nm to 70 nm.
The variation in the surface recombination velocity, $S_{\text{eff}}$, as a function of a-SiC:H thickness is shown in Figure 4.19. The observed trend is similar to that reported for hydrogenated amorphous silicon passivation of crystalline silicon. In a-Si films, as the thickness increases, the lifetime reaches a maximum around 40 nm and then deteriorates as films become thicker; the drop in lifetime with thickness increase beyond 40 nm is attributed to an increase in the stress in the film and hence at the interface [76]. With the DCSF deposited a-SiC:H, the passivation performance was also observed to improve as thickness increases and reached a minimum value of $S_{\text{eff}}$ at approximately 50 nm, then degraded with additional film growth. This differs from results reported in literature using RF PECVD where $S_{\text{eff}}$ decreases rapidly as film thickness increases.
increases to 50 nm and then saturates to a thickness of 100 nm [11]. In view of this, the 40 minute deposition experiment was repeated to determine whether the change in trend was a real effect or a spurious result; the repeated test yielded essentially the same film thickness and carrier lifetime. Other properties such as the Tauc gap and elemental composition were found to remain constant as a function of thickness.

**Figure 4.19:** The $S_{\text{eff}}$ is plotted as a function of film thickness. The surface passivation of DCSF a-SiC:H improves as thickness increases, and reaches a minimum value of $S_{\text{eff}}$ at around 50 nm, then degrades as the film becomes thicker.

Using the Olibet recombination model, the interface fixed charge density and the interface defect density were extracted as a function of the film thickness; the data is summarized in Table 4.10
below. Additionally, the interface defect density is plotted as a function of thickness in Figure 4.20.

**Table 4.10:** The thickness scan summary of data

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Deposition Time (minutes)</th>
<th>Thickness (nm)</th>
<th>Lifetime (µs)</th>
<th>$S_{\text{eff}}$ (cm/s)</th>
<th>Interface Fixed Charge Density $\times 10^{11}$ (cm$^{-2}$)</th>
<th>Interface Defect Density $\times 10^{10}$ (cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY26</td>
<td>5</td>
<td>10.3</td>
<td>23.1</td>
<td>607</td>
<td>1.3</td>
<td>15.6</td>
</tr>
<tr>
<td>JY27</td>
<td>10</td>
<td>18.1</td>
<td>32.1</td>
<td>435</td>
<td>2.0</td>
<td>10.6</td>
</tr>
<tr>
<td>JY10</td>
<td>20</td>
<td>36.0</td>
<td>62.3</td>
<td>225</td>
<td>2.5</td>
<td>8.0</td>
</tr>
<tr>
<td>JY11</td>
<td>30</td>
<td>52.0</td>
<td>112.0</td>
<td>124</td>
<td>2.0</td>
<td>3.4</td>
</tr>
<tr>
<td>JY28</td>
<td>40</td>
<td>66.5</td>
<td>30.8</td>
<td>454</td>
<td>2.0</td>
<td>11.4</td>
</tr>
</tbody>
</table>

**Figure 4.20:** The inferred interface defect density is plotted as a function of thickness. It decreases as thickness increases and reaches a minimum around 50 nm, and then increases as the film grows even thicker.
Although the fixed charge density varies with thickness, it suggests that any potential field passivation could be induced by the fixed charge located in the first 10 nm of the a-SiC:H film since the magnitude of the charge increases and then decreases with thickness [77]. On the other hand, the magnitude of the fixed charge density is relatively small and does not correlate with the lifetime data; this implies that the fixed charge does not significantly contribute to the passivation of the surface.

The passivation quality improves as the thickness of the passivation film increases from 10 to 50 nm. This can be attributed to in-situ hydrogenation which involves the diffusion of hydrogen atoms to the c-Si and a-SiC:H interface [15], [58]; the hydrogen atoms saturate the dangling bonds and hence enhances the passivation quality as shown by the reduction of interface defect density in the 10 to 50 nm range. With subsequent growth of film above 50 nm, the interface defect density increased resulting in degradation of surface passivation. The more defective interface may be caused by the buildup of mechanical stress at the interface due to the growth of thicker layers [26], [78].

In the context of practical photovoltaic device designs, one needs to consider the tradeoff between better passivation for thicker layers (up to 50 nm) and increased absorption within the film with thickness [50]. Ideally, the passivation layer which may be used as the intrinsic buffer layer needs to be as thin as possible so as to allow maximum transmission of light and thus its absorption in the bulk of the wafer.

### 4.5 Repeatability

While the deposition conditions are kept constant, a number of variables can affect the quality of the film. This includes the HF acid dip time, HF acid concentration, the amount of time the sample is exposed to air before pumping down the chamber to a good vacuum, the tightness of the clamps holding the wafer down on the substrate holder, the amount of heat up time and pump down time before deposition, etc. In order to ensure repeatability, a number of depositions were dedicated to investigate the consistency of sample properties using the same deposition parameters. A set of six separate depositions of a-SiC:H films under 500 °C, 0.5 gas ratio, and 30 minute deposition time were carried out at different times throughout the entire experimental
study. The various film characteristics measured from Sinton lifetime tester, SE, and XPS are displayed in Table 4.11 below. Although the thickness of the film varied from 51 μm to 61 μm, the film elemental composition stayed relatively constant with a carbon content of approximately 15 atomic %. In addition, the Tauc Gap was constant across all samples with a value of around 2.00 eV. Finally, the lifetime of the samples varied from around 68 μs to 112 μs. While this equates to approximately 65% difference, the lifetime values lie within the upper range of all effective time values measured. With further improvements in optimizing film lifetime, the variance of the data may be minimized. For the purpose of this thesis, Gen 1 depositions are considered to be repeatable to the zeroth order.

Table 4.11: Summary of sample characteristics of films deposited under identical conditions.

<table>
<thead>
<tr>
<th></th>
<th>JY23A</th>
<th>JY23B</th>
<th>JY24A</th>
<th>JY24B</th>
<th>JY11A</th>
<th>JY11B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lifetime (μs)</td>
<td>88.11</td>
<td>86.76</td>
<td>67.82</td>
<td>71.67</td>
<td>112.00</td>
<td>92.00</td>
</tr>
<tr>
<td>Seff (cm/s)</td>
<td>158.44</td>
<td>160.80</td>
<td>206.56</td>
<td>195.33</td>
<td>124.35</td>
<td>152.00</td>
</tr>
<tr>
<td>a-SiC:H thickness (μm)</td>
<td>60.67</td>
<td>55.41</td>
<td>60.17</td>
<td>51.83</td>
<td>51.96</td>
<td>50.90</td>
</tr>
<tr>
<td>Tauc Gap (eV)</td>
<td>2.02</td>
<td>2.01</td>
<td>2.05</td>
<td>2.04</td>
<td>2.02</td>
<td>2.06</td>
</tr>
<tr>
<td>Silicon Content (At. %)</td>
<td>82.93</td>
<td>81.48</td>
<td>83.59</td>
<td>79.80</td>
<td>82.27</td>
<td>83.20</td>
</tr>
<tr>
<td>Carbon Content (At. %)</td>
<td>15.69</td>
<td>16.21</td>
<td>14.65</td>
<td>17.40</td>
<td>15.34</td>
<td>15.06</td>
</tr>
<tr>
<td>Oxygen Content (At. %)</td>
<td>1.38</td>
<td>2.24</td>
<td>1.71</td>
<td>2.72</td>
<td>2.27</td>
<td>1.63</td>
</tr>
<tr>
<td>Fluorine Content (At%)</td>
<td>0.00</td>
<td>0.07</td>
<td>0.06</td>
<td>0.08</td>
<td>0.12</td>
<td>0.11</td>
</tr>
</tbody>
</table>

4.6 Uniformity

The uniformity of the film was investigated through μPCD lifetime scans and SE measurements. Since the lifetime of the bulk is assumed to be constant throughout the wafer, the lifetime map corresponds to the variation in quality of surface passivation by a-SiC:H film. In Figure 4.21, the lifetime map of sample JY23A is shown. A clear non-uniformity is observed with patches of low lifetimes on the right side of the wafer and high lifetimes near the bottom of the wafer. The red shapes at the top and bottom of the wafer represent low lifetime areas which were covered by wafer clamps holding down the wafer. In Figure 4.22, the histogram is fitted to a Gaussian distribution centered at $\tau_{peak} = 67.8 \mu s$ with a large standard deviation of $\sigma = 34.4 \mu s$ compared to literature reported values of $\tau_{peak} = 953 \mu s$ and $\sigma = 83 \mu s$ [12]. The wide main peak in the
Gaussian fit implies a wide distribution of lifetime values, and hence non-uniformity in surface passivation quality.

**Figure 4.21:** μPCD lifetime map of sample JY23A.
Figure 4.22: Gaussian fit of the lifetime histogram data with $\tau_{\text{peak}} = 67.8$ $\mu$s and $\sigma = 34.4$ $\mu$s.

Furthermore, the SE measurements confirm a thickness variation across the wafer. The wafer was mapped as shown in Figure 4.23, and the thicknesses are displayed accordingly. The thickness increases monotonically from the right side of the wafer to the left, while the vertical scan shows a lesser degree of thickness deviation. The top- and bottom- most values are influenced by the wafer clamps that hold the sample down and hence have different thicknesses as the centre of the wafer. This thickness variation was also reported for amorphous silicon depositions in the same DCSF PECVD system [79]. The non-uniformity of Gen 1 deposition system can be attributed to the asymmetric position of the gas inlet and outlet ports. It is possible to solve the issue with system improvements by introducing feed gas from both sides of the chamber, and relocating the outlet port to the centre of the system. In addition, a ring clamp could be used to hold the wafer down from the entire circumference of the wafer, providing a constant pressure on the entire outer edge. Since lifetime non-uniformity exists on the wafer, all
Sinton and SE measurements were taken at the centre of the wafer to maintain consistency across all deposited samples.

**Figure 4.23:** SE measurement map (top) and the corresponding thicknesses (bottom). The gas inlet is located on the left side of the wafer and the thickness was found to vary monotonically from thickest to thinnest from the left to right of the wafer.
4.7 Annealing

Post-deposition annealing has been known to improve the passivation quality through the restructuring of silicon bonds at the interface and the diffusion of hydrogen [27]. In addition, thermal annealing can relieve internal film stress by releasing hydrogen molecules from the film [80]. All a-SiC:H samples from the various scans were thermally treated to investigate the passivation characteristics, as well as the thermal stability. A hot plate capable of reaching 550 °C was utilized to carry out the annealing experiments. In order to suppress any undesirable absorption of impurities from the ambient atmosphere, most notably oxygen and carbon dioxide, the annealing was carried out in a nitrogen glove box with oxygen levels below 50 parts per million (ppm). Lastly, two extra minutes were added to the specified annealing time to account for the rise time associated with temperature ramping to the set temperature.

4.7.1 Single Step Annealing

Annealing the samples at 300 °C for 15 minutes was shown to improve the passivation quality of low deposition temperature samples, while causing degradation to samples prepared at higher temperatures, as illustrated in Figure 4.24 below.

![Figure 4.24](image)

**Figure 4.24**: $S_{\text{eff}}$ improves after annealing treatment for the 250 °C sample and degrades for higher temperatures.
The trends observed in the plot above can be correlated with the microstructure parameter determined by FTIR measurements. The microstructure is defined as a ratio of SiH$_2$ to SiH content and a high R-value represents a-SiC:H layers with a higher void fraction [48]. For higher deposition temperatures of 400 °C and above, hydrogen molecules can effuse out of the film more easily via the interconnected voids and thereby deteriorating the interface properties and reducing the effective lifetime. On the other hand, the 250 °C sample with a lower microstructure prevents such effusion and maintains the hydrogen content within the film. Also, the enhancement in passivation can be attributed to the restructuring the silicon bonds at the interface by reducing strained Si-Si bonds, hence decreasing the defect density [81].

![Graph showing microstructure vs. deposition temperature](image)

**Figure 4.25:** The microstructure parameter increases as the deposition temperature increases. This suggests a more compact film at lower temperatures with fewer microvoids.

The effect of annealing time on passivation quality was also investigated for the 250 °C samples; the passivation quality was observed to improve by the same degree for 15-minute, 30-minute, and all the way up to 240-minute experiments with no degradation detected. The high temperature gas ratio scan and the thickness scan samples all displayed degradation after a one-
time annealing treatment at 300 °C, while the low temperature gas ratio scan samples showed improvement. Based on the microstructure data, it is deduced that the degraded samples likely have a high microstructure parameter as they were all deposited at 500 °C. The thermal stability of the low temperature gas ratio scan a-SiC:H films is analyzed in the next subsection.

4.7.2 Thermal Stability

In addition to the one-time annealing experiments described above, sequential annealing steps were performed from 150 °C to 400 °C to demonstrate the thermal stability of amorphous silicon carbide. The effective lifetime for low temperature gas ratio scan samples and its thermal stability are shown to depend strongly on the gas ratio as seen in Figure 4.26 below.

![Figure 4.26: The effective lifetime is plotted as a function of annealing temperature for 0.1 to 0.7 feed gas ratios. The smallest gas ratio samples have the highest thermal stability while the highest gas ratio samples have enhanced lifetime at low annealing temperatures.](image-url)
The lifetime plot as a function of stepwise annealing temperatures shown above demonstrates a number of concepts. Firstly, the films deposited with the lowest gas ratios are most thermally stable, reaching peak lifetimes at higher annealing temperatures around 320 °C. These low carbon content samples also showed the best improvement in surface passivation quality when compared to the peaks at all compositions. On the other hand, higher carbon incorporation in a-SiC:H layers boosted the lifetime at lower annealing temperatures and resulted in an elevated lifetime enhancement rate. However, these samples are less temperature stable as they began to degrade around 250 °C, while the lifetime values for the low gas ratio films continued to increase with further increase in annealing temperature. The point that divides the thermal stability of high and low gas ratio occurs at around 275 °C, where the lifetime curves intersect. At higher annealing temperatures above 350 °C, drastic decrease in effective lifetime occurs for all gas ratios as visualized by the large arrow in the plot. This is due to the thermal and mechanical stress on the film from the annealing procedure, as well as the hydrogen effusion out of the amorphous layers. Hydrogen effusion plays a key role in the thermal stability of a-SiC:H films as hydrogen starts to leave the film at around 350 °C [82], compared to 250 °C for a-Si:H [27]. This can be explained based on the higher bond dissociation energy of C-H (337.2 kJ/mol) than that of Si-H (298.49 kJ/mol) [75]. It requires less energy for hydrogen to break away from Si-H bonds than C-H bonds; hence, hydrogen diffusion out of the amorphous films is suppressed for a-SiC:H samples with variable C-H bond content depending on the gas ratio. However, from the results presented above, the high carbon content samples were not able to withstand high temperature annealing. This could be linked to the previous studies of microstructure parameter which found the formation of less compact films with higher carbon content [82], implying that higher gas ratio samples have a high fraction of voids. Atomic hydrogen desorbs and forms molecular hydrogen in these interconnected voids, forming a path for hydrogen to effuse out of the film [49]. Thus, the thermal stability of high carbon content films is reduced since the saturation of dangling bonds requires high atomic hydrogen content. Samples with low carbon content have a lower microstructure parameter and accordingly are more dense films; these compact films tend to relatively hinder the diffusion of hydrogen atoms to the interface at low annealing temperatures, and correspondingly a slow rate of rise in effective lifetime with annealing temperature is observed in the plot. Also, the effusion of hydrogen is not prevalent until at higher annealing temperatures, thus displaying better thermal stability for compact films with small microstructure parameters. In summary, low gas ratio films yield the most thermally
stable passivation, withstanding annealing temperatures up to around 320 °C, while high gas ratio films show quick improvement in passivation at lower annealing temperatures.

4.8 XPS Analysis

4.8.1 Depth Profile

The depth profile of a-SiC:H films is determined using XPS with in situ sputtering. The instrument uses an Argon ion gun of 1000 eV to sputter off the surface of the sample for 10 second intervals and followed by an XPS measurement to determine the elemental composition. Figure 4.27 shows the depth profile of sample JY23 with SE thickness of 60 nm. The interface of a-SiC:H film and c-Si substrate can be seen at 600 seconds of etch time where the carbon content drops quickly, while the silicon content increases to around 99%. Hence, the etch rate can be calculated to be roughly 0.1 nm/s.
Figure 4.27: The depth profile displays the concentration of silicon, carbon and oxygen at each etch level until the a-SiC:H film is completely etched away. This plot shows high oxygen concentration at the surface, and can be removed by sputtering for approximately 30 seconds.

At the surface of the film, approximately 20 atomic (at.) % of oxygen atoms exist due to absorbed oxygen and surface oxidation from exposure of the sample the atmosphere. This is detrimental in determining the film elemental composition; therefore it is desirable to etch away the contamination layer. The oxygen level is brought down to less than 3% after around 30 seconds of sputtering and remains at a constant level throughout the rest of the film depth. Therefore, the elemental composition of the samples was determined by XPS after 30 seconds of sputtering, in addition to the first measurement of the unsputtered or as-is sample. The next section presents the data for as-is and after sputtering data and compares the elemental composition and chemical bonding between the two sets of data.
4.8.2 Sputtering Analysis

A survey scan is a low resolution measurement of electron counts for a binding energy of 0 to 1250 eV. The as-is and after 30 seconds of sputtering survey scans are shown in Figure 4.28 and Figure 4.29 below, respectively. The O1s peak decreases sharply after the sputtering has taken place, thus surface oxidation has less of an impact on the determination of elemental composition.

![Survey Chart]

**Figure 4.28:** As-is XPS survey scan shows a large O1s peak from surface oxidation effects.
**Figure 4.29:** After sputtering XPS survey scan show a sharp decrease in the O1s peak after etching off surface contamination.

Furthermore, the C1s and Si2p peaks were investigated to observe the changes in chemical bond composition before and after sputtering as shown in Figure 4.30 to Figure 4.33. The charge shifting effect of XPS was first corrected by shifting the silicon peak to the reported value of 99.3 eV and hence shifting the entire spectrum [43]. Then the Shirley background was applied to cancel out the background noise as shown labeled “Background” in the peak fitting plots below [44]. It is important to note that the binding energy of C-C and C-H peaks has a small difference of the order of 0.1 eV [74]. Hence, these peaks were combined in one peak and not deconvolved further. Similarly, the Si-Si and S-H peak energy positions also have a small difference within 0.1 eV [45], therefore it is not possible to accurately distinguish between the two bonding configurations.
Figure 4.30: As-is C1s peak fit shows C=O and C-O-H peaks from surface contamination.

Figure 4.31: Sputtered C1s peak fit shows removal of surface contamination.
Figure 4.32: As-is Si2p peak fit shows significant quantity of Si-O bonds at the surface.

Figure 4.33: Sputtered Si2p peak fit shows the disappearance of surface oxide contamination.
The chemical bond content from peak fitting the Si2p and C1s peaks is shown in Table 4.12 for as-is and sputtered samples. In both sets of after-sputter plots above, the surface oxide peaks have disappeared, including Si-O<sub>x</sub>, C-O-H, and C=O bonds. This is seen in Table 4.12 which coincides with the survey scans which show a sharp decrease in the O1s peak. In addition, the C-C/C-H bond content dropped from around 50% to 19% after sputtering; this may be attributed to the removal of surface contamination due to adsorbed ambient hydrocarbons. Moreover, the charge shift effect is observed in both C1s and Si2p peaks after sputtering where the entire spectrum has shifted slightly to the right in the direction of decreasing binding energy.

Table 4.12: Chemical bond content of as-is and sputtered XPS measurements of sample K9A.

<table>
<thead>
<tr>
<th>Peak Type</th>
<th>Chemical Bond</th>
<th>As-is Content (At. %)</th>
<th>Sputtered Content (At. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si2p</td>
<td>Si-Si (99.19 eV)</td>
<td>29.18</td>
<td>94.33</td>
</tr>
<tr>
<td></td>
<td>Si-C (100.87 eV)</td>
<td>5.01</td>
<td>5.67</td>
</tr>
<tr>
<td></td>
<td>Si-O&lt;sub&gt;x&lt;/sub&gt; (102.48 eV)</td>
<td>65.81</td>
<td>0.00</td>
</tr>
<tr>
<td>C1s</td>
<td>C-Si (283.14 eV)</td>
<td>26.79</td>
<td>80.99</td>
</tr>
<tr>
<td></td>
<td>C-C/C-H (285.00 eV)</td>
<td>49.50</td>
<td>18.94</td>
</tr>
<tr>
<td></td>
<td>C-O-H (286.71 eV)</td>
<td>14.65</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>C=O (287.80 eV)</td>
<td>9.06</td>
<td>0.07</td>
</tr>
</tbody>
</table>

For the Si2p peak fit, the Si2p<sub>3/2</sub>- Si2p<sub>1/2</sub> spin-orbit splitting was taken into account for the deconvolution [83]. Each chemical bond peak is represented by two distinct peaks 0.61 eV apart, with a branching ratio of 0.52 [84]. The area ratios of the bonds were then determined using either Si2p<sub>3/2</sub> or Si2p<sub>1/2</sub>, exclusively.

In summary, XPS analysis of a-SiC:H film was more accurately determined after 30 seconds of sputtering which removes any surface contamination from oxide and hydrocarbon molecules.
4.9 System Improvements

A number of trial depositions were performed initially to test the system stability of a-SiC:H depositions. As higher temperatures were desired, numerous system improvements were imposed on the Gen 1 vacuum system including lamp heater, temperature controller, high amperage power line, water cooling for the decomposition chamber, and thermocouple to detect flange temperature. However, during the process of increasing lamp wattage, the increased rate of heating caused the stainless steel substrate holder to bend and deform, which caused non-uniformity in film deposition due to the uneven surface. In addition, the high temperature created mechanical deformation on the lamp structure, which in turn caused electrical contact issues between the halogen bulbs and power rails. As a result, and given the time constraints, the original coil heater was used to carry out the depositions for this thesis. Nonetheless, the lamp heating system did demonstrate the advantages of rapid heating, rapid cool-down, and very uniform heating all of which can be availed following key enhancements in the design of the lamp heater.

4.10 Error Analysis

The potential sources of errors and the estimated error in the measurements are presented in this section. The Gen 1 DCSF PECVD vacuum system has several sources of error in terms of deposition parameters. The deposition temperature is kept within ± 10 °C of the set temperature by the temperature controller, and the gas pressure monitored by a capacitance manometer has a maximum error of approximately ± 10 Torr, leading to the same error in calculating the gas ratio. Moreover, the hot plate used for annealing has a temperature error of ± 15 °C.

For the effective lifetime measured by the Sinton lifetime tester, there exists a 5% error in the QSS-PC method due to uncertainty in the optical constant in calculating the generation rate. In addition, solving for the effective surface recombination velocity involves the wafer thickness parameter which is nominally 280 µm ± 20 µm. The modeling from Spectroscopic Ellipsometry presents a regression fitting error as well as a thickness error as shown on all thickness plots presented. The source of the thickness error arises from inaccuracies in instrument measurement as well as fitting. All SE fits achieved an R² greater than 0.99 with some measurements reaching
0.999. In addition, the Olibet recombination model fits have a least square mean (LSM) of less than 0.0015 while all FTIR fits have an $R^2$ value greater than 0.994.

The XPS elemental composition calculated from the area ratios of various peaks has roughly 5% error that can be attributed to instrument resolution and computation error. The peak fitting performed on C1s and Si2p peaks have reported values of Chi squared, but the accuracy of the fit is typically determined by eye. The fitting error is not quantified in XPS publications, but rather determined by observing the plot of the fitted curve overlapping the raw data.

### 4.11 Summary

The deposition temperature was found to have the most dominant effect on surface passivation quality, with increasing deposition temperature resulting in lower $S_{\text{eff}}$ values. The lowest $S_{\text{eff}}$ achieved was 28 cm/s through a series of repeatability experiments at the optimum temperature of 500 °C under the same deposition conditions of 0.5 gas ratio and 30 minute deposition time. The repeatability experiments data are shown in Figure 4.34 as illustrated by the dotted line.

![Figure 4.34](image)

**Figure 4.34**: The $S_{\text{eff}}$ plotted as a function of the deposition temperature, with a series of repeatability experiment data points shown by the dotted line at 500° C.
The variation in the cluster of data points at 500 °C can be attributed to process variations and for the purpose of this research, the DC saddle field system is considered to be repeatable to the zeroth order. In comparison to the state of the art $S_{\text{eff}}$ result of 22 cm/s for n-type wafers, the DC saddle field a-SiC:H accomplished comparable passivation quality with $S_{\text{eff}}$ of 28 cm/s, corresponding to a lifetime of around 0.5 ms. This set of results from the first study of DCSF a-SiC:H shows promise, and lower $S_{\text{eff}}$ values closer to the state of the art result is expected with further improvements in process control.

In addition, the gas ratio scan obtained Tauc gaps in the range of 1.7 to 2.3 eV, compared to reported values of 1.8 – 3.85 eV for RF PECVD a-SiC:H. The difference in the upper end of the range can be attributed to the difference in carbon content. The 2.3 eV Tauc gap was obtained for a sample with less than 25 at. % carbon content, while the RF PECVD achieved higher Tauc gaps by incorporating higher carbon content in the film. This is due to the higher power used in RF PECVD systems; the DCSF anode power can be increased in order to raise the carbon content for a higher Tauc gap. The drop of the optical band gap beyond around 0.55 (55 at. %) carbon content is due to the onset of sp2 hybridization which causes the gap to become narrower.

![Figure 4.35: Optical gap values as a function of carbon content for RF PECVD a-SiC:H [71].](image)
5 Conclusions

5.1 Conclusions

The fundamental study of intrinsic hydrogenated amorphous silicon carbide (a-SiC:H) films grown by the novel DC saddle field (DFSF) PECVD technique has been carried out in this thesis. The dependence of passivating, structural, and optical properties of a-SiC:H films on the deposition conditions was investigated and compared with literature results for a-SiC:H films grown using RF PECVD.

The excess carrier lifetime results demonstrate the potential of amorphous silicon carbide as a high lifetime and thermally stable surface passivation material for high efficiency thin silicon photovoltaic applications. The highest lifetime achieved was 0.5 ms, corresponding to an effective surface recombination velocity, \( S_{\text{eff}} \), value of 28 cm/s using a deposition temperature of 500 °C, 0.5 gas ratio, and 30 minutes of deposition time.

The deposition temperature was found to have the most critical effect on the passivating qualities of the film. The effective surface recombination velocity, \( S_{\text{eff}} \), decreases dramatically as the deposition temperature rises, representing an improvement in surface passivation characteristics. By fitting the \( S_{\text{eff}} \) data as a function of the excess carrier density to the Olibet recombination model, an essentially constant interface fixed charge density was found while the interface defect density decreased with higher deposition temperatures. This indicates that field effect passivation from the fixed charge in the film is not the predominant cause of improvement in surface passivation rather the sharp drop of interfacial defect density corresponds directly to the saturation of silicon dangling bonds by atomic hydrogen. Increasing the deposition temperature promotes hydrogen redistribution within the film to fill the surface defects and provides better interface properties, hence lower \( S_{\text{eff}} \).

The dependence of film and interface properties on feed gas ratio, defined as \([\text{CH}_4]/([\text{CH}_4]+[\text{SiH}_4])\), was determined by carrying out a series of depositions at the optimum deposition temperature of 500°C. In addition, another gas ratio scan was performed at a lower temperature of 250 °C to compare and contrast the properties of film at the two ends of the temperature
spectrum. Both sets of experiments showed $S_{\text{eff}}$ local minima of 536 cm/s and 124 cm/s at 0.3 and 0.5 gas ratios for 250 °C and 500 °C, respectively. This dependence of surface passivation on the gas ratio is similarly observed for RF PECVD deposited films with a minimum at just under 0.5 gas ratio, which suggests similar growth mechanisms between DCSF and RF PECVD a-SiC:H films. Furthermore, both gas ratio scans demonstrated the adjustable band gap of a-SiC:H with the Tauc gap varying from 1.70 eV to 2.22 eV with increasing methane concentration in the feed gas. The widening effect of the Tauc gap is attributed to the incorporation of carbon atoms, which replaces Si-Si bonds with stronger Si-C and C-C bonds.

The structural and optical properties of the two gas ratio scans showed similar results, while the passivating qualities were significantly better for higher deposition temperatures.

The DCSF PECVD a-SiC:H film growth was found to be uniform in thickness within the 5-40 minutes deposition time regime. A linear fit of thickness as a function of deposition time provided a growth rate of 1.68 nm/minute, which is much less than the reported growth rates in using RF-PECVD systems owing to their use of higher power to operate the plasma discharges. The RF systems can reach deposition rates from 8 nm/min [58] to as high as 18 nm/minute [59].

The passivation quality improved as thickness was increased to 50 nm, corresponding to an optimum deposition time of 30 minutes then degraded rapidly as film thickness was increased further. The improvement can be attributed to in-situ hydrogenation as hydrogen atoms diffuse towards the interface to fill dangling bonds and reduce interface defect density. With subsequent growth of film above 50 nm, the buildup of mechanical stress from thick layers results in a more defective interface, and thus degrades the surface passivation quality.

Post-deposition annealing results exhibited improvement of passivation quality through the diffusion of atomic hydrogen and the restructuring of silicon bonds at the interface. The enhancement in effective lifetime were only observed for low deposition temperature samples (250 °C), while films deposited at higher temperature (500 °C) showed dramatic degradation with annealing. This outcome was correlated to the increase of the microstructure parameter as the deposition temperature rises, which suggests an increase in the microvoid fraction in films deposited at high temperature. Therefore, hydrogen molecules can effuse out of the film more easily via the interconnected voids and thus lead to deterioration in interface properties and accordingly the passivation quality. Additionally, annealing of the films grown as part of the gas ratio scans revealed that low gas ratio films yield the most thermally stable passivation,
withstanding annealing temperatures up to around 320 °C, while high gas ratio films exhibit an improvement in passivation quickly at low annealing temperatures then degrading rapidly as the annealing temperature is raised further.

In summary, the properties of the c-Si and a-SiC:H interface were found to be critical to the resulting surface passivation qualities. The variation of deposition parameters allows for the improvement or degradation of these properties. Through the range of systematic experiments, a-SiC:H films grown for the first time using the DC saddle field technique have been shown to achieve very good passivation quality, adjustable band gap, and thermal stability making it amenable for low-temperature synthesis of high efficiency silicon photovoltaics.

5.2 Future Work

Further characterization studies on Gen 1 DCSF PECVD system can be performed by varying other deposition parameters such as the anode voltage, base pressure, and electrode configuration. This allows for a broader scan of the system’s capabilities for depositing a-SiC:H films and optimizing the surface passivation quality. In addition, variations in the anode voltage can be experimented to attempt achieving higher carbon incorporation to provide wider Tauc gaps in the 3-4 eV range. Further annealing studies examining the effect on the microstructure of films can be done along with observing changes in hydrogen content with annealing temperature so as to better understand the correlation between annealing and hydrogen content of the films.

Moreover, the effective lifetime of the amorphous films can be enhanced through a number of system improvements such as: i) a high temperature heater capable of achieving higher than 500 °C, ii) symmetric gas inlet and outlet ports on the system to provide a more uniform gas distribution, iii) a nitrogen-filled glove box connected to a load lock for the chamber so samples could be loaded without contamination due to the atmosphere after the HF acid dip, and iv) a ring clamp to hold the wafer down on the entire circumference of the sample, providing equal pressure all around. It is suggested that these enhancements and especially the ability to deposit films at higher temperatures can lead to the attainment of even higher lifetimes, exceeding 1 ms. Upon achieving such effective lifetime values, device fabrication is desirable to demonstrate the
proof of concept of amorphous silicon carbide as an excellent surface passivation material that is thermally stable and has a wide band gap.

Lastly, it is worth highlighting that hydrogenated amorphous silicon carbide has a number of other applications in optical communications, optical sensors, LEDs, and MEMS. Its mechanical properties and inert composition makes it amenable for bio-applications as encapsulation materials. Its low surface roughness lends it as a potential buffer layer in piezoelectric based devices. Accordingly, the exploration of a-SiC:H for these applications is a worthy future endeavor.
References


56. Hoex, B., et al., *State of the art surface passivation by hydrogenated amorphous silicon deposited at rates > 1nm/s by the expanding thermal plasma technique*.


Appendix

The elemental composition raw data for 250 °C and 500 °C shown in Tables A1 and A2, respectively. For both deposition temperatures, the carbon content increases from approximately 3 at. % to 25% as more methane is added to the feed gas. Consequently, the silicon content decreases, while the oxygen and fluorine content remained constant at less than 3 at. % and 0.3 at. %, respectively.

Table A1: Elemental composition of gas ratio scan films deposited at 250 °C.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Gas Ratio</th>
<th>Silicon (At. %)</th>
<th>Carbon (At. %)</th>
<th>Oxygen (At. %)</th>
<th>Fluorine (At. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY33</td>
<td>0.1</td>
<td>93.41</td>
<td>3.84</td>
<td>2.45</td>
<td>0.29</td>
</tr>
<tr>
<td>JY34</td>
<td>0.3</td>
<td>88.66</td>
<td>9.07</td>
<td>2.12</td>
<td>0.14</td>
</tr>
<tr>
<td>JY35</td>
<td>0.5</td>
<td>82.09</td>
<td>15.26</td>
<td>2.48</td>
<td>0.17</td>
</tr>
<tr>
<td>JY36</td>
<td>0.7</td>
<td>71.89</td>
<td>25.15</td>
<td>2.80</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Table A2: Elemental composition of gas ratio scan films deposited at 500 °C.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Gas Ratio</th>
<th>Silicon (At. %)</th>
<th>Carbon (At. %)</th>
<th>Oxygen (At. %)</th>
<th>Fluorine (At. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY18</td>
<td>0.1</td>
<td>94.57</td>
<td>3.11</td>
<td>2.20</td>
<td>0.12</td>
</tr>
<tr>
<td>JY17</td>
<td>0.2</td>
<td>92.10</td>
<td>5.52</td>
<td>2.19</td>
<td>0.20</td>
</tr>
<tr>
<td>JY16</td>
<td>0.3</td>
<td>89.98</td>
<td>7.59</td>
<td>2.30</td>
<td>0.14</td>
</tr>
<tr>
<td>JY15</td>
<td>0.4</td>
<td>86.93</td>
<td>11.10</td>
<td>1.83</td>
<td>0.14</td>
</tr>
<tr>
<td>JY11</td>
<td>0.5</td>
<td>82.27</td>
<td>15.34</td>
<td>2.27</td>
<td>0.12</td>
</tr>
<tr>
<td>JY19</td>
<td>0.6</td>
<td>78.29</td>
<td>19.88</td>
<td>1.72</td>
<td>0.11</td>
</tr>
<tr>
<td>JY20</td>
<td>0.7</td>
<td>74.41</td>
<td>23.30</td>
<td>2.19</td>
<td>0.10</td>
</tr>
</tbody>
</table>
Tables A3 and A4 present the Tauc gap data with reference to the gas ratio and carbon content of samples deposited at 500 °C and 250 °C, respectively. As more carbon gets incorporated into the film, the Tauc gap increases as Si-Si bonds are replaced by stronger Si-C bonds. The Tauc gap is slightly higher for the 250 °C samples than that of 500 °C for the same gas ratios. The difference is due to a slightly higher carbon content for the higher Tauc gap samples.

**Table A3:** Tauc gap and carbon content data for 500 °C samples. Tauc gap increases as more carbon content is incorporated in the film.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Gas Ratio</th>
<th>Carbon Content (At. %)</th>
<th>Tauc Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY18</td>
<td>0.1</td>
<td>3.11</td>
<td>1.70</td>
</tr>
<tr>
<td>JY17</td>
<td>0.2</td>
<td>5.52</td>
<td>1.79</td>
</tr>
<tr>
<td>JY16</td>
<td>0.3</td>
<td>7.59</td>
<td>1.86</td>
</tr>
<tr>
<td>JY15</td>
<td>0.4</td>
<td>11.10</td>
<td>1.94</td>
</tr>
<tr>
<td>JY11</td>
<td>0.5</td>
<td>15.34</td>
<td>2.02</td>
</tr>
<tr>
<td>JY19</td>
<td>0.6</td>
<td>19.88</td>
<td>2.16</td>
</tr>
<tr>
<td>JY20</td>
<td>0.7</td>
<td>23.30</td>
<td>2.23</td>
</tr>
</tbody>
</table>

**Table A4:** Tauc gap and carbon content data for 250 °C samples. The Tauc gap increases as more carbon content is incorporated in the film.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Gas Ratio</th>
<th>Carbon Content (At. %)</th>
<th>Tauc Gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY33</td>
<td>0.1</td>
<td>3.84</td>
<td>1.83</td>
</tr>
<tr>
<td>JY34</td>
<td>0.3</td>
<td>9.07</td>
<td>1.95</td>
</tr>
<tr>
<td>JY35</td>
<td>0.5</td>
<td>15.26</td>
<td>2.09</td>
</tr>
<tr>
<td>JY36</td>
<td>0.7</td>
<td>25.15</td>
<td>2.26</td>
</tr>
</tbody>
</table>
The chemical composition determined from fitting the XPS C1s peak is presented in Tables A5 and A6 below for 500 °C and 250 °C, respectively. A higher carbon incorporation forming C-Si bonds is observed as more methane is added to the feed gas for both deposition temperatures.

**Table A5:** The chemical composition of for 500° C gas ratio samples; an increase of C-Si bond content is observed as gas ratio increases.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Gas Ratio</th>
<th>C-Si (At. %)</th>
<th>C-C/C-H (At. %)</th>
<th>C-O-H (At. %)</th>
<th>C=O (At. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY18</td>
<td>0.1</td>
<td>41.95</td>
<td>51.81</td>
<td>6.15</td>
<td>0.09</td>
</tr>
<tr>
<td>JY17</td>
<td>0.2</td>
<td>57.62</td>
<td>35.79</td>
<td>6.54</td>
<td>0.05</td>
</tr>
<tr>
<td>JY16</td>
<td>0.3</td>
<td>63.86</td>
<td>32.77</td>
<td>3.34</td>
<td>0.03</td>
</tr>
<tr>
<td>JY15</td>
<td>0.4</td>
<td>69.79</td>
<td>27.95</td>
<td>2.23</td>
<td>0.02</td>
</tr>
<tr>
<td>JY11</td>
<td>0.5</td>
<td>72.25</td>
<td>25.80</td>
<td>1.95</td>
<td>0.01</td>
</tr>
<tr>
<td>JY19</td>
<td>0.6</td>
<td>81.47</td>
<td>18.00</td>
<td>0.52</td>
<td>0.01</td>
</tr>
<tr>
<td>JY20</td>
<td>0.7</td>
<td>83.53</td>
<td>15.99</td>
<td>0.47</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**Table A6:** The chemical composition of for 250° C gas ratio samples; an increase of C-Si bond content is observed as gas ratio increases.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Gas Ratio</th>
<th>C-Si (At. %)</th>
<th>C-C/C-H (At. %)</th>
<th>C-O-H (At. %)</th>
<th>C=O (At. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JY33</td>
<td>0.1</td>
<td>33.47</td>
<td>58.08</td>
<td>8.21</td>
<td>0.24</td>
</tr>
<tr>
<td>JY34</td>
<td>0.3</td>
<td>55.18</td>
<td>43.93</td>
<td>0.59</td>
<td>0.29</td>
</tr>
<tr>
<td>JY35</td>
<td>0.5</td>
<td>63.41</td>
<td>35.62</td>
<td>0.85</td>
<td>0.12</td>
</tr>
<tr>
<td>JY36</td>
<td>0.7</td>
<td>68.88</td>
<td>30.52</td>
<td>0.56</td>
<td>0.05</td>
</tr>
</tbody>
</table>