Interface properties of the amorphous silicon/crystalline silicon heterojunction photovoltaic cell

by

Basia Halliop

A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Electrical and Computer Engineering
University of Toronto

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Abstract

Amorphous-crystalline silicon (a-Si:H/c-Si) heterojunctions have the potential of being a very high efficiency silicon photovoltaic platform technology with accompanying cost and energy budget reductions. In this research a heterojunction cell structure based on a-Si:H deposited using a DC saddle field plasma enhanced vapour deposition (DCSF PECVD) technique is studied, and the a-Si:H/c-Si and indium tin oxide/a-Si:H interfaces are examined using several characterization methods.

Photocarrier radiometry (PCR) is used for the first time to probe the a-Si:H/c-Si junction. PCR is demonstrated as a carrier lifetime measurement technique – specifically, confirming carrier lifetimes above 1 ms for 1-5 Ω.cm phosphorous-doped c-Si wafers passivated on both sides with 30 nm of i-a-Si:H. PCR is also used to determine surface recombination velocity and mobility, and to probe recombination at the a-Si:H/c-Si interface, distinguishing interface recombination from recombination within the a-Si:H layer or at the a-Si:H surface.
A complementary technique, lateral conductivity is applied over a temperature range of 140 K to 430 K to construct energy band diagrams of a-Si:H/c-Si junctions. Boron doped a-Si:H films on glass are shown to have activation energies of 0.3 to 0.35 eV, tuneable by adjusting the diborane to silane gas ratio during deposition. Heterojunction samples show evidence of a strong hole inversion layer and a valence band offset of approximately 0.4 eV; carrier concentration in the inversion layer is reduced in $p$-a-Si:H/$i$-a-Si:H/c-Si structures as intrinsic layer thickness increases, while carrier lifetime is increased.

The indium tin oxide/amorphous silicon interface is also examined. Optimal ITO films were prepared with a sheet resistance of $17.3 \ \Omega/\square$ and AM1.5 averaged transmittance of 92.1%, for a film thickness of approximately 85 nm, using temperatures below 200°C. Two different heat treatments are found to cause crystallization of ITO and to change the properties of the underlying a-Si:H film.

Finally, an open circuit voltage of 699 mV was achieved using DCSF PECVD in the tetrode configuration to fabricate a metal/ITO/$p$-a-Si:H/$i$-a-Si:H/$n$-c-Si/$i$-a-Si:H/$n^+$/a-Si:H/metal photovoltaic cell on a texturized wafer. The 4 cm$^2$ cell had an efficiency of 16.5%, a short circuit current of 36.4 mA/cm$^2$ and a fill factor of 64.7%.
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\( A \) area \([\text{cm}^2]\)

\( B_n, B_p \) electron and hole capture coefficients \([\text{cm}^3/\text{s}]\)

\( B_{rad} \) radiative recombination coefficient \([\text{cm}^3/\text{s}]\)

\( C \) arbitrary constant

\( c \) speed of light in vacuum, 2.998x10^{10} \([\text{cm/s}]\)

\( C_{th} \) heat capacity \([\text{J/K}]\)

\( c_{th} \) specific heat capacity \([\text{J/gK}]\)

\( D^*, D_n, D_p \) ambipolar diffusion constant, electron diffusion constant, hole diffusion constant \([\text{cm}^2/\text{s}]\)

\( D_{a-Si}, D_{c-Si} \) ambipolar diffusion constant in a-Si, in c-Si \([\text{cm}^2/\text{s}]\)

\( d_{AR} \) thickness of antireflective coating \([\text{cm}]\)

\( d_{a-Si:H} \) thickness of amorphous silicon \([\text{cm}]\)

\( E, \bar{E}, E_{\alpha}, \bar{E}_{\text{int}}, \bar{E}_{\text{th}} \) electric field, applied electric field, internal electric field, thermoelectric field \([\text{V/cm}]\)

\( E \) energy \([\text{eV}]\)

\( E_c, E_v \) conduction band minimum, valence band maximum \([\text{eV}]\)

\( E_{corr} \) correlation energy \([\text{eV}]\)

\( E_F \) Fermi level \([\text{eV}]\)

\( E_{F,\text{int}} \) Fermi level at a-Si :H/c-Si interface \([\text{eV}]\)

\( E_g \) band gap \([\text{eV}]\)

\( F \) diffusion wave damping coefficient \([\text{cm}^2]\)
$F_1, F_2$  spectral coefficients of PCR system  

$FF$  fill factor  

$f(E, E_F(x))$  probability of electron occupation for a state at energy $E$  

$f_o^+ (E, E_{F, \text{int}}), f_o^- (E, E_{F, \text{int}})$  probability of electron occupation for positive, negative interface defects at energy $E$  

$f_t$  probability of electron occupation for trap state  

$G$  carrier generation rate [cm$^{-3}$s$^{-1}$]  

$G_0$  DC carrier generation rate (for modulated photoluminescence) [cm$^{-3}$s$^{-1}$]  

$G_1$  amplitude of the AC carrier generation rate (for modulated photoluminescence) [cm$^{-3}$s$^{-1}$]  

$G_{\text{cond}}$  conductance [S]  

$G_{\text{ne}}, G_{\text{pc}}$  electron and hole trap release rates [cm$^{-3}$s$^{-1}$]  

$G_{s}$  sheet conductance [S]  

$h$  Planck’s constant, $6.625 \times 10^{-34}$ [J-s]  

$h$  Dirac’s constant, $h/2\pi$ [J-s]  

$h, L$  electrode dimensions [cm]  

$h_{\text{air, cooling}}$  heat transfer coefficient [W/cm$^2$K]  

$I_o$  optical intensity [W/cm$^2$]  

$I_{AM1.5} (\lambda)$  optical intensity of AM1.5 solar spectrum [W/cm$^2$/nm]  

$J, \tilde{J}$  current density [A/cm$^2$]  

$J_{\text{dark}}$  dark current density [A/cm$^2$]  

$\tilde{J}_{\text{diff}n}, \tilde{J}_{\text{diff}p}$  electron diffusion current density, hole diffusion  

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current density [A/cm²]

\( \vec{J}_{\text{drift}_n} \)  
\( \vec{J}_{\text{drift}_p} \)  
\( \vec{J}_n, \vec{J}_p \)  
\( J_{n=1, J_{n=2}} \)  
\( J_o \)  
\( J_{o1, J_{o2}} \)  
\( J_{sc} \)  
\( k \)  
\( L \)  
\( L_{ac} \)  
\( L_{Di} \)  
\( L_{D(a-Si:H)} \)  
\( L_n, L_p \)  
\( m_n^*, m_p^* \)  
\( N(z, \omega) \)  
\( N(E_F) \)  
\( N_A, N_D \)  
\( N_A^*, N_D^+ \)  
\( N_c, N_v \)
\( N_{DB}(E) \)
dangling bond density of states \([\text{cm}^{-3}]\)

\( N_t \)
trap density \([\text{cm}^{-3}]\)

\( n \)
ideality factor (if in expression \( q/nkT \))

\( \Delta n, \Delta p \)
excess electron, hole concentration \([\text{cm}^{-3}]\)

\( \Delta n_0 \)
DC excess carrier generation (for modulated photoluminescence) \([\text{cm}^{-3}]\)

\( \Delta n_1 \)
amplitude of AC excess carrier generation (for modulated photoluminescence) \([\text{cm}^{-3}]\)

\( n, p \)
total electron, hole concentration \([\text{cm}^{-3}]\)

\( n_{bulk}, p_{bulk} \)
total electron, hole concentrations in bulk silicon, far from the interface \([\text{cm}^{-3}]\)

\( n_i \)
intrinsic carrier concentration \([\text{cm}^{-3}]\)

\( n_n, p_n \)
equilibrium electron, hole concentration in \( n \)-type semiconductor \([\text{cm}^{-3}]\)

\( n_p, p_p \)
equilibrium electron, hole concentration \([\text{cm}^{-3}]\)

\( n_{p0}, p_{p0} \)
equilibrium electron, hole concentration in \( p \)-type semiconductor \([\text{cm}^{-3}]\)

\( n_r \)
refractive index

\( n_t \)
electron concentration when Fermi level is equal to the trap state energy \([\text{cm}^{-3}]\)

\( P \)
power density \([\text{W/cm}^2]\)

\( P_{input} \)
input power density \([\text{W/cm}^2]\)

\( P_m \)
maximum power density \([\text{W/cm}^2]\)

\( P_s \)
sheet hole density \([\text{cm}^{-2}]\)

\( Q_{v-Si}, Q_{a-Si:H}, Q_{int} \)
charge in crystalline silicon, in amorphous silicon, and at interface \([\text{C}]\)
$Q$  
  elementary charge, $1.6 \times 10^{-19}$ [C]

$Q_{\text{heat laser}}$  
  heat flow into sample from laser [W]

$R_l, R_b$  
  fraction of radiative power reflected from front surface, backing for PCR

$R_s$  
  series resistance [Ω]

$R_{sh}$  
  shunt resistance [Ω]

$R_{th}, R_{th\text{(wafer)}}, R_{th\text{(slab)}}, R_{\text{air transfer}}$  
  thermal resistance, thermal resistance of wafer, thermal resistance of slab, equivalent heat transfer resistance [K/W]

$r, x, y, z$  
  spatial coordinates [cm]

$S$  
  surface recombination velocity [cm/s]

$S_1, S_2$  
  front and back surface recombination velocities [cm/s]

$S_{it}$  
  interface recombination velocity [cm/s]

$S_{\text{seebeck}}$  
  seebeck coefficient [V/K]

$T$  
  temperature [K]

$\Delta T_{\text{wafer+slab}}, \Delta T_{\text{wafer}}$  
  temperature drop across wafer-slab system, temperature drop across wafer [K]

$T_{av}$  
  average optical transmittance [%]

$T_{opt}(\lambda)$  
  optical transmittance [%]

$T$  
  time [s]

$U$  
  carrier recombination rate $[\text{cm}^{-3}\text{s}^{-1}]$

$U_{\text{Aug}}$  
  Auger recombination rate $[\text{cm}^{-3}\text{s}^{-1}]$

$U_{nc}, U_{pc}$  
  electron and hole trap capture rates $[\text{cm}^{-3}\text{s}^{-1}]$

$U_{\text{rad}}$  
  radiative recombination rate $[\text{cm}^{-3}\text{s}^{-1}]$
\( u(x), u_{\text{bulk}}, u_{\text{int}} \) energy difference from Fermi level to intrinsic Fermi level (as a function of \( x \), in bulk, and at a-Si:H/c-Si interface), expressed as a ratio with respect to \( kT \)

\( V \) voltage [V]

\( V_{bi} \) built-in voltage [V]

\( V_{bi(a-Si:H)}, V_{bi(c-Si)} \) built-in voltage component in a-Si :H, in c-Si [V]

\( V_{th} \) thermoelectric voltage [V]

\( V_{oc} \) open circuit voltage [V]

\( W \) wafer thickness[cm]

\( W_{eR} \) spectral power per unit wavelength from radiative recombination (for PCR) [W/cm]

**Greek symbols**

\( \beta \) absorption coefficient [cm\(^{-1}\)]

\( \chi_{a-Si:H} \) electron affinity of amorphous silicon [eV]

\( \chi_{c-Si} \) electron affinity of crystalline silicon [eV]

\( \delta_{c-Si}, \delta_{a-Si:H} \) energy difference between Fermi level and nearest band edge (closer of conduction band minimum or valence band maximum) in bulk crystalline silicon, amorphous silicon [eV]

\( \delta_{\text{skin}} \) optical skin depth [cm]

\( \varepsilon, \varepsilon_0 \) dielectric permittivity, dielectric permittivity in a vacuum [F/cm]

\( \varepsilon(\omega), \varepsilon_1(\omega), \varepsilon_2(\omega) \) relative dielectric permittivity, real and imaginary parts of relative dielectric permittivity
\( \varepsilon_\infty \)  
high frequency relative dielectric permittivity

\( \phi_b \)  
injection barrier for carrier recombination across interface [eV]

\( h \nu \)  
photon energy [J]

\( \Gamma_1, \Gamma_2, \gamma_1, \gamma_2 \)  
ratios used to simplify PCR equations

\( \eta \)  
efficiency

\( \eta_0 \)  
quantum yield for excess carrier generation

\( \eta_R \)  
radiative recombination efficiency for PCR

\( \varphi_{c-Si} \)  
crystalline silicon band bending [eV]

\( \lambda \)  
wavelength [cm]

\( \lambda_1, \lambda_2 \)  
PCR filter wavelengths [cm]

\( \mu, \mu_e, \mu_h \)  
carrier mobility, electron mobility, hole mobility [cm\(^2\)/V-s]

\( v_n \)  
electron thermal velocity [cm/s]

\( \rho \)  
resistivity [\( \Omega \text{.cm} \)]

\( \rho_{th} \)  
thermal resistivity [Kcm/W]

\( \rho_{a-Si:H}, \rho_{c-Si} \)  
charge density in amorphous silicon, crystalline silicon [C/cm\(^3\)]

\( \sigma \)  
conductivity [S/cm]

\( \sigma_{ITO} \)  
conductivity of ITO [S/cm]

\( \sigma_n \)  
electron capture cross section [cm\(^2\)]

\( \tau_{Auger} \)  
Auger recombination lifetime [s]

\( \tau_{bulk} \)  
bulk excess carrier lifetime [s]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{\text{eff}}$</td>
<td>effective excess carrier lifetime [s]</td>
</tr>
<tr>
<td>$\tau_{n,\text{SRH}}, \tau_{p,\text{SRH}}$</td>
<td>electron and hole lifetimes due to SRH recombination [s]</td>
</tr>
<tr>
<td>$\tau_{n,\text{rad}}, \tau_{p,\text{rad}}$</td>
<td>electron and hole lifetimes due to radiative recombination [s]</td>
</tr>
<tr>
<td>$\tau_{n,\text{Aug}}, \tau_{p,\text{Aug}}$</td>
<td>electron and hole lifetimes due to Auger recombination [s]</td>
</tr>
<tr>
<td>$\tau_{n}, \tau_{p}$</td>
<td>electron and hole bulk lifetimes [s]</td>
</tr>
<tr>
<td>$\tau_{\text{rad}}$</td>
<td>radiative recombination lifetime [s]</td>
</tr>
<tr>
<td>$\tau_{\text{SRH}}$</td>
<td>Schockley-Read-Hall recombination lifetime [s]</td>
</tr>
<tr>
<td>$\tau_{\text{surface}}$</td>
<td>effective excess carrier lifetime due to surface recombination [s]</td>
</tr>
<tr>
<td>$\omega$</td>
<td>angular frequency [rad/s]</td>
</tr>
<tr>
<td>$\omega_P$</td>
<td>angular plasma frequency [rad/s]</td>
</tr>
<tr>
<td>$\xi_{\text{int}}$</td>
<td>effective electric field at the a-Si:H/c-Si interface [V/cm]</td>
</tr>
<tr>
<td>$\psi$</td>
<td>diffusion wave function</td>
</tr>
</tbody>
</table>
1. Introduction

1.1. The solar resource and history of photovoltaic energy

Worldwide, the average surface irradiance of the earth is approximately 170 W/m² which over a year corresponds to 5.4 GJ/m² [1]. This means that on average for every 1 m² the amount of incident solar energy in a year is approximately the same as the energy that can be extracted by burning one barrel of oil, 200 kg of coal, or 140 m³ of natural gas [1]. Moreover, solar irradiation is a resource that will not run out within the foreseeable future and cannot be said to contribute to environmental pollution.

One way of transforming the solar resource into other forms of energy is by converting it first to electrical energy through the photovoltaic effect. Table 1 shows the average number of kilowatt-hours of electricity that can be actually generated per year per kilowatt of installed photovoltaic capacity (equivalent to the average integrated yearly PV potential in hours) in a number of Canadian cities and elsewhere. Canadian cities rank average in the group, above both Germany and Japan. In Canada the prairie provinces have the most solar resource.
Table 1 - Yearly PV potential in several Canadian cities and elsewhere [2]

<table>
<thead>
<tr>
<th>Canadian Cities</th>
<th>Average yearly energy harvest/installed power (kWh/kW)</th>
<th>Cities Worldwide</th>
<th>Average yearly energy harvest/installed power (kWh/kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Regina, Saskatchewan</td>
<td>1361</td>
<td>Cairo, Egypt</td>
<td>1635</td>
</tr>
<tr>
<td>Calgary, Alberta</td>
<td>1292</td>
<td>Cape Town, South Africa</td>
<td>1538</td>
</tr>
<tr>
<td>Winnipeg, Manitoba</td>
<td>1277</td>
<td>New Delhi, India</td>
<td>1523</td>
</tr>
<tr>
<td>Edmonton, Alberta</td>
<td>1245</td>
<td>Los Angeles, U.S.A.</td>
<td>1485</td>
</tr>
<tr>
<td>Ottawa, Ontario</td>
<td>1198</td>
<td>Mexico City, Mexico</td>
<td>1425</td>
</tr>
<tr>
<td>Montréal, Québec</td>
<td>1185</td>
<td>Regina, Canada</td>
<td><strong>1361</strong></td>
</tr>
<tr>
<td>Toronto, Ontario</td>
<td>1161</td>
<td>Sydney, Australia</td>
<td>1343</td>
</tr>
<tr>
<td>Fredericton, New Brunswick</td>
<td>1145</td>
<td>Rome, Italy</td>
<td>1283</td>
</tr>
<tr>
<td>Québec, Québec</td>
<td>1134</td>
<td>Rio de Janeiro, Brazil</td>
<td>1253</td>
</tr>
<tr>
<td>Charlottetown, Prince Edward Island</td>
<td>1095</td>
<td>Beijing, China</td>
<td>1148</td>
</tr>
<tr>
<td>Yellowknife, Northwest Territories</td>
<td>1094</td>
<td>Washington, D.C., U.S.A.</td>
<td>1133</td>
</tr>
<tr>
<td>Victoria, British Columbia</td>
<td>1091</td>
<td>Paris, France</td>
<td>938</td>
</tr>
<tr>
<td>Halifax, Nova Scotia</td>
<td>1074</td>
<td>St John’s, Canada</td>
<td><strong>933</strong></td>
</tr>
<tr>
<td>Iqaluit, Nunavut</td>
<td>1059</td>
<td>Tokyo, Japan</td>
<td>885</td>
</tr>
<tr>
<td>Vancouver, British Columbia</td>
<td>1009</td>
<td>Berlin, Germany</td>
<td>848</td>
</tr>
<tr>
<td>Whitehorse, Yukon</td>
<td>960</td>
<td>Moscow, Russia</td>
<td>803</td>
</tr>
<tr>
<td>St. John’s, Newfoundland and Labrador</td>
<td>933</td>
<td>London, England</td>
<td>728</td>
</tr>
</tbody>
</table>

The primary challenge that solar photovoltaics must meet for greater penetration into the Canadian and world electricity markets is improving the cost of power produced. The cost per watt at peak production, or $/W_p$, is the usual figure of merit used to characterize the cost of solar photovoltaics. There are several approaches for decreasing the $/W_p$. Some focus on improving cell efficiency, while others focus on developing low cost technologies. In fact a more useful metric may be the cost per watt of installed power, which includes the costs of module integration, AC/DC power conversion (where applicable), and installation. This is because in recent years the cost of photovoltaic cells has decreased to the point that it now makes up a minority of the installed cost of a
photovoltaic module or array; module costs themselves make up only approximately half of the installed cost of a system, and up to half of the module cost typically comes from non-cell components such as environment protection, framing and wiring [3] [4]. One consequence of this is that changes in cell efficiency have a disproportionate effect on cost per installed watt compared to changes in cell cost, although both are clearly important. Thus, it will be important to focus attention on increasing cell efficiency followed by reducing cell production cost. In this context crystalline semiconductor photovoltaics are of great interest.

1.2. The amorphous-crystalline silicon heterojunction

The amorphous-crystalline silicon heterojunction consists of a crystalline silicon wafer on which is deposited one or more hydrogenated amorphous silicon layers. The crystalline and amorphous layers may be doped in order to create a $p$-$n$ or $p$-$i$-$n$ junction, which can form the basis for a photovoltaic cell. Additional features such as back surface fields and other optical and electrical layers are typically added in order to improve performance. An example of such a cell structure is shown in Figure 1.
1.2.1. History of the amorphous-crystalline silicon heterojunction photovoltaic cell

In 1974, Fuhs et al. reported an amorphous-crystalline silicon heterojunction with very weakly rectifying behaviour [5]. Throughout the 1980s, a number of research groups began to show interest in a-Si:H/c-Si heterojunctions. Matsuura et al. described some of the electrical properties of a-Si:H/c-Si heterojunctions on $p$-type crystalline silicon, and demonstrated that the behaviour fit an abrupt heterojunction model [6]. Rubinelli calculated through modeling that heterojunctions with thin hydrogenated amorphous silicon layers could have a good spectral response and showed potential for photovoltaic applications [7]. Cuniot and Marfaing [8] and also Mimura and Hatanaka [9] investigated the energy band discontinuities of a-Si:H/c-Si heterojunctions by photoemission spectroscopy. There was no consensus between these groups regarding the values of the band offsets [8]. Additionally, several researchers found that intrinsic
amorphous silicon can be used to lower carrier recombination at the crystalline silicon surface [9][10].

In 1992, Tanaka et al. demonstrated a p-a-Si:H/n-c-Si cell with 12.3% efficiency and a p-a:Si/i-a-Si:H/n-c-Si cell with more than 18% efficiency[11]. The addition of an i-layer at the interface led to an increase of $V_{oc}$ by approximately 30 mV and a fill factor of 80%. This p-a-Si:H/i-a-Si:H/n-c-Si cell architecture has been named a HIT cell, or heterojunction with intrinsic thin layer. Over the years, the HIT cell efficiency has improved. Recently 100 cm$^2$ HIT cells with an efficiency of 24.7% have been reported [12].

1.2.2. Optimizing heterojunction photovoltaics

A number of processing steps are required to produce an a-Si:H/c-Si heterojunction cell. The device is made using a doped crystalline silicon wafer, and depositing thin layers of intrinsic and doped amorphous silicon on the front illuminated surface to create a junction, and on the back surface to create a back surface field. Very shallow and abrupt junctions can be formed in this way, which is advantageous for capturing short wavelength photons. The low process temperatures are also very advantageous, for both device performance and manufacturing cost reasons. Heterojunction cells are produced at temperatures of 180-300 °C. In contrast c-Si homojunction cells are typically processed at temperatures close to 1000 °C and above[13]. Lower temperatures have the potential to reduce the cost of manufacturing, and consequently the cost of photovoltaic energy. High temperatures not only require more energy, they also cause unwanted effects including dopant and defect diffusion and thermal stresses in the wafer. The latter problem is particularly important when we attempt to reduce material costs by using thinner silicon wafers for the substrate, as such cells are fragile under thermal stresses.

Amorphous silicon is also highly effective for surface passivation of crystalline silicon, particularly when intrinsic material is used [14] [15]. In relatively high quality
wafers with high bulk carrier lifetimes, the surface recombination is often the limiting factor in cell performance. Therefore, the use of amorphous silicon passivation leads to higher effective minority carrier lifetime, which in turn leads to higher open circuit cell voltage and higher cell efficiency.

Although both \textit{n}- and \textit{p}-\textit{c-Si} can be used as the basis for amorphous silicon/crystalline silicon heterojunction photovoltaic cells, this thesis focuses on a \textit{n}-\textit{c-Si} based structure. The \textit{n}-\textit{c-Si} substrate gives the advantage of higher open circuit voltage and resistance to light-induced degradation [16] [17].

\textbf{1.2.3. State of the art in a-Si:H/c-Si photovoltaics}

The highest recorded efficiency for a large area amorphous silicon/crystalline silicon heterojunction cell is 24.7\%, reported by Panasonic in 2013 [12]. The Panasonic cell had an area of 101.8 cm\(^2\), and was made on a texturized, \textit{n}-doped Float zone silicon wafer with a thickness of 98 \(\mu\)m. Its short circuit current density was 39.5 mA/cm\(^2\), open circuit voltage was 750 mV, and fill factor was 83.2\% [12]. Panasonic credited low substrate surface damage during amorphous silicon deposition for the high open circuit voltage, and high metallization aspect ratio for the high fill factor. They also reported that they achieved their high short circuit current by reducing grid shadowing losses and high optical transmittance of their transparent conducting oxide layer. Although they did not report the effective minority carrier lifetime in their cells, their high \(V_{oc}\) points to a high minority carrier lifetime, consistent with a minority carrier lifetime that is limited by bulk recombination rather than by surface recombination, implying a more effective surface passivation than in the earlier record cell reported by this group in 2012 [16]. I-V measurements are shown in Figure 2 for a cell with 23\% efficiency.
When compared to other high efficiency cell architectures, HIT cells are notable for their high open circuit voltages, and the relatively small negative temperature coefficient, leading to improved performance in the field [18]. Other high-efficiency silicon cells infrequently exceed an open circuit voltage of 700 mV even in the highest efficiency cells. The best recorded passivated emitter and rear locally diffused (PERL) cell, for example, achieved an efficiency of 25% with an open circuit voltage of 706 mV, a short circuit current density of 42.7 mA/cm², and a fill factor of 82.8%, for a cell with an area of 4 cm²[19].

1.2.4. Progress in understanding

Despite the high efficiencies achieved experimentally, the internal mechanism of the HIT cell is not completely understood by the research community. A number of research groups have investigated and modeled a-Si:H/c-Si heterojunctions with either n- or more
frequently \( p \)-type crystalline silicon absorbers, however many questions are still under debate and in some cases it is unclear under which conditions particular models apply \[20][21][22][23][24]. Even when the cell layers are reasonably well understood in isolation as bulk materials, their interaction necessarily produces new and more complex phenomena: A variety of values are reported for the conduction and valence band offsets and different models have been proposed to explain the values and determine the neutral branch-point energy[25]. Transport mechanisms across the heterojunction are also incompletely understood and modeled, and different modes of transport will dominate depending on the cell properties, including bulk and interface defect densities and band offsets[24][26].

The indium tin oxide (ITO) – amorphous silicon interface has been relatively less studied, although modeling studies have suggested that its properties may play a crucial role in the cell’s performance[27] [28]. Some research has also indicated the possibility that the ITO deposition process may cause diffusion of indium into the a-Si:H or into the crystalline absorber [29], which could introduce defects or dopants.

1.3. Motivation and research objectives

1.3.1. DC saddle field plasma enhanced chemical vapour deposition technique

A number of methods can be used to form amorphous silicon films, generally divided into physical and chemical methods. Physical methods include evaporation and sputtering. However, these methods produce a highly defective amorphous silicon film that can not be effectively doped to create \( n \)- or \( p \)-type films [30]. Chemical vapour deposition methods (CVD), in contrast, allow the incorporation of hydrogen, which can satisfy dangling bonds, thereby increasing excess carrier lifetime. Accordingly, CVD is preferred for photovoltaic applications. The most common form of CVD used to deposit
hydrogenated amorphous silicon films for photovoltaic applications is plasma enhanced chemical vapour deposition, or PECVD (also sometimes called glow discharge deposition), and in particular RF PECVD.

An alternative technique for amorphous silicon deposition, the DC saddle-field PECVD (DCSF-PECVD), has been recently developed to deposit high quality amorphous silicon films on crystalline silicon substrates [14][15][31][32]. This technique, developed at the University of Toronto, is scalable thereby making it amenable for large area solar cell production. Furthermore, the basic grid elements of the technique can be integrated into RF based systems, resulting in advanced tunable PECVD for the growth of high quality interface and thin film materials and thus high performance devices [33]. Accordingly, there is potential for low-cost large area device processing.

This research uses the tetrode configuration of DCSF-PECVD. This configuration uses two semitransparent electrodes and one solid electrode to create the saddle-field plasma, and a fourth electrode to hold the substrate [34]. The saddle field plasma is thus quite asymmetrical, as it has a solid metal electrode on one side of the saddle field and a semi-transparent one on the other side.

Heterojunctions made with this technique are investigated in this thesis.

1.3.2. Cell architecture

The basic structure under investigation in this thesis is the ITO/p-a-Si:H/i-a-Si:H/n-c-Si stack, where the a-Si:H layers are all deposited using DCSF PECVD and the ITO is prepared by RF magnetron sputtering. Various simpler structures are made to study the interactions of the different layers in the stack, and these layers are ultimately incorporated into a full photovoltaic cell on a texturized silicon substrate, with the addition of i-a-Si:H and n⁺-c-Si back surface field layers and front and back metallization with silver.
1.3.3. Cell interfaces (a-Si:H/c-Si and ITO/a-Si:H)

The objective of this thesis research is to improve the understanding of the physical properties of the ITO/p-a-Si:H/i-a-Si:H/n-c-Si/i-a-Si:H/n⁺-c-Si stack, particularly to develop a better understanding of the interactions between the different cell layers, especially the interaction of the amorphous silicon with adjacent cell layers, i.e., the a-Si:H/c-Si interface and the ITO/a-Si:H interface. Although the ultimate ambition of this thesis is to aid in the understanding of the a-Si:H/c-Si and the ITO/a-Si:H interfaces and in advancing the development of interface characterization techniques it is hoped that it will also assist in developing high efficiency, low cost photovoltaic cells using the novel DCSF PECVD technique.

There are a number of areas of interest concerning the amorphous silicon interfaces.

a-Si:H/c-Si interface:

- Passivation quality of the a-Si:H;
- Electrical interaction of the doped a-Si:H and c-Si layers, including band bending and band offsets;
- Effect of buffer i-layers of varying thicknesses.

ITO/a-Si:H interface

- Deposition of high performance ITO while respecting temperature constraints of a-Si:H;
- a-Si:H changes during ITO deposition and processing.

The a-Si:H studied in this research is deposited with the DCSF PECVD technique, using the tetrode configuration.
The cell layers studied are also integrated into a complete cell, with a resulting measured open circuit voltage of 699 mV under air mass 1.5 (AM1.5) solar illumination, – the highest $V_{oc}$ HIT cell produced to-date using the DCSF technique.

1.3.4. Characterization techniques

The cell layers, interfaces, and PV cell are characterized using a number of well-established tools; two characterization tools, photocarrier radiometry (PCR) and coplanar conductivity, are then considered in more depth.

Photocarrier radiometry (PCR) is used to look at excess carrier properties in the wafer, namely the bulk carrier lifetime, diffusion coefficient, and front and back surface recombination velocities. In particular, for the first time we develop the use of PCR to examine how these properties change with passivation of the surface by amorphous silicon. PCR is a non-contact technique in which an AC modulated superbandgap laser is used to excite carriers in the sample, and their eventual radiative recombination is detected and analyzed. With this technique it is possible to determine the bulk lifetime separately from the lifetimes associated with the front and back surface recombination. This technique is compared to more standard techniques for measuring carrier lifetimes in wafers, namely transient and quasi-steady state photoconductive decay measurements with microwave or eddy current detection of conductivity.

Coplanar conductivity measurements are used to better understand the band structure of the heterojunction. This technique makes use of lateral conductance through a surface inversion layer in the crystalline silicon near the $p-n$ junction. The conductance is a measure of the concentration of carriers, and thus of the strength of the inversion layer; the temperature dependence of this conductivity provides additional insights into the band structure of the junction. Using coplanar conductivity measurements, heterojunctions using different doped amorphous silicon deposition conditions are compared, as are heterojunctions with and without intrinsic layers. The passivation of
these structures is also measured using standard techniques, including modulated photoluminescence and photoconductive decay. In this way the band diagrams of different structures can be considered in the context of the need for good passivation.

1.3.5. Thesis outline

The thesis is organized in the following way:

Chapter 2 provides general theoretical background of amorphous-crystalline silicon heterojunction photovoltaics and of transparent conducting oxides. It begins by introducing basic single and two diode models of a photovoltaic cell, then a more physically accurate model of a $p$-$n$ homojunction. Heterojunctions are discussed next, including how they differ from homojunctions. Finally, the role of the antireflective transparent conducting oxide coating is briefly outlined.

In Chapter 3, the experimental apparatus and procedures are outlined. The deposition systems used to deposit the various layers are described and the experimental techniques used in the characterization of the stacks are described. Next, the different sample structures that are made are described in detail, and finally the standard tools used to characterize the structures are discussed.

The photocarrier radiometry technique is described in Chapter 4. The chapter begins with an overview of the theory of carrier recombination. Next, diffusion wave fields are introduced and two mathematical models for their solution are presented, followed by a discussion of the assumptions made in the models and the introduction of metrics that may be used to judge the appropriateness of the assumptions. The experiments undertaken are described and the results discussed and compared to standard measurements.

The coplanar conductance technique is described in Chapter 5, beginning with a more in depth discussion of the theory behind the technique, followed by details of the
experiments that were undertaken. A discussion of the results follows, including a comparison to standard measurements as appropriate.

Chapter 6 examines the integration of the heterojunction into a complete cell structure, with a particular emphasis on the integration of the indium tin oxide layer and its effect on the cell. The theory of how transparent conducting oxides work is presented, followed by results of an optimization study to develop an indium tin oxide deposition process that is compatible with the amorphous silicon/crystalline silicon structure and fabrication process. The ITO/a-Si:H interface is next examined in more detail. Finally, fabrication of a complete HIT cell, incorporating the ITO and a-Si:H layers as well as more advanced cell features including a back surface field and texturization is described, concluding with cell characterization.

In Chapter 7 the conclusions of the thesis are presented, which include a summary of the work done, the key findings, and suggestions for future research.

In the Appendix, a model of a p-n homojunction is developed beginning from basic physical properties of semiconductors and the current-voltage relationship is derived.
2. Background theory

2.1. PN junction cell

Empirically, the behaviour of an idealised photovoltaic cell can be simply modeled by a current source in parallel with a diode, as in Figure 3.

![Figure 3 – Ideal single diode model for a photovoltaic cell.](image)

Using the convention that photocurrent is positive, the cell behaviour can be described by Equation 2.1, where \( J_o \) is a device property primarily determined by the bandgap of the cell materials, \( J_{sc} \) is the short circuit current density, \( k \) is Boltzmann’s constant, and \( T \) is the temperature\[35\]. The term \( n \) in the exponent is called the ideality factor and is primarily determined by the dominant excess carrier recombination processes in the cell; it typically varies between 1 and 2 depending on the materials and physical dimensions of the cell, although in some cases it may be higher than 2:

\[
J(V) = J_{sc} - J_{dark} = J_{sc} - J_o(e^{qV/nkT} - 1)
\]  

2.1

The bulk and surface recombination current density \( J_{n=1} \) is described by the following equation, with an ideality factor of 1 and a reverse saturation current density of \( J_{o1} \)\[36\].

\[
J_{n=1} = J_{o1}(e^{qV/kT} - 1)
\]  

2.2

while the junction recombination current density \( J_{n=2} \) has an ideality factor of 2 and a reverse saturation current density of \( J_{o2} \)\[36\].
The full two diode equation with series and shunt resistances is given in Equation 2.4:

\[ J(V) = J_{sc} - J_{0n}\left(e^{\frac{q(V+JAR_s)}{kT}} - 1\right) - J_{0p}\left(e^{\frac{q(V+JAR_s)}{2kT}} - 1\right) - \frac{(V + JAR_s)}{R_{sh}} \]

A more physical model can also be derived based on the material properties of the semiconductors and the physical processes within the cell. A detailed derivation of such a model is developed in the Appendix for the case of a \( p-n \) homojunction, with \( p \) and \( n \) layers both thick compared to the minority carrier diffusion lengths, and with recombination in the bulk assumed to be the dominant recombination mechanism.

This gives the classic diode equation [37]:

\[ J(V) = J_{sc} - \left[\frac{qD_p}{L_p}P_{n0} + \frac{qD_n}{L_n}n_{p0}\right]\left[e^{\frac{qV}{kT}} - 1\right] \]

\[ J(V) = J_{sc} - J_0\left[e^{\frac{qV}{kT}} - 1\right] \approx J_{sc} - J_0 e^{\frac{qV}{kT}} \]

Here \( P_{n0} \) and \( n_{p0} \) are the minority carrier hole and electron concentrations in the bulk \( n \) and \( p \) regions far from the space charge region, \( J_{sc} \) is the short circuit current density due to photogenerated carriers, \( D_n \) and \( D_p \) are the diffusion coefficients of minority carrier electrons and holes, and \( L_n \) and \( L_p \) are the diffusion lengths of minority carrier electrons and holes, respectively.

\( V_{oc} \) can be found from Equation 2.6, using the definition of open circuit voltage, \( J(V_{oc})=0 \).
\[ V_{oc} = \frac{kT}{q} \ln \left( \frac{J_{sc}}{J_0} \right) \] \hspace{2cm} 2.7

In the case where \( J_0 \) is dominated by bulk recombination and where the \( p \) side is much more strongly doped than the \( n \) side, the \( V_{oc} \) equation can be simplified [38]:

\[ V_{oc} = \frac{E_g}{q} - \frac{kT}{q} \ln \left( \frac{qD_pN_eN_v}{L_pN_dJ_{sc}} \right) \] \hspace{2cm} 2.8

The maximum open circuit voltage in this cell will be determined primarily by the doping densities and by the excess carrier lifetime, with the latter influencing Equation 2.8 through \( J_{sc} \) and \( L_p \).

Clearly the excess carrier lifetime is a particularly important property of the semiconductor in the context of photovoltaic cells. The excess carrier lifetime is a material parameter that describes the rate of recombination of carriers; it is the average length of time an excess minority carrier will survive in the material before it recombines with a majority carrier. The recombination rate, \( U \), is inversely proportional to the effective excess carrier lifetime.

\[ U = \frac{\Delta n}{\tau_{eff}} \] \hspace{2cm} 2.9

The excess carrier injection level \( \Delta n \) is determined by the generation rate \( G \) and the effective minority carrier lifetime \( \tau_{eff} \) [37]:

\[ \Delta n = G\tau_{eff} \] \hspace{2cm} 2.10
The bulk carrier lifetime is determined by adding the inverses of the lifetimes given by the different recombination mechanisms - Auger, Shockley-Read Hall, and Radiative recombination, in the bulk, each characterised by a lifetime $\tau_{\text{Aug}}$, $\tau_{\text{SRH}}$, and $\tau_{\text{rad}}$. The recombination mechanisms are described in more detail in Section 4.1. The effect on excess carriers, of the front surface recombination velocity $S_1$ and the back surface recombination velocity $S_2$, can also be expressed as a lifetime $\tau_{\text{surface}}$, and the bulk and surface lifetimes can be combined into an effective lifetime for the sample [39]:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{bulk}}} + \frac{1}{\tau_{\text{surface}}}$$  \hspace{1cm} 2.11

If the sample is thin, so that the carrier diffusion length is much greater than the sample thickness, $W$, and the front and back surface recombination velocities are equal, the effective lifetime can be expressed as follows[39]:

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{Aug}}} + \frac{1}{\tau_{\text{SRH}}} + \frac{1}{\tau_{\text{rad}}} + \frac{2S}{W}$$  \hspace{1cm} 2.12

### 2.2. a-Si:H/c-Si heterojunction

In high quality crystalline silicon wafers, bulk lifetimes $\tau_{\text{bulk}}$ can be as high as several milliseconds, while surface lifetimes $\tau_{\text{surface}}$ are typically lower by several orders of magnitude; surface recombination therefore constitutes the primary limiting factor to high effective lifetimes, and has a critical impact on open circuit voltage.

Crystalline silicon has the largest part of the photovoltaic market. Its band gap at 1.12 eV is close to the theoretical Schockley-Queisser optimum of 1.4 eV for a single junction cell, leading to a theoretical maximum efficiency of 29% [35][40]. Silicon is abundant and it can be doped with boron or phosphorous; additionally, silicon has a long
history of use in integrated circuits so many technological processes can be readily applied to solar cell processing. The highest quality silicon wafers have electron and hole mobilities of approximately 1500 and 500 cm$^2$/Vs, and electron and hole diffusion coefficients of approximately 40 and 10 cm$^2$/s, respectively [35]. The bulk lifetime is also relatively high. Therefore, recombination at the surfaces becomes the dominant factor in determining carrier lifetime in devices and accordingly, surface passivation has a dramatic effect on effective carrier lifetimes, leading to an increase in minority carrier injection, and by extension, open circuit voltage in photovoltaic devices.

In bulk crystalline silicon, each silicon atom has a tetrahedral bonding structure and bonds to four neighbouring silicon atoms. However, at the surface, the lattice ends abruptly, leaving a layer of atoms that are not four-fold bonded. These “dangling bonds” act as electron and hole trap states. There may also be additional crystal defects or impurities at the surface as a result of wafer processing. Hydrogenated amorphous silicon (a-Si:H) has been found to be very effective for passivating dangling silicon bonds. By doping the a-Si:H it is possible to simultaneously create a $p$-$n$ junction, or if an ultra-thin intrinsic a-Si:H layer is deposited between the doped layers, a $p$-$i$-$n$ junction.

Amorphous silicon differs from crystalline silicon in a number of ways. At the structural level, amorphous silicon is four-fold tetrahedrally bonded as crystalline silicon. However, small variations exist in bond lengths and angles, leading to a lack of long-range order, as well as a large number of dangling bonds in the bulk. These dangling bonds act as traps which make it impossible in practice to substantially change the energy of the Fermi level of pure amorphous silicon by doping. However, the addition of hydrogen passivates dangling bonds sufficiently to allow effective doping, although the doping efficiency is lower than in crystalline silicon and a significant number of dangling bond states remain within the band gap.
The variation in bond length and angle has the effect of ‘smearing’ the edges of the conduction and valence bands: instead of an abruptly defined maximum allowable energy level for valence band states and minimum allowable energy level for conduction band states, there is a gradual decrease in allowed states leading to band tails rather than definitive band edges. These regions of decreased density of states are known as the Urbach tails in the energy gap. As the density of states decreases in the tails, extended states yield to localized states and the dominant mechanism of carrier transport becomes hopping rather than extended state conduction, leading to drastically reduced mobility. Optical and mobility band gaps in amorphous silicon are defined with reference to the decrease in the density of states and mobility in the valence and conduction bands, respectively. In hydrogenated amorphous silicon the electrical and optical band gaps are close in value.

The energy gap is larger than that of crystalline silicon, and can vary in size primarily depending on hydrogen content of the amorphous silicon; it may range between approximately 1.7 eV-1.9 eV[41].

Transport is also different in amorphous silicon than in crystalline silicon, due to the lesser degree of order, essentially equivalent to a very high defect density. This leads to greatly decreased and widely varying mobility, with electron mobilities on the order of $10^{-2} - 1 \text{ cm}^2/\text{Vs}$ and hole mobilities on the order of $10^{-3}$ to $10^{-1} \text{ cm}^2/\text{Vs}$, compared to electron and hole mobilities of approximately 1500 and 500 cm$^2$/Vs respectively in high quality crystalline silicon [30][35][42][43][44]. Also, as mentioned previously, there is a significant degree of hopping transport due to the large number of defects, particularly in the band tails.

A typical density of states for amorphous silicon is modeled in Figure 4, showing the valence and conduction band Urbach tails, and defect states in the band gap.
In an a-Si:H/c-Si heterojunction, the difference in energy band gaps creates valence and conduction band offsets which can act as barriers to carrier transport. These offsets also have an effect on the electric field in the space charge region, and may increase the electric field for a given doping level [25].

In the derivation in the Appendix, bulk recombination was assumed to be the dominating form of recombination. If instead interface recombination dominates, the current will depend on the interface recombination velocity $S_{it}$ and the excess minority carrier concentration in the $p$-type amorphous silicon space charge region ($n_p - n_{p0}$), as well as the carrier injection barrier $\phi_b$ across the interface [38][46]:

$$J_{dark}(V) = q S_{it} (n_p - n_{p0}) = q S_{it} N_D e^{\left(\frac{V_{bi}}{e}\right)} \left( \frac{qV}{nkT} - 1 \right)$$  \hspace{1cm} (2.13)
$J_o = qS_{it}N_C e^{\left( \frac{-\Phi_B}{n_kT} \right)}$  \hspace{1cm} 2.14

where $N_D$ is the donor doping concentration in the $n$-type crystalline silicon, $N_C$ is the conduction band density of states, $n$ is the diode ideality factor, and $q$, $k$, and $T$ have their usual definitions.

In a $p$-a-Si:H/$n$-c-Si heterojunction, the injection barrier corresponds to the difference between the Fermi level and the crystalline silicon conduction band minimum at the interface (for a $n$-a-Si:H/$p$-c-Si heterojunction it would be the difference between the Fermi level and the crystalline silicon valence band maximum at the interface). This barrier is analogous to the Schottky barrier in a metal-semiconductor junction as it determines the activation energy required for recombination of carriers across the interface. Because of the relationship between $J_o$ and $V_{oc}$, any increase in $J_o$ will lead to a decrease in $V_{oc}$, hence low interface recombination is important for high cell efficiency. A large injection barrier would therefore be desirable, as it reduces interface recombination. However, there remains debate about the dominant current mechanism or mechanisms in heterojunction cells, and it appears that different current mechanisms dominate for different cells and at different voltage biases. Interface recombination, multistep tunneling with capture and emission (MTCE), and diffusion all appear to dominate in certain situations. The highest efficiency HIT cells appear to be diffusion-dominated in the high voltage bias range, which is attributed to their high interface passivation [23] [47].

Band alignment is also an important consideration. The difference between the band gaps of the two materials leads to discontinuities in the conduction and valence bands at the junction of the two materials.
These band offsets have a number of important influences on the cell performance: they can block desired carrier transport by acting as a barrier, or alternatively force carrier transport to occur through tunneling; they can act as a barrier for undesirable carrier diffusion; and their values are directly related to the injection barrier for recombination and to the built-in voltage.

A number of models have been proposed to predict and explain the relative sizes of the conduction and valence band offsets. The most commonly quoted is the Electron Affinity rule, also known as Anderson’s rule, which uses the vacuum level as a common reference point such that the conduction band offset is presumed to be equal to the difference in electron affinities of the two materials. However, measured values appear to range much more widely than would be predicted by this rule, with some groups reporting that the band offset is entirely in the conduction band, and some reporting that it is entirely in the valence band [25] [47]. Another model, which may be more accurate, is the neutral lineup, or branch-point energy model, which instead uses the branch-point energy as a common reference point; this is, the energy level within the band-gap which separates the acceptor-like states from the donor-like states, equivalent to the position of the Fermi level which would result in a neutral charge [25]. Because amorphous silicon has a variable structure, including variable band gap and density of states, the band offsets may also have some variability.

The sizes of the band offsets have a significant impact on carrier transport. In the case of a p-a-Si:H/n-c-Si junction photovoltaic cell as shown in Figure 5, when electron-hole pairs are created, electrons are swept towards the n-side by the electric field, while holes are swept towards the p-side. In the case of electrons in a p-a-Si:H/n-c-Si heterojunction a band offset in the conduction band poses no problem to carrier
collection, and in fact may be beneficial as it impedes the diffusive flow of electrons back across the junction [47]. However holes experience a barrier whose size is determined by the valence band offset and the relative doping concentrations of the two materials. A large valence band offset may significantly reduce the transport of holes, leading to electron-dominated transport, while a small valence band offset would not. On the other hand, if the barrier is sufficiently narrow, as in a case of a strongly doped a-Si:H layer, a tunneling junction may be formed.

![Figure 5 - Energy band diagram of a p-a-Si:H/n-c-Si heterojunction, showing electron affinities of both materials, conduction and valence band offsets, Fermi level $E_F$, carrier injection barrier for interface recombination $\Phi_b$, and movement of electrons ($e^-$) and holes ($h^+$) due to drift and diffusion.](image)

The carrier injection barrier across the interface is also determined in part by the band offsets; for the same doping concentrations, a larger conduction band offset leads to a lower carrier injection barrier (and hence higher interface recombination) as the voltage drop across the space charge region is reduced. This is plotted in Figure 6 using AFORS-HET simulation software, which is described in Section 3.5.
Figure 6 - Energy band diagram and carrier concentrations for weakly doped p-a-Si:H/n-c-Si heterojunction with large conduction band offset.

It can also be seen from Figure 7 that the use of a heterojunction changes the doping concentrations required to establish a given level of built-in voltage; the same degree of band bending in a homojunction would require a significantly more strongly doped p-
layer. Similarly, by strongly doping the $p$-layer it is possible to create a higher built-in voltage than would be possible in a homojunction.

Figure 7 - $p$-a-Si:H/$n$-c-Si heterojunction with strongly doped a-Si:H layer and large degree of band bending.

2.3. **Transparent conducting oxide**

Although we usually refer to amorphous silicon-crystalline silicon heterojunction cells, in fact such cells are more accurately ITO/a-Si:H/c-Si heterostructures, as a transparent conducting layer is typically applied to improve cell performance and typically this layer is indium tin oxide (ITO). The ITO layer is included for both optical and electrical reasons, as it acts as both an anti-reflective coating and an electrical contact. Since it must form an electrical contact with the amorphous silicon, its work function can also affect the behaviour of the cell.
A smooth silicon surface reflects approximately 30% of the power in the solar spectrum. This constitutes a very significant loss that will reduce $J_{sc}$ by a similar proportion. Hence, high efficiency photovoltaic cells invariably include antireflective coatings and other light trapping features such as texturization at the front of the cell to reduce reflective losses. Similarly, light trapping features at the back of the cell can reduce transmittance losses and make thinner cells possible. A basic single layer optical antireflective coating uses a tuned refractive index and thickness to create an optical path length that causes destructive interference at certain wavelengths. Light reflected from the air/coating interface is 180 degrees out of phase from the light reflected at the coating/a-Si:H interface. This necessitates a total path length difference of half a wavelength.

For normally incident light, the path length difference is twice the optical thickness of the antireflective coating, so the desired relationship is:

$$2n_r d_{AR} = \frac{\lambda}{2}$$  \hspace{1cm} 2.16

where $n_r$ is the refractive index and $d_{AR}$ is the thickness of the antireflective coating.

This corresponds to an optical thickness of a quarter wavelength:

$$n_r d_{AR} = \frac{\lambda}{4}$$  \hspace{1cm} 2.17

The wavelength chosen for minimization should be such as to maximize useful incident light (i.e., chosen with reference to the cell function and to the AM 1.5 spectrum).
In a typical c-Si homojunction cell, the top of the cell is covered with an antireflective optical coating, often SiN, and the metal contact fingers are fired through the optical coating. Since crystalline silicon has a high electrical conductivity, carriers can move laterally across the silicon to the nearest metal contact without introducing a large series resistance. Amorphous silicon has the disadvantage of much lower conductivity, so a conducting layer is deposited to permit improved lateral conduction and thus to minimize series resistance, while maintaining a reasonable metal finger spacing. This layer must be as optically transparent as possible to prevent shading losses. It may also be used as an antireflective coating, or there may be two layers, one a transparent conductor and the other an antireflective coating. Most transparent conductors are transparent conducting oxides (TCOs), of which one of the best performing is indium tin oxide (ITO). Panasonic credits improvements in the TCO layer for increasing their short circuit current density to 39.5 A/cm$^2$ [12]; however it may still be an area where improvement can be made, as the lower $J_{sc}$ of the HIT cell compared to the PERL cell may be explained by higher absorption losses, particularly in the UV and IR [48].

The TCO layer can also affect open circuit voltage and transport within the cell, depending on its work function, the work function of the amorphous silicon layer, and the thickness of the doped amorphous layer; modeling suggests that if these values are poorly matched, a potential barrier can form at the TCO/a-Si:H interface which may reduce the $V_{oc}$ and $FF$ of the cell [27] [28].
3. Experimental

3.1. Overview of experiments

Three series of experiments were carried out in order to study the interfaces of the hydrogenated amorphous silicon in contact with crystalline silicon and with indium tin oxide. A complete photovoltaic cell was also fabricated.

First a study of the passivation properties of a-Si:H on c-Si was undertaken using both well-established and novel measurement techniques. n-type crystalline silicon wafers were passivated using intrinsic hydrogenated amorphous silicon on one or both surfaces of the wafer. Effective minority carrier lifetime was measured using 1) microwave photoconductive decay using a Semilab WT-2000, 2) eddy current photoconductive decay using a Sinton WCT120 in either transient or quasi-steady-state mode as appropriate, and 3) photocarrier radiometry using near infrared and ultraviolet lasers.

Next, a coplanar conduction method was used in order to better understand the electrical properties of the p-a-Si:H/n-c-Si heterojunction with and without an intrinsic layer. p-a-Si:H layers with various doping concentrations were fabricated on resistive glass and on n-c-Si wafers and Cr/Ag electrical contacts were deposited on the top surface in order to measure the lateral conductance. By comparing the lateral conductance of a-Si:H/glass, a-Si:H/c-Si, and etched a-Si:H/c-Si samples, it is possible to determine the conductivity provided by the build-up of carriers at the a-Si:H/c-Si interface. This technique provides information about the electric field and carrier concentration in the crystalline silicon near the interface, which is related to the band offsets and to the open circuit voltage. Conductance was measured over a large range of temperatures both above and below room temperature so as to determine the activation energy of the conductance. The effective minority carrier lifetime of these samples was also measured using microwave and eddy current photoconductive decay and modulated photoluminescence.
Subsequently, the interface between a-Si:H and a transparent conducting oxide, indium tin oxide (ITO), was studied. Indium tin oxide typically has optimal electrical and optical properties when deposited at high temperature, however the heterojunction photovoltaic cell architecture requires that it be deposited directly onto the heat-sensitive hydrogenated amorphous silicon, so a series of experiments were carried out to deposit high quality RF-sputtered ITO at low temperature. UV-vis spectroscopy and four point probe measurements were used to optimize the optical transmittance and sheet resistance. X-ray diffraction (XRD) and secondary ion mass spectroscopy (SIMS) were used to inspect the ITO film and the ITO/a-Si interface.

Finally, the ITO/p-a-Si:H/i-a-Si:H/n-c-Si structure was incorporated into a full photovoltaic cell on a textured (100) Si substrate including the back surface field layers (i-a-Si:H/n-a-Si:H), full back metallization, and a front metallization grid. I-V measurements of this cell were taken before and after annealing under dark and AM1.5 conditions.

3.2. Apparatus

3.2.1. DCSF-PECVD System

Hydrogenated amorphous silicon needs to be deposited at relatively low temperatures - well below 450°C to prevent crystallization [41]. The crystallization temperature is dependent on a number of factors, including the hydrogen content, however low temperature deposition techniques are crucial. Plasma enhanced chemical vapour deposition (PECVD) [49] [50] is the most common technique used; other alternatives are hot wire chemical vapour deposition (HWCVD)[51] [52] and reactive sputtering [53] [54] [55]. Other purely physical techniques such as non-reactive sputtering [55] can be used to make amorphous silicon films, however chemical methods are required in order
to incorporate sufficient hydrogen, which is necessary to create films of practical use for photovoltaics [30].

In PECVD, precursor gases are ionized to create a plasma containing high-energy electrons. These electrons have sufficient energy to induce chemical processes that would otherwise not occur at lower temperatures. DC or RF plasmas (typically 13.56 MHz) can be used, however RF plasmas are preferred when depositing amorphous silicon for a number of reasons: they can be used to deposit insulating films without the plasma being extinguished by a build-up of dielectric material on the electrodes, and RF plasmas are stable at lower pressures, reducing potential substrate damage [56] [57]. However, RF plasmas also have certain disadvantages; for example, they require a complex matching circuit [56] [57].

In this study a DC-saddle field PECVD (DCSF-PECVD) technique in a tetrode configuration was used to deposit hydrogenated amorphous silicon. The DC saddle field plasma was sustained within a vertical stack of three electrodes: a grounded solid metal cathode, a high voltage semitransparent metal grid anode, and a grounded semitransparent metal grid cathode (Figure 8). This electrode configuration allowed electrons in the plasma to oscillate about the central electrode, leading to a longer effective path length than would be possible in a basic DC diode configuration [58]. This path extension led to a greater number of ionizing collisions and thus allowed a stable DC plasma to be maintained at pressures as low as a few mtorr [31]. The substrate was placed remotely on a fourth, grounded, solid electrode above the other electrodes, and gas/plasma species reached it by escaping the saddle field through the semitransparent cathode. Because the substrate was remote from the plasma, plasma damage was reduced and local substrate variables such as temperature and electrical bias could be controlled separately from the plasma variables.
The tetrode DCSF-PECVD system differed from previous DCSF-PECVD systems, which used symmetrical configurations of three or five electrodes. The three electrode configuration used a semitransparent anode in the centre of the chamber, with substrates positioned at either of two cathodes on either end of the chamber [31]. The five electrode configuration, in contrast, introduced a separation/demarcation between the substrates and the plasma/anode, by introducing semitransparent cathodes, and extending the deposition chamber in either direction past the anode-cathode region [59].

The DCSF-PECVD system used in this study is described in detail in the Appendix of reference [14]. Process variables that could be directly controlled included anode current, deposition chamber pressure, gas flow rate into the chamber, substrate temperature, and doping gas ratio. Anode current was held at 34.5 mA in all cases, which led to an anode voltage between 500V and 700V depending on other parameters and on the system
deposition and cleaning history. The voltage rose gradually with system use as a layer of low conductivity intrinsic amorphous silicon built up on the grids; periodic cleaning of the grids ensured that the anode voltage remained within the target range. Chamber pressure and gas flow rate were held constant at 160 mtorr and 30 sccm, respectively. The thickness of the deposited layers was not measured in-situ but was controlled by depositing for pre-determined lengths of time, based on calibrations of the deposition rate derived by measuring sample thicknesses post-deposition. The system was designed to accommodate wafers with a diameter of 4 inches.

The substrate was heated using conductive heating. The back side of the substrate was in direct contact with a silicon nitride coated silicon wafer, which was in direct contact with the heater (a heated copper block). A proportional-integral-derivative (PID) controller was used to regulate the heater temperature; a pre-heat time of 30 minutes was used to allow the substrate to reach the desired temperature. The relationship between heater temperature and substrate temperature was previously calibrated for the substrates used (silicon and glass).

The main precursor gas used was silane (SiH$_4$), which was decomposed by collisions with electrons, primarily into H and SiH$_x^+$ or SiH$_x$ [41]; this led to the incorporation of hydrogen into the amorphous silicon as it was deposited, creating hydrogenated amorphous silicon films [14]. Small percentages of diborane (B$_2$H$_6$) or phosphine (PH$_3$) were added to the gas mixture to create $p$- or $n$- doped a-Si:H films respectively. When doped films were to be deposited, the desired partial pressures of the component gases were combined in mixing bottles which were then flowed into the PECVD chamber via a mass flow controller.

The plasma was controlled by holding the anode current constant, and anode voltage fluctuated over a small range (approximately 500V-700V) during deposition due to the build-up of insulating or conducting films on the electrodes. After several depositions the
chamber was opened and the electrodes were cleaned in heated KOH, as were the protective metal shields covering the chamber walls.

Because $i$-, $p$- and $n$-a-Si:H were deposited in the same vacuum chamber, cross-contamination prevention measures were necessary. Each time the film doping was changed, a ‘dummy’ substrate was used between samples, on which an intrinsic film approximately 10 nm thick was deposited, thus coating the walls and electrodes with $i$-a-Si:H. The dummy wafer was then removed and the next sample was loaded.

The DCSF-PECVD chamber was connected via a load-lock to a glove box containing dry nitrogen atmosphere. In this way pre-deposition substrate processing were completed in a low oxygen and low moisture environment, and the substrates were then loaded directly into the PECVD system without exposure to ambient air.

In the case of glass substrates, the substrates were brought into the load-lock as received from the manufacturer in a sealed box, opened in the glove box, and loaded directly into the PECVD system. For silicon substrates, immersion in HF was used to etch the native oxide and passivate the silicon dangling bonds by hydrogen termination before depositing the a-Si:H films.

3.2.2. E-beam deposition system

Metal contacts in this study were deposited using electron beam evaporation. In this method, an electron beam is used to evaporate metal, which is contained in a crucible under the substrate; the evaporated metal atoms traverse to the substrate and lead to the formation of a solid film upon contact with the substrate.

Samples were loaded into the load lock from the ambient, and from there were transferred into the E-beam chamber. The E-beam evaporator has a base pressure of less than $1 \times 10^{-7}$ torr and can be used to deposit up to four different metals without needing to
open the chamber. When the E-beam is ignited, an electron beam is focused down onto the metal held in a crucible, which either sublimates directly or first melts and then evaporates. The evaporated metal was deposited upwards onto the rotating substrate, which faced downwards in relation to the source. Deposition rate and layer thickness were monitored in real-time using a crystal thickness monitor. When beginning the deposition of a new layer, a shutter was used to mask the substrate until stable evaporation was established at the desired rate.

For the 1 µm thick silver contacts used in the coplanar conductivity study, a 5 nm layer of chromium was first deposited at a rate of 0.2-0.5 Å/s, then the E-beam was powered down and the crucibles were rotated to select silver before repowering the E-beam. The silver deposition rate was ramped up in a series of steps, with lower deposition rates being used closer to the metal/substrate interface: the first 100 nm of silver were deposited at a rate of 2 Å/s, then the rate was gradually ramped up to approximately 10 Å/s over the next 100 nm, then it was ramped up to 20-40 Å/s for the final 800 nm. For the cells where 2 µm thick metal contacts were used, in this case the last 1 µm of silver was also deposited at 20-40 Å/s. No heating was done during the metal deposition, and circulating cold water was used to limit substrate heating.

Shadow masks were used to deposit selectively. For larger contacts with dimensions above several millimeters, as in the coplanar conductivity study, a shadow mask was made by cutting a pattern in a 280 µm thick silicon wafer with a machining laser. The mask was then cleaned in acetone, isopropyl alcohol, and de-ionized water before use. For front metallization of the photovoltaic cell, a higher resolution mask was required, and hence photolithographic resist was used for masking.
3.2.3. Sputtering systems

Indium tin oxide layers were deposited by sputtering. In sputter deposition an electric field causes ions in a non-reactive gas plasma to bombard a solid target consisting of the material to be deposited; through transfer of momentum, ions colliding with the target eject atoms and molecules or clusters from the target into gas phase, which subsequently traverse and deposit onto the substrate to form a solid film. Two different systems were used in this study: a Materials Research Corporation (MRC) DC magnetron sputtering system, and a Kurt J. Lesker (KJL) RF magnetron sputtering system. In both cases the sputtering gas used was argon, and the target was a ceramic block of sintered indium oxide (In$_2$O$_3$) and tin oxide (SnO$_2$) powders, with a composition of 90% indium oxide and 10% tin oxide.

The MRC system is a DC based sputtering system with a target-substrate distance of 3 cm. Target dimensions are 12 cm x 37.5 cm, the substrate holder dimensions are 35 cm x 35 cm, and there is a minimum base pressure of $10^{-6}$ torr. The substrate holder and target are both oriented vertically. During deposition the target is stationary while the substrate is passed through the target line of sight parallel to it, at a constant speed; layer thickness is controlled by varying the speed at which the substrate passes by the target. Heating in this system is done by moving the sample holder to another part of the system (out of the line of sight of the target) and using 1.3 kW halogen lamps that have a clear optical path to the front surface of the sample. Heated depositions are done by heating the sample prior to sputtering. This system does not provide the capability to adjust sputtering pressure and gas flow rate independently. The substrate is loaded into the system from the ambient via a load lock.

The KJL system is an RF based sputtering system with a diagonally-oriented target-substrate distance of 20 cm, a target radius of 3.8 cm and a minimum base pressure on the order of $10^{-8}$ torr. The target is oriented at an angle while the substrate is positioned
horizontally; the downward facing substrate is rotated to attain uniform deposition. In this system, halogen lamps are also used, but they are incident on the back of the sample holder rather than the front, they can be used during deposition, and this system includes a PID temperature controller and independent pressure and gas flow control. A gas ring positioned near the substrate and can be used to add oxygen to the sputtering gas. This system is part of a cluster tool that also includes the E-beam evaporation system described in Section 3.2.2; the two deposition chambers share a common load lock, although samples can generally not be moved directly from one chamber to the other to deposit consecutive layers in a structure, because of the need to position masks or flip wafers between layers.

3.3. Sample preparation

3.3.1. DCSF-PECVD amorphous silicon films

All a-Si:H layers were deposited using the deposition parameters described in Table 2. Other deposition parameters such as thickness or doping vary from sample to sample and are described where appropriate. Samples were heated for 30 minutes before deposition began, to allow the temperature to stabilize. The deposition process is described in detail by Bahardoust [14].

<table>
<thead>
<tr>
<th>Table 2 - DCSF-PECVD deposition parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>chamber pressure</td>
</tr>
<tr>
<td>anode current</td>
</tr>
<tr>
<td>gas flow rate</td>
</tr>
<tr>
<td>substrate temperature</td>
</tr>
<tr>
<td>base vacuum</td>
</tr>
</tbody>
</table>
3.3.2. Samples for photocarrier radiometry experiment

The first sample structure examined consisted of an $n$-type silicon wafer (#451) which was divided, using masks, into four sections. The substrate used was a 4 inch diameter, 280 $\mu$m thick, 1-5 $\Omega$ cm, (100) oriented float zone silicon wafer. Intrinsic hydrogenated amorphous silicon ($i$-a-Si:H) films were deposited by DCSF-PECVD using the parameters in Table 2. A mask, depicted in Figure 9, was used to cover half the wafer while a nominally 30 nm thick $i$-a-Si:H film was deposited on the front, then the wafer was turned to expose the back and the mask was rotated 90 degrees to deposit an $i$-a-Si:H film of the same thickness on the back. In this way four distinct areas on the wafer were made depending on whether the front, back, neither, or both were masked during deposition. The resulting wafer is shown in Figure 10.

Figure 9 - Shadow mask for PCR sample deposition used for wafer #451. a-Si:H was deposited onto the first side (side A) of the $n$-c-Si wafer through the mask, then the wafer was flipped and the mask was rotated by 90° before depositing a-Si:H onto the second side (side B).
Three additional samples were made with $i$-a-Si:H deposited on one side only, with film thicknesses of 10 nm (#437), 30 nm (#438) and 90 nm (#439). The substrate properties and $i$-a-Si:H deposition parameters were the same as for sample #451.

### 3.3.3. Samples for coplanar conductivity experiment

The next set of samples were made with the structures shown in Figure 11 and Figure 12.
Figure 12 – Amorphous silicon on insulating substrate sample structure for coplanar conductivity measurements.

Thin amorphous silicon films were deposited on 100 mm diameter silicon and glass substrates using DCSF-PECVD. The silicon substrates were 10 cm diameter 1-5 Ohm-cm float zone wafers with (100) orientation and of 280 μm thickness, while the glass substrates were Corning Eagle 2000 wafers of 700 μm thickness.

The substrate heater used for the depositions was calibrated and adjusted so as to ensure that the surface temperatures of the silicon and glass wafers were the same during the separate depositions on the two substrate materials. The deposition parameters are given in Section 3.3.1. Doping of the hydrogenated amorphous silicon layer was controlled through the precursor gas composition. For p-type doping, a diborane-silane gas mixture was used, with the diborane concentration, \([B_2H_6]/([B_2H_6] + [SiH_4])\), varied to achieve the change in doping concentration. A series of samples was prepared with varying diborane gas fraction while holding all other deposition parameters constant at the values in Table 2. The rate of film deposition was determined through spectroscopic ellipsometry measurements, and this rate was then used to choose a deposition time of 25 min, yielding films of approximately 20 nm thickness on c-Si and on glass. 20 nm a-Si:H films were made on glass and on crystalline silicon for diborane concentrations of 0.5%,
0.75%, and 1%. Additionally, a much thicker amorphous silicon layer of approximately 160 nm was deposited on glass using 0.75% diborane concentration. In the case of films on c-Si substrates, the samples were symmetrical, i.e., \( p\text{-a-Si:H}/n\text{-c-Si}/p\text{-a-Si:H} \). Samples on glass substrates had a-Si:H films only on one side.

<table>
<thead>
<tr>
<th>Sample (thickness 20 nm except HC2)</th>
<th>( \frac{\text{B}_2\text{H}_6}{\text{B}_2\text{H}_6 + \text{SiH}_4} )</th>
<th>i-layer thickness</th>
<th>substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC2 (160nm)</td>
<td>0.75</td>
<td>0</td>
<td>glass</td>
</tr>
<tr>
<td>HC3</td>
<td>0.5</td>
<td>0</td>
<td>glass</td>
</tr>
<tr>
<td>HC7</td>
<td>0.75</td>
<td>0</td>
<td>glass</td>
</tr>
<tr>
<td>HC6</td>
<td>1</td>
<td>0</td>
<td>glass</td>
</tr>
<tr>
<td>HC4</td>
<td>0.5</td>
<td>0</td>
<td>n-c-Si</td>
</tr>
<tr>
<td>HC1</td>
<td>0.75</td>
<td>0</td>
<td>n-c-Si</td>
</tr>
<tr>
<td>HC5</td>
<td>1</td>
<td>0</td>
<td>n-c-Si</td>
</tr>
<tr>
<td>HC8</td>
<td>0.75</td>
<td>4 min</td>
<td>n-c-Si</td>
</tr>
<tr>
<td>HC9</td>
<td>0.75</td>
<td>10</td>
<td>n-c-Si</td>
</tr>
</tbody>
</table>

Lastly, two samples were also made to test the effect of introducing an intrinsic amorphous layer in between the doped amorphous layer and the silicon substrate. The intrinsic layers, which were deposited using only silane as a precursor gas, were approximately 4 nm and 10 nm in thickness. The sample structure was therefore \( p\text{-a-Si:H}/i\text{-a-Si:H}/n\text{-c-Si}/i\text{-a-Si:H}/p\text{-a-Si:H} \), and the \( p \)-layers were deposited using 0.75% diborane concentration.
Electrical contacts were deposited by E-beam evaporation using a shadow mask. The contacts consisted of a 5 nm chromium adhesion layer followed by 1 µm of silver. Each sample had electrical contacts 10 mm x 5 mm in area with interelectrode spacings of 0.5 mm, 1 mm, 2 mm, and 4 mm in a transmission line pattern. The interelectrode area used in this research was 1 mm wide and 10 mm long; other interelectrode spacings were used only to confirm that the contact resistance between the electrical contacts and the amorphous silicon layers was not significant.

In summary, a series of different samples were made with different doping gas concentrations on n-c-Si and on glass. Two samples with an i-layer/p-layer stack were also made on n-c-Si. In the case of samples on n-c-Si, each sample was double-sided, with the same deposition parameters used to deposit films on each side, while the samples on glass were single-sided. A thicker i-a-Si:H sample (approximately 160 nm) was also deposited on glass for comparison. Electrodes were then deposited by E-beam evaporation using a shadow mask: the electrodes consisted of a 5 nm thick chromium adhesion layer followed by a 1 µm thick layer of silver, with an interelectrode spacing of 1 mm x 10 mm.

3.3.4. Samples to study ITO/a-Si:H interface

Samples of low temperature sputter deposited ITO were made on resistive Corning 1737 glass, on (100) crystalline silicon, and on amorphous silicon-crystalline silicon heterojunctions.

The first series of samples on glass were deposited by DC magnetron sputtering, in the MRC deposition system (Table 4). Preheating and annealing of samples was with a 1.3 kW lamp, which drew a 6.4 A current when operating. The speed of movement of the substrate across the line of sight of the target was used to control the film thickness to approximately 80 nm.
<table>
<thead>
<tr>
<th>Sputtering power (W)</th>
<th>Preheat time (min)</th>
<th>Anneal time (min)</th>
<th>Sputtering pressure (mtorr)</th>
<th># of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>750</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>9</td>
</tr>
<tr>
<td>750</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>0</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>0</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>5</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>10</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>300</td>
<td>0</td>
<td>15</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

A second series of samples on Corning 1737 glass were deposited by RF magnetron sputtering, in the KJL deposition system (Table 5). In this system heating was done using halogen lamps incident on the back of the substrate holder, which could be used during deposition as well as after the deposition. A heater temperature calibration was performed before making the samples, so as to determine the required temperature settings to reach the desired glass substrate temperature. The sputtering power was 100 W, the total gas flow rate was 19.5 sccm, and a crystal thickness monitor was used to deposit films of approximately 85 nm. When oxygen was used, it was injected into the sputtering chamber via a gas ring positioned near the substrate.
Table 5 - ITO samples deposited on glass in KJL RF magnetron sputtering system

<table>
<thead>
<tr>
<th>sample</th>
<th>sputtering pressure (mtorr)</th>
<th>deposition temperature (°C)</th>
<th>oxygen partial pressure in argon (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF#35</td>
<td>2.14</td>
<td>room temperature</td>
<td>0</td>
</tr>
<tr>
<td>RF#39</td>
<td>6.90</td>
<td>room temperature</td>
<td>0</td>
</tr>
<tr>
<td>RF#40</td>
<td>3.47</td>
<td>room temperature</td>
<td>0</td>
</tr>
<tr>
<td>RF#52</td>
<td>6.90</td>
<td>room temperature</td>
<td>0</td>
</tr>
<tr>
<td>RF#53</td>
<td>1.39</td>
<td>room temperature</td>
<td>0</td>
</tr>
<tr>
<td>BH6</td>
<td>2.08</td>
<td>room temperature</td>
<td>0</td>
</tr>
<tr>
<td>BH32</td>
<td>5.5</td>
<td>room temperature</td>
<td>0</td>
</tr>
<tr>
<td>BH11</td>
<td>2.14</td>
<td>room temperature</td>
<td>0.025%</td>
</tr>
<tr>
<td>BH12</td>
<td>2.14</td>
<td>room temperature</td>
<td>0.075%</td>
</tr>
<tr>
<td>BH13</td>
<td>2.14</td>
<td>room temperature</td>
<td>0.125%</td>
</tr>
<tr>
<td>BH14</td>
<td>2.14</td>
<td>room temperature</td>
<td>0.175%</td>
</tr>
<tr>
<td>BH15</td>
<td>2.14</td>
<td>room temperature</td>
<td>0.225%</td>
</tr>
<tr>
<td>BH4</td>
<td>2.14</td>
<td>60</td>
<td>0</td>
</tr>
<tr>
<td>BH3</td>
<td>2.14</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>BH8</td>
<td>2.14</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>BH9</td>
<td>2.14</td>
<td>120</td>
<td>0</td>
</tr>
</tbody>
</table>

A third set of ITO samples was prepared using the KJL sputtering system, with each film deposited on three different substrates simultaneously in the same deposition: Corning 1737 glass, 1-5 Ω.cm n-type (100) float zone Si wafer, and a p-a-Si:H/n-c-Si
heterojunction (Table 6). The heterojunction was made by depositing 10 nm of p-a-Si:H (with boron gas partial pressure of 0.75% and substrate temperature of 170 °C) onto a 1-2 Ω.cm n-type float zone (100) Si wafer. The sputtering power was 100 W and the Ar gas flow rate was 19.5 sccm. No oxygen was used.

Table 6 - ITO films deposited on glass, (100) n-c-Si, and p-a-Si:H/n-c-Si heterojunctions, with three different heat treatments

<table>
<thead>
<tr>
<th>sample set</th>
<th>anneal time (min)</th>
<th>operating pressure (mtorr)</th>
<th>deposition temperature (degrees C)</th>
<th>anneal temperature (degrees C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B21</td>
<td>0</td>
<td>2.14</td>
<td>room temperature</td>
<td>NA</td>
</tr>
<tr>
<td>B23</td>
<td>0</td>
<td>2.14</td>
<td>140</td>
<td>NA</td>
</tr>
<tr>
<td>B26</td>
<td>50</td>
<td>2.14</td>
<td>room temperature</td>
<td>200</td>
</tr>
</tbody>
</table>

3.3.5. HIT cell with texturization and ITO layer

A HIT cell was made by depositing a-Si:H and ITO on a textured crystalline silicon substrate and then depositing chromium/silver metal layers on the front and back; a lithographic process was used to deposit the front metal grid. The substrate was a 1-5 Ω.cm phosphorous doped, (100) float zone silicon wafer, 280 μm thick. An optical lithography mask was used to create an inverted pyramid texture with a 4 μm pyramid base width and 1 μm mesa between pyramids, corresponding to a total pitch of 5 μm [60] [61]. Before the amorphous silicon layers were deposited, the wafer was treated by dipping in a 5% solution of HF for 84 seconds. i-a-Si:H and n⁺-a-Si:H layers were deposited on the back surface (with thicknesses of 10 nm and 24 nm respectively,
and a phosphine concentration of 0.75% for the $n^+$-a-Si:H deposition), then the wafer was removed to the N\textsubscript{2} glove box where it was flipped over and dipped again in 5% HF, this time for 42 seconds, before depositing the front side $i$-a-Si:H and $p$-a-Si:H layers (with thicknesses of 14 nm and 8.67 nm respectively, and a diborane concentration of 0.75% for the $p$-layer). All a-Si:H films were deposited at 170 °C, with a chamber pressure of 160 mtorr and an anode current of 34.5 mA. A final 5% HF, 42 second dip was done before sputtering 90 nm of ITO (100 W, 19.5 sccm Ar gas flow, 2.14 mtorr, no substrate heating) using the KJL system.

Front and back metallization were completed using E-beam deposition of 5 nm of chromium followed by 1 $\mu$m of silver on the back and 2.5 $\mu$m at the front. The finger spacing for front metallization was 1 mm, with finger width of 100 $\mu$m. The metal fingers extend from either side of a trapezoidal centre busbar of 1 mm width at the wide end and 100 $\mu$m at the narrow end. A photolithographic mask was used to deposit the front metal, followed by a lift-off process consisting of immersion in acetone to remove the photoresist. Each cell was 2 cm x 2 cm, for a total of nine cells on one 4 inch diameter wafer.

The cell was annealed twice for 30 minutes each time, once at 187 °C and once at 200 °C. The ramp up and cool down times were each approximately 2 minutes.

3.4. **Standard characterization tools**

3.4.1. **Photoconductivity and carrier lifetime measurement**

A number of methods for non-contact carrier lifetime measurement exist. When there is no net current in a semiconductor, the rate of change of excess carriers is a function only of generation and recombination:
This equation can be used to determine the effective excess carrier lifetime $\tau_{\text{eff}}$ in a wafer.

$$\frac{d\Delta n(t)}{dt} = G(t) - U(t)$$  \hspace{1cm} (3.1)

$$U(t) = \frac{\Delta n(t)}{\tau_{\text{eff}}}$$  \hspace{1cm} (3.2)

If the wafer is exposed to a known illumination producing a uniform excess carrier concentration throughout the wafer, and the change in excess carrier concentration is measured (i.e., by measuring the change in conductivity of the wafer), the effective lifetime can be extracted. The conductance $\sigma$ of a semiconductor wafer depends on the carrier densities $n$ and $p$, the carrier mobilities $\mu_n$ and $\mu_p$, and the width of the wafer $W$.

When the concentration of carriers is increased by $\Delta n$ due to generation, the conductance changes in direct proportion, making it possible to calculate $\Delta n$ from the change in conductance:

$$\Delta \sigma = \Delta n (\mu_n + \mu_p) W$$ \hspace{1cm} (3.4)

Two special cases in particular yield simplifications to the relationship in Equation 3.3. In the transient photoconductive decay method, the sample is illuminated with a light which is abruptly turned off, such that $G(t) = 0$ for $t > 0$. In this case the excess carrier concentration decays exponentially with a time constant of $1/\tau_{\text{eff}}$. This technique is
effective when the lifetime is relatively large, and is easy to calibrate as only the rate of the change of the conductivity needs to be measured.

When the carrier lifetime is very small, the excess carrier concentration may decay too rapidly to be accurately measured, however the quasi-steady state photoconductance (QSSPC) method can be used instead. Under steady-state illumination, \( d\Delta n/dt \) is approximately equal to zero, and the equation for effective lifetime becomes:

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

In quasi-steady state photoconductance measurements, the level of illumination is varied very slowly compared to the lifetime, so that a steady-state approximation can be used with good accuracy. A disadvantage of this method is that the generation rate and carrier mobility must be known a priori.

### 3.4.2. Eddy current photoconductance lifetime measurement

In this research the Sinton WCT120 lifetime tester, shown in Figure 13, was used for both transient and quasi-steady-state photoconductance measurements [62]. The Sinton measures conductance using an inductive coil in a resonant RF circuit. The wafer is placed above the coil and changes in conductivity in the wafer disrupt the resonant circuit. A sensor next to the coil measures the intensity of light when a broad-spectrum lamp above the stage is illuminated.
The Sinton lifetime tester is controlled via a Microsoft Excel program, which also collects the data and uses it to calculate the effective lifetime. Results are obtained over a range of carrier densities, so lifetime as a function of excess carrier concentration can be measured. In this research measurements were reported for an excess carrier concentration of $1 \times 10^{15}$ cm$^{-3}$ and an infrared filter was used to limit the wavelength range of the incident light so that the absorption would be more uniform throughout the wafer depth. Lifetime measurements are average results over the area of the inductive coil, which has a 40 mm diameter.

### 3.4.3. Microwave photoconductive decay (μPCD) lifetime measurement

Microwave photoconductive decay lifetime measurements are made by illuminating an area of the sample with a laser beam and determining the change in carrier concentration by measuring the change in microwave reflectance. The analysis method used may be either transient or quasi-steady-state, however in this research transient results are reported. The system used was the Semilab WT-2000; it has a laser with a wavelength of 905 nm and the microwave frequency used to measure carrier concentration is 10 MHz [63]. Because the illumination is localized with a laser, the lifetime is measured as a function of position in the wafer, with a resolution of 1 mm.
This spatial resolution refers only to the plane of the wafer, as the results given are averages over the depth of the sample. The laser source is described in Table 7; the penetration depth of the laser is approximately 30 μm in silicon.

<table>
<thead>
<tr>
<th>Type</th>
<th>EG&amp;G PGAU4S12 InGaAs laser diode</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength</td>
<td>905 ± 10 nm</td>
</tr>
<tr>
<td>Pulse width</td>
<td>200 ns</td>
</tr>
<tr>
<td>Maximum repetition frequency</td>
<td>2.5 kHz</td>
</tr>
<tr>
<td>Laser beam divergence</td>
<td>0.4 radian</td>
</tr>
<tr>
<td>Maximum output</td>
<td>8.5 mW average, 17 W during 200 ns</td>
</tr>
</tbody>
</table>

3.4.4. Modulated photoluminescence

Modulated photoluminescence is a method in which the photoluminescence of a sample in response to a modulated excitation beam can be used to measure lifetime. The light source is made up of a bias source combined with a modulated source. If we consider a constant bias source which creates generation \( G = G_0 \), a steady state excess carrier concentration \( \Delta n_0 = G_0 \tau_{\text{eff}} \) would result. A modulated beam is added to create generation \( G(t) = G_0 + G_1 e^{i\omega t} \), where generation \( G_1 e^{i\omega t} \) is the generation in response to the modulated beam, and \( \omega \) is the modulation frequency [64]. A modulated excess carrier concentration \( \Delta n = \Delta n_0 + \Delta n_1 e^{i\omega t} \) is likewise created in response to the time varying source, where \( \Delta n_1 \) is a complex number defined by Equations 3.6 and 3.7 [64]. The phase is defined with respect to the generation \( G_1 \) (and hence to the phase of the excitation source).
\[ |\Delta n_1| = \frac{\tau_{eff} G_1}{\left(1 + \omega^2 \tau_{eff}^2\right)^{1/2}} \]

3.6

\[ tan(\angle \Delta n_1) = -\omega \tau_{eff} \]

3.7

The amplitude and phase of the modulated portion of the carrier concentration, and hence of the photoluminescence, can therefore be used to extract \( \tau_{eff} \).

Modulated photoluminescence measurements were done in an in-house tool at the Laboratoire de Génie Électrique de Paris.

3.4.5. IV measurements

Current-voltage measurements were measured using a Neonsee solar simulator which used a custom in-house two-point probe system. The probe tips were gold and the voltage was applied across two probe contacts using a voltage source, with current measurements being recorded through a LabView program. Dark and light I-V curves were measured with this device, with the illumination being provided by a xenon arc lamp with a power density of 100 mW/cm\(^2\); the spectrum of this lamp approximates an AM1.5 solar spectrum.

3.4.6. UV-vis spectroscopy

Optical spectroscopy was used to measure the spectral transmittance and reflectance of a given sample over a range of 190 nm to 900 nm. The system used was a Perkin Elmer Lambda 18 UV/VIS spectrometer. The system consists of a deuterium light source in series with a monochromator; the monochromator uses diffraction gratings and mirrors to select a narrow wavelength range out of a white light. This light is then directed at the sample and the transmitted or reflected light is collected and measured. In the case of reflectance measurements, a calibration mirror is used as a reference, while in the case of
transmittance measurements, the films measured are deposited on glass substrates, which are used as a reference.

3.4.7. Four point probe resistance

The sheet resistance of indium tin oxide films was measured using the four point probe method. Four probes are arranged in line with equidistant spacing and are lowered onto the surface of the sample, a current is applied to the two outer probes, and the voltage is measured between the two inner probes with a high impedance voltmeter. Since the probes which are used for measurement do not have a significant current flowing through them, the contact resistance of the probes is effectively eliminated.

3.4.8. Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)

Secondary Ion Mass Spectroscopy (SIMS) is a surface analysis technique which is used to determine the chemical composition of a surface or film. A primary ion source is used to sputter species from the surface; these ‘secondary ions’ which are removed from the surface are then analysed to determine their composition. In the case of time of flight SIMS, the secondary ions are accelerated towards a detector, and their time of travel is used to infer their mass; in this way the surface composition is detected. In order to do depth analysis, a second sputtering source is used to etch the material and expose layers of material below the original surface. ToF-SIMS is described in more detail by Sodhi [65]. All SIMS sputter depth analyses in this thesis were done at SI-Ontario in an ION-TOF TOF SIMS IV system, sputtering from the front (ITO side) of the sample. For the SIMS analysis described in Section 6.5.4, argon at 500 eV was used to etch the film and bismuth at 25 keV was used as the analysis species.

3.4.9. X-Ray Diffraction (XRD)

X-ray diffraction can be used to understand the crystal structure of a thin film, by bombarding it with X-rays, which are elastically scattered by the planes of the crystal.
The reflected rays interfere constructively or destructively according to Bragg’s law, to form a diffraction pattern of spots when projected onto a two-dimensional plane. The diffraction pattern is dependent on the crystal structure of the sample, and by rotating the sample and bombarding it with X-rays from different angles, different crystal planes are detected. XRD analysis was done at the X-Ray Powder Diffraction Laboratory in the Chemistry Department at the University of Toronto using a Siemens D5000 θ/2θ Diffractometer with Cu-Kα source operating at 50kV, 35 mA. The secondary beam was monochromatized by a Kevex Solid State Detector, and data was processed by DiffracPlus™ software.

3.5. **AFORS-HET simulation tool**

AFORS-HET (Automat for Simulation of Heterostructures) is a software tool developed by the Hahn-Meitner-Institute in Berlin for use in numerical simulation of heterojunction solar cells [66]. Version 2.4.1 was used for the modeling in this research. This version of AFORS-HET allows simulation of an arbitrary one-dimensional structures made up of semiconductor layers and interfaces, with properties such as band gap and defect densities defined by the user; external parameters such as voltage, illumination, and temperature can also be varied.

The model numerically solves the one dimensional semiconductor equations with appropriate boundary conditions, using the Newton-Raphson iteration scheme. Either drift-diffusion or thermionic emission models can be used at semiconductor interfaces: in this research thermionic emission is used at the amorphous-crystalline silicon interface, so the interface is modeled as a boundary. Analytical approximations are used as starting conditions to first solve the structures under equilibrium conditions, then parameters are changed incrementally with each last calculated solution serving as a starting solution for the next problem.

The full set of equations used in AFORS-HET is described in detail by R. Stangl [66].
4. Photocarrier radiometry

4.1. Carrier recombination in semiconductor wafers

The excess minority carrier lifetime is a key optimization parameter in order to ensure good photovoltaic cell performance, and in particular to attain high open circuit voltages. In this chapter photocarrier radiometry is used to study recombination in crystalline silicon wafers with hydrogenated amorphous silicon passivating layers deposited by the DCSF PECVD method.

Carrier recombination in crystalline silicon can be divided into radiative, Auger, and Shockley Read Hall (or trap–assisted) recombination mechanisms. The first two are unavoidable physical processes, while the third is highly dependent on variable material properties, and as such can be minimized. In each case, a carrier lifetime can be defined such that the rate of recombination is inversely proportional to the carrier lifetime.

Radiative recombination is also known as spontaneous emission and is the reverse process to photon absorption: in photon absorption, the energy of a photon is used to raise an electron from one energy state (in the valence band) to a higher energy state above the material band gap (in the conduction band), which we model mathematically as the creation of an electron-hole pair; in spontaneous emission, an electron-hole pair recombine as an electron drops down from the conduction band into the vacant electronic state in the valence band, and in doing so emits the lost energy in the form of a photon. The radiative recombination rate is lower in indirect band-gap materials, as the process requires phonons. The rate of radiative recombination $U_{\text{rad}}$ is dependent on the carrier concentration, as well as on the radiative recombination coefficient, $B_{\text{rad}}$, a property of the material [35]:

\[ U_{\text{rad}} = B_{\text{rad}}(np - n_t^2) \]  

4.1
For an $n$-type material $N_d > n_i$, hence Equation 4.1 is simplified [35]:

$$U_{rad} \approx B_{rad} \Delta n N_d$$  \hspace{1cm} 4.2

$$B_{rad} = \frac{1}{n_i^2} \frac{2\pi}{\hbar^2 c^2} \int_0^\infty n_i^2 \beta(E) e^{-E/kT} E^2 dE$$  \hspace{1cm} 4.3

$B_{rad}$ is independent of carrier concentration, but is dependent on the absorption coefficient $\beta$ and refractive index $n_i$, as well as the intrinsic density of states $n_i$; $h$, $c$, $k$, $T$, and $E$ are used with their usual definitions. From Equation 4.3 it can be seen that materials with higher absorption also have higher emission; for this reason direct band-gap materials generally have higher radiative recombination. Also, the exponential term amplifies the effect of transitions at lower energies, so radiative recombination involving trap states inside the band can be very significant, despite the relatively small absorption at those levels. The rate of radiative recombination is inversely proportional to the minority carrier radiative recombination lifetime, $\tau_{p,rad}$, in the case of $n$-doped material (and analogously for $p$-doped material) [35]:

$$\tau_{p,rad} = \frac{1}{B_{rad} N_d}$$  \hspace{1cm} 4.4

The second type of recombination in semiconductors is Auger recombination, a non-radiative recombination process involving the creation of kinetic rather than radiative energy. It requires the collision of two similar carriers (two electrons or two holes). For example, one electron transfers its energy to another: the first electron loses energy as it recombines with a hole, while the second electron increases its kinetic energy. A total of
three carriers are therefore involved, and the rate $U_{Aug}$ is proportional to the density of all three.

In the case of two-electron collisions [35]:

$$U_{Aug} \propto (n^2p - n_0^2p_0)$$  \hspace{1cm} 4.5

Similarly, for two-hole collisions [35]:

$$U_{Aug} \propto (np^2 - n_0p_0^2)$$  \hspace{1cm} 4.6

The Auger lifetime, $\tau_{p,Aug}$, in $n$-doped material is therefore strongly dependent on carrier concentration, and so Auger recombination is most important in highly doped materials, or at high temperatures.

$$\tau_{p,rad} \propto \frac{1}{N_d^2}$$  \hspace{1cm} 4.7

Auger recombination can also be trap-assisted, where a free carrier collides with one in a trap, in which case the minority carrier lifetime is proportional to either $\frac{1}{N_dN_a}$ or $\frac{1}{N_eN_d}$, depending whether electrons or holes are involved in the collision[35]. Auger recombination can occur in either direct or indirect bandgap materials, since the creation of a phonon allows the total momentum in the system to be conserved.

Although radiative and Auger recombination can be significant in the limit of very high quality materials, generally in most practical situations Shockley Read Hall (SRH) recombination dominates. SRH recombination occurs when a free carrier is captured by a trap, and remains in the trap until an oppositely charged carrier is captured by the same
The rate of SRH recombination therefore depends on the capture rates for both holes and for electrons, as well as on the average time between capture and release of a carrier by the trap state.

The capture rate $U_{nc}$ for an electron in a given trap state depends on the trap density, $N_t$, the electron concentration, $n$, the probability that the trap is empty, $(1-f_t)$, where $f_t$ will be derived, and a constant $B_n$ which combines the capture cross section $\sigma_n$ and the thermal velocity $v_n$ of the electron [35].

$$U_{nc} = B_n n N_t (1 - f_t) \quad 4.8$$

$$B_n = v_n \sigma_n \quad 4.9$$

The lifetime for SRH electron capture is therefore:

$$\tau_{nSRH} = \frac{1}{B_n N_t} \quad 4.10$$

and the rate of release of electrons from the trap is:

$$G_{nc} = B_n n_t N_t f_t \quad 4.11$$

where $n_t$ is the electron concentration when the Fermi level is equal to the trap level:

$$n_t = n_t e^{\frac{E_i - E_t}{kT}} \quad 4.12$$
The equations for hole capture and release are completely analogous, except that the probability that a trap state is empty is replaced by the probability that it is filled, and vice versa. Given that charge must not build up in the traps in the steady state, it can be shown that the probability of trap occupation is given by Equation 4.14.

\[ U_{nc} - G_{nc} = U_{pc} - G_{pc} \]  

And so the net recombination rate is

\[ f_t = \frac{B_n n - B_p p_t}{B_n (n + n_t) + B_p (p + p_t)} \]  

And so the net recombination rate is

\[ U_{SRH} = \frac{np - n_t^2}{\tau_{n,SRH} (p + p_t) + \tau_{p,SRH} (n + n_t)} \]  

In the case of an \( n \)-doped semiconductor, if \( \tau_{n,SRH} \approx \tau_{p,SRH} \) and \( n_t \approx p_t \) this simplifies to

\[ U_{SRH} \approx \frac{\Delta p}{\tau_{p,SRH}} \]  

The total bulk minority carrier lifetime, \( \tau_p \), depends on all of the different recombination processes:

\[ \frac{1}{\tau_p} = \frac{1}{\tau_{p,rad}} + \frac{1}{\tau_{p,Aug}} + \frac{1}{\tau_{p,SRH}} \]  

A background level of thermal generation and recombination of electrons and holes occurs in all semiconductors at temperatures higher than 0 K even without light, with the generation and recombination rates being equal. However, when light is incident on the
semiconductor it induces further generation, and the total generation rate of electrons and holes increases, producing excess carriers in addition to the equilibrium population; the recombination rate is similarly increased in response to the increased number of minority carriers. A steady-state will be reached where generation and recombination are equal, with new electron and hole concentrations determined by the excess carrier lifetime.

In most cases, the excess electron and excess hole concentrations can be considered equal at any given point in space; this assumption is referred to as the charge neutrality assumption and will be discussed in detail in Section 4.3.1. When the charge neutrality assumption is made, the bulk excess carrier lifetime \( \tau_{\text{bulk}} \) is given by Equation 4.18:

\[
\frac{\Delta n}{\tau_{\text{bulk}}} = \frac{n}{\tau_n} - \frac{n_0}{\tau_{n0}} = \frac{p}{\tau_p} - \frac{p_0}{\tau_{p0}}
\]

where \( \tau_n \) and \( \tau_p \) are the total electron and hole recombination rates, and \( \tau_{n0} \) and \( \tau_{p0} \) are the electron and hole recombination rates at thermal equilibrium.

**4.2. Photocarrier radiometry theory**

Photocarrier radiometry (PCR) is a measurement technique which probes direct and trap assisted (SRH) radiative recombination in a semiconductor sample, using carrier waves created in response to an AC-modulated incident superbandgap laser. Since the incident photons have an energy greater than the bandgap of the semiconductor, the sample is highly absorbing and the laser light is absorbed near the surface of the sample; carriers are generated which diffuse into the sample in an electronic carrier diffusion wave that oscillates at the AC modulation frequency. As carriers recombine and emit radiation, this resultant radiation provides information about the diffusion wave which was created, which in turn provides information about the diffusion constant, carrier lifetime, and, implicitly, the depth-dependent trap densities in the sample.
Diffusion waves are a family of physical phenomena which have only a first-order time derivative [67]. The behaviour of this group of phenomena is governed by diffusion in response to an oscillatory driving force, and can be described using ‘wave’ terminology. However, the diffusion wave is a distinct form of wave that behaves quite differently from the more familiar plane wave; in particular it has no wavefront and is highly damped. Diffusion waves have the basic form given in Equation 4.19, where $\psi$ is the wave function, $q(r)e^{i\omega t}$ is a sinusoidal driving function, and $F(r)$ is the inverse of the square of the characteristic decay length and defines how rapidly the wave is damped [67].

$$\nabla^2 \psi(z,t) - \frac{1}{D} \frac{\partial}{\partial t} \psi(z,t) + F(z)\psi(z,t) = q(z)e^{i\omega t} \quad 4.19$$

The excess carrier concentration $\Delta p$ in an $n$-type semiconductor sample behaves according to the continuity equation [37]:

$$D^*\nabla^2 \Delta p(z,t) - \frac{\partial \Delta p(z,t)}{\partial t} - \frac{\Delta p(z,t)}{\tau_{bulk}} + \mu^* E\nabla \Delta p(z,t) + G = 0 \quad 4.20$$

where $D^*$ is the ambipolar diffusion coefficient, $\tau_{bulk}$ is the excess hole bulk lifetime, and $\mu^*$ is the ambipolar carrier mobility. $E$ is the electric field and $G$ is the carrier generation rate.

The ambipolar diffusion coefficient $D^*$ describes how rapidly electrons and holes diffuse in a concentration gradient; because they are oppositely charged, an electric field is created between the electrons and the holes, so that they diffuse together with a common diffusion coefficient. It can be shown that the ambipolar diffusion coefficient is given by Equation 4.21 [37]:

$$\mu^* = \frac{D^*}{\tau_{bulk}}$$

where $\tau_{bulk}$ is the excess hole bulk lifetime.
\[ D^* = \frac{D_n D_p (n + p)}{D_n n + D_p p} \]  

and similarly the ambipolar mobility is given by Equation 4.22 [37]:

\[ \mu^* = \frac{\mu_n \mu_p (p - n)}{\mu_n n + \mu_p p} \]

In certain conditions the ambipolar diffusion coefficient can be approximated by a constant value. It is given by \( D^* \approx D_p \) in the case of an \( n \)-type semiconductor in low injection, where \( p_o \ll n_o \) and \( \Delta n \ll n_o \), or \( D^* \approx \frac{2D_n D_p}{D_n + D_p} \) for a semiconductor in high injection, where \( p_o \ll n_o \ll \Delta n \). At moderate injection levels the ambipolar diffusion coefficient has a value intermediate between the two extremes. In the case of crystalline silicon, \( D_n \) and \( D_p \) are of the same order of magnitude, with \( D_n \) typically 2-3 times larger than \( D_p \) [37]. Thus, the ambipolar diffusion coefficient is only weakly dependent on carrier concentration, as throughout the full range of injection levels, its value is expected to range only from \( D_p \) to approximately 1.5\( D_p \). It will be shown in Section 4.2.1 that the carrier wave is only weakly dependent on \( D^* \) over a realistic range of values; the ambipolar diffusion coefficient is therefore modeled as a constant value.

In the case of amorphous silicon, \( D_n \) is typically larger than \( D_p \) by several orders of magnitude, hence the ambipolar diffusion coefficient again has a value approximately equal to \( D_p \) in the high injection case [30] [41]. The semiconductor can be put in high injection by choosing a sufficiently high laser intensity for photoexcitation.

If there is no applied electric field, in most cases the electric field can be assumed to be zero; this approximation is discussed further in Section 4.3.1. Simplifications can also be made to the ambipolar mobility in certain conditions. In the case of high injection,
where \( p_0 \ll n_0 \ll \Delta n \), it follows that \( p \approx n \approx \Delta n \), so \( \mu^* \approx 0 \). Similarly, in an intrinsic semiconductor, \( p \approx n \), so \( \mu^* \approx 0 \). In any of these cases, the electric field term in Equation 4.20 becomes negligible and the equation can be simplified to:

\[
D^* \nabla^2 \Delta p(z, t) - \frac{\partial \Delta p(z, t)}{\partial t} - \frac{\Delta p(z, t)}{\tau_{bulk}} + G = 0
\]

4.23

When the generation has a harmonic time dependence (due to a harmonically modulated laser photogenerating excitation source of amplitude \( g(r, t) \)) the excess carrier distribution can be described by Equation 4.24:

\[
\nabla^2 \Delta p(z, t) - \frac{1}{D^*} \frac{\partial}{\partial t} \Delta p(z, t) - \frac{\Delta p}{D^* \tau_{bulk}} = g(z, t)e^{i\omega t}
\]

4.24

This is the form of a diffusion wave and can also be described using its Fourier transform (using \( \Delta N \) to represent excess carriers):

\[
\nabla^2 \Delta N(z, \omega) - \left( \frac{1 + j\omega \tau_{bulk}}{D^* \tau_{bulk}} \right) \Delta N(z, \omega) = G(z, \omega)
\]

4.25

The coefficient \( \left( \frac{1 + j\omega \tau_{bulk}}{D^* \tau_{bulk}} \right) \) provides information about the characteristics of the wave. Since the imaginary part is dependent on the frequency, the ratio of the real to imaginary parts varies with frequency, and at low frequencies, when \( \omega \ll \frac{1}{\tau_{bulk}} \), the imaginary part is insignificant. In this case there is no phase lag in the diffusion wave field and hence the field oscillates in time, but does not have a wave nature in space. At higher frequencies the phase lag appears; the transition frequency is dependent on the carrier lifetime, and occurs when \( \omega \approx \frac{1}{\tau_{bulk}} \). As this transition appears, the amplitude of the carrier wave also decreases.
A diffusion wave propagates at infinite speed, however it is spatially damped and its amplitude is small at large distances. The characteristic AC diffusion length $L_{ac}$ for an electronic carrier diffusion wave in a sample of thickness $L$ is defined as the centroid of the excess carrier distribution, i.e., [68]:

$$L_{ac}(\omega) \equiv \left[ \frac{\int_{0}^{L} z \Delta N(z, \omega) \, dz}{\int_{0}^{L} \Delta N(z, \omega) \, dz} \right]$$

The ambipolar diffusion constant $D^*$ is given by $D^* \approx D_p$ in the case of a strongly extrinsic $n$-type semiconductor. If the thickness of the sample is longer than the AC diffusion length, then the carrier wave will not extend to the back surface of the sample.

The incident laser which is used to create the carrier wave also creates thermal changes in the wafer, leading to a related thermal diffusion wave in addition to the carrier wave. Specifically, when carriers (e.g. electrons) are first created by a superbandgap light source, they have an energy higher than the conduction band edge, and the carriers within the conduction band rapidly reach an equilibrium energy through phonon emission, thus raising the local temperature. The carriers then diffuse until they recombine through either radiative or non-radiative recombination, either of which can occur directly from the conduction and valence bands, or via intermediate trap states. In the case of non-radiative recombination, the result is phonon emission, which leads to localised temperature changes in the wafer.
The carrier diffusion wave $\Delta N(z, \omega)$ and thermal diffusion wave $\Delta T(z, \omega)$ each emit infrared radiation; the carrier diffusion wave emits radiation due to radiative and SRH recombination, while the thermal diffusion wave emits radiation due to Planck emissions. All of the infrared radiation can be collected by a detector, whose signal is then processed by a lock-in amplifier tuned to the modulation frequency, to remove background radiation.

The wafer is placed on a reflective surface (the backing) and the input laser beam is directed at the front surface. Parabolic mirrors are used to collect the emitted radiation, with the mirrors placed in such a way that they do not collect the specular reflection of the input laser beam. The collected signal $P(\omega)$ at a given modulation frequency $\omega$ is expressed by Equation 4.28, where $F_{PTR}$ and $F_{PCR}$ are functions dependent on the spectral properties of the filters and detector [69].

$$P(\omega) \approx F_{PTR}(\lambda_1, \lambda_2) \int_0^L \Delta T(z, \omega) dz + F_{PCR}(\lambda_1, \lambda_2) \int_0^L \Delta N(z, \omega) dz \quad 4.28$$

Optical filters and tuned IR detectors can be used to separate the thermal wave and carrier wave components of the radiation. In the case of photocarrier radiometry, it is the carrier wave component which is of interest.

$$P_{PCR}(\omega) \approx F_{PCR}(\lambda_1, \lambda_2) \int_0^L \Delta N(z, \omega) dz \quad 4.29$$

Here $(\lambda_1, \lambda_2)$ is the spectral range of the filters and optical detector, and $F_{PCR}(\lambda_1, \lambda_2)$ is a function of the radiative emission of the sample per unit wavelength and of the reflectances of the various surfaces (front and back wafer surfaces and the backing on which the wafer is placed) [69].
where $R_f$ is the front surface reflectance, $R_b$ is the backing material reflectance, $W_{eR}$ is the spectral power per unit wavelength (i.e., the rate of recombination multiplied by the energy difference between initial and final states), $\eta_R$ is the quantum yield for infrared radiative emission from those states, $m^*$ is the effective mass of a carrier, $\mu$ is the ambipolar mobility, $\varepsilon$ is the dielectric constant, $n_r$ is the refractive index, $q$ is the charge of an electron, and $c$ is the speed of light in a vacuum.

### 4.2.1. Single layer model

The excess carrier concentration $\Delta N(z, \omega)$ can be determined by solving Equation 4.25. In the case of excitation with an 830 nm laser, nearly all of the absorption occurs in the crystalline silicon substrate, and the wafer is modelled as a single layer, with the amorphous silicon layer affecting the boundary conditions. In the case of a semiconductor of thickness $L$, photoexcited with a beam whose diameter is sufficiently large compared to $L$, the carrier distribution can be approximated as one-dimensional. The excess carrier generation will be given by the Beer-Lambert Law [68]:

$$G(z, \omega) = \frac{\beta n Q I_0}{2 h \nu} e^{-\beta z}$$

where $\beta$ is the absorption coefficient, $n_Q$ is the quantum yield for carrier generation, and $I_0$ and $h \nu$ are the optical intensity and incident photon energy of the beam respectively.
By combining Equations 4.25 and 4.31, in the case where there is no external electric field, it can be shown that the resulting carrier concentration wave field is given by Equation 4.32 [68].

\[
\Delta N(z, \omega) = \frac{\beta \eta_0 I_0}{2 h v D^* (\beta^2 - L_{ac}^{-2})} \left( \frac{\Gamma_2 Y_1 - Y_2 \Gamma_1 e^{-(L_{ac}^{-1} + \beta)L}}{\Gamma_2 - \Gamma_1 e^{-2L/L_{ac}}} \right) e^{-z/L_{ac}} e^{-z/L_{ac}}
\]

where \( \Gamma_1, \Gamma_2, \gamma_1, \) and \( \gamma_2 \) represent the following ratios:

\[
\Gamma_1 = \frac{D_p L_{ac}^{-1}(\omega) - S_1}{D_p L_{ac}^{-1}(\omega) + S_1}
\]

\[
\Gamma_2 = \frac{D_p L_{ac}^{-1}(\omega) + S_2}{D_p L_{ac}^{-1}(\omega) - S_2}
\]

\[
\gamma_1 = \frac{D_p \beta(\omega) + S_1}{D_p L_{ac}^{-1}(\omega) + S_1}
\]

\[
\gamma_2 = \frac{D_p \beta(\omega) + S_2}{D_p L_{ac}^{-1}(\omega) + S_2}
\]

\( S_1 \) and \( S_2 \) correspond to the front and back surface recombination velocities, and \( \tau_{\text{bulk}} \) is the minority excess carrier lifetime in the bulk.

The above equation is complex, has many terms, and is not easily visualized or solved analytically. However, it can be solved using numerical methods. In Figure 14 - Figure
18, the amplitude and phase of the integrated carrier concentration wave field \( \int_0^L \Delta N(\omega) \, dx \) are plotted with respect to the laser modulation frequency. Different material properties can be varied to investigate their effect on the carrier concentration wave.

In Figure 14, the optical absorption of the sample is varied, which shifts the amplitude, without changing the frequency dependence of the amplitude; it also has minimal effect on the phase of the carrier concentration wave field. Bulk lifetime is varied in Figure 15, which changes the carrier concentration wave amplitude at low frequencies and changes the high-frequency cutoff at which the amplitude decreases and the phase begins to shift; at higher frequencies the curves for the various values of bulk lifetime converge. The phase relationship, though shifted in frequency, retains its shape as the bulk lifetimes is varied.

When front surface recombination velocity is investigated, in Figure 16, the relationship is slightly more complex. The carrier concentration wave amplitude is higher when the surface recombination velocity is decreased, as would be expected, but additionally at frequencies above the cutoff frequency, the rates at which the amplitude and phase change are now both dependent on surface recombination velocity. For high front surface recombination velocities, the phase tends to saturate before it reaches 90 degrees.

The back surface recombination velocity and the diffusion coefficient, shown in Figure 17 and Figure 18, have very similar effects on the carrier concentration wave. In both cases the low frequency amplitude is modified, and the cutoff frequency is shifted. This pattern is similar to the one found when varying carrier lifetime, however the effect is less pronounced within a realistic range of values of diffusion coefficient and back surface recombination velocity; the effect of back surface recombination velocity, in
particular, is rather weak, with even changes of surface recombination velocity of several orders of magnitude having only a very slight effect on the carrier concentration wave.

Figure 14 – Integrated excess carrier density $\int_0^L \Delta N(\omega) d\omega$ with varying optical absorption coefficient top) amplitude bottom) phase; $L = 280$ $\mu$m, $\tau = 100$ $\mu$s, $D^* = 30$ cm$^2$/s, $S_1 = 10^2$ cm/s, $S_2 = 10^5$ cm/s
Figure 15 - Integrated excess carrier density $\int_0^L \Delta N(\omega) d\tau$ with varying bulk excess carrier lifetime (top) amplitude (bottom) phase; $L = 280 \, \mu m$, $D^* = 30 \, \text{cm}^2/\text{s}$, $S_1 = 10^2 \, \text{cm/s}$, $S_2 = 10^5 \, \text{cm/s}$, $\beta = 650 \, \text{cm}^{-1}$. 
Figure 16 - Integrated excess carrier density $\int_0^L \Delta N(\omega) \, dx$ with varying front surface recombination velocity (top) amplitude and (bottom) phase; $L = 280 \, \mu\text{m}$, $D^* = 30 \, \text{cm}^2/\text{s}$, $\tau = 100 \, \mu\text{s}$, $S_z = 10^5 \, \text{cm/s}$, $\beta = 650 \, \text{cm}^{-1}$. 
Figure 17 - Integrated excess carrier density $\int_0^L \Delta N(\omega) d\omega$ with varying back surface recombination velocity (top) amplitude and (bottom) phase; $L = 280 \mu m$, $D^* = 30 \text{ cm}^2/\text{s}$, $\tau = 100 \mu s$, $S_1 = 10^2 \text{ cm/s}$, $\beta = 650 \text{ cm}^{-1}$. 
Figure 18 - Integrated excess carrier density $\int_0^L \Delta N(\omega) \, dx$ varying diffusion coefficient top) amplitude bottom) phase; $L = 280 \, \mu m$, $\tau = 100 \, \mu s$, $S_1 = 10^2 \, \text{cm/s}$, $S_2 = 10^5 \, \text{cm/s}$, $\beta = 650 \, \text{cm}^{-1}$. 
4.2.2. Two layer model

If the absorption in the amorphous silicon layer is sufficiently high, or if the film is sufficiently thick, a significant portion of the carrier excitation may occur in the amorphous silicon. This is the case when the PCR excitation frequency is much higher than the amorphous silicon cutoff frequency, for example when the sample is excited with a UV laser. In this case, it is useful to model the system using a two layer model. The carrier diffusion wave equation, Equation 4.25, is solved in each layer to account for the different properties of the two layers, and boundary conditions are described at the interface as well as at the front and back. The difference between the carrier concentration wave concentrations $\Delta N$ at either side of the amorphous-crystalline silicon interface is set to equal the unfilled trap density, $n_T$, such that if there are no unfilled traps, $\Delta N$ is continuous at the interface (discontinuities due to the heterojunction band offsets are thus neglected). $n_T$ has units of $\text{cm}^{-3}$, and when multiplied by the interface recombination velocity, it determines the carrier flux at the interface.

$$-D_{a-Si:H} \frac{d}{dx} \Delta N_{a-Si:H}(x, \omega)|_{interface} + D_{c-Si} \frac{d}{dx} \Delta N_{c-Si}(x, \omega)|_{interface} = S_I n_T$$

The model is described in further detail in reference [70].

4.3. Model assumptions

Certain assumptions are made in the photocarrier radiometry calculations; methods for determining the accuracy of these assumptions will be described in this section, following the method of analysis shown by McKelvey [71]. The first assumption is the electrical neutrality assumption which is used in the derivation of the well-known ambipolar transport equation [37]. The next assumption is the assumption of zero electric field, which is made in deriving the solution to the carrier concentration wave field [68].
Since there is no applied electric field, the assumption of zero electric field amounts to two assumptions: that the internal field created by ambipolar diffusion is negligible, and that the electric field created by the thermoelectric effect is negligible. Ambipolar transport will be discussed in section 4.3.1, and the thermoelectric effect will be discussed in section 4.3.2.

**4.3.1. Ambipolar transport**

The single layer and two layer models described in sections 4.2.1 and 4.2.2 are derived using the ambipolar transport equation, Equation 4.20, which is derived by combining the continuity equations for holes and electrons [71]. Excess holes and excess electrons in a semiconductor have different diffusion coefficients and mobilities, and if they could move completely independently, they would drift and diffuse at different rates. However, they do not move independently, but rather are held together by an electric field which arises when they begin to separate; the excess electrons and holes thus travel together with an effective ambipolar diffusion coefficient and ambipolar mobility. This phenomenon is known as ambipolar transport.

Ambipolar transport is quite complicated to calculate exactly, and has no analytical solution, hence an approximation is normally made which is reasonable in the vast majority of cases. Electrical neutrality is assumed, i.e., it is assumed that the concentrations of excess electrons and holes are equal at any point in space. Although this can not be exactly correct or there would be no ambipolar transport, the separation of charge required to create the field necessary for ambipolar transport is normally extremely small and can be reasonably neglected in the calculations. Once the carrier densities are calculated, they can then be used to calculate the internal field, which in turn can be used to calculate the excess charge separation and evaluate the consistency of the assumption.
The continuity equations for holes and for electrons are given by Equations 4.38 and 4.39.

\[ D_p \nabla^2(\Delta p) - \mu_p \left( \bar{E} \cdot \nabla \Delta p + p \bar{V} \cdot \bar{E} \right) + G_p - \left( \frac{p}{\tau_p} - \frac{p_0}{\tau_{p0}} \right) = \frac{\partial \Delta p}{\partial t} \quad 4.38 \]

\[ D_n \nabla^2(\Delta n) - \mu_n \left( \bar{E} \cdot \nabla \Delta n + n \bar{V} \cdot \bar{E} \right) + G_n - \left( \frac{n}{\tau_n} - \frac{n_0}{\tau_{n0}} \right) = \frac{\partial \Delta n}{\partial t} \quad 4.39 \]

If we make the charge neutrality assumption, \( \Delta n = \Delta p \), several simplifications can be made to Equations 4.38 and 4.39: both equations may be expressed in terms of \( \Delta n \), the recombination term in each equation can be simplified to \( \Delta n/\tau_{\text{bulk}} \) using Equation 4.18. We can also reasonably assume that the generation terms are equal \((G_n=G_p=G)\). This allows the two equations to be combined and the \( \bar{V} \cdot \bar{E} \) term to be eliminated, giving Equation 4.40:

\[ \frac{(n + p)D_n D_p}{n D_n + p D_p} \nabla^2(\Delta n) - \frac{(n - p)\mu_p \mu_n}{n \mu_n + p \mu_p} \left( \bar{E} \cdot \nabla \Delta n \right) + G - \frac{\Delta n}{\tau_{\text{bulk}}} = \frac{\partial \Delta n}{\partial t} \quad 4.40 \]

This is the familiar ambipolar transport equation (Equation 4.20), and the coefficients of the first two terms are \( D^* \) and \( \mu^* \), the ambipolar diffusion coefficient and ambipolar mobility (Equations 4.21 and 4.22).

The electrical neutrality assumption can be evaluated by calculating the internal field and the disparity between \( \Delta n \) and \( \Delta p \) necessary to create that internal field. This may be done by writing the total electrical current density and solving for the electric field:
\[ \tilde{J} = \tilde{J}_n + \tilde{J}_p = \sigma \tilde{E} + q(D_n - D_p)\nabla \Delta n \]  

\[ \tilde{E} = \frac{\tilde{J}}{\sigma} - \frac{q}{\sigma} (D_n - D_p) \nabla \Delta n \]

Expressing \( \sigma \), \( D_n \) and \( D_p \) in terms of electron and hole mobilities, this becomes:

\[ \tilde{E} = \frac{\tilde{J}}{\sigma} - \frac{kT}{q} \left( \frac{\frac{\mu_n}{\mu_p} - 1}{\frac{\mu_n}{\mu_p} n + p} \right) \nabla \Delta n = \tilde{E}_a + \tilde{E}_{int} \]

where \( \tilde{E}_a \) and \( \tilde{E}_{int} \) are the applied and internal electric fields. So, the internal electric field is given by Equation 4.44:

\[ \tilde{E}_{int} = - \frac{kT}{q} \left( \frac{\frac{\mu_n}{\mu_p} - 1}{\frac{\mu_n}{\mu_p} n + p} \right) \nabla \Delta n \]

Using Poisson’s equation it is now possible to calculate the disparity between the excess electron and excess hole concentrations.

\[ \nabla \cdot \tilde{E}_{int} = \frac{4\pi q}{\varepsilon} (\Delta p - \Delta n) = \frac{kT}{q} \left( \frac{\frac{\mu_n}{\mu_p} - 1}{\frac{\mu_n}{\mu_p} n + p} \right) \nabla^2 \Delta n \]

In order for the charge neutrality assumption to be reasonable, it must be shown that the relative disparity in the excess electron and hole populations is small:
which, from Equation 4.45, is equivalent to the condition

\[ \frac{\Delta p - \Delta n}{\Delta p} \ll 1 \]  

where \( L_{Di} \) is the intrinsic Debye length, and is given by \( \left( \frac{\varepsilon kT}{4\pi q^2 n_i} \right) \). Equation 4.47 will be used to test the charge neutrality assumption, and thus to determine whether it is accurate to use the ambipolar transport equation in the photocarrier radiometry model.

The second assumption made in the photocarrier radiometry model is that the internal electric field due to ambipolar diffusion is negligible. Since there is no applied electric field, the assumption is reasonable if the effect of the internal electric field on the carrier distribution is small compared to the effect of diffusion. In order to make this comparison, we define a characteristic drift length in the semiconductor, analogous to the characteristic diffusion length. The characteristic drift length is the distance that an average carrier will travel due to the electric field before it recombines. This characteristic drift length is equal to \( \mu^* \left| E \right| \tau_{bulk} \), and the effect of an electric field will be negligible if the characteristic drift length is much smaller than the characteristic diffusion length.

So, the effect of the internal electric field can be neglected if:

\[ \mu^* \left| E_{int} \right| \tau_{bulk} \ll \sqrt{D^* \tau_{bulk}} \]
Using the equation for the internal electric field, Equation 4.44, this condition can be expressed in terms of the material parameters and carrier concentrations:

\[
\frac{|\nabla(\Delta n)|}{\sqrt{D^*\tau_{\text{bulk}}}} \left(\frac{\mu_n}{\mu_p} - 1\right)\frac{(n + p)(n\frac{\mu_n}{\mu_p} + p)}{(n_0 - p_0)} \ll 1
\]

4.49

The ratio on the left side of Equation 4.49 gives a metric for how reasonable the assumption of negligible internal electric field is. This condition will be used to test if and when it is reasonable to neglect the internal electric field in the photocarrier radiometry model.

4.3.2. Thermoelectric effect

When a semiconductor is exposed to a source of energy such as a laser, heating can occur leading to thermal gradients within the semiconductor. In addition to motion of carriers due to concentration gradients or electric fields, there is also motion of free carriers due to diffusion down a temperature gradient if one exists. If there is no net current through the material, a potential gradient develops which is proportional to the thermal gradient:

\[
\bar{\nabla}V_{th} = -S_{\text{seebeck}}\bar{\nabla}T
\]

4.50

where \(V_{th}\) is the thermoelectric potential and \(S_{\text{seebeck}}\) is the Seebeck coefficient, a property of the material. In the case where the carriers are predominantly negatively charged, the Seebeck coefficient will be negative, as the carriers will move from a higher temperature to a lower temperature region.

The electric field due to the thermoelectric effect is thus given by:
\[ \vec{E}_{th} = -S_{\text{seebeck}} \nabla T \]

4.51

In the PCR model described in sections 4.2.1 and 4.2.2, it is assumed that there is no electric field. The significance of the thermoelectric field can be quantified similarly to the internal electric field, as in Equation 4.48 in section 4.3.1. The thermoelectric effect can thus be reasonably neglected under the following condition:

\[ \frac{\mu^* |S_{\text{seebeck}} \nabla T| \tau_{\text{bulk}}}{\sqrt{D^* \tau_{\text{bulk}}}} \ll 1 \]

4.52

The temperature gradient \( \nabla T \) is determined based on the specific details of the samples and experimental setup. These calculations will be presented in section 4.5.4 and used to test the assumption of negligible thermoelectric effect.

4.4. Experiment

A phosphorous doped crystalline silicon wafer (sample #451) was divided into four sections, each of which underwent a different passivation procedure, using intrinsic hydrogenated amorphous silicon. One section was passivated on both sides A and B with 30 nm of amorphous silicon; one section was passivated only on side A; one section was passivated only on side B; and the fourth section was not passivated at all. Each of the four sample quadrants was measured from both sides A and B, to confirm the symmetry of the measurements. Additionally, three samples (samples #437, #438, and #439) were made with i-a-Si:H on only one side, using three different thicknesses of i-a-Si:H: the i-a-Si:H layers were 10, 30, and 90 nm respectively. In all cases, the i-a-Si:H layers were deposited by DCSF-PECVD using the deposition parameters described in Section 3.3.1.
In photocarrier radiometry, an incident photon with an energy above that of the bandgap is used to excite an electron to the conduction band, and when it decays its energy is converted to some combination of phonons and photons. These photons, which have a wavelength either equal to the bandgap energy (in the case of band-to-band radiative recombination) or less than the bandgap energy (in the case of trap-assisted recombination) are collected and form the PCR signal.

The experimental setup used is pictured in Figure 19. A sample was placed on an aluminum stage which functioned as both a reflective backing and a thermal mass, whose position could be adjusted in the x, y, and z, directions. For the IR measurements, an 830 nm laser was used as the excitation source, with the power and spot diameter adjusted to 27.4 mW and 500 μm respectively (giving an incident photon flux of $5.8 \times 10^{19}$ cm$^{-2}$s$^{-1}$). For the UV measurements, the laser wavelength was 355 nm, the power was 27 mW, and the spot diameter was 850 μm (giving an incident photon flux of $8.5 \times 10^{18}$ cm$^{-2}$s$^{-1}$). This incident laser light was modulated with an AC function generator, and the resulting PCR signal was collected via a lock-in-amplifier. A gradium lens and mirrors directed the laser onto the sample, and the radiation emitted from the sample was collected by parabolic mirrors. These parabolic mirrors were positioned so as to exclude the specular reflection from the excitation source, however they capture radiation from a wide range of angles, which is then passed through a long pass filter (1042 nm – 2198 nm) to exclude the diffuse reflection from the excitation source. An InGaAs photodetector (800-1750 nm, 1550 nm peak) collected the light and sent the signal to the lock-in amplifier. A MATLAB interface was used to control the stage and instruments and to acquire the data.
The 830 nm near infrared laser corresponds to a photon energy of 1.49 eV, which is slightly below the bandgap energy of hydrogenated amorphous silicon (approximately 1.8-1.9 eV), so amorphous silicon layer is not highly absorbing at this wavelength; with an a-Si:H thickness of only 30 nm, the a-Si:H layer did not absorb a significant portion of the light. Instead, the absorption occurred essentially entirely in the crystalline silicon bulk, largely in the front 20-30 μm (assuming an absorption coefficient of 650 cm$^{-1}$), and the electron-hole pairs diffused further into the bulk [73]. The PCR signal measured from near infrared excitation provides a picture of the crystalline silicon bulk wafer properties, with the hydrogenated amorphous silicon layer influencing the surface boundary conditions.

The 355 nm ultraviolet laser, in contrast, corresponds to a photon energy of 3.49 eV, which is strongly absorbed in amorphous silicon, with the majority of the power absorbed in the first 10 nm of the film if we assume an absorption coefficient of $10^6$ cm$^{-1}$ [73]. Hence, the majority of carriers were created in the amorphous silicon and reached the
crystalline silicon by diffusion, so the UV PCR signal, in contrast to the IR PCR signal, was more directly influenced by the a-Si:H properties.

4.5. Results and discussion

4.5.1. Excitation with 830 nm laser

Sample #451 was examined using PCR with a 830 nm excitation source. The surface of the wafer was scanned in 0.5 mm steps with a 0.5 mm spotsize laser, at a series of different modulation frequencies, to create amplitude and phase colour maps of the four differently-passivated quadrants of the wafer (i-a-Si:H passivation on both sides of the wafer, on the front only, on the back only, and no passivation). The colour maps are shown in Figure 20. The PCR measurement is able to clearly distinguish between the four different passivation schemes. In particular, by comparing results at different modulation frequencies we can distinguish between front surface or back surface recombination: at high modulation frequencies the back-surface passivated quadrant resembles the unpassivated quadrant, as the high modulation frequency excludes data from the back of the sample.
Figure 20 - Amplitude and phase of x-y scans of a sample with four different surface passivation schemes, scanned at three different laser modulation frequencies. Quadrants 1 through 4 represent passivation on both sides, front only, back only, and no passivation respectively [72].

The results of the IR PCR measurements for a representative point in each quadrant are shown in Figure 21 as a function of modulation frequency; a single layer model is used for fitting. Each quadrant of the sample was measured from both sides of the wafer, and so there are eight measurements in total. However, it is evident from the graphs that equivalent samples give essentially equivalent results; e.g., comparing the case where only side A is passivated and the measurement was taken from side A, versus the case where only side B is passivated and the measurement was taken from side B, the two sets
of results match closely. This is expected and confirms the symmetry of the samples and reproducibility of the films. It also provides additional data for fitting.

Figure 21 - Photocarrier radiometry amplitude (top) and phase (bottom) for phosphorous-doped c-Si wafer #451 with and without 30 nm i-a-Si:H layers for surface passivation, using near infrared laser excitation at 830 nm. Measurement data at each point is plotted, and curves of best fit are drawn [72].
The next observation concerns the large range of amplitudes in Figure 21. The PCR amplitude ranges by nearly three orders of magnitude from the lowest amplitude signal to the highest, corresponding to a proportionally large difference in the carrier concentration wave integrals. This demonstrates the effectiveness of the passivation layers. It is also notable that there is a very significant difference between the samples which were passivated on both sides and those that were passivated only at the front, despite the fact that carrier generation occurs only near the front. Lastly, above 10kHz the amplitudes of the back-side passivated sample and unpassivated sample begin to merge, and above 50 kHz they are indistinguishable. This marks the frequency where the carrier concentration wave no longer reaches the back surface.

The measurement data was fitted to a theoretical model using a square deviation minimum and setting the bulk lifetime, diffusion coefficient, and front surface recombination velocity as fitting parameters [72] [74]. Because the back surface recombination velocity has only a very weak effect on the PCR results it was not set as a fitting parameter in the least-squares minimization, rather the symmetry of the samples was used to determine an appropriate approximate value of the back surface recombination velocity, by minimizing the difference between the front and back surface recombination velocities in the symmetrical samples, as well as between measurements of the same surface when it is at the front or back. The bulk lifetime and diffusion coefficient were both modeled as constants, giving weighted effective values over the depth of the layer. Additionally, the lifetime, diffusion coefficient, and surface recombination velocities were all assumed to be independent of PCR modulation frequency; since the excess carrier density amplitude can vary significantly depending on modulation frequency, this amounts to modeling the parameters as constant over a range of carrier injection levels.

Self-normalized data was used in the fitting, i.e., the PCR amplitude measured at the lowest frequency point and the theoretically calculated PCR amplitude at the same point
were both normalized to 1 prior to fitting. This method allowed us to avoid the problem of finding an accurate reference sample with precisely known optoelectronic properties, and to avoid the fitting error caused by a reference sample with imprecisely known properties [74].

The data fits the theoretical model closely at low frequencies, but at very high frequencies the phase lag shows large deviations from what is predicted by the model. This may be due to the build up of charge at the c-Si/air or a-Si-H/c-Si interfaces, which may confine the carrier wave centroid closer to the surface, reducing the phase lage. Also, it is important to consider the effect of the internal electric field which is created by a separation of excess electrons and holes due to ambipolar transport, which is more pronounced at high frequencies. The effect of ambipolar transport at high frequencies is discussed in Section 4.5.3.

Results of the fitting are seen in Table 8, together with the effective lifetimes measured by microwave and eddy current photoconductive decay. The least-squares fitting error for the PCR results is 2.6% for sample passivated on both sides, 1.7% for the front side passivated sample, 4.3% for the back side passivated sample, and 14% for the unpassivated sample. For eddy current measurements, samples with effective lifetime above 200 µs were measured by transient analysis, and those with smaller lifetimes were measured with quasi-steady-state analysis. The µPCD, eddy current, and PCR measurements are expected to be different, as they use different light sources (with µPCD and PCR both using near infrared lasers, while the eddy current measurements use a broad-spectrum light source), different illumination levels, and different analysis techniques. The basic trends are similar for the effective lifetimes measured by µPCD and eddy current, although there are a few notable differences. The effective lifetimes for the eddy current measurements of the double-side passivated wafers are substantially higher than those for the µPCD measurements of the same samples, and the eddy current
measurements distinguish much more between the samples passivated on the front and those passivated on the back, suggesting that the photogeneration is not uniform through the depth of the wafer.

Table 8 - Lifetime, diffusion constant, and surface recombination velocities for \textit{i-a-Si:H} passivated silicon, wafer #451. Effective lifetime, $\tau_{\text{eff}}$, is measured using $\mu$PCD and eddy current photoconductivity measurements. Additionally, numerical fitting using the single-layer PCR model is used to extract the bulk lifetime, $\tau_{\text{bulk}}$, ambipolar diffusion coefficient, $D_{\text{c-Si}}$, and the front and back surface recombination velocities, $S_1$ and $S_2$, from the PCR measurements.

<table>
<thead>
<tr>
<th></th>
<th>$\tau_{\text{eff}}$ (µs) $\mu$PCD</th>
<th>$\tau_{\text{eff}}$ (µs) Eddy current</th>
<th>$\tau_{\text{bulk}}$ (µs) PCR</th>
<th>$D_{\text{c-Si}}$ (cm$^2$/s) PCR</th>
<th>$S_1$ (cm/s) PCR</th>
<th>$S_2$ (cm/s) PCR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i$-$a$-$\text{Si:H}$/\text{n-$c$-$\text{Si}$/i-$a$-$\text{Si:H}$ (measured from side A)</td>
<td>718</td>
<td>1595.7</td>
<td>1036</td>
<td>3.1</td>
<td>1.8</td>
<td>0.5</td>
</tr>
<tr>
<td>$i$-$a$-$\text{Si:H}$/\text{n-$c$-$\text{Si}$ (measured from side A)</td>
<td>34.4</td>
<td>28.3</td>
<td>206</td>
<td>5.3</td>
<td>3.8x10$^2$</td>
<td>1.7x10$^5$</td>
</tr>
<tr>
<td>$\text{n-$c$-$\text{Si}$/i-$a$-$\text{Si:H}$ (measured from side A)</td>
<td>30.9</td>
<td>8.8</td>
<td>203</td>
<td>4.0</td>
<td>5.4x10$^6$</td>
<td>3.2x10$^2$</td>
</tr>
<tr>
<td>$\text{n-$c$-$\text{Si}$ (measured from side A)</td>
<td>8.3</td>
<td>3.8</td>
<td>19</td>
<td>7.2</td>
<td>1.7x10$^5$</td>
<td>4.0x10$^4$</td>
</tr>
<tr>
<td>$i$-$a$-$\text{Si:H}$/\text{n-$c$-$\text{Si}$/i-$a$-$\text{Si:H}$ (measured from side B)</td>
<td>660.1</td>
<td>1578.6</td>
<td>1051</td>
<td>3.2</td>
<td>1.3</td>
<td>0.4</td>
</tr>
<tr>
<td>$i$-$a$-$\text{Si:H}$/\text{n-$c$-$\text{Si}$ (measured from side B)</td>
<td>33.9</td>
<td>28.0</td>
<td>146</td>
<td>5.6</td>
<td>3.2x10$^2$</td>
<td>1.7x10$^7$</td>
</tr>
<tr>
<td>$\text{n-$c$-$\text{Si}$/i-$a$-$\text{Si:H}$ (measured from side B)</td>
<td>31.1</td>
<td>9.6</td>
<td>95</td>
<td>3.8</td>
<td>3.4x10$^6$</td>
<td>3.8x10$^2$</td>
</tr>
<tr>
<td>$\text{n-$c$-$\text{Si}$ (measured from side B)</td>
<td>8.3</td>
<td>3.6</td>
<td>21</td>
<td>7.3</td>
<td>1.7x10$^5$</td>
<td>3.8x10$^4$</td>
</tr>
</tbody>
</table>
The eddy current measurements in Table 8 are quoted at a calculated excess carrier density of $1 \times 10^{15} \text{ cm}^{-3}$. Using the PCR model and the measured data, it is possible to estimate the excess carrier density in the sample for the laser power and modulation frequencies used in the experiment. The range of excess carrier densities is estimated to be on the order of $10^{14}$ to $10^{15} \text{ cm}^{-3}$ for the unpassivated sample, $10^{15}$ to $10^{16} \text{ cm}^{-3}$ for the single side passivated samples, and on the order of $10^{17} \text{ cm}^{-3}$ for the sample passivated on both sides. The measurement setup used for the eddy current measurements was not capable of achieving an excess carrier density of $10^{17} \text{ cm}^{-3}$, however the effective lifetime of the double side passivated wafer was measured at $10^{16} \text{ cm}^{-3}$ using the eddy current method, giving $1385 \mu\text{s}$ and $1383 \mu\text{s}$ respectively when measured from side A or side B.

The PCR bulk lifetimes extracted from the model also follow the same trends as the $\mu$PCD effective lifetimes, although in the one-side passivated or unpassivated cases the PCR bulk lifetimes are higher: this difference is expected as the bulk lifetimes do not directly incorporate the effect of surface recombination. Bulk lifetimes and effective lifetimes are both, however, lower when surface recombination is higher, which is clearly reflected in the PCR results. This is because the bulk lifetime is strongly affected by free carrier concentration: as the free carrier concentration decreases, the trap state occupation likewise decreases, and at any given time there are more states available to act as recombination centres, thus unpassivated wafer surfaces, by decreasing free carrier concentration, decrease the measured bulk lifetime[75] [76]. The surface recombination velocity shows a similar link to free carrier concentration, so passivation on one side of the wafer has an effect on the surface recombination velocity seen on the other side of the wafer. For well-passivated wafers, bulk recombination dominates and so the bulk and effective lifetimes should be very similar, as is indeed the case in our experiments. Finally the diffusion coefficient also decreases with higher carrier concentration, due to free carrier scattering.
The correlation of carrier recombination and transport properties to the front and back passivation draw attention to the vital importance of good passivation on both surfaces, even when light generation occurs in a shallow region near the front of the wafer: when one or both surfaces are unpassivated, it acts as a sink for carriers, lowering the carrier concentration throughout the wafer, which in addition to directly reducing the short circuit current, also very negatively affects the recombination and transport properties. Even if one surface of the wafer is passivated, that surface still demonstrates a much higher surface recombination velocity than it would when both surfaces are passivated.

4.5.2. Excitation with 355 nm laser

The same sample, #451, that was measured with 830 nm laser excitation was also measured with 355 nm laser excitation. Additionally, samples #437, #438, and #439 were also examined. The PCR amplitude and phase data are plotted in Figure 22, Figure 23, and Figure 24. The PCR plots using the 355 nm excitation source are similar to those using the 830 nm excitation source, however certain differences appear.

![Figure 22](image-url) - PCR frequency scans in four quadrants of c-Si wafer #451 with 30 nm i-a-Si:H deposited on both sides, only front side, only back side, and without deposition. left) amplitude, right) phase [69].
The PCR amplitude data for UV excitation of sample #451, shown in Figure 22, demonstrates a different dependence on sample structure than does the analogous PCR data for IR excitation, seen in Figure 21. In the IR case, the front-side passivated structure has a lower PCR amplitude than the back-side passivated one, due to the dominance of the \(i\)-\(a\)-Si:H and interface properties in the PCR signal, specifically the low lifetime in the amorphous silicon and the carrier trapping at the interface.

In Figure 23, UV PCR results are shown for three samples with different thicknesses of \(i\)-\(a\)-Si:H layers on the front side, and no back side passivation. It is clear that the thicker the \(i\)-\(a\)-Si:H film, the more pronounced are the effects of the \(i\)-\(a\)-Si:H and interface dominance in the PCR signal. In contrast, when the excitation source is incident on the unpassivated side of the wafer, so that the carrier generation occurs in the crystalline silicon, the plots in Figure 24 do not show a phase minimum, and the 10 nm film has a lower PCR amplitude than the thicker films, suggesting a decreased passivation effectiveness, leading to a lower carrier concentration and hence a lower bulk crystalline silicon lifetime due to an increase in unfilled trap states.
The two-layer fitting results are shown in Table 9. There is not a large difference in parameters extracted for the 10 nm, 30 nm, and 90 nm $i$-layers. There is, however, a significant difference between the c-Si and surface properties extracted using UV excitation and the two-layer model compared to the results in Table 8. The bulk lifetimes extracted for #451 using UV excitation are higher by approximately a factor of 1.5-2, the diffusion constants show a greater variation between the single and double-sided sample, and the front and back surface recombination velocities for the double sided sample are higher by more than two orders of magnitude.

The large discrepancy in the surface recombination velocities between the two models can be explained by the difference between the one-layer and two-layer models. In a one-layer model, the amorphous silicon layer is modeled as being infinitely thin, and the model does not distinguish between recombination at the amorphous-crystalline interface, in the amorphous silicon, and at the amorphous silicon-air interface; all these types of recombination are combined in the term $S_i$, the front surface recombination velocity [68]. The two-layer model, in contrast, considers several locations for recombination at the front of the wafer separately [70]. Thus the term $S_i$ in the two-layer

![Figure 24 - PCR frequency scans of the same silicon wafers as in Figure 23 with the sample flipped over so that $i$-a-Si:H was on the back side. left) amplitude, right) phase [69].](image-url)
model refers to the recombination at the amorphous silicon-air interface, and should not be directly compared to $S_i$ as determined by the one-layer model. The improvement in passivation quality with the double side passivated sample can however be seen in the unfilled trap density at the interface, $n_T$, which is more than two orders of magnitude lower in the double side passivated sample than it is in the single side passivated samples.

<table>
<thead>
<tr>
<th>Fitted parameter</th>
<th>#451</th>
<th>#451</th>
<th>#437</th>
<th>#438</th>
<th>#439</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_{c-Si}$, us</td>
<td>1440</td>
<td>454</td>
<td>701</td>
<td>600</td>
<td>640</td>
</tr>
<tr>
<td>$D_{c-Si}$, cm$^2$/s</td>
<td>1.73</td>
<td>8.11</td>
<td>8.48</td>
<td>8.01</td>
<td>8.61</td>
</tr>
<tr>
<td>$S_i$, cm/s</td>
<td>$1.19 \times 10^2$</td>
<td>$2.26 \times 10^2$</td>
<td>$9.57 \times 10^2$</td>
<td>$8.16 \times 10^2$</td>
<td>$6.61 \times 10^2$</td>
</tr>
<tr>
<td>$S_{i_2}$, cm/s</td>
<td>$2.57 \times 10^1$</td>
<td>$3.03 \times 10^1$</td>
<td>$8.69 \times 10^1$</td>
<td>$3.90 \times 10^1$</td>
<td>$7.89 \times 10^1$</td>
</tr>
<tr>
<td>$S_{i_3}$, cm/s</td>
<td>$3.56 \times 10^1$</td>
<td>$1.5 \times 10^1$</td>
<td>$3.5 \times 10^4$</td>
<td>$1.62 \times 10^4$</td>
<td>$3.26 \times 10^4$</td>
</tr>
<tr>
<td>$D_{a-Si}$, cm$^2$/s</td>
<td>$1.62 \times 10^{-5}$</td>
<td>$9.02 \times 10^{-4}$</td>
<td>$7.14 \times 10^{-4}$</td>
<td>$9.59 \times 10^{-4}$</td>
<td>$3.43 \times 10^{-4}$</td>
</tr>
<tr>
<td>$\tau_{a-Si}$, ns</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>$\beta_{a-Si}$, cm$^{-1}$</td>
<td>$2.24 \times 10^6$</td>
<td>$2.48 \times 10^6$</td>
<td>$9.45 \times 10^6$</td>
<td>$3.97 \times 10^5$</td>
<td>$7.64 \times 10^6$</td>
</tr>
<tr>
<td>$n_T$, cm$^{-3}$</td>
<td>$7.58 \times 10^{11}$</td>
<td>$2.77 \times 10^{14}$</td>
<td>$3.76 \times 10^{14}$</td>
<td>$2.81 \times 10^{14}$</td>
<td>$2.91 \times 10^{14}$</td>
</tr>
</tbody>
</table>

The UV PCR results also allow us to extract parameters for $i$-a-Si:H properties. The excess carrier lifetimes extracted range from 1 to 10 nanoseconds, and the ambipolar diffusion constants range from $10^{-5}$ to $10^{-3}$ cm$^2$/s. The lifetime values are at the low end of the range reported for intrinsic amorphous silicon; electron lifetimes in bulk intrinsic amorphous silicon have been measured as low as $10^{-8}$ s and as high as $10^{-2}$ s, depending on sample properties and measurement conditions[30][41]. This is consistent with earlier findings that the method used produces $i$-a-Si:H films with a high ratio of SiH$_2$ to SiH,
which is associated with a high defect density and hence low lifetimes[14][77]. Carrier mobilities for intrinsic amorphous silicon are reported in literature as being on the order of 1 cm$^2$/Vs for electrons and on the order of $10^{-3}$ to $10^{-2}$ cm$^2$/Vs for holes[30][41], corresponding to diffusion constants in the range of $10^{-2}$ cm$^2$/s for electrons and $10^{-5}$ to $10^{-4}$ cm$^2$/s for holes, or ambipolar diffusion coefficients in the range of $10^{-5}$ to $10^{-4}$ cm$^2$/s.

It is clear that PCR measurements offer somewhat different information than photoconductivity measurements; they are able to distinguish more directly when there are changes to bulk lifetime, surface recombination velocity, and diffusion coefficient, unlike the photoconductivity measurements, which group these into an effective lifetime. This greater degree of qualitative detail may be beneficial in understanding the means by which different processes affect the cell performance, and hence may be of use in the research and development of better photovoltaic cells.

### 4.5.3. Ambipolar transport assumptions and potential sources of error

Two approximations are made in the photocarrier radiometry model that relate to ambipolar diffusion. The first is electrical neutrality, which allows us to use the ambipolar diffusion equation; the second is negligible internal electric field, which allows us to assume an electric field strength of zero, removing one term from the ambipolar transport equation. These two conditions are each expressed, in Section 4.3.1, as a ratio which should be significantly less than one. However, the measured PCR signal which was used for fitting is proportional to an integral of the carrier concentration throughout the depth of the wafer. So, a weighted-average figure of merit was defined for each ratio. These two figures of merit are calculated for each sample using MATLAB.

\[
\text{figure of merit}(f) = \frac{\int \text{Ratio}(x,f) \Delta ndx}{\int \Delta ndx}
\]

4.53
Assumptions used in the tests described here are as follows: $D^*$, $\tau_{\text{bulk}}$, and back surface recombination velocity were as reported in Table 8 in Sections 4.5.1, $\Delta n$ was calculated in all cases using the single-layer PCR model as referenced in Section 4.2.1 and using the parameters calculated in Sections 4.5.1 and the reported illumination conditions described in Section 4.4. The resistivity of the wafer was assumed to be 1 $\Omega \cdot \text{cm}$, and $\mu_n/\mu_p$, $n_0$, and $p_0$ were calculated assuming c-Si electron and hole mobilities of 1350 and 480 cm$^2$/Vs respectively [37].

The figure of merit for the electrical neutrality assumption is plotted in Figure 25 for sample #451 for the four different structures excited with 830 nm, and for one structure excited using 355 nm excitation. All of the $i$-a-Si:H layers are approximately 30 nm thick. In all cases the electrical neutrality figure of merit is below $3 \times 10^{-7}$, i.e., it is much smaller than unity, so the ambipolar transport equation can be used without any significant error. The figure of merit does rise at high frequencies, demonstrating that there is an increase in charge separation at high frequencies, however the value remains insignificant.
Figure 25 - Figure of merit for electrical neutrality approximation, for four different structures on sample #451 measured using 830 nm excitation and one measured using 355 nm excitation.

The figure of merit for the zero internal field approximation is plotted in Figure 26. At low frequencies, the figure of merit is in every case less than 0.25, with the best sample having a low-frequency figure of merit of $4 \times 10^{-4}$. The error increases significantly at high frequencies, with the figure of merit approaching unity at the high end of the measured range for some samples; this may explain the discrepancy between the measured and theoretical values at very high frequencies (above 30 kHz) in the 855 nm PCR experiment shown in Figure 21. The figure of merit is much less than one over several orders of magnitude, allowing for fitting over this range, and the parameters extracted match expected results (obtained by other measurement methods) to a good first-order approximation.
Figure 26 - Figure of merit for zero internal field approximation, for four different structures from wafer #451 measured using 830 nm excitation and one measured using 355 nm excitation.

4.5.4. Thermoelectric effect assumption and potential sources of error

In both the single layer and two layer PCR fitting models, it is assumed that there is no significant electric field due to the thermoelectric effect. In order to evaluate this assumption, the temperature gradient and hence the actual thermoelectric field will be estimated.

The silicon wafer samples used for the PCR measurements are placed on an aluminum slab, and subsequently the surface of the wafer is illuminated with a laser.
There is a delay of 5 minutes before the measurements are carried out in order to allow a steady state to be reached, and when the frequency is changed there is another 15 second delay prior to the measurements. The wafer has a diameter of approximately 4 inches or approximately 10 cm and a thickness of 280 \( \mu \)m, while the aluminum slab is approximately 5 cm by 5 cm in area and approximately 1 cm in thickness. For the IR experiment, the laser has a power of 27 mW and a spot diameter of 500 \( \mu \)m; for the UV experiment the laser power is the same but the spot diameter is 800 \( \mu \)m. The experiment was carried out at room temperature.

The temperature drop across the combined wafer-slab system in response to heating by the laser can be calculated using the following equation for heat flow, assuming that the wafer has a thermal resistance \( R_{th,wafer} \), the aluminum slab has a thermal resistance \( R_{th,slab} \), the rate of cooling of the slab to the ambient air is expressed by an equivalent resistance \( R_{air,transfer} \) and the combined system has a heat capacity \( C_{th} \). \( Q_{heat,laser} \) is the power input from the laser:

\[
Q_{heat,laser} = \frac{\Delta T_{wafer+slab}}{\left( R_{th(wafer)} + R_{th(slab)} + R_{air,transfer} \right)} + C_{th} \frac{d\Delta T_{wafer+slab}}{dt} \quad 4.54
\]

where the thermal resistance of an object is a function of its length \( l \), cross-sectional area, \( A \), and its thermal resistivity \( \rho_{th} \), a material property. The thermal resistivity of silicon used is 0.6 Kcm/W and that of aluminum is 0.4 Kcm/W [78] [79]. The expression for resistance is

\[
R_{th} = \frac{\rho_{th} l}{A} \quad 4.55
\]

while the equivalent air cooling resistance is given by
where $h_{air\text{-}cooling}$ is a parameter characterising the heat transfer between the aluminum slab and the ambient air, and is taken to be 10 K/cm²W for non-circulating air.

The heat capacity, $C_{th}$, is a measure of the system’s ability to store heat and is given by:

$$C_{th} = c_{th}(mass)$$

where $c_{th}$ is the specific heat capacity of the material, which is 0.9 J/g.K for aluminum and 0.7 J/g.K for silicon [80] [81]. In the PCR experiment the aluminum slab is so much more massive than the silicon wafer that the heat capacity of the system is almost entirely determined by that of the aluminum slab.

The temperature drop across the wafer is then defined as follows:

$$\Delta T_{\text{wafer}} = \frac{R_{th(\text{wafer})} \Delta T_{\text{wafer+slab}}}{(R_{th(\text{wafer})} + R_{th(\text{slab})} + R_{air\text{-}transfer})}$$

The electric field due to the thermoelectric effect can therefore be calculated, and the assumption that it is negligible can be tested. For the calculations, the magnitude of the Seebeck coefficient is assumed to be 1.5 mV/K [82]. The ambipolar mobility and ambipolar diffusion coefficient are assumed to be the 450 cm²/Vs and 12 cm²/s, respectively; these are the hole mobility and hole diffusion coefficient for crystalline silicon [37]. Depending on the carrier injection in a particular experiment, the ambipolar mobility may be much lower and the ambipolar diffusion coefficient may be higher, so these numbers represent a worst-case scenario. Similarly, the carrier lifetime used is the highest that was calculated from the PCR measurements, 1.3 ms.
In the case of the laser-wafer-aluminum slab system, we simplify the thermal resistance and air cooling calculations by ignoring the spreading of the heat laterally; further, in the resistance and air cooling calculations it is assumed that the heat can only travel downwards directly below the laser beam, i.e., we assume that the area $A$ is the area of the laser spot. We also neglect radiative recombination, and instead assume that the entire power of the laser is transformed into heat. Lastly, we assume that all power is absorbed at the surface of the wafer. Thus, the calculations are a conservative estimate and can be expected to lead to an overestimate of the thermoelectric effect.

The input power of the laser is modulated, however there is a DC offset as the average power is finite. The DC offset is assumed to be one half the maximum laser power.

The DC component of the temperature difference across the silicon wafer is thus estimated to be a maximum of 0.11 K for the IR experiment, which implies a maximum thermoelectric voltage of 0.17 mV, maximum electric field of 0.006 V/cm, and a maximum drift-diffusion ratio of 0.03. The equivalent estimates for the UV experiment are a maximum temperature difference of 0.05 K, maximum thermoelectric voltage of 0.07 mV, maximum electric field of 0.002 V/cm, and maximum drift-diffusion ratio of 0.01. The electric field is in the positive direction, i.e., directed downward into the sample, and will add to the tendency of the carriers to move away from the surface and into the sample.

The AC results show an extremely weak effect, with the magnitude of the thermoelectric effect decreasing rapidly at higher laser modulation frequencies, due to the damping effect of the aluminum slab, which has a significant heat capacity. At a frequency of 3 Hz, the maximum temperature difference is on the order of $10^{-7}$ K, the maximum thermoelectric voltage is on the order of $10^{-8}$ V, and the maximum drift-
diffusion ratio is on the order of $10^{-7}$. These values decrease further at higher modulation frequencies.

### 4.5.5. Additional limitations of the model

Numerical fitting of multivariable models is used to extract material parameters from the measured PCR amplitude and phase data. Hence, multiple low-error solutions may be possible, and there is a danger of finding the wrong solution. It may be possible in the future to mitigate this danger by simplifying the model and more judiciously choosing the assumptions. For example, the single layer model is very insensitive to certain parameters, such as the diffusion coefficient, and very sensitive to others, such as the lifetime. It might therefore be useful to choose a reasonable value for the diffusion coefficient based on data from literature, and treat it as a constant rather than a fitting variable. Similarly, the two-layer model is much more sensitive to the top layer parameters than to the lower layer parameters.

A second limitation of the current PCR models is that they assume that parameters such as lifetime and surface recombination velocity are independent of laser modulation frequency. In reality, excess carrier density in the sample can vary depending on laser modulation frequency, and bulk and surface recombination rates are expected to be dependent on excess carrier density. For example, at very high carrier densities, Auger recombination will increase, while at lower carrier densities, SRH recombination is expected to be more significant. Hence, the lifetime that is extracted from the data will be an average over a range of carrier densities.

Lastly, although it has to date been proposed that the lifetime determined by PCR fitting is the bulk lifetime rather than an effective lifetime as is measured by photoconductive decay methods [68] [72], this topic may need to be further investigated in the future as the values obtained here for unpassivated FZ wafers are more consistent with an effective lifetime.
5. Coplanar conductance

5.1. Current research on band bending and offsets

Although the basic shape of the amorphous silicon/crystalline silicon heterojunction band diagram is known, some details are not yet fully understood. For example, a large range of values have been suggested for the band offsets, which in turn also contributes to the persistence of competing theories about the mechanisms of carrier transport across the heterojunction.

The most commonly used model to predict the band offsets is Anderson’s rule, which predicts that the conduction band offset at a semiconductor heterojunction will be equal to the difference in electron affinities of the two semiconductors [25].

A variety of tools have been used to determine information about band offsets, including internal photoemission and capacitance spectroscopy [8] [25] [83]. A large range of values have been reported, with valence band offsets as high as 0.71 eV and as low as 0 eV measured, although values closer to 0.4 or 0.5 eV, close to the values predicted by Anderson’s rule, appear to be more common [25]. The large range of values could be due to either or both of two factors: inaccuracies in the measurement methods, and actual variability in the samples.

In this chapter lateral conductance measurements are investigated, and used to study amorphous/crystalline silicon heterojunctions deposited using DCSF PECVD in the tetrode configuration.
5.2. Heterojunction inversion layer theory

5.2.1. Heterojunction inversion layer

In a $p$-$n$ homojunction, the difference in Fermi levels in the $p$ and $n$ semiconductors normally causes a depletion of majority carriers in both materials near their interface; an inversion layer can occur only in the presence of dipoles or charges at the $p$-$n$ interface. In a heterojunction, in contrast, it is much more likely for this depletion to be accompanied by an inversion layer of minority carriers in the crystalline silicon, since the conduction or valence band discontinuity can form a barrier allowing minority carriers to collect near the interface. The degree of inversion is dependent in part on the band discontinuity in the valence band in the case of a $p$-a-Si:H/$n$-c-Si heterojunction, or in the conduction band in the case of an $n$-a-Si:H/$p$-c-Si heterojunction. A $p$-a-Si:H/$n$-c-Si heterojunction is shown in Figure 27 with two different values of the valence band offset; the larger valence band offset is clearly associated with a higher degree of inversion in the crystalline silicon near the interface. The concentration of minority carriers in this inversion layer can be determined by measuring the lateral conductivity.
Figure 27 – Typical band diagram of $p$-a-Si:H/n-c-Si heterojunction with two different conduction band offsets, simulated in AFORS-HET using Anderson’s rule. The hole inversion layer in the $n$-c-Si is highlighted: as the valence band edge approaches the Fermi level, the hole concentration increases.

The degree of inversion may be described using the excess minority carrier concentration in the crystalline silicon near the a-Si:H/c-Si interface; specifically the hole concentration $\Delta p$ in the case of a $p$-a-Si:H/n-c-Si heterojunction. A closely related term is the sheet hole density, $P_s$, which is the integral with respect to depth of the excess hole concentration, i.e.,

$$P_s = \int_{\text{interface}}^{\infty} (p(x) - p_{\text{bulk}}) dx \approx \int_{\text{interface}}^{\infty} p(x) dx$$  \hspace{1cm} 5.1
where, if there is an inversion layer, we assume that the bulk hole concentration does not make a significant contribution to the integral, and can be neglected. The sheet hole density is a useful parameter because it is directly related to the lateral conductance through the sample, which can be measured.

Lastly, since the inversion layer correlates with band bending in the crystalline silicon near the $p$-$n$ junction interface, it provides an indirect way of probing the built-in voltage of the junction; a strong inversion layer implies a high built-in voltage, which allows for a higher open circuit voltage in the device.

AFORS-HET can be used to estimate the relationship between the degree of inversion (characterised by the minority carrier concentration) and the band offsets, using a model based on Poisson’s equation. The model is described in more detail in Section 5.2.3.

5.2.2. Valence band offsets

The degree of band bending is closely related to the valence band offset, $\Delta E_v$. The valence band offset increases the total built-in potential $V_{bi}$ in the junction, which is made up of the voltage drops in the amorphous silicon and crystalline silicon, $V_{bi(a-Si:H)}$ and $V_{bi(c-Si)}$.

$$qV_{bi} = qV_{bi(a-Si:H)} + qV_{bi(c-Si)} = E_{g(c-Si)} + \Delta E_v - \delta_{c-Si} - \delta_{a-Si:H}$$

where $\delta_{c-Si}$ and $\delta_{a-Si:H}$ are the distances between the Fermi level and the conduction band in the $n$-type crystalline silicon and between the Fermi level and the valence band in the $p$-type amorphous silicon respectively. And since a hole inversion layer forms in $n$-$c$-$Si$ when the the Fermi level is closer to the valence band at the interface than it is to the conduction band in the bulk, i.e.,
$$ (E_F - E_V)_{\text{c-Si} \text{(int)}} \leq \delta_{\text{c-Si}} $$ 5.3

This is equivalent to

$$ \Delta E_V \geq \delta_{\text{a-Si:H}} \cdot \delta_{\text{c-Si}} + qV_{\text{bi(a-Si:H)}} $$ 5.4

That is, an inversion layer forms when the valence band offset is large enough, and when the amorphous silicon layer is sufficiently strongly doped. Similarly, as the interface layer goes more deeply into inversion, this implies a larger valence band offset. Hence, information about the degree of inversion can provide insight into the valence band offset.

### 5.2.3. Band bending and charge

The band bending $\varphi_{\text{c-Si}}$ in c-Si can be defined according to Equation 5.5, and can be expressed in terms of $u(x)$ (Equation 5.6), where $u(x)kT$ is the deviation of the Fermi level $E_F$ from the intrinsic Fermi level $E_i(x)$, and $u_{\text{bulk}}$ and $u_{\text{int}}$ are the values of $u(x)$ evaluated in the bulk c-Si and at the a-Si:H/c-Si interface respectively, $k$ is Boltzman’s constant, and $T$ is the temperature in kelvin.

$$ \varphi_{\text{c-Si}} = kT(u_{\text{bulk}} - u_{\text{int}}) $$ 5.5

$$ u(x) = \frac{E_F - E_i(x)}{kT} $$ 5.6
The relationships in Equation 5.6 are shown graphically in Figure 28.

![Heterojunction Energy Band Diagram](image)

**Figure 28 - A heterojunction energy band diagram, referencing Fermi level deviation $u(x)kT$**

Expressing the band bending in this way allows the relationship between the carrier concentrations $n$ and $p$, the intrinsic carrier concentration $n_i$, and the band bending to be expressed in a straightforward way, if the carrier concentrations obey the Boltzmann approximation.

$$n(x) = n_i e^{u(x)}$$  \hspace{1cm} 5.7

$$p(x) = n_i e^{-u(x)}$$  \hspace{1cm} 5.8

It is possible to calculate the degree of band bending in an a-Si:H/c-Si heterojunction, using an approach based on charge neutrality. The total charge in the structure is equal to zero

$$Q_{c-Si} + Q_{a-Si:H} + Q_{int} = 0$$  \hspace{1cm} 5.9
where \( Q_{c-Si} \), \( Q_{a-Si:H} \), and \( Q_{int} \) are the charge concentrations in the c-Si, in the a-Si:H, and at the interface respectively. If this equation can be expressed entirely in terms of \( u_{int}, u_{bulk} \) and material parameters, it will be possible to solve for \( u_{bulk} - u_{int} \) and hence for the degree of band bending.

The total charge density \( \rho_{c-Si}(x) \) at any point in the crystalline silicon is given by the sum of the free carrier concentrations \( p \) and \( n \) and the donor and acceptor ions \( N_D^+ \) and \( N_A^- \):

\[
\rho_{c-Si}(x) = q[p(x) - n(x) + N_D^+ - N_A^-]
\]

Assuming charge neutrality in the bulk \((\rho_{bulk}=0)\), assuming complete ionization of donors, and combining Equations 5.7, 5.8, and 5.10, this implies that in the bulk n-c-Si, the net negative charge concentration is given by [84]:

\[
n_{bulk} - p_{bulk} = N_D - N_A = 2n_isinh(u_{bulk})
\]

where \( n_{bulk} \) and \( p_{bulk} \) are the concentrations of electrons and holes in the crystalline silicon, far from the interface, \( n_i \) is the intrinsic carrier concentration, and \( N_D \) and \( N_A \) are the active donor and acceptor doping concentrations.

But \( u(x) \) is linearly related to the electrostatic potential, \( V \):

\[
 u(x) = C + \frac{qV(x)}{kT}
\]

where \( C \) is a unitless constant.

Poisson’s equation \( \frac{d^2V(x)}{dx^2} = -\frac{\rho_{c-Si}(x)}{\varepsilon} \) can hence be expressed using \( u(x) \) and hyperbolic trigonometric functions [84]:
\[
\frac{d^2 u(x)}{dx^2} = \frac{2q^2 n_i}{\varepsilon kT} (\sinh(u(x)) - \sinh(u_{\text{bulk}}))
\]

where \(\varepsilon\) is the dielectric constant of the material.

By integrating this equation it is possible to solve for \(u(x)\) and hence for the electric field in the crystalline silicon, using the relationship between \(u(x)\) and \(V(x)\) in Equation 5.12. Gauss’ law can then be used to find the total space charge \(Q_{c-Si}\) in the crystalline silicon, by considering a Gaussian cylinder with one face deep in the bulk (where the electric field is zero) and the other face at the edge of the a-Si:H/c-Si interface, just within the crystalline silicon (where the electric field will be normal to the interface and to the face of the Gaussian cylinder). This derivation can be found in Frankl [84]; only the result is shown here:

\[
|Q_{c-Si}| = 2 \sqrt{\frac{n_i \varepsilon kT}{q}} \sqrt{\cosh(u_{\text{int}}) - \cosh(u_{\text{bulk}}) - (u_{\text{int}} - u_{\text{bulk}}) \sinh(u_{\text{bulk}})}
\]

where \(Q_{c-Si}\) is positive if \(u_{\text{int}} > u_{\text{bulk}}\) and negative if \(u_{\text{int}} < u_{\text{bulk}}\).

The above derivation assumes that the carrier distribution can be modeled classically (i.e., without quantum confinement). However, in a \(p\)-a-Si:H/\(n\)-c-Si heterojunction with strong band bending near the interface, a more accurate model can be derived by considering the effect of quantum confinement of minority carriers in a triangular potential well formed in the c-Si inversion layer. In this case, \(Q_{c-Si}\) is a function of both the a-Si:H and c-Si properties rather than only the c-Si properties as it is in the classical case. However, \(Q_{c-Si}\) can still be written in terms of \(u_{\text{int}}\) and \(u_{\text{bulk}}\) [45].
In order to determine the charge in the amorphous silicon, it is necessary to consider the trapped charge in the defects; because of the high defect density in amorphous silicon, this charge is very significant and may in fact be the dominant charge contribution in the amorphous silicon [85]. The trapped charge density \( \rho(x)_{aSi:H} \) is given by

\[
\rho_{aSi:H}(x) = -q \int_{E_F(aSi:H)}^{E_c(aSi:H)} N_E(E_F)[f(E, E_F(x))] \left[ f(E, E_F(-\infty)) \right] dE
\]

where \( f(E, E_F(x)) \) is the Fermi-Dirac function at the energy level \( E \) in the a-Si:H, which gives the probability that a trap state at energy \( E \) is occupied, and \( N_E(E_F) \) is the density of states in the amorphous silicon, which is modeled by using the density of states at the Fermi level and assuming that the density of states is constant throughout the band gap [45].

Equation 5.15 can be further simplified if the Fermi-Dirac function is approximated as a step function. The amorphous silicon charge density \( \rho_{aSi:H} \) is then integrated over the a-Si:H thickness \( d_{aSi:H} \) to eventually obtain the total charge \( Q_{aSi:H} \) in the amorphous silicon [45].
where $L_{D(a-Si:H)}$ is the debye length in amorphous silicon:

$$L_{D(a-Si:H)} = \sqrt{\frac{\varepsilon}{q^2 N(E_F)}}$$

The last significant charge concentration is due to the distribution of dangling bonds, $N_{DB}(E)$, in the interface.

$$Q_{int} = \int_{E_v(a-Si)}^{E_c(a-Si)} N_{DB}(E) [f_0^+(E, E_F) - f_0^-(E, E_F)] dE$$

where $f_0^+$ and $f_0^-$ are the occupation functions for positive and negative defects [86].

$$f_0^+(E, E_F) = \frac{1}{1 + 2 e^{\frac{(E_F - E_{corr} + u_{int})}{kT}} + e^{\frac{(2(E_F - E_{corr} + u_{int})}{kT}}}$$
\[ f_0(E, E_F) = e^{\frac{2(E_F - E - E_{corr}) + u_{int}}{kT}} f_0^+(E, E_F) \]  

5.20

where \( E_{corr} \) is the correlation energy between the positive and negative defects, and \( E_F \) is the Fermi energy, which can be expressed with respect to the c-Si valence band \( E_{v_{c-Si}}(0^+) \).

\[ E_F - E_{v_{c-Si}}(0^+) = E_{g}^{c-Si} - \varphi_{c-Si} - \delta_{c-Si} \]
\[ = E_{g}^{c-Si} - kT(u_{bulk} - u_{int}) - \delta_{c-Si} \]  

5.21

The total charge in the amorphous silicon layer, in the crystalline silicon, and in the interface should sum to zero. So, Equations 5.9, 5.14, 5.16, and 5.18 can be combined and solved numerically to determine the degree of band bending in a particular heterojunction structure.

### 5.2.4. Temperature dependence of sheet hole density

Once the relationships between band bending, sheet hole density, and other heterojunction properties are known, it is useful to look more closely at the temperature dependence of the sheet hole density; the function \( P_s(T) \) will be dependent on a number of parameters, with band bending having a strong effect. If the sheet hole density can be measured at different temperatures, the function \( P_s(T) \) can be plotted and its shape used to infer information about the band offsets and other properties of the junction. The sheet hole density can also be expressed in terms of \( u \),
While the band-bending itself is explicitly temperature dependent, the function also makes use of material parameters which are temperature dependent, namely the effective density of states in the valence and conduction bands of the crystalline silicon (and hence $n_i$), and the crystalline and amorphous silicon bandgaps.

$P_s(T)$ can be solved numerically and fitted over a given temperature range to an Arrhenius equation with activation energy $E_a$.

$$P_s(T) = Ae^{-\frac{E_a}{kT}}$$

where $A$ is a constant. A characteristic of Arrhenius equations is that their natural logarithm has a linear form with respect to $1/T$. Hence, by plotting $P_s$ on a graph whose x-axis is $1/T$ and whose y-axis uses a logarithmic scale, as in Figure 29, the activation energy $E_a$ can be easily extracted from the slope of the graph.

$$\ln(P_s(T)) = \ln A - \frac{E_a}{kT}$$

Varache has demonstrated that the sheet hole densities of a-Si:H/c-Si heterojunctions fit most closely to a model that assumes that the valence band gap is independent of temperature, while changes in the semiconductor bandgaps are reflected in the conduction band gaps [45]. Varache modeled the effect on the Arrhenius plot when three
specific parameters are varied: the density of defect states in the amorphous silicon, the built-in voltage, and the interface dangling bond density, all shown in Figure 29 [87].

Figure 29 - Temperature dependence of sheet hole density: (a) varying $p$-a-Si:H density of states, where the density of states is modeled as a constant equal to $N(E_F)$; (b) varying built-in-voltage; (c) varying interface dangling bond density [87].
Changing the density of defect states in the amorphous silicon (while holding the other parameters constant) primarily has the effect of changing the sheet hole density, without significantly affecting its temperature dependence. It is also interesting to note that a higher density of defect states in the amorphous silicon leads to a higher sheet hole density, if all other parameters are held constant.[45].

Increasing the interface dangling bond density slightly increases the activation energy of the sheet hole density. Thus, processes that reduce interface states may be expected to decrease the activation energy of the lateral conductance. The built in voltage has a particularly large effect on the slope of the graphs, which suggests that the measurement of sheet hole density may be useful to provide insight into the built-in-voltage (and by inference the open circuit voltage), as a small activation energy is strongly correlated with a higher built-in voltage.

The effect of band offsets is simulated in Figure 30, in which the sheet hole density of a $p$-a-Si:H/$n$-c-Si heterojunction is plotted, demonstrating that a larger valence band offset results in a smaller activation energy.
5.3. Experiment

5.3.1. Overview of experiment

Two types of samples are made by depositing rectangular coplanar metal contacts on top of a) heterojunction structures or b) amorphous silicon layers on an insulating glass substrate. Both samples are illustrated in Figure 31. Since the width $h$ of the contacts is very large in comparison to the distance $L$ between the contacts (greater than 10 times as large), edge effects are negligible. The contacts are made of silver, with a thin chromium layer for adhesion to the amorphous silicon, and the electrical probe wires are connected to the silver contacts with silver paste. In this way the contact resistances are minimized; the low contact resistance was confirmed using contacts deposited in a transmission line pattern. The samples were placed in a cryostat and voltages were applied across the contacts at different temperatures, with current measured and recorded at each temperature.

Figure 30 - Simulated Arrhenius plot of sheet hole density of a $p$-a-Si:H/$n$-c-Si heterojunction with varying amorphous silicon electron affinity. Higher a-Si:H electron affinities correspond to larger valence band offsets and to smaller sheet hole density activation energy.
In a heterojunction structure three transport paths could potentially contribute to the measured lateral planar conductance: current could be carried in the top a-Si:H layer; across the interfaces and in the c-Si; and finally in a strongly inverted c-Si surface layer that is created due to the differences in doping and the particular band alignment of the two semiconductors, which lead to a build-up of mobile holes near the crystalline silicon surface. The analogous electron inversion layer has been measured on n-a-Si:H/p-c-Si substrates by scanning capacitance measurements and by planar conductance measurements [29][88]. The first two paths provide only a negligible contribution in the p-a-Si:H/n-c-Si heterostructure since a-Si:H is weakly conductive and one reverse diode is blocking the current traversing through the Si substrate. This has been shown by Kleider et al., by comparing coplanar measurements made using three types of samples[88]:

a) heterojunction sample, i.e., p-a-Si:H on n-c-Si
b) amorphous silicon layer on glass, i.e., p-a-Si:H on glass
c) etched heterojunction sample, i.e., sample a with p-a-Si:H etched away between the metal contacts using SF₆O₂. This removes the p-a-Si:H and inversion layer conduction
paths, while retaining the n-c-Si path, including the contact resistances and diode structures directly under the contacts.

Kleider demonstrated that the heterojunction sample, structure a, had a coplanar conductivity several orders of magnitude higher than either the etched heterojunction, structure c, or amorphous silicon layer on glass, structure b, and a much lower activation energy, indicating a different conduction mechanism[88]. Hence, the high conductivity of the heterojunction sample cannot be explained by the simple parallel addition of the conductances of the amorphous silicon and crystalline silicon layers, but must be attributed to a third conduction path, through the hole inversion layer.

Hence, by measuring coplanar conductance in samples of the structure a, it is possible to measure the conductance of the hole inversion layer, and from this determine the concentration of holes and the strength of the inversion layer. The temperature dependence of the planar conductance is of particular interest, as it can be used to calculate the activation energy of the conductance, and this activation energy relates closely to the valence band offset.

Additional information can be extracted by depositing a layer of amorphous silicon followed by coplanar contacts on an insulating substrate such as glass (structure b): the activation energy of the coplanar conductance then provides insight into the position of the Fermi level, and thus tracks the effect of doping.

5.3.2. Lifetime measurements

Because surface passivation has such a significant effect on cell performance, and since one of the major goals of using amorphous silicon layers is to improve passivation of the wafer surface, passivation quality is an important metric to compare the quality of different cell structures and amorphous silicon recipes. For this reason, all of the samples
that were used in the coplanar conductance measurements were first characterised to determine their effective excess minority carrier lifetime.

Minority carrier lifetime was measured to assess the quality of passivation using several tools such as the Sinton WCT120 eddy-current transient photoconductive decay, microwave photoconductive decay (µ-PCD), and modulated photoluminescence (MPL). The measurements were carried out on all the heterojunction samples, and are summarized in Table 10. Photoluminescence measurements yield lower lifetime values than those obtained from the photoconductive decay measurements due to the small-signal analysis but have the advantage that they can be performed in between the electrodes[89]. We find that the trends between the techniques are the same, and that higher gas dopant concentration decreases lifetime, likely due to an increase in defect density in the amorphous layer resulting in more recombination states at the interface. Additional discrepancies between the three methods are caused by differences in carrier concentration and absorption depth during measurement, as the eddy current measurement uses a white light, while the µ-PCD and MPL each use higher intensity monochromatic light in the form of lasers. Adding an intrinsic layer increases lifetime owing to improved interfacial passivation. The µ-PCD measurement and the first eddy current measurement, carried out in Toronto and shown in Table 10, were carried out on the entire wafer prior to the deposition of the electrical contacts; the eddy current measurements were repeated post E-beam evaporation at LGEP on smaller cut samples, and were observed to be within 5-15% of the original values.
Table 10 – Minority carrier lifetime measurements. Eddy current measurements were done first at the University of Toronto, and then repeated at LGEP after the wafers were cleaved in half and shipped.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\text{B}_2\text{H}_6$ conc. (%)</th>
<th>$\mu\text{PCD } \tau_{\text{eff}}$ (μs)</th>
<th>Eddy current $\tau_{\text{eff}}$ (μs) (Toronto/LGEP)</th>
<th>MPL $\tau$ (μs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC4</td>
<td>0.5</td>
<td>263</td>
<td>269/287</td>
<td>122</td>
</tr>
<tr>
<td>HC5</td>
<td>1</td>
<td>147</td>
<td>167/136</td>
<td>79</td>
</tr>
<tr>
<td>HC1</td>
<td>0.75</td>
<td>189</td>
<td>217/149</td>
<td>79</td>
</tr>
<tr>
<td>HC8 (4 nm i)</td>
<td>0.75</td>
<td>370</td>
<td>509/485</td>
<td>147</td>
</tr>
<tr>
<td>HC9 (10 nm i)</td>
<td>0.75</td>
<td>456</td>
<td>523/466</td>
<td>265</td>
</tr>
</tbody>
</table>

5.3.3. Planar conductance measurements

Planar conductance measurements were carried out on the $p$-doped amorphous layers deposited on glass and on crystalline silicon. The conductance value $G_{\text{cond}}$ actually depends on the geometry of the electrodes (length, $h$, and interelectrode distance, $L$). In order to remove this dependence and to provide data that can be easily compared with data from the literature or obtained with another electrode configuration, we calculate the sheet conductance $G_s$:

$$G_s = G_{\text{cond}} \times \left(\frac{h}{L}\right)$$ \hspace{1cm} (5.25)

which is independent of the electrode geometry. The samples deposited on glass are presumed to be uniform in thickness, and the conductivity of the a-Si:H layer, $\sigma_{\text{a-Si:H}}$, can
be deduced from the sheet conductance by dividing it by the layer thickness, \( d_{a-Si:H} \), i.e., \( \sigma = G_s / d_{a-Si:H} \). For the samples deposited on c-Si, where the conductance is attributed to a hole surface channel in c-Si, the sheet conductance can be expressed as:

\[
G_s = q \mu_p P_s
\]

where \( q \) is the positive unit charge, \( \mu_p \) the hole mobility in the channel, and \( P_s \) the sheet hole concentration defined as the integral of hole concentration in c-Si:

\[
P_s = \int_0^{d_{c-Si}} p(x) dx
\]

The contribution is essentially from the strongly inverted surface layer, since holes are minority carriers in the bulk of the \( n \)-type c-Si wafer. For the samples on c-Si, the sheet conductance can be viewed as a surface conductance and is thus an intrinsic characteristic of the surface conduction channel.

### 5.4. Results and discussion

The samples were first heated from 300 K to 430 K then cooled down to 140 K, with conductance measurements taken at 10 K intervals during heating and cooling. The temperature dependence of the sheet conductance is shown in Figure 32. The samples were then further heated to 460 K and showed a further increase in conductance, as seen for the glass samples in Figure 33. The conductivities and activation energies are summarized in Table 11. For samples on c-Si, the activation energy was calculated in the range of 200-300 K; for samples on glass, it was calculated in the range of 300-400 K. Heating of the samples was up to 430 K. For all samples except HC2, thickness of p-a-Si:H layer was 20 nm. For p-a-Si:H layers deposited on glass, activation energies (i.e.,
The position of the Fermi level with respect to the valence band) were approximately 0.3 eV, which is promising for device applications as the proximity of the Fermi level to the valence band implies effective p-type doping. We can see from the glass samples that as gas doping concentration increases, conductivity increases. This is likely caused by pushing the Fermi level towards the valence band, i.e., increasing the free carrier concentration. We can also see that annealing decreases the activation energy, which would be consistent with a reduction in interface defects (in the case of heterojunction samples) or an increase in effective doping.

Table 11 - Dark conductivity, sheet conductance and activation energy. Heating is at 430 K.

<table>
<thead>
<tr>
<th>sample</th>
<th>B$_2$H$_6$ conc. (%)</th>
<th>substrate</th>
<th>$G_0$(S) [300 K] before heating</th>
<th>$\sigma$(S cm$^{-1}$) [300 K] before heating</th>
<th>$G_0$(S) [300 K] after heating</th>
<th>$\sigma$(S cm$^{-1}$) [300 K] after heating</th>
<th>$E_a$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC2</td>
<td>0.75</td>
<td>glass</td>
<td>1.97x10$^{-7}$</td>
<td>1.23x10$^{-2}$</td>
<td>2.90x10$^{-7}$</td>
<td>1.81x10$^{-2}$</td>
<td>0.354</td>
</tr>
<tr>
<td></td>
<td>160 nm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HC3</td>
<td>0.5</td>
<td>glass</td>
<td>1.06x10$^{-10}$</td>
<td>5.3x10$^{-5}$</td>
<td>5.48x10$^{-9}$</td>
<td>2.74x10$^{-3}$</td>
<td>0.346</td>
</tr>
<tr>
<td>HC7</td>
<td>0.75</td>
<td>glass</td>
<td>3.36x10$^{-10}$</td>
<td>1.68x10$^{-4}$</td>
<td>1.21x10$^{-8}$</td>
<td>6.05x10$^{-3}$</td>
<td>0.343</td>
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<tr>
<td>HC6</td>
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<td>glass</td>
<td>8.35x10$^{-10}$</td>
<td>4.18x10$^{-4}$</td>
<td>4.43x10$^{-8}$</td>
<td>2.22x10$^{-2}$</td>
<td>0.305</td>
</tr>
<tr>
<td>HC4</td>
<td>0.5</td>
<td>n-c-Si</td>
<td>2.40x10$^{-3}$</td>
<td></td>
<td>3.67x10$^{-3}$</td>
<td></td>
<td>0.0142</td>
</tr>
<tr>
<td>HC1</td>
<td>0.75</td>
<td>n-c-Si</td>
<td>6.31x10$^{-3}$</td>
<td></td>
<td>9.15x10$^{-3}$</td>
<td></td>
<td>0.0197</td>
</tr>
<tr>
<td>HC5</td>
<td>1</td>
<td>n-c-Si</td>
<td>5.00x10$^{-3}$</td>
<td></td>
<td>6.23x10$^{-3}$</td>
<td></td>
<td>0.0099</td>
</tr>
<tr>
<td>HC8</td>
<td>0.75</td>
<td>n-c-Si /i-a-Si</td>
<td>3.55x10$^{-3}$</td>
<td></td>
<td>3.81x10$^{-3}$</td>
<td></td>
<td>0.0121</td>
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<tr>
<td>(4 min i)</td>
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</tr>
<tr>
<td>HC9</td>
<td>0.75</td>
<td>n-c-Si /i-a-Si</td>
<td>7.06x10$^{-4}$</td>
<td></td>
<td>7.36x10$^{-4}$</td>
<td></td>
<td>0.153</td>
</tr>
<tr>
<td>(10 min i)</td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 32 - Temperature dependence of sheet conductance of $p$-a-Si:H on glass vs on $n$-c-Si.
Figure 33 - Activation energy and absolute conductivity values at 300 K of p-doped a-Si:H layers deposited on glass with varying gas doping concentration as defined by the diborane in silane precursor gas fraction. Activation energy and conductivity values are shown for the samples after annealing at 430 K (below the original deposition temperature) and after annealing at 460 K (above the original deposition temperature).

Figure 34 shows the conductance versus the inverse of the temperature of several samples on glass and on crystalline silicon, where the gas doping concentration is held constant for all samples. The surface conductances for the films grown on crystalline silicon substrates correspond to increasing i-layer thickness (0, 4, and 10 minutes of deposition at a nominal deposition rate of 1 nm/min). As expected from studies on RF PECVD a-Si:H films, the samples on crystalline silicon have a much higher conductance and a weaker temperature dependence, i.e. a lower activation energy (see Table 11), which suggests the presence of a strong inverted layer at the interface [45][88]. We also see that for the same doping concentration on glass, increased film thickness results in higher conductance with no significant change in activation energy.
Figure 34 - Sheet conductance versus the inverse of temperature showing a comparison of (above) three different thicknesses of the intrinsic layer on crystalline silicon, with a constant doped amorphous layer of 20 nm thickness, and (below) two different thicknesses of the doped layer on glass with no intrinsic layer in these samples. The thicknesses for the samples with intrinsic layers are determined using a nominal deposition rate of 1 nm/min.

From Table 11, we note that for samples on glass, conductance also increases with gas dopant concentration. From analytical calculations performed on n-a-Si:H/p-c-Si and p-a-Si:H/n-c-Si heterojunctions, it has been shown that, for negligible interface states density, either a shift of the a-Si:H Fermi level position towards the nearest band or an increase of the a-Si:H density of states at the Fermi level results in an increased planar conductance[87]. However the samples on crystalline silicon do not follow the expected trend as doping concentration increases; instead the intermediate doped sample shows a higher conductance than the highest doped sample. A possible explanation is that as doping increases, the increased defect density at the heterojunction interface traps more
charge, causing changes to the band bending at the interface which counteract the effect of increased doping. After annealing at 430 K, the conductive properties improved slightly even though the heating temperature did not exceed the deposition temperature. This may be caused by changes to the film due to annealing even at the relatively low temperature. Another possible cause of this change is the removal of water adsorbed on the surface of the samples, which could slightly influence the a-Si:H/c-Si interface due to the very small thickness of the emitter. The effect is far less pronounced in the thicker film, which would be expected if it is caused by water adsorption, as surface effects are less significant for a thicker film.

From Table 10 (sample numbers HC1, 8, 9) one can see that the insertion of an intrinsic layer between the emitter and the absorber increases the effective lifetime, indicating that the interface is better passivated. However, it is observed that while the activation energy increases with increasing thickness of the passivation layer, the surface conductance at 300 K decreases. This can be understood as a consequence of the potential drop through the $i$-a-Si:H layer. In Figure 35 we performed simulations with varying $i$-a-Si:H layer thickness. The total potential drop over the junction is the same since the $p$-a-Si:H work function has not changed. However, the part of this potential drop that occurs in a-Si:H increases with the $i$-a-Si:H layer thickness, and the band bending in the crystalline part of the junction is thus reduced. The theoretical reduction in potential in the c-Si layer is 15 mV and 32 mV for 4 nm and 10 nm $i$- layers, respectively, leading to a weaker inversion layer and to a potentially weaker open circuit voltage. However, the experimental data show a smaller effect on the conductance than predicted by the AFORS-HET simulations; this could be ascribed to increasing interface charge also playing a bigger role in the case of unpassivated layers. This suggests that an optimal intrinsic layer thickness must be found: a good passivation without excessive lowering of the band bending in c-Si should provide the best open circuit voltage. This is in agreement with Fujiwara and Kondo who have reported on the strong effect of i-layer
thickness and the existence of an optimum thickness, and adds evidence to their claim that increasing the i-layer thickness causes a reduction of the electric field in the c-Si wafer [90]. Overall, the magnitude and activation energies measured here for the p-a-Si:H/n-c-Si interfaces obtained from a-Si:H layers deposited using the DCSF technique are comparable to those measured on interfaces obtained by Kleider et al. using the conventional RF PECVD technique[91]. This would imply that the values of the band offsets are also similar, giving a valence band offset near 0.4 eV, close to that predicted by Anderson’s rule.

![Figure 35 - Change in built-in voltage across p-a-Si:H/i-a-Si:H/n-c-Si heterojunction as i-layer is varied in thickness, modelled in AFORS-HET. Interface defect density is not included in this band model [92].](image)

Figure 35 - Change in built-in voltage across p-a-Si:H/i-a-Si:H/n-c-Si heterojunction as i-layer is varied in thickness, modelled in AFORS-HET. Interface defect density is not included in this band model [92].
6. Indium tin oxide in a $p$-$a$-Si:H/$n$-c-Si heterojunction photovoltaic cell

6.1. Transparent conducting oxides

The amorphous silicon-crystalline silicon heterojunction photovoltaic cell uses a transparent conducting oxide layer to create a front electrical contact; this oxide layer forms a heterojunction with the amorphous silicon layer of the cell. In this chapter the transparent conducting oxide layer is studied, with a focus on its incorporation into the photovoltaic cell.

Known transparent conducting oxides (TCOs) are mainly $n$-type. Building blocks include binary oxide compounds $\text{In}_2\text{O}_3$, $\text{SnO}_2$, $\text{ZnO}$, $\text{CdO}$, $\text{Ga}_2\text{O}_3$, and $\text{MgO}$ (the most commonly used being the first three), along with ternary compounds of the same elements, and multicomponent combinations of the binary or ternary compounds[93]. Additional common dopants include $\text{Al}$ and $\text{F}$.

Indium tin oxide (ITO) is the most widely used TCO, consisting of indium oxide ($\text{In}_2\text{O}_3$) combined with a smaller amount (commonly 10%) of tin oxide ($\text{SnO}_2$). ITO is popular because of its high performance, particularly its high electrical conductivity[93][94]. It acts as a degenerately doped $n$-type semiconductor, which we define as a semiconductor that has a Fermi level either inside the conduction band or within a few $kT$ of the conduction band edge; the free electrons are thus degenerate and exhibit metallic behaviour. Both the tin itself and oxygen vacancies can act as $n$-type dopants[95][96]. However, other TCOs may have other advantages for use in amorphous silicon-crystalline silicon heterojunctions, such as higher work function, larger optical band gap, or low deposition temperature[97].

The TCO can also have an effect on band bending in the heterojunction structure [22][27][28]. The key TCO property in this case is work function, which for ITO has been measured by various researchers to be between 4.3 eV and 5.1 eV [27]. Unlike
other properties like resistivity or optical properties, the desired TCO work function depends strongly on whether the heterojunction silicon is an amorphous $p$ on crystalline $n$ structure or an $n$ on $p$ structure; for a $p$ on $n$ structure, a high TCO work function is required, and for an $n$ on $p$ structure, a low TCO work function is required. For a $p$-a-Si:H/$n$-c-Si heterojunction, the work function of the TCO should ideally be higher than that of the $p$-doped amorphous silicon layer, and the top metal contact should have the highest work function. Models have predicted a strong effect of work function on open circuit voltage, fill factor and device efficiency, and an unsuitable work function is expected to decrease performance or even prevent cell operation [27] [28].

In this study, ITO was used, due to its potential for high transparency and conductivity. A series of samples were made with ITO layers deposited on glass, on crystalline silicon, and on $p$-a-Si:H/$n$-c-Si heterojunctions. Deposition and post-processing conditions were varied and changes in the electrical, optical, and structural properties of the ITO were measured. The question of how the ITO deposition process may influence the underlying layers of amorphous and crystalline silicon was addressed. Finally, complete cells were made incorporating the films.

6.2. **Transparent conducting oxide physical theory**

Transparent conducting oxides are very wide bandgap semiconductors. With an optical bandgap in the ultraviolet, they have low absorption at visible wavelengths, however when degenerately doped, they can be electrically conducting while still retaining their transparency to visible wavelengths [95]. Reflection will increase at frequencies below the plasma frequency.

Indium tin oxide is a combination of indium oxide and tin oxide, each of which is a transparent conducting oxide; when combined their electrical and optical properties can be further improved compared to either alone. Indium oxide has a complex cubic bixbyite crystal structure, with a unit cell containing 80 atoms. The structure consists of
a face-centered cubic $\text{In}^{3+}$ array, with 75% of the tetrahedral interstices replaced by $\text{O}^{2-}$ [98]. Indium oxide is often slightly reduced when it is prepared, such that it is really $\text{In}_2\text{O}_{3-x}$. The conductivity of indium oxide comes from this oxygen depletion, as a missing $\text{O}^{2-}$ ion can act as a shallow donor dopant contributing two free electrons. If there are sufficient oxygen vacancies, i.e., if $x$ is sufficiently large, then an oxygen vacancy impurity band forms at the inner edge of the bandgap, possibly overlapping with the conduction band, and a degenerate free-electron gas is formed [95]. As it retains its bandgap of approximately 3.75 eV, it will not absorb photons in the visible range. The next higher level state above the impurity band is also spaced such as to prevent visible wavelength photons from exciting carriers in the impurity band to higher states [98]. There is additionally some degree of $\text{O}^{2-}$ ion movement from vacancy to vacancy, acting as a $p$-type dopant, however this effect is insignificant compared to the $n$-type conduction [98]. A band diagram of indium tin oxide is shown in Figure 36.

In indium tin oxide, some percentage of the In atoms are replaced by Sn atoms, which changes the nature of the doping, as the tin acts as a substitutional donor providing one electron. However, the two types of $n$-type dopants, namely oxygen vacancies and tin atoms, coexist and create a combined impurity band. In the simplest case the chemical formula becomes $\text{In}_{2-x}\text{Sn}_x\text{O}_{3-2x}$, and the electron concentration is proportional to $n=x+y$ [98]. It is however possible for more complex interactions to take place, such as the creation of an $\text{Sn}_3\text{O}_4$ phase, which is undesirable and causes darkening of the film.
Figure 36 - A simplified band diagram of indium tin oxide for small x (a) and large x (b). Here, the outermost part of the valence band is formed by the oxygen atoms, while the conduction band is formed by the indium 5s shell. Donor doping is provided by both tin ions and by oxygen vacancies: tin ions donate one carrier each while oxygen vacancies donate two[98].

6.3. Optical and electrical properties of indium tin oxide

The properties of indium tin oxide are highly variable. Oxygen incorporation, tin doping, defects, and crystal structure all play a role in the optical and electrical properties. This is especially true of films deposited and processed at lower temperatures as they are likely to have a more amorphous nature and a higher defect density, and a higher risk of different phases developing within the material. The multiple goals can also create a trade-off, as the electrical and optical requirements of a transparent conductor are to some extent contradictory: a very metallic material will conduct better, but the free electrons will also lead to increased optical absorption. The nature of the trade-off can be better understood (and minimized) by considering the equations that describe the conductivity and absorption.
The conductivity of indium tin oxide relates simply to its free carrier concentration and carrier mobility. Given that the free carriers in this case are electrons, the conductivity $\sigma_{\text{ITO}}$ is described by Equation 6.1.

$$\sigma_{\text{ITO}} = qn\mu_n \tag{6.1}$$

That is to say, it increases with rising electron density $n$ and electron mobility $\mu_n$.

The optical behaviour is more complex and varies depending on the ranges of several material properties as well as on the wavelengths in question. However, in the case of a degenerately doped material, the free electrons can be modeled as an electron gas, and the conductivity in response to a time-dependent electric field (such as an electromagnetic wave) can be described using the Drude model [95]. Two parameters can thus be determined which are useful in describing the transparency of a film, namely the plasma frequency and the skin depth.

The frequency-dependent relative dielectric function $\varepsilon_r(\omega)$ is given by:

$$\varepsilon_r(\omega) = \varepsilon_1(\omega) - j\varepsilon_2(\omega) \tag{6.2}$$

where $\varepsilon_1$ and $\varepsilon_2$ are the real and imaginary parts of the relative dielectric function [95]:

$$\varepsilon_1(\omega) = \varepsilon_\infty - \frac{nq^2\tau_n^2}{\varepsilon_0 m_n^* (1 + \omega^2\tau_n^2)} \quad \varepsilon_2(\omega) = \frac{1}{\varepsilon_0 m_n^* \omega} \frac{nq^2\tau_n^2}{1 + \omega^2\tau_n^2} \tag{6.3}$$

where $\varepsilon_\infty$ is the high frequency relative permittivity of the ITO, $\varepsilon_0$ is the dielectric permittivity in vacuum, $m_n^*$ is the effective electron mass in the ITO, and $\tau_n$ is the bulk electron lifetime in the ITO.
The plasma frequency $\omega_p$ is the frequency when the relative dielectric constant $\varepsilon(\omega)$ becomes fully imaginary, i.e., when $\varepsilon_i(\omega) = 0$; below this frequency the material becomes highly reflective. It therefore represents an upper bound on the wavelength of light that can be transmitted through the film, and in photovoltaic applications it should ideally be such as to allow the transmittance of the entire visible light spectrum up to the cutoff wavelength of the photovoltaic absorbing layer. The plasma frequency occurs at: 

$$\omega_p = \sqrt{\frac{nq^2}{\varepsilon_\infty \varepsilon_0 m_n^*} - \frac{1}{\tau_n^2}}$$

The plasma frequency increases with increasing $n$, and for sufficiently high values of $\tau_n$ and $n$, such as those in highly conductive films, the plasma frequency is mainly controlled by $n$.

A second optical metric that may be useful to consider is the optical skin depth. This describes how rapidly light traveling through a film is reduced in intensity both by reflection and by absorption, and is thus a measure of the transmittance of the material. The skin depth $\delta_{\text{skin}}$ at a given wavelength is defined as the depth at which the intensity of the incident radiation $I(0)$ is reduced by a factor of $e$ compared to the incident intensity. That is,

$$\frac{I(\delta_{\text{skin}})}{I(0)} = e^{-1}$$

For high transparency, a large skin depth is required at the relevant wavelengths. It can be shown that the skin depth for a free electron gas following the Drude model is given by
\[
\delta_{\text{skin}} = \frac{c}{\omega} \left( \frac{2}{\sqrt{\varepsilon_1^2 + \varepsilon_2^2 - \varepsilon_1}} \right)^{1/2}
\]

where \( c \) is the speed of light in vacuum [95].

This equation can be simplified in different ways depending on the wavelength range and properties of the oxide film. In particular, for frequencies above the plasma frequency (i.e., in the visible range) and for mobilities and carrier densities that are reasonable in practical indium tin oxide films, that is [95].

\[
\omega_p < \omega < \frac{E_g}{\hbar}, \omega \tau_n \gg 1, \varepsilon_2 \approx \frac{nq^2}{\varepsilon_0 m^* \omega^2 \tau_n} \ll \varepsilon_1
\]

then the skin depth becomes [95]

\[
\delta_{\text{skin}} \approx \frac{2m^* \sqrt{\varepsilon_\infty}}{377q^2} \frac{\omega^2 \tau_n}{n}
\]

Since lifetime is proportional to mobility, the general trend for skin depth is given by Equation 6.9:

\[
\delta_{\text{skin}} \propto \frac{\omega^2 \mu_n}{n}
\]

So, skin depth increases with higher mobility and decreases with higher carrier density.

In summary, the electrical conductivity is proportional to both carrier density and mobility, and optical characteristics are generally improved by increasing mobility, however high carrier densities can increase the plasma frequency (risking reflectance in the near infrared) and decrease the skin depth in the visible range.
6.4. **Work function**

Since the transparent conducting oxide forms an electrical contact with the amorphous silicon, its work function is very important. For example, in the case of a $p$-a-$\text{Si}:\text{H}/n$-$\text{c}$-$\text{Si}$ cell, if the work function is too small, a rectifying contact will be formed which functions as a barrier against carrier transport, reducing the maximum $V_{oc}$ of the cell [27] [28].

More generally, it is relevant to note that ITO is a strongly doped $n$-type semiconductor. Hence, in the case of a $p$-a-$\text{Si}:\text{H}/n$-$\text{c}$-$\text{Si}$ photovoltaic cell, the structure is more accurately an $n+/p/n$ structure, which one would not typically expect to result in a good photovoltaic cell; when the cell is forward biased, the ITO/$p$-a-$\text{Si}:\text{H}$ creates a reverse biased diode. Kanavce and Metzger have demonstrated through modeling that band-to-band tunneling through the ITO/$p$-a-$\text{Si}:\text{H}$ interface can explain the observed I-V behaviour of both poor and good cells, and must be taken into account when designing cells; for this tunneling to happen effectively, the $p$-a-$\text{Si}:\text{H}$ layer must be sufficiently highly doped and sufficiently thick, otherwise $V_{oc}$ will suffer [99]. Fujiwara and Kondo also analysed the I-V characteristics of cells with different $p$-a-$\text{Si}:\text{H}$ layer thicknesses and saw effects consistent with ITO/$p$-a-$\text{Si}:\text{H}$ tunneling [90].

6.5. **Indium tin oxide in a-$\text{Si}:\text{H}/c$-$\text{Si}$ heterojunction photovoltaics**

Particular constraints come into play when indium tin oxide or other transparent conducting oxides are used in amorphous silicon-crystalline silicon heterojunction photovoltaics. It is much more common for TCOs to be used in applications where they are deposited directly onto a glass superstrate, onto which any subsequent layers are then deposited; this is the most common architecture for thin film photovoltaics, although it is also possible to use a substrate architecture, where a substrate such as stainless steel is used and thin layers are deposited on top. The heterojunction architecture uses a
variation of this second processing order, where amorphous silicon layers are deposited first onto a crystalline silicon substrate and ITO is then deposited onto the heterojunction. The difference in processing order introduces different challenges, as the processing constraints of the a-Si:H/c-Si heterojunction must be respected, and the ITO deposition process must not damage the thin a-Si:H layer, which may be only a few nanometers thick. Mixing and diffusion of species either into or out of the silicon layers are also a possible concern.

Additionally, in this architecture the ITO has a dual purpose, that is, in addition to providing an optically transparent electrical contact it also serves as an antireflective (AR) coating layer. The requirements of the single-layer AR coating necessitate a particular optical thickness, i.e., the product of the refractive index and the physical thickness is constrained. This prevents us from compensating for weak electrical conductivity by making much thicker films.

The most immediately obvious constraint is temperature. Generally the most highly conducting and transparent ITO films are deposited at high temperatures, well above the 170-250°C range at which the amorphous silicon is deposited, and the use of such high temperatures is not possible in heterojunction cells without risking the crystallization of the amorphous silicon. So it is necessary to create films with good transparency and conductivity at low temperatures. In this study, the method of deposition is sputtering, and both DC and RF magnetron sputtering are explored.

Sputtering systems are highly individual, with many parameters that vary from system to system: substrate-target distance, target size and shape, substrate-target angles, and exact target compositions can all vary, with significant consequences. Hence optimization of film parameters is system-specific, although general trends may sometimes be observed. The two sputtering systems used in this study are described in more detail in Section 3.2.3.
6.5.1. Experiment

A series of indium tin oxide films were deposited on Corning glass substrates at low temperatures (below 200°C) to determine the effect of different sputtering process parameters and to attempt to create a film that could be incorporated into the a-Si:H/c-Si PV architecture. Transparency and conductivity were the initial concerns.

Conductivity is determined by considering the sheet resistance of the films, which is a metric used to describe the lateral resistance through a sheet or film for fixed thickness and a square geometry. The resistance laterally through a sheet of any material is determined by the resistivity $\rho$, the length $l$ and width $w$, and the thickness $t$, i.e., $R = \frac{\rho l}{tw}$ (Figure 37).

![Figure 37 - Lateral resistance through a film](image)

The sheet resistance $R_s$ is defined by assuming the length and width are equal, thus giving a parameter that is characteristic of the film and not dependent on the geometry of the particular sheet. It has units of $\Omega$, although $\Omega/\square$ (ohms per square) are often used to avoid ambiguity between resistance and sheet resistance. The sheet resistance was measured using a four-point probe.

To compare the optical properties of the different films, a weighted average transmittance, $T_{av}$, was used, to correct for the fact that different parts of the solar
spectrum have a higher intensity and hence are more important to solar cell functioning. The percent optical transmittance of the film as a function of wavelength \( T_{opt}(\lambda) \), normalized to the transmittance of the glass substrate, was averaged over the wavelength range of the spectrometer (200 nm-900 nm), weighted over the AM1.5 solar spectrum \( I_{AM1.5} \), where \( \lambda \) is the wavelength.

\[
T_{av} = \frac{\int I_{AM1.5}(\lambda)T_{opt}(\lambda)d\lambda}{\int I_{AM1.5}(\lambda)d\lambda}
\]

6.5.2. Results

An initial series of experiments were carried out using DC magnetron sputtering in the MRC system, depositing films on Corning 1737 glass. Figure 38 shows the average percent transmittance compared to the sheet resistance for varying sputtering power and with and without heating. Heating has a large effect, improving both sheet resistance and transmittance. In fact, almost all of the samples follow the pattern of higher transmittance being correlated with lower sheet resistance. This trend was seen throughout all the experiments. Based on the discussion in Section 6.2, this leads to the observation that it is likely that the main variation between different samples is due to the carrier mobility.
A variation in sputtering pressure also changed film parameters, with lower pressures (and therefore a longer mean free path of sputtered species) being more desirable, as shown in Figure 39. The minimum pressure was set at the point where the system was able to maintain a stable plasma.

The highest quality films made in this system, particularly in terms of conductivity, were those that were either deposited on heated substrates or annealed post-deposition. Sheet resistance and transmittance of films annealed for different lengths of time are shown in Figure 40. In fact, with 15 minutes of annealing the sheet resistance was under 30 Ω/□ and the average transmittance was approaching 90%. The improvement with annealing was time-dependent, but most striking for small annealing times, with a plateau reached after approximately 15 minutes.

**Figure 38** – Average transmittance and sheet resistance for three sets of samples deposited on glass under various conditions in MRC system.
Figure 39 – Average transmittance and sheet resistance for samples deposited at various sputtering pressures in the MRC system, with a power of 300 W.

Figure 40 – Average transmittance and sheet resistance for samples annealed for different lengths of time under 1.3 kW lamps. The samples were deposited at room temperature in MRC system, with a power of 300 W.
Further experiments were performed in the Kurt J. Lesker (KJL) system, using RF magnetron sputtering; data is plotted in Figure 41. Again, lower sputtering pressure was desirable, but in this system below 3 mTorr further reduction did not lead to further film property improvement. Also, in this case there was no clear effect on average transmittance.

![Figure 41](image)

**Figure 41 - Transmittance and sheet resistance for films sputtered in KJL system, with varying sputtering pressure**

The effect of oxygen is of particular interest, as the addition of oxygen can be expected to change the stoichiometry of the film, and to influence a number of processes within the film. Oxygen gas is frequently added during ITO sputtering or evaporation to improve film qualities, and reactive sputtering or evaporation of In/Sn with the addition
of oxygen gas can also be used in order to control oxygen content independently of the In and Sn components [100].

Since oxygen vacancies act as dopants in ITO, increasing oxygen content may be expected to reduce carrier concentration, leading to an increase in sheet resistance but also an increase in optical transmittance. However, in reality the full effect of oxygen is slightly more complex. The presence of oxygen can suppress the tendency of Sn\textsubscript{3}O\textsubscript{4} to be created and to form a distinct (darkening) phase, in which case the addition of oxygen may also improve the doping efficiency of the tin, and thus improve the conductivity[98]. Additionally, it is possible for oxygen to be incorporated into the film without taking its place in the crystal structure, instead contributing to interstitial defects which limit the mobility of the film. Hence, the effect of oxygen in a given system is not necessarily reliably predictable by a simple oxygen vacancy doping model. Nevertheless, a number of research groups have found that adding oxygen to the sputtering gas does increase both sheet resistance and optical transmittance [101][102].

When oxygen gas was added to the sputtering chamber in the KJL system (via a gas ring positioned near the target), an immediate and large detrimental effect was seen on sheet resistance. This is shown in Figure 42. Oxygen also had a detrimental effect on transmittance (albeit less drastic than the effect on conductivity), which would not be expected purely from a reduction in carrier concentration. Instead, it seems likely that the oxygen gas is also having some other effect, perhaps increasing the defect density. The sheet resistance and optical transmittance were not improved with annealing.
As in the MRC system, the biggest improvements in film properties came with the use of heat. Figure 43 shows the effect of deposition temperature on depositions in the KJL system. Substrate temperature was varied from room temperature to 155°C. Transmittance and sheet resistance both improved at higher deposition temperatures, particularly above 100°C. The best film was obtained at the highest temperature, with a sheet resistance of 17.3 Ω/□ and average transmittance of 92.1%, for a film thickness of approximately 85 nm.
A small number of samples were also made by using the standard room temperature deposition parameters, followed immediately by a period of annealing in the vacuum chamber. This process also resulted in significant improvements in sheet resistance and transmittance, as shown in Table 12. Annealing at 200°C for a period of 50 minutes, including ramp up time, results in a remarkable sheet resistance of $25 \ \Omega/\square$ and an average transmittance approaching 93%. A possible explanation for this increase in both resistance and transmittance is that the film is likely to have been substantially crystallized during the annealing, leading to increased carrier mobility. The crystallization is examined using XRD in Section 6.5.3.
Table 12 - Post-deposition annealing in vacuum of samples deposited in KJL system (100 W RF, 2.14 mtorr, 20 sccm Ar, room temperature deposition)

<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Annealing time, including ramp up (minutes)</th>
<th>Sheet resistance, $R_s$ ($\Omega/\square$)</th>
<th>Average transmittance, $T_{av}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>54.0</td>
<td>86.3</td>
</tr>
<tr>
<td>150</td>
<td>40</td>
<td>48.0</td>
<td>87.1</td>
</tr>
<tr>
<td>200</td>
<td>50</td>
<td>25.1</td>
<td>92.2</td>
</tr>
<tr>
<td>200 (repeated)</td>
<td>50</td>
<td>25.4</td>
<td>92.7</td>
</tr>
</tbody>
</table>
6.5.3. X-ray diffraction measurements

The sheet resistance and transmittance results in Section 6.5.2 suggest that improvements in film performance with heat treatment are primarily due to improvements in mobility, which may be due to crystallization. XRD characterization was done for ITO films deposited on (100) $n$-c-Si with three different sets of deposition parameters, detailed in Table 6, in Section 3.3.4. Sample B21 was deposited with no heat treatment either during or after deposition; sample B23 was deposited with the substrate temperature held at 140°C during deposition, and sample B26 was deposited with no heating during deposition, but annealed post-deposition at 200°C. All three samples were deposited by RF magnetron sputtering in the KJL system. The XRD results can be seen in Figure 44.

![Figure 44 - X-ray diffraction measurements of three different samples of ITO on (100) $n$-c-Si, deposited using the KJL system. B21 is deposited at room temperature, B23 is deposited at 140°C, and B26 is deposited at room temperature then annealed at 200°C. Strong $<200>$ and $<400>$ signals are detected from the substrate in all cases. Additional signals from several different crystal planes are detected from the two heat-treated ITO samples.](image)
The sample with no heat treatment, B21, showed only some slight broadening at 30°, and no clear peaks other than the substrate peaks. This was true regardless of whether the film was deposited directly on crystalline silicon, or whether there was an amorphous silicon layer. This is to be expected for a low-temperature, amorphous film; the broadening would indicate a slight tendency to (222) orientation. B23 and B26 each showed a number of additional crystal peaks, consistent with polycrystallinity. Although B23 and B26 had similar optical and electrical properties, they showed a different pattern of XRD peaks, indicating different dominant crystal planes, with B26 indicating a particularly strong (222) orientation, which is typical of pure In$_2$O$_3$ in a body-centred-cubic structure [103] [104]. They also had a slightly different lattice constant, with B23 measuring $a = 10.147$ Å, compared to B26 which had a lower lattice constant of 10.108 Å. Pure In$_2$O$_3$, in contrast, has a lattice constant of 10.118 Å [104]. Overall the annealed sample, B26, has a structure more similar to In$_2$O$_3$, while the sample that was heated during deposition, B23, has a different structure, suggesting that the tin is incorporated differently (for example by occupation of interstitial sites, which would increase the lattice constant).

The XRD measurements support the conclusion that the improvements in film resistivity and transmittance seen with heating during or after deposition are likely due to crystallization of the ITO, leading to higher electrical mobility.

### 6.5.4. PV Cell Integration

ITO films B21, B23, and B26, were also deposited onto a $p$-a-Si:H/$n$-c-Si heterojunction that had been previously cleaved into sections, and time of flight secondary ion mass spectroscopy (ToF-SIMS) analysis was done to detect the depth-dependent composition of the ITO/$p$-a-Si:H/$n$-c-Si structures. The $n$-c-Si and $p$-a-Si:H/$n$-c-Si substrates were loaded simultaneously into the sputtering chamber so that the films could be deposited simultaneously on both substrates, i.e., under otherwise identical process conditions. In Figure 45, Figure 46, and Figure 47, the $x$-axis represents the time...
into the experiment, and as such is an indirect measure of depth into the sample. Silicon and boron are used as markers to detect the boundaries of the $p$-a-Si:H layer. The inflection point of the silicon curve is used to detect the ITO/$p$-a-Si:H interface, while the $p$-a-Si:H/$n$-$c$-Si interface is defined as the point where the boron level detected is below 10 counts. Using these markers, a number of observations can be made.

Firstly, a significant amount of indium is detected within the two silicon layers in all three films, and oxygen is detected in the amorphous silicon layer. However, it can not be confirmed that these species are actually present in the silicon layers, because the etching process in depth-dependent SIMS may drive species into the sample, so it is possible that these signals may be an artifact of the measurement process [105].

Secondly, the apparent thickness of the boron layer is thicker in the two heat treated films, B23 and B26, than in the non-heat treated film, B21. This implies certain changes in the heterojunction after heat treatment, whether during or after ITO deposition. It is possible that the structure of the amorphous silicon layer is changed in such a way as to modify the etch rate after heat treatment. Alternatively, it is possible that the boron has diffused into the crystalline silicon, which could cause unintended $p$-type doping in the crystalline silicon.
Figure 45 - ToF-SIMS measurement of ITO/p-a-Si:H/n-c-Si structure, with no heat treatment during or after ITO deposition.

Figure 46 - ToF-SIMS measurement of ITO/p-a-Si:H/n-c-Si structure, with ITO deposited at 140°C.
6.6. Heterojunction cell IV measurements

A HIT cell was fabricated on a textured wafer using the DCSF-PECVD hydrogenated amorphous silicon and RF sputtered indium tin oxide described in previous sections. The cell fabrication is described in detail in Section 3.3.5.

Light and dark I-V measurements were taken and short circuit current, open circuit voltage, and fill factors were extracted. The cell was then annealed at 187°C for 30 minutes and re-characterized, then annealed a second time at 200°C for 30 minutes and characterized once again. The measured light and dark I-V curves are plotted in Figure 48, and the cell parameters are summarized in Table 13. After annealing, the best cell efficiency was 16.5%, and the open circuit voltage was 699 mV. Short circuit current was 36.4 mA/cm². Although the fill factor was improved by annealing, it is still
relatively low at only approximately 65%. The $V_{oc}$ is the highest reported to date for a HIT cell made using DCSF-PECVD.

![Graph showing I-V curves](image-url)

**Figure 48 -** Dark and light I-V curves of best cell as deposited and after two anneals. Cell has an area of 4.02 cm$^2$. Annealing improves the open circuit voltage, short circuit current, and fill factor.
Table 13 – Measured I-V parameters of textured HIT cell

<table>
<thead>
<tr>
<th></th>
<th>after 2nd anneal (200°C)</th>
<th>after 1st anneal (187°C)</th>
<th>as deposited</th>
</tr>
</thead>
<tbody>
<tr>
<td>Efficiency</td>
<td>16.46%</td>
<td>16.36%</td>
<td>14.91%</td>
</tr>
<tr>
<td>Voc</td>
<td>699 mV</td>
<td>697 mV</td>
<td>679 mV</td>
</tr>
<tr>
<td>Jsc</td>
<td>36.4 mA/cm²</td>
<td>36.1 mA/cm²</td>
<td>35.5 mA/cm²</td>
</tr>
<tr>
<td>FF</td>
<td>64.68%</td>
<td>65.09%</td>
<td>61.83%</td>
</tr>
</tbody>
</table>

In order to better understand the cell performance, the I-V results were numerically fit to the two diode model (Equation 6.11) using a MATLAB script developed by group member Zahidur Chowdhury. The two diode model is still a simplification, as it only considers two current mechanisms, however it gives more information than a one diode model. The fitting results are summarized in Table 14 and Figure 49. The model provides some insights into the effect of annealing. The series resistance extracted from the model is significant, as visible in Figure 48. The two diode model also gives a value of $J_{o2}$, the junction recombination current density parameter, four to five orders of magnitude larger than $J_{o1}$, the bulk and surface recombination current density parameter. With annealing the photocurrent increases, while junction recombination current density inferred from the two-diode model is slightly increased. The two-diode series resistance is also decreased, which would lead to an improved fill factor.

$$J(V) = J_{sc} - J_{o1} \left( e^{\frac{q(V+JRs)}{knT}} - 1 \right) - J_{o2} \left( e^{\frac{q(V+JRs)}{2knT}} - 1 \right) - \frac{(V + JR_s)}{R_{sh}}$$  \hspace{1cm} 6.11
Table 14 - Two diode model parameters for textured HIT cell

<table>
<thead>
<tr>
<th></th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$J_{o1}$ (mA/cm$^2$)</th>
<th>$J_{o2}$ (mA/cm$^2$)</th>
<th>$R_s$(Ω/cm$^2$)</th>
<th>$R_{sh}$(Ω/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited</td>
<td>37.8</td>
<td>$1.2 \times 10^{-10}$</td>
<td>$1.4 \times 10^{-6}$</td>
<td>2.9</td>
<td>90</td>
</tr>
<tr>
<td>2nd anneal (200°C)</td>
<td>38.3</td>
<td>$4.9 \times 10^{-11}$</td>
<td>$2.1 \times 10^{-6}$</td>
<td>2.3</td>
<td>101</td>
</tr>
</tbody>
</table>

Figure 49 - Two diode fitting to measured IV results under AM1.5 illumination

The model fits the measured results more closely in the higher forward bias, with a greater error in the low bias, suggesting that the true shunt resistances may be somewhat higher than those in Table 14.

Improvements in series resistance are consistent with the observation in Section 6.5.2, that is, that the ITO sheet resistance is decreased by annealing. Short circuit current is also expected to increase, due to the increase in lifetime seen with annealing[14].
Schulze and Korte found that the high-forward bias ideality factors of a-Si:H/c-Si heterojunctions increased with increasing passivation quality[24][106]; this is consistent with the observation that the bulk and surface recombination current density is inversely dependent on the minority carrier diffusion length, and could explain the dominance of the two diode model recombination current, $J_{o2}$, in our cells. It is clear that series resistance needs to be further decreased in order to achieve higher fill factors and higher efficiencies in our cells. This may be achieved in part by improvement of the front metallization layer, and by optimization of the thicknesses of the different layers in the cell.
7. Conclusions

7.1. Thesis overview

Amorphous-crystalline silicon heterojunctions can be used to fabricate high efficiency silicon photovoltaic cells. This cell structure is made at lower processing temperatures which are less energy intensive as well as being more compatible with thinner silicon substrates than standard crystalline silicon cells. Hence, the amorphous-crystalline silicon heterojunction has the potential for lower fabrication costs compared to homojunction crystalline silicon cells. In order to further improve cell designs and processes, a greater understanding of why this concept is effective and how it works will be useful; this will aid in reducing cell fabrication costs and usage of materials and energy while achieving high performance. The research reported here focuses on developing methods to better understand the amorphous-crystalline silicon heterojunction photovoltaic cell, and specifically the interfaces between the front-side amorphous silicon layer and the materials on either side of it, i.e., the a-Si:H/c-Si interface and the ITO/a-Si:H interface. The cell design that was studied uses an n-type crystalline silicon substrate with i-a-Si:H and p-a-Si:H front layers and i-a-Si:H and n-a-Si:H back surface field all deposited by DC Saddle Field PECVD in the tetrode configuration, and ITO deposited by sputtering.

The a-Si:H/c-Si interface was studied with a variety of established methods, and two characterisation techniques were investigated in more depth. One of the important benefits of the a-Si:H layer is its surface passivating effect, and this was the first area of study. Photocarrier radiometry was used for the first time to extract the bulk carrier lifetimes, surface recombination velocities, and diffusion coefficients of crystalline silicon samples passivated with i-a-Si:H. The technique was also used to extract more detailed information about the heterojunction interface, including carrier lifetime in the i-a-Si:H, and recombination velocities at the front surface and at the amorphous-crystalline silicon interface. Calculations were also done to understand the limits of the model used.
The electric field and band alignment at the a-Si:H/c-Si interface were considered next, using lateral conductivity measurements over a range of temperatures. This technique provides information about the energy band bending and energy barriers at the junction, specifically by probing the minority carrier inversion layer near the junction. The effects of different $p$-a-Si:H doping levels and of different thickness $i$-a-Si:H layers on the built-in voltage in the crystalline silicon were examined, and these observations were correlated with carrier lifetime measurements for the same samples, using eddy current, $\mu$PCD, and modulated photoluminescence measurements.

The ITO/a-Si:H interface was subsequently studied, beginning with the development of an optimized process for low-temperature deposition of ITO onto an a-Si:H/c-Si substrate. X-ray diffraction was used to compare the crystal structure of thin ITO layers which had undergone different heat treatments, and ToF-SIMS depth probing was used to look at the effects of these same heat treatments on ITO/$p$-a-Si:H/$n$-c-Si structures.

Finally all the layers were combined to fabricate a photovoltaic cell with metal/ITO/$p$-a-Si:H/$i$-a-Si:H/$n$-c-Si/i-a-Si:H/$n^+$-a-Si:H/metal structure, on a textured wafer. The voltage-current characteristics of this cell were measured in the dark and under AM1.5 solar illumination, and short circuit current, open circuit voltage, and fill factor were extracted. The measured results were then analysed with the two-diode model.

7.2. Thesis conclusions

A number of conclusions can be drawn from the experiments and analyses that were completed during this research.

Photocarrier radiometry (PCR) was successfully used for the first time to analyse amorphous-crystalline silicon heterostructures to determine recombination and transport properties. PCR is a contactless technique, does not require a large surface area, and can
provide depth-dependent information. By choosing different excitation wavelengths, it is possible to further tune the parts of the sample which are analyzed, and to extract information about different layers of the heterojunction structure.

- Photocarrier radiometry using laser excitation can be used to extract information about the effect of wafer passivation with intrinsic hydrogenated amorphous silicon films: the bulk excess carrier recombination lifetime, front and back surface recombination, and diffusion constant can be determined by numerically fitting measurement results to a theoretical model. Carrier recombination lifetimes of approximately 1 ms were extracted for films passivated on both sides by 30 nm of intrinsic hydrogenated amorphous silicon deposited by DCSF PECVD. The lifetimes determined using PCR were also similar to those determined using microwave and eddy current photocurrent decay, confirming the accuracy of the PCR technique for measuring carrier lifetime.

- The PCR technique can distinguish between bulk and surface recombination, and can measure the diffusion constant of the wafer. Surface recombination velocities below 2 cm/s were measured for films passivated on both sides by 30 nm of intrinsic hydrogenated amorphous silicon deposited by DCSF PECVD. Measured bulk lifetimes were shown to be strongly dependent on surface passivation, which is expected due to the strong effect of surface passivation on bulk excess carrier concentration. Similarly, the presence or absence of a passivating layer on one wafer surface was shown to affect the recombination rate on the other surface, as an unpassivated surface acts as a carrier sink and lowers the carrier concentration throughout the wafer, thus decreasing the occupation of traps. Hence, recombination needs to be low on all surfaces as well as in the bulk to ensure good device performance.
• PCR can further be used to study the heterojunction with UV laser excitation, with results fitted to a more detailed, two-layer model. Recombination and transport properties were extracted for both the amorphous silicon and the crystalline silicon, as were the surface and interface recombination velocities and the unfilled interface trap state density. It was thus possible to distinguish between different types of recombination processes in the heterostructure. The bulk excess carrier lifetime in the crystalline silicon was measured to be 1.4 ms by this method. Amorphous silicon lifetimes obtained were between 1 and 10 ns, and amorphous silicon mobilities were in the range of $10^{-4}$ to $10^{-1}$ cm$^2$/Vs, suggesting that the defect density in the amorphous silicon may be relatively high. However, double-side passivation with intrinsic amorphous silicon was shown to decrease the unfilled interface trap state density at the interface by approximately three orders of magnitude compared to single side passivation, to less than $10^{12}$ cm$^{-3}$.

• Photocarrier radiometry uses pulsed laser excitation, which results in a sinusoidal carrier generation rate and a time-varying carrier distribution. Ambipolar diffusion can result in charge separation at higher frequencies, giving rise to an internal electric field. This field may be significant or may even dominate carrier transport in some experiments and should be considered when interpreting photocarrier radiometry measurements. Detailed calculations were carried out in the context of the PCR parameters used in the experiments to show that the approximation of negligible effects due to ambipolar transport approximation was valid.
Photocarrier radiometry involves illumination of a semiconductor sample with a laser, which heats the sample non-uniformly and can create an electric field through the thermoelectric effect. This effect can be quantified and addressed, and the thermoelectric effect can be neglected in the model if there is adequate heat management.

The a-Si:H/c-Si heterojunction interface was further studied using coplanar conductivity measurements. A minority carrier inversion layer is created in the crystalline silicon in the presence of an oppositely doped amorphous silicon layer if the doping is sufficiently strong; lateral conductance measurements under varying temperature conditions can be used to measure this inversion layer and to infer information about the band bending and band offsets. Additionally, they can be used to gain insight into the doping efficiency in a film. Using this technique, information was gained about the energy band diagram of the DCSF PECVD amorphous silicon and of the heterojunction it forms with crystalline silicon.

The deposition method produces effectively doped films and the carrier concentration can be tuned. Conductivity and activation energy were determined for boron doped amorphous silicon films deposited on glass substrates. For a thick (160 nm) film deposited with an intermediate diborane to silane gas ratio, lateral conductivity was $1.2 \times 10^{-2}$ S/cm as deposited, and $1.8 \times 10^{-2}$ S/cm after annealing. Thinner (approximately 20 nm) films had conductivities of $5.5 \times 10^{-5}$ to $4.2 \times 10^{-4}$ S/cm as deposited and $2.7 \times 10^{-3}$ to $2.2 \times 10^{-2}$ S/cm after annealing; conductivity increased as diborane to silane gas ratio increased. Activation energy was found to be 0.354 eV in the thick sample and 0.305 to 0.346 eV in the thin samples; for samples of constant thickness, the activation energy decreased with increasing diborane to silane gas ratio.
Heterojunctions made by depositing boron-doped amorphous silicon on phosphorous-doped crystalline silicon wafers using DCSF PECVD form a strong hole inversion layer in the crystalline silicon, and this hole inversion layer is weakened with the addition of an intrinsic amorphous silicon layer, with increasing $i$-a-Si:H thickness corresponding to a weaker hole inversion layer, and by extension, a reduction in crystalline silicon band bending. Heterojunctions made with no $i$-layer had a lateral sheet conductance of $2.4 \times 10^{-3}$ to $5.0 \times 10^{-3}$ S/cm as deposited or $3.7 \times 10^{-3}$ to $6.2 \times 10^{-3}$ S/cm after annealing, and an activation energy between 0.01 and 0.02 eV, suggesting a valence band offset of approximately 0.4 eV, which is similar to that predicted by Anderson’s rule. The lateral sheet conductance was decreased by approximately a factor of two with the insertion of an intrinsic amorphous silicon layer (approximately 4 nm) between the doped amorphous layer and the crystalline silicon layer, suggesting that the intrinsic layer does decrease the band bending in the crystalline silicon; the sheet conductance was further decreased to $7.0 \times 10^{-4}$ S/cm with a thicker intrinsic layer (approximately 10 nm). The effective carrier lifetime, however, is improved by the addition of these films, and is improved more with a thicker film than with a thinner film. It is concluded that there is a trade-off between passivation and band-bending, and that intrinsic amorphous silicon layer thickness can and should be optimized in photovoltaic cells.

The interface between amorphous silicon and indium tin oxide was characterised and optimised using sheet resistance measurements, spectroscopy, XPS, and ToF-SIMS.

A recipe was developed to make high quality indium tin oxide films using temperatures that are compatible with deposition onto amorphous silicon thin films. ITO films were made with a sheet resistance of $17.3 \ \Omega/\square$ sheet and average transmittance of 92.1%, for a film thickness of approximately 85 nm.
• It was determined that the highest quality ITO films are made using heat treatment either during or after deposition. In both cases the improvement is shown to be likely due to an increase in carrier mobility rather than to a change in carrier concentration. ITO films are amorphous as deposited at room temperature, and show significant crystallinity if heated during or after deposition, with a different crystal orientation depending on whether heating is during or after deposition. Heating during ITO deposition allows for greater improvements in film quality with a lower maximum temperature, compared to post-deposition annealing.

• Heat treatment during or after ITO deposition on a heterojunction causes changes in the amorphous silicon layer such that the sputtering etch rate is reduced.

Finally, a photovoltaic cell was made on a textured wafer using front and back $i$-$a$-$Si$:H passivation, a front $p$-$a$-$Si$:H layer and a $n^+$-$a$-$Si$:H back surface field, all deposited using DCSF PECVD in the tetrode configuration, followed by ITO deposition by room temperature RF sputtering, and front and back metallization by E-beam evaporation.

• An open circuit voltage of 699 mV was achieved, which is the highest open circuit voltage to date in a HIT cell made using DCSF PECVD.

• A cell efficiency of 16.46% was achieved, with a short circuit current of 36.4 mA/cm$^2$ and a fill factor of 64.68%. Two diode modeling suggests a junction recombination current dominated device with a fill factor limited by both series and shunt resistances.
Annealing the cell leads to substantial improvements, from an as-deposited efficiency of 14.91%, with open circuit voltage of 679 mV, short circuit current of 35.5 mA/cm², and fill factor of 61.83%. Annealing improves both shunt and series resistances, with a greater relative change seen in the series resistance. It also improves both open circuit voltage and short circuit current. These improvements can be attributed to a number of causes, including crystallization of the ITO layer and reduction in heterojunction interface defect density [14]. Several other changes were observed with annealing: an increase in the a-Si:H conductivity, a decrease in a-Si:H activation energy, an increase in interface inversion layer strength, and changes to the a-Si:H layer that resulted in a decreased sputter etch rate. It is possible that some of these annealing-based changes may also contribute to the improvement in cell performance with annealing.

7.3. Future work

This research raises a number of questions which would be interesting to investigate further.

Photocarrier radiometry can provide further information by probing samples with doped a-Si:H layers deposited on crystalline silicon, as well as p-a-Si:H/i-a-Si:H/n-c-Si structures, in order to see the effects of doped layers on passivation effectiveness and on film and interface properties. This research is already underway. Secondly, it would be useful to use PCR to examine the effect of annealing on different cell structures, in order to better understand the causes for annealing-related improvement. Thirdly, it might be possible to examine ITO/a-Si:H/c-Si samples, by using a laser wavelength that is not absorbed in the ITO.
Heat treatment has positive results in more than one area related to cell operation. However, the various mechanisms by which heating changes the cell can still be better understood and optimized. For example, in Section 6.5.2 it was demonstrated that heating ITO during deposition rather than afterwards produces films with a different structure and different conductivity. It would be useful to examine the cell layers and interfaces after heat treatment at different stages of cell processing (e.g., after a-Si:H deposition, during ITO deposition, after ITO deposition, after metallization).
8. Works Cited


[70] A. Melnikov, A. Mandelis, B. Halliop and N. P. Kherani, “Effective interface state effects in hydrogenated amorphous-crystalline silicon


9. Appendix – PN junction photovoltaic cell

9.1. Single diode model of a photovoltaic cell

Empirically, the behaviour of an idealised photovoltaic cell can be simply modeled by a current source in parallel with a diode, as seen in Figure 50.

\[
J(V) = J_{sc} - J_{dark} = J_{sc} - J_o (e^{qV/nkT} - 1)
\]

Using the convention that photocurrent is positive, the cell behaviour can be described by Equation 9.1, where \( J_o \) is a device property primarily determined by the bandgap of the cell materials, \( J_{sc} \) is the short circuit current density, \( k \) is Boltzmann’s constant, \( q \) is the charge of an electron, and \( T \) is the temperature[35]. The term \( n \) in the exponent is called the ideality factor and is primarily determined by the dominant excess carrier recombination processes in the cell; it typically varies between 1 and 2 depending on the materials and physical dimensions of the cell, although in some cases it may be higher than 2:

The JV curve of the photovoltaic cell under illumination therefore resembles a shifted diode curve, plotted in Figure 51, with the \( x \) and \( y \) intercepts respectively giving the open circuit voltage, \( V_{oc} \), and the short circuit current density, \( J_{sc} \). When a load is connected the cell will operate at an intermediate point \((V, J)\) along the curve.
Figure 51 – Plots of current density vs. voltage and power vs. voltage for ideal PV cell, showing maximum power point and fill factor

Since the power per unit area output by the cell is equal to $VJ$, the power at any given operating point is easily seen to be equal to the area of the rectangle between $(V, J)$ and the origin, and a maximum power point can be defined at $(V_m, J_m)$. An additional metric, fill factor, $FF$, is defined as the ratio between $V_mJ_m$ and $V_{oc}J_{sc}$; in this way the maximum power density $P_m$ that can be produced by the cell can be easily expressed in terms of $V_{oc}$ and $J_{sc}$:[35].

$$P_m = V_{oc}J_{sc}FF$$  \hspace{1cm} 9.2

The efficiency $\eta$ of the cell is therefore equal to the maximum power density, $P_m$, divided by the power density of the light incident on the cell, $P_{input}$.

$$\eta = \frac{P_m}{P_{input}} = \frac{V_{oc}J_{sc}FF}{P_{input}}$$  \hspace{1cm} 9.3

The solar illumination used in this research is an air mass 1.5 (AM1.5) solar spectrum, that is, it is the solar illumination when the sun is at an angle of 48.2° from the
normal, which is used to approximate the average angle of the sun at temperate latitudes [107].

To make the model somewhat more realistic, series and shunt resistances $R_s$ and $R_{sh}$ are added, as in Figure 52.

The equation is thus modified [35]:

$$J(V) = J_{sc} - J_o \left( e^{\frac{q(V+JAR_s)}{kT}} - 1 \right) - \frac{(V + JAR_s)}{R_{sh}}$$

where $A$ is the cross-section area of the cell. The effect of series and shunt resistances on the JV curve will be to lower $V$ and $J$, respectively. Both lead to a decrease in fill factor and cell efficiency.

9.2. Two diode model of a photovoltaic cell

The empirical model can be further refined by the addition of a second diode with different characteristics from the first, shown in Figure 53. This makes it possible to distinguish between different current mechanisms within the cell, e.g., diffusion vs. recombination currents, and to take into account the fact that different mechanisms may dominate depending on the bias voltage.

The bulk and surface recombination current density $J_{n=1}$ is described by the following equation, with an ideality factor of 1 and a reverse saturation current density of $J_{o1}$ [36]:
\[ J_{n=1} = J_{o1}(e^{qV/kT} - 1) \]

while the junction recombination current density \( J_{n=2} \) has an ideality factor of 2 and a reverse saturation current density of \( J_{o2} \) [36]:

\[ J_{n=2} = J_{o2}(e^{qV/2kT} - 1) \]

![Two diode model of photovoltaic cell with series and shunt resistances](image)

**Figure 53 - Two diode model of photovoltaic cell with series and shunt resistances**

The full two diode equation with series and shunt resistances is given in Equation 9.7 [35]:

\[
J(V) = J_{sc} - J_{o1}\left(e^{\frac{q(V+JAR_{sh})}{kT}} - 1\right) - J_{o2}\left(e^{\frac{q(V+JAR_{sh})}{2kT}} - 1\right) - \frac{(V + JAR_{sh})}{R_{sh}}
\]

### 9.3. PN junction

The single diode model does demonstrate the behaviour of the cell to first degree, and it can be further modified with the addition of a second diode to match cell behaviour more accurately. However, the one and two diode models give only limited insight into the physics that give rise to the behaviour and so are less helpful in understanding the reasons why different cell architectures or material parameters have the effects that they do. For this we need a more physical model.
A semiconductor is characterized by an energy gap $E_g$ between allowed electron energy bands, where the lower range is almost fully occupied and the upper range is almost empty. Typically (e.g. in solid state, crystalline semiconductors) this means that electrons are attached to most of the valence orbitals of individual atoms in the material, and occupy some of the delocalized higher energy conduction states. A significant gap $E_g$, two to three orders of magnitude greater than $kT$, separates the highest energy valence band state from the lowest energy conduction band state, and energy equal to $E_g$ is required to move electrons from the valence band to the conduction band. The Fermi-Dirac distribution function, $f(E)$, gives the probability that a state at a given energy $E$ will be occupied by an electron [37].

$$f(E) = \frac{1}{1 + e^{(E-E_F)/kT}}$$  \hspace{1cm} (9.8)

The Fermi level $E_F$ is the energy level at which a state has an equal probability of being occupied or unoccupied, and it can vary depending on factors including the valence and conduction band state densities, the trap state density and impurity doping concentrations. At zero degrees Kelvin, all states below $E_F$ will be occupied by electrons and all states above it will be unoccupied; at higher temperatures there is a more gradual transition between states with a high probability of occupation and states with a low probability of occupation. If the Fermi level is within the band gap and sufficiently far from the conduction band, several times $kT$, the electrons are said to be nondegenerate, and the Fermi-Dirac distribution can be approximated by a Boltzmann function, given in Equation 9.9 [37].

$$f(E) \approx e^{-(E-E_F)/kT}$$  \hspace{1cm} (9.9)
In the case of the valence band, which is almost completely full of electrons, we keep track of missing electrons, i.e., holes, for the sake of convenience and mathematical simplicity, as they behave like mobile positive charges. If the Fermi level is several $kT$ above the maximum energy of the valence band, the holes obey Boltzmann statistics and are said to be nondegenerate. The electron and hole concentrations $n$ and $p$ are determined by the temperature, impurity doping concentrations, and intrinsic properties of the semiconductor.

When the semiconductor has been isolated from its environment for a sufficiently long time, i.e., with no incident light and no electrical current or heat transfer, it is considered to be at thermal equilibrium. Thermal equilibrium electron and hole concentrations $n_o$ and $p_o$ for a nondegenerate semiconductor, one in which both electrons and holes are nondegenerate, are related to the Fermi level by the following equations:

\[
\begin{align*}
n_o &= N_c e^{-\frac{(E_c-E_F)}{kT}} \\
p_o &= N_v e^{-\frac{(E_F-E_v)}{kT}}
\end{align*}
\]

Where $N_c$ and $N_v$ are the effective density of conduction and valence band states in the material, respectively. $E_c$ and $E_v$ are the minimum conduction band energy and the maximum valence band energy respectively, such that $E_c-E_v=E_g$ [37].

Electron-hole pairs are created by random thermal generation events allowing an electron to move from the valence to the conduction band, and destroyed in random recombination events where an electron moves back from the conduction band to the valence band. The rate of recombination is determined by the concentration of carriers.
and by the material properties of the semiconductor. Because a recombination event requires an electron and a hole, it is limited by whichever carrier has a lower concentration. If the semiconductor is doped with donor atoms, the free electron concentration will rise while the hole concentration will be reduced due to increased recombination; the Fermi level will move closer to the conduction band. Similarly, if it is doped with acceptor atoms, the Fermi level will move closer to the valence band. However, for a nondegenerate semiconductor at equilibrium, from Equations 9.10 and 9.11, the product of the hole and electron concentrations is always given by Equation 9.12 [37].

\[ n_o p_o = N_c N_v e^{-\frac{E_g}{kT}} \quad \text{9.12} \]

When no dopants are present, the thermal equilibrium electron and hole concentrations are both equal to the intrinsic carrier concentration, \( n_i \). This intrinsic carrier concentration \( n_i \) is determined by the temperature, the band gap, and the density of states in the conduction and valence bands. For \( n_0 = p_0 = n_i \) we have from Equation 9.12:

\[ n_i^2 = N_c N_v e^{-\frac{E_g}{kT}} \quad \text{9.13} \]

Electric currents occur in a semiconductor when there is a net movement of charged particles, which can be caused by electric fields or by concentration gradients (we do not consider here temperature gradients or other possible driving forces). In the case of a concentration gradient of holes or electrons, the random thermal motion of the particles will cause a net diffusion of particles from the region of higher concentration to the region of lower concentration; since the carriers are charged, this flow corresponds to a current. In sum there are four components that make up the total current flow at any point in a semiconductor: the movement of electrons due to an electric field (electron
drift current density, $J_{\text{drift}}$), the movement of holes due to an electric field (hole drift current density, $J_{\text{driftp}}$), the movement of electrons due to diffusion along a concentration gradient (electron diffusion current density, $J_{\text{diffn}}$), and the movement of holes due to diffusion along a concentration gradient (hole diffusion current density, $J_{\text{diffp}}$) [37].

\[
\mathbf{J} = qE\mu_n \mathbf{n} + qE\mu_p \mathbf{p} + qD_n \nabla \mathbf{n} - qD_p \nabla \mathbf{p} \tag{9.14}
\]

\[
\mathbf{J} = \mathbf{J}_{\text{driftn}} + \mathbf{J}_{\text{driftp}} + \mathbf{J}_{\text{diffn}} + \mathbf{J}_{\text{diffp}} = \mathbf{J}_n + \mathbf{J}_p \tag{9.15}
\]

where $\mu_n$, $\mu_p$, $D_n$ and $D_p$ are mobilities and diffusion coefficients of electrons and holes, respectively.

We will assume that the semiconductor has acceptor doping $N_A$, donor doping $N_D$, electron concentration $n$, hole concentration $p$, electric field $E$, electron and hole mobilities $\mu_n$ and $\mu_p$, electron and hole diffusion lengths $L_n$ and $L_p$, electron and hole diffusion constants $D_n$ and $D_p$ (where the relationship between each $\mu$ and $D$ pair is given by the Einstein relationship, $D/\mu = kT/q$. $U_n$ and $G_n$ are the recombination and generation rates for electrons, and $U_p$ and $G_p$ are the recombination and generation rates for holes, which in the most general case may be different due to the presence of electrons or holes in trap states.

Two other equations must also be valid at every point in the semiconductor: Poisson’s equation, and the continuity equation.

Poisson’s equation gives the relationship between the electric field and the charge density [108]:

\[
\]
where \( N_D^+ \) and \( N_A^- \) are the ionized donor and acceptor impurity concentrations, and the continuity equations express conservation of electrons and holes [35]:

\[
\frac{\partial n}{\partial t} = -\frac{1}{q} (\nabla \cdot \vec{j}_n) + G_n - U_n \tag{9.17}
\]

\[
\frac{\partial p}{\partial t} = -\frac{1}{q} (\nabla \cdot \vec{j}_p) + G_p - U_p \tag{9.18}
\]

To model a photovoltaic cell we begin by considering a \( p-n \) homojunction diode at equilibrium, as shown in Figure 54. An \( n \)-type semiconductor (doped with donor impurities, and thus containing more free electrons than holes) is in contact with a \( p \)-type semiconductor (doped with acceptor impurities, thus containing more holes). Diffusion occurs as the free carriers move along concentration gradients, with electrons near the interface diffusing from the \( n \) side into the \( p \) side and holes near the interface diffusing from the \( p \) side into the \( n \) side. Since these particles are charged, their net movement constitutes a diffusion current. Far away from the interface the bulk properties remain essentially unchanged, however near the interface there are a number of interesting effects. A depletion region or space charge region is created which is (to first approximation) empty of free carriers. Within this depletion region on each side of the \( p-n \) interface there is now a net electrical charge caused by the donor or acceptor ions, with each side of the depletion region containing an equal and opposite total charge (thus the space charge region is proportionally wider on the more lightly doped side). This charge gives rise to an electric field, which leads to electron and hole currents, known as the drift
currents. The electron and hole drift currents are equal and opposite to the electron and hole diffusion currents, such that an equilibrium is maintained.

Together with the electric field, a built-in voltage, \(V_{bi}\), is established between the \(p\)-side bulk and the \(n\)-side bulk, which also relates the equilibrium carrier concentrations on each side of the junction. The subscripts \(n\) and \(p\) refer to the \(n\)- and \(p\)-type semiconductor [37].

\[
n_{p0} = n_{n0} e^{\left(-\frac{qV_{bi}}{kT}\right)}
\]
An energy band diagram is useful to visualize key features of the junction. The modeling software AFORS-HET (Automat for Simulation of Heterostructures, by the Hahn-Meitner Institut, described in more detail in Section 3.5) is used to make the diagrams, using an acceptor doping density of $1 \times 10^{19}$ cm$^{-3}$, a donor doping concentration of $1 \times 10^{16}$ cm$^{-3}$, and the bandgap of crystalline silicon. The built-in voltage, seen in Figure 55, is proportional to the disparity in conduction band levels by a factor of $q$, i.e., the disparity in conduction band levels is equal to the energy that must be gained or lost by a single electron at the conduction band edge, as it moves across the built-in voltage. This voltage falls mainly across the more lightly doped $n$-region, which makes up the majority of the space charge region.

$$p_{n0} = p_{p0} e^{-\frac{qV_{bb}}{kT}}$$

9.20
Figure 55 - \( p-n \) junction: energy band diagram and carrier concentration profiles with zero applied bias

When a forward bias voltage, \( V \), is applied, as in Figure 56, the voltage barrier across the junction is decreased by the applied voltage, reducing the electric field in the barrier region and the electron and hole drift currents in the barrier region. The electron and hole diffusion currents are not affected and therefore are now larger than the electron and hole drift currents. The diffusing minority carriers carry the net current in the device. Since the
semiconductor is no longer in equilibrium it is not accurate to speak of a Fermi level, however electron and hole quasi-Fermi levels can be defined which have a mathematically analogous relationship with the non-equilibrium electron and hole populations. The quasi Fermi levels are now changed from the equilibrium Fermi level to reflect the fact that both minority carrier electrons and holes have increased at the edges of the depletion region from the equilibrium concentrations [37].

\[
n_p = n_{p0} e^{\frac{qV}{kT}} \tag{9.21}
\]

\[
p_n = p_{n0} e^{\frac{qV}{kT}} \tag{9.22}
\]

As before, the subscripts \( n \) and \( p \) are used to refer to the \( n \)- or \( p \)- type semiconductor.
Figure 56 - p-n junction with applied forward voltage bias: energy band diagram and carrier concentration profiles.

The difference between the actual and equilibrium values of the electron or hole concentrations in any semiconductor (e.g., $n-n_0$ for electrons) can be referred to as the excess electron or excess hole concentration, $\Delta n$ or $\Delta p$. When light is incident on the
cell, the electron and hole concentrations at a given location in the cell are both increased by the same absolute value due to the creation of electron-hole pairs, i.e., $G_n = G_p$ and $\Delta n = \Delta p$. However, in strongly doped semiconductors under typical solar illumination and open circuit conditions this injection of new carriers has a negligible impact on the majority carrier concentrations (the electrons in $n$-type silicon or the holes in $p$-type silicon), while it is large enough to dominate the much smaller minority carrier concentrations. The energy difference between the electron and hole minority carrier quasi Fermi levels, when divided by $q$, provides the open circuit voltage, $V_{oc}$ of the cell. The upper limit to $V_{oc}$ is $V_{bi}$.

When a load is connected to the illuminated cell a current is drawn from the device, the voltage drop across the cell drops and the voltage across the depletion region is increased, back towards $V_{bi}$, by the potential drop across the load. This case can be seen in Figure 57.
Figure 57 - $p$-$n$ junction under illumination: energy band diagram and carrier concentration profiles.

In the case of a device where both of the $p$ and the $n$ sides of the junction are thick compared to the minority carrier diffusion lengths, where bulk recombination dominates over interface recombination, the current-voltage behaviour of the device can be derived
by solving the Equations 9.14, 9.21, and 9.22 at the boundaries of the space charge region, using the assumption that recombination within the space charge region is negligible.

This gives the classic diode equation [37]:

\[ J(V) = J_{sc} - \left[ \frac{qD_p p_{n0}}{L_p} + \frac{qD_n n_{p0}}{L_n} \right] \frac{qV}{e^{kT} - 1} \]  
\[ J(V) = J_{sc} - J_0 \left[ e^{kT} - 1 \right] \approx J_{sc} - J_0 e^{kT} \]

Here \( p_{n0} \) and \( n_{p0} \) are the minority carrier hole and electron concentrations in the bulk \( n \) and \( p \) regions, far from the space charge region, and \( J_{sc} \) is the short circuit current density due to photogenerated carriers and \( L_n \) and \( L_p \) are the diffusion lengths of minority carrier electrons and holes, respectively. \( V_{oc} \) can be found from Equation 9.24 using the definition of open circuit voltage, \( J(V_{oc}) = 0 \).

\[ V_{oc} = \frac{kT}{q} \ln \left( \frac{J_{sc}}{J_0} \right) \]

In the case where \( J_0 \) is dominated by bulk recombination and where the \( p \) side is much more strongly doped than the \( n \) side, the \( V_{oc} \) equation can be simplified [38]:

\[ V_{oc} = \frac{kT}{q} \ln \left[ \frac{J_{sc}}{qD_p p_{n0} / L_p} \right] \]
The maximum open circuit voltage in this cell will be determined primarily by the doping densities and by the excess minority carrier effective lifetime, with the latter influencing 9.28 through $J_{sc}$ and $L_p$.

\[
V_{oc} = \frac{kT}{q} \ln \left[ \frac{J_{sc}}{qD_pN_eN_v e^{\frac{E_g}{kT}}} \right] \quad 9.27
\]

\[
V_{oc} = \frac{E_g}{q} - \frac{kT}{q} \ln \left[ \frac{qD_pN_eN_v}{L_pN_D J_{sc}} \right] \quad 9.28
\]