Atmospheric Pressure Chemical Vapor Deposition of Functional Oxide Materials for Crystalline Silicon Solar Cells

Kristopher Davis

University of Central Florida

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ATMOSPHERIC PRESSURE CHEMICAL VAPOR DEPOSITION OF FUNCTIONAL OXIDE MATERIALS FOR CRystalline silicon solar cells

by

KRISTOPHER O. DAVIS

B.S. in Electrical Engineering, University of Central Florida, 2007

M.S. in Optics, University of Central Florida, 2011

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the College of Optics and Photonics at the University of Central Florida Orlando, Florida

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2015

Major Professor: Winston V. Schoenfeld
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ABSTRACT

Functional oxides are versatile materials that can simultaneously enable efficiency gains and cost reductions in crystalline silicon (c-Si) solar cells. In this work, the deposition of functional oxide materials using atmospheric pressure chemical vapor deposition (APCVD) and the integration of these materials into c-Si solar cells are explored. Specifically, thin oxide films and multi-layer film stacks are utilized for the following purposes: (1) to minimize front surface reflectance without increasing parasitic absorption within the anti-reflection coating(s); (2) to maximize internal back reflectance of rear passivated cells, thereby increasing optical absorption of weakly absorbed long wavelength photons (λ > 900 nm); (3) to minimize recombination losses by providing excellent surface passivation; and (4) to improve doping processes during cell manufacturing (e.g., emitter and surface field formation) by functioning as highly controllable dopant sources compatible with in-line diffusion processes. The oxide materials deposited by APCVD include amorphous and polycrystalline titanium oxide (a-TiOₓ and pc-TiOₓ, respectively), aluminum oxide (AlOₓ), boron-doped AlOₓ (AlOₓ:B), silicon oxide (SiOₓ), phosphosilicate glass (PSG), and borosilicate glass (BSG). The microstructure, optical properties, and electronic properties of these films are characterized for different deposition conditions. Additionally, the impact of these materials on the performance of different types of c-Si solar cells is presented using both simulated and experimental current-voltage (I-V and J-V) curves.
ACKNOWLEDGMENTS

First, I would like to express gratitude toward my advisor, Dr. Winston V. Schoenfeld, for his scientific and technical input, professional guidance, and mentorship through the course of my Ph.D. research. I would like to also thank Dr. Schoenfeld, Dr. Dirk Habermann, and Steve Pauve (both formerly with SCHMID Group) for providing me with the incredible opportunity of living and working in the idyllic Schwarzwald region of Germany. The entire staff at SCHMID Group were very accommodating and patient, and my research and education in both CVD processes and c-Si solar cell manufacturing would be woefully incomplete without the assistance of: Dr. Kaiyun Jiang (a big thank you!); Heiko Zunft; Carsten Demberger; Dr. Helge Haverkamp; Dr. Robin Nissler; Michael Wiedorn; and many others. I would also like to Dr. Keith McIntosh (PV Lighthouse) for numerous technical discussions ranging on topics from recombination, to optics, to manufacturing. I would like to thank Dr. Simeon Baker-Finch (First Solar) for his insight in front side cell optics, and I’d like to thank Dr. J. Patrick Looney (Brookhaven National Laboratory) for his insight into oxide/semiconductor interfaces. I would also like to express my gratitude to the other members of my dissertation advisory committee, Dr. M.G. Moharam, Dr. Patrick L. LiKamWa, and Dr. Dirk Habermann.

Most importantly, I would like to thank my wife, Shelley Easter, for her unwavering support throughout my Doctorate program.
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<tr>
<th>Symbol</th>
<th>Description (Common Unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>device area (cm$^2$)</td>
</tr>
<tr>
<td>$A_{ARC}$</td>
<td>parasitic absorption within the anti-reflection coating</td>
</tr>
<tr>
<td>$A_{b,FCA}$</td>
<td>free carrier absorption within the bulk of a solar cell</td>
</tr>
<tr>
<td>$A_{e,FCA}$</td>
<td>free carrier absorption within the emitter of a solar cell</td>
</tr>
<tr>
<td>$A_r$</td>
<td>parasitic absorption at the rear side of a solar cell</td>
</tr>
<tr>
<td>$d_{a-TiO}$</td>
<td>thickness of amorphous titanium oxide film</td>
</tr>
<tr>
<td>$D_B$</td>
<td>diffusivity of boron in extrinsically doped silicon (cm$^2$·s$^{-1}$)</td>
</tr>
<tr>
<td>$d_{EMA}$</td>
<td>thickness of the rough effective medium approximation layer for a crystalline or polycrystalline titanium oxide film</td>
</tr>
<tr>
<td>$D_i$</td>
<td>interface defect density (eV$^{-1}$·cm$^{-2}$)</td>
</tr>
<tr>
<td>$D_{i,midgap}$</td>
<td>interface defect density at midgap (eV$^{-1}$·cm$^{-2}$)</td>
</tr>
<tr>
<td>$d_{TiO}$</td>
<td>thickness of crystalline or polycrystalline titanium oxide film</td>
</tr>
<tr>
<td>$E$</td>
<td>energy level (eV)</td>
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<td>conduction band energy level (eV)</td>
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<td>$E_g$</td>
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<td>$E_{ph}$</td>
<td>photon energy (eV)</td>
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<td>$E_t$</td>
<td>energy level of bulk defect or trap (eV)</td>
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<tr>
<td>$E_V$</td>
<td>valence band energy level (eV)</td>
</tr>
<tr>
<td>$f_{EMA}$</td>
<td>Effective medium approximation fraction (i.e., fraction of one material to another using the effective medium approximation for modeling the complex refractive index)</td>
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<tr>
<td>$G$</td>
<td>carrier generation rate (cm$^3$·s$^{-1}$)</td>
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<td>$G_{STC}$</td>
<td>irradiance of 1000 W·m$^{-2}$</td>
</tr>
<tr>
<td>$I$</td>
<td>current (A)</td>
</tr>
<tr>
<td>$I_{01}$</td>
<td>saturation current of $m = 1$ diode</td>
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<td>$I_1$</td>
<td>recombination current due to $m = 1$ diode</td>
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<td>$I_2$</td>
<td>recombination current with $m = 2$ diode</td>
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<td>$I_G$</td>
<td>photogenerated current (A)</td>
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<tr>
<td>$I_H$</td>
<td>recombination current due to resistance-limited enhanced recombination</td>
</tr>
<tr>
<td>$J$</td>
<td>current density (mA·cm$^{-2}$)</td>
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<tr>
<td>$J_0$</td>
<td>saturation current density (fA·cm$^{-2}$)</td>
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<tr>
<td>$J_{01}$</td>
<td>saturation current density of $m = 1$ diode (fA·cm$^{-2}$)</td>
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<tr>
<td>$J_{02}$</td>
<td>saturation current density of $m = 2$ diode (fA·cm$^{-2}$)</td>
</tr>
<tr>
<td>$J_{0b}$</td>
<td>saturation current density contribution from the bulk of a cell (fA·cm$^{-2}$)</td>
</tr>
<tr>
<td>$J_{0BSF}$</td>
<td>saturation current density contribution from back surface field region (fA·cm$^{-2}$)</td>
</tr>
<tr>
<td>$J_{0e}$</td>
<td>emitter saturation current density (fA·cm$^{-2}$)</td>
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<td>Symbol</td>
<td>Description (Common Unit)</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>$J_{0f}$</td>
<td>saturation current density contribution from the front of a cell ($\text{fA}\cdot\text{cm}^{-2}$)</td>
</tr>
<tr>
<td>$J_{0\text{met}}$</td>
<td>saturation current density contribution from a metallized region ($\text{fA}\cdot\text{cm}^{-2}$)</td>
</tr>
<tr>
<td>$J_{0n^+}$</td>
<td>saturation current density contribution from a $n^+$ doped region ($\text{fA}\cdot\text{cm}^{-2}$)</td>
</tr>
<tr>
<td>$J_{0r}$</td>
<td>saturation current density contribution from the rear of a cell ($\text{fA}\cdot\text{cm}^{-2}$)</td>
</tr>
<tr>
<td>$J_{0s}$</td>
<td>saturation current density contribution from a surface ($\text{fA}\cdot\text{cm}^{-2}$)</td>
</tr>
<tr>
<td>$J_A$</td>
<td>equivalent current density of light parastically absorbed by an anti-reflection coating ($\text{mA}\cdot\text{cm}^{-2}$)</td>
</tr>
<tr>
<td>$J_G$</td>
<td>photogenerated current density ($\text{mA}\cdot\text{cm}^{-2}$)</td>
</tr>
<tr>
<td>$J_{G,max}$</td>
<td>maximum generation current density for a given wafer or cell thickness and optical pathlength enhancement ($\text{mA}\cdot\text{cm}^{-2}$)</td>
</tr>
<tr>
<td>$J_{MP}$</td>
<td>current density at max power ($\text{mA}\cdot\text{cm}^{-2}$)</td>
</tr>
<tr>
<td>$J_{SC}$</td>
<td>short-circuit current density ($\text{mA}\cdot\text{cm}^{-2}$)</td>
</tr>
<tr>
<td>$k$</td>
<td>extinction coefficient</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$k_{a\text{-TiO}}$</td>
<td>extinction coefficient of amorphous titanium oxide</td>
</tr>
<tr>
<td>$k_{EMA}$</td>
<td>extinction coefficient of the rough effective medium approximation layer for crystalline or polycrystalline titanium oxide</td>
</tr>
<tr>
<td>$k_{TiO}$</td>
<td>extinction coefficient of crystalline or polycrystalline titanium oxide</td>
</tr>
<tr>
<td>$m$</td>
<td>diode ideality factor</td>
</tr>
<tr>
<td>$n$</td>
<td>refractive index</td>
</tr>
<tr>
<td>$n$</td>
<td>electron concentration ($\text{cm}^{-3}$)</td>
</tr>
<tr>
<td>$n_0$</td>
<td>electron concentration under thermal equilibrium ($\text{cm}^{-3}$)</td>
</tr>
<tr>
<td>$n_0$</td>
<td>refractive index of an incident medium</td>
</tr>
<tr>
<td>$n_{0s}$</td>
<td>electron concentration under thermal equilibrium at the surface ($\text{cm}^{-3}$)</td>
</tr>
<tr>
<td>$N_A$</td>
<td>background dopant concentration of acceptor species ($\text{cm}^{-3}$)</td>
</tr>
<tr>
<td>$n_{a\text{-TiO}}$</td>
<td>refractive index of amorphous titanium oxide</td>
</tr>
<tr>
<td>$n_{ARC}$</td>
<td>refractive index of a single layer anti-reflection coating</td>
</tr>
<tr>
<td>$n_{ARC,\text{bot}}$</td>
<td>refractive index of the bottom layer of a double layer anti-reflection coating</td>
</tr>
<tr>
<td>$n_{ARC,\text{top}}$</td>
<td>refractive index of the top layer of a double layer anti-reflection coating</td>
</tr>
<tr>
<td>$N_D$</td>
<td>background dopant concentration of donor species ($\text{cm}^{-3}$)</td>
</tr>
<tr>
<td>$n_{EMA}$</td>
<td>refractive index of the rough effective medium approximation layer for crystalline or polycrystalline titanium oxide</td>
</tr>
<tr>
<td>$n_i$</td>
<td>intrinsic carrier concentration ($\text{cm}^{-3}$)</td>
</tr>
<tr>
<td>$n_{ie}$</td>
<td>effective intrinsic carrier concentration ($\text{cm}^{-3}$)</td>
</tr>
<tr>
<td>$N_{ph}$</td>
<td>incident photon flux ($\text{cm}^{-2}\cdot\text{s}^{-1}$)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description (Common Unit)</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>$n_s$</td>
<td>electron concentration at the surface (cm$^{-3}$)</td>
</tr>
<tr>
<td>$n_{Si}$</td>
<td>refractive index of silicon</td>
</tr>
<tr>
<td>$N_t$</td>
<td>density of defect (traps) in the bulk material (cm$^{-3}$)</td>
</tr>
<tr>
<td>$n_{TiO}$</td>
<td>refractive index of crystalline or polycrystalline titanium oxide</td>
</tr>
<tr>
<td>$p$</td>
<td>hole concentration (cm$^{-3}$)</td>
</tr>
<tr>
<td>$p_0$</td>
<td>hole concentration under thermal equilibrium (cm$^{-3}$)</td>
</tr>
<tr>
<td>$p_{0s}$</td>
<td>hole concentration under thermal equilibrium at the surface (cm$^{-3}$)</td>
</tr>
<tr>
<td>$P_{MP}$</td>
<td>maximum power point (W)</td>
</tr>
<tr>
<td>$P_{ph}$</td>
<td>power of photons incident on a given area</td>
</tr>
<tr>
<td>$p_s$</td>
<td>hole concentration at the surface (cm$^{-3}$)</td>
</tr>
<tr>
<td>$q$</td>
<td>elementary charge (C)</td>
</tr>
<tr>
<td>$Q_f$</td>
<td>fixed charge at a dielectric/semiconductor interface (cm$^{-2}$)</td>
</tr>
<tr>
<td>$R$</td>
<td>carrier recombination rate (cm$^{-3}$s$^{-1}$)</td>
</tr>
<tr>
<td>$R_{esc}$</td>
<td>component of the measured front surface reflectance due to light escaping from within the wafer or cell after being internally reflected at the back (only important for long wavelengths)</td>
</tr>
<tr>
<td>$R_{ext}$</td>
<td>front surface reflectance</td>
</tr>
<tr>
<td>$R_{f1}$</td>
<td>internal front reflectance for the “first bounce”</td>
</tr>
<tr>
<td>$R_H$</td>
<td>resistance due to resistance-limited enhanced recombination</td>
</tr>
<tr>
<td>$R_r$</td>
<td>aggregated internal back reflectance accounting for all “bounces”</td>
</tr>
<tr>
<td>$R_{r1}$</td>
<td>internal back reflectance for the “first bounce”</td>
</tr>
<tr>
<td>$R_m$</td>
<td>internal back reflectance for light undergoing multiple internal reflections</td>
</tr>
<tr>
<td>$R_S$</td>
<td>series resistance (Ω or Ω·cm$^{-2}$)</td>
</tr>
<tr>
<td>$R_{SH}$</td>
<td>shunt resistance (Ω or Ω·cm$^{-2}$)</td>
</tr>
<tr>
<td>$R_{sheet}$</td>
<td>sheet resistance (Ω/☐)</td>
</tr>
<tr>
<td>$R_W$</td>
<td>weighted average front surface reflectance</td>
</tr>
<tr>
<td>$S$</td>
<td>surface recombination velocity (cm·s$^{-1}$)</td>
</tr>
<tr>
<td>$S_{n0}$</td>
<td>electron surface recombination velocity (cm·s$^{-1}$)</td>
</tr>
<tr>
<td>$S_{p0}$</td>
<td>hole surface recombination velocity (cm·s$^{-1}$)</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature (°C or °K)</td>
</tr>
<tr>
<td>$T_1$</td>
<td>fraction of light transmitted through the front surface of a solar cell</td>
</tr>
<tr>
<td>$T_2$</td>
<td>fraction of light redirected back into the wafer after the “first bounce”</td>
</tr>
<tr>
<td>$T_{dep}$</td>
<td>deposition temperature (°C or °K)</td>
</tr>
<tr>
<td>$T_n$</td>
<td>fraction of light redirected into the wafer following multiple internal reflections</td>
</tr>
<tr>
<td>$u$</td>
<td>ultimate efficiency (%)</td>
</tr>
<tr>
<td>$U$</td>
<td>net carrier recombination rate (cm$^{-3}$s$^{-1}$)</td>
</tr>
<tr>
<td>$U_{b,SRH}$</td>
<td>net carrier recombination rate due to bulk defects or traps (cm$^{-3}$s$^{-1}$)</td>
</tr>
<tr>
<td>$U_{s,SRH}$</td>
<td>net carrier recombination rate due to surface defect states (cm$^{-3}$s$^{-1}$)</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description (Common Unit)</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>V</td>
<td>voltage (V or mV)</td>
</tr>
<tr>
<td>V_{MP}</td>
<td>voltage at max power (V or mV)</td>
</tr>
<tr>
<td>V_{OC}</td>
<td>open-circuit voltage (V or mV)</td>
</tr>
<tr>
<td>v_{th}</td>
<td>thermal velocity of carriers (cm·s⁻¹)</td>
</tr>
<tr>
<td>W</td>
<td>cell thickness (µm)</td>
</tr>
<tr>
<td>Z</td>
<td>optical pathlength enhancement</td>
</tr>
<tr>
<td>α</td>
<td>optical absorption coefficient (cm⁻¹)</td>
</tr>
<tr>
<td>α_{EHP}</td>
<td>component of the optical absorption coefficient leading to electron-hole pair generation (cm⁻¹)</td>
</tr>
<tr>
<td>α_{FCA}</td>
<td>component of the optical absorption coefficient leading to free carrier absorption (cm⁻¹)</td>
</tr>
<tr>
<td>Δn</td>
<td>injection level or excess concentration of electrons (cm⁻³)</td>
</tr>
<tr>
<td>Δn_s</td>
<td>excess carrier concentration at the surface (cm⁻³)</td>
</tr>
<tr>
<td>Δρ</td>
<td>excess concentration of holes (cm⁻³)</td>
</tr>
<tr>
<td>η</td>
<td>power conversion efficiency (%)</td>
</tr>
<tr>
<td>θ₁</td>
<td>primary ray angle for light transmitted into a wafer or cell (°)</td>
</tr>
<tr>
<td>θ_{c,AlO}</td>
<td>critical angle at the interface between aluminum oxide and silicon (°)</td>
</tr>
<tr>
<td>θ_{c,SiO}</td>
<td>critical angle at the interface between silicon oxide and silicon (°)</td>
</tr>
<tr>
<td>θ_n</td>
<td>ray angle for light undergoing multiple internal reflections (°)</td>
</tr>
<tr>
<td>σ_n</td>
<td>electron capture cross section (cm²)</td>
</tr>
<tr>
<td>σ_p</td>
<td>hole capture cross section (cm²)</td>
</tr>
<tr>
<td>τ</td>
<td>carrier recombination lifetime (s)</td>
</tr>
<tr>
<td>τ_A</td>
<td>Auger carrier recombination lifetime (s)</td>
</tr>
<tr>
<td>τ_b</td>
<td>carrier recombination lifetime due to all recombination processes occurring in the bulk (s)</td>
</tr>
<tr>
<td>τ_{b,SRH}</td>
<td>carrier recombination lifetime due to bulk defects or traps (s)</td>
</tr>
<tr>
<td>τ_{eff}</td>
<td>effective carrier recombination lifetime due to all recombination processes (s)</td>
</tr>
<tr>
<td>τ_{n0}</td>
<td>electron recombination lifetime or electron capture time constant due to bulk defects in p-type semiconductor (s)</td>
</tr>
<tr>
<td>τ_{p0}</td>
<td>hole recombination lifetime or hole capture time constant due to bulk defects in n-type semiconductor (s)</td>
</tr>
<tr>
<td>τ_r</td>
<td>radiative carrier recombination lifetime (s)</td>
</tr>
<tr>
<td>τ_{s,SRH}</td>
<td>carrier recombination lifetime due to surface states (s)</td>
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## LIST OF ACRONYMS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>a-Si:H</td>
<td>hydrogenated amorphous silicon</td>
</tr>
<tr>
<td>AC</td>
<td>alternating current</td>
</tr>
<tr>
<td>Al-BSF</td>
<td>aluminum back surface field</td>
</tr>
<tr>
<td>ALD</td>
<td>atomic layer deposition</td>
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<tr>
<td>AlO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>aluminum oxide</td>
</tr>
<tr>
<td>AlO&lt;sub&gt;x&lt;/sub&gt;:B</td>
<td>boron-doped aluminum oxide</td>
</tr>
<tr>
<td>APCVD</td>
<td>atmospheric pressure chemical vapor deposition</td>
</tr>
<tr>
<td>ARC</td>
<td>anti-reflection coating</td>
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<td>B&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>diborane</td>
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<td>BC</td>
<td>back contact</td>
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<tr>
<td>BJ</td>
<td>back junction</td>
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<td>BNL</td>
<td>Brookhaven National Laboratory</td>
</tr>
<tr>
<td>BSF</td>
<td>back surface field</td>
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<tr>
<td>BSG</td>
<td>borosilicate glass</td>
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<tr>
<td>c-Si</td>
<td>crystalline silicon</td>
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<td>C-V</td>
<td>capacitance-voltage</td>
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<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>Cz</td>
<td>Czochralski</td>
</tr>
<tr>
<td>DC</td>
<td>direct current</td>
</tr>
<tr>
<td>DLARC</td>
<td>double layer anti-reflection coating</td>
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<tr>
<td>EDX</td>
<td>energy-dispersive X-ray spectroscopy</td>
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<td>EELS</td>
<td>electron energy loss spectroscopy</td>
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<tr>
<td>EHP</td>
<td>electron-hole pair</td>
</tr>
<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
</tr>
<tr>
<td>EWT</td>
<td>emitter wrap-through</td>
</tr>
<tr>
<td>FCA</td>
<td>free carrier absorption</td>
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<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<td>FZ</td>
<td>float zone</td>
</tr>
<tr>
<td>I-V</td>
<td>current-voltage</td>
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<tr>
<td>IBC</td>
<td>interdigitated back contact</td>
</tr>
<tr>
<td>IBR</td>
<td>internal back reflectance</td>
</tr>
<tr>
<td>IQE</td>
<td>internal quantum efficiency</td>
</tr>
<tr>
<td>LCOE</td>
<td>levelized cost of energy ($/kWh)</td>
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<tr>
<td>LPCVD</td>
<td>low pressure chemical vapor deposition</td>
</tr>
<tr>
<td>LPD</td>
<td>liquid phase deposition</td>
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<td>MOCVD</td>
<td>metal organic chemical vapor deposition</td>
</tr>
<tr>
<td>mono-Si</td>
<td>monocrystalline silicon</td>
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<tr>
<td>multi-Si</td>
<td>multicrystalline silicon</td>
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<tr>
<td>MWT</td>
<td>metal wrap-through</td>
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<tr>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>ammonia</td>
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<tr>
<td>nPERL</td>
<td>n-type passivated emitter and rear locally diffused cell</td>
</tr>
<tr>
<td>nPERT</td>
<td>n-type passivated emitter and real totally diffused cell</td>
</tr>
<tr>
<td>NREL</td>
<td>National Renewable Energy Laboratory</td>
</tr>
<tr>
<td>O&amp;M</td>
<td>operation &amp; maintenance</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>O₃</td>
<td>ozone</td>
</tr>
<tr>
<td>PCD</td>
<td>photoconductance decay</td>
</tr>
<tr>
<td>PECVD</td>
<td>plasma-enhanced chemical vapor deposition</td>
</tr>
<tr>
<td>PH₃</td>
<td>phosphine</td>
</tr>
<tr>
<td>pPERC</td>
<td>p-type passivated emitter and rear cell</td>
</tr>
<tr>
<td>pPERL</td>
<td>p-type passivated emitter and rear locally diffused cell</td>
</tr>
<tr>
<td>PSG</td>
<td>phosphosilicate glass</td>
</tr>
<tr>
<td>PV</td>
<td>photovoltaic</td>
</tr>
<tr>
<td>PVD</td>
<td>physical vapor deposition</td>
</tr>
<tr>
<td>QSSPC</td>
<td>quasi-steady-state photoconductance</td>
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<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
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<tr>
<td>SiH₄</td>
<td>silane</td>
</tr>
<tr>
<td>SIMS</td>
<td>secondary ion mass spectroscopy</td>
</tr>
<tr>
<td>SiNx</td>
<td>silicon nitride</td>
</tr>
<tr>
<td>SRH</td>
<td>Shockley-Read-Hall</td>
</tr>
<tr>
<td>STC</td>
<td>Standard Test Conditions</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>TEOS</td>
<td>tetraethoxysilane</td>
</tr>
<tr>
<td>TiOₓ</td>
<td>titanium oxide</td>
</tr>
<tr>
<td>TMA</td>
<td>trimethylaluminum</td>
</tr>
<tr>
<td>TMM</td>
<td>transfer matrix method</td>
</tr>
<tr>
<td>TPT</td>
<td>tetraisopropyl titanate</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
CHAPTER 1 - INTRODUCTION

With global energy consumption expected to increase over 30% by 2035 [1] and growing concerns regarding climate change, the world is actively looking to both energy efficiency and new forms of energy production. With significant cost reductions in both wind and solar energy, renewables are expected to account for a third of the total global electricity output by 2035, with solar growing more rapidly than any other form of renewable energy [1]. Photovoltaics (PV), a form of solar energy wherein light is directly converted to electricity typically using a semiconductor material, has been the primary driver of the incredible growth of solar in recent years. This growth can be clearly seen by tracking the evolution of the cumulative global installed PV capacity over time, as shown in Figure 1-1 in units of peak gigawatts (GWp) [2]. In the first half of 2014, solar (primarily PV, with some concentrating solar power) accounted for 53% of all new electricity generation capacity in the U.S., (beating out natural gas (30%) and wind (14%)) [3]! The European Photovoltaic Industry associations anticipates the global annual market for PV to be between 35-69 GWp per year over the next four years [2].
PV offers a number of advantages over fossil fuel energy sources, nuclear energy, and even other renewable resources. Critical advantages include the following:

- **No fuel required**: PV systems do not require fuel, thereby eliminating the risk associated with fluctuating fuel costs. This is the advantage over fossil fuel resources and is an advantage shared by many other (but not all!) renewable resources. There is also no requirement to dispose of fuel, like there is with nuclear energy. The economic and safety issues associated with nuclear fuel disposal are still disputed and carry with them a certain level of financial risk, which is why organizations like the IEA expect a reduced role for nuclear power in the future compared to expectations in years past [1].

- **No emissions**: The energy produced by PV systems is free of pollutants and greenhouse gas emissions. While this represents a long-term and politically
controversial advantage associated with the growing concerns around climate change [4], it should also be noted that recent reports indicate hidden health care costs associated with populations living near coal fired power plants [5, 6]. These hidden costs aren’t typically accounted for in cost estimates comparing PV to coal.

- **Modular and distributed**: PV systems are modular and can be operated anywhere on the planet, so the potential generation capacity of PV is virtually limitless. As pointed out in a recent study by the National Renewable Energy Laboratory (NREL), the U.S. currently uses approximately 4,000 TWh/year of electricity, which is roughly the same amount of solar energy incident on continental U.S. land in only a few hours of daylight [7]. In fact, PV has a larger generation potential in the U.S. than all other renewable energy technologies combined [8]. Since PV can be installed and operated at the point of use (i.e., distributed generation), transmission and distribution costs are significantly reduced [9]. This is also of critical importance in rural developing nations, where the construction of large centralized power plants with vast transmission and distribution networks is cost prohibitive. Finally, the modularity of PV systems provides added flexibility for utilities due to much shorter construction lead times compared to large scale centralized power plants [9]. This means utilities can respond to increases in demand in a much faster, more targeted way.

- **Minimal O&M**: PV systems are comprised of highly reliable, solid-state devices with low operation and maintenance (O&M) requirements. The
current O&M costs for PV are a much lower percentage of the total levelized cost of energy (LCOE) when compared to other power generation technologies [10], with potential to be reduced even further with advances in module level electronics and diagnostics.

- **Ancillary services**: Thanks to improvements in fast switching power semiconductor devices [11] and improvements to inverter technology [12, 13], integration of PV into the utility grid can now be carried out in a way that significantly enhances the stability of the grid and provides added value, like power factor control and dispatchable reactive power (referred to as “ancillary services” in the utility sector) [9, 14, 15].

- **Little to no water usage**: More than any other sector, the power sector withdraws the most water in the U.S., accounting for >40% of all freshwater withdrawals in 2005 [16]. Macknick *et al.* studied water withdrawal and consumption for different electric power generation technologies, and found PV and wind (i.e., non-thermal renewables) to have the lowest water consumption [16]. The heavy dependence on available water resources for fossil fuel-based and nuclear generation can impact the reliability of these technologies.

The potential disadvantages associated with PV are listed below [14], and :

- **Intermittency**: PV is an intermittent power source, similar to other renewable resources (e.g., wind), and is dependent on the fluctuating sunlight local to the area in which it is installed. Unlike wind however, PV produces most of its power during times of peak electrical demand for utilities. This and the
added predictability of the diurnal solar cycle make PV less of a liability than wind when it comes to intermittency [14]. The larger intermittency challenge for PV is due to rapid changes in production due to moving clouds completely or partially shading the array. This issue can be addressed both by dispersing PV systems over a large geographic area (i.e., geographic smoothing [17]) and by the use of advanced solar forecasting [18] and cloud detection methods [19].

- **Lack of utility control**: Although PV deployment is increasing at a very high rate, it still represents a rather small share of the total electricity produced in the U.S. and abroad. It is still a relatively new generation technology, from the perspective of utility companies, and there are many outdated policies and standards that affect how PV can and can’t be utilized. One of the most important advantages of PV mentioned earlier is that it can be used to help support the overall stability of the utility grid [9]. However, when utilities don’t have the policies or technical resources in place to safely and effectively control PV systems, that advantage can’t be fully realized. In recent years, there have been significant advantages in PV system integration technologies that facilitate utility control of PV [12-15, 20, 21], and changes are expected for outdated interconnection standards [12]. However, the issue of utility control for PV remains a potential barrier to adoption.

- **High capital cost**: Despite incredible reductions in PV component and system costs, including a 5-7% drop per year in the installed system cost from 1998-2011 (11-14% in 2010-2011 alone) [22], the levelized cost of
energy (LCOE) of PV is still currently higher than energy from fossil fuels in many places [10]. To become truly competitive with fossil fuels, cost reductions at the material, cell, module and system level must occur.

Table 1-1. Table listing the advantages and potential disadvantages associated with PV.

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Potential Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>No fuel required</td>
<td>Intermittency</td>
</tr>
<tr>
<td>No emissions</td>
<td>Lack of utility control</td>
</tr>
<tr>
<td>Modular and distributed</td>
<td>High capital cost</td>
</tr>
<tr>
<td>Minimal O&amp;M</td>
<td></td>
</tr>
<tr>
<td>Ancillary services</td>
<td></td>
</tr>
<tr>
<td>Little to no water usage</td>
<td></td>
</tr>
</tbody>
</table>

Where the first two disadvantages described are both inherently system-related issues, the issue of high capital cost can be addressed at the material and cell level, in addition to the system level. The scope of this research will be related to making improvements in cell technology that lead to higher energy conversion efficiencies, while also reducing the cost to manufacture cells by using novel process technologies. In particular, functional oxide materials deposited via atmospheric pressure chemical vapor deposition (APCVD) will be explored as a means to fabricate highly efficient crystalline silicon (c-Si) cells.

1.1 Overview of the Photovoltaic Industry

The role of a PV system is to efficiently and safely convert incident sunlight into useable electricity [23]. In most cases, useable electricity refers to alternating current (AC) power at voltages compatible with standard electrical loads in homes and buildings. However, PV applications now span a wide range of sizes and variations, from small cells designed to recharge batteries to massive, ground mounted PV systems directly tied into transmission level utility voltages. Normally
the application dictates the form factor of the PV devices and ancillary components needed to manage, convert, and distribute the energy produced.

Despite the application, the actual source of power is the photovoltaic (or solar) cell, a semiconductor device that uses the built-in field of a \textit{p-n} junction and the conversion of photons to charge carriers to produce voltage and current. These cells are commonly connected together electrically, in series or in a series-parallel configuration, to increase the voltage and current of the interconnected ensemble. Those cells are also typically encapsulated to protect the semiconductor device and current carrying electrodes from the environment in which they were designed to operate. This final component is called a PV module (specifically, a flat plate module), aptly named because a system designer can simply add the required amount of modules together to reach the system size desired for the specific application.

In a grid-connected PV system (i.e., a system that is electrically interconnected to a utility network), modules are connected electrically to increase operating voltages and currents to desired levels (as is the case with cells within a module). This collection of modules is referred to as an array, and the output of the array, a direct current (DC) source of power, is fed to a component called an inverter that performs many tasks [24]. These include maximum power point tracking the current-voltage \((I-V)\) characteristics of the array, converting DC to AC power, synchronizing the AC output to match the sine wave of the interconnected utility network, performing critical safety functions and acting as the primary human machine interface for the entire system. Figure 1-2 features an array of c-Si PV
modules mounted on a rooftop and an array of ground mounted thin film PV modules.

Figure 1-2: (a) An array of rooftop mounted c-Si PV modules; and (b) an array of ground mounted thin film PV modules.

Besides standard grid applications, another application of flat plate modules is stand-alone, or off-grid PV systems. As the name implies, these systems are not connected to a utility network and are normally the only source of power for that building or residence (hybrid systems including fossil-fuel generators [25] or small wind turbines [26] are also possible, but less common). In this case, energy storage is required if loads are to be served at night or during very cloudy days. The inverter and other supplementary power electronics (e.g., charge controllers) for these applications therefore differ from a standard grid-connected system [24].

In another type of application called concentrator, or concentrating, photovoltaics, lenses or mirrors are used to concentrate light onto a small, individual cell [23, 27]. This technology differs from flat plate module designs in many ways. Due to the limited field of view, which is dependent of the level of concentration used, concentrating PV modules must be installed on tracking systems. The benefit is that a smaller area semiconductor device is used, which can allow higher cost, higher efficiency materials and cell architectures to be used.
Also, due to the tracking arrangement, more solar energy is incident on the same given area through the course of a day. However, the downsides are that the added optical and mechanical components can negatively impact the cost and reliability of the overall system. Also, the added size and mechanical components needed limit these systems to very large, ground mounted installations and the smaller field of view of the concentrating optics limits these systems to climate zones with minimal cloud cover due to an inability to collect diffuse light.

1.1.1 Conversion Technologies

Since the first silicon $p$-$n$ junction solar cell was created in 1954 at Bell Laboratories [28], there have been a wide assortment of new cell and module technologies that have been introduced to the PV community with varying levels of success entering the market place. c-Si has been the most successful technology by far, holding at least 80% market share every year and a $\approx$90% market share in 2011 in terms of manufacturing production [29]. Traditionally, c-Si cells have been fabricated from Si wafers, which are sawed from either monocrystalline Si (mono-Si) ingots or multicrystalline Si (multi-Si) bricks [30]. Subsequently, cell fabrication is carried out in a method similar to that of integrated circuits (dopant diffusion, wet chemical etching, metallization), but with a drastically different cost model [31].

To compete with c-Si, thin film PV technologies were developed to lower the cost of module manufacturing by reducing the processing steps and amount of active material required to create a module, at the expense of lower efficiencies. In general, this is accomplished by depositing a thin inorganic semiconductor film
(<4 \mu m \text{ thick} \ [32, 33]), called the absorber layer, onto a substrate or superstrate. The absorber normally features a direct bandgap in the range of 1-1.75 eV, allowing for strong optical absorption of the visible and near-infrared wavelengths available from the solar spectrum on Earth. Cell fabrication is then carried out using a combination of steps involving chemical treatments, buffer layer deposition, laser scribing, and transparent conductive oxide deposition. Various thin film material systems have been utilized by industry. The most successful absorber materials have been hydrogenated amorphous silicon (a-Si:H), cadmium telluride (CdTe), and copper indium gallium diselenide (CIGS), or variations therein. For a-Si:H, homojunctions with a $p-i-n$ structure have been commonly utilized, while later developments have involved the use of tandem structures with microcrystalline Si as the bottom layer used to absorb the red portion of the spectrum [33]. In the case of CdTe and CIGS, a heterojunction is normally formed using cadmium sulfide (CdS) [32]. Many other materials have also been investigated, but with limited success (e.g., Cu$_2$S/CdS devices [34]). An emerging potential material system based on kesterite absorbers that has recently garnered the interest of the PV community is copper zinc tin sulfide and copper zinc tin sulfide selenium. Recent work at IBM has lead to efficiencies exceeding 10% using Cu$_2$ZnSn(Se,S)$_4$ [35]. The advantage of this material over CdTe and CIGS is that it consists of low cost, earth-abundant elements [36]. Limited availability and/or concerns of increasing prices for Te and In is a current cause of concern according to many economic experts and technologists working in the PV industry [37].
Where thin films were developed to offer a cheaper, but lower performing alternative to c-Si, multijunction III-V solar cells were developed to push the envelope of solar cell efficiencies. While this comes at an incredibly high cost, in terms of both cost per area and cost per power/energy produced, efficiencies as high as 46% have been achieved under concentrated light and 38.8% under “one sun” [38]! This higher cost is due to both the materials requirements (e.g., substrates) and the expensive, low throughput epitaxial crystal growth methods (e.g., metal-organic chemical vapor deposition, molecular beam epitaxy) required to create these devices, which is why concentration of light is normally used to reduce the amount of active material needed [39]. From a scientific and engineering perspective however, the performance of these multijunction cells, also known as tandem cells, is nothing less than extraordinary. Spire Semiconductor, Sharp, Soitec, Boeing-Spectrolab, Solar Junction, NREL and Fraunhofer ISE are all organizations that have exceeded the 40% efficiency mark [40]. The efficiency boost primarily comes from the use of multiple p-n junctions stacked on top of each other, each with a bandgap engineered to absorb light with a certain range of wavelengths.

In addition to c-Si, thin film and multi-junction III-V technologies, other materials and device concepts have been developed at the laboratory-scale, but with little to no commercial impact. Perhaps the most notable technology in this category would be organic photovoltaics, which is based on the use of organic semiconductor materials. Dye-sensitized solar cells are another technology of current interest to the PV community. More recently, perovskite materials have
emerged as a potentially attractive technology based on the demonstration of a non-stabilized cell efficiency of 20.1% [40]. Concerns over both the short-term and long-term stability of organic photovoltaics, dye-sensitized solar cells, and perovskite cells are current market barriers for these technologies.

Other emerging PV technologies seek to break the well-known Shockley-Queisser limit by exploiting quantum confinement or by using some other novel energy conversion process (e.g., hot carrier solar cells, multiple exciton generation, frequency conversion, intermediate band solar cells). The majority of these disruptive technologies are at the very early stages of the R&D cycle (e.g., theoretical investigations, proof of principle studies, early prototype development) [41]. Figure 1-3 features the famous chart of best PV cell efficiencies that is maintained and updated by NREL [40]. Here, one can track the progression in cell efficiencies dating back to the mid-1970’s.
1.2 Metrics and Economic Drivers for PV Technologies

1.2.1 Performance

Typically, PV performance refers to power conversion efficiency ($\eta$), or the amount of electrical power produced from the solar radiation incident on the cell or module. The evaluation of conversion efficiency for a cell or modules is generally carried out under standard test conditions (STC), also known as standard reporting conditions. This refers to normally incident light with an irradiance of 1000 W·m$^{-2}$ ($G_{STC}$), a defined spectral distribution of light called AM1.5G and a device temperature of 25°C [42]. This is done to provide an effective “apples-to-apples” comparison of cells and modules from different laboratories or different manufacturers, and the testing can be performed in a laboratory setting using
broadband light sources designed for the appropriate irradiance and spectral
distribution. Efficiency is determined by measuring the \( I-V \) characteristics of the PV
device under these test conditions. Simply divide maximum power point \( (P_{MP}) \) by
the product of irradiance and the illuminated device area \( (A) \) to calculate \( \eta \):

\[
\eta = \frac{P_{MP}(W)}{G_{STC}(Wm^{-2}) \cdot A(m^2)} \cdot 100\%.
\]

Note, the power output of a cell or module does vary under changing test
conditions (i.e., not STC). In fact, modules operating in the field rarely (if ever!) actually experience STC. As the sun moves across the sky, the angle of incidence is constantly changing throughout the day. The incident irradiance also varies throughout the course of the day and from season to season, with a peak irradiance varying significantly from location to location. The same can be said for cell and module temperatures, which normally operate at temperatures much higher than 25ºC. Also, weather patterns also affect incident irradiance, temperature, and even the spectral distribution of light, which is affected by atmospheric conditions (e.g., aerosol optical depth) [42]. If the change in power output due to varying operating conditions was the same for all types of cells and modules, this wouldn’t really be an issue. But this isn’t the case, different cell technologies have different temperature coefficients and some module designs perform better than others when the angle of incidence is not zero [43]. There are various methods to address this discrepancy, including the following two examples [44]:
• Translation of module performance data collected in the field to STC or some other alternative reporting conditions [42];

• Measure energy yield of the module (i.e., integral of power over time) and divide by the total solar energy incident on the module over that same period of time (e.g., hourly, daily, monthly, yearly) [45, 46].

1.2.2 Cost

Cost is arguably the most critical metric affecting market penetration of a given PV technology and there are various ways to define cost for PV cells, modules and systems. The two most common cost metrics for comparing PV to other forms of energy (or for comparing different PV technologies) are:

• **Cost per watt**: Sale price, manufacturing cost or installed system cost divided by the STC rated power output at the cell, module or system level given in dollars per watt ($/W_p);

• **Levelized cost of energy (LCOE)**: Total cost of a PV system, including upfront capital costs (e.g., modules, inverters, ancillary equipment/materials, installation) and O&M costs over the life of the system divided by total amount of energy produced by the system – given in dollars per kilowatt hours ($/kWh).

Cost per watt is typically referred to more often, because it is much simpler and easier to determine. This is the common metric used to compare one PV technology or product to another, particularly at the cell and module level. LCOE requires more assumptions (e.g., performance under non-STC conditions, operational lifetime, degradation rates, O&M cost) and some predictive modeling
of performance over the entire life of the system. However, LCOE ultimately tells
the real story and is the better metric when comparing PV to other form of energy,
particularly considering the fact that reliability and durability are completely ignored
in cost per watt comparisons. Freely available software tools like the NREL Solar
Advisor Model have made LCOE calculations much simpler and more accessible
[47].

1.2.3 Reliability and Durability

While the long-term performance of PV technologies is a critically important
metric, both in terms of reliability (i.e., ability to withstand failure) and durability
(i.e., ability to withstand degradation), this topic falls outside the scope of this paper.

1.2.4 Environmental Sustainability

Similarly, environmental sustainability of the manufacturing materials and
methods used to produce PV cells and modules is also critically important,
particularly since one of PV’s most prominent advantages is being environmentally
friendly. However, issues of material abundance, end-of-life recycling and disposal
and energy payback time all fall outside the scope of this paper.
CHAPTER 2 - OVERVIEW OF CRYSTALLINE SILICON PHOTOVOLTAICS

2.1 Introduction

According to the Shockley-Queisser formalism, the efficiency limit of an ideal c-Si solar cell with a single junction is ≈33%, assuming no non-radiative recombination occurs. This value is known as the Shockley-Queisser limit, named after the authors of the seminal paper on the detailed balance limit of efficiency for solar cells [48]. The so-called ultimate efficiency (\(u\)) of any single junction technology is determined using the following equation:

\[
u = \frac{E_g \cdot N_{ph(E_{ph}>E_g)}}{P_{ph}} \cdot 100\%.
\] (2-1)

Here, \(E_{ph}\) refers to photon energy, \(N_{ph(E_{ph}>E_g)}\) is the number of photons with energy greater than the absorber material’s bandgap \(E_g\) incident on a given area per unit time (i.e., flux), and \(P_{ph}\) is the incident power of all photons incident on that same area (i.e., the incident solar energy per unit time). This number provides the absolute upper limit of efficiency solely based on the bandgap of the absorber material, with no consideration of recombination or any other loss mechanisms. Figure 2-1(a) shows the dependence of \(u\) on \(E_g\), while Figure 2-1(b) provides both \(E_g\) and \(u\) for a variety of different absorber materials of interest to the PV community [37]. Note, the maxima occurs at approximately 1.1 eV, which happens to be the indirect bandgap of c-Si.
Figure 2-1: (a) Ultimate efficiency given as a function of $E_g$. (b) Calculated ultimate efficiency for different absorber materials of interest to the PV community.

The so-called Shockley-Queisser limit of 33% is the radiative recombination-limited efficiency of an ideal material with a step-function optical absorption at $E_g$ and assuming AM1.5G spectral distribution [49]. Tiedje et al. found that when accounting for other fundamental limitations to c-Si like Auger recombination, free carrier absorption and actual optical absorption coefficients, the limiting efficiency of c-Si cells is approximately 30%.

The world record efficiency for a c-Si solar cell stood at 25.0% for 15 years, a record set by Green et al. at the University of New South Wales [38, 50, 51]. This record was just recently surpassed by Panasonic in 2014 with a 25.6% efficient cell, with two other companies also achieving 25% cell efficiencies in 2014 (SunPower, Sharp) [40]. However, the c-Si cells used in mass production today have typical efficiencies closer to 16-19%, with cells made from multi-Si wafers on the low end and mono-Si wafers on the high end. While there are notable examples of companies producing higher efficiency cell architectures (e.g., interdigitated back contact, silicon heterojunction), most cells produced in mass production today
typically utilize a aluminum back surface field (Al-BSF) architecture with a silicon nitride (SiNₓ) front side coating, which acts as an anti-reflection coating (ARC) and passivation layer, and screen printed metal contacts on the front and rear of the cell (Figure 2-2). In the following sections, the energy conversion process for c-Si cells is discussed, along with key loss mechanisms leading to reduced efficiency.

Figure 2-2. Al-BSF cell architecture commonly used in mass production today. This architecture is implemented on 156 mm x 156 mm c-Si wafers (either mono-Si or multi-Si) and then encapsulated into a PV module for installation.

2.2 The Process of Energy Conversion

2.2.1 Optical Absorption

When considering the energy conversion process for a c-Si solar cell, the absorption of light within the cell is the natural place to start. A widely used optical model for c-Si cells is given in Figure 2-3, created to reflect an Al-BSF cell in this case [52]. The following sections provide insight on the various optical loss mechanisms shown in Figure 2-3, and descriptions for all of the parameters shown can be found in the LIST OF SYMBOLS.
Reflection from the front surface of a solar cell is one of the first loss mechanisms encountered. For an unencapsulated, planar c-Si wafer, the Fresnel reflections at the air/Si interface are very high: 35% at a wavelength ($\lambda$) of 600 nm and normal incidence, while increasing for larger angles of incidence. The most common method of mitigating these reflection losses at the surface of a cell is to texture the cells using either an alkaline or acid based chemical solution for mono-Si and multi-Si wafers, respectively. In addition to this geometrical approach to photon management, an ARC is used to provide an intermediate refractive index and provide destructive interference of the incident optical wave. In the common Al-BSF cells used by industry, this film is an approximately 75 nm SiN$_x$ film.
deposited using plasma-enhanced chemical vapor deposition (PECVD). Figure 2-4 illustrates the impact of texturing and the ARC on the front surface reflectance \((R_{\text{ext}})\) of a c-Si wafer.

![Figure 2-4. \(R_{\text{ext}}\) as a function of \(\lambda\) for a bare, planar mono-Si wafer, a bare textured mono-Si wafer, and a textured mono-Si wafer with a SiN\(_x\) ARC. Calculated using OPAL 2 [53] with a complex refractive index for SiN\(_x\) taken from [54].](image)

Clearly, a significant reduction in \(R_{\text{ext}}\) is achieved through the use of a textured front surface and ARC, but the solution isn’t perfect. By integrating \(R_{\text{ext}}(\lambda)\) over the relevant wavelengths of interest (\(\lambda \approx 380-1200\) nm) and accounting for the photon flux of a reference solar spectrum (e.g., AM1.5G), one can determine the weighted average front surface reflectance \((R_{W})\) of a given front surface and ARC [55]. This equation is given below:

\[
R_{W} = \frac{\int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} R_{\text{ext}}(\lambda) \cdot N_{\text{ph}}(\lambda) d\lambda}{\int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} N_{\text{ph}}(\lambda) d\lambda},
\]

(2-2)
where $\lambda_{\text{max}}$ and $\lambda_{\text{min}}$ are the maximum and minimum wavelengths of interest, respectively, and $N_{\text{ph}}(\lambda)$ is the incident photon flux given as a function of $\lambda$ in this case. While this is a quick and effective way to evaluate ARCs, a critical weakness is that it doesn’t account for absorption within the ARC layer ($A_{\text{ARC}}$), which is especially important for high index SiN$_x$ ARCs. Figure 2-5 illustrates the increasing extinction coefficient ($k$) with increasing refractive index ($n$). The increasing $n$ is achieved by increasing the SiH$_4$/NH$_3$ ratio during PECVD.

![Figure 2-5](image.png)

**Figure 2-5.** Increasing $k$ associated with higher index SiN$_x$ films, which leads to increased parasitic absorption within the ARC for short wavelengths ($\lambda > 500$ nm) [54].

An alternative method of evaluating the optical performance of a solar cells front surface is to calculate the so-called generation current density ($J_G$), which is amount of current that could be generated based on, not only $R_{\text{ext}}$ and $A_{\text{ARC}}$, but also the absorption coefficient and optical thickness of the cell [53]. McIntosh and Baker-Finch argue that $J_G$, which can be thought of as a photon current, is a more meaningful metric than $R_W$ because the actual finite absorption of a cell is accounted for and the wavelength limits aren’t arbitrarily defined. $J_G$ is given by the following equation (assuming normal incidence):

$$J_G$$
\[ J_G = q \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} [1 - R_{\text{ext}}(\lambda) - A_{\text{ARC}}(\lambda)] N_{ph}(\lambda) e^{-\alpha(\lambda) Z \cdot W} d\lambda, \]  

(2-3)

where \( q \) is the elementary charge of \( 1.602 \times 10^{-19} \) C, \( \alpha \) is the absorption coefficient of the absorber material, \( W \) is the thickness of the absorber layer, and \( Z \) is the optical pathlength enhancement of the cell. Note, \( (1 - R_{\text{ext}}(\lambda) - A_{\text{ARC}}(\lambda)) \) equals the amount of light transmitted into the cell. \( Z \) is commonly calculated using a number of assumptions regarding the propagation angle of light transmitted into the cell, the reflectance and (to a lesser extent) the optical diffusivity of the rear side of the cell, and escape reflectance at the front side of the cell [53, 56, 57]. In reality, \( Z \) is a function of \( \lambda \), but it is often calculated at a long wavelength (e.g., \( \lambda = 1-1.2 \) \( \mu \)m) and assumed to be independent of \( \lambda \), since it is only the long wavelengths that reach the rear side of the cell. The quantify of light reflected from the front surface and the amount of light parasitically absorbed by the ARC can also be converted to photon currents, \( J_R \) and \( J_A \), respectively, using the following:

\[ J_R = q \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} R_{\text{ext}}(\lambda) N_{ph}(\lambda) e^{-\alpha(\lambda) Z \cdot W} d\lambda, \]  

(2-4)

\[ J_A = q \int_{\lambda_{\text{min}}}^{\lambda_{\text{max}}} A_{\text{ARC}}(\lambda) N_{ph}(\lambda) e^{-\alpha(\lambda) Z \cdot W} d\lambda. \]  

(2-5)

The sum of \( J_G, J_R, \) and \( J_A \) equals the maximum photogenerated current \((J_{G,\text{max}})\) possible for a given \( Z \) and \( W \). For example, a 180 \( \mu \)m cell with \( Z = 4 n^2 \) results in a \( J_{G,\text{max}} \) of 44.5 mA·cm\(^{-2}\) or a \( J_{G,\text{max}} \) of 44.0 mA·cm\(^{-2}\) using a more realistic
Z taken from [58]. \( J_R \) and \( J_A \) are useful metrics in that they relate a measured optical loss (\( R_{ext} \) and \( A_{ARC} \)) directly to the amount current lost for a solar cell. This current loss can then be used to easily calculate the reduction in cell efficiency associated with these optical losses.

Because Si is an indirect bandgap semiconductor, incident photons with photon energies near the band edge (1.12 eV) are inefficiently absorbed. Figure 2-6 illustrates this reality by showing the fractional absorption in Si as a function of \( \lambda \) for four different optical path lengths (i.e., the product \( Z \cdot W \)) [59]. Absorption begins to become severely impacted for \( \lambda > 900 \) nm range, particularly for the 50 \( \mu \)m and 10 \( \mu \)m optical path lengths. The internal back reflectance is therefore another important metric when considering the optical performance of c-Si solar cells, since it directly impacts \( Z \). Various cell architectures are known to enhance the short-circuit current density (\( J_{SC} \)) by increasing the internal back reflectance, particularly rear passivated solar cells [60].

![Figure 2-6. Fractional absorption in c-Si for four different optical path lengths (\( Z \cdot W \)) [59].](image-url)
It is important to note that when seeking to enhance absorption near the band edge, losses due to free carrier absorption (FCA) become more important to consider. Like optical absorption leading to the formation of electron-hole pairs (EHP), FCA is dependent on $\lambda$. FCA is also dependent on doping concentration [61]. The optical absorption coefficient can therefore be written as the following:

$$\alpha(\lambda) = \alpha_{EHP}(\lambda) + \alpha_{FCA}(\lambda),$$

(2-6)

where $\alpha_{EHP}$ is the component of optical absorption leading to EHP generation and $\alpha_{FCA}$ is the component leading to FCA. Highly doped regions of the cell are more susceptible to FCA due to the doping dependence. Therefore, FCA within emitter ($A_{e,FCA}$) and BSF ($A_{BSF,FCA}$) regions of cells is normally higher than the level of FCA occurring in the bulk of the wafer itself ($A_{b,FCA}$) despite the fact that the wafer’s bulk is much thicker.

Another important consideration related to optical losses in c-Si solar cells is shading due to the metallization at the front of the cell. The Ag-based contacts and busbars used to collect carriers and conduct current reflect (and to a lesser extent absorbs) light, making this region opaque to the active Si material underneath. While there are ways of mitigating losses due to front contact shading in front contact cell architectures (e.g., Al-BSF), all back contact cell architectures avoid this loss mechanism altogether, which will be discussed later.
2.2.2 Carrier Generation, Recombination and Transport

EHPs are created as a result of optical absorption, excluding FCA. These EHPs act as charge carriers, which produce current if effectively transported to the electrical contacts of the cell. The generation rate of EHPs \( G \) is dependent on \( N_{ph}(\lambda) \), as follows [62]:

\[
G = \int_{\lambda_{min}}^{\lambda_{max}} \alpha_{EHP}(\lambda) N_{ph}(\lambda) d\lambda.
\] (2-7)

\( N_{ph}(\lambda) \), and therefore \( G \), is dependent on position within the cell, as the number of photons are attenuated through the absorption process. While the generation of multiple EHPs from a single photon can occur in c-Si for photon energies in excess of 3.5 eV, the probably is quite low and the effect on \( J_{SC} \) is minimal to non-existent [62].

Once EHPs are created, the goal is to transport these carriers to the cell junction and then the contacts before recombination of the EHP occurs. The carrier recombination lifetime \( \tau \) can be given by the following [63]:

\[
\tau = \frac{\Delta n}{U},
\] (2-8)

where \( \Delta n \) refers to the injection level and \( U \) refers to the total net recombination rate \( (U = R - G, \text{ where } R \text{ is the recombination rate}) \). The injection level is the excess concentration of electrons \( (\Delta n = n - n_0) \) or holes \( (\Delta p = p - p_0) \), since \( \Delta n = \Delta p \) in the absence of charge carrier trapping and electric fields. Here, \( n \) and \( p \) are...
the electron and hole concentrations and \( n_0 \) and \( p_0 \) are the concentrations of each at thermal equilibrium [63]. The dependence of recombination processes on \( \Delta n \) is often divided into two regimes: (1) low-injection conditions refer to injection levels wherein \( \Delta n \) is much smaller than the background doping concentration (i.e., \( N_D \) or \( N_A \), for \( n \) and \( p \)-type material, respectively); and (2) high-injection conditions refer to the case where \( \Delta n \) greatly exceeds the background doping level.

While radiative and non-radiative recombination processes are known to occur in semiconductor materials, it is non-radiative recombination that is dominant in Si (again, due to the indirect bandgap). For c-Si solar cells, the three recombination processes of greatest importance are: (1) band-to-band Auger recombination; (2) recombination via bulk defects; and (3) surface recombination.

2.2.2.1 Band-to-Band Auger Recombination

In the case of band-to-band Auger recombination, the energy associated with the recombination of the EHP is transmitted to a third charge carrier (an electron in the conduction band or hole in the valence band) [63]. The Auger recombination lifetime \( \tau_A \) decreases as the dopant concentration increases and with increasing \( \Delta n \).

2.2.2.2 Recombination via Bulk Defects

Recombination via bulk defects, or traps, refers to allowed energy levels within the forbidden gap of the semiconductor, which are formed by impurities, dislocations, or other disturbances in the crystal lattice. This type of recombination is modeled using Shockley-Read-Hall (SRH) statistics [64]. The net recombination
rate due to SRH recombination \((U_{b,SRH})\) for a single-level bulk defect at a given energy level within the forbidden band \((E_i)\) is given by the following \([63]\):

\[
U_{b,SRH} = \frac{np-n_i^2}{\tau_p(n+n_ie^{E_t-E_i/kT})+\tau_n(p+n_ie^{E_i-E_t/kT})},
\]  

(2-9)

where \(n_i\) is the intrinsic carrier concentration with is equal to \(\sqrt{n_0p_0}\), and \(\tau_{p0}\) and \(\tau_{n0}\) are the hole and electron capture time constants due to recombination via bulk defects, respectively. These parameters are given by:

\[
\tau_{p0} = \frac{1}{\sigma_p v_{th} N_t},
\]

(2-10)

\[
\tau_{n0} = \frac{1}{\sigma_n v_{th} N_t},
\]

(2-11)

where \(\sigma_n\) and \(\sigma_p\) are the electron and hole capture cross sections, respectively, \(v_{th}\) is the thermal velocity of the charge carriers and \(N_t\) is the density of defects (i.e., traps) in the bulk material. For deep level defects (i.e., defects with energy levels near middle of \(E_g\)) at low-injection, the SRH carrier lifetime is equal to \(\tau_{n0}\) and \(\tau_{p0}\) in \(p\) and \(n\)-type materials, respectively, meaning the minority carrier lifetime dictates the recombination rate. Unlike Auger recombination, at high-injection levels the SRH carrier lifetime is larger than the low-injection case (i.e., slower recombination for large \(\Delta n\)). Additionally, at high-injection levels, SRH
recombination is no longer dependent on $\Delta n$ or the background doping concentration [63].

2.2.2.3 Surface Recombination

Finally, surface recombination occurs to the presence of surface states. Similar to bulk defects, these are allowed energy levels within the forbidden gap that present a disturbance in the crystal lattice. The primary reason is due to the non-saturated (i.e., “dangling”) bonds, but other reasons include chemical residues and metal impurities remaining on the surface during processing, as well as dislocations [63]. Again, as with bulk defects, SRH theory is applied to model this type of recombination. In this case, the net recombination rate due to surface defects ($U_{s,SRH}$) is defined as:

$$U_{s,SRH} = S \cdot \Delta n_s,$$  \hspace{1cm} (2-12)

Where $S$ is the surface recombination velocity and $\Delta n_s$ is the excess carrier concentration at the surface. The following equation provides more insight into $U_{s,SRH}$ [65]:

$$U_{s,SRH} = (n_s p_s - n_{ie}^2) \int_{E_V}^{E_C} \left( \frac{dE}{E_L - E_i} \right) \left( \frac{E_L - E_i}{s_{p0}(E)} + \frac{E_i - E_T}{s_{n0}(E)} \right),$$  \hspace{1cm} (2-13)

where $n_s$ and $p_s$ are electron and hole concentrations at the semiconductor surface (i.e., $n_s = \Delta n_s + n_{0s}$), $n_i$ is the so-called effective intrinsic carrier concentration (i.e,
\( \sqrt{n_{0s}p_{0s}} \), and \( S_{p0}(E) \) and \( S_{n0}(E) \) are the energy level dependent fundamental surface recombination velocity parameters for holes and electrons, respectively. Note that \( U_{s,SRH} \) must be determined by integrating from \( E_C \) to \( E_V \) due to the large number of defects present at surfaces resulting in a quasi-continuum of surface states [63]. \( S_{p0}(E) \) and \( S_{n0}(E) \) are given by the following:

\[
S_{p0}(E) = v_{th} D_{it}(E) \sigma_p(E),
\]

\[
S_{n0}(E) = v_{th} D_{it}(E) \sigma_n(E),
\]

where \( D_{it}(E) \) is the interface defect density, or the energy level dependent number of defects per unit area at the surface of the semiconductor, given in units of eV\(^{-1}\).cm\(^{-2}\). Because deep level defects have the strongest impact on recombination, \( D_{it}(E) \) is often reported as a single value at midgap \( (D_{it,midgap}) \) where \((E_t - E_i) = 0\). It should be noted that the shape of the defect density can also impact the resulting \( U_{s,SRH} \) in addition to \( D_{it,midgap} \) [65]. For surface recombination, a strong injection level dependence can be observed in the case asymmetrical capture cross sections (i.e., \( \sigma_n \neq \sigma_p \)) and/or band bending at the surface due to electric fields [63].

2.2.2.4 Effective Carrier Recombination Lifetime

The actual, or effective, carrier recombination lifetime \((\tau_{eff})\) is dependent on all of these recombination processes, as follows:
\[
\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_b} + \frac{1}{\tau_{s,\text{SRH}}},
\]

(2-16)

\[
\frac{1}{\tau_{\text{eff}}} = \left(\frac{1}{\tau_r} + \frac{1}{\tau_A} + \frac{1}{\tau_{b,\text{SRH}}}\right) + \frac{1}{\tau_{s,\text{SRH}}},
\]

(2-17)

where \(\tau_b\) is the carrier lifetime due to all recombination processes occurring in the bulk (i.e., not surface) of the wafer, \(\tau_{s,\text{SRH}}\) is the carrier lifetime due to surface recombination, \(\tau_r\) is the carrier lifetime due to radiative recombination (neglected in the case of Si), \(\tau_A\) is the carrier lifetime due to Auger recombination, and \(\tau_{b,\text{SRH}}\) is the carrier lifetime due to SRH recombination in the bulk of the wafer.

A large part of the energy conversion process is essentially a race to transport carriers to the cell junction and contacts before recombination occurs. This means that increasing \(\tau_{\text{eff}}\) is critical in maximizing energy collection from a solar cell. Minimization of both bulk and surface recombination is important elements of designing cells. Bulk recombination is driven primarily by doping levels, trace metal impurities, and crystallographic defects (e.g., dislocations), which depends on the quality of the material resulting from polysilicon production, crystallization, and wafering, and (to a lesser extent) gettering steps performed during cell processing (e.g., Fe gettering in multi-Si from POCl\(_3\) diffusion). Surface recombination in c-Si solar cells is reduced primarily using one or both of the following methods: (1) reducing \(D_{it}\) (i.e., chemical passivation); and reducing the number of electrons or holes at the surface using a “surface field” (i.e., field effect passivation). A reduction in \(D_{it}\) is accomplished by growing or depositing an
appropriate passivation film on the surface of the wafer, while field effect passivation is achieved by either doping the surface of the wafer to form back and front surface fields (BSF and FSF, respectively) or by using dielectric films that possess stable fixed electrostatic charges [63].

2.2.2.5 Saturation Currents

In addition to net recombination rates, carrier lifetimes, and surface recombination velocities, another way to express recombination is via saturation currents. The saturation current density of a cell \( J_0 \) has a strong impact on the efficiency of a solar cell. It is often useful to decouple the various contributions to the cell \( J_0 \) to better prioritize what improvements should be made to the cell. For example, one might break \( J_0 \) into front \( (J_{0f}) \), base \( (J_{0b}) \), and rear \( (J_{0r}) \) components, wherein the total \( J_0 \) is the sum of all three [66]. Within these three components, recombination currents can be further sub-divided to evaluate the contribution of different types of regions within each part of the cell, like passivated surfaces, metallized surfaces, and diffused regions (Figure 2-7). The emitter saturation current density \( (J_{0e}) \) is a particularly useful metric for evaluating the level of recombination in heavily doped regions and can be measured directly from symmetrically doped wafers [67-71]. Descriptions for all of the parameters shown in Figure 2-7 can be found in the LIST OF SYMBOLS.
2.2.3 Carrier Extraction and Equivalent Circuit Models

When charge carriers are successfully transported to the cell contacts they must then be extracted by an external electrical circuit. This is the load in which the cell is delivering power to. Various equivalent circuit models can be used to model the electrical characteristics of solar cells with varying degrees of complexity and sophistication. The simplest model considered in this work is the one diode model, which is governed by the Shockley ideal diode equation plus a photogenerated current component ($I_G$) [72]:

$$I = I_G - I_{01} \left( e^{\frac{qV}{kT}} - 1 \right), \quad (2-18)$$

where $I$ and $V$ are the current and voltage, respectively, at the terminal of the cell, $T$ is the temperature of the cell and $I_{01}$ is the saturation current. $I_i$ is essentially the
recombination current due to SRH recombination, wherein the ideality factor \((m)\) is equal to 1. It should also be noted that in the case of solar cells, it is common to express \(I-V\) equations in terms of current density \((J)\), as well as the other current terms \((J_G\) rather than \(I_G\) and \(J_{01}\) rather than \(I_{01}\)). This is to allow for an easier comparison of the performance of various cells with different physical dimensions. The \(J-V\) relationship for the ideal one diode model is given by the following equation:

\[
J = J_G - J_{01} \left( e^{\frac{qV}{kT}} - 1 \right). \tag{2-19}
\]

When finite series and shunt resistances \((R_S\) and \(R_{SH}\), respectively) are considered, \(J\) is given by the following equation, and a schematic is shown in Figure 2-8(a) [73]:

\[
J = J_G - J_{01} e^{\frac{q(V+JR_S)}{kT}} + \frac{V + JR_S}{R_{SH}}. \tag{2-20}
\]
Both $R_S$ and $R_{SH}$ can critically impact the fill factor (FF), and therefore $\eta$, of a solar cell. Ideally, $R_S = 0$ and $R_{SH} = \infty$, but this doesn’t happen in reality, so cell manufacturing processes must be optimized to reduce $R_S$ as much as possible and ensure $R_{SH}$ is large enough to not negatively impact $\eta$. Good process control can typically ensure a sufficiently large $R_{SH}$, and it normally doesn’t affect the FF. $R_S$ on the other hand is dependent on many different individual components [74] that must be optimized to ensure a maximum FF, and therefore $\eta$, is achieved.

When analyzing $J$-$V$ curves of actual c-Si solar cells, often a second diode with an ideality factor of 2 is added, as shown in Figure 2-8(b). This diode with $m = 2$ has been attributed to various mechanisms. McIntosh demonstrated that, in the case of c-Si solar cells, the cause of the $e^{qV/2kT}$ recombination current ($I_2$) is likely...
due to edge recombination and not depletion-region recombination as previously thought [73].

Note the exponential term is sometimes given as $e^{\frac{qV}{mKT}}$, where $m$ is the diode ideality factor. In this case, $m$ is varied and, often in the case of c-Si cells, will end up being something between 1-2, which multi-Si cells often featuring a larger $m$ than mono-Si cells. This model is shown schematically in Figure 2-8(c).

Finally, isolated regions of cells featuring resistance-enhanced recombination necessitate the need for an additional resistance component ($R_H$) and diode with a recombination current $J_H$ [75], as shown in Figure 2-8(d). This was initially proposed as a method of accounting for surface damage on textured emitters [75], but has since also been used to account for cell edge recombination, localized Schottky contacts, and grain boundaries (for multi-Si cells) [73].

Ultimately, these various modifications can allow for: more accurate modeling of the dark and illuminated $J$-$V$ characteristics of solar cells; and/or more useful information to be extracted from the data (e.g., which recombination mechanisms need to be addressed to increase $\eta$). While dark $J$-$V$ curves can be very useful in analyzing specific details about a solar cell, ultimately the illuminated $J$-$V$ curves are of the most importance, since they dictate the maximum power point and efficiency of the cell. A typical $J$-$V$ curve modeled using the one diode model is given in Figure 2-9 with some important cell parameters annotated including the open-circuit voltage ($V_{OC}$), $J_{SC}$, $P_{MP}$, as well as the current density and voltage at $P_{MP}$ ($J_{MP}$ and $V_{MP}$, respectively). This curve is representative of a typical, industry standard Al-BSF cell.
Figure 2-9. Simulated $J$-$V$ curve for a typical Al-BSF cell ($\eta \approx 18.4\%$) at STC. A one diode model with the following assumptions was used: $J_G = 37 \text{ mA-cm}^2$; $J_{01} = 840 \text{ fA-cm}^2$; $m = 1$; $R_{SH} = 10^4 \Omega$-cm$^2$; $R_S = 0.8 \Omega$-cm$^2$.

2.3 Advanced Cell Architectures

In the Al-BSF cell, an $n^+$ emitter is formed on the front (i.e., sunny) side of a $p$-type wafer, as shown in Figure 2-2. Emitter passivation is most commonly carried out using SiNx, since it can both lower the interface defect density ($D_{it}$) and deflect minority carriers (holes, in this case) through the presence of positive fixed charge ($Q_f$) at the dielectric/Si interface [76]. For the rear side of the cell, an Al-Si eutectic is formed during firing of the metal contacts, and this eutectic forms a $p^+$ BSF, which provides a moderate level of field effect passivation [77]. The typical $J_0$ contribution of an Al doped $p^+$ BSF ($J_{0BSF}$) is in the range of 400-700 fA-cm$^2$ [78]. Common Al-BSF cell efficiencies are around 18.4% in production [79].

Advanced c-Si cell architectures (i.e., non-Al-BSF) offer several pathways to increasing cell efficiency, and dielectric films play an important role for each. According to the most recent International Technology Roadmap for Photovoltaics
(ITRPV), the expected market share of advanced c-Si cell architectures is expected to grow substantially over the next decade, growing from less than 10% market share in 2013 to ≈85% by 2024 (Figure 2-10 [80]). Notable advanced architectures are described below and are broken into “evolutionary approaches” and “revolutionary approaches”, where the former represents a small change to existing cell manufacturing process flows and the latter requires significant changes. Selective emitters and rear passivated cells represent two primary evolutionary approaches gaining traction with industry and are often used together to increase cell efficiencies into the 20-22% range without increasing cost per $W_p$ compared to Al-BSF cells. Revolutionary approaches, like all back contact cells and silicon heterojunction cells, have demonstrated the ability to push efficiencies beyond 22%. However, currently these types of cells do significantly increase cell manufacturing cost and complexity and typically come at a higher cost per $W_p$ at the module and system level than Al-BSF cells.

![Figure 2-10. Expected market share for Al-BSF cells and advanced c-Si cell architectures over time, according to the most recent ITRPV, showing a dramatic shift from Al-BSF cells to higher efficiency cells [80].](image-url)
2.3.1 Evolutionary Approaches

2.3.1.1 Selective Emitter

Emitter formation requires a careful balance between reducing sheet resistance ($R_{\text{sheet}}$) to reduce contact resistance (and therefore $R_s$) and minimizing both Auger and SRH recombination in the emitter, which both increases at higher doping concentrations [81]. A selective emitter eliminates the need to compromise between contact resistance and SRH recombination by selectively doping regions underneath the front metal contacts at higher levels ($R_{\text{sheet}} \approx 30-50 \Omega/\square$) than the rest of the front side of cell ($R_{\text{sheet}} \approx 80-110 \Omega/\square$). This approach has been used for lab-scale solar cells for a long time, but has only recently begun to experience larger scale adoption by industry [79]. This approach is evolutionary in that it can still be applied to an Al-BSF cell, only now with locally doped regions on the front surface. It can therefore be relatively easily integrated into standard manufacturing lines and can provide cell manufacturers with a $\approx 0.5\%$ absolute increase in cell efficiency due to an increased $V_{\text{OC}}$ and better QE in the blue region. It should be noted though, depending on the spectral response of the encapsulation material used, some of the increased blue response might be lost when the cell is laminated within a module. Additionally, improved Ag paste formulations now make it possible to effectively contact emitters with high $R_{\text{sheet}}$ [82], which might reduce the value proposition of this technology.
2.3.1.2 Rear Passivated Cells

Rear passivated solar cells featuring front and rear side contacts come in a variety of forms, including the passivated emitter and rear cell (PERC), the passivated emitter and real totally diffused (PERT) cell and passivated emitter and rear locally diffused (PERL) cell, the latter of which was, until recently, the highest efficiency c-Si cell ever measured [38]. These cell architectures are quite similar to the Al-BSF cell, particularly p-type PERC (pPERC) cells, as shown in Figure 2-11. For these cells, rather than covering the entire rear with Al and forming a full area $p^+$ BSF, the rear side is covered with a passivating dielectric film and local openings are made in which the Al can then form a local BSF [83, 84]. Using this approach, the $J_0$ contribution of the rear side of the cell (which is a combination of recombination at the dielectric/Si interface and the local back contacts) can be drastically reduced leading to a boost in $V_{OC}$. Also, the increased internal back reflectance due to the low index dielectric increases the QE near the band edge (i.e., $J_{SC}$ increase). PERT and PERL cells feature a diffused rear side (either totally or locally), and though they are mostly of interest for $n$-type wafers, they can be applied $p$-type wafers as well [50, 51, 85]. As shown in Figure 2-10, rear passivated cells are expected to increase in market share from less than 5% in 2013 to nearly 50% in 2024, more than any other c-Si cell architecture.
It should be noted that both rear passivation schemes and selective emitters can be (and are) used together to increase cell efficiency.

2.3.2 Revolutionary Approaches

2.3.2.1 Back Contact Cells

Back contact (BC) cells come in a few different variations, most notable of which are emitter wrap-through (EWT), metal wrap-through (MWT), and back junction (BJ) cells [86], the latter of which are often referred to as interdigitated back contact (IBC) cells. There are various advantages to BC cells, but the most obvious is the elimination of shading from the bus bars placed on the front side of more conventional cells, which leads to a $J_{SC}$ enhancement of 5-10% [87]! While EWT and MWT technologies have had trouble gaining adoption by industry, the
world leader in producing high efficiency c-Si modules, SunPower, currently uses the IBC architecture in their high efficiency cells and modules [88].

![IBC Diagram]

Figure 2-12. Schematic of an interdigitated back contact (IBC) cell.

2.3.2.2 Silicon Heterojunction Cells

Another revolutionary approach to increase cell efficiency is through the use of a-Si:H films to both provide surface passivation and form a heterojunction emitter. A schematic for these silicon heterojunction (SHJ) cells, often referred to as heterojunction with thin intrinsic layer (HIT) cells, is given in Figure 2-13. The development of this technology by Panasonic has lead independently confirmed world record $V_{oc}$ values approaching 750 mV, compared to 721 mV for the 24.2% efficient SunPower IBC cell and 706 mV for the world record holding 25.0% efficient PERL cell [38].
2.3.2.3 Hybrid Cell Designs

A new development in the PV industry is the recent announcement of an independently confirmed world record of 25.6% for c-Si solar cells achieved by Panasonic [89]. For this new cell, Panasonic has merged the $J_{SC}$ advantage of back contacted cells with the $V_{OC}$ advantage of SHJ cells by creating a hybrid back contacted SHJ cell.

Figure 2-13. Schematic of a silicon heterojunction (SHJ) cell.
CHAPTER 3 - ATMOSPHERIC PRESSURE CHEMICAL VAPOR DEPOSITION

3.1 Introduction

Thin film deposition processes are used in numerous applications, from manufacturing integrated circuits and optoelectronic devices to the use of protective surface coatings in mechanical components (e.g., drill bits, automotive parts). For a more comprehensive list of thin film applications, see [90]. Thin solid films play an important role in manufacturing all types of solar cells (not just thin film solar cells, which is perhaps the most obvious application). Thin films have many functions in c-Si cells. Examples of important functionalities include reducing carrier recombination, reducing optical losses, acting as dopant sources and masking layers during manufacturing, and forming contact layers. This chapter is focused on the actual deposition processes of interest to c-Si cell manufacturing, in particular atmospheric pressure chemical vapor deposition.

There are many ways to group and classify the various processes used to deposit thin films. Three commonly used classifications are: (1) physical vapor deposition (PVD); (2) chemical vapor deposition (CVD); and (3) liquid phase deposition (LPD). PVD methods are very common in integrated circuit and optoelectronic device manufacturing and include thermal evaporation and sputtering. In both PVD and CVD processes, a vapor is used to transfer material from one or more sources to a growth/deposition surface to form the thin solid film [91]. To better control the characteristics of the vapor, these processes are often performed in vacuum chambers. The primary difference for CVD processes is that
a chemical reaction using volatile chemical precursors is used to form the nonvolatile thin solid film. In LPD, a liquid is used for material transference. This broad category includes plating (e.g. electroplating, electroless plating), as well as depositing a sol-gel or a colloidal solution (e.g., via spin-coating, spraying, or inkjet printing) and then exposing that material to a thermal treatment. An attractive feature of LPD methods, like sol-gel films, is that it eliminates the need for costly vacuum system used in most PVD and CVD processes. However, the resulting material properties and film characteristics (e.g., purity, thickness, uniformity) are typically inferior to that of PVD and CVD films.

3.2 Overview of Chemical Vapor Deposition Technology

3.2.1 Components of a CVD System

A CVD system can typically be broken up into the following three components [90]: (1) precursor delivery; (2) the CVD reactor; and (3) exhaust management.

3.2.1.1 Precursor Delivery

The role of the precursor delivery system is to transport the appropriate quantity and composition of gas phase reactants to the CVD reactor, which is where the deposition takes place. The precursors used in CVD processes can come in the form of gases, liquids, and solids, so the delivery system must also convert liquid and solid materials to gas phase reactants when they are used. For liquids and solids, the delivery system must either directly heat the materials to the boiling or sublimation point, respectively, or apply heat and supply an inert carrier
gas to convert and transport these materials to the reactor. For liquid phase precursors, bubblers are used to create the desirable vapor pressure via heat and supply the carrier gas, which results in delivery of a diluted precursor to the reactor, as shown in Figure 3-1 [92]. The molar flow rate for a bubbler-based delivery system can be calculated based on the total pressure, vapor pressure of the liquid precursor, and volumetric flow rate of the carrier gas [92]. The temperature-dependent vapor pressure of the liquid precursor is a critical parameter during the materials selection process. In some cases, reactants can also be generated in situ within the gas dispensing system (e.g., Al reacting with HCl to form AlCl$_3$, the desired reactant for some aluminum oxide CVD processes) [90]. Gas flows are commonly measured with mass flow controllers, which provide excellent accuracy and can be integrated into the control system of the CVD tool.

![Figure 3-1](image)

**Figure 3-1.** Schematic of a bubbler system used in CVD processes to convert liquid phase precursors to a diluted vapor and deliver the vapor to the reactor. Adapted from [92].
3.2.1.2 Reactor

The CVD reactor is where the actual deposition takes place. Here, the reactants encounter the substrate on which they will react. Gas transport to the substrate is dictated in large part to the reactor design and is a very important component in controlling film uniformity, deposition rates, and precursor utilization efficiencies [93]. Two common categories of CVD reactors include hot wall and cold wall reactors.

In hot wall reactors, the substrate and the reactor wall are at comparable temperatures [90]. Film growth takes place on the walls, which can cause powders and flakes to break off and fall onto the substrate. Homogeneous vapor phase reactions are also common in this type of reactor. Depletion of reactant from the gas entrance to exit can also occur, potentially impacting batch uniformity. However, these types of reactors lend themselves well to batch processing and are rather simple to implement.

In cold wall reactors, the substrate is at a significantly higher temperature than the wall of the reactor. Deposition on the walls and homogeneous reactions in the vapor phase are minimized and the importance of reactions at the substrate surface is increased. Large temperature gradients near the substrate can impact gas flow and cause non-uniform depositions (in terms of thickness and microstructure), which is why much care and attention must be given to gas flow dynamics in these systems.
3.2.1.3 Exhaust Management System

Finally, the exhaust management system includes the vacuum pumps, sensors, and control systems needed to maintain the desired total pressure of the system [90]. It also includes the appropriate scrubbers and abatement systems to dispose of potentially harmful materials.

3.2.2 Types of CVD Processes

There are a large variety of different CVD processes that can be categorized in many different ways. Below are five different CVD processes worth noting due to their use in PV manufacturing and R&D.

1. Atmospheric pressure chemical vapor deposition (APCVD): As the name suggests, APCVD processes occur at atmospheric pressure (i.e., 1 atmosphere = 101,325 Pa = 760 Torr). APCVD is compatible with vacuum-free, continuous in-line processes, making it very attractive for cost sensitive, high volume manufacturing applications like PV cell manufacturing.

2. Low pressure chemical vapor deposition (LPCVD): In LPCVD processes, vacuum systems are used to pump the chamber down to low pressure. This aids mass transport to the growth substrate and results in for uniform films with fewer defects [93], at the expense of adding cost and complexity.

3. Metal organic chemical vapor deposition (MOCVD): The name MOCVD refers to the type of precursors used during the deposition. Metal organic compounds are comprised of metals and organic ligands and are typically liquid phase at room temperature and atmospheric pressure. A bubbler
system (Figure 3-1) is typically used to deliver vapor phase metal organic precursors to the reactor. MOCVD processes are most often associated with the epitaxial growth of compound semiconductors for optoelectronic devices. However, MOCVD processes are also used in the deposition of metals and metal oxides for other applications [93].

4. Plasma enhanced chemical vapor deposition (PECVD): In PECVD processes, a glow-discharge plasma is used to decompose gas molecules into reactive species allowing for CVD reactions to occur at much lower temperatures than traditional thermal CVD processes [93]. One of the most common PECVD processes is the deposition of SiNx using silane (SiH₄) and ammonia (NH₃), a process used in both integrated circuit and PV cell manufacturing.

5. Atomic layer deposition (ALD): ALD is a type of CVD process that relies on introducing the chemical reaction partners (i.e., precursors) one at a time, alternating between each to allow for deposition in a self-limiting way [94]. This layer-by-layer deposition process provides improved control of thickness, uniformity, and composition of the deposited film. This improvement comes at the expense of throughput, since ALD processes are often associated with very low deposition rates.

3.3 Dynamic In-Line APCVD of Oxide Films

In this work, a dynamic in-line APCVD system manufactured by SCHMID Thermal Systems, Inc. (STI), formerly SierraTherm, Inc., is utilized. N₂-diluted precursors are delivered to a CVD injector zone that is separated from the rest of
the system by N₂ gas curtains, as shown in Figure 3-2. Because the deposition is performed at atmospheric pressure and the CVD injectors are separated, multiple CVD injectors can be included in one system allowing for multi-layer films to be deposited within a single process run.

Figure 3-2. Diagram highlighting the dynamic in-line APCVD process used in this work, with aluminum oxide being the example.

The primary single-lane system used in this work, shown in Figure 3-3(a), features a continuously moving Ni alloy (Inconel 601) belt that transports the wafers through preheating zones followed by three N₂ isolated CVD injectors. A newer high-throughput model featuring five-lanes and a ceramic roller transport system was also utilized in this work, to a lesser extent, and is shown in Figure 3-3(b). In the past, these types of system were primarily used in integrated circuit applications to deposit SiOₓ and doped SiOₓ using N₂-diluted SiH₄ and O₂ or tetraethoxysilane (TEOS) and O₃ as precursors [95-97]. However, both systems can also deposit metal oxide films using metal organic compounds delivered via a bubbler system.
Figure 3-3. The two STI APCVD systems used in this work: (a) the single-lane belt APCVD system featuring three CVD injectors (primary system used in this development effort); and (b) the five-lane ceramic roller APCVD system with two CVD injectors.

The following sections provide a description of the materials deposited and investigated in this work and the specific functions they can perform in c-Si solar cells. An overview is given in Table 3-1.

Table 3-1. Overview of the oxide materials explored in this work and how they can be used in c-Si solar cells.

<table>
<thead>
<tr>
<th>Oxide Material</th>
<th>Functions within c-Si Solar Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon oxide (SiOₓ)</td>
<td>• Intermediate rear reflector in rear passivated cells</td>
</tr>
<tr>
<td></td>
<td>• Capping layer during doping processes</td>
</tr>
<tr>
<td>Phosphosilicate glass (PSG)</td>
<td>• Phosphorus dopant source</td>
</tr>
<tr>
<td>Borosilicate glass (BSG)</td>
<td>• Boron dopant source</td>
</tr>
<tr>
<td>Titanium oxide (TiOₓ)</td>
<td>• Optical coating in single and double layer ARC structures</td>
</tr>
<tr>
<td></td>
<td>• Capping layer in rear passivated cells to protect the passivation layer from the Al during firing</td>
</tr>
<tr>
<td>Aluminum oxide (AlOₓ)</td>
<td>• Surface passivation for p-type surfaces at any doping level and for lightly doped n-type surfaces (i.e., undiffused)</td>
</tr>
<tr>
<td></td>
<td>• Top layer ARC in double layer ARC structures</td>
</tr>
<tr>
<td>Boron doped aluminum oxide (AlOₓ:B)</td>
<td>• Boron dopant source and surface passivation layer</td>
</tr>
</tbody>
</table>

3.3.1 Silicon Oxide

The deposition of SiOₓ by APCVD has been studied extensively, particularly within the integrated circuit R&D community. Perhaps the most common process
uses SiH₄ and O₂ as precursors at a substrate deposition temperature ($T_{dep}$) of ≈400-450°C [94, 95]. With the appropriate precursor gas ratio (O₂ to SiH₄), this results in a near stoichiometric SiO₂ film. This is the primary process used in this work, resulting in SiOₓ films ($x \approx 2$) with identical optical properties to SiO₂. In this work, intrinsic SiOₓ is used as an intermediate rear reflector layer for rear passivated cells and as a capping layer during doping processes to prevent the escape of phosphorus and boron atoms.

3.3.2 Phosphosilicate Glass

Phosphosilicate glass (PSG) films, or phosphorus-doped SiOₓ films, can be deposited by adding phosphine (PH₃) to the process described above for SiOₓ. The phosphorus concentration within APCVD PSG films is highly controllable, and because the dopant drive-in is performed ex situ, it lends itself to well to localized doping techniques (e.g., mask and etch processes before drive-in). In this work, PSG is used as a dopant source to form high quality $n^+$ emitters for $p$-type cells.

3.3.3 Borosilicate Glass

Borosilicate glass (BSG) films are similar to PSG in that they can be formed by adding a dopant-containing hydride (diborane in this case, B₂H₆) to the process above for SiOₓ consisting of SiH₄ and O₂ precursors. And similar to PSG, the boron concentration within these silicate films is highly controllable. In this work, BSG is considered as a boron dopant source for c-Si solar cells. This is especially of interest in the formation of $p^+$ emitters in $n$-type cell architectures.
3.3.4 Titanium Oxide

To deposit titanium oxide (TiO\textsubscript{x}), tetraisopropyl titanate (TPT) and H\textsubscript{2}O are used as precursors. Since TPT is a metal organic precursor, this may be considered an AP-MOCVD process, however, it will continue to be referred to as an APCVD process for simplicity. A wide range of temperatures were investigated in this work ($T_{\text{dep}}$ from $\approx$250-570°C), leading to films with different optical properties due to a phase change from amorphous to polycrystalline (anatase) at around 300°C. Precursor gas ratios (H\textsubscript{2}O to TPT) were varied and found to have an impact on the deposition rate, but minimal impact on the optical properties. This is particularly useful for single and double ARC structures in c-Si solar cells. Another application for TiO\textsubscript{x} considered is its use as a capping layer for rear passivating cells, to protect the underlying passivation material from the Al contact layer upon firing.

3.3.5 Aluminum Oxide

The process for depositing aluminum oxide (AlO\textsubscript{x}) in this work uses trimethylaluminum (TMA) and O\textsubscript{2} at a $T_{\text{dep}}$ $\approx$500°C at varying precursor gas ratios (O\textsubscript{2} to TMA). As with TiO\textsubscript{x}, this is technically an AP-MOCVD process. In this work, AlO\textsubscript{x} is primarily used as a surface passivation material, due to the incredibly low effective surface recombination velocities demonstrated on $p$ and $n$-type wafers of varying resistivities. However, heavily doped (i.e., diffused) $n$-type surfaces, like $n^+$ and $n^{++}$ emitters and BSFs, are not compatible with AlO\textsubscript{x} passivation due to the polarity of the large fixed charge at the AlO\textsubscript{x}/Si interface. AlO\textsubscript{x} is also used as the top layer in double layer ARC structures in this work.
3.3.6 Boron-Doped Aluminum Oxide

To deposit boron doped AlO$_x$ (AlO$_x$:B) films, B$_2$H$_6$ is added to the process above for AlO$_x$. These films are considered as potential BSG replacements for boron doping, with potential applications for both $p$ and $n$-type cells. AlO$_x$:B is of particular interest due to its ability to potentially operate as a multi-functional film, acting as both a dopant source and surface passivation layer.
CHAPTER 4 - ANTI-REFLECTION COATINGS USING APCVD OXIDE FILMS

4.1 Introduction

Dielectric films have long been used in c-Si solar cells to reduce reflection at the front surface ($R_{ext}$ in Figure 2-3). As mentioned previously, the PV industry is predominantly using a ≈75 nm layer of SiN$_x$ deposited by PECVD as a front side ARC. Titanium oxide (TiO$_2$ or TiO$_x$) was commonly used in the past, but was displaced due to its inability to provide effective surface passivation unless accompanied by an oxidation step [98]. When used simply as an optical layer, though, TiO$_x$ has advantages over SiN$_x$, the primary one being cost since it is compatible with non-vacuum deposition processes like APCVD [55]. Similar to SiN$_x$, the refractive index can be tuned by modifying the process parameters, allowing for low cost implementation of double layer ARCs (DLARC) with improved broadband performance [55].

Unlike high index SiN$_x$ films, however, which suffer from significant absorption in the blue region [54], TiO$_x$ can potentially achieve a high index with minimal absorption, which can enable effective DLARCs using a thin passivation film (≈5-20 nm thick). To realize this, either two TiO$_x$ ARCs can be used, the bottom film featuring a higher index polycrystalline TiO$_x$ (pc-TiO$_x$) film deposited at a higher deposition temperature ($T_{dep} > 300^\circ$C) followed by an amorphous TiO$_x$ (a-TiO$_x$) film (i.e., single material DLARC [55]), or pc-TiO$_x$ paired with another lower index material like SiO$_x$ or, better yet, AlO$_x$ [99].
In this chapter, the focus is on reducing the front surface reflectance of anisotropically textured mono-Si solar cells using oxide-based DLARC structures formed using APCVD. To accomplish this, changes in the optical properties of the APCVD TiO$_x$ films are investigated and exploited. Conventional single layer SiN$_x$ ARC and oxide-based DLARC structures featuring intermediate passivation layers are modeled and fabricated. Simulated and experimental reflectance data is presented for unencapsulated ARCs and simulated data for encapsulated ARCs. Two of the four oxide-based DLARC structures outperform SiN$_x$ in the unencapsulated case, and all four outperform SiN$_x$ in the simulated encapsulated case. These front side DLARCs can be used in any cell architecture compatible with an oxide-passivated emitter, including Al-BSF, $p$PERC, nPERT, and nPERT (Figure 4-1), as well as IBC cells.
Figure 4-1. Cross-sectional diagrams highlighting (in red) how oxide-based DLARCs can be applied to Al-BSF, pPERC, nPERT, and nPERL cells to reduce front surface reflectance.

The majority of the work in this chapter is from [100].

4.2 Modeling Methodology

Anisotropically textured mono-Si cells are the focus of this work. Random upright pyramids formed by the anisotropic etching result in a characteristic base angle that is commonly assumed to be 54.74°, but in actuality is around 50-52° for industrial cells [101]. To model the transmission of light into the wafer from incident media (e.g., air, polymeric encapsulation), accounting for front surface reflectance and optical absorption in the front side passivation layer and/or ARC(s), the freeware program OPAL 2 is used [53].
To simulate the reflectance of the ARC structures with some confidence, reliable optical models for each of the films used is required. All of the amorphous films explored in this work (i.e., SiN$_x$, AlO$_x$, SiO$_x$, and a-TiO$_x$) can be modeled as single thin films, as shown for a-TiO$_x$ in Figure 4-2(a). Rough and/or porous films, like pc-TiO$_x$, can be slightly more complicated to model, but can be accounted for by using two separate layers in the model (Figure 4-2(b)): a dense TiO$_x$ film on the bottom (nearest the underlying Si substrate) and a porous top layer modeled using an Bruggeman effective medium approximation (EMA) [55]. This enables the extraction of the complex refractive index of pc-TiO$_x$ films from spectroscopic ellipsometry measurements and allows for TMM calculations of reflectance, transmittance, and absorption to be performed.

Experimentally measured complex refractive index values for the a-TiO$_x$, pc-TiO$_x$, and rough EMA layer are used within OPAL 2 to design and optimize the oxide-based DLARC structures. Published $n$ and $k$ values are used for the SiO$_x$/SiO$_2$ [102], SiN$_x$ [54], and AlO$_x$ films [103], upon successful comparison with experimentally measured values from the films used in this work. Optical losses are converted into the amount of photogenerated current lost due to front surface
reflectance ($J_R$) and parasitic absorption within the ARC(s) ($J_A$) using equations (2-4) and (2-5), respectively, using the methodology from [53] and assumptions outlined in section 2.2.1.

4.3 Experimental Details

The processes described in section 3.3 are used to deposit a-TiO$_x$, pc-TiO$_x$, AlO$_x$, and SiO$_x$, and TiO$_x$ films via APCVD, and a standard batch PECVD process was used for the SiN$_x$ films. APCVD SiO$_x$ films ($x \approx 2$) are used as substitutes for thermal SiO$_2$ passivation layers in the optical experiments. The APCVD films are indistinguishable optically from thermal SiO$_2$ layers even though they don’t provide the same level of surface passivation in the as-deposited state.

Polished Si wafers are used for spectroscopic ellipsometry measurements and materials characterization, while anisotropically textured wafers are used for reflectance measurements. Four different oxide-based DLARC structures with intermediate oxide passivation layers are investigated in this work, as well as a reference group consisting of a single $\approx$75 nm layer of PECVD SiN$_x$ (Figure 4-3).
Figure 4-3. Illustrations of the four different multi-layer oxide film stacks investigated in this work and the SiN$_x$ single-layer ARC reference case used as a benchmark. Note that two of the groups feature a SiO$_2$ passivation layer and two an AlO$_x$ passivation layer.

Ellipsometry measurements are carried out using a SENTECH SE800 PV spectroscopic ellipsometer and a SENTECH SE400 laser ellipsometer ($\lambda = 632.8$ nm). Reflectance measurements are performed using a Cary 5000 spectrophotometer with integrating sphere and calibrated reflectance standards. Reflectance was measured for wavelengths relevant to c-Si solar cells ($\lambda \approx 380$-1200 nm). Cross-sectional Transmission Electron Microscopy (TEM) has been performed using a FEI Tecnai F30 TEM, with sample preparation carried out with a FEI 200 TEM Focused Ion Beam (FIB).
4.4 Results and Discussion

4.4.1 Optical and Microstructural Properties of APCVD Titanium Oxide

A change in the crystal structure from amorphous to polycrystalline (anatase phase) occurs in TiO\textsubscript{x} thin films at deposition temperatures \((T_{\text{dep}})\) around 300°C [55]. The \(n_{\text{TiO}}(\lambda)\) and \(k_{\text{TiO}}(\lambda)\), measured using spectroscopic ellipsometry, for both a-TiO\textsubscript{x} and pc-TiO\textsubscript{x} are given in Figure 4-4. Absorption coefficients calculated from \(k_{a,TiO}\) and \(k_{TiO}\) indicate little to no absorption within the TiO\textsubscript{x} films for \(\lambda > 380\) nm, which is very important in the effort to minimize parasitic optical losses as much as possible.

![Graph showing refractive index (n) and extinction coefficient (k) for a-TiO\textsubscript{x} (T\textsubscript{dep} = 250°C) and pc-TiO\textsubscript{x} (T\textsubscript{dep} = 400°C).](image)

Figure 4-4. Refractive index \(n\) and extinction coefficient \(k\) for a-TiO\textsubscript{x} \((T_{\text{dep}} = 250^\circ C)\) and polycrystalline TiO\textsubscript{x} \((T_{\text{dep}} = 400^\circ C)\) given as a function of \(\lambda\).

The assumption of a fixed EMA fraction \(f_{\text{EMA}}\) of 0.5 for air to TiO\textsubscript{x} (i.e., half air, half TiO\textsubscript{x}) has been used (a larger \(f_{\text{EMA}}\) means a larger fraction of air than TiO\textsubscript{x} and vice versa) due to concerns that varying \(f_{\text{EMA}}\) could lead to nonphysical results.
during the analysis of the measured ellipsometry data [55]. In this work however, it was found that varying $f_{EMA}$ was actually indicative of a trend in the film microstructure, as shown in the cross-sectional TEM images of TiO$_x$ films in Figure 4-5. As expected, the a-TiO$_x$ films, shown in Figure 4-5(a), exhibit no rough surface layer ($f_{EMA} = 0$). For the pc-TiO$_x$ films, larger $f_{EMA}$ values and larger ratios of the EMA layer thicknesses ($d_{EMA}$) to dense TiO$_x$ layer thicknesses ($d_{TiO_x}$) were found as $T_{dep}$ is increased. The observation appears to be substantiated by the TEM images shown in Figure 4-5(b), (c). The rougher, more columnar structure for the film deposited at 570°C compared to the one at 400°C is due to the change in nucleation during growth/deposition.

(a) Amorphous TiO$_x$
$T_{dep} = 250^\circ$C, $f_{EMA} = 0$

(b) Polycrystalline TiO$_x$ (anatase)
$T_{dep} = 400^\circ$C, $f_{EMA} = 0.44$

(c) Polycrystalline TiO$_x$ (anatase)
$T_{dep} = 570^\circ$C, $f_{EMA} = 0.57$

Figure 4-5. Cross-sectional TEM images of: (a) amorphous TiO$_x$ samples ($T_{dep} = 250^\circ$C) showing no rough EMA layer ($f_{EMA} = 0$); (b) polycrystalline TiO$_x$ (anatase) samples deposited at $T_{dep} = 400^\circ$C ($f_{EMA} = 0.44$); and (c) polycrystalline TiO$_x$ (anatase) samples deposited at $T_{dep} = 570^\circ$C showing a thicker, rougher EMA layer ($f_{EMA} = 0.57$) due to more columnar growth during the CVD process.

4.4.2 Double Layer Anti-Reflection Coatings

For a single layer ARC, the optimum refractive index ($n_{ARC}$) is given by the following equation:

$$n_{ARC}^2(\lambda) = n_0 \cdot n_{Si}(\lambda),$$  \hspace{1cm} (4-1)
where $n_0$ is the refractive index of the incident medium and $n_{Si}$ is the refractive index of Si. For a DLARC, the optimal refractive indices of the top ($n_{ARC, top}$) and bottom ($n_{ARC, bot}$) ARCs are [55, 104]:

$$n_{ARC, top}^3(\lambda) = n_0^2 \cdot n_{Si}(\lambda),$$  \hspace{1cm} (4-2)

$$n_{ARC, bot}^3(\lambda) = n_0 \cdot n_{Si}^2(\lambda).$$  \hspace{1cm} (4-3)

The progression of refractive indices from the incident medium to the Si wafer is $n_{Si} > n_{ARC, bot} > n_{ARC, top} > n_0$ [55]. Figure 4-6 shows how close some of the materials discussed in this work come to the ideal values calculated from equations (4-2) and (4-3) for the case of an unencapsulated cell ($n_0 = 1$).
Figure 4-6. Refractive index as a function of wavelength for Si, air, the oxide materials of interest in this work (pc-TiO\textsubscript{x}, a-TiO\textsubscript{x}, AlO\textsubscript{x}, SiO\textsubscript{2}), along with that of the ideal top and bottom ARCs calculated from Equations 5 and 6 for an unencapsulated cell ($n_0 = 1$).

Clearly, the pc-TiO\textsubscript{x} films is an excellent match with $n_{ARC,bot}$, while both AlO\textsubscript{x} and SiO\textsubscript{2} are well matched to $n_{ARC,top}$. SiO\textsubscript{2} is commonly used as a top layer ARC for reducing reflectance in unencapsulated cells tested in air, but it is known that any benefit of this second ARC would be eliminated in the encapsulated case since the refractive index of SiO\textsubscript{2} is less than 1.5. AlO\textsubscript{x}, on the other hand, has a refractive index slightly greater than 1.5 meaning the $n_{ARC,top} > n_0$ condition still holds. A similar plot of $n$ vs. $\lambda$ is given for the encapsulated case ($n_0 = 1.5$) in Figure 4-7. The increase in $n_0$ results in an increase in $n_{ARC,bot}$ and $n_{ARC,top}$. In this case,
pc-TiO$_x$ is still best suited for the bottom ARC, but it isn’t as well matched in the encapsulated case. For the top ARC, a-TiO$_x$ is a perfect match to $n_{ARC,top}$.

![Figure 4-7](image-url)

Figure 4-7. Refractive index as a function of wavelength for Si, glass/EVA, the oxide materials of interest in this work (pc-TiO$_x$, a-TiO$_x$, AlO$_x$, SiO$_2$), along with that of the ideal top and bottom ARCs calculated from Equations 5 and 6 for an encapsulated cell ($n_0 = 1.5$).

The reflectance of four different oxide-based film stacks was measured in this work, as well as a reference group featuring a single ≈75 nm layer of PECVD SiN$_x$ (Figure 4-3). Each of the oxide films stacks investigated features a thin, intermediate passivation layer, which in this case could be a thermally grown SiO$_2$ layer or an AlO$_x$ film. They are therefore all compatible with cell designs consisting of well-passivated front surfaces (e.g., Al-BSF, $p$PERC, $p$PERL, nPERT, nPERL,
IBC cells). These four film stacks, all deposited on anisotropically textured wafers (i.e., alkaline chemical treatment), include:

(I) 10 nm SiO$_2$ passivation layer followed by a pc-TiO$_x$ film then an a-TiO$_x$ film (i.e., pc-TiO$_x$/a-TiO$_x$ DLARC);

(II) 10 nm SiO$_2$ passivation layer followed by a pc-TiO$_x$/AlO$_x$ DLARC;

(III) 20 nm AlO$_x$ passivation layer followed by a pc-TiO$_x$/a-TiO$_x$ DLARC; and

(IV) 10 nm AlO$_x$ passivation layer followed by a pc-TiO$_x$/AlO$_x$ DLARC.

While an intermediate low index passivation layer is known to slightly reduce the performance of an ARC stack, Figure 4-8 clearly shows the APCVD DLARC stacks deposited onto the AlO$_x$ and SiO$_2$ passivation films perform quite well compared to a single SiN$_x$ ARC. In fact, the pc-TiO$_x$/AlO$_x$ DLARCs outperform SiN$_x$ when unencapsulated.
Figure 4-8. Results of reflectance measurements comparing the standard SiN\(_x\) single-layer ARC to the following: (a) two SiO\(_2\) passivated stacks; and (b) two AlO\(_x\) passivated stacks. In both cases, the pc-TiO\(_x\)/AlO\(_x\) DLARCs outperform the SiN\(_x\) reference. The sharp increase at \(\lambda \approx 1000\) nm is due to light internally reflected from the rear side (i.e., escape reflectance).

Figure 4-9 shows \(J_G\), \(J_R\), and \(J_A\) for all five structures calculated from Equations 1-3. In the unencapsulated case, all five enable a maximum \(J_G\) of \(\geq 42.5\) mA-cm\(^{-2}\), meaning the sum of the losses due to front surface reflectance and parasitic absorption within the ARC are \(\leq 1.5\) mA-cm\(^{-2}\). Knowing the reflectance of unencapsulated ARCs is useful and can be measured rather conveniently. However, in a deployed PV system c-Si solar cells are encapsulated into modules.
using glass and transparent polymeric materials (e.g., EVA), which changes the
refractive index directly above the cells surface (i.e., $n_0 \neq 1$). Based on equations
(4-1)-(4-3), the higher refractive index of EVA compared to air increases the
optimal refractive indices of single-layer ARCs and both the top and bottom films
in DLARCs, as shown in Figure 4-7. Figure 4-9 also shows $J_G$, $J_R$, and $J_A$ calculated
for the encapsulated case using OPAL 2. For these modeled structures, the
thicknesses of the oxide-based DLARC layers were optimized to maximize $J_G$. All
four structures outperform the standard SiN$_x$ ARC, although by a small amount in
each case. Based on Figure 4-7, it may be surprising that the pc-TiO$_x$/AlO$_x$ perform
slightly better than the pc-TiO$_x$/a-TiO$_x$. The reason for this is the finite absorption
of the a-TiO$_x$ films limits the thickness, whereas the AlO$_x$, with negligible absorption
throughout the solar spectrum, can be made thicker allowing it to be used for
destructive interference (i.e., $\lambda/4$) with longer wavelengths.
In this work, the optical and microstructural properties of TiO\text{x} films deposited by in-line APCVD have been investigated by spectroscopic ellipsometry and cross-sectional TEM imaging. A modified optical model for pc-TiO\text{x} films has been proposed wherein the EMA fraction is permitted to act as a variable rather than being fixed at 0.5. This modification allows for improved understanding of the film properties for various deposition conditions, which can be used during process optimization.

Figure 4-9. Calculated $J_A$, $J_R$, and $J_A$ for the SiN\text{x} reference and all four oxide-based DLARCs both for the unencapsulated and encapsulated cases.

4.5 Summary
All-oxide DLARC structures have been fabricated on textured Si wafers featuring a thin (10-20 nm) SiO$_x$ or AlO$_x$ film, meant to simulate either a thermal SiO$_2$ or ALD/CVD AlO$_x$ passivation layer. Low broadband reflectance has been demonstrated experimentally with these oxide-based DLARCs. The pc-TiO$_x$/AlO$_x$ DLARCs are experimentally shown to outperform a traditional SiN$_x$ ARC for unencapsulated cells, and optical modeling of encapsulated structures shows that all four oxide-based DL ARCs can outperform SiN$_x$ if packaged within a module. These results offer significant promise as a low cost in-line solution for front side ARCs, particularly for cell architectures featuring a thin thermal SiO$_2$ passivation layer or n-type wafers with AlO$_x$ passivated $p^+$ emitters. The possibility of using APCVD AlO$_x$, which provides excellent surface passivation (see sections 6.1-6.4), followed by an APCVD DLARC is particularly interesting since a three layer film can be deposited in one process run with this in-line APCVD technique.
CHAPTER 5 - IMPROVED LIGHT TRAPPING USING APCVD OXIDE FILMS

5.1 Introduction

As previously mentioned, one of the advantages of rear passivated cells is the increased internal back reflectance when compared to Al-BSF cells. The internal back reflectance of cells of Al-BSF is actually lower than one might expect from an Al/Si interface. This is because the Al pastes used and the resulting Al-Si eutectic formed following screen printing and contact firing are quite different than an abrupt pure Al layer in contact with the Si wafer (see Figure 5-1) [105, 106]. Even when PVD Al is used, which is essentially pure Al in the as deposited state, the composition changes upon firing due to diffusion of Si atoms into the Al contact layer resulting in a reduction in internal back reflectance [107].

![Figure 5-1. Model of an actual Al-BSF cell’s rear side. Taken with permission from [105].](image)

Rear passivated devices feature a dielectric layer on the majority of the back side of the cell, as shown in the optical model in Figure 5-2. The two primary materials used, thermal silicon oxide (SiO\textsubscript{2}) and aluminum oxide (AlO\textsubscript{x}), both have
relatively low refractive indices compared to Si. This results in a higher internal back reflectance, which improves the QE of these cells near the band edge [60]. This improvement in the long-\(\lambda\) QE can increase \(J_{SC}\) by \(\approx 1.1\) to \(1.8\) mA cm\(^{-2}\) [83, 84, 108-110].

Figure 5-2. Optical model for PERC and PERL cells [52]. Note this model is similar for PERT cells, but FCA within the full area BSF should be considered.

Often in \(p\)PERC or \(p\)PERL cells, a capping layer is used to prevent the Al contact layer from firing through the rear side dielectric (inadvertently creating an Al-BSF cell!). While SiN\(_x\) has often been used in the past [83, 84, 111, 112], it has recently been proposed that the use of a thicker low index passivation layer or a low index capping layer (e.g., SiO\(_x\)) should be used to ensure a high IBR [59, 113-116]. Using an 8 nm AlO\(_x\) passivation layer, Bullock \textit{et al.} used 2D optical
simulations to predict a 0.125 mA·cm$^2$ increase in $J_{SC}$ for low index, spin coated SiO$_x$:H and AlO$_x$SiO$_y$:H films as capping layers compared to SiN$_x$. Using experimental data on $p$PERL cells, Cornagliotti et al. have shown an increase in both internal back reflectance and $J_{SC}$ when using either a SiO$_x$ capping layer or intermediate SiO$_x$ layer between the AlO$_x$ passivation film and SiN$_x$ capping layer [117].

The work in this chapter focuses how capping layers deposited on top of a thin passivation influence internal back reflectance. This work is relevant to any rear side passivated cell architecture, including $p$PERC, nPERT, and nPERT (Figure 5-3), as well as IBC cells, but is aimed primarily at $p$PERC cells.

Figure 5-3. Cross-sectional diagrams highlighting (in red) how oxide-based rear reflectors can be applied to $p$PERC, nPERT, and nPERL cells to improve light trapping.
The majority of the work in this chapter is from [59, 118].

5.2 Modeling Methodology

The basic optical model used in this work (Figure 5-2) is inspired by the popular model introduced by Basore to determine an aggregated internal back reflectance value \( R_i \) from internal quantum efficiency measurements (IQE) of c-Si solar cells [52]. The focus of this work is primarily on the use of mono-Si wafers featuring an anisotropically textured front side and planar rear side. Most cell architectures with a passivated rear surface feature a planarized rear side to limit surface recombination by reducing the surface area and fraction of exposed \(<111>\) facets [119].

At normal incidence, \( \approx 76\% \) of the total incident light (primary ray) is transmitted into the wafer at an angle \( \theta_1 \) in Figure 2-3) of \( \approx 41^\circ \) and \( \approx 19\% \) of the light at \( \theta_1 \approx 59^\circ \) [60]. \( \theta_1 \) is a very important parameter because it dictates the angle of incidence on the rear side of the cell and the calculated internal reflectance is highly sensitive to angle of incidence. The \( \theta_1 \approx 41^\circ \) value for the primary ray applies to unencapsulated cells. It should be noted that for encapsulated cells (i.e., cells within a module), \( \theta_1 \) is actually \( \approx 35^\circ \) due to the different \( n \) for the incident medium \( (n \approx 1.5 \text{ for EVA, rather than } n = 1 \text{ for air}) \) [59]. The secondary ray angle of \( \theta_1 \approx 59^\circ \) is also important because \( 60^\circ \) is commonly assumed to be the angle at which randomized light is reflected (i.e., light reflected from a rough, or non-specular, surface), which is the case for light confined within the cell through front and rear internal reflection(s) \( (\theta_i \text{ in Figure 5-2}). \)
To model the $R_r$ of c-Si solar cells, two different modeling methods were used: (1) a MATLAB program was written to perform transfer matrix method (TMM) calculations of reflectance at the dielectric/Si interface as a function of angle of incidence at the rear of the cell using either published or measured $n$ and $k$ data for the different layers [59]; and (2) OPAL 2 is used to calculate the wavelength-dependent IBR (i.e., $R_{rr}(\lambda)$, $R_{rn}(\lambda)$) at specific angles of interest that represent common ray angles ($\theta_1 = 41^\circ$, $60^\circ$) for light transmitted into Si featuring random upright pyramids [59, 60].

5.3 Experimental Details

The processes described in section 3.3 were used to deposit AlO$_x$, SiO$_x$, and TiO$_x$ films via APCVD. A standard batch PECVD process was used for the SiN$_x$ films.

Test samples were fabricated to supplement and validate the results and conclusions obtained from the optical modeling. For these experiments, two different wafer types have been used: 250 µm thick, 150 mm round float zone (FZ) $p$-type wafers with 2 $\Omega\cdot$cm resistivity and polished front and rear; and 180 µm thick, full area (243 cm$^2$ square) $p$-type Cz wafers with 1-3 $\Omega\cdot$cm resistivity, an anisotropically etched front side, and a rear side chemically planarized using a HF/HNO$_3$ etching process. 200 nm Al films were thermally evaporated on the rear side of the wafers.

Ellipsometry measurements were carried out on the polished substrates using the aforementioned SENTECH SE800 and SE400 ellipsometers. Reflectance measurements for these samples were carried out using an Ocean
Optics HR2000+ high resolution spectrometer, Mikropack DH-2000-BAL light source, Mikropack integrating sphere, and Labsphere reflectance standards. Reflectance was measured for wavelengths between 250-1100 nm.

Finally, to characterize the optical properties of screen printed Al pastes, four groups of 156 mm x 156 mm Al-BSF cells (manufactured from p-type Cz wafers) each featuring a different screen printed Al paste were used for complex refractive index \((n, k)\) measurements. Spectroscopic ellipsometry measurements were used to determine the wavelength-dependent complex refractive index of these films using a J.A. Woollam M-2000XI T-Solar system with data acquisition and analysis performed using the CompleteEASE software package.

5.4 Results and Discussion

5.4.1 Multi-Layer Rear Side Film Stacks

By plotting 2D contour maps of \(R_{\text{r}}\) versus dielectric layer thickness and \(\theta_t\), some interesting trends can be seen that provide insight into the origin of non-unity IBR in rear passivated cells [59]. Using a single AlO\(_x\) rear passivation layer as an example, there are three critical regions with respect to \(\theta_t\) shown in Figure 5-4. \(\theta_{c,\text{AlO}}\) refers to the critical angle for an AlO\(_x\)/Si interface, which is \(\approx 26^\circ\) for \(\lambda > 1000\) nm. Note that a similar trend is observed for thermal SiO\(_2\) passivation, where the critical angle (\(\theta_{c,\text{SiO}}\)) is \(\approx 24^\circ\).
Figure 5-4. 2D contour maps of $R_{r1}$ versus $\text{AlO}_x$ thickness and $\theta_1$ for an $\text{AlO}_x$/Si interface, where $\text{AlO}_x$ is assumed to have a refractive index of 1.63 ($\lambda > 1000$ nm) resulting in a critical angle ($\theta_{c,\text{AlO}}$) of 26° [59]. The complex refractive index of pure Al was used in these calculations. A description of each of the regions shown is given in the text.

- Region I ($\theta_1 < \theta_{c,\text{AlO}}$): In this region, the electromagnetic wave propagates through the dielectric film(s) and interference effects play a key role in the resulting reflectance. The alternating constructive and destructive interference gives the periodic dependence of $R_{r1}$ on layer thickness. These smaller angles of incidence are less interesting for anisotropically etched mono-Si cells due to refraction of primary beams, but could be of interest in cells with different texturing and ARC configurations (e.g., nanostructured black Si or any graded index structure).
Region II ($\theta_1$ near $\theta_{c,\text{AlO}_x}$): At the critical angle, total internal reflection occurs and rather than propagating into the film, the wave propagates parallel to the AlO$_x$/Si interface (i.e., surface wave). This surface wave propagating parallel to the interface allows for rather efficient energy transfer to the lossy Al layer. The region should be avoided if light trapping is to be maximized.

Region III ($\theta_1 > \theta_{c,\text{AlO}_x}$): As the angle of incidence increases above the critical angle, less energy is transferred to Al layer. The energy carried by the evanescent wave propagating parallel to the AlO$_x$/Si interface is attenuated as the distance from the higher index media (i.e., Si) is increased. This attenuation increases with $\theta_1$ and is why the larger angles of incidence and thicker dielectric layers result in higher $R_{r1}$. The primary reason for a less than unity $R_{r1}$ in pPERC cells is coupling of the evanescent wave to the Al contact layer. The transfer of energy through the dielectric film(s) to the Al contact layer is dependent on the complex refractive index of this Al layer in addition the $n$ and $k$ of the dielectric(s) and Si. Therefore, knowledge of $n$ and $k$ are critical to accurately modeling $R_{r1}$.

A very practical case to consider is an AlO$_x$ passivation layer capped with a higher index like SiN$_x$ or TiO$_x$, which is used to protect the AlO$_x$ passivation from the Al upon firing. Depending on the situation, these capping layers can either have a positive or negative impact on the overall light trapping ability of the cell. Figure 5-5 shows a similar 2D contour plot of $R_{r1}$, but this time a fixed 20 nm AlO$_x$ rear passivation layer is assumed with a SiN$_x$ capping layer of varied thickness and $n = 2.06$ at $\lambda = 1000$ nm.
Two key differences observed in the case of the SiN$_x$-capped AlO$_x$ layer are: (1) for an unencapsulated cell (labeled air) with $\theta_t > 40^\circ$, $R_{rt}$ increases with the capping layer thickness, as described in the Region III case; and (2) the lossy Region II has been “pushed up”, meaning for $\theta_t < 40^\circ$ (like the case of an EVA encapsulated cell) significantly lower IBR ($R_{rt} < 0.7$ or 70%) are calculated as the SiN$_x$ capping layer thickness is increased. The conclusions from the simulation results are substantiated by the experimental reflectance data shown in Figure 5-6. On anisotropically textured Cz wafers, a clear progression of increasing $R_{esc}^*$ is observed.

Because no internal back reflectance parameters (e.g., $R_r$, $R_{rf}$, $R_m$) can be directly measured, they must be inferred. $R_{esc}$ is a relatively good measure of $R_r$ and can be extracted by measuring reflectance and subtracting $R_{ext}$. However,
evident going from: no dielectric present between the Si and PVD Al layer → AlOₙ
only → AlOₙ/SiNₓ → SiOₓ. The SiNₓ layer enhances the \( R_{esc} \) of the AlOₙ-coated as predicted from Figure 5-5 for an unencapsulated sample. SiOₓ has a lower \( n \) than AlOₙ and therefore exhibits the highest \( R_{esc} \).

there is uncertainty due to difference in the internal reflectance on the front side (see \( R_{f1} \) in Figure 5-2) for different samples. In fact, a high \( R_{esc} \) is not necessarily a good thing, since that light is still lost. Therefore, both a high \( R_{r1} \) and a high \( R_{f1} \) are ideal for effective light trapping. \( R_{f1} \) can be increased by having a Lambertian type of surface on the rear as opposed to a perfectly planar surface with specular reflection.
Figure 5-6. Measured reflectance for the following samples, all featuring a PVD Al layer at the rear: no dielectric coating between the Si and Al; \( \approx 27 \text{ nm AlO}_x \) film between the Si and Al; \( \approx 27 \text{ nm AlO}_x \) followed by \( \approx 80 \text{ nm SiN}_x \); and \( \approx 86 \text{ nm SiO}_x \) [59].

One way to drive toward unity \( R_{r1} \) and eliminate any potential reduction in \( R_{r1} \) due to a high index capping layer (particularly for encapsulated cells) is to use a low cost intermediate reflector with a very low index. SiO\(_x\) works well in this case because it is very inexpensive to deposit and has a low index. In the case of APCVD, multi-layer films consisting of AlO\(_x\)/SiO\(_x\)/TiO\(_x\) can be deposited in a single process run, wherein AlO\(_x\) provides surface passivation, SiO\(_x\) ensures unity \( R_r \), and
TiO$_x$ acts as a capping layer to protect the AlO$_x$ and SiO$_x$ from Al upon firing. 2D contour plots of $R_{r1}$ for this AlO$_x$/SiO$_x$/TiO$_x$ rear films stack are shown in Figure 5-7.

![Contour plot](image)

Figure 5-7. 2D contour plot of $R_{r1}$ versus SiO$_2$/SiO$_x$ intermediate reflector layer thickness and $\theta_1$ with a fixed 20 nm AlO$_x$ passivation layer and 60 nm a-TiO$_x$ capping layer ($\lambda = 1000$ nm).

5.4.2 Optical Properties of Screen Printed Aluminum Contacts

The wavelength-dependent complex refractive index of the screen printed Al pastes was determined by performing the spectroscopic ellipsometry on the rear side of the cells. These pastes have also been used to fabricate $p$PERC cells, but Al-BSF cells were used for these measurements due to sample availability. The Al pastes are optically thick and incident light is completely absorbed by this layer. The pastes are therefore optically modeled as a semi-infinitely thick substrate and the complex refractive index was determined using a Kramers-Kronig consistent
B-spline layer. Due to paste absorption, no information about the underlying Al-Si eutectic region can be detected. This complicates the ability to analytically model the IBR of Al-BSF cells, since the refractive index of the Al-Si eutectic region cannot be accurately determined and light transmitted into the wafer from the front side of the cell encounters the Al-Si eutectic layer before the Al contact layer.

In the case of pPERC cells, the majority of the rear side features a dielectric layer (or stack) with well-known and easily measurable optical properties separating the actual wafer from the Al contact layer. The $n$ and $k$ values measured in this work are therefore directly applicable to IBR calculations of pPERC cells.

![Figure 5-8](image)

**Figure 5-8.** Complex refractive index data for four different screen printed Al pastes compared to pure Al [102, 118].

Figure 5-8 features the measured complex refractive index of the four screen printed and fired Al pastes compared to the published $n$ and $k$ for pure Al [102]. While the data for the four pastes are quite similar, clearly there is a large discrepancy in both $n$ and $k$ for the screen printed Al pastes compared to the pure
Al. While $n$ (top of Figure 5-8) shows a gradual increase from 300-700 nm for both the pastes and the pure Al, the pure Al exhibits a peak at $\approx$800 nm. This feature doesn’t exist for the Al pastes, which seems to level off at around $\approx$700 nm and not decline. In the case of the extinction coefficient, $k$ (bottom of Figure 5-8), this value is much lower for the pastes.

This change in $n$ and $k$ does impact the internal back reflectance and could make the need for a low index reflector more of a priority. This is evident in Figure 5-9, which shows the simulated $R_{r1}(\lambda)$ of AlO$_x$/a-TiO$_x$ stacks (with and without a 150 nm SiO$_x$ intermediate reflector) at an angle of incidence of 41° using the $n$ and $k$ of pure Al and screen printed Al.

![Figure 5-9. OPAL 2 modeling results of the internal back reflectance for the first pass ($R_{r1}(\lambda)$) at an AOI of $\theta_1 = 41^\circ$ using both the complex refractive index of pure Al and that of the screen printed (SP) Al, paste A in this case. Additionally, rear side dielectric stacks featuring AlO$_x$/a-TiO$_x$ (no intermediate SiO$_x$ layer) and AlO$_x$/SiO$_x$/a-TiO$_x$ were considered [118].](image-url)
5.5 Summary

The internal back reflectance has been modeled as a function of AlO$_x$ thickness and the rear side angle of incidence at the AlO$_x$/Si interface. AlO$_x$ passivated structures with different capping layers are considered. The 2D contour plots of the internal back reflectance, calculated using the transfer matrix method, clearly show three critical regions with respect to the backside angle of incidence ($\theta_1$): small angles with $\theta_1 < \theta_{c,AlO}$; $\theta_1$ near $\theta_{c,AlO}$; and large angles with $\theta_1 > \theta_{c,AlO}$, where $\theta_{c,AlO}$ is the critical angle of the AlO$_x$/Si interface. Higher index capping layers like SiN$_x$, a-TiO$_x$, or pc-TiO$_x$ can either positively or negatively influence the light trapping capability of pPERC cells, depending on which of these three regions the cell is operating in, which depends in part on whether the cells are encapsulated into a module or not.

Finally, the measured complex refractive index of screen printed Al is presented and compared to that of pure Al. A clear discrepancy in the wavelength-dependent $n$ and $k$ is found, likely originating in the major differences in the composition and microstructure of the two forms of Al. These results are relevant to the PV community because accurate modeling of the internal back reflectance, and therefore light trapping capability of a cell, is dependent on knowledge of the actual complex refractive index of the actual materials used.
6.1 Introduction

A reduction in the recombination of charge carriers at the surfaces of c-Si solar cells, also known as surface passivation, is commonly obtained by using thin dielectric films. As described in section 2.2.2, both a reduction in $D_{nl}(E)$ (i.e., chemical passivation) and a reduction in the concentration of electrons or holes at the surface (i.e., field effect passivation) result in a reduction in the surface recombination velocity and therefore the $J_0$ contribution associated with that surface ($J_{0s}$). Surface recombination rates are lowest in the case of accumulation or inversion of the majority carriers and highest in the case of depletion (wherein $n \approx p$ at the surface) since the SRH process requires an electron and hole. Additionally, the impact of field effect passivation is greatly diminished at increasingly higher injection levels.

For symmetrically passivated samples (equivalent surface recombination at the front and rear of the sample), solving the second order differential equation that governs carrier decay leads to two useful equations arising from two extremes (very good passivation and very poor passivation). For well passivated surfaces ($S_{eff} < D/4W$, where $D$ is the diffusion constant of the excess carriers), $S_{eff}$ can be calculated from $\tau_{eff}$ measurements using the following equation [120]:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{2S_{eff}}{W}. \quad (6-1)$$
For poorly passivated surfaces with very large $S_{eff}$, the following approximation can be assumed:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \left(\frac{\pi}{W}\right)^2 D. \quad (6-2)$$

The most common passivation materials used by the PV industry today include SiO$_2$, SiNx, and a-Si:H. Among the various other potential materials of interest, AlO$_x$ has attracted much attention due to its ability to very effectively passivate $p$-type and $p^+$ c-Si surfaces [121]. This is of significant interest for rear side passivation of c-Si solar cells made from standard $p$-type wafers, and also of interest for front surface (emitter) passivation of $n$-type wafers, since it is known the positive fixed charge exhibited in SiNx forms a inversion layer $p$-type materials, which leads to parasitic shunting [122]. High efficiency ($\eta$) solar cells have been realized using an AlO$_x$ film for front surface passivation of $n$-type cells ($\eta > 23\%$ [123]) and rear surface passivation of $p$-type cells ($\eta = 20.7\%$ for full-sized 243 cm$^2$ screen printed cells using APCVD AlO$_x$ films [124, 125]). The effective passivation of $p$-type c-Si surfaces by AlO$_x$ is due to both the presence of a large fixed negative charge ($Q_f$) in the range of $10^{12}$-$10^{13}$ cm$^{-2}$, as well as excellent chemical passivation due to a reduction in interface defect density ($D_{it}$) down to $\approx 10^{11}$ cm$^{-2}$·eV$^{-1}$, which is associated with the incorporation of H in the layer [126-128]. A significant reduction in $D_{it}$ after post-deposition annealing at $\approx 400$-500$^\circ$C has been attributed to the diffusion of H species from the film to the AlO$_x$/Si interface [129, 130]. The
observed formation of a SiO$_2$ or sub-oxide (i.e., SiO$_x$ with $x < 2$) interlayer, between the Si surface and bulk AlO$_x$ film, and film relaxation (i.e., reduction in strain near the interface) are speculated to also play a role in reducing $D_{it}$ upon annealing [121].

Various deposition techniques have been investigated for AlO$_x$ surface passivation. Hezel and Jaeger were the first to report AlO$_x$ passivation in 1989, via pyrolysis of aluminum-triisopropanoxide at atmospheric pressure [131]. However, most of the recent work in this area has been using thermal atomic layer deposition (ALD) and plasma-assisted ALD (PA-ALD) processes (see [121] and references therein). Excellent passivation has been achieved with these films, with reported effective surface recombination velocities ($S_{eff}$) as low as 0.8 cm/s on p-type substrates [127]. However, the relatively low deposition rates of standard ALD processes (< 10 nm/min) have lead to an interest in higher throughput methods including: spatial ALD [132, 133]; plasma-enhanced CVD (PECVD) [134-136]; physical vapor deposition (PVD) (i.e., sputtering [128]); and a recent report using APCVD with triethyldialuminum tri-(sec-butoxide) (TEDA-TSB) and water vapor as precursors [137]. PECVD and APCVD have both been shown to provide comparable levels of surface passivation as the ALD processes. On the other hand, the preliminary data from PVD-based processes have to date exhibited lower passivation quality, due to larger $D_{it}$ values presumably caused by a reduced concentration of interfacial H [128].

Despite all of the recent activity in AlO$_x$ passivation, the demonstration of a high-throughput, industrially scalable AlO$_x$ deposition process that doesn’t require
vacuum systems and is compatible with the low cost deposition of multi-layer film stacks within a single process run remains a compelling topic for c-Si solar cell manufacturing R&D. In this chapter, low surface recombination velocities ($S_{\text{eff, max}} < 10 \text{ cm/s}$) for 10-20 $\Omega \cdot \text{cm}$ $p$-type Si wafers passivated with APCVD AlO$_x$ are demonstrated. This is due to AlO$_x$ providing excellent field effect passivation ($|Q_f| > 2 \cdot 10^{12} \text{ cm}^2$) and reducing the number of interface defects ($D_{it, midgap} < 4 \cdot 10^{11} \text{ ev}^{-1} \cdot \text{cm}^2$). The precursor gas ratio (i.e., $O_2$/TMA) is shown to impact both the deposition rate and the surface recombination velocity.

AlO$_x$ can be applied as a surface passivation layer for lightly doped (i.e., undiffused) $n$-type surfaces and any level of doping for $p$-type surfaces, and is therefore relevant to $p$PERC, nPERT, and nPERT cells (Figure 6-1), as well as IBC cells.
6.2 Experimental Details

In this work, AlO$_x$ films are deposited using the process outlined in section 3.3.5. The physical properties and passivation performance of APCVD AlO$_x$ films have been investigated for different processing conditions. To investigate the effect of the O$_2$/TMA ratio ($I$) on the film characteristics and passivation performance, TMA gas flow has been fixed while varying O$_2$ gas flow so that $I$ is adjusted from 10 to 90. The substrate temperatures at the deposition zone (i.e. deposition temperature) were kept at $\approx$500°C. Round <100> $p$-type Cz wafers with 150 mm diameter, 500 $\mu$m thickness, a resistivity of 10-20 $\Omega$·cm, and planar front and rear surfaces were used in this study.
The thickness and refractive index ($n$) of AlO$_x$ films were determined using a laser ellipsometer (SENTECH SE400, $\lambda = 632.8$ nm). Film composition was analyzed by energy dispersive X-ray analysis (EDX) using an EDAX Genesis 2000 detector implemented on a JEOL JSM-6480 scanning electron microscope (SEM). Film crystallinity was determined by means of grazing incidence X-ray diffraction (XRD) using a Siemens D5000 system with a step size of 0.01°, angle of incidence of 1° and diffraction 2θ angle of 25 to 55°. Cross-sectional high-resolution transmission electron microscopy (HR-TEM) imaging was performed using a FEI Tecnai F30 TEM following in situ focused ion beam (FIB) lift-out with a FEI 200 TEM FIB.

The $\tau_{\text{eff}}$ of wafers symmetrically coated with the AlO$_x$ films have been measured as a function of excess minority carrier density ($\Delta n$) using contactless photoconductance decay (PCD) measurements (Sinton WCT-120) [138]. The maximum effective surface recombination velocity ($S_{\text{eff, max}}$) values have been extracted from $\tau_{\text{eff}}$ by assuming $S_{\text{eff, max}} = W/2\tau_{\text{eff}}$ [120], where $W$ is the wafer thickness and $\tau_b$ is assumed to be infinite. This is a commonly used approximation that assumes all recombination occurs at the surface rather than the bulk and is therefore a very conservative estimate of the ability of the film to passivate the Si surface.

Non-contact corona-voltage measurements of $D_\text{it}$ and $Q_\text{f}$ in the AlO$_x$ films were carried out using a Semilab PV-2000A metrology tool [139]. The technique uses a corona discharge in air to deposit an electric charge on a dielectric thus changing the electric field in the dielectric and in the semiconductor. The response
of the dielectric/semiconductor system is monitored in a non-contact manner by measuring the contact potential difference.

6.3 Results and Discussion

Figure 6-2 presents the influence of the $O_2$/TMA precursor ratio ($I$) on the AlO$_x$ film deposition rate. As $I$ increases from 10 to 30, the growth rate doubles, reaching a value of 150 nm·min$^{-1}$ (assuming wafers 156 mm in length). A further increase in $I$ results in a drop of deposition rate, however all values reported in this study (from $I$ = 10-90) are relatively high (>70 nm·min$^{-1}$). Two reasons likely attribute to the high deposition rates obtained with this APCVD system. One reason is the higher pressure of the APCVD process leads to a higher precursor flux directed toward the substrate surface, when compared to a typical vacuum process [140]. A second reason is that compared to other APCVD systems, this system effectively limits pre-mixing of the gas phase precursors (TMA and $O_2$) by the N$_2$ gas curtain separator. Powder formation is consequently avoided and high TMA reaction efficiencies can be achieved.

The deposition rate decrease for $I$ > 30, where a dark cloud under the CVD injector was observed, indicates an enhanced gas reaction due to excess $O_2$. For $I$ < 30, we conclude that a lack of $O_2$ reaching the surface limits the reaction with the surface-adsorbed TMA molecules, hence the increasing deposition rate with increasing $I$ up to 30. Film thickness was found to be quite uniform from wafer-to-wafer, with a standard deviation of ±5%.
Figure 6-2. The deposition rate of the APCVD AlOₓ films as a function of \( \Gamma \), the O₂/TMA ratio. Error bars here represent the standard deviation in deposition rate as a result of ellipsometry mapping of a single polished wafer for each \( \Gamma \) [124].

![Graph showing deposition rate vs. O₂/TMA ratio](image)

Figure 6-3. Cross-sectional TEM and HR-TEM images showing (a) the bulk of the AlOₓ film and (b) the AlOₓ/Si interface [124].

![Cross-sectional TEM images](image)

Crystallinity of the films has been investigated directly after deposition (i.e., as-deposited) and after a firing step using grazing incidence XRD analysis. This analysis exclusively showed flat patterns with the typical amorphous hump at 2θ at 40°. No crystalline peaks have been observed. The chemical composition of the as-deposited layers, determined from EDX with a sapphire standard, features an
over stoichiometric O/Al ratio ($x \approx 1.60-1.75$) due to possible OH groups incorporated inside the layer [141]. A small amount of residual carbon (3-4 at.%) was found for all films. No clear dependence of $\Gamma$ on the film composition was observed. The AlO$_x$ film and AlO$_x$/Si interface are shown in the cross-sectional TEM and HR-TEM images in Figure 6-3(a-b).

No blistering was observed for the SiO$_x$-capped and uncapped AlO$_x$ films following a firing step. The blistering problem has been reported for AlO$_x$ films deposited using low temperature processes, including ALD [142] and PECVD [135]. The blistering in the ALD and PECVD films occurs during post-deposition thermal treatments at temperatures over the deposition temperature, and is reportedly due to out-gasing of H$_2$O as the AlO$_x$ films acts as a gas diffusion barrier [135, 143]. Additionally, Vermang et al. have shown that high temperature depositions (>350°C) of PECVD SiO$_x$ and SiN$_x$ capping layers on ALD AlO$_x$ have been shown to form blisters, while using a 600°C annealing step after prior to capping layer deposition can prevent blistering [144]. The relatively high deposition temperature used in this study (500°C) is the most likely reason for the blister free films, even after a firing step. Additional experiments by the authors on APCVD AlO$_x$ capped with PECVD SiN$_x$ and other dielectric films have also not shown signs of blister formation. Black et al. have also demonstrated firing stability of SiN$_x$-capped APCVD AlO$_x$ (using different precursors for the APCVD AlO$_x$ film deposition) [145].

The passivation performance of the samples has been evaluated after deposition and following post-deposition firing using PCD. As frequently addressed
in the literature, a post-deposition annealing step, with or without forming gas, is commonly used to “activate” the passivation of the AlO$_x$ layer [25,26], although the post-deposition anneal becomes less important at higher deposition temperatures [137]. This latter point is crucial, as it allows for “activation” of the AlO$_x$ passivation to be carried during the co-firing process (i.e. the step after screen printing) rather than as a separate post-deposition annealing step, which would add another thermal process to cell manufacturing (e.g., 400°C for >15 min. is commonly cited in the literature for ALD and PECVD).

The firing step used in this work is based on a standard industrial process used to co-fire the front and rear side screen printed metallization in a c-Si solar cell. During the firing step, the samples undergo approximately 4 min. at 400°C followed by a brief exposure (few seconds) at 860°C. In the case of the films without a SiO$_x$ capping layer (i.e., AlO$_x$ only), a clear increase of $\tau_{\text{eff}}$ from less than 1 ms to $\approx$3-4 ms is achieved at $\Delta n < 10^{15}$ cm$^{-3}$. In the case of the AlO$_x$ films capped with SiO$_x$, the surprisingly low as-deposited $S_{\text{eff,max}}$ values obtained are likely due to the additional thermal energy resulting from the APCVD SiO$_x$ deposition (i.e., in situ annealing).

The influence of $I^*$ on $S_{\text{eff,max}}$ for the APCVD AlO$_x$ passivated wafers is demonstrated in Figure 6-4. For samples measured both in the as-deposited state and after firing, lower $S_{\text{eff,max}}$ values are obtained for the higher O$_2$/TMA ratios. This observation is consistent with the work from Miyajima et al. where a decrease in $S_{\text{eff,max}}$ was reported with an increase in the CO$_2$/TMA ratio in the case of PECVD AlO$_x$ [134]. However, the authors did not provide any possible explanation for this
relationship. We suggest that this could be associated with varied film composition (i.e. varying levels of OH group incorporated into the film). The role of the interfacial SiO$_2$ layer, which may be affected by $\Gamma^-$, might also play a role in reducing $D_{it}$. Nevertheless, the chemical composition data obtained from EDX is not sufficient to judge this and a more detailed experimental investigation of the interfacial properties of these films is ongoing.

To investigate both the chemical and field effect passivation of the APCVD AlO$_x$ films, $D_{it}$ and $Q_f$ for the samples were extracted using the non-contact corona-voltage measurement technique outlined previously ($\Gamma^-$ = 40 was used for these samples). As found in previous studies on AlO$_x$, $D_{it}$ is reduced following post-deposition annealing. However, the $D_{it}$ of the as-deposited samples ($\approx 2 \times 10^{12} \text{ eV}^{-1} \text{cm}^2$) is approximately an order of magnitude lower than that of typical ALD AlO$_x$ samples in the as-deposited state [129]. Again, this is likely due to the higher deposition temperatures, consistent with other studies on APCVD AlO$_x$ [137]. The resulting $Q_f$ of the APCVD AlO$_x$ films was found to negative in all cases, with $|Q_f| > 2 \times 10^{12} \text{ cm}^2$. $Q_f$ changes with post-deposition annealing, but is less dependent on annealing than $D_{it}$. The increase in $\tau_{eff}$ associated with annealing is due to reduced $D_{it}$ for the samples investigated in this work.
Figure 6.4. $S_{\text{eff,max}}$ of APCVD AlO$_x$ passivated $p$-type Cz Si wafers (bulk resistivity $\approx$ 10-20 $\Omega\cdot$cm, 500 $\mu$m thick) with and without a SiO$_x$ capping layer in the as-deposited state and following a firing step for three different O$_2$/TMA ratios. For these measurements, $\tau_{\text{eff}}$ was measured at $\Delta n = 10^{15}$. Error bars represent the standard deviation in $S_{\text{eff,max}}$ from the six wafers used for each process condition [124].

6.4 Summary

To date, an effective process for the deposition of AlO$_x$ passivation layers on c-Si surfaces has been demonstrated using an in-line APCVD technology with O$_2$ and TMA as precursors. This approach combines high deposition rates (up to 150 nm·min$^{-1}$ per wafer) with excellent passivation performance for $p$-type Si wafers, while eliminating the need for vacuum systems. The excellent passivation is due to the presence of large negative fixed charge ($|Q_f| > 2\cdot10^{12}$ cm$^2$) and low interface defect density ($D_{\text{it,midgap}} < 4\cdot10^{11}$ ev$^{-1}$·cm$^2$). The results presented suggest this approach is a promising alternative to ALD AlO$_x$ for rear side passivation of $p$-
type wafers and emitter passivation for $n$-type wafers in industrial c-Si solar cell manufacturing. In addition, the APCVD AlO$_x$ films described in this work have been used by collaborators to create 20.7% efficient, full area (243 cm$^2$) $p$-type Cz rear passivated solar cells with screen printed contacts (independently confirmed by Fraunhofer ISE CalLab) [125].
7.1 Introduction

The starting point for cell manufacturing is the acquisition and inspection of incoming c-Si wafers, which are uniformly doped with either phosphorus or boron depending on whether n or p-type wafers are being used. The background doping level and resulting wafer resistivity is typically in the range of $\approx 10^{14}$-$10^{16}$ cm$^{-3}$ and $\approx 0.5$-$10$ $\Omega$-cm, respectively, and are highly dependent on the cell architecture and cell design selected.

The incorporation of additional dopant atoms into c-Si wafers is one of the most critical types of processes performed during cell manufacturing. Emitters (i.e., p-n homojunctions) and surface fields are carefully designed to maximize the conversion efficiency for all relevant cell architectures, including Al-BSF, pPERC, nPERT, nPERL, and IBC cells. As is the case with the background doping of incoming wafers, P and B represent the most common dopants used to form emitters and surface fields in c-Si cells. An important exception to this would be the use of Al to form the BSF in p-type Al-BSF cells. The application of P doped and B doped regions in common c-Si cell architectures are shown in Figure 7-1 and Figure 7-2, respectively.
Figure 7-1. Cross-sectional diagrams highlighting (in red) where phosphorus doped regions can be applied to Al-BSF, pPERC, nPERT, and nPERL cells.

Figure 7-2. Cross-sectional diagrams highlighting (in red) where boron doped regions can be applied to nPERT and nPERL cells.

The majority of the work in this chapter is from [146].
7.1.1 Relevant Doping Methods for c-Si Solar Cell Manufacturing

Various process technologies exist for doping Si wafers with P and B, most of which leverage experience and development from the methods of integrated circuit industry. The most relevant examples are described below.

- Gas phase delivery of liquid halogen-based precursors using bubbler systems in a tube furnace and subsequent high-temperature drive-in diffusion is one of the most common methods of doping c-Si solar cells. Common precursors include phosphorus oxychloride (POCl$_3$) [147, 148], boron tribromide (BBr$_3$) [123, 149], and, more recently, boron trichloride (BCl$_3$) [150, 151]. POCl$_3$ diffusion is currently the primary method of forming the $n^+$ emitter in Al-BSF cells [152].

- Spraying and spin-coating diluted phosphoric acid (H$_3$PO$_4$) [153] and boric acid (H$_3$BO$_3$) [154] mixtures have been used as P and B dopant sources, respectively. P doping via H$_3$PO$_4$ has actually been used by industry as an in-line (i.e., not a batch process) doping technique for manufacturing Al-BSF cells. However, challenges in limiting the P concentration at the surface have been a barrier to widespread adoption [153].

- Spin-on-dopant solutions and screen printable pastes incorporated with P and B have also been utilized in the fabrication of c-Si cells. Spin-on-dopants are typically low viscosity solutions that are spin-coated or sprayed, then dried, and finally exposed to a high temperature drive-in diffusion step [155, 156]. Screen printed dopant
pastes are similar in principle, but with a different rheology (i.e., higher viscosity), and are compatible with screen printing systems that are already used in industry for the metallization of cells [157-159]. Additionally, this method offers the possibility of selectively doping regions, something of critical importance to higher efficiency cell architectures (e.g., selective emitter, PERL, IBC). In both cases, impurities (e.g., organics) from the solutions and pastes can contaminate the wafers resulting in a reduction in the bulk carrier lifetime [159]. This remains a barrier for the widespread adoption of this approach.

- Ion implantation has long been used in integrated circuit manufacturing due to better control of dopant location and concentration. It is fundamentally different than all of the other methods described here, which all rely on the diffusion of a species from a high concentration source (e.g., $P_2O_5$, $B_2O_3$) into the lower concentration Si wafer under elevated temperatures. In ion implantation (as the name suggests), impurity ions are accelerated and directed toward the surface of the Si wafer followed by a activation and annealing step [160]. Recently, new implantation tools tailored for the higher throughput demands of PV manufacturing, compared to integrated circuit manufacturing, have created a strong interest in ion implantation for c-Si cell manufacturing [161, 162]. The ability to selectively dope regions via in situ patterning is particularly attractive.
for higher efficiency cell architectures [163]. Concerns regarding cost and throughput remain potential barriers for the widespread adoption of this technology.

- Finally, chemical vapor deposition of doped oxides (e.g., PSG, BSG) followed by an *ex situ* drive-in step represents the doping process covered in this work. This process is similar to the other three diffusion processes described, except in this case a thin solid film deposited via CVD is used as the dopant source.

For a more complete review of the different doping methods used in c-Si solar cell manufacturing, please see [81, 155, 164]. Other methods of forming emitters and BSFs like epitaxial growth of doped single crystalline Si films onto a wafer [165] or the formation of heterojunctions [166] are not covered here.

### 7.1.2 Importance of Well Controlled Doping Concentrations

The requirements for dopant concentration levels of different regions of a solar cell are highly dependent on the cell architecture selected. For Al-BSF and *p*PERC cells, the formation of the *n*+ emitter is one of the most important steps during cell manufacturing and strongly influences the resulting cell efficiencies achievable. A lower emitter sheet resistance emitter (i.e., higher total dopant concentration) allows for better electrical contact with the cell and improved fill factor. However, a low $R_{\text{sheet}}$ can also lead to increased Auger recombination and a thicker “dead layer” at the surface with excess P atoms acting as Shockley-Read-Hall (SRH) recombination centers [81].
As mentioned in section 2.3.1.1, selective emitters solve this issue by selectively doping regions more heavily under the contacts and more lightly for the uncontacted regions of the front surface. However, this approach adds additional process steps and increase manufacturing cost. Another approach to improve efficiency without adding process steps is to engineer the actual emitter dopant profile, in terms of concentration, shape, and depth, in order to minimize recombination losses while limiting contact resistance. To target the best performance for uniform emitters, the P diffusion profile should be optimized with a deep emitter while limiting excess P concentration ($<7 \times 10^{20} \text{ cm}^{-3}$) to minimize the impact of high P concentration at the surface [147].

The two most common doping methods used in recent years by the industry are POCl$_3$ tube furnace diffusion and in-line H$_3$PO$_4$ spray-based diffusion, each with strengths and weaknesses. The H$_3$PO$_4$ spray method lacks control of excess P concentration at the wafer surface [153], but can be performed in-line under atmospheric conditions, which is compatible with very high throughput production and also better suited for processing thinner wafers. The POCl$_3$ process is limited to batch processing in a closed furnace, but provides better control of P at the surface and Cl$_2$ (a by-product) is known to getter metal ions.

In this work, a low cost, an industrially scalable method of forming highly uniform $n^+$ emitters is proposed by depositing PSG/SiO$_x$ films via APCVD followed by drive-in diffusion in an in-line (atmospheric) furnace. This method allows for excellent control of the emitter dopant profile and has a large potential for
application in the PV industry since it is compatible with high volume, in-line manufacturing.

7.2 Experimental Details

In this work, PSG, BSG, AlOₓ:B, and SiOₓ films were deposited using the processes outlined in section 3.3. 65-70 nm PSG layers were deposited with varying concentration levels of P, a step easily realized by simply changing the PH₃ flow rate. Subsequently, a ≈40 nm SiOₓ capping layer was then deposited onto the wafers in the second CVD injection chamber to protect the hygroscopic PSG layer from moisture. After deposition of the PSG and SiOₓ films, subsequent drive-in diffusion was conducted using an in-line furnace (atmospheric conditions) for 12 minutes at varied temperatures between 840-910°C.

The P concentrations were determined as a function of distance into the wafer by secondary ion mass spectroscopy (SIMS) depth profiling on polished p-type Cz Si wafers. A PHI Adept 1010 Dynamic SIMS System was used with a 50 nA Cs beam at 3 kV primary energy and 200 µm x 200 µm raster with 5% detection area. After deposition of the PSG/SiOₓ films and subsequent drive-in diffusion, these samples were submerged in a buffered oxide etch solution to remove the PSG/SiOₓ.

For the fabrication of Al-BSF solar cells (Figure 7-3), 156 mm x 156 mm p-type Cz Si wafers with a resistivity of ≈1-3 Ω·cm were used. Prior to the APCVD PSG/SiOₓ deposition process described above, these samples underwent an alkaline-based anisotropic texturing process and HCl/HF cleaning step for the removal of any native oxide and surface contamination. Following the drive-in
diffusion, a wet chemical edge isolation and PSG/SiO\textsubscript{x} removal step was performed. Then, a SiN\textsubscript{x} passivation and ARC layer was deposited on the front surface via PECVD, followed by screen printing and co-firing of the front and rear metallization pastes. $R_{\text{sheet}}$ measurements were carried out on diffused wafers using a Signatone four-point probe system with $R_{\text{sheet}}$ mapping capability. Four sample groups (all with ≈60 Ω/□ emitters, but varied dopant profiles) were created by varying the amount of P within the PSG layer and using different diffusion temperatures. Illuminated $I-V$ curves were measured at STC using a calibrated flash solar simulator.

### Process Flow

<table>
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<tr>
<th>Process Flow</th>
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<tr>
<td>156 mm x 156 mm p-type Cz wafers</td>
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<tr>
<td>Anisotropic (alkaline-based) texturing</td>
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<tr>
<td>HC/IF cleaning</td>
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<tr>
<td><strong>Group 1</strong></td>
</tr>
<tr>
<td>PSG (13.0 wt.% P)</td>
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<tr>
<td>SiO\textsubscript{x} capping layer</td>
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<tr>
<td>Diffusion temp. = 905°C</td>
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<tr>
<td>$R_{\text{sheet}}$ = 58±2 Ω/□</td>
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<tr>
<td><strong>Group 2</strong></td>
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<tr>
<td>PSG (14.5 wt.% P)</td>
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<tr>
<td>SiO\textsubscript{x} capping layer</td>
</tr>
<tr>
<td>Diffusion temp. = 890°C</td>
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<tr>
<td>$R_{\text{sheet}}$ = 58±2 Ω/□</td>
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<td><strong>Group 3</strong></td>
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<tr>
<td>PSG (15.7 wt.% P)</td>
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<tr>
<td>SiO\textsubscript{x} capping layer</td>
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<tr>
<td>Diffusion temp. = 870°C</td>
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<td>$R_{\text{sheet}}$ = 58±2 Ω/□</td>
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<tr>
<td><strong>Group 4</strong></td>
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<td>PSG (16.7 wt.% P)</td>
</tr>
<tr>
<td>SiO\textsubscript{x} capping layer</td>
</tr>
<tr>
<td>Diffusion temp. = 855°C</td>
</tr>
<tr>
<td>$R_{\text{sheet}}$ = 64±2 Ω/□</td>
</tr>
<tr>
<td>Edge isolation and PSG removal</td>
</tr>
<tr>
<td>PECVD SiN\textsubscript{x}</td>
</tr>
<tr>
<td>Screen printing and co-firing of front and rear contacts</td>
</tr>
</tbody>
</table>

Figure 7-3. Process flow for the fabrication of Al-BSF solar cells using the APCVD-based doping process to form the $n^+$ emitter. Four groups were created, all with approximately equivalent emitter $R_{\text{sheet}}$ values (≈60 Ω/□) but varied dopant profiles.

### 7.3 Results and Discussion

#### 7.3.1 Phosphorus Doping

Figure 7-4 shows the SIMS depth profile data for the four sample groups with varied APCVD and process conditions and diffusion temperatures. Control of both the P concentration at the surface ($N_s$), where $x$ is the distance into the wafer) and emitter depth can be seen from the SIMS depth profiles. Groups 1-3 all have nearly equal $R_{\text{sheet}}$, achieved by varying the diffusion temperatures, but the actual
profiles differ. This is a key point for emitter design since both \( N_s \) and emitter depth play a critical role in determining the final solar cell efficiency [12].

![Phosphorus depth profiles measured via SIMS for the four groups with approximately equivalent emitter \( R_{\text{sheet}} \) values (\( \approx 60 \, \Omega/\square \)). The insert in to the top right of the figure provides a zoomed in view of the P concentrations near the wafer surface.](image)

**Figure 7-4.** Phosphorus depth profiles measured via SIMS for the four groups with approximately equivalent emitter \( R_{\text{sheet}} \) values (\( \approx 60 \, \Omega/\square \)). The insert in to the top right of the figure provides a zoomed in view of the P concentrations near the wafer surface.

For the typical diffusion temperatures used in PV and in this work, the solid solubility of electronically active P atoms in Si is known to be in the range 2-3\( \times 10^{20} \) cm\(^{-3} \) [167] and has been measured using electrochemical-capacitance-voltage profiling [168, 169]. Relatively low P concentrations at the surface (\( N_s < 7\times 10^{20} \) cm\(^{-3} \)) and deep emitter depths for all four groups lead to promising cell efficiencies for these full-sized, industrially-processed wafers (Table 1-1Table 7-1). While Groups 1-3 indicate the ability to control the P surface concentration and emitter depth while retaining equivalent \( R_{\text{sheet}} \), Group 4 illustrates the known effects of higher doping at the surface on \( I_{\text{SC}} \) and \( V_{\text{OC}} \). Although the Group 4 samples have
a slightly larger $R_{\text{sheet}}$ than Groups 1-3, the higher concentration of inactive P atoms at the surface leads to a reduced $I_{\text{SC}}$ and $V_{\text{OC}}$. This runs counter to the conventional rule of thumb, which is that a higher $R_{\text{sheet}}$ leads to higher $I_{\text{SC}}$ and $V_{\text{OC}}$ at the expense of reduced fill factor ($FF$), but is in agreement with recent investigations using POCl$_3$ diffusion [147, 148]. An additional group of samples consisting of 80±3 Ω/□ emitters was also fabricated to show the potential for achieving higher efficiencies with further optimization of the deposition and diffusion parameters, as well as the pastes and firing profiles.
Table 7-1. Characteristics of the P-doped emitters and resulting solar cell performance for the four ≈60 Ω/□ emitters and an additional ≈80 Ω/□ group.

<table>
<thead>
<tr>
<th>Group</th>
<th>No. of Cells</th>
<th>R_{sheet} (Ω/□)</th>
<th>N_s (cm⁻³)</th>
<th>Emitter Depth at N_D=5·10¹⁹ cm⁻³</th>
<th>Emitter Depth at N_D=1·10¹⁸ cm⁻³</th>
<th>η (%)</th>
<th>I_{SC} (A)</th>
<th>V_{OC} (mV)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13</td>
<td>59±2</td>
<td>3.4·10²⁰</td>
<td>0.11 µm</td>
<td>0.36 µm</td>
<td>17.8±0.1</td>
<td>8.62±0.02</td>
<td>625±1</td>
<td>79.1±0.5</td>
</tr>
<tr>
<td>2</td>
<td>13</td>
<td>58±2</td>
<td>4.0·10²⁰</td>
<td>0.08 µm</td>
<td>0.31 µm</td>
<td>18.1±0.1</td>
<td>8.68±0.02</td>
<td>628±1</td>
<td>79.5±0.2</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>58±2</td>
<td>4.7·10²⁰</td>
<td>0.07 µm</td>
<td>0.25 µm</td>
<td>18.0±0.1</td>
<td>8.72±0.02</td>
<td>627±1</td>
<td>78.8±0.5</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>64±1</td>
<td>6.4·10²⁰</td>
<td>0.05 µm</td>
<td>0.21 µm</td>
<td>17.9±0.1</td>
<td>8.62±0.03</td>
<td>624±1</td>
<td>79.6±0.4</td>
</tr>
<tr>
<td>80 Ω/□</td>
<td>26</td>
<td>80±3</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>18.4±0.1</td>
<td>8.96±0.03</td>
<td>631±1</td>
<td>79.5±0.3</td>
</tr>
</tbody>
</table>

More importantly, these results show that the control of the phosphorus concentration at the surface and emitter depth can be obtained with standard in-line diffusion furnaces originally used for H₃PO₄ doping. This allows for cost-effective insertion into existing production lines and has the potential for significant cost savings for cell manufacturing in three important ways: (1) in-line processes are more compatible with the manufacturing of thin wafers (<100 µm) than batch processes, allowing for wafer formats that significantly increase Si utilization efficiency; (2) the elimination of vacuum components enables a significant reduction in the cost of ownership for emitter formation equipment for cell manufacturers; and (3) increased throughput – recent experiments on a newer model of the APCVD system (with ceramic rollers, five wafers-wide) and a standard diffusion furnace have demonstrated a throughput of up to 4,000 wafers/hour. The primary barrier for this emitter formation technology when compared to POCl₃ has been limited demonstration using industrial-scale tools.
7.3.2 Boron Doping

The ability to perform boron doping by depositing BSG via CVD and then performing a drive-in diffusion step is very attractive prospect for manufacturing different $n$-type cell architectures, notably $nP$ERT, $n$PERL, and IBC cells. All of these architectures offer the promise of stabilized efficiencies even higher than $p$PERC cells due to the elimination of light induced degradation. Many of the alternatives methods of doping Si wafers with B (e.g., BBr$_3$, ion implantation) feature many disadvantages. The diffusion of B from CVD BSG has been explored using PECVD [170, 171] and (recently) APCVD [172, 173] by other research groups. Various challenges exist in B diffusion, including the high temperatures (>900°C) and long times required for driving in B, the impact of these diffusion on the bulk carrier lifetime, and control of the B concentration near the surface (e.g., formation of a boron rich layer).

Figure 7-5 features SIMS depth profiles for B from diffused wafers featuring four different B sources: APCVD BSG films with different drive-in conditions; and APCVD AlO$_x$:B. In all cases, no separate processes for removal of any boron rich layer was performed. This is evident in BSG Group 2 and BSG Group 3, which both feature a boron rich layer. Appropriate control of the environment (e.g., amount of N$_2$ and O$_2$) during the ex situ drive-in can prevent the formation of this boron rich layer, as shown in BSG Group 1 and the AlO$_x$:B sample. These results also demonstrate the possibility of using APCVD AlO$_x$:B as a dopant source, which can potentially provide excellent surface passivation while acting as a dopant.
source. Future work on B doping via APCVD will explore how these films can be used to create optimized doped regions for different cell architectures.

Figure 7-5. Boron depth profiles measured via SIMS using three different APCVD BSG films and one APCVD AlOx:B film as dopant sources. The insert in to the top right of the figure provides a zoomed in view of the B concentrations near the wafer surface.

7.4 Summary

In this chapter, it is shown that PSG films deposited by APCVD can be used to provide excellent control of the dopant profile during emitter formation. In addition to the ability of creating deep emitter profiles with low concentrations of phosphorus at the surface ($N_s < 7 \times 10^{20}$ cm$^{-3}$), APCVD has many economic advantages including the elimination of vacuum systems and the higher throughput associated with in-line processing.
Preliminary results using BSG and AlO$_x$:B also highlight the ability to form boron doped regions in Si wafers without a boron rich layer. Boron doping via APCVD is a planned topic of future R&D.
CHAPTER 8 - MODELING THE POTENTIAL IMPACT OF APCVD OXIDE FILMS ON CRYSTALLINE SILICON SOLAR CELLS

8.1 Introduction

The incorporation of oxide films and film stacks into c-Si solar cells offers potential efficiency gains through reduced optical and recombination losses compared with the standard Al-BSF cells with SiNx ARC and passivation. The use of APCVD to deposit the oxide films offers a lower cost alternative to traditional vacuum based deposition processes. Together, the ability to increase performance and reduce the cost of cells using a process technology that is highly compatible with high volume manufacturing is the primary reason for investigating APCVD oxide films in this work. In this chapter, the impact of incorporating APCVD oxide films on the performance Al-BSF and pPERC cells is explored.

8.1.1 The Baseline

In this work, conventional mono-Si Al-BSF cells with an efficiency of 18.4% will be used as the baseline (Al-BSF I) for comparing other cell designs. This represents an achievable and common level of performance for mono-Si Al-BSF cells featuring SiNx passivated, homogeneously doped emitters. The process flow for this type of cell is shown in Figure 8-1.
It should be noted that recently efficiencies as high as 19.9% have been independently confirmed using full area (243 cm$^2$) Cz wafers and various specialized processes (e.g., etched back emitter with thermal SiO$_2$ passivation) [110]. However, this efficiency level is likely pushing the practical limits in terms of
what is possible with Al-BSF cells considering the aforementioned high recombination at the rear of the cell ($J_{0\text{BSF}} \approx 400\text{-}700 \text{ fA}\cdot\text{cm}^{-2}$ [78]), which limits the maximum $V_{OC}$ to $\approx 650 \text{ mV}$ in the very best case (very minimal front and rear recombination). Additionally, $J_{SC}$ is also limited by poor internal back reflectance at the rear side of the cell.

8.2 Modeling Methodology

A one diode is used to model the $J$-$V$ characteristics of the different types of cells considered in this work. Since mono-Si wafers are being used, $m$ is assumed to be unity. $R_{SH}$ is assumed to be $10^4 \Omega \cdot \text{cm}^2$, and $R_S$ is assumed to be $0.8 \Omega \cdot \text{cm}^2$ in all cases. The primary input parameters for this work are $J_G$ and $J_{01}$, which strongly impact $J_{SC}$ and $V_{OC}$, respectively. Assuming a large enough $R_{SH}$, the following relationships hold:

$$J_{SC} = J_G,$$

$$V_{OC} = \frac{kT}{q} \ln \frac{J_G}{J_{01}}.$$  \hfill (8-2)

The $J_G$ and $J_{01}$ selected for the baseline Al-BSF cell are 37 mA$\cdot$cm$^{-2}$ and 840 fA$\cdot$cm$^{-2}$, respectively, resulting in the $J$-$V$ curve given in Figure 2-9. $J_G$ and $J_{01}$ are selected for each type of cell based on a combination of published results from the literature as well and measurements and simulations performed directly for this
work. Each type of cell considered represents an incremental improvement over the baseline Al-BSF cells.

8.3 Results and Discussion

8.3.1 Al-BSF Cells

To reduce $J_0$ (Figure 2-7) and improve the short wavelength IQE of an Al-BSF cell, a selective emitter passivated with thermal SiO$_2$ and featuring a PECVD SiN$_x$ ARC can be used, which will refer to as Al-BSF II. The $J_G$ of this SiO$_2$ passivated cell can be further improved by using a pc-TiO$_x$/AlO$_x$ DLARC deposited by APCVD (Al-BSF III) rather than a SiN$_x$ ARC. In all three of these Al-BSF cells, APCVD can be used for P doping (i.e., emitter formation), and again, the ability to form locally doped regions (e.g., selective emitter) could be facilitated by the deposition of these thin solid PSG films which are driven in *ex situ*. The estimated performance benefits relative to the baseline are given in Table 8-1. A 0.3 mA·cm$^{-2}$ increase in $J_G$ and a 110 fA·cm$^{-2}$ reduction in $J_0$ were input into the model for Al-BSF II, leading to increases shown. An additional increase in $J_G$ of 0.3 mA·cm$^{-2}$ for Al-BSF III is attributed to the reduced front surface reflectance of the DLARC structure.
Table 8-1. $J_{SC}$, $V_{OC}$, and efficiency ($\eta$) of the baseline Al-BSF cell, as well as the performance increases of the alternative cell designs.

<table>
<thead>
<tr>
<th>Cell Design</th>
<th>$J_{SC}$ ($\Delta J_{SC}$) (mA cm$^{-2}$)</th>
<th>$V_{OC}$ ($\Delta V_{OC}$) (mV)</th>
<th>$\eta$ ($\Delta \eta$) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-BSF I: Homogeneous emitter with SiNx front</td>
<td>37</td>
<td>630</td>
<td>18.4</td>
</tr>
<tr>
<td>Al-BSF II: Selective emitter with SiO$_2$/SiNx front</td>
<td>37.3 (+0.3)</td>
<td>633 (+3)</td>
<td>18.7 (+0.3)</td>
</tr>
<tr>
<td>Al-BSF III: Selective emitter with SiO$_2$/pc-TiO$_x$/AlO$_x$ front</td>
<td>37.6 (+0.6)</td>
<td>634 (+4)</td>
<td>18.9 (+0.5)</td>
</tr>
<tr>
<td>$p$PERC I: Homogeneous emitter with SiNx front and AlO$_x$/SiNx rear</td>
<td>38.5 (+1.5)</td>
<td>650 (+20)</td>
<td>19.9 (+1.5)</td>
</tr>
<tr>
<td>$p$PERC II: Selective emitter with SiO$_2$/SiNx front and AlO$_x$/SiNx rear</td>
<td>38.8 (+1.8)</td>
<td>659 (+29)</td>
<td>20.3 (+1.9)</td>
</tr>
<tr>
<td>$p$PERC III: Selective emitter with SiO$_2$/pc-TiO$_x$/AlO$_x$ front and AlO$_x$/SiO$_x$/TiO$_x$ rear</td>
<td>39.6 (+2.6)</td>
<td>659 (+29)</td>
<td>20.7 (+2.3)</td>
</tr>
</tbody>
</table>

8.3.2 $p$PERC Cells

As shown in Figure 2-10, rear passivated cells like $p$PERC cells are expected to gain significant market share in the coming years. An important advantage of $p$PERC cells compared to $n$PERT and $n$PERL is that the industry can still utilize the majority of its current manufacturing infrastructure with only a few unit processes added to the overall process flow. Additionally, B-doped $p$-type Cz wafers can still be used, which are produced in high volumes at relatively low cost. However, these wafers suffer from lower bulk minority carrier lifetimes ($\tau_b < 1$ ms) and are susceptible to light induced degradation, a phenomena in which $\tau_b$ is reduced upon exposure to light due to the formation of recombination-active B-O complexes [174].

As previously mentioned, $p$PERC cells provide an efficiency boost by reducing $J_0$, and therefore the total $J_{01}$ of the cell, which is shown in Figure 8-2. Additionally, there is an increase in the internal back reflectance due to the rear side dielectric, which results in a $J_G$ boost. First consider a $p$PERC cell featuring
the same front side and bulk properties of the baseline Al-BSF cell, but featuring an AlO\textsubscript{x}/SiN\textsubscript{x} rear side passivation stack and local \(p^+\) back contacts (\(p\)PERC I). The reduction in \(J_{01}\) (due to \(J_{0r}\)) is estimated to be 470 fA-cm\(^{-2}\) (from 840 down to 370 fA-cm\(^{-2}\)) and the increase in \(J_G\) estimated to be 1.5 mA-cm\(^{-2}\) (due to \(R_i\)). These improvements yield the results shown in Table 8-1.

Another obvious improvement is to again apply a selective emitter with thermal SiO\textsubscript{2} passivation and SiN\textsubscript{x} ARC (\(p\)PERC II), resulting in the same \(J_{01}\) and \(J_G\) reductions described for Al-BSF II compared to Al-BSF I. Finally, a SiO\textsubscript{2} passivated selective emitter with the pc-TiO\textsubscript{y}/AlO\textsubscript{x} DLARC and AlO\textsubscript{y}/SiO\textsubscript{y}/TiO\textsubscript{x} rear side stack (\(p\)PERC III) results in an additional \(J_G\) increase of 0.8 mA-cm\(^{-2}\) compared to \(p\)PERC II. Simulated \(J-V\) curves for all of the Al-BSF and \(p\)PERC cell designs are shown in Figure 8-3. Clearly the \(p\)PERC III demonstrates the highest

![Recombination model for a PERC or PERL cell highlighting some of the critical recombination parameters and the region of the cell in which they occur.](image)
performance, and all of the key aspects of this cell can be implemented in a low cost way using multi-layer front and rear side film stacks deposited via APCVD.

![Simulated J-V curves for all of the p-type cell designs considered in this work, with the pPERC III cell featuring the front and rear APCVD oxide stacks showing the best performance.](image)

Figure 8-3. Simulated $J$-$V$ curves for all of the $p$-type cell designs considered in this work, with the $p$PERC III cell featuring the front and rear APCVD oxide stacks showing the best performance.

8.4 Summary

In this chapter, five different cell designs are compared against an 18.4% efficient Al-BSF cell, two of which are improvements on the Al-BSF design and the other three are different $p$PERC cells. Aside from the use of APCVD, all of the cell designs included make use of standard materials (e.g., $p$-type Cz wafers) and processes. A one-diode model was used with equivalent input parameters used in each case except for variations in $J_G$ and $J_{01}$ that were taken based on a combination of published results from the literature and measurements and
simulations performed directly for this work. Based on these estimated performance improvements, the highest performing cell design ($p$PERC III) results in a calculated efficiency of 20.7% or an absolute efficiency increase of 2.3% over the baseline. This large improvement can be attributed to: reduced front surface reflectance by using the pc-TiO$_x$/AlO$_x$ DLARC ($J_G$ increase); rear side passivation using AlO$_x$ ($J_{01}$ reduction); and improved light trapping using the intermediate SiO$_x$ reflector layer in the rear side stack ($J_G$ increase).
CHAPTER 9 - CONCLUSION

Dielectric films are utilized in c-Si solar cells for a number of functions. In the case of c-Si Al-BSF cells, the most obvious use is SiN\textsubscript{x} as an ARC and passivation layer. Alternatives to SiN\textsubscript{x} also exist, and in this work, the use of functional oxide films for photon management, surface passivation, and doping in Al-BSF and advanced c-Si cell architectures will be explored. The primary thrust of my proposed research is on atmospheric pressure chemical vapor deposition (APCVD) of functional oxide films and film stacks for c-Si solar cells. The primary motivation of integrating APCVD oxide films into c-Si cell manufacturing is to reduce manufacturing cost by eliminating vacuum-based processing during film deposition and increase efficiency through improved surface passivation and photon management, which can also reduce cost (per W\textsubscript{p}) by increasing power output per cell.

Process development for the APCVD film deposition and integration of these films into various cell architectures has been performed at a R&D facility owned and operated by SCHMID Group in Freudenstadt, Germany. Measurements and characterization of various samples (e.g., films, processed wafers, cells) have been carried out at numerous sites around the world, including multiple SCHMID Group facilities in Germany, the University of Konstanz (Konstanz, Germany), Brookhaven National Laboratory (New York, U.S.), Tau Science (Oregon, U.S.), National Renewable Energy Laboratories (Colorado, U.S.), JA Woollam Co. (Nebraska, U.S.), Semilab SDI (Florida, U.S.), and the University of Central Florida.
Key contributions to the field of c-Si PV made in this body of work are given below:

- Double layer anti-reflection coatings consisting of pc-TiO$_x$/AlO$_x$ are shown to exhibit a lower reflectance, particularly at short wavelengths ($\lambda < 500$ nm), compared to the industry standard plasma-enhanced chemical vapor deposition silicon nitride (SiN$_x$).

- To maximize internal back reflectance of rear passivated cells, different rear reflector designs (with and without SiN$_x$ capping) are evaluated, with AlO$_x$/SiO$_x$/TiO$_x$ the preferred choice for maximizing the long wavelength quantum efficiency.

- Low surface recombination velocities ($S_{eff,max} = 8$ cm/s) are achieved for APCVD AlO$_x$. This is due to AlO$_x$ providing excellent field effect passivation (|$Q| > 2 \cdot 10^{12}$ cm$^2$) and reducing the number of interface defects ($D_{it,midgap} < 4 \cdot 10^{11}$ ev$^{-1}$cm$^2$).

- Improved control of phosphorus surface concentration during in-line diffusion is demonstrated in this work using APCVD PSG as a dopant source, and potential applications for APCVD BSG and AlO$_x$:B as boron dopant sources for $n$-type cell architectures are also explored.
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