Characterization and Modeling of Ion Transport Kinetics in p-Si Photovoltaic Modules

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in

NanoEngineering

by

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2020
The dissertation of Erick Rolando Martinez Loran is approved, and it is acceptable in quality and form for publication on microfilm:

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University of California, San Diego

2020
DEDICATION

To my family, who has supported me through this journey.
The world stands out on either side

No wider than the heart is wide;

Above the world is stretched the sky,—

No higher than the soul is high.

—Edna St. Vincent Millay
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List of Abbreviations

AC  Alternating current.

Al-BSF  Aluminum back-surface field.

ARC  Anti-reflective coating.

BTS  Bias-temperature-stress.

C-V  Capacitance-voltage.

DC  Direct current.

EDX  Energy dispersive X-ray spectroscopy.

EVA  Ethylene-vinyl acetate.

FEM  Finite element method.

HRTEM  High-resolution transmission electron microscopy.

J-V  Current-density-voltage.

MIS  Metal-insulator-semiconductor.
n-Si $n$-type silicon.

p-Si $p$-type silicon.

n$^+$-Si Highly-doped $n$-type silicon.

PDE Partial differential equation.

PECVD Plasma-enhanced chemical vapor deposition.

PID Potential-induced degradation.

PID-s Potential-induced degradation of the shunting type.

PNP Poisson-Nernst-Planck.

PV Photovoltaic.

SF Stacking Fault.

SIMS Secondary-ion mass spectroscopy.

ToF-SIMS Time-of-flight secondary-ion mass spectroscopy.

XPS X-ray photoelectron spectroscopy.
**List of Symbols**

116 $\epsilon_0$  Permittivity of free space

117 $\epsilon_r$  Relative permittivity

118 $\mu$  Mobility (ionic or electronic)

119 $\nabla$  The Nabla operator

120 $\phi$  Electric Potential

121 $E$  Electric field

122 $C$  Concentration

123 $k_B$  Boltzmann’s constant

124 $q$  Elementary charge

125 $Q_S$  Image charge in the semiconductor.

126 $R_{sh}$  Shunt resistance

127 $T$  Temperature

128 $V$  Voltage
$V_{FB}$  Flatband voltage
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ABSTRACT OF THE DISSERTATION

Characterization and Modeling of Ion Transport Kinetics in p-Si Photovoltaic Modules

by

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Doctor of Philosophy in NanoEngineering

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Professor Prabhakar R. Bandaru, Chair

Though generally reliable, silicon solar modules can be subject to unforeseen degradation, leading to a duty life shorter than the expected 25-year life cycle. Potential-induced degradation (PID) has proven difficult to characterize and study. This dissertation is dedicated to developing a physical model to understand the kinetics of PID of the shunting type, and explain the factors that may lead to the design of PID-robust modules.

A bias-temperature stress (BTS) methodology to study ion migration in dielectric films is presented, which accounts for the contribution of bulk traps in the dielectric. Using this method, an Arrhenius relationship for the diffusivity of Na⁺ in SiNx is determined, for which the prefactor is \( D_0 = 1.4 \times 10^{-14} \text{ cm}^2/\text{s} \), and the activation energy is \( E_a = 0.14 \text{ eV} \), with a 95% confidence interval of [0.07, 0.21] eV. Based on this result, we bound the transit time of sodium ions, through highly resistive SiNx anti-reflective coatings, within 1 h and 2 d, under temperature and electric fields relevant to PV operation.
A numerical solution to the coupled Poisson-Nernst-Planck system of equations is presented, based on the finite element method (FEM), that can accurately simulate ionic transport in dielectrics and stacks of materials. The FEM implementation adequately describes the accumulation of charge in the semiconductor interface of metal-insulator-semiconductor capacitors (MIS). Using this model, we evaluate diffusion coefficients of Na\(^+\) in SiO\(_2\) under BTS conditions.

A methodology to simulate PID degradation in PV modules is derived, which uses the result from the ion transport model to simulate the characteristic J-V of the devices. PID is adequately described by the presence of metallic shunt at the p-n junction of the cell, for which, the metal conductivity depends on the sodium concentration. An upper bound for the diffusivity of Na in stacking faults that result in PID is estimated to be \(10^{-14}\) cm\(^2\)/s, based on comparison of the simulated PID time series with experimental reports of PID-s.
The photovoltaic industry has made outstanding progress over the last decades to bring the promise of a low-carbon economy closer than ever. One of the main advantages of photovoltaic energy is the low cost of operation inherent to silicon photovoltaic (PV) modules, which largely compensates for the considerable initial investment of solar developments. Silicon PV modules are required to operate with minimal power degradation over an average lifespan of 25 years in order to meet commercial warranties \[1,2\]. Driven by this concern, reliability studies have become a subject of interest. Several procedures have been developed to test the reliability of modules under normal operation and under accelerated conditions. The latter are devised to forecast the performance of PV modules over the course of many years; provided that the acceleration protocols adequately relate to long term PV module operation. While some of the mechanisms of degradation seem evident (e.g. mechanical failure, loss of transparency of the encapsulant, delamination, shattering, among others) and have been addressed, the type of degradation studied in this dissertation is intrinsically more complex and remediation requires comprehensive knowledge of the properties of all the materials in the module.

A brief introduction on potential-induced degradation of the shunting type is be given in this chapter, followed by an overview, in chapter 2, of the transport of Na in PV modules.
In chapter 3, a quantification methodology for the transport of Na in silicon nitride (SiNx) is be presented. It is be shown that, for low ionic concentrations with respect to the applied electric stress, the kinetics of Na transport can be described as a diffusion-advection problem. A methodology to quantify ion migration in SiNx metal-insulator-semiconductor (MIS) capacitors is be demonstrated. A detailed analysis on the characteristic transit time is be presented, beyond which accumulation at the semiconductor interface occurs and leakage of Na to the silicon can occur at a larger scale.

In chapter 4, a finite element solution to the coupled Poisson-Nernst-Planck system of equations is derived, which is used to model transport of charged species in metal-insulator-semiconductor devices and other stacks of materials, beyond the assumptions of low contaminant concentration with respect to the applied electrical stress. A comparison with experimental data is given which agrees well with the predictions of the model.

In chapter 5, a modeling framework is presented, which mechanistically describes the kinetics of PID-s degradation in p-Si modules, based on the bill of materials in the PV module and the operating conditions. Based on the results of the model, and comparison with PID reports, an upper bound for the diffusion coefficient of Na in the stacking fault is be estimated.

1.1 What is Potential-Induced Degradation?

Solar panels incorporate several individual solar cells connected in series, in order to achieve typical load requirements of several hundreds to thousands of volts. Fig. 1.1 shows a simplified schematic of a solar module, where each individual cell is connected in series to achieve a load of 1000 V. As these devices are mounted on a metal frame that is grounded, the voltage
differential between the metal frame ($V = 0$) and the floating potential of the cells becomes considerable at the extremes of the array. Also in Fig. 1.1 a simplified schematic of the cross-section of a mono-facial module is shown, consisting of a solar cell with a SiN$_x$ anti-reflective coating (ARC), encapsulated within a polymer (typically ethylene-vinyl acetate or EVA), and a glass window on the front side, usually made from soda lime glass. It has been observed that the cells subject to a more negative potential with respect to the metal frame suffer from degradation in the output power [3–5]. This degradation mode is called potential-induced degradation (PID) and is known to affect $n$-type silicon (n-Si) and $p$-type silicon (n-Si) devices differently. In the n-Si case, it has been reported that degradation is the result of surface polarization and is almost completely reversible [6], whereas in p-Si, the degradation is due to a reduction in the shunt resistance $R_{sh}$ of the device [5] as is illustrated in Fig 1.2. While recovery has been documented for p-Si modules affected by PID [5, 7–15], in general, only partial recovery is observed, and it requires the application of a temperature stress and/or inverting the polarity of the voltage between the cell and the frame. This makes the study of this type degradation on p-Si of special interest, and is the focus of this research.
PID in p-Si occurs as a result of several factors facilitating the formation of electrical shunts in the emitter of the device. Initial investigations suggested corrosion played an important role in degradation [3], which led to the characterization of leakage currents across the module stack, aimed at determining the physical pathways of the degradation process [5, 6, 16, 17]. These experiments helped to identify ionic currents and, particularly, sodium ions (Na+) as the main factor involved in PID in p-Si solar modules [17, 18].

1.2 Root cause of PID

The mechanism by which Na induces shunting has been elucidated by a combination of energy dispersive X-ray spectroscopy (EDX) and high-resolution transmission electron microscopy (HRTEM) studies performed at the Fraunhofer Center for Silicon Photovoltaics, which showed incorporation of Na inside stacking faults (SFs) in the silicon emitter, on severely shunted regions of PID-affected devices [9, 12, 13, 19]. These findings indicate that Na introduces a large con-
centration of defect states in the band energy diagram, within the p-n junction of a solar cell, which induce undesirable recombination. These defects are ultimately responsible for a substantial decrease in $R_{sh}$ [9]. The mechanism is illustrated in Fig. 1.3 where it is depicted how ionic Na is transported through the SiNx anti-reflective coating of the module, driven by the electric field. Then, a large concentration of Na builds up at the interfacial silicon oxide film, followed by in-diffusion to the stacking faults in the silicon emitter. Once a critical concentration of Na is accumulated in the SF, the defect results in shunting of the junction of the solar cell. Therefore this mode of degradation is referred to as PID of the shunting type or PID-s.

### 1.3 Origin of Na contamination

The front cover glass has been pointed out as the most likely source of Na ions in the module stack [7, 18, 20, 21], mediated by an activation process involving temperature and humidity.
 Nevertheless, PID-s has been reported to occur in the absence of a front cover glass and even in the absence of the polymer encapsulant, when the electric field is supplied by a corona discharge. Evidence of Na contamination has been reported within the EVA polymer encapsulant specially close to the surface of SiN\textsubscript{x}. This suggests that Na contamination introduced during the module lamination. Nevertheless, introduction of Na contamination from the front cover glass can not be ruled out, especially in combination with high contents of moisture and elevated temperatures.

### 1.4 Electric Potential in the module

The magnitude of the electric field in the module stack and, specifically in the SiN\textsubscript{x} film determines to a large extent the ingress of Na in the emitter of the device and hence, susceptibility to PID-s. The potential drop across the module stack has been explained by a voltage divider model. This model assumes that the main path of current occurs through a circuit of series resistors corresponding to the glass, polymer encapsulant, and SiN\textsubscript{x} layers, as shown in Fig. 1.4. Since the highly doped emitter (n*-Si) has a resistivity in the order of m\(\Omega\) cm, its contribution can be safely neglected. The leakage current \(I_{\text{leak}}\) is given by

\[
I_{\text{leak}} = \frac{V_{\text{stress}}}{R_{\text{module}}} = \frac{AV_{\text{stress}}}{\sum_{n=1}^{3} \rho_{n}l_{n}}, \tag{1.1}
\]

where \(V_{\text{stress}}\) is the voltage stress applied to the module stack, \(R_{\text{module}} = R_{\text{glass}} + R_{\text{poly}} + R_{\text{SiN}}\), \(A\) is the area of the device and \(\rho_{n}, l_{n}\) are the electrical resistivity and thickness of the \(n\)th-layer (1 \(\rightarrow\) glass, 2 \(\rightarrow\) encapsulant, 3 \(\rightarrow\) SiN\textsubscript{x}). Then, the voltage drop \(V_{n}\) at each material is given by

\[
V_{n} = I_{\text{leak}}R_{n} = \frac{\rho_{n}l_{n}}{\sum_{m=1}^{3} \rho_{m}l_{m}}V_{\text{stress}} \tag{1.2}
\]
1.5 Sodium Transport

While some phenomenological models to describe the kinetics of PID-s have been proposed [14, 28, 29], in order to provide adequate solutions to prevent PID-s, a mechanistic understanding of the processes behind the shunt formation is required. In that sense, very few attempts have been made to propose a physical description of PID-s kinetics [15]. Transport of Na\(^+\) in the module stack is governed by Nernst-Planck equation

\[
\frac{\partial C(x,t)}{\partial t} = -\nabla \cdot \mathbf{J} = -\nabla \cdot [-D \nabla C - \mu C \nabla \phi(x,t)],
\]

where \(C(x,t)\) is the concentration of Na\(^+\) in units of ions per unit volume, as a function of the position \(x\) and time \(t\), \(\mathbf{J}\) represents the total flux in units of ions per unit area per time, \(D\) is the diffusion coefficient of Na\(^+\) in the material in units of unit area per time, \(\mu = qD/k_BT\) is the ionic mobility in units of cm\(^2\)/V/s, \(q\) is the elementary charge, \(k_B\) is Boltzmann’s constant, \(T\) is the absolute temperature and \(\phi(x,t)\) is the electric potential.
We shall see that, due to the discontinuity of the properties (e.g. diffusion coefficient, equilibrium Na concentration), numerical integration generally is required, except for a very limited subset of conditions where coarse approximations can simplify the problem [15].

1.6 Summary

Engineering solutions to alleviate PID-s requires a mechanistic model to describe the processes behind shunt formation. While understanding of the mechanisms leading to loss of performance has remarkably advanced over the past decade, the kinetics of degradation still needs clarification. Phenomenological models can successfully predict some of the trends and timescales for PID degradation but fail to correlate material properties that can be used to engineer PID-robust silicon modules.

The motivation of this work is to propose a physical model that mechanistically explains potential-induced degradation in the solar module. The overarching goal is to parametrize the kinetics of PID-s and explain the factors that make a module PID-robust.
Na transport kinetics in the module stack

The decoration of stacking faults in the n⁺-Si emitter of the PV module follows the transport of Na contamination through the different materials in the module stack. This process is driven by the large voltage differential between the frame and the cell at the extremes of the array. Transport is governed by Nernst-Planck equation (1.3)

\[
\frac{\partial C(x,t)}{\partial t} = \nabla \cdot (D \nabla C) + \mu C \nabla \cdot \nabla \phi(x,t) + \mu \nabla C \cdot \nabla \phi(x,t),
\] (2.1)

Eqn. (2.1) needs to be solved for each material and coupled with adjacent materials by means of adequate boundary conditions. This is illustrated in Fig. 2.1 where the module stack is schematically drawn alongside with the potential drop due to the applied voltage stress on the layer stack.

The first difficulty in this approach is the fact that the values of the diffusion coefficient of Na in the module stack are either not available for the materials, or are extrapolated from measurements performed at temperatures not relevant to PID [30–32]. It is required that characterization of Na kinetics is performed under conditions as close as possible to operational, or with accelerated testing.

As a first approximation, we assume that Na⁺ in the front cover glass is accessible directly at the glass/encapsulant interface in such a way that release is not rate limiting. This is in agreement with the assumption that Na⁺ transport is a temperature- and humidity- activated process in soda
According to the voltage divider model, application of a voltage stress over the module leads to a potential drop of different magnitude in each material. The resulting electric field induces a drift term that adds to the otherwise diffusive transport through the materials. The potential in the silicon emitter is neglected due to the large conductivity of this region, hence transport is assumed to occur just by diffusion in Si.

In other words, we assume that the front cover glass plays the role of a source of ions at the glass/encapsulant interface, which reduces the number of materials on which Eq. (2.1) needs to be solved.

We also assume that the electric field $E = -\nabla \phi$ is normal to the glass/encapsulant interface. Furthermore, it is be assumed that diffusion can be approximated as a one-dimensional problem which simplifies the computation without loss of generality.

### 2.1 Approximate voltages in the module stack

As discussed in Sec. 1.4, the potential drop in each material depends on the resistivity and thickness of all of the other materials in the module stack. Table 2.1 shows typical literature values of the resistivities and thicknesses of the different materials in the module stack. The estimated electric field is based upon an applied stress voltage of $V_{\text{stress}} = 1000 \text{ V}$. Notice that the real values of the resistivities can be subject to orders of magnitude variations depending on the specific pro-
Table 2.1: Typical thicknesses and resistivities of the materials in a c-Si module

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<thead>
<tr>
<th>Layer</th>
<th>Material</th>
<th>Thickness (cm)</th>
<th>Resistivity (Ω cm)</th>
<th>Estimated $E$ (kV/cm)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Glass$^b$</td>
<td>0.32</td>
<td>$3 \times 10^{12}$</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>EVA$^c$</td>
<td>$4.5 \times 10^{-2}$</td>
<td>$10^{12} - 10^{15}$</td>
<td>$10^{-1} - 10^{4}$</td>
</tr>
<tr>
<td>3</td>
<td>SiN$_x$$^d$</td>
<td>$75 \times 10^{-7}$</td>
<td>$10^{4} - 10^{19}$</td>
<td>$10^{-2} - 10^{5}$</td>
</tr>
</tbody>
</table>

$^a$ Assuming a stress voltage of 1000 V.

$^b$ Ref. [34]

$^c$ Ref. [3, 34]

$^d$ Fit to the ohmic regime in Ref. [27] and Ref. [33].

$^e$ Ref. [34]

cessing conditions of the materials, as well as on the relative humidity and temperature [3, 22, 27].

In particular, electronic transport in SiN$_x$ processed by plasma-enhanced chemical vapor deposition (PECVD) can range between $10^4$ to $10^{19}$ Ω cm depending on the Si/N ratio introduced during deposition [33].

2.2 Transport of Na in EVA

The widespread use of EVA as encapsulant in Si solar modules makes it important to determine the impact of Na$^+$ transport in this polymer. Induced-coupled plasma (ICP) measurements have successfully identified Na contamination in Si modules within the EVA encapsulant, close to the SiN$_x$ ARC, even prior to PID test [26]. To validate this assumption, Na drift-diffusion experiments were performed in metal-EVA-metal structures to determine the penetration depth of Na under conditions as close as possible to the ones referenced in Table 2.1.
2.2.1 Experiment

Metal-insulator-metal (MIM) structures were prepared by coating aluminum foil with EVA. Prior to the coating, aluminum foil is cleaned with acetone, isopropyl alcohol and deionized water. After curing, the exposed surface of EVA was intentionally contaminated with Na by thermally evaporating NaCl at $\sim 800 \, ^\circ$C. After contamination, silver paste was deposited onto the contaminated surface to complete the MIM structure. The thickness of EVA was determined from multiple point measurement using scanning electron microscopy (SEM). The average value of the thickness of EVA is $440 \, \mu m$.

The MIM structures were put on a hot plate at $80 \, ^\circ$C and subject to a voltage stress of 100 V, equivalent to $2.3 \, kV/cm$ (roughly one third of the value estimated in Table 2.1). Three repetitions were performed for the same conditions. Relative humidity was not monitored.

The samples were sent to the National Renewable Energy Laboratory to perform time-of-flight secondary-ion mass spectroscopy characterization (ToF-SIMS). After contact removal, the samples were rinsed in deionized water to remove excess Na. For ToF-SIMS analysis the samples were sputtered from the side onto which Na contamination was introduced.

2.2.2 Results

Fig. 2.2 shows a representative SIMS profile of a sample stressed at $80 \, ^\circ$C and $2.3 \, kV/cm$ for 12 h. Due to the large concentration of ions at the interface, a large memory effect is observed in the concentration profile, due to repositioning of Na during sputtering. During this timescale, Na reached a depth of $\sim 15 \, \mu m$, beyond which, the concentration drops below detectable limits. By fitting the concentration profile to Eq. (3.7), we estimated a diffusion coefficient of $4 \times 10^{-14} \, cm^2/s$. 
Figure 2.2: Representative Na drift-diffusion profile obtained by SIMS of a metal-EVA-metal structure intentionally contaminated with Na on one of the ends stressed for 12 h under an electric field of 2.3 kV/cm at a temperature of 80 °C.

Using Eq. (3.9), we determined that the characteristic Na transit time, for a 300 µm thick EVA encapsulant stressed at 7 kV cm$^{-1}$ is $\approx$ 36h. This finding contrasts with the trends on the normalized power output observed on PID-susceptible devices from reports of p-Si devices stressed under similar conditions [5, 35–38], and those from normalized $R_{sh}$ [24, 39–41] for which a 5% degradation of the initial condition occurs within an average time of $\approx$ 13 h. While Eq. (3.7) does not consider the contribution of the ionic concentration to the electric potential, the net effect of this is to screen the applied electric stress. This means that, when considering the image charge effect of the ion distribution, drift decreases considerably close to the source. This result indicates that transport in EVA has a limited impact in the kinetics of PID. Given this result, we think that transport of Na to the cell interface occurs during lamination, or that Na is already present on cell
2.3 Summary

The typical electrical stress in each material of the PV module was estimated using a voltage divider model, for which a potential drop ranging from $10^{-2}\,\text{V cm}^{-1}$ to $10^{4}\,\text{V cm}$ in the $\text{SiN}_x$ film was estimated. Drift-diffusion experiments in EVA showed that $\text{Na}^+$ is not expected to traverse the full depth of the encapsulant at significant concentrations to cause PID-s in the timescales within which degradation is typically reported on PID-prone devices. This finding is in agreement with reports suggesting the presence of $\text{Na}^+$ on the surface of $\text{SiN}_x$ prior to PID tests. It is possible that damp-heat tests at a high relative humidity (85 % RH) lead to electrochemical reactions that are not accounted for in the scope of this work. Nevertheless, changes in the conductivity of EVA associated to different levels of water content and temperature might have an impact on the magnitude of the electric field in $\text{SiN}_x$. 
3 | Transport of Na in SiN$_x$

Sodium moves through SiN$_x$ as an ionic species subject to the kinetics described by Eq. (3.7). In this chapter we show that transport in SiN$_x$ is very sensitive to the magnitude of the applied electric potential, as well as the average concentration of Na$^+$. We also establish a number of conditions within which, we can simplify Eq. (3.7), in order to derive analytical approximations that allow us to characterize the drift-diffusion kinetics of Na contamination in dielectrics.

While some reports suggest that SiN$_x$ films of the sort used in solar modules can act as barriers against mobile charge contamination [42–44], there is also evidence that, under an electric field of 0.5 MV/cm, sodium can drift across an 80 nm thick layer of SiN$_x$ in just 25 min at 80 °C [32].

Given the large variations in the resistivities of the different materials in p-Si modules, electric fields of the order of 0.5 MV/cm can’t be discarded. Therefore, accurate knowledge of Na kinetics in silicon nitride under typical module operating conditions is necessary.
3.1 Characterization of drift-diffusion kinetics using C-V measurements

Mobility of ionic charge in dielectrics has been addressed in the past by means of transient current measurements [45–48]. This method assumes that mobile charges drift over the entire length of the dielectric during the measurement. This assumption is adequate for ions with mobilities fast enough to enable drift across the dielectric within the time scale of the experiment or less [48]. Nevertheless, ions with lower diffusivities might not satisfy this criterion, especially at low temperatures. In contrast, methods relying on the determination of the flatband voltage ($V_{FB}$) from capacitance-voltage (C-V) methods, enable the detection of ion migration in dielectrics on a broader temperature range. Among these methods, the bias-temperature-stress (BTS) method has been widely used to determine ionic migration [43–45, 49–52].

3.2 Trap-corrected bias-temperature-stress method

In the standard BTS method, ionic contribution to flatband voltage measurements can be obfuscated by carrier trapping effects and hence, modifications are required to adequately quantify ion kinetics. A signature due to trapping effects has in fact been identified in dielectrics that are known to have a large density of trap centers, including SiNx [49, 53, 54] and high-$k$ dielectrics such as hafnium oxide [55]. Conflation of flatband shift due to carrier trapping in ionic mobility measurements results in incorrect attribution of drift characteristics as seen in porous SiOx [51], which precludes reliable analysis of migration in the dielectric. We developed a time-resolved
capacitance-voltage method which incorporates a kinetics model to estimate the ionic diffusivity in dielectrics. We used this method to quantify the diffusion coefficient of Na$^+$ in SiN$_x$ which is necessary to study the ingress of Na in the emitter of p-Si modules leading to PID.

### 3.2.1 Flatband fitting

In the BTS method, the barrier for ionic diffusion is lowered by providing a thermal stress (i.e. heating the device above room temperature) and an electrical stress, by applying an electrostatic potential $V_{\text{stress}}$ to the dielectric. The flatband voltage at time $t$ with respect to its value at $t = 0$ is determined by integration of Poisson’s equation in the dielectric

$$\frac{d^2 \phi}{dx^2} = -q \frac{n(x,t)}{\epsilon_{\text{ins}}}, \quad n(x,t) \equiv z_{\text{ion}} C(x,t) + z_{\text{traps}} n_{\text{traps}}(x,t),$$

(3.1)

where $z_{\text{ion}}, z_{\text{traps}}$ are the valency of ionic species and traps respectively ($z_{\text{ion}} = 1$, for Na$^+$ and $z_{\text{traps}} = \pm 1$, depending on the type of carrier captured), $C(x,t), n_{\text{traps}}(x,t)$ are the concentration of mobile ions and occupied traps respectively, and $\epsilon_{\text{ins}}$ is the permittivity of the dielectric. Eq. (3.1) is integrated from a position in the insulator to the position $x = L$, located at the surface of the semiconductor. The boundary conditions assumed are that the band bending and the potential vanish at the silicon surface in the flatband condition ($d\phi/dx \to 0$ and $\phi \to 0$ as $x \to L$) and, that $\phi(x = 0) = V_{\text{FB}} - W_{\text{ms}}$, where $W_{\text{ms}}$ represents the difference between the work function of the metal and that of the semiconductor. This leads to the general expression for $V_{\text{FB}}$ [56]:

$$V_{\text{FB}}(t) = W_{\text{ms}} - \frac{q}{\epsilon_{\text{ins}}} \int_0^L x' n(x',t) dx'.$$

(3.2)
Assuming that the concentration of Na$^+$ and occupied traps is negligible at $t = 0$, we can define the shift in flatband voltage as

$$\Delta V_{FB}(t) \equiv V_{FB}(t) - V_{FB}(t = 0) = -\frac{q}{\epsilon_{\text{ins}}} \int_0^L x' C(x', t) dx' - \frac{q \tilde{C}_{\text{traps}}}{\epsilon_{\text{ins}}} \int_0^L x' n_{\text{traps}}(x', t) dx', \quad (3.3)$$

which is independent of $W_{\text{ms}}$ and captures the effect of occupied traps in the dielectric.

Eq. (3.3) also implies that, if ions and traps do not interact, their contribution can be decoupled which is the basis of the trapping correction.

The ionic contribution to the flatband voltage shift $\Delta V_{FB}^{\text{ion}}(t)$ can be now estimated by subtracting the component due to electronic trapping $\Delta V_{FB}^{\text{traps}}(t)$, measured on devices without intentional ion contamination $C(x, t) = 0$, from the flatband voltage shift measured on ion-contaminated devices:

$$\Delta V_{FB}^{\text{ion}}(t) = \Delta V_{FB}(t) - \Delta V_{FB}^{\text{traps}}(t). \quad (3.4)$$

### 3.3 Kinetics of ion diffusion and drift in SiN$_x$

The kinetics of ion transport is then obtained by relating $\Delta V_{FB}^{\text{ion}}(t)$ to the ionic concentration as prescribed by Eq. (2.1). From Eq. (3.1), we see that the electric potential is a function of the ionic and trap concentrations in the dielectric itself, which implies that Nernst-Planck and Poisson’s equations are coupled. Nevertheless, at times less than a critical value $\tau_c$, beyond which accumulation of ions at the interface leads to surface charges induce $E = Q/\epsilon$ comparable with $V_{\text{stress}}/L$, the concentration can assume a limiting constant value $C(x) = C$. In such a case, the solution to
the ionic component of (3.1) is simply $\phi = -\left(\frac{q}{\epsilon_{\text{ins}}}\right)L^2C$. This means that for concentrations

$$C \ll C_{\text{th}} \equiv \frac{2\epsilon_{\text{ins}}}{qL^2}V_{\text{stress}}$$

(3.5)

the magnitude of the ionic charge distribution is much less than the applied electric potential, and

the electric field can be assumed to be $V_{\text{stress}}/L$. The Na-contaminated SiN$_x$ films prepared for this

work were analyzed using X-ray photoelectron spectroscopy (XPS) which has a detection limit of

$5 \times 10^{18}$ cm$^{-3}$ and no signal corresponding to Na was detected. In comparison, the magnitude of

the applied voltage is 8.6 V over a 86 nm thick layer of SiN$_x$ ($\epsilon_r \approx 7$), which sets the right hand side

of (3.5) on the order of $10^{18}$ cm$^{-3}$, indicating that, indeed $C$ is low compared to $V_{\text{stress}}$ and hence,

$E = -\nabla \phi \rightarrow V_{\text{stress}}/L$. This allows us to assume a constant drift velocity $v_d = -\mu \partial_x \phi = zqDE/k_B T$

and remove Laplacian term in (2.1):

$$\frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) - v_d \frac{\partial C}{\partial x},$$

(3.6)

where we have reduced the problem to one-dimension. The advection term in (3.6) can be elimi-

nated by introducing the moving reference frame $[57, 58]$

$$x' = x - v_d, \quad t' = t,$$

which transforms Eq. (3.6) to a pure diffusion equation in the primed reference frame. We assume

a constant source of ions at the surface of SiN$_x$: $C(x = 0,t) = C_s$ and a closed boundary at the

Si interface: $[-D\partial_x C + v_d C]_{x=L} = 0$. Given these assumptions, we can now define the analytical

solution of Eq. (3.6) for this set of boundary conditions, before the onset of accumulation ($t < \tau_c$, discussed in Sec. 3.6) as follows

$$C(x,t) = \frac{C_s}{2B} \left[ \text{erfc}\left( \frac{x - \mu Et}{2\sqrt{Dt}} \right) + \text{erfc}\left( -\frac{x - 2L + \mu Et}{2\sqrt{Dt}} \right) \right],$$

(3.7)
with a normalization constant $B \equiv \text{erfc}(\mu Et/2\sqrt{Dt})$.

The diffusivity of ionic species $D$ and concentration of ions at the source $C_s$ can be determined from the experimental $\Delta V_{FB}$ by fitting the theoretical flatband shift obtained from (3.3) and (3.7) to the experimental flatband shift obtained through (3.4).

The fitting is performed using trust-region reflective nonlinear least squares. The uncertainty of the fitted parameters is taken from the 95% confidence intervals estimated from the covariance matrix of the fit and using the $t$-student distribution.

### 3.4 Experiment

Metal-insulator-semiconductor (MIS) structures were fabricated on $n$-type silicon (100) wafers with a resistivity of 2.7 $\Omega$ cm. The wafers were cleaned with acetone, ethanol and isopropyl
alcohol and then cleaned with RCAI and RCAII procedures, followed by a 1% hydrofluoric acid dip. SiN\textsubscript{x} films were grown on the polished side of the wafer using PECVD with a NH\textsubscript{3}/SiH\textsubscript{4} ratio of 7. This ratio was chosen to obtain high SiN\textsubscript{x} resistivity\textsuperscript{[59]} to ensure a significant potential drop across the dielectric, which leads to drift times within reasonable timescales in the experiments. Additionally, SiO\textsubscript{2} films were grown by dry oxidation at a temperature of 1100 °C. The thickness and refractive index of the as-grown films were mapped using spectroscopic ellipsometry. An average thickness of 86 nm and an average index of refraction of 1.89 at 600 nm were estimated for the SiN\textsubscript{x}. The dielectric layers were subsequently cleaned with isopropyl alcohol and ethanol to remove surface contaminants and the back surface was swabbed with hydrofluoric acid. Aluminum gate electrodes of approximately 200 nm were deposited by thermal evaporation onto SiN\textsubscript{x}. The electrodes were defined by a shadow mask with 1 mm diameter circles and a pitch of 2.54 mm. A layer of aluminum was deposited on the bottom side of the wafer to produce the back contact. In devices with intentional contamination, 25 nm of NaCl were thermally evaporated at 800 °C, followed by the deposition of the gate without breaking vacuum.

An in-situ C-V setup with automated BTS capabilities was developed to perform migration studies. As illustrated in Fig. 3.1, the temperature stress is provided by a temperature-controlled hotplate with feedback from a thermocouple directly placed underneath the sample. A software-controlled relay was used to switch between stressing and measuring modes in order to periodically monitor ΔV\textsubscript{FB} as a function of stress BTS time. Contact to the back of the sample was achieved by placing the sample on an Al-coated silicon wafer, which provides adequate thermal distribution. Contact to the Al-coated wafer and the gate was achieved by means of Au-plated spring-loaded contacts. The system applied BTS stress to the MIS capacitors in 1 or 4 h intervals using a programmable hotplate and a Keithley 2401 source meter to apply a direct current (DC) bias. It has
been reported that an electric field on the order of 1 MV cm$^{-1}$ is required to observed PID in silicon PV modules, which contrasts with the voltage-divider estimation in Table 2.1. The reason for this discrepancy is unknown [60], but it could be attributed to large variations in the electrical properties introduced during the PECVD deposition of SiN$_x$. An electric field of 1 MV cm$^{-1}$, is adequate for our experiments since it satisfies Eq. (3.5) and was thus applied to the MIS structures during migration experiments, in agreement with other studies [32]. After each BTS interval, a fan (Fig. 3.1) was used to cool down the devices to room temperature within 15 min. Once cooled, C-V curves were acquired with a HP4194A impedance analyzer at 1 MHz, to ensure that ions were unaffected by the 100 mV (peak to peak) alternating current (AC) signal from the impedance analyzer. During the C-V acquisition, the DC voltage was swept from $-8.6$ to $8.6$ V and each measurement was averaged 32 times with a dwell time of 5 ms per point. The flatband voltage as a function of BTS time was estimated from the C-V curves using a second-derivative method described in Ref. [61].

3.5 Results

The need to correct for traps in the dielectric to obtain the ionic component to $\Delta V_{FB}$ is shown in Fig. 3.2. In devices without intentional Na contamination, $\Delta V_{FB}$ increases as a function of time, which is explained by an increase in negative charge in the dielectric according to (3.3). This effect originates from electron trapping as demonstrated in a previous study [54], and can be further quantified by integrating Frenkel-Poole emission current [63]. A first-order kinetics model [64] was used to determine a trapping time constant of 2.5 h. Because each C-V sweep is completed in 2 min, it is not expected that the DC bias from the C-V measurement influences
Figure 3.2: Flatband shift as a function of time and temperature: (a) in SiN<sub>x</sub> capacitors stressed at 1 MV cm<sup>−1</sup>. An example of raw flatband shift including both Na<sup>+</sup> and trapping is shown in black empty squares with a dotted line as a guide to the eye. Trapping-corrected flatband voltage shifts are shown at different temperatures. The fits obtained from the Nernst-Planck migration model are depicted by solid lines. (b) SiO<sub>x</sub> capacitors without trapping correction (pure ionic shift) in both Na-free and Na-contaminated devices at 0.5 MV cm<sup>−1</sup> and 50 °C. Reproduced from Ref. [62].

The raw ΔV<sub>FB</sub> signal (before trapping correction) in a Na-contaminated sample is shown in solid black circles in Fig. 3.2, which includes the contributions from both, electron trapping (negative charging) and Na migration (positive charging). To account for charge due electron trapping in SiN<sub>x</sub> [49, 53, 54], we estimated ΔV<sub>FB</sub><sup>traps</sup> by averaging the flatband shift from four Na-free devices and subtracted its contribution from ΔV<sub>FB</sub>, as prescribed by Eq. (3.4). After applying this correction, a negative flatband shift is observed as a function of time, as expected from the ingress of positive ions into the dielectric. Note that the error bars originate from variations in
the concentration of trapped charge in Na-free devices used in the estimation of $\Delta V_{\text{FB}}^{\text{traps}}$. Overall, our trapping-corrected data captures the resulting $\Delta V_{\text{FB}}$ in Na-contaminated devices across device-relevant temperatures.

To confirm the applicability of the trapping-corrected BTS method to isolate ion migration, experiments were conducted on thermal SiO$_2$ capacitors, which are known to exhibit very little to no carrier trapping in the bulk of the dielectric compared to SiN$_x$ [46, 63, 65]. Fig. 3.2 shows the measured $\Delta V_{\text{FB}}$ without trapping correction in Na-free and Na-contaminated SiO$_2$ capacitors. As expected, we observed little-to-no variation in the flatband voltage in control samples without intentional Na contamination. In Na-contaminated SiO$_2$ capacitors, a flatband shift of $\approx$ 0.5 V was detected without the need for trapping correction. This trend is well fit by our ion migration model. This result confirms that the experimental conditions and detection method are suitable to detect ion migration within the timescales of the experiment.

Using the described trapping-corrected BTS method, we determined the Arrhenius relationship for the migration of Na$^+$ in SiN$_x$ by averaging the diffusivities of measurements collected over 4–8 devices at each temperature. Fig. 3.3 shows the extracted diffusivities of Na$^+$ in SiN$_x$ at different temperatures together with the 95% confidence interval. The results of the fit to the Arrhenius relationship give a diffusion coefficient prefactor of $D_0 = 1.4 \times 10^{-14}$ cm$^2$/s with a 95% confidence interval of $[1.2 \times 10^{-15}, 1.6 \times 10^{-13}]$ cm$^2$/s and an activation energy of $E_a = 0.14$ eV, with a 95% confidence interval of $[0.07, 0.21]$ eV. Note that the deviation from the higher-temperature results of Wilson et al. [32] indicates a large difference in the activation energy compared to the range of temperatures in this work.
Figure 3.3: Arrhenius relationship for the diffusivity of Na\(^+\) in SiN\(_x\) evaluated by the trapping-corrected BTS method and by Wilson et al. \([32]\), using a Kelvin-probe-based method. The estimated prefactor for the diffusion coefficient is \(D_0 = 1.4 \times 10^{-14} \text{ cm}^2/\text{s}\) with a 95\% confidence interval of \([1.2 \times 10^{-15}, 1.6 \times 10^{-13}] \text{ cm}^2/\text{s}\). The estimated activation energy is \(E_a = 0.14 \text{ eV}\), with a 95\% confidence interval of \([0.07, 0.21] \text{ eV}\).

3.6 Characteristic Na\(^+\) transit time

To provide context to the results of the ion-migration experiments with respect to PID-s, we estimate how the Na\(^+\) concentration at the SiN\(_x\)/Si interface changes over time. Since Na transport can eventually lead to PID-s, we consider the characteristic time \(\tau_c\) at which Na\(^+\) drifts across the dielectric, as the solution to the equation

\[
L = 2\sqrt{D \tau_c} + \mu E \tau_c
\]  

(3.8)
If the magnitude of the electric field in SiN\(_x\) is low with respect to the diffusive term, \(-D\nabla^2 C \ll \mu EC\), then \(\tau_c \to L^2/D\). If the drift term dominates \(\tau_c \to L/\mu E\). This can be expressed as

\[
\tau_c = \inf \left\{ t = \frac{L^2}{D}, \quad t = \frac{L}{D} \left(\frac{v_{th}}{E}\right) + \frac{2}{D} \left(\frac{v_{th}}{E}\right)^2 \left\{ 1 \pm \left[ 1 + \left(\frac{E}{v_{th}}\right)L \right]^{1/2} \right\} \right\} \quad \text{for} \quad t \in \mathbb{R}^+ \quad \text{,} \quad (3.9)
\]

where \(v_{th} = k_B T/q\) is the thermal voltage. The complete derivation of Eq. (3.9) is shown in Appendix A.

Fig. 3.4 shows the characteristic transit time across a typical nitride thickness of 65 nm as a function of the module temperature and electric field across the SiN\(_x\) in ranges relevant to solar module operation. The range of values selected for the electric field in SiN\(_x\) account for a large variability on the resistivities of the materials in the module [3, 12, 22, 33, 34, 66]. To estimate the values on the resistivity axis in Fig. 3.4 we consider a borosilicate glass with a resistivity \(\rho_{\text{glass}} \approx 3 \times 10^{12} \Omega \text{ cm} [67]\), ethylene-vinyl acetate EVA with a resistivity \(\rho_{\text{EVA}} \approx 5 \times 10^{13} \Omega \text{ cm}\) and a voltage differential of 1000 V, to estimate the silicon nitride resistivity corresponding to
the electric field in the left axis. Under such conditions, Na migration through the dielectric can occur between a few hours to a few days depending primarily on the potential drop across SiN$_x$. Such times are lower than the observed degradation times after accelerated experiments at high temperature and in the field [38, 68]. However, $\tau_c$ only reflects the transport across SiN$_x$ and does not represent the actual time to PID in the full module stack.

It is worth considering scenarios in which the assumptions made to derive Eq. (3.7) do not longer hold, namely (1) large ion concentrations $C_s \approx 2\varepsilon_{ins}V_{stress}/qL^2$ where the distribution of mobile ions does affect the local potential within the dielectric, (2) long stress times: $t > \tau_c$ where the flatband potential becomes sensitive to the accumulation of ions at the dielectric/semiconductor interface, and (3) finite sources of ions.

3.7 Conclusions

We derived a method to quantify Na$^+$ diffusion kinetics in SiN$_x$ using a drift-diffusion model to analyze the corresponding flatband voltage shift in MIS structures. We developed a C-V setup for measuring MIS capacitors under BTS. We developed a model to correct nonidealities from charge trapping in the dielectric. This description of a C-V based approach to parametrize ion migration should allow reliable quantification of ion diffusion kinetics broadly in dielectrics. We presented an analytical approximation to bound the transport times of Na$^+$ in SiN$_x$ within the context of PID. We showed that migration through PV-relevant, 65 nm-thick silicon nitride films can occur within a few days in field-operating conditions. We can easily extend this study to a variety of SiN$_x$ of different compositions and electrical properties. Furthermore, quantification of the transport kinetics from this study is especially significant to determine the overall kinetics of
PID-s in the full module stack.

Sodium contamination is known to be deleterious to semiconductor devices since the early days of the semiconductor industry. The need to mitigate this problem opened the way for studying mobile charge transport in dielectrics commonly used in the industry \[42, 45, 69-73\]. In silicon photovoltaic (PV) modules, Na contamination has been determined as the root cause for PID-s, and linked to failure within a timescale of a few hours to a few days under accelerated testing \[5, 24, 35, 36, 38, 39, 41, 74\]. In section 3.3 we described a simplified model to estimate the kinetics of Na\(^+\) migration under the limiting case of short migration times \((t < \tau_c)\) and low ionic concentrations with respect to the applied electric field \((C \ll 2\epsilon_{\text{ins}}/qL^2)\). In this chapter, as general solution to Eq. (2.1) is presented, using only a limited set of assumptions. We then expand the model to accommodate for a flux of ions out of the dielectric and into the semiconductor. This is useful in modeling PID-s kinetics on p-Si modules.
4.1 Modeling mobile charge kinetics in MIS structures

The conditions assumed to derive an analytical approximation to Eq. (3.6) are generally not held for long-time experiments nor for a wider range of mobile charge concentrations, as would be expected for PID-s in the case of Si PV modules [23,75,76]. In metal-insulator-semiconductor (MIS) structures, the concentration of ions near the metal gate induces an image charge in the metal, with the opposite sign of the ion. The resulting electric field points in the negative direction of $x$, leading to a diffusion dominated region in the vicinity of the metal gate [69]. It is also typical to assume a closed boundary at the dielectric/semiconductor interface [56,69], which leads to ion accumulation at that interface due to ion drift towards the semiconductor. Just as in the metal gate, accumulation of ions at the dielectric/semiconductor interface induces an image charge of the opposite sign in the semiconductor—which we measure as $\Delta V_{\text{FB}}^{\text{ion}}$ in Eq. (3.4), but in this case the resulting image charge acts on the same direction of the applied electric field. This effect was first reported by Snow et al. [69], where the authors introduced a boundary layer approximation to estimate the image charge in the semiconductor. This approach has the advantage of avoiding the need to solve the coupled Poisson-Nernst-Planck (PNP) system of equations. Nevertheless, this model does not mechanistically account for the image charge effect at the source and semiconductor interfaces or the depletion of ions near the gate. In such cases the Poisson’s equation for the ion distribution:

$$\nabla \cdot \nabla \phi_{\text{ion}} = -\frac{zqC(x,t)}{\epsilon_{\text{ins}}}$$  (4.1)

needs to be solved self-consistently with (2.1). Analytical solutions to Poisson-Nernst-Planck equations are available just for a few limiting cases, namely, low applied voltages and binary
electrolytes close to charge neutrality. In this chapter, we present a finite-element-method (FEM) solution to the Poisson-Nernst-Planck coupled system of equations. This methodology has the advantage of fully describing the kinetics of ion migration in MIS structures and providing a framework to model transport across stacks of materials. This is specially useful, for instance to describe ion ingress leading to shunt formation in PID-s.

The boundary conditions for Eq. (4.1) can be set by estimating the image charges induced by the ion distribution. The contribution of image charge of ionic origin \( Q_{\text{ion}} = q \int_{0}^{L} C(x', t) dx' \) to the drift term in Eq. (2.1) arises from \( \text{Na}^+ \) charge being imaged at both, the metal gate \( Q_G \) and the semiconductor \( Q_S \) interfaces of the MIS structure. The surface charge distribution of image charges due to ionic migration are determined by:

\[
Q_G = q \int_{0}^{L} \left( \frac{x' - L}{L} \right) C(x', t) dx' \leq 0 \tag{4.2a}
\]
\[
Q_S = -q \int_{0}^{L} \left( \frac{x'}{L} \right) C(x', t) dx' \leq 0, \tag{4.2b}
\]

with \( L \) the thickness of the dielectric. It follows that \( -Q_{\text{ion}} = Q_G + Q_S \). The electric fields associated with these charge distributions have opposite directions inside the dielectric:

\[
- \nabla \phi_{\text{ion}}|_{x=0} = E_{\text{ion,G}} = \hat{x} \frac{q}{\epsilon_{\text{ins}}} \int_{0}^{L} \left( \frac{x' - L}{L} \right) C(x', t) dx' \tag{4.3a}
\]
\[
- \nabla \phi_{\text{ion}}|_{x=L} = E_{\text{ion,S}} = -\hat{x} \frac{q}{\epsilon_{\text{ins}}} \int_{0}^{L} \left( \frac{x'}{L} \right) C(x', t) dx' \tag{4.3b}
\]

Thus, for \( \mathbf{E} = E \hat{x} \), the image charge field at the gate opposes the external electric field, while the image charge field at the semiconductor interface adds to it. Eq. (4.3) can be introduced
as the boundary conditions to Poisson’s equation

\[
\nabla \phi(x = 0) \cdot \hat{n}_G = E_{\text{stress}} + \frac{q}{\varepsilon_{\text{ins}}} \int_0^L \left( \frac{x' - L}{L} \right) C(x', t) \, dx' \\
\n\nabla \phi(x = L) \cdot \hat{n}_S = -E_{\text{stress}} - \frac{q}{\varepsilon_{\text{ins}}} \int_0^L \left( \frac{x'}{L} \right) C(x', t) \, dx',
\]

(4.4a)

(4.4b)

where \( \hat{n}_G = -\hat{x} \) and \( \hat{n}_S = \hat{x} \) are the normal vectors to the gate and semiconductor surfaces enclosing the insulator volume in the MIS structure.

4.2 Finite Element Method Implementation of the PNP coupled system

The general solution to the Poisson-Nernst-Planck system requires integration over the space and time. Spatial integration is relatively straightforward using the finite element method. The general approach to impose the boundary conditions require writing the spatial part of the partial differential equation (PDE) as an integral equation (i.e. the “weak form”), which has the advantage of reducing the computational load of evaluating second order spatial derivatives [81, 82]. This formulation also allows us to easily introduce both, the Dirichlet and Neumann boundary conditions [81]. Time integration must be addressed by a finite difference scheme using the solutions computed by the FEM solver.

Among the different time integration schemes, the two-step trapezoidal-second order backward difference (TR-BDF2) method has proven to be very reliable for semiconductor modeling [83, 84] because of its strong stability [83–86] compared to other time stepping approaches like the Crank-Nicholson method, which is known to introduce spurious oscillations if un-damped [87].
The TR-BDF2 advances the system

\[ \frac{\partial C}{\partial t} = F[C(t), \phi(t), t] \] (4.5)

from \( t_n \) to \( t_{n+1} = t_n + \Delta t_n \) in two steps \[83, 84\]. In Eq. (4.5), \( F \) corresponds in this case to the right hand side of (2.1). The first step consists of a trapezoidal time integration by which the system is advanced from \( t_n \) to \( t_{n+\gamma} = t_n + \gamma \Delta t_n \) (0 < \( \gamma < 1 \)):

\[ C^{n+\gamma} - \frac{\Delta t_n}{2} F^{n+\gamma} = C^n + \frac{\Delta t_n}{2} F^n. \] (4.6)

The system is then advanced from \( t_{n+\gamma} \) to \( t_{n+1} \) using the second order differentiation (BDF2):

\[ C^{n+1} - \frac{1-\gamma}{2-\gamma} \Delta t_n F^{n+1} = \frac{1}{\gamma(2-\gamma)} C^{n+\gamma} - \frac{(1-\gamma)^2}{\gamma(2-\gamma)} C^n. \] (4.7)

In equations (4.6) and (4.7) we have used the notation \( C^{n+\gamma} = C(x, t_n + \gamma \Delta t_n) \) and \( C^{n+1} = C(x, t_n + \Delta t_n) \), for the discretization of time.

The derivation of the weak form for the coupled system is shown in Appendix C. For the TR step, the system is advanced by

\[ \int_{\Omega} u_c^{n+\gamma} v_c d\Omega - \frac{\gamma}{2} \frac{\Delta t_n}{2} (A_{NP}^{n+\gamma} + A_P^{n+\gamma}) = \int_{\Omega} u_c^n v_c d\Omega + \frac{\Delta t_n}{2} (A_{NP}^n + A_P^n), \] (4.8)

and, for the BDF2 time step we get

\[ \int_{\Omega} u_c^{n+1} v_c d\Omega - \frac{1-\gamma}{2-\gamma} \Delta t_n (A_{NP}^{n+1} + A_P^{n+1}) = \frac{1}{\gamma(2-\gamma)} \int_{\Omega} u_c^{n+\gamma} v_c d\Omega - \frac{(1-\gamma)^2}{\gamma(2-\gamma)} \int_{\Omega} u_c^n v_c d\Omega. \] (4.9)

In Eqs. (4.8) and (4.9), \( u_c \) and \( u_p \) are trial functions for \( C \) and \( \phi \), respectively, \( v_c, v_p \) are test functions for \( C \) and \( \phi \), respectively, and \( A_{NP} \) and \( A_P \) are the linear forms corresponding to the weak form of \( F[C(t), \phi(t), t] \) in Eq. (4.5), and the weak formulation of Poisson’s equation,
respectively (See Appendix B):

\[
A_{NP} = -D \int_{\Omega} \nabla u_c \cdot \nabla v_c \, d\Omega + D \int_{\partial \Omega} (\nabla u_c \cdot \hat{n}) v_c \, ds - \mu \int_{\Omega} u_c \nabla u_p \cdot \nabla v_c \, \Omega + \mu \int_{\partial \Omega} (\nabla u_p \cdot \hat{n}) u_c v_c \, ds
\]  
(4.10a)

\[
A_p = -\int_{\Omega} (\nabla u_p \cdot \nabla v_p) \, d\Omega + \int_{\partial \Omega} (\nabla u_p \cdot \hat{n}) v_p \, ds + \frac{q}{\epsilon_{\text{ins}}} \int_{\Omega} u_c v_p \, d\Omega
\]  
(4.10b)

4.3 Modeling charge transport in SiO\textsubscript{2}

To validate the model, we ran transport simulations in SiO\textsubscript{2}, to reproduce the experimental trends described by Snow et al. [69]. An initial distribution of Na\textsuperscript{+} with a surface concentration \(Q_0 = 29 \times 10^{11} / \text{cm}^{-2}\), uniformly distributed over the first 140 Å of a 0.2 µm-thick layer of SiO\textsubscript{2} was assumed. The diffusion coefficient of Na\textsuperscript{+} was set to \(5 \times 10^{-16} \text{ cm}^2 / \text{s}\) and no-flux boundary conditions for the concentration where set to

\[-D \nabla C - \mu C \nabla \phi = 0\]  
(4.11)

at \(x = 0\) and \(x = L = 0.2 \mu \text{m}\). The gradient of the potential \(\nabla \phi\) is obtained self-consistently from (4.4). For the electric potential we set \(\phi(x = 0) = 10 \text{ V}\) and \(\phi(x = L) = 0\). As an initial condition, we set a uniform finite concentration of ions in the layer to a negligible value (we used \(C \rightarrow 10^{-20} / \text{cm}^3\)) and a linear potential drop within the dielectric, consistent with a potential at the gate of \(\phi(x = 0) = 10 \text{ V}\).

Equations (4.8) and (4.9), together with the boundary conditions are solved self consistently. At each time step, \(\nabla \phi\) was estimated from (4.4), by integrating the latest concentration profile. The mesh was refined close to the boundaries with a minimum element size \(\Delta x = 1.67 \text{ Å}\).
Figure 4.1: Simulated image charge in the semiconductor of a MIS structure as a function of time. Experimental points are taken from Snow et al. [69].

and a maximum element size $\Delta x = 6.67 \text{Å}$. The time step was set to a fixed value of $\Delta t = 50 \text{s}$ to reduce time truncation error in the TR-BDF2 integration as much as possible. The solution was computed using FEniCS [82, 88] and the auxiliary numerical tools for this framework [89–94]. The results for a $\sim 6.25 \text{h}$ drift-diffusion simulation at a 140 $^\circ\text{C}$ temperature stress are shown in Fig. 4.1. The normalized image charge in the semiconductor as a function of dimensionless time $t/\tau$, predicted by the model is plotted in red, together with the experimental excess surface charge in the semiconductor, reported by Snow et al. [69]. The model successfully predicts a linear relationship of $Q_S/Q_0$ as a function of $\bar{t} = \sqrt{t/\tau}$ for $\bar{t} \lesssim 1.4$, after which the curvature changes and the surface concentration saturates. This is consistent with the boundary layer approximation [69]. From the boundary layer theory [69]

$$\left| \frac{Q_S}{Q_0} \right| \approx \frac{4}{\pi^{3/2}} \left( \frac{t}{\tau} \right)^{1/2}, \text{ for } t \ll \tau$$

(4.12)

$$\left| \frac{Q_S}{Q_0} \right| \approx 1 - \frac{8}{\pi^2} \exp \left( \frac{t}{\tau} \right), \text{ for } t \gg \tau,$$

(4.13)
with

$$\tau \equiv 4x_1^2/\pi^2 D.$$ 

The value of $x_1$ in Eq. (4.14) corresponds to the thickness of the boundary layer. Eq. (4.12) establishes the slope and time constant for the linear and exponential regime. Deviation from the experimental slope arises from a different constant of proportionality originating from (1) the discrepancy introduced by the boundary layer width $x_1$ which is no longer a constant in the numerical simulation and, (2) on the effective magnitude of the electric field when taking the superposition of the applied electric stress and the electric potential due to the ion concentration.
In Fig. 4.2, a selection of concentration profiles used to compute the image charge in Fig. 4.1 is plotted as a function of time indicated in color scale. Shown in yellow is the shape of the initial concentration profile. At early times, we notice that the initial profile is pulled in opposite directions: the image charge at the gate pulls in the negative direction of $x$, and the applied bias drifts the ions in the positive direction. Because of the balancing effect of the image charge potential and the applied bias, the region closest to the gate is in fact dominated by diffusion. As a consequence of the image charge effect drifting Na$^+$ driving ions towards the gate, and the applied bias driving ions towards the Si interface, the concentration around the original profile depletes. Then, the magnitude of $\mu E C$ decreases, leading to slower transit times during the early stages of the simulation, as is evidenced in the region for $t \lesssim 0.25\, h$ in Fig. 4.1. At intermediate times, Na$^+$ piles up at the semiconductor interface driven by the applied bias and the local image charge effect at that interface. Ions are lost from the region around the vicinity of the gate to the drift
Figure 4.3: Simulated $V_{FB}$ as a function of time for a SiO$_2$ MIS structure using $D = 4 \times 10^{-17}$ cm$^2$/s. Empty circles indicate the experimental results of samples stressed at 60 °C under a bias of 4 V.

dominated region, driven by a large concentration gradient close to this interface. This causes further depletion of the gate interface, which is identified by profiles with positive concentration gradients moving towards the semiconductor interface. This result quantitatively describes the kinetics of Na migration in MIS structures, suggesting that the initial concentration profile might lay further into the bulk of SiO$_2$ (leading to lower initial concentration which in turn reduces image charge effect at the gate).

To provide further validation of the model with more recent experimental data, following the experiment by Snow et al. [69], we prepared SiO$_2$ MIS capacitors by dry oxidation of n-type Si (100) wafers at a temperature of 1100 °C. Prior to oxidation, the silicon wafers were cleaned with acetone, ethanol and isopropyl alcohol, followed by RCAI and RCAII cleaning procedures. The thickness of the SiO$_2$ layer was mapped by spectroscopic ellipsometry. An average thickness of 100 nm was measured. Sodium contamination was introduced by thermal evaporation at 800 °C.
from a NaCl source, followed by contact deposition without breaking the vacuum. The rate of
deposition of the NaCl layer was monitored using a quartz microbalance up to value of 25 nm.
A pattern of \( \sim 1 \text{mm} \) diameter circles with a pitch of 2.54 mm was deposited using a shadow
mask. Approximately 200 nm of aluminum were deposited as front and back contacts. The bottom
surface of the wafer was swabbed with hydrofluoric acid prior to metallization.

The as-prepared samples were subject to a bias-temperature stress of 60 \(^\circ\)C and 4 V in
intervals of 1 h. Between stress intervals, the samples were cooled down to room temperature and
capacitance-voltage measurements were collected. The flatband voltage shift \( \Delta V_{FB} \) was extracted
as described in our previous work \[62\].

To simulate the transport of Na\(^+\) in the SiO\(_2\) MIS capacitor, we used \( Q_0 = 1.4 \times 10^{11} \text{cm}^{-2} \).
This value was selected based on a quick estimation of the expected saturation \( V_{FB} \approx -0.6 \text{V} \approx
-\frac{Q_0}{\epsilon_{ins}L} \) from the experimental results. A diffusivity of \( 4 \times 10^{-17} \text{cm}^2/\text{s} \) was used to match the
temporal dependence of \( \Delta V_{FB} \). For comparison, this value is two orders of magnitude larger than
the one we would expect from the extrapolation of the Arrhenius relationship reported by Frischat \[95\] taken within the range of 170 \(^\circ\)C to 250 \(^\circ\)C for commercial SiO\(_2\) glasses. The initial concentra-
tion profile was set to reach a 25 nm depth from the gate, in accordance to the monitored thickness
during NaCl evaporation. As can be seen in Fig. 4.3, the simulated profile matches well the exper-
imental data within errorbars. For consistency with Fig. 4.1, the results were plotted against \( t^{1/2} \).
In this representation, a quadratic dependence of \( \Delta V_{FB} \) is indicative of drift-dominated transport.
4.4 Behavior before the characteristic transit time

In section 3.6 the concept of characteristic transit time was introduced to account for a simplified behavior whenever the concentration was below the threshold value $C_{th} \equiv 2e_{ins}/qL^2V_{stress}$.

To cross reference our transport model with this behavior at short times and under low concentrations we modified the boundary conditions to accommodate for a constant source of ions at the gate. Then, we ran simulations on a MIS structure with a thickness of 80 nm at a temperature of 80°C, with an applied bias of 4 V. The corresponding concentration profiles as a function of time are shown in Fig. 4.4, where the drift-diffusion time is indicated in color scale. Fig. 4.4(a) illustrates the transport kinetics at short times as modeled by the numerical solution to Poisson-Nernst-Planck coupled system with a constant source and a closed boundary at the semiconductor interface. The estimated characteristic time for this system is $\tau_c \approx 8.4h$, beyond which the concentration profile begins to pile up at the semiconductor interface, due to the effect of drift and accumulation of negative image charges in the semiconductor. As expected from the boundary conditions, we do not see depletion at the metal gate interface, in contrast with the closed system described is Section 4.3. In fact, when $t < \tau_c$, this boundary condition behaves identically to the approximation at short times given by (3.7), shown in Fig. 4.4(b). A variation of only 2.8 mV in $V_{FB}$ at $t = \tau_c$ was estimated between the two models, which is less than the thermal voltage $k_B T \approx 30$ mV at the simulated temperature. This is expected due to the fact that, for the given bias and thickness, our threshold concentration is $C_{th} \approx 5 \times 10^{17}$ cm$^{-3}$, compared to our average concentration of $10^{16}$ cm$^{-3}$.
Figure 4.4: Concentration profiles as a function of time, indicated in color scale, modeled by (a) a FEM simulation of the full Poisson-Nernst-Planck coupled system (PNP) and (b) the approximate solution (ERF) at short times given by (3.7). To the right of each pane is plotted the corresponding $\Delta V_{FB}$ due to the ionic charge distribution as a function of time. In the same plot is indicated the characteristic transit time within the approximation described in Sec. 3.6. The difference between the estimated $V_{FB}$ at $t = \tau_c$ is of only 2.8 mV.

4.5 Na transport in stacks of materials

The finite element implementation of the present model can be easily re-formulated to study the kinetics of transport of ionic species in stacks of materials. We can model the transport of Na\textsuperscript{+} through the dielectric and into the silicon, by treating both systems independently, and connecting them with a flux boundary condition. Given the discontinuity in the diffusion coefficients, impurity equilibrium concentrations and electrical properties in the layer stack, segregation needs to be considered. To account for impurity segregation at the dielectric/semiconductor interface we use a
phenomenological, first order kinetics description of the flux \( J_s \):

\[
J_s \equiv h \left( C_{\text{ins}}(L,t) - \frac{C_{\text{Si}}(L,t)}{m} \right),
\]

(4.14)

where \( L \) is the thickness of the insulating film, \( C_{\text{ins}}(L,t) \), \( C_{\text{Si}}(L,t) \) are the impurity concentrations defined in the insulator and in the semiconductor, respectively, \( h \) is the surface mass transfer coefficient given in units of distance over unit time, and

\[
m \equiv \left( \frac{C_{\text{Si}}}{C_{\text{ins}}} \right) \text{ in equilibrium}
\]

(4.15)

is the segregation coefficient.

The total flux at \( x = L \) from the dielectric side is given by

\[
-D_{\text{SiN}} \nabla C - \mu C \nabla \phi = J_s.
\]

(4.16)

Because silicon is assumed to have an electrical resistivity several orders of magnitude less than the insulating films (from \( \sim 10^{-3} \, \Omega \, \text{cm} \) to \( \sim 10^5 \, \Omega \, \text{cm} \), compared to typical insulating resistivities on the order of \( 10^{11} \, \Omega \, \text{cm} \)), it is possible to neglect drift in silicon. As it turns out, in PV devices, the high doping concentration of the emitter side puts an upper bound on the resistivity of Si on the order of \( 10^{-2} \, \Omega \, \text{cm} \). Hence, transport in silicon is governed by pure diffusion. And the total flux at \( x = L \) from the side of silicon is given by

\[
-D_{\text{Si}} \nabla C = J_s.
\]

(4.17)

Eqs. (4.16) and (4.17) are introduced easily as Neumann boundary conditions on the surface element terms \( ds \) in Eq. (4.10).

Incoming flux at the metal gate interface can also be easily instrumented in the model by considering a source of ions with surface concentration \( S \) given in atoms per unit area flowing in
to the insulating layer at a rate $k$ in units of inverse time:

$$J_{\text{source}} = kS$$  \hspace{1cm} (4.18)

To account for the finite size of the source, we consider that the source is depleted after a time $1/k$ after which we set $J_{\text{source}} = 0$.

To demonstrate transport through stacks of materials, we simulated the kinetics of Na$^+$ through the SiN$_x$/Si stack by means of Eqs. (4.8) and (4.9), and setting the boundary conditions defined by equations (4.16), (4.17) and (4.18). The thickness of the SiN$_x$ was set to 75 nm, in accordance to typical values used in PV modules [27]; and the thickness of silicon was set to 1 µm which is long enough to be considered infinite within the timescale of the simulation (96 h) for the selected value of the diffusivity of Na in Si. We set the temperature to 85 °C and considered a diffusivity of Na$^+$ in SiN$_x$ of $\sim 4 \times 10^{-16}$ cm$^2$/s in accordance to our trapping-corrected BTS estimates (Gastrow et al. [62]), and a value of $10^{-16}$ cm$^2$/s for the diffusivity of Na in Si. The latter is larger than the expected values of $\sim 10^{-21}$ cm$^2$/s from extrapolation of experimental Arrhenius curves taken at temperatures above 1000 °C [97], but lower than the bounds estimated based upon typical failure times of PID-s affected PV modules, which put an upper bound of $\sim 10^{-7}$ cm$^2$/s [98]. An electric stress of 75 mV was applied, corresponding to an electric field of $10^4$ V cm, which is in range with the estimations from the voltage divider model shown in Table 2.1 for low resistivity nitrides. For the source term, we chose a surface concentration of $S = 10^{10}$ cm$^{-2}$ which is two orders of magnitude less than the values corresponding to intentional contamination in [32, 69], and a rate of ingress $k = 10^{-5}$ s$^{-1}$, for which the source is partially depleted within the simulation time of $\sim 3.5 \times 10^5$ s (96 h). For the segregation flux, we used a surface mass transfer coefficient of $h = 10^{-12}$ cm s$^{-1}$ and a segregation coefficient $m = 1$. The results are plotted in
Figure 4.5: Simulated concentration profiles as a function of time across a SiN\textsubscript{x}/Si material stack.

Fig. 4.5, where the concentration profiles are shown as a function of time in color scale. Notice that, because the flux at the source is maintained constant and the rate is $k = 10^{-5} \text{ s}^{-1}$, depletion becomes evident after the $\sim 28$ h. In fact, the concentration profile almost flattens within the SiN\textsubscript{x} over the course of the simulation. Furthermore, because the diffusion coefficient in the silicon is set to a higher value ($10^{-14} \text{ cm}^2/\text{s}$) with respect to the value in SiN\textsubscript{x} ($4 \times 10^{-16} \text{ cm}^2/\text{s}$), Na\textsuperscript{+} is transferred to silicon and is diffused into the bulk of Si relatively easily. Additionally, due to the low magnitude of the electric field in SiN\textsubscript{x}, no accumulation of Na is observed at the SiN\textsubscript{x}/Si interface, and ionic transport in the dielectric film is dominated by diffusion, as can be observed in Fig. 4.5 by the slopes of the concentration profiles.
4.6 Conclusions

We developed a model to simulate the kinetics of ion diffusion in MIS devices. Validation with experimental results resulted in good agreement of the simulated trend of the image charge in the semiconductor interface. Reference with BTS experiments also results in agreement of the predicted $\Delta V_{FB}$ due to ion migration. Under the limiting case of low concentration and short times, we verified that the solution can be correctly approximated using a constant electric field which simplifies to a pure diffusion problem, as described in Sec. 3.3. The estimated solution to Poisson-Nernst-Planck coupled system yields all the information required to study ion transport kinetics with respect to the charge distribution. This is especially important to visually understand the assumptions behind boundary layer theory and extend upon it. Our model allows for direct extrapolation to other type of dielectric structures and material stacks which are of interest for modeling reliability of semiconductor devices.

Chapter 4, in part, is being prepared for submission in the Journal of Applied Physics under the title “Numerical Solution to Poisson-Nernst-Planck Equations for Ion Transport in MIS structures and Solar Cells” by E. Martinez-Loran, G. von Gastrow, J. Clenney, F. Contreras-Torres, R. Meier, M.I. Berton, P. Bandaru and D.P. Fenning. The dissertation/thesis author was the primary investigator and author of this paper.
5 | Device degradation modeling

The photovoltaic industry has made huge efforts to engineer efficient and reliable solar modules and to test the long-term performance of modules. Reliability tests have shown potential-induced degradation can lead device failure before the average warranty time in silicon solar modules [1, 3–5]. Over the last decade, much work has been put to standardize reliability tests [5, 7, 14, 24, 27, 68, 99–102] and to develop predictive models to estimate the progression of PID [14, 15, 68].

5.1 Introduction

Power law models have demonstrated some use to describe the loss in power output, albeit with limitations on the applicability to weeks-long simulations. Since PID in p-Si solar modules has been ascribed to electrical shunting of the emitter, empirical models describing the progression of the shunt resistance $R_{\text{sh}}$ have phenomenologically described the progression of $R_{\text{sh}}$ with stress time, and even incorporated environmental conditions [14, 29, 103]. More recently Schulze et al. [15], proposed a simplified drift-diffusion model of a shunt that adequately fits the PID progression and recovery in $R_{\text{sh}}$ for p-Si modules. While this model provides insights into the physical parameter space that impacts ion transport and can potentially be engineered to
reduce PID, the introduced level of simplification weakens the connection to describe engineerable parameters, which can be determined through the bill of materials.

The assumed mechanism behind PID-s in p-Si PV modules is that Na contamination from different depths in the module migrates to the silicon emitter where it is responsible for shunting behavior \([5, 9, 12, 13, 18, 19]\). Microscopy analyses have established that Na-decorated \{111\} stacking faults in p-type silicon lead to the formation of electrical shunts in the emitter of the solar cell leading to PID \([12, 19]\). It has been proposed that the introduction of Na in these defects occurs through electric-field assisted transport, whereupon Na contamination in the silicon nitride (SiN\(_x\)) anti-reflective coating of the solar cell moves towards the emitter of the solar cell \([12]\). Once Na reaches silicon, it tends to concentrate in the \{111\} stacking faults \([9, 12, 13, 19]\). These defects shunt the p-n junction and result in the loss of carrier collection efficiency \([9, 12, 19, 104]\).

In this chapter we describe a mechanistic model to describe the formation of the electrical...

Figure 5.1: Proposed modeling framework aimed at predicting PID-s and engineering PID-robust PV modules.
shunts in the module which takes into account the full kinetics of ion transport formulated in
Chapter 4. The present model allows to parametrize the power output degradation and $R_{sh}$ in terms
of intrinsic properties, like the diffusion coefficients of Na in the different layers, and engineerable
parameters like the resistivity of the encapsulant layer and the incorporation of blocking layers
between the SiN$_x$ and the Si emitter.

The overarching goal of this modeling framework is to develop a full physical analysis
aimed at understanding the impact of the properties of the materials in the PV module, the operating
voltages, and environmental conditions in PID-s. As proposed in Fig. 5.1, this iterative analysis
allows a comprehensive study of the multiple factors leading to PID-s. This methodology will
provide guidance to optimize the bill of materials for PID-robust PV modules. The proposed inputs
of the model are the electrical resistivity of the front-cover glass, encapsulant layer and SiN$_x$. As
a proxy for the electrical resistivity of SiN$_x$, refractive index measurements have shown good
 correlation with PID-s resistance [5 27 59 74 105 106]. Also of interest, is the average surface
concentration of stacking fault defects in the emitter of the module and, the string voltage, which
determines to what extent ions drift towards the emitter. These parameters can be used in transport
simulations to model the ingress of Na through the module stack and determine the concentration
profile of Na in the stacking faults. The Na concentration in the defect and this information,
together with the area of the shunt and density of defects is mapped to a shunt conductivity and
the kinetics model is used by a device simulation tool that determines the current-voltage (J-V)
characteristic of the PV module. The kinetics of degradation is then estimated by analyzing the
J-V characteristic of the device. Simulated $R_{sh}$ and power output is subsequently validated against
experimental data.
Figure 5.2: Boundary conditions used for Na transport simulations in p-Si PV modules. As a first approximation we set a constant source boundary condition at the EVA/SiNx located at $x = 0$. At the bottom of Si, located at $x = L_{Si}$, a zero-flux boundary condition is imposed. The two materials are connected by a first order kinetics segregation flux boundary condition. The boundary condition for the electric potential is determined by the electric field induced by the image charges at the EVA and Si interfaces, due to the Na$^+$ concentration in SiNx.
5.2 Modeling Na migration kinetics

In PID-s, Na contamination is assumed to reach the n$^+$-Si emitter of the PV module, where it “decorates” the stacking faults, after migrating through the encapsulation and the SiN$_x$ anti-reflective coating. The process is driven by the large potential difference between the cell at a floating negative potential $V \geq 1000$ V and the metal frame which is grounded at $V = 0$ [5, 12].

We assume that the electric field in the module stack can be estimated on the basis of the voltage divider introduced in Sec. 1.4. In Table 2.1 we show typical ranges of the equivalent electric field in each material of the PV module, based on typical values of the thickness.

The origin of Na contamination in solar modules has been historically ascribed to the front cover soda-lime glass [4, 5, 7]. For instance, it has been shown that replacement of soda-lime glass with a quartz glass widow mitigates pseudo fill factor losses in Si modules subject to damp heat-PID tests [7, 18]. Nevertheless, more recent reports show that PID can occur in the absence of a front-cover glass and even in the absence of an encapsulant [23–25]. This suggests that Na contamination might have been introduced during lamination of the module. This hypothesis has been supported by the presence of Na contamination within EVA, particularly, close to the EVA/SiN$_x$ interface, prior to PID testing [26]. In Sec. 2.2 we provided further evidence that, migration through the EVA might have a limited impact on PID-s due to the fact that Na does not drift through the whole thickness of the encapsulant in the time scale of PID degradation. Therefore, we assume that Na contamination is present at the EVA/SiN$_x$ prior to PID stressing.

It is assumed that PID-s occurs by Na contamination present at the EVA/SiN$_x$ interface being drifted through the SiN$_x$ anti-reflective coating and diffused into the n$^+$-Si emitter of the PV
Figure 5.3: Schematic of the Aluminum Back Surface used to simulate the module degradation.

Transport in SiN\(_x\) is governed by drift and diffusive flux. The relative contribution of the drift and diffusive terms is determined by the magnitude of the electric field in the SiN\(_x\).

Transport is then simulated using the FEM modeling framework described in Sec. 4.5. The boundary conditions that we used are described in Fig. 5.2. For small source concentrations, we assume that a constant source boundary condition can suffice to describe ion ingress at the EVA/SiN\(_x\) interface. At the bottom of the Si simulation volume, we impose a zero-flux boundary condition. Transport is modeled independently in each layer with a coupling boundary condition given by a first order kinetics segregation flux \[96\]. The electric field is assumed to be negligible in the n\(^+-\)Si emitter, hence transport is well described by pure diffusion in this material. In SiN\(_x\), the electric stress is usually non-negligible and transport is governed by Nernst-Planck’s equation. Due to the introduction of Na\(^+\), the electric potential is determined by the superposition of the applied bias and the potential induced by the Na\(^+\) charge distribution. Therefore, as discussed in Sec. 3.6, the complete solution for times \(t > \tau_c\) is coupled to the solution of Poisson’s equation for the charge distribution in SiN\(_x\). We set the Neumann boundary conditions to the electric potential self-consistently, based on the determination of the image charges at the EVA and Si interface due to the Na\(^+\) concentration profile.
5.3 Device simulations

To determine the amount of degradation as a function of Na ingress into the silicon substrate, we model the effect of introducing an electrical shunt in the emitter of a typical p-Si, aluminum back surface field (Al-BSF) PV module. The schematic of the simulated devices is shown in Fig. 5.3. The boron concentration in the base, emitter phosphorus concentration and Al-BSF concentration used in the simulation are listed in Table 5.1. Both, the emitter and Al-BSF are defined using a Gaussian concentration profile which reaches a value of $10^{16}$ cm$^{-3}$ at a depth of 300 nm from the front and back surfaces, respectively. Device simulations are performed using Synopsys Sentaurus FEM solver[1]. Carrier generation is estimated using OPAL[2] at 1 Sun, considering an SiN$_{x}$ anti-reflective coating of 75 nm. Shockley-Read-Hall bulk recombination is activated and a bulk lifetime of 5 ms. The selected bulk lifetime is consistent with several reports of high quality float zone Si wafers at the same level of doping [107]. The surface recombination velocity at the SiN$_{x}$/Si interface was estimated using Altermatt’s parametrization [108], and Fermi–Dirac statistics is activated to account for the large doping concentration at the emitter.

To model PID-s, we introduce a metallic structure within the emitter of the cell as illustrated in Fig. 5.4. We define the conductivity profile along the SF according to the spreading resistance measurements taken by Korol [97] on Na-implanted silicon. To avoid introducing spurious shunting at early stages of the simulation due to the presence of a metallic structure, we neglected the regions of the shunt with conductivity less than $10^{-10}$ S cm$^{-1}$. Concentration profiles as a function of time were modeled according to the parameters in Table 5.1.

Table 5.1: Parameters used to model transport across the SiN\textsubscript{x}/Si stack.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simulation temperature</td>
<td>( T )</td>
<td>85</td>
<td>°C</td>
</tr>
<tr>
<td>Thickness of SiN\textsubscript{x}</td>
<td>( L_{\text{SiN}} )</td>
<td>75</td>
<td>nm</td>
</tr>
<tr>
<td>Thickness of Si</td>
<td>( L_{\text{Si}} )</td>
<td>1</td>
<td>µm</td>
</tr>
<tr>
<td>Electric field in SiN\textsubscript{x}</td>
<td>( E_{\text{SiN}} )</td>
<td>0.5</td>
<td>MV cm(^{-1})</td>
</tr>
<tr>
<td>Electric field in Si</td>
<td>( E_{\text{Si}} )</td>
<td>0</td>
<td>V cm(^{-1})</td>
</tr>
<tr>
<td>Diffusion coefficient of Na\textsuperscript{+} in SiN\textsubscript{x} (^a)</td>
<td>( D_{\text{SiN}} )</td>
<td>( 4 \times 10^{-16} )</td>
<td>cm(^2)/s</td>
</tr>
<tr>
<td>Concentration of the source</td>
<td>( C_{s} )</td>
<td>( 10^{16} )</td>
<td>cm(^{-3})</td>
</tr>
<tr>
<td>Doping concentration in the p-Si base</td>
<td>( N_{A} )</td>
<td>( 10^{16} )</td>
<td>cm(^{-3})</td>
</tr>
<tr>
<td>Doping concentration in the n-Si emitter</td>
<td>( N_{D} )</td>
<td>( 10^{19} )</td>
<td>cm(^{-3})</td>
</tr>
<tr>
<td>Al-BSF doping level</td>
<td>( N_{D} )</td>
<td>( 10^{19} )</td>
<td>cm(^{-3})</td>
</tr>
<tr>
<td>Surface mass transfer coefficient at the SiN\textsubscript{x}/Si interface</td>
<td>( h )</td>
<td>( 10^{-12} )</td>
<td>cm s(^{-1})</td>
</tr>
<tr>
<td>Segregation coefficient at the SiN\textsubscript{x}/Si interface</td>
<td>( m )</td>
<td>1.0</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\) Based on high resistivity SiN\textsubscript{x} measurements Gastrow et al. \[62\].
Figure 5.4: Schematic of a metallic shunt introduced in the n⁺-Si emitter of the PV module to model PID-s. The triangular plane represents a metallic region over a {111}-stacking fault, with a resistivity profile determined by the Na concentration.

Fig. 5.5 shows a PID-s kinetics simulation for a device stressed at 85 °C under a voltage equivalent to 0.5 MV cm⁻¹, according to the parameters described in Table 5.1. Fig. 5.5(a) shows the corresponding concentration profiles in the module stack used in the determination of the shunt conductivity and subsequently, to simulate the J-V characteristic. Due to the small value of the surface mass transfer coefficient ($h = 10^{-12}$ cm s⁻¹), sinking into the emitter occurs at a slower rate, compared to the rate at which ions drift within the SiNₓ. This leads to a build-up in the concentration on the SiNₓ side of the SiNₓ/Si, which reaches concentrations up to $\sim 10^{19}$ cm⁻³.

For the selected value of the diffusion coefficient of Na in the SF, Na reaches concentrations $\gtrsim 10^{14}$ cm⁻³ within a few hours leading to values of the conductivity $\gtrsim 10^{-3}$ S cm⁻¹ within the p-n junction of the device, as can be seen in Fig. 5.5(b). The simulated J-V characteristic due to PID is shown in Fig. 5.5(c). The first J-V curve shown in bright yellow, at time zero corresponds to the device in the absence of the shunt. Below the threshold value of $\sigma_{\text{shunt}} < 10^{-3}$ S cm⁻¹, only a
Figure 5.5: Simulated PID-s kinetics degradation for device stressed at 85 °C under a voltage equivalent to 0.5 MV cm⁻¹. (a) Shows the corresponding Na concentration profiles as a function of PID stress indicated in color scale. Accumulation at the Si interface occurs due to the effect of the segregation flux allowing only a fraction of Na to sink into the n⁺-Si emitter. In Si, Na transport is entirely governed by diffusion. For the selected value of the diffusion coefficient of Na in the SF (10⁻¹⁴ cm²/s), Na reaches the p-n junction of the devices in a few hours. (b) The corresponding conductivity from the Na concentration in the Si emitter, estimated from spreading resistance measurements by Korol [97]. (c) Simulated J-V characteristic as a function of PID time for device. For short times, before the conductivity reaches the value of 10⁻³ S cm⁻¹, the device loses efficiency by increased recombination. Indicated in red circles is the maximum power point $P_{mpp}$ for each curve.
loss of fill factor is observed. This is assumed to be due to an increase in the diode recombination current. Once this threshold is surpassed, an unambiguous decrease in $R_{sh}$ is seen at further times, as expected in PID-s. Note that the 42 mA/cm$^2$ short circuit current ($J_{sc}$) is due to the fact that no surface recombination current is considered for the contacts of the cell. This fact does not change the analysis, since the kinetics is estimated normalizing with respect to the initial performance metrics (e.g. $R_{sh}$ and $P_{mpp}$) of the device.

5.4 Bounding the value of the diffusion coefficient of Na in the SF

From the simulated J-V characteristic like the one shown in Fig. 5.5, it can be seen that a threshold value of the conductivity at the vicinity of the $p$-$n$ junction is required in order to observe PID. This indicates that, in order to observe PID, the diffusion length of Na in Si should be around the value of the depth of the $p$-$n$ junction. It follows that this requirement can be used to set the bounds of the diffusivity of Na in the stacking fault, by using order of magnitude analysis.

Robust device simulations require full 3D implementation to avoid current collection losses artificially introduced by reduction of current pathways in 2D simulations. This increases the computational load due to the large number of elements required to adequately capture the physics on elements of very dissimilar scales. For instance, the dimensions of the quasi-2D shunt give elements with minimum mesh size of 5 nm, while the distance between finger electrodes is 1 mm. To reduce computational time, when working with numerous parameter scans, we recreated the FEM model, by means a, Machine Learning algorithm that uses the concentration profiles as pre-
Figure 5.6: Simulated PID-s progression as a function of Na diffusivity in the stacking fault $D_{SF}$ for a PV module stressed at 85 °C and a voltage stress equivalent to a 0.5 MV cm$^{-1}$ in the SiN$_x$ film. Failure time decreases with increasing $D_{SF}$, from being less than 10 %, within the timescale of the simulation for $D_{SF} = 10^{-18}$ cm$^2$/s, to less than 4 h in the case of $D_{SF} = 10^{-14}$ cm$^2$/s. For reference, experimental PID-s reported for similar temperatures and device architectures are plotted alongside: Masuda et al. [35] (2016), Hacke et al. [36] (2013), Oh et al. [37] (2017), Pingel et al. [5] (2010), Hacke et al. [38] (2015).

Figure 5.7: Arrhenius relationship for the diffusion coefficient of Na in Si, as estimated from fitting SIMS profiles of thermally diffused Na in n-Si wafers. For reference, the dashed red curve represents an extrapolation from from Arrhenius curves within the range of 350 to 800 °C by [97]. Adapted from Clenney et al. [109].
dictors and previously computed $P_{\text{mpp}}$ as targets. This is justified, since device simulations do not explicitly incorporate ion transport kinetics, and the characteristic J-V is only a function of the shunt conductivity for the geometry shown in Fig. 5.4, albeit this approach is specific to the device geometry defined in 5.3. To implement this, we used the Scikit-learn [110] library distributed with Python to train a Random Forest regressor with a set of 121 concentration profiles ($\approx 70\%$) and their respective $P_{\text{mpp}}$ from a total sample size of 172 simulations. We tested the regressor against the remaining dataset of 52 profiles ($\approx 30\%$) with their respective $P_{\text{mpp}}$, from which we got a coefficient of determination [111] $R^2 = 0.999$ for $P_{\text{mpp}}$.

In order to bound the values of $D_{\text{SF}}$, we used the trained model to predict the decay in the maximum power from the simulated concentration profiles of devices stressed according to the parameters in Table 5.1. The diffusion coefficient of Na in the SF is varied logarithmically from $10^{-18}$ to $10^{-14}$ cm$^2$/s. Fig. 5.6 shows the simulated power output ($P_{\text{mpp}}$) normalized to the initial $P_{\text{mpp}}$ as a function of PID time, for different values of $D_{\text{SF}}$. As expected, failure time decreases with increasing $D_{\text{SF}}$, from a few hours for $D_{\text{SF}} = 10^{-14}$ cm$^2$/s, to the order of days for $D_{\text{SF}} = 10^{-18}$ cm$^2$/s. Overlayed in Fig. 5.6 are experimental degradation times reported for p-Si PV modules stressed under similar conditions reported by Pingel et al. [5], Masuda et al. [35], Hacke et al. [36], Oh et al. [37], and Hacke et al. [38]. Comparison with literature data for PID-susceptible devices like the ones reported by Masuda et al. [35], indicates that the upper bound for $D_{\text{SF}}$ is of the order of $10^{-14}$ cm$^2$/s. It is notable that the devices which experience faster degradation kinetics (Masuda et al. [35] and Hacke et al. [36]) are multi-crystalline Si modules, whereas devices exhibiting smaller degradation rates (Pingel et al. [5], Oh et al. [37], and Hacke et al. [38]) are mono-crystalline devices. Recent results from ab-initio calculations on the interstitial barrier for Na diffusion in intrinsic stacking faults suggested that diffusion along the extend defects
might have a larger energy penalty than bulk diffusion \cite{112}. This result seemed to indicate that the mechanism behind shunt decoration is dominated by bulk diffusion followed by segregation to the intrinsic SF. Fig. 5.7 shows the Arrhenius relationship of Na diffusivity in Si as obtained by fitting the diffusion profiles of Na measured by SIMS \cite{109}. Based on SIMS measurements, the expected diffusivity of Na in the bulk of Si is \( \approx 3 \times 10^{-19} \text{cm}^2/\text{s} \) at 85 °C \cite{109}, which contrasts with the upper bound of \( 10^{-14} \text{cm}^2/\text{s} \) required to match the degradation kinetics seen on multicrystalline samples \cite{35}. Our result indicates that segregation to the SF from bulk-diffused Na is incompatible with the timescales associated with degradation in PID-prone devices. This suggests a diffusive mechanism through the SF as described by the DFT calculations by Ziebarth et al. \cite{113}, in which the energetic barrier for interstitial diffusion along the SF is lowered for a filled defect, driven by an increase in the Si–Si bond distance.

5.5 Finite Source Analysis

The considerable amount of Na accumulation in SiN\(_x\) near the Si interface shown in Fig. 5.5 (reaching concentrations \( > 10^{18} / \text{cm}^{-3} \)) is in part due to the low value of \( h \) (\( 10^{-12} \text{cm/s} \)) used in the simulation. However, a significant contribution to the accumulation comes from the fact that we have assumed an infinite reservoir of Na\(^+\) keeping the concentration \( C_s \) fixed at all times. A more physical assumption is to consider the effect of a finite source by means of Eq. (4.18),

\[
J_{\text{source}} = kS
\]

where a constant flux of Na\(^+\) at the source is given by the product of a rate of ingress \( k \) and a surface concentration \( S \).
Table 5.2: Parameters taken as the reference base case in PID kinetics simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
<th>Consideration</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>85</td>
<td>°C</td>
<td>Accelerated testing</td>
</tr>
<tr>
<td>$E$</td>
<td>$10^4$ V/cm</td>
<td></td>
<td>Within the order of magnitude of the upper bound in Table 2.1.</td>
</tr>
<tr>
<td>$D_{SiN}$</td>
<td>$4 \times 10^{-16}$ cm$^2$/s</td>
<td></td>
<td>Ref. [62] (at 85 °C).</td>
</tr>
<tr>
<td>$D_{SF}$</td>
<td>$10^{-14}$ cm$^2$/s</td>
<td></td>
<td>Upper bound from Sec. 5.4.</td>
</tr>
<tr>
<td>$S$</td>
<td>$10^{10}$ cm$^{-2}$</td>
<td></td>
<td>Two order of magnitude less than intentionally contaminated devices in Wilson et al. [32].</td>
</tr>
<tr>
<td>$k$</td>
<td>$10^{-4}$ s$^{-1}$</td>
<td></td>
<td>Depletion of the source within the first 24 h.</td>
</tr>
<tr>
<td>$h$</td>
<td>$10^{-12}$ cm s$^{-1}$</td>
<td></td>
<td>Inefficient leakage to Si</td>
</tr>
<tr>
<td>$m$</td>
<td>1</td>
<td>–</td>
<td>No jump discontinuity.</td>
</tr>
<tr>
<td>$L_{SiN}$</td>
<td>75 nm</td>
<td></td>
<td>Ref. [34]</td>
</tr>
<tr>
<td>$L_{Si}$</td>
<td>1 µm</td>
<td></td>
<td>Capture the emitter thickness.</td>
</tr>
</tbody>
</table>

The value of $k$ can be defined based upon whether depletion of the source occurs during the time scale of the simulation or not, whereas $S$ can be taken from experimental estimations on the surface concentration like the ones given by Naumann et al. [104], Wilson et al. [32] and Snow et al. [69].

As shown in Fig. 4.5, the consideration of a finite source leads to (1) less accumulation at the SiN$_x$/Si interface and, (2) depletion of the source within the timescale of the simulation.

To understand the effect of individual variations of the parameters $D_{SF}$, $S$, $k$, $E$ and $h$ from the base case indicated in Table 5.2, we performed PID kinetics simulations using a finite source.
In Fig. 5.8, the simulated kinetics of PID-s is shown for different values of $D_{\text{SF}}$, indicated in color scale. As could be expected, larger values of $D_{\text{SF}}$ result in a more rapid accumulation of Na at the $p$-$n$ junction of the device leading to faster degradation rates. This is by far the parameter that induces the most significant variation in the degradation kinetics of p-Si PV modules. Depending on the quality of the initial wafer and the manufacturing quality control during the formation of the emitter, the number of SF defects can vary from device to device, leading to effective variations in $D_{\text{SF}}$. Furthermore, it is expected for multi-crystalline Si devices to have grain boundaries with different defect orientations, with respect to the typical $54^\circ$ orientation of the $\{111\}$ SF in mono-crystalline Si. Some of these orientations would lead to shorter SF path lengths to the emitter junction. This could explain difference on the effective $D_{\text{SF}}$, which would be averaged over the crystallite boundaries at the surface of the emitter.

In Fig. 5.9, the simulated time series of PID is plotted for different values of the surface source concentration, $S$ indicated by the color scale. It can be observed that even for a variation
Increasing $S$

Figure 5.9: Simulated PID-kinetics as a function of the surface concentration of Na at the source $S$ (indicated by the color scale).

Increasing $k$

Figure 5.10: Simulated PID-kinetics as a function of the rate of ingress of Na at the source $k$ (indicated by the color scale)
of three orders of magnitude in $S$, the equivalent time required to reach a 50% degradation of the initial power output is still within the range of 4 to 8 hours. Nevertheless, the degradation reaches almost the same level, regardless of the value of $S$, after $\sim 20$ h of PID stress.

In contrast, in Fig. 5.10 it is shown that the rate of ingress of Na to the SiN$_x$ has a significant impact on the magnitude and the rate of degradation of the PV module. It can be seen that the time required to reach a 50% degradation varies from around 16 h for $k = 10^{-8}$ s$^{-1}$, to $\approx 8$ h for $k = 10^{-5}$ s$^{-1}$. An increase in the flux from the source leads to a larger accumulation of Na in the SiN$_x$ film, compared with lower values of $k$. Since the magnitude of the segregation flux is dependent on the difference of the Na concentration at both sides of the SiN$_x$/Si interface, a larger value of the concentration at the SiN$_x$ increases the magnitude of the flux to the Si emitter. This explains why larger values of $k$ increase the rate and the magnitude of degradation of the module.

As discussed in Sec. 1.4, it is expected that the magnitude of the electric field $E$ in SiN$_x$ determines the amount of drift of Na through the dielectric and hence, a reduction of $E$ should translate to a decrease in the decay rate. In Fig. 5.11 the simulated PID time series of a PV modules
Increasing $h$ 

$10^{-12}$ cm/s

$10^{-10}$ cm/s

$10^{-8}$ cm/s

Figure 5.12: Simulated PID-kinetics as a function of the magnitude of the surface mass transfer coefficient $h$ at the SiN$_x$/Si interface (indicated by the color scale).

is shown, as a function of $E$, indicated in color scale. It can be observed that, indeed, a reduction of the $E$ from $10^6$ to $10^5$ MV/cm leads to a $< 4$ h delay in the time the device is expected to degrade 50% with respect to the initial value. Nevertheless, variations in the degradation kinetics for for $E < 10^4$ MV/cm are minimal. This behavior is explained by the fact that, at $85^\circ$C, the diffusion coefficient of Na$^+$ in SiN$_x$ is such, that transit time can occur in less than 36 h for $E < 10^4$ MV/cm, as can be seen in Fig. [3.4]. This indicates that it is likely that highly resistive SiN$_x$ films preclude the fabrication of PID-robust devices. It might be possible that the energetic barrier for Na$^+$ diffusion in less resistive SiN$_x$ can be larger compared to high resistivity SiN$_x$, leading to a decrease in the rate of decay with respect to the indicated in Fig. [5.11].

In Fig. [5.12], the variation in the simulated PID kinetics as a function of the surface mass transfer coefficient $h$ at the SiN$_x$/Si interface is shown. It can be observed that for $h > 10^{-10}$ cm/s, the difference in the time series of PID becomes negligible. The effect of $h$ is conflated with the relative values of $D$ in the SiN$_x$ film and in the SF, as well as with the relative Na concentrations at both sides of the SiN$_x$/Si interface.
Figure 5.13: Estimated time required to reach a 5% performance degradation in a p-Si PV module due to potential induced degradation as a function of (1) the diffusion coefficient of Na in the stacking fault $D_{SF}$, (2) the electric field in the SiN$_x$ $E$, (3) the surface concentration of ions at the source $S$, (4) the rate of ingress of Na from the source $k$, (5) the segregation surface mass transfer coefficient at the SiN$_x$/Si interface $h$. For comparison, a “high” and a “low” value of each parameter is shown with a 2 orders of magnitude variation in each case.
To quantitatively compare the effect of the variation in the transport parameters, we estimate the time required to incur in a 5% decrease in the initial power output ($\tau_5$) for each of the time series shown in Figs. 5.8, 5.9, 5.10, 5.11 and 5.12. The comparison is made for a two orders of magnitude variation of each parameter with respect to the base case shown in Tab. 5.2. The values are plotted in Fig. 5.13. It can be seen that $\tau_5$ decreases almost 75% when increasing $E$ from $10^4$ to $10^6$ V/cm which is the largest percentage change between the five parameters. Nevertheless, it has been shown that below $10^4$ V/cm, diffusive transport dominates leading to a negligible change in the kinetics of PID-s, for the SiN$_x$ composition analyzed in this work. The second largest change occurs when varying $D_{SF}$ from $10^{-16}$ to $10^{-14}$ cm$^2$/s, which results in a $\approx 64\%$ reduction in $\tau_5$. Similarly $\tau_5$ drops $\approx 55\%$, when increasing $k$ from $10^{-6}$ to $10^{-4}$ s$^{-1}$. Finally, $\tau_5$ drops $\approx 50\%$ when increasing $S$ from $10^{10}$ to $10^{12}$ /cm$^2$, which is just about the same amount it decreases when varying $h$ from $10^{-12}$ to $10^{-8}$ cm/s. These results indicate that control over the electric field in SiN$_x$ is very important, particularly in film compositions that have lower Na diffusivities. Additionally the diffusion coefficient of Na remains a significant parameter which could be subject of improvement by using monocrystalline Si wafers and through optimization of the process of emitter diffusion [9]. A final remark is that, the considerable change in $\tau_5$ introduced by the variation of $k$ suggests that engineering the encapsulant/SiN$_x$ interface might be a potential workaround to increase segregation at the polymer, and hence increase the robustness of the device against PID.
5.6 Summary

We developed a framework to model PID-s degradation kinetics that describes the kinetics of shunt formation and the decay in the power output as a function of the diffusivity of Na in the PV module, surface concentration and rate of ingress of Na at the EVA/SiN$_x$ interface, segregation surface mass transfer coefficient, and the string bias. This parametrization can be correlated with the bill of materials in the module. Extension to estimate the kinetics of $R_{sh}$ decay is straightforward. We identified that the shunt conductivity around the $p-n$ junction of the device must be above $10^{-3}$ S cm$^{-1}$ in order to observe PID. Furthermore, we established an upper bound for the diffusivity of Na in the stacking fault on the order of $10^{-14}$ cm$^2$/s, which suggests that diffusion occurs along the SF.

We established that finite source simulations could be advantageous to avoid unphysical accumulation of Na across the interface. By simulating the effect of varying one parameter at a time, we were able to identify that $D_{SF}$ has the largest impact on the kinetics of PID. This indicates that the crystallinity and number concentration of SF in the emitter can average to an effective diffusion coefficient. It is expected then, that quality control during the emitter formation could help decrease the susceptibility to PID. Notably, the kinetics of PID is very sensitive to the rate of ingress of Na in the SiN$_x$. This means that interface design between the encapsulant and SiN$_x$ is very likely to reduce the impact of PID in Si PV modules, by increasing segregation to the encapsulant. We also identified that, for highly resistive SiN$_x$, the reduction of $E$ has a limiting effect on PID, due to the large value of the diffusivity of Na associated to the Si-N composition we studied.
Overall, this framework has enabled us to identify the rate limiting processes in PID. Further fitting of the degradation time series to accelerated PID experiments will allow us to determine more accurate values on the parameter space. Our model provides a description of the PID's physics which renders not only the time series of the power decay, but also the kinetics of Na transport and J-V characteristic of stressed devices. This will enable reference with multiple characterization techniques (e.g. BTS measurements, SIMS characterization, I-V characterization), to validate the sensitivity to the different components in the module and. Upon parameter refinement, this framework will be of use in the design of PID-robust PV modules.

Chapter 5, in part, is being prepared for submission in IEEE Journal of Photovoltaics under the title “Finite Element Simulation of Potential Induced Degradation Kinetics in p-Si Solar Modules” by E. Martinez-Loran, G. von Gastrow, J. Clenney, R. Meier, P. Bandaru, Mariana I. Bertoni, D.P. Fenning. The dissertation/thesis author was the primary investigator and author of this paper.
6 | Summary and Suggestions for Future Work

A framework for the characterization and modeling of potential-induced degradation has been developed for p-Si photovoltaic modules. The proposed methodology includes quantification methods to determine the transport kinetics of Na in the passivation layers of Si solar cells using measurement techniques that enable characterization at device operating temperatures. The advantage of this measurement is that it can provide a more accurate parametrization of ion kinetics with respect to the extrapolation of the diffusivities from measurements at higher temperature ranges, which can incur orders of magnitude variations in the estimated diffusion coefficient.

Transport in SiN$_x$ films with index of refraction 1.89 (at 600 nm) reveals that anti-reflective coatings with this Si–N composition, are not an effective barrier against Na diffusion in silicon photovoltaic modules.

A numerical solution to the transport of charged species in dielectrics was developed which can describe the ingress of Na contamination in silicon photovoltaic modules. The advantage of the numerical solution is that: (1) it can solve Poison and Nernst-Planck’s equations self consistently to completely describe the kinetics of Na transport for contamination levels consistent with PID,
extension of the solution to stacks of materials can be implemented through first order kinetics segregation fluxes [96]. (3) It allows to reference the numerical results with electrical measurements and other quantitative experimental techniques to characterize the concentration of Na ions (e.g. secondary-ion mass spectroscopy).

A complete framework to describe the kinetics of potential-induced degradation was proposed which uses transport simulations to estimate the resistivity profile of a metallic shunt in the emitter of a photovoltaic module. This model has allowed us to set an upper bound of $10^{-14} \text{cm}^2\text{s}$ (at 85°C) on the diffusivity of Na in the Si emitter. This result indicates that bulk diffusion, which occurs with $D \approx 3 \times 10^{-19} \text{cm}^2/\text{s}$ at the simulated temperature [109], is not the predominant mechanism in PID-prone devices. Instead, transport is dominated by diffusion through the SF as suggested by ab-initio studies by Ziebarth et al. [113].

6.1 Applications of PID kinetics quantification and modeling

The methodology developed to quantify the kinetics of Na transport in SiN$_x$ is of interest to other device architectures and dielectric compositions. Determination of transport kinetics is applicable to other semiconductor architectures like perovskite PV devices, which are very attractive for solar energy harvesting [114].

The general goal of this modeling framework is to be able to parametrize PID-s in terms of the materials used in the photovoltaic module and the operating conditions. This model will provide guidance in the design of ion blocking layers that can reduce the ingress of Na to the emitter of the module by means of (1) reduction of the drift and, (2) interface design to increase segregation on the outermost layers of materials in the device.
6.2 Future work

6.2.1 Quantification of composition-dependent transport in SiN\textsubscript{x}

Based on the voltage divider model, modification of the Si to N composition in SiN\textsubscript{x} films impacts PID kinetics by changing the electrical resistivity of the film and hence, the magnitude of the electric field driving transport. Nevertheless, transport of Na can also be influenced by local electrostatic interactions determined by the coordination environment of (N–Si–N)\textsuperscript{−} in the film \cite{115}. To quantify this effect, the trapping corrected BTS method can be used to study sodium transport in SiN\textsubscript{x} films as a function of Si to N composition. It would be expected that SiN\textsubscript{x} of higher Si content \cite{33} would experience a higher activation energy for diffusion.

6.2.2 Incorporation of environmental factors

To adequately reproduce accelerated testing protocols, incorporation of temperature- and humidity-activated resistivity \cite{3} values is required. This could help elucidate whether transport in the polymer encapsulants can be enhanced by an electrochemical reaction at elevated water contents, in addition to the electrostatic considerations of this model.

PID kinetics simulations will be of use to better understand the applicability of accelerated testing protocols. Accelerated testing assumes long term damage can be characterized by continuous application of temperature, voltage and humidity stress to the PV modules. Under regular operation, such extreme conditions do not occur. Diurnal variations can be implemented on our transport modeling framework to account for realistic ingress of Na under conditions closer to field operation.
6.2.3 Three-dimensional considerations

The present model assumes that Na transport is predominantly occurring in the direction normal to the material interfaces which simplifies some of the derivations and saves computing resources. Nevertheless, three-dimensional extension can be easily implemented, and can provide further information on the effect of in-plane diffusion, especially in the context of interfacial oxide layers that might play a significant role in reducing the ingress of Na contamination to the Si emitter.

6.2.4 PID-recovery

The process of PID recovery has been reported experimentally in p-Si PV modules by means of the application of a thermal stress with and without the reversal of the electric field in the PV module [5, 11, 14, 15, 28, 35, 103, 116, 117]. While full PID recovery is usually not observed, the process remains poorly understood from a physical perspective.

The present model considers that transport of Na impurities in the Si emitter of PV devices is dominated by 1D diffusion along the direction normal to the SiNₓ/Si interface. Under these conditions, the typical negative concentration gradients inside the silicon emitter preclude out-diffusion as proposed by Lausch et al. [11]. In the context of this model, we hypothesize that recovery could be possible for a specific combination of source concentrations and recovery electric fields. A full combinatorial analysis on the parameter space could shed light on such conditions. An alternative answer might arise from the three-dimensional consideration of transport kinetics, where out-diffusion to the bulk of Si might explain thermal PID recovery. In this sense, Density Functional Theory studies have shown that, once Na occupies interstitial positions in the
SF, there is a large barrier to diffuse back into the bulk \[112\], which explains the irreversibility of this degradation mode.

### 6.2.5 Incorporation of SiN\(_x\) trap kinetics

In our trapping corrected BTS method we considered the effect of bulk traps in SiN\(_x\) capturing, driven by the applied voltage stress. The rate at which traps are filled is dependent on the magnitude of the applied field, and the energy position of the traps with respect to the conduction band edge of SiN\(_x\) as prescribed by Frenkel-Poole emission current \[63\]:

\[
J = C_1E \exp \left\{ -\frac{q}{k_B T} \left[ \phi_1 - \left( \frac{qE}{\pi \varepsilon_0 \varepsilon_d} \right)^{1/2} \right] \right\}, \tag{6.1}
\]

where \(E\) is the electric field, \(\phi_1\) is the barrier height of the trap with respect to the conduction band edge, \(\varepsilon_d\) is the dynamic dielectric constant of SiN\(_x\) and the proportionality constant \(C_1\) is a function of the density of the trapping centers.

During operating conditions, the voltage differential in the SiN\(_x\) anti-reflective coating, albeit low, might be enough to fill a finite concentration of bulk traps with electrons leading to positive image charges in the semiconductor. Based upon the 1 V saturation flatband voltage shift (see Fig. 3.2) from our BTS measurements at 1 MV cm\(^{-1}\) and Eq. (6.1), we assumed that the concentration of occupied traps at \(E = 10\) kV cm\(^{-1}\) typically used for our simulations, will be at least two orders of magnitude less. Hence, we neglected the concentration of trapping centers in the computation of image charges in PID degradation kinetics. Nevertheless, this aspect could be of interest for SiN\(_x\) compositions with larger concentration of traps. To characterize this, we propose to fit \(\Delta V_{FB}\) in SiN\(_x\) MIS capacitors without intentional Na contamination to the flatband voltage obtained by integration of Frenkel-Poole current in Eq. (6.1), to extract \(C_1\) and \(\phi_1\). This
will allow us to determine the extent of positive image charges in Na transport simulations, which will modify the electric potential at the SiNₓ/Si interface and consequently Na accumulation and ingress to the Si emitter.
A Derivation for the characteristic time for drift-diffusion

We defined the characteristic time for drift-diffusion as the solution to the equation

\[ L = 2\sqrt{D \tau_c} + \mu E \tau_c \]

\( \tau_c \) is then given by the solution to the quadratic equation

\[ \mu^2 E^2 \tau_c^2 - 2(\mu EL + 2D)\tau_c + L^2 = 0, \]

which is given by

\[ \tau_c = \frac{L}{\mu E} + \frac{2D}{\mu^2 E^2} \pm \frac{2\sqrt{\mu ELD + D^2}}{\mu^2 E^2}. \]

Rearranging the terms within the square root term:

\[ \tau_c = \frac{L}{\mu E} + \frac{2D}{\mu^2 E^2} \pm \frac{2D}{\mu^2 E^2} \left( 1 + \frac{\mu EL}{D} \right)^{1/2}. \]

Equation (A.3) can be further simplified to

\[ \tau_c = \frac{L}{\mu E} + \frac{2D}{\mu^2 E^2} \left[ 1 \pm \left( 1 + \frac{\mu EL}{D} \right)^{1/2} \right]. \]
Writing the mobility term explicitly \((\mu = qD/k_B T)\):

\[
\tau_c = \frac{L}{D} \left( \frac{k_B T}{qE} \right) + \frac{2}{D} \left( \frac{k_B T}{qE} \right)^2 \left\{ 1 \pm \left[ 1 + \left( \frac{qE}{k_B T} \right) L \right]^{1/2} \right\}. \tag{A.5}
\]

Equation (A.5) can also be expressed in term of the thermal voltage \(v_{th} \equiv k_B T / q\):

\[
\tau_c = \frac{L}{D} \left( \frac{v_{th}}{E} \right) + \frac{2}{D} \left( \frac{v_{th}}{E} \right)^2 \left\{ 1 \pm \left[ 1 + \left( \frac{E}{v_{th}} \right) L \right]^{1/2} \right\}. \tag{A.6}
\]

The solution to the equation (3.8) assumes that the drift flux \(\mu EC\) is in fact considerable with respect to the diffusive flux \(-DV^2C\). Equation (A.6) depends on the inverse of \(E\). This causes \(\tau_c \to \infty\) as \(E \to 0\), which is not physical because the diffusive term dominates as \(E \to 0\). Then the solution needs to be given by the lowest bound of the time between (A.6) and the characteristic diffusion time \(L/D\).
Derivation of the spatial part of Nernst-Planck equation in the weak form

Behind scenes, the weak formulation of a PDE works by transforming the differential operator to a variational problem \[81, 82, 118\]. Discretization prescribes formulating the problem \( L(x) = f \) in matrix form. The solution \( u \) in the vector space \( V \) is then given by:

\[
Au = f. \tag{B.1}
\]

The function space \( V \) has the minimum requirements of being equipped with a norm \( \| \cdot \| \) to compute distances within vectors, and we require that every Cauchy sequence in \( V \) converges to an element in the same space (Banach space) \[119\]. The variational formulation states that this problem is equivalent to finding \( u \) such that

\[
[Au](v) = f(v) \tag{B.2}
\]

for all \( v \) in the vector space \( V \). In the FEM, \( u \) are called trial functions and \( v \) are known as test functions. An additional requirement is placed on \( V \) so that for all test functions \( v^2 \) and \( \|v^2\| \) have finite integrals over the volume (Sobolev space) \[81\].

The finite-element-method approach to integrate the spatial part of the coupled Poisson-Nernst-Planck system with the finite element method is to write it in the variational formulation.
The right hand side of Eq. (2.1) and Poisson’s equation can be written in terms of trial functions

\[ L_{NP}[u_c] \equiv \nabla \cdot (D \nabla u_c) + \mu u_c \nabla \cdot \nabla u_p + \mu \nabla u_c \cdot \nabla \phi (u_p, t), \quad (B.3a) \]

\[ L_p[u_p] \equiv \nabla \cdot \nabla u_p + \frac{q}{\varepsilon_{ins}} u_c \quad (B.3b) \]

where \( u_c, u_p \) are trial functions for the concentration and electric potential respectively, \( L_{NP} \) and \( L_p \) are the differential operators for the spatial part of (2.1) and for Poisson’s equation, respectively.

Multiplying \( L \) by the test function \( v \) and integrating over the volume \( \Omega \):

\[ A_{NP}(u, v) \equiv D \int_{\Omega} \nabla \cdot (\nabla u_c) v_c d\Omega + \mu \int_{\Omega} u_c \nabla \cdot \nabla u_p v_c d\Omega + \mu \int_{\Omega} \nabla u_c \cdot \nabla u_p v_c d\Omega \quad (B.4a) \]

\[ A_p(u, v) \equiv \int_{\Omega} \nabla \cdot \nabla u_p v_p d\Omega + \frac{q}{\varepsilon_{ins}} \int_{\Omega} u_c v_p d\Omega \quad (B.4b) \]

The order of the derivatives of Laplacian terms in (B.4) can be reduced by integrating by parts and using Gauss theorem (See Appendix [D]):

\[ A_{NP}(u, v) \equiv -D \int_{\Omega} \nabla u_c \cdot \nabla v_c d\Omega + D \int_{\partial \Omega} (\nabla u_c \cdot \hat{n}) v_c ds - \mu \int_{\Omega} \nabla u_p \cdot \nabla (u_c v_c) \Omega \\
+ \mu \int_{\partial \Omega} (\nabla u_p \cdot \hat{n}) u_c v_c ds + \mu \int_{\Omega} \nabla u_c \cdot \nabla u_p v_c d\Omega, \quad (B.5) \]

for \( A_{NP}(u, v) \) and

\[ A_p(u, v) \equiv -\int_{\Omega} (\nabla u_p \cdot \nabla v_p) d\Omega + \int_{\partial \Omega} (\nabla u_p \cdot \hat{n}) v_p ds + \frac{q}{\varepsilon_{ins}} \int_{\Omega} u_c v_p d\Omega \quad (B.6) \]

for \( A_p(u, v) \).
Expanding $\nabla (u_c v_c) = u_c \nabla v_c + v_c \nabla u_c$ in (B.5):

$$A_{NP}(u, v) \equiv -D \int_\Omega \nabla u_c \cdot \nabla v_c \, d\Omega + D \int_{\partial \Omega} (\nabla u_c \cdot \hat{n}) v_c \, ds - \mu \int_\Omega \nabla u_p \cdot u_c \nabla v_c \, d\Omega$$

$$- \mu \int_\Omega \nabla u_p \cdot v_c \nabla u_c \, d\Omega + \mu \int_{\partial \Omega} (\nabla u_p \cdot \hat{n}) u_c v_c \, ds + \mu \int_\Omega \nabla u_c \cdot \nabla u_p v_c \, d\Omega,$$

The bilinear forms can now be written as

$$A_{NP} = -D \int_\Omega \nabla u_c \cdot \nabla v_c \, d\Omega + D \int_{\partial \Omega} (\nabla u_c \cdot \hat{n}) v_c \, ds - \mu \int_\Omega u_c \nabla u_p \cdot \nabla v_c \, d\Omega + \mu \int_{\partial \Omega} (\nabla u_p \cdot \hat{n}) u_c v_c \, ds$$

(B.7a)

$$A_p = -\int_\Omega (\nabla u_p \cdot \nabla v_p) \, d\Omega + \int_{\partial \Omega} (\nabla u_p \cdot \hat{n}) v_p \, ds + \frac{q}{\varepsilon_{ins}} \int_\Omega u_c v_p d\Omega$$

(B.7b)
We will use the results from Appendix B to derive the time stepping system in the variational form. We start by defining Equations (4.6) and (4.7) in terms of the trial functions for the concentration $u_c$ and the electric potential $u_p$, followed by multiplication by the test functions $v_c$ and $v_p$ and subsequently, by integration within the simulation volume $\Omega$ [82].

For the TR step we have

$$
\int_{\Omega} u_c^{n+1} v_c d\Omega - \frac{1 - \gamma}{2 - \gamma} \Delta t_n \int_{\Omega} \langle F^{n+1}(u_c, v_c), (v_c, v_p) \rangle d\Omega = \int_{\Omega} u_c^n v_c d\Omega + \frac{\gamma}{2} \Delta t_n \int_{\Omega} \langle F^n(u_c, u_p), (v_c, v_p) \rangle d\Omega,
$$

(C.1)

and for the BDF2 step

$$
\int_{\Omega} u_c^{n+1} v_c d\Omega - \frac{1 - \gamma}{2 - \gamma} \Delta t_n \int_{\Omega} \langle F^{n+1}(u_c, v_c), (v_c, v_p) \rangle d\Omega = \frac{1}{\gamma(2 - \gamma)} \int_{\Omega} u_c^{n+1} v_c d\Omega
$$

$$
- \frac{(1 - \gamma)^2}{\gamma(2 - \gamma)} \int_{\Omega} u_c^n v_c d\Omega,
$$

(C.2)

where $F$ refers to the spatial part of the problem $\partial C / \partial t = F(C, \phi, x)$, and we have defined the inner product

$$
\langle F(u_c, u_p), (v_c, v_p) \rangle \equiv \underbrace{F_c(u_c, u_p)v_c}_{\text{Nernst-Planck}} + \underbrace{F_p(u_c, u_p)v_p}_{\text{Poisson}}
$$

(C.3)
Equations (C.1) and (C.2) can be expressed in terms of the linear forms (B.7).

For the TR step

\[ \int_{\Omega} u^n_{c} v_c d\Omega - \frac{\Delta t^n}{2} (A^{n+\gamma}_{NP} + A^{n+\gamma}_{P}) = \int_{\Omega} u^n_{c} v_c d\Omega + \frac{\Delta t^n}{2} (A^{n}_{NP} + A^{n}_{P}), \]

and for the BDF2 step

\[ \int_{\Omega} u^{n+1}_{c} v_c d\Omega - \frac{1 - \gamma}{2 - \gamma} \Delta t^n (A^{n+1}_{NP} + A^{n+1}_{P}) = \frac{1}{\gamma(2 - \gamma)} \int_{\Omega} u^{n+\gamma}_{c} v_c d\Omega - \frac{(1 - \gamma)^2}{\gamma(2 - \gamma)} \int_{\Omega} u^n_{c} v_c d\Omega. \]
Writing the weak form of Laplacian terms

Re-formatting the weak form for Laplacian terms $\nabla \cdot \nabla u$ is quite useful to reduce the order of the PDE and, to introduce Neumann boundary conditions. The starting equation for the weak form is

$$\int_{\Omega} \nabla \cdot (\nabla u) v d\Omega$$  \hspace{1cm} (D.1)

We use the result from taking the divergence of $v \nabla u$:

$$\nabla \cdot (v \nabla u) = v \nabla \cdot \nabla u + \nabla v \cdot \nabla u.$$  

to integrate by parts Eq. (D.1)

$$\int_{\Omega} \nabla \cdot (\nabla u) v d\Omega = \int_{\Omega} \nabla \cdot (v \nabla u) d\Omega - \int_{\Omega} (\nabla v \cdot \nabla u) d\Omega$$

Applying the Gauss theorem to the first term on the RHS:

$$\int_{\Omega} \nabla \cdot (v \nabla u) d\Omega = \int_{\partial \Omega_D \cup \partial \Omega_N} (\nabla u \cdot \hat{n}) v ds,$$  \hspace{1cm} (D.2)

where $\partial \Omega_D \cup \partial \Omega_N$ is the union of the Dirichlet and Neumann surfaces. Typically, $v$ is defined such that the integral over the Dirichlet part of the surface vanishes. Then

$$\int_{\Omega} \nabla \cdot (\nabla u) v d\Omega = - \int_{\Omega} (\nabla u \cdot \nabla v) d\Omega + \int_{\partial \Omega_N} (\nabla u \cdot \hat{n}) v ds.$$  \hspace{1cm} (D.3)

The Neumann BC $g = \nabla u$ can then be imposed on the second term on the RHS of (D.3).
References


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