From Femtoseconds to Gigaseconds: The SolDeg Project to Analyze Si Heterojunction Cell Degradation with Machine Learning

I. Degradation in Si-only heterojunctions
II. Development of a Machine-Learning trained Si-H interatomic potential
III. Experimental degradation study
IV. Degradation in c-Si/a-Si:H heterojunctions

Supported by DOE SETO

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Motivation

* Si Heterojunction cells hold Si world record efficiency of 26.7%
* Si HJ cells are a leading candidate for tandem bottom cells
* HJ efficiency degradation rates of 1%/yr were reported, twice the usual. The extra 0.5%/yr degradation was attributed to Voc
* Eliminating this 0.5%/yr degradation would have the effect of increasing the efficiency by 1.5-2% in terms of LCOE, based on the System Advisor Model


On the other hand, the modeling reveals that during the 28-month storage period the density of defect states at the interface, N_s, has increased by an order of magnitude,

D. Jordan et al., IEEE J. of Photovoltaics, 8, 177 (2018)
I. The SolDeg platform

We developed the SolDeg platform to analyze the formation of defects at the c-Si/a-Si interface. This requires:

1. Connecting extreme time scales from femtoseconds to gigaseconds (30 years)
2. Simulation of large number of large samples with extreme precision

**Si-only HJs**

1. Create c-Si/a-Si stacks
2. Generate blasted clusters at the c-Si/a-Si interface as likely hosts of electronic defects
3. Identify blasted clusters that actually host electronic defects
4. Determine the energy barriers that control the generation of these electronic defects
5. Determine the distribution of these barriers
6. Determine the defect generation dynamics from the energy barrier distribution
1. Create c-Si/a-Si stacks using Molecular Dynamics. For the Si-Si potential we chose the Machine-Learning trained Gaussian Approximation Potential Si GAP. (developed by Csanyi)
Timestep: femtoseconds

GAP reproduces DFT much better than other interatomic potentials.
Creating and identifying electronic defects

2. Generate shocked clusters at the c-Si/a-Si interface with “cluster-blaster” as likely hosts of electronic defects

“Dangling bond locator” with DFT: Inverse Participation Ratio (IPR) is an efficient indicator of an electronic state being localized:

\[
IPR_n = \frac{\sum_{i=1}^{I} a_{ni}^4}{(\sum_{i=1}^{I} a_{ni}^2)^2}
\]

~ O(1) for localized states
~ O(1/N) for extended states

We created 1,500 blasted clusters

500 blasted clusters supported electronic defects

3. Identify blasted clusters that actually host electronic defects: IPR

(a) IPR as a function of energy, (b) IPR as a function of z-depth
4. Determine energy barriers that control the generation of the electronic defects: Nudged Elastic Band method
   Start with a path that connects initial and final state over barrier, then nudge it. The relaxing band finds lowest energy barrier/saddlepoint.

5. Determine the barrier distribution for 500 barriers

(b) Energy barrier distributions
6. Use Kinetic Monte Carlo dynamics of thermally activated processes over barriers. But simulation gets stuck in deep valleys. We accelerated simulation: 1. Identify deep valleys (“superbasins”); 2. Help simulation to break free from them.

**Accelerated Superbasin Kinetic Monte Carlo**
Integrate out fast degrees of freedom as in Renorm Group

\[
\tau_0 \exp \left( \frac{1.3 \text{eV}}{300 \text{K}} \right) \sim 10^9 \text{sec} \ (\text{gigasec}) = 30 \text{ years}
\]

Data are well fitted by stretched exponential
Why? Because \( P(E) \) can be fitted by \( P(E) \sim \exp(-E/E^*) \)

\[
N(t) = N_{\text{sat}}(1 - \exp\left[-\left(\frac{t}{\tau_0}\right)^\beta\right])
\]

\[
\beta = kT/E^*
\]
**Time correspondence curve for accelerated testing**

**Accelerated testing at elevated temperature:**

Construct Time correspondence curve

\[ N(T=350K,t_{acc}) = N(T=300K,t_{norm}) \]

Stretched exponential analytically predicts:

\[ t_{(norm)} \sim t_{(acc)}^{\left(\frac{T_{(acc)}}{T_{(norm)}}\right)} \]

350K/300K = 1.17

Fitting the simulation:

\[ t_{(norm)} \sim t_{(acc)}^s \]

\[ s = 1.17 \]
II. SolDeg for c-Si/a-Si:H: High precision needs Machine-Learning trained Si-H GAP

Problem: no Machine Learning-based Si-H (GAP) potential
We developed the world’s first Si-H Machine Learning-trained GAP potential

<table>
<thead>
<tr>
<th>Iteration</th>
<th>Structure Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Optimized structures (all phases)</td>
</tr>
<tr>
<td>2</td>
<td>Optimized structures (all phases)</td>
</tr>
<tr>
<td>3</td>
<td>Low T anneal of a-Si:H</td>
</tr>
<tr>
<td>4</td>
<td>High T anneal of liq-Si:H</td>
</tr>
<tr>
<td>5</td>
<td>High T anneal of liq-Si:H</td>
</tr>
<tr>
<td>6</td>
<td>Med T anneal (1100K) of a-Si:H</td>
</tr>
<tr>
<td>7</td>
<td>Heating a-Si:H from 500K to 800K at 10^13 K/s</td>
</tr>
<tr>
<td>8</td>
<td>Heating a-Si:H from 800K to 1100K at 10^13 K/s</td>
</tr>
<tr>
<td>9</td>
<td>Heating a-Si:H from 1100K to 1400K at 10^13 K/s</td>
</tr>
<tr>
<td>10</td>
<td>Heating a-Si:H from 1100K to 1400K at 10^13 K/s</td>
</tr>
<tr>
<td>11</td>
<td>Heating a-Si:H from 800K to 1400K at 10^13 K/s</td>
</tr>
<tr>
<td>12</td>
<td>Added new a-Si:H structures</td>
</tr>
<tr>
<td>13</td>
<td>Added new a-Si:H structures</td>
</tr>
<tr>
<td>14</td>
<td>Added c-Si/a-Si:H interface structures</td>
</tr>
<tr>
<td>15</td>
<td>Added c-Si/a-Si:H interface structures</td>
</tr>
<tr>
<td>16</td>
<td>Added new c-Si divacancy structures</td>
</tr>
<tr>
<td>17</td>
<td>Added new liq-Si:H structures</td>
</tr>
<tr>
<td>18</td>
<td>Added new c-Si vacancy structures</td>
</tr>
<tr>
<td>19</td>
<td>Added new c-Si interstitial structures</td>
</tr>
<tr>
<td>20</td>
<td>Low T anneal of c-Si/a-Si:H interface structures</td>
</tr>
<tr>
<td>21</td>
<td>Optimization of c-Si/a-Si:H interface structures</td>
</tr>
<tr>
<td>22</td>
<td>NPT high T anneal of liq-Si:H structures</td>
</tr>
<tr>
<td>23</td>
<td>NPT high T anneal of liq-Si:H structures</td>
</tr>
<tr>
<td>24</td>
<td>Quenching liq-Si:H from 2000K to 1500K at 10^13 K/s</td>
</tr>
<tr>
<td>25</td>
<td>Annealing quenched liq-Si:H structures at 1500K</td>
</tr>
<tr>
<td>26</td>
<td>Quenching liq-Si:H from 1500K to 1400K at 10^13 K/s</td>
</tr>
<tr>
<td>27</td>
<td>Added hydrogen passivated c-Si surface (100) and c-Si surface (111) structures</td>
</tr>
</tbody>
</table>

Forces: Deviation from DFT substantially reduced
Energies: reproduces DFT within 4 meV/atom

RMSE: 0.004 eV/atom
Machine-Learning based Si-H GAP: Validation, comparison

Our Si-H GAP reproduces DFT correlator qualitatively better than Tersoff
Machine-Learning based Si-H GAP: Validation, comparison

Our Si-H GAP is closer to experiments than DFT or Tersoff
Si-H GAP: Reaching the unreachable in size and precision

Run time scaling: GAP $O(N)$; DFT $O(N^3)$
DFT can simulate 400-500 atoms
Si:H GAP simulation: 4,096 Si and 558 H atoms

Si:H GAP Molecular Dynamics simulations can reach unparalleled sizes and number of realizations
III. Experimental analysis of SHJ degradation: samples, stressors

**Samples**
- a-Si:H(i) ~50 nm
- c-Si (160-270 μm)
- a-Si:H(i) ~50 nm

**Deposition Conditions**

<table>
<thead>
<tr>
<th>Name</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>13.56 MHz</td>
</tr>
<tr>
<td>Pressure</td>
<td>3.2 Torr</td>
</tr>
<tr>
<td>Power</td>
<td>200 W</td>
</tr>
<tr>
<td>$H_2$</td>
<td>200 sccm</td>
</tr>
<tr>
<td>$SiH_4$</td>
<td>40 sccm</td>
</tr>
<tr>
<td>Temperature</td>
<td>220 °C</td>
</tr>
<tr>
<td>Deposition rate</td>
<td>0.5 nm/sec</td>
</tr>
</tbody>
</table>

**Characterization**

![Graph showing absorbance against wavenumber (cm⁻¹) with peaks at different points for SiH and SiH₂ with baseline.]  

<table>
<thead>
<tr>
<th>Bandgap (eV)</th>
<th>H conc. (at.%)</th>
<th>$\rho$ (g/cm³)</th>
<th>$E_g$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.68</td>
<td>15</td>
<td>2.25</td>
<td>48</td>
</tr>
</tbody>
</table>

**Ageing conditions**

- Dark, Ambient (DA): 0 Sun, T=25 °C
- Light, Ambient (LA): 1 Sun, T=25 °C
- Dark, Heated (DH): 0 Sun, T=80 °C
- Light, Heated (LH): 1 Sun, T=80 °C
Data collection, processing

Minority carrier effective lifetimes at 4 thicknesses

SRV

\[
\frac{1}{\tau_{\text{eff}}} = \left( \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{aug}}} + \frac{1}{\tau_{\text{SRH}}} \right) + 2 \times \frac{SRV}{W}
\]

Defect density, \(N(t)\)

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III. Experimental analysis of SHJ degradation

\[ \frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{aug}}} + \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{SRH}}} + \frac{2 \times \text{SRV}}{W} \]

* Determine SRV at each $\Delta n$ from slope of $1/\tau_{\text{eff}}$ vs. $1/W$
* Repeat for every $\Delta n$ for each $T$ to obtain $\text{SRV}(\Delta n, T)$
* Determine neutral interface defect density $N_s$ by fitting $\text{SRV}(\Delta n, T)$ at three values of $\Delta n$ with the amphoteric defect model of Olibet, Baliff et al.

$Q_s = -(1 \pm 0.3) \times 10^{11}$ cm$^{-2}$
IV. Repeat SolDeg for c-Si/a-Si:H with Si-H GAP

Created 60 c-Si/a-Si:H stacks. 
H content: 12%, 15%

Matched the z-dependent averaged density $D(z)$ at the interface

![Graph showing $D(z)$ against z (Angstrom)]
Observe: Defects are generated by hydrogen drifting from interface

Movement of one H induces the collective motion of 10-20 atoms

We use the Inverse Participation Ratio IPR to verify that the H creates a new dangling bond as it drifts from the interface.
Hydrogen induced defects are low charge/"neutral"

As H drifts, with DFT we track partial charge of all ~500 atoms: Si-blue, H-red
Partial charges remain in -0.2...+0.2 range: generated defects are approximately neutral
Why is hydrogen drifting? H energy is measured to exhibit gradient

We inserted “probe” Hs to ~400 interstitial positions in each of the 60 stacks and measured its “hydrogen energy”. This represents 25,000 calculations.

The hydrogen energy exhibits a gradient across interface. This creates a force that drives H atoms away from interface.
Energy barrier distributions of main processes

- **bond breaking:**
  - $E_{(bb)} = 1.34 \text{ eV}$
  - $\sigma_{(bb)} = 0.34 \text{ eV}$

- **recapture:**
  - $E_{(re)} = 0.26 \text{ eV}$
  - $\sigma_{(re)} = 0.26 \text{ eV}$

- **drift return:**
  - $E_{(dr)} = 0.56 \text{ eV}$
  - $\sigma_{(dr)} = 0.31 \text{ eV}$

- **drift away:**
  - $E_{(da)} = 0.44 \text{ eV}$
  - $\sigma_{(da)} = 0.18 \text{ eV}$
Novelty: Distributions from collective dynamics; H energy gradient

Matching up with previous work

<table>
<thead>
<tr>
<th></th>
<th>Si-H bond-breaking (eV)</th>
<th>Barrier to drift/diffusion (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>1.34</td>
<td>0.49</td>
</tr>
<tr>
<td>Santos et al. 1993</td>
<td>1.3</td>
<td>0.5</td>
</tr>
<tr>
<td>van de Walle 1994</td>
<td>1.2-1.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Biswas 1998</td>
<td>1.4-1.5</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Novelty:
Distribution of barrier energies from collective dynamics
Hydrogen energy gradient
Gradient allows simplifying model to three barriers

1. The $k_i$ rates are the thermal activation factors with the SolDeg-determined $E_i$ energies of the barrier crossing processes.
2. Equations analytically solved for $N_i(t)$.
3. The $N_i(t)$ are averaged over the SolDeg-determined $P(E_i)$ distributions.
Defect generation with SolDeg-simulated energies reproduces data well

* Modelled $N(t)$ with SolDeg-determined energies, averaged over SolDeg-determined distributions (line)
* Correspondence with experimental values (dots) is remarkable
* Not a fit – adjusted only within our narrow error bars

$N(t)$ from AS-KMC without analytics or model truncation validates three barriers model
Broadened barrier distribution needed to provide active barriers

Degradation between 1 week and 1 year is driven by the barriers between 1.1 eV and 1.2 eV.

The 1.34 eV barriers are completely frozen between 1 week and 1 year. Broadening of $P(E)$ around 1.34 eV provides barriers that are active in 1wk-1yr time window, and thus drive the time evolution of $N(t)$.
Hydrogen energy gradient is in blue. Measured Si density is in red. The Si density gradient correlates with, and likely causes, the hydrogen energy gradient. The increasingly porous a-Si offers more room/lower energy spots for H.
How to stop H-driven degradation? Reverse Si density gradient!

The H energy gradient was created by the Si density gradient. Idea: Reverse the H energy gradient by reversing the Si density gradient! This will create a density minimum at interface that traps the H and stabilizes the passivation.

We created 60 new c-Si/a-Si:H stacks where the Si density had a minimum at the interface. We again measured the H energy at 25,000 positions. Found that the H energy gradient has been changed into a minimum!
Related experiments

Ru et al. Hanergy SolMat (2020)

In summary, a 0.5–1 nm $i_1$ a-Si:H buffer layer deposited by RF-PECVD with high hydrogen content and large microstructure factor ($R^*$) was introduced, which improved the c-Si surface passivation effectively.

Duan et al. Prog. in PV (2021)

By using a denser and thinner second part of the intrinsic a-Si:H layer, a reduced vertical rear resistance loss was achieved. This favored vertical carrier transport and led to a higher $FF$. 
Related experiments


Underdense a-Si:H film capped by a dense film as the passivation layer of a silicon heterojunction solar cell

for passivating the a-Si:H/c-Si interface. However, if the structure-loose a-Si:H of Passi-Underdense is not capped with a densely doped a-Si:H layer, the temperature step may induce H mobility in the a-Si:H passivation layer, which helps H to escape towards a vacuum. This can explain why the $\tau_{\text{eff}}$ of

Lee et al. ECS Solid State letters (2014)

Improved Surface Passivation Using Dual-Layered a-Si:H for Silicon Heterojunction Solar Cells

Empty symbols: second, underdense i-a-Si layer added
Related experiments

(i)a-Si:H monolayer vs bilayer

Arno Smets, Y. Zhao

<table>
<thead>
<tr>
<th>(i)-layers on (n)-(p)-side</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$FF$ (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i2/i2$</td>
<td>694.40 ± 4.67</td>
<td>36.92 ± 0.08</td>
<td>79.72 ± 0.46</td>
<td>20.44 ± 0.20</td>
</tr>
<tr>
<td>$i2/i1+i2$</td>
<td>698.60 ± 5.27</td>
<td>37.01 ± 0.17</td>
<td>80.26 ± 0.29</td>
<td>20.75 ± 0.14</td>
</tr>
<tr>
<td>$i1+i2/i1+i2$</td>
<td>704.20 ± 2.28</td>
<td>37.15 ± 0.05</td>
<td>80.55 ± 0.33</td>
<td>21.07 ± 0.03</td>
</tr>
</tbody>
</table>
Can \( N(t) \) be fitted with stretched exponential?

The 1 week-1 year time interval probes the \( P(E) \) barrier distribution only in the narrow range of 1.1-1.2 eV. In this range \( P(E) \) can be well approximated with a simple exponential \( P(E) \sim e^{(E_0-E)/\sigma} \).
Stretched exponential $N(t)$ unavoidably predicts:

$$t(\text{norm}) \sim t(\text{acc})^{(T(\text{acc})/T(\text{norm}))}, \ T(\text{acc})/T(\text{norm})=1.17$$

Consistent with stretched exponential behavior

Exponent $s = \text{ratio of temperatures } 350/300 = 1.17$

Delayed start modifies this relationship.
Related theories and stretched exponentials

De Wolf, Olibet, Ballif 2008: Reported stretched exponential. But:
(1) $\tau$ was increasing, (2) on short time scales, (3) via annealing.

(1) Our $\tau$ is decreasing, (2) on longer time scales, (3) during normal thermal degradation.

Stabler-Wronskii
Divacancies + nanovoids
Anomalous diffusion with distribution of time scales
Hydrogen collision
Stretched exp. in opposite direction
Anomalous diffusion with hierarchy of time scales:

Stabler, Wronskii 1977
Smets, Melskens 2000-2016
Street, Kakalios, Johnson 1993
Brantz 1999
de Wolf, Ballif 2008; Edholm Blomberg 2000;
Anderson, Palmer, Stein
1. Developed SolDeg platform to analyze defect dynamics over 24 orders of magnitude in time
2. In Si-only SHJs found that defect generation follows a stretched exponential scaling law of accelerated testing: \( t(\text{norm}) \sim t(\text{acc})^{(T(\text{acc})/T(\text{norm}))} \)
3. Developed Machine-Learning-based Si-H GAP potential for most accurate Molecular Dynamics simulation of c-Si/a-Si:H heterojunctions.
4. Reported experimental analysis: Neutral defect generation at interface drives degradation
5. Performed SolDeg simulation of c-Si/a-Si:H HJs to analyze neutral defect generation
6. H energy gradient drives H drift from HJ interface. This degrades the cell passivation
7. Computed N(t) with Soldeg energies & distributions: it was consistent with experimental data
   Key: H energy gradient at interface; Wide distribution of barrier energies
8. How to suppress degradation by H drift?
   a-Si layer: low density at interface, higher density away from interface: bilayer or gradient
   • Increases Voc by 10-15 mV
   • Reduces Voc degradation: 0.5 %/yr \( \rightarrow \) 0.1%/yr

SUMMARY

This talk, PVSC proceedings

ACS App. Mat. & Interfaces p. 32424 (2021)

arxiv 2106.02946; Phys. Rev. Mat., in press

submitted to SolMat

This talk, PVSC proceedings

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- Mariana Bertoni
  ASU

- Gabor Csanyi
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He is handsome too
THANK YOU