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

1. Degradation in Si-only heterojunctions
2. Development of a Machine-Learning trained Si-H interatomic potential
3. Experimental HJ degradation study
4. Degradation in c-Si/a-Si:H heterojunctions
5. Degradation in TOPCon cells

Supported by DOE SETO
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Aareschlucht

Lucerne
ITPRV: The two leading designs of the next generation: HJ and TOPCon

2023 edition of ITRPV

Today PERC dominates

By early 2030s, the share of TOPCon will reach 60%, and Heterojunction 20%

What factors will impact the relative acceptance of these leading designs:
- Efficiency
- Type of wafer
- Silver needs

We wish to assist this decision by shining the light on one more factor:
Degradation rates, mitigation possibilities
High HJ Degradation rates were reported

- Si Heterojunction cells hold Si world record efficiency of 26.7%
- Si HJ cells are a leading candidate for tandem bottom cells
- 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 close to 1.5-2% in terms of LCOE, based on the System Advisor Model

1. 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 with Machine-Learning (ML)-developed Si-Si potential: Gaussian Approximation Potential Si GAP. -- Timestep: femtoseconds

GAP reproduces DFT much better than other interatomic potentials.
2. Generate shocked clusters at the c-Si/a-Si interface with "cluster-blaster" as likely hosts of electronic defects. We created 1,500 blasted clusters.

3. Identify shocked clusters that actually host electronic defects: Inverse Participation Ratio (IPR) method. 500 of the clusters supported electronic defects.
**UC DAVIS**

**Connect Decades of Time Scales: Nudged Elastic Band Method**

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**

![Energy barrier distributions](image)
6. Use Kinetic Monte Carlo dynamics of thermally activated processes over barriers.

But simulation gets stuck in deep valleys. We accelerated simulation:
- Identify deep valleys (superbasins)
- Accelerate break out from valleys

**Accelerated Superbasin Kinetic Monte Carlo**

Integrate out fast degrees of freedom as in Renorm Group

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

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

\[
\beta = kT/E^*
\]

Data are well fitted by stretched exponential

**Why? Because** $P(E)$ can be fitted by $P(E)\sim\exp(-E/E^*)$
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:**
\[ t(\text{norm}) \sim t(\text{acc})^{(T(\text{acc})/T(\text{norm}))} \]

\[ 350K/300K = 1.17 \]

Fitting the simulation:
\[ t(\text{norm}) \sim t(\text{acc})^s \]
\[ s = 1.17 \]
Problem: no Machine Learning-based Si-H (GAP) potential

We developed the world’s first Si-H Machine Learning-trained GAP potential that delivers the highest precision.

Forces: Deviation from DFT substantially reduced
27 Rounds of ML-training Created Precise, Efficient Si-H GAP

1. Energies: reproduces DFT within 4 meV/atom
2. Accuracy of reproducing DFT forces improved by 35%.

3. Radial correlation function
4. Bond angle distribution function
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
3. 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**

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

**Characterization**

**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
Experimental specifics

Bertoni, Manzoor (ASU):

* Double-side polished float zone (FZ) quality n-type c-Si wafers with (100) crystal orientation, 2.5 Ωcm resistivity and starting thickness of ~275 μm. These wafers went through rigorous cleaning procedure, during which they were cleaned in Piranha (H₂SO₄:H₂O₂|4:1) and RCA-b (H₂O:HCl:H₂O₂|6:1:1) solutions. For thinning the wafers, they were etched for variable time in an HNA (HF: HNO₃:CH₃COOH|10:73:17) mixture, ending with a dip in a buffered oxide (HF:H₂O|10:1) etch solution. Four different thicknesses were achieved in the range of 160–260 μm.

* These wafers were symmetrically passivated by depositing 50 nm of a-Si:H(i) on both sides using plasma enhanced chemical vapor deposition (PECVD) technique in Octopus I tool from INDEOtec SA.

* Effective minority carrier lifetime measurements at temperatures between 30–230 °C were performed with WCT-120TS tool from Sinton Instruments, where measurements were taken as temperature decreased from 230 °C. Data were collected in transient mode owing to the high lifetime of samples.

* The deposited a-Si:H(i) films were characterized with Fourier transform infrared spectroscopy (FTIR) technique using Nicolet 6700 spectrometer from Thermo Electron to determine the microstructure and hydrogen content of the films. Moreover, M2000 ellipsometer from JA Woollam was employed to characterize the thickness, bandgap ($E_g$), refractive index and lack of crystallinity in a-Si:H(i) film. Ellipsometric spectra were collected at multiple incident angles of 65, 70 and 75 degrees in reflection mode. Resulting spectra were fitted with a single Tauc-Lorentz oscillator and yielded a $E_g$ of 1.68 eV.
1. Determine SRV at each $\Delta n$ from slope of $1/\tau_{\text{eff}} (1/W)$
2. Repeat for every $\Delta n$ for each $T$ to obtain SRV($\Delta n$, $T$)
3. Determine neutral interface defect density $N_s$ by fitting SRV($\Delta n$, $T$) at three values of $\Delta n$ with the amphoteric defect model of Olibet, Baliff et al.

$$\frac{1}{\tau_{\text{eff}}} = \frac{1}{\tau_{\text{aug}}} + \frac{1}{\tau_{\text{rad}}} + \frac{1}{\tau_{\text{SRH}}} + \frac{2\times \text{SRV}}{W}$$
Interface Defect Density $N(t)$ with Various Stressors

$N_s$ (cm$^{-2}$)

$Q_s(t) = -(1 \pm 0.3) \times 10^{11}$ cm$^{-2}$

Dark ambient
Light ambient
Light heated
Previous expt.

$Q_s(t)$ was approximately constant
4. Repeat SolDeg for c-Si/a-Si:H with Si-H GAP

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

Dominant dynamics:
H drifts away from interface

1. Movement of one H induced the collective motion of 10-20 atoms
2. We used the Inverse Participation Ratio (IPR) to verify that the H created a new dangling bond when it drifted away from the interface.
3. We verified that the dangling bond created a neutral defect
Why is hydrogen drifting? H energy exhibits a gradient across the interface. This creates the force that drives H atoms away from the interface.

We measured the hydrogen energy at 25,000 locations.
4 types of barriers control H dynamics

- **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 away:**
  - \( E(da) = 0.44 \text{ eV} \)
  - \( \sigma(da) = 0.18 \text{ eV} \)

- **drift return:**
  - \( E(dr) = 0.56 \text{ eV} \)
  - \( \sigma(dr) = 0.31 \text{ eV} \)

Energy barrier distributions of main processes
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><strong>This work</strong></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:
Barrier energies are widely distributed: collective dynamics
Hydrogen energy has a gradient
Coupled dynamics across barriers: Analytic solution, SolDeg averaged

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.

\[
\begin{align*}
\frac{\partial}{\partial t} N_1 &= -k_1 N_1 + k_2 N_2 \\
\frac{\partial}{\partial t} N_2 &= -k_2 N_2 - k_3 N_2 + k_1 N_1 \\
\frac{\partial}{\partial t} N_3 &= k_3 N_2 \\
N_1(t) &= N_0 e^{-\frac{\alpha t}{2}} \left( \cosh \left( \frac{\beta t}{2} \right) - \frac{k_1 - k_2 - k_3}{\beta} \sinh \left( \frac{\beta t}{2} \right) \right) \\
\alpha &= k_1 + k_2 + k_3 \\
\beta &= \sqrt{\alpha^2 - 4k_1 k_3}
\end{align*}
\]
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 – The six parameters are simulated, not fitted

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).
The impact of light on defect generation

How light impacts defect generation:
Photo-induced electrons, when localized at interface dangling bonds, modify the barriers of hydrogen drift. Intuition: the recapture barrier will be impacted the most, as the captured photo-electron enhances the barrier against recapture.
Photo-induced electrons increase defect generation, moderately

We modified the bond-breaking and the recapture barriers accordingly in our Three Barrier Model, and recalculated the $N(t)$ in the presence of light – shown with red line.

Our simulation results match the ASU data at long times - purple.

The majority of the defect generation is driven by thermal processes, not by light.
“In this work, we showed that, for well-optimized SHJ solar cells, light soaking treatment results in improved efficiency. However, this treatment can also cause degradation, e.g., when the (p) layer is too thin and exposed to light.”

The ASU data did not show such LS effect at long times and ambient T. But its stacks did not have a doped layer or ITO, both of which effected the LS results. (LS also may saturate? LS at higher T?)

We did observe the barriers that control H diffusion to be lowered by light. Maybe this helps H to diffuse to the interface and to increase passivation. This may be related to the observed Light Soaking enhancement.
Cause of H energy gradient? Si density gradient

Hydrogen energy gradient is in blue. -- 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. Again measured the H energy at 25,000 positions. Found that the H energy gradient has been changed into a minimum!
Bilayer adaptation of Reverse Si Gradient Improved Voc/Passivation

- Ru et al. Hanergy SolMat (2020): a-Si:H bilayer improved passivation
- Duan et al. Prog. in PV (2021): a-Si:H bilayer led to higher FF
- A. Smets et al. (2022): Increased Voc by 10 mV and efficiency by 0.6%
- Lee et al. ECS Solid State Lett.: (2014) Increased Voc by up to 25 mV

In our view, Voc was improved in these bilayer HJ cells because the degradation of Voc was suppressed from femtosec to the kilosec test times.
Trilayer Reversed Gradients started to appear in products in 2023

Meyer Burger as well
N(t) can be fitted with stretched exponential

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

![Stretched Exponential Fit to Three Barrier Model and DA Sample](image)
5. SolDeg analysis of TOPCon cells: Passivation is Sensitive to H

The excellent performance of TOPCon comes from the SiOx/poly-Si contacts providing excellent passivation, good carrier selectivity, and low contact resistance via the highly doped poly-Si. But passivation is sensitive to temperature of fabrication.

Passivation is also sensitive to hydrogen. The recombination parameter J0 decreases up to an optimal H concentration, but increases for higher H concentrations. Dynamics of passivation needs to be analyzed to optimize TOPCon cell performance.


Kang et al. ACS Appl. Mater. Interfaces (2021)
TOPCon cells use SiOx/poly-Si passivating contact.
SiOx layer thickness ~1.6 nm (POLO 2 nm)
The primary transport across insulating SiOx is quantum tunneling. An Ohmic contribution was also reported and attributed to pinholes in the SiOx.
A pinhole is a Si-rich region that partially or completely pierces through the SiOx resulting in unpassivated surface states and thus enhances recombination.

Proposed Driver of Pinhole Nucleation: Phase Separation of SiO\textsubscript{x}

The SiO\textsubscript{x} layer is non-stoichiometric for x<2. Non-stoichiometric compounds:
At higher T: Homogeneous mixed phase.
At lower T: Phase separation by minority phase nucleating in majority phase. -> Spinodal decomposition

Upon crossing the phase separation line (solid) from the homogeneous phase, the free energy of SiO\textsubscript{x} is lowered by stoichiometric Si bubbles/pinholes nucleating within a background that evolves towards stoichiometric SiO\textsubscript{2}. The nucleation is controlled by barriers.
To simulate the thermal stress of the firing process, TOPCon cells (stacks) were formed with a c-Si wafer and a 1.6 nm SiOx layer on top; x ~ 1.6-1.8.

The periodic boundary conditions provided a structure consistent to c-Si/SiOx/poly-Si.

Stacks were heated to temperatures ~1500 °C, followed by a quench back down to 25 °C.

All Simulations were performed using the LAMMPS molecular dynamics simulator, with the ReaxFF developed for simulating c-Si/SiO2 interface [1].

The results of our TOPCon firing simulations clearly show that pinholes form via nucleated phase separation.

Temperature of 1500 °C, above representative values. Top view:

Sideview of the evolution of iso-surface surrounding the x < 0.5 volume in our simulations.
Using our initial structures we added hydrogen in various concentrations, $1.4 \times 10^{14} - 2.5 \times 10^{15} \text{cm}^{-2}$ average areal density.

Stacks were heated to fabrication-realistic lower temperatures between 700 $^\circ$C-1300 $^\circ$C, followed by quenching back to 25 $^\circ$C.

The simulation showed distinct regimes for low, $[\text{H}] < 4 \times 10^{14} \text{cm}^{-2}$, and high $[\text{H}] > 4 \times 10^{14} \text{cm}^{-2}$ concentrations of hydrogen.

low $[\text{H}] < 4 \times 10^{14} \text{cm}^{-2}$

Si-Red, O-Blue and H-Yellow.
At low [H], < $4 \times 10^{14} cm^{-2}$, hydrogen migrates to the interface, passivates the Si dangling bonds and relaxes the strained bonds. No pinholes formed during the representative simulation time.

At low [H] the density of interface Si dangling bonds (DB) decreases with increasing [H]

(These dangling bonds are consistent with the known Pb0 defects)

The total number of strained bonds is large, thus we find that ideal passivation requires [H] >> DB
At high [H], > $4 \times 10^{14} \text{cm}^{-2}$, the interface region becomes saturated, and a significant concentration of H remained within the SiO$_x$ layer. H in the bulk SiO$_x$ layer primarily resides in bond center configurations. We observed extensive pinhole formation.

The addition of hydrogen changed the competing terms in the free energy of the system. Hydrogen lowered the energy of the phase separated configuration.

For SiO$_x$ layers that did not support pinhole formation, the addition of sufficient amount of H drove the SiO$_x$ layer across the binodal line and nucleated pinhole formation.

Simulated firing with [H] = 0

Simulated firing with [H] = $1.2 \times 10^{15} \text{cm}^{-2}$
High [H] Regime – Hydrogen Induces Nucleation of Pinholes

At high [H], $> 4 \times 10^{14} \text{cm}^{-2}$, the interface region becomes saturated, and a significant concentration of H remained within the SiOx layer. H in the bulk SiOx layer primarily resides in bond center configurations. We observed extensive pinhole formation.

The addition of hydrogen changed the competing terms in the free energy of the system. Hydrogen lowered the energy of the phase separated configuration.

For SiOx layers that did not support pinhole formation, the addition of sufficient amount of H drove the SiOx layer across the binodal line and nucleated pinhole formation.
Nucleation is driven by H shifting balance of competing energy terms

The nucleation energy barrier barely changes as [H] grows from $3 \times 10^{12}$ cm$^{-2}$ to $3 \times 10^{14}$ cm$^{-2}$, but once it exceeded $3.6 \times 10^{14}$ cm$^{-2}$, the barrier rapidly decreased as [H] approached $1 \times 10^{15}$ cm$^{-2}$.

$$\Delta F = [NF_{Si} + (N_{0} - N)F_{SiO2}] + \sigma N^{2/3} - N_{0} F_{SiOx} =$$

$$= \text{const.} - [F_{SiO2} - F_{Si}]N + \sigma N^{2/3}$$

energy of pinhole surface
Hydrogen Induced Pinhole Nucleation

High [H] lowers the nucleation barrier of pinholes.

\[ [H] < 4 \times 10^{14} \text{ cm}^{-2} \] pinholes did not form within the timeframe of the simulation.

\[ [H] > 4 \times 10^{14} \text{ cm}^{-2} \] pinholes did form.

At higher [H] pinholes form faster.

Pinhole formation rate as a function of [H] for pinholes within simulation timeframe.
At high $[H]$, $H$ induces nucleation of pinholes that act as recombination centers at the c-Si interface.

At low $[H]$, hydrogen increasingly passivates dangling bonds at the interface.
Kang et al. reported that upon extracting H by N2 annealing at high [H], they could lower J0.
In our theory, pinhole formation is the consequence of SiOx being driven across the binodal line by adding H. In this picture, subsequent removal of H drives the system back across the line. This makes pinhole formation energetically unfavorable and dissolves the pinholes.
Predicting Electronic Defects from Structural Info by Machine Learning

DFT is much slower and computer intensive than Molecular Dynamics (MD) that is used for Structural Simulations.

<table>
<thead>
<tr>
<th>Training/validation accuracy</th>
<th>cSi</th>
<th>cSi/aSi</th>
<th>cSi/aSi:H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond lengths only</td>
<td>68%/68%</td>
<td>61%/61%</td>
<td>60%/60%</td>
</tr>
<tr>
<td>3-body angles only</td>
<td>97%/94%</td>
<td>85%/78%</td>
<td>77%/77%</td>
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<tr>
<td>Bond lengths + subset of 3-body angles</td>
<td>98%/95%</td>
<td>75%/75%</td>
<td>76%/76%</td>
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<tr>
<td>Bond lengths + 3-body angles</td>
<td>98%/97%</td>
<td>90%/81%</td>
<td>78%/78%</td>
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<tr>
<td>Bond lengths + 3-body angles + 4-body angles</td>
<td>99%/97%</td>
<td>93%/83%</td>
<td>80%/78%</td>
</tr>
</tbody>
</table>

We ML-trained algorithms on cSi; cSi/aSi interfaces; and cSi/aSi:H structures to find electronic defects. We achieved 78%-97% accuracy to predict quantum electronic defect properties from structural info alone.
1. Developed **SolDeg** platform to analyze defect dynamics over 24 orders of magnitude in time

2. For Heterojunction cells, developed 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: Degradation is driven by neutral defect generation at interface

5. **SolDeg**-simulated defect generation was remarkably consistent with experiments

6. **SolDeg**: H drift from interface causes degradation. **Proposed Reverse Si Density Gradient to suppress** $V_{oc}$ degradation from 0.5%/yr to 0.1%/yr. This also increases $V_{oc}$ by 10-15 mV

7. **SolDeg** modelled TOPCon passivation dynamics:
   - low [H]: interface passivation lowers recombination
   - high [H]: induces nucleation of pinholes that increase recombination
   - passivation can be optimized by well-chosen hydrogen concentration

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ACS App. Mat. & Interfaces p. 32424 (2021)
Phys. Rev. Mat. 6, 065603 (2022)
Nature Comm. Mat. /doi.org/10.1038/s43246-023-00347-6 (2023)
TOPCon: submitted
THANK YOU