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

Davis Unruh (UCD – Argonne)
Reza Vatan (ASU)
Zitong Zhao (UCD)
Salman Manzoor (ASU)
Andrew Diggs (UCD)
Mariana Bertoni (ASU)
Stephen Goodnick (ASU)
Gabor Csanyi (Cambridge, UK)
Gergely Zimanyi (UCD)

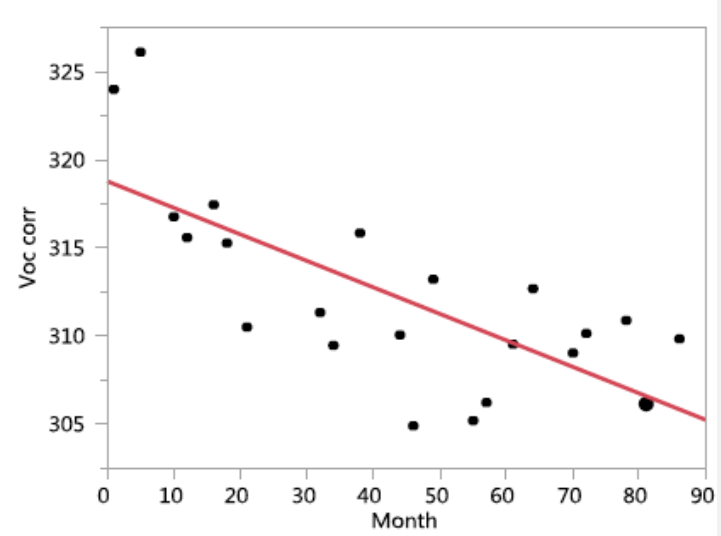
Supported by DOE SETO

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

Possible driver? Defects at interface! Bertoni Phys. Stat. Sol. 2018

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

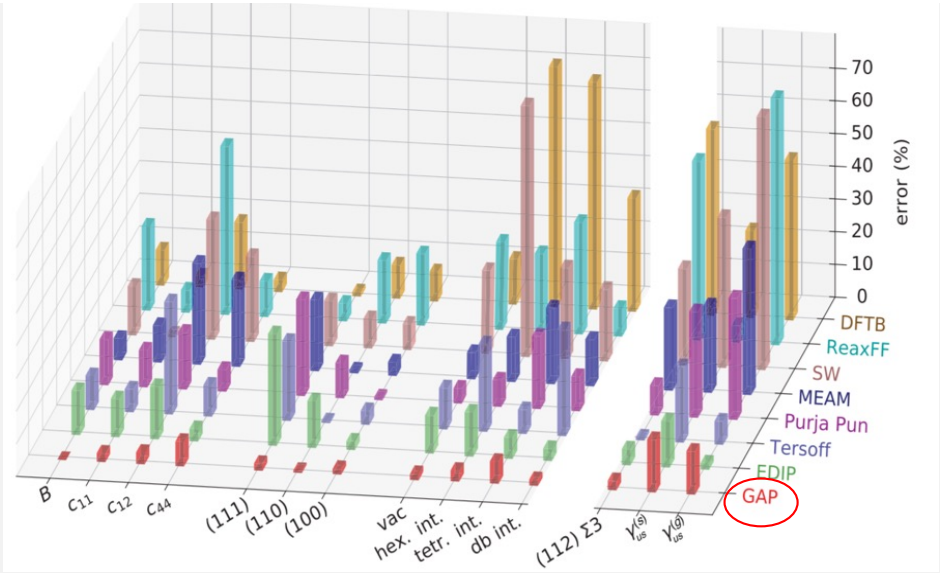
5. Determine the distribution of these barriers

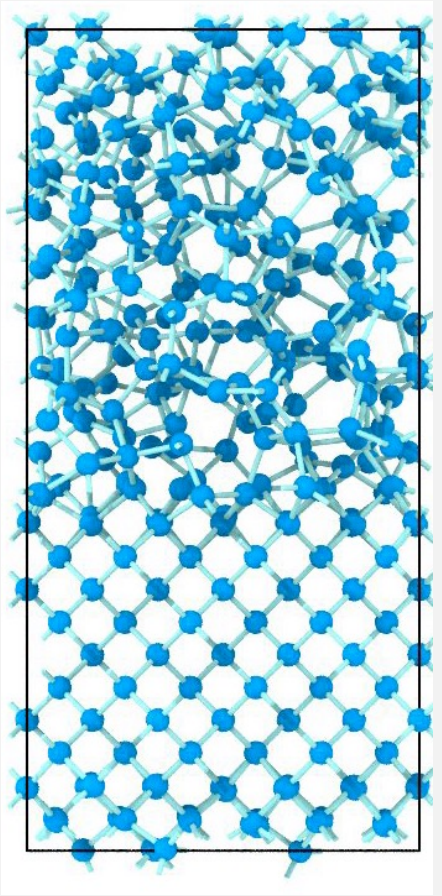
6. Determine the defect generation dynamics from the energy barrier distribution

Si-only HJs: Precise structures by Machine Learning-trained Potentials

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.



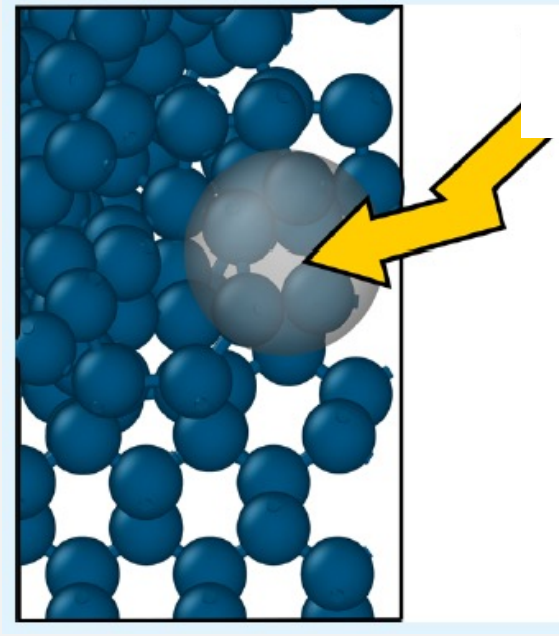


Typically 432 Si atoms

Secret Weapon SW1

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



We created 1,500 blasted clusters

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

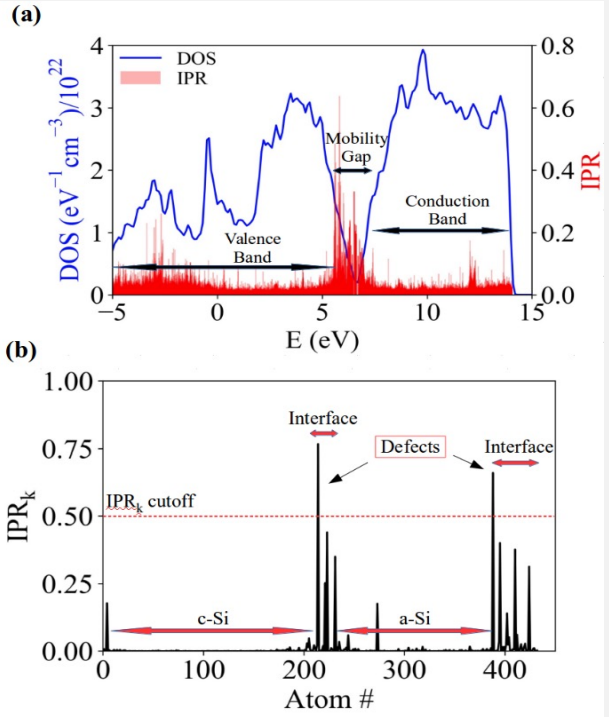
$$IPR_n = \frac{\sum_{i=1}^{I} a_{ni}^4}{(\sum_{i=1}^{I} a_{ni}^2)^2}$$

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

SW2

500 blasted clusters supported electronic defects

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



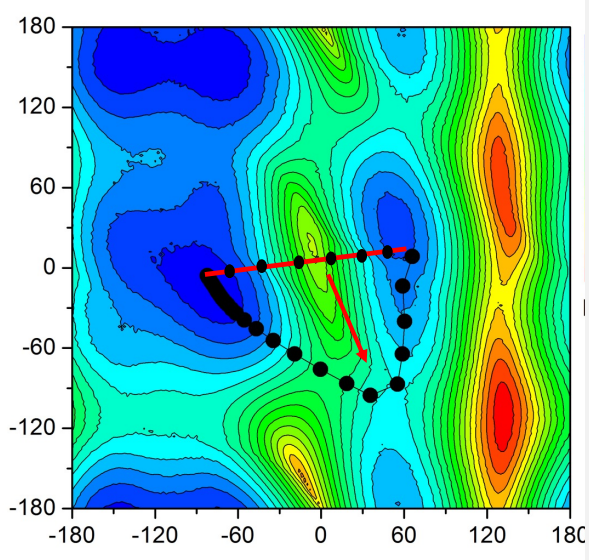
(a) IPR as a function of energy, (b) IPR as a function of z-depth

Connect decades of time scales: Nudged Elastic Band method

4. Determine energy barriers that control the generation of the electronic defects:

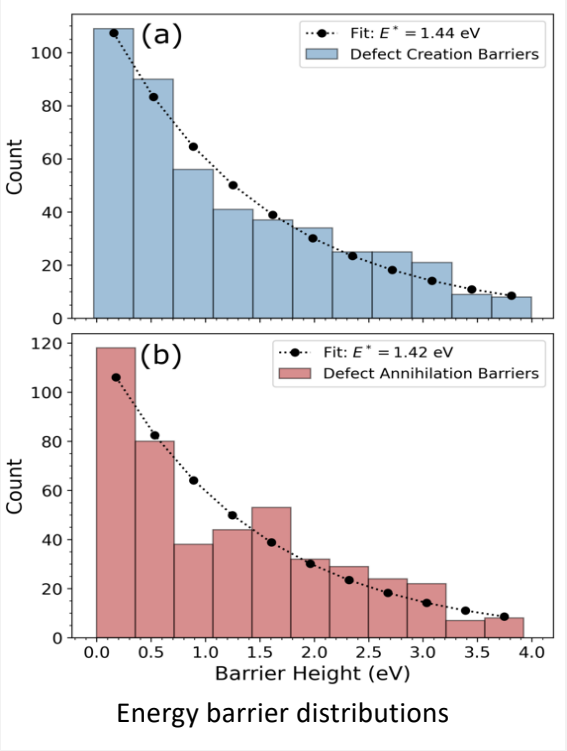
Nudged Elastic Band method

Start with a path that connects initial and final state over barrier, then nudge it. The relaxing band finds lowest energy barrier/saddlepoint.



SW3

5. Determine the barrier distribution for 500 barriers



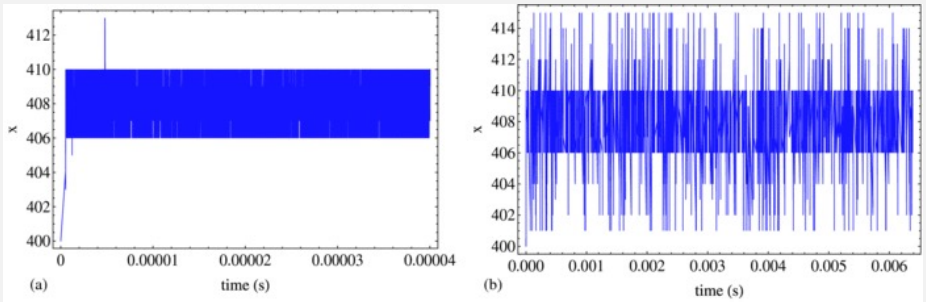
Energy barrier distributions

Determine and Analyze Dynamics of Defect Generation

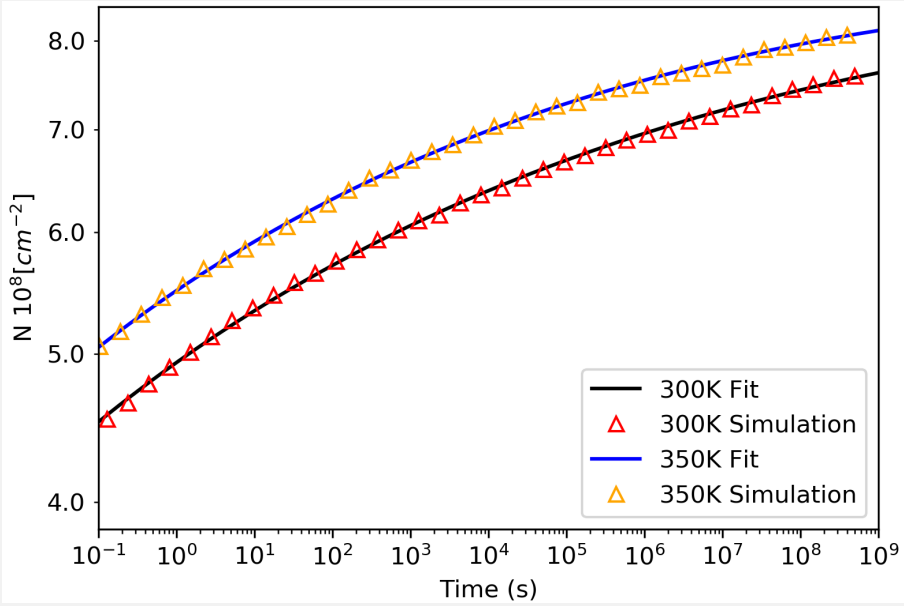
6. Use Kinetic Monte Carlo dynamics of thermally activated processes over barriers. But simulation gets stuck in deep valleys. We accelerated simulation: 1. Identify deep valleys ("superbasins"); 2. Help simulation to break free from them.

Accelerated Superbasin Kinetic Monte Carlo

Integrate out fast degrees of freedom as in Renorm Group



SW4



τ_0(ps) exp $^{(1.3eV/300K)}$ ~ 10^9sec (gigasec)=30 years

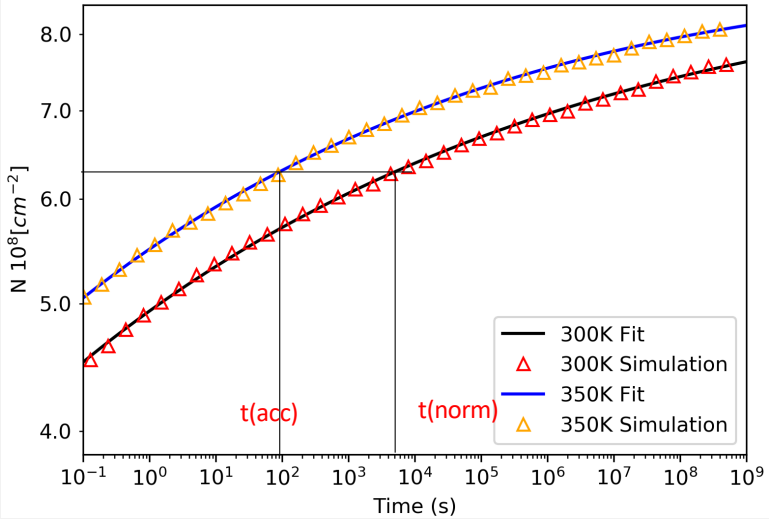
$$N(t) = N_{sat}(1 - \exp[-(t/\tau_0)^{\beta}])$$

β =kT/E*

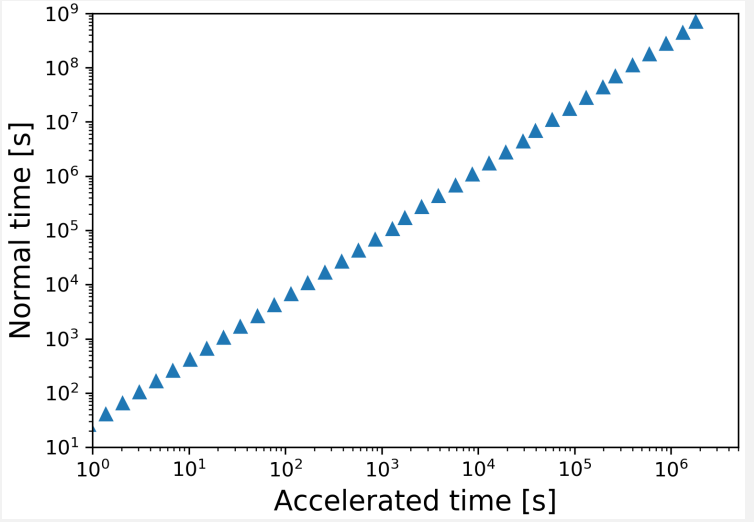
Data are well fitted by stretched exponential
Why? Because P(E) can be fitted by P(E)~exp(-E/E*)

Time correspondence curve for accelerated testing

Accelerated testing at elevated temperature:
Construct Time correspondence curve
N(T=350K,tacc)=N(T=300K,tnorm)



Stretched exponential analytically predicts:
$t(norm) \sim t(acc)^{(T(acc)/T(norm)}$
350K/300K=1.17

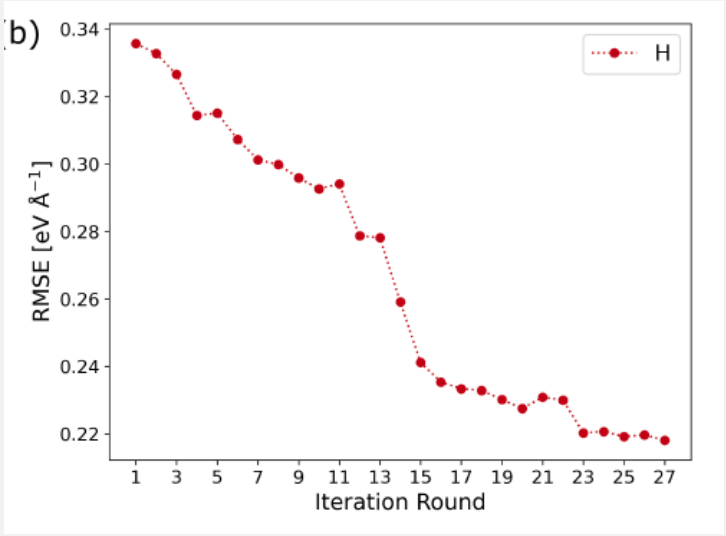


Fitting the simulation: $t(norm) \sim t(acc)^s$
s = 1.17

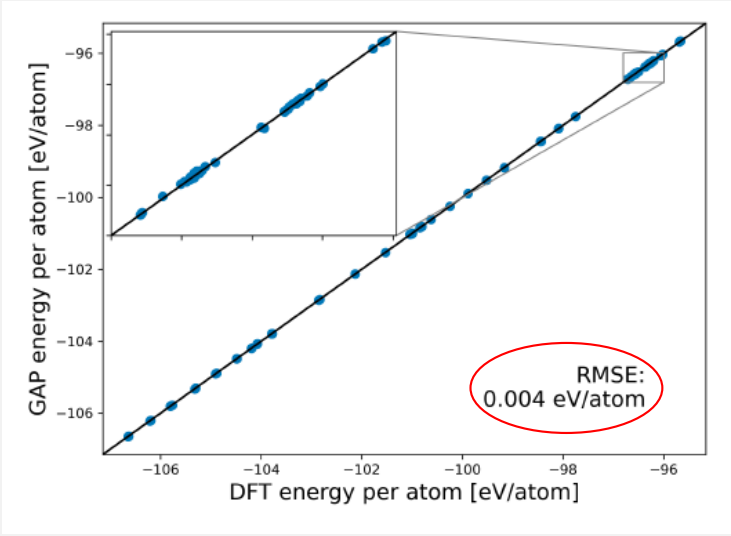
II. SolDeg for c-Si/a-Si:H: High precision needs Machine-Learning trained Si-H GAP

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

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



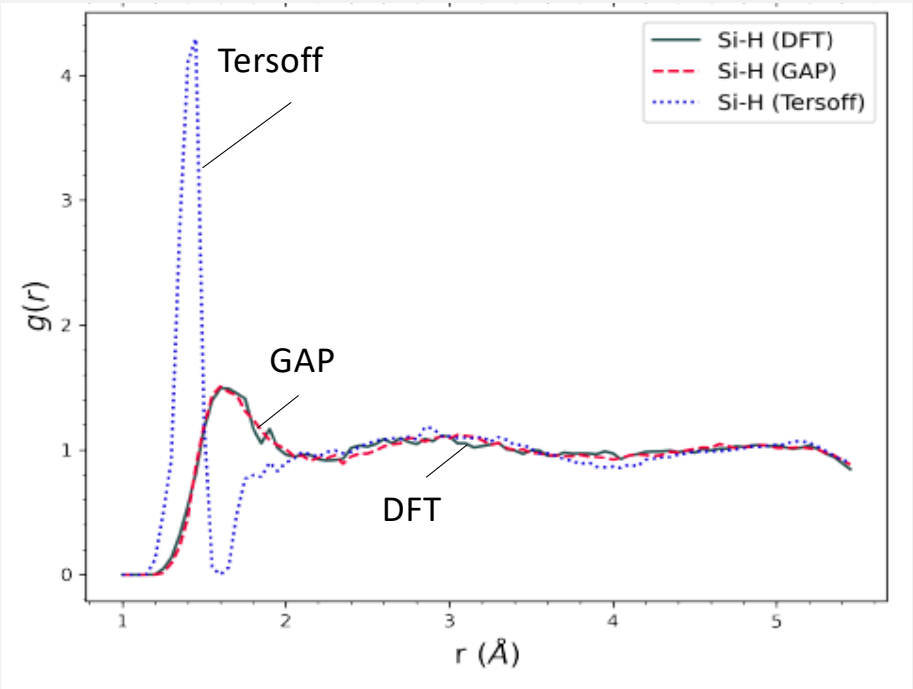
Forces: Deviation from DFT substantially reduced



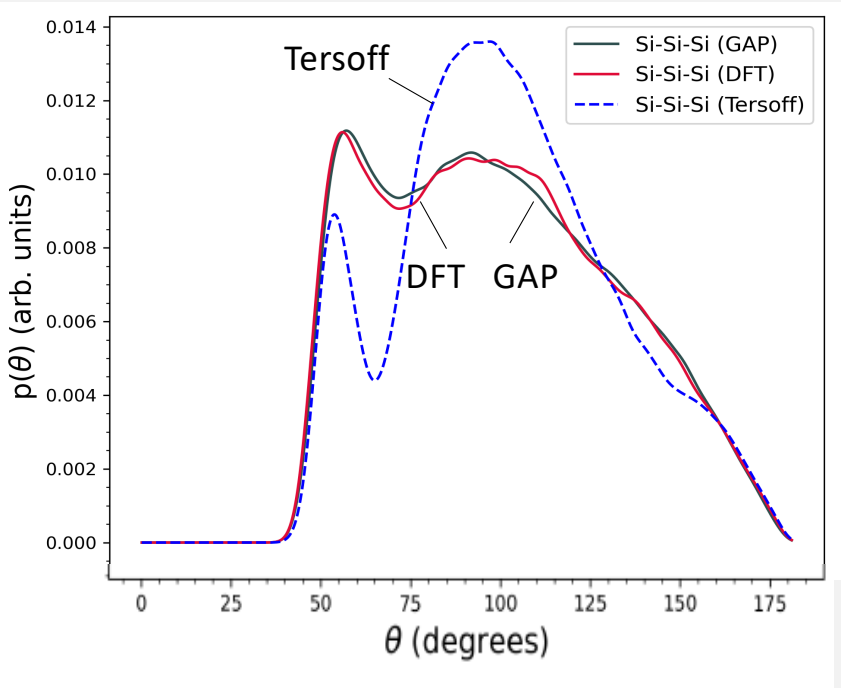
Energies: reproduces DFT within 4 meV/atom

Machine-Learning based Si-H GAP: Validation, comparison

Radial correlation function – liquid Si:H



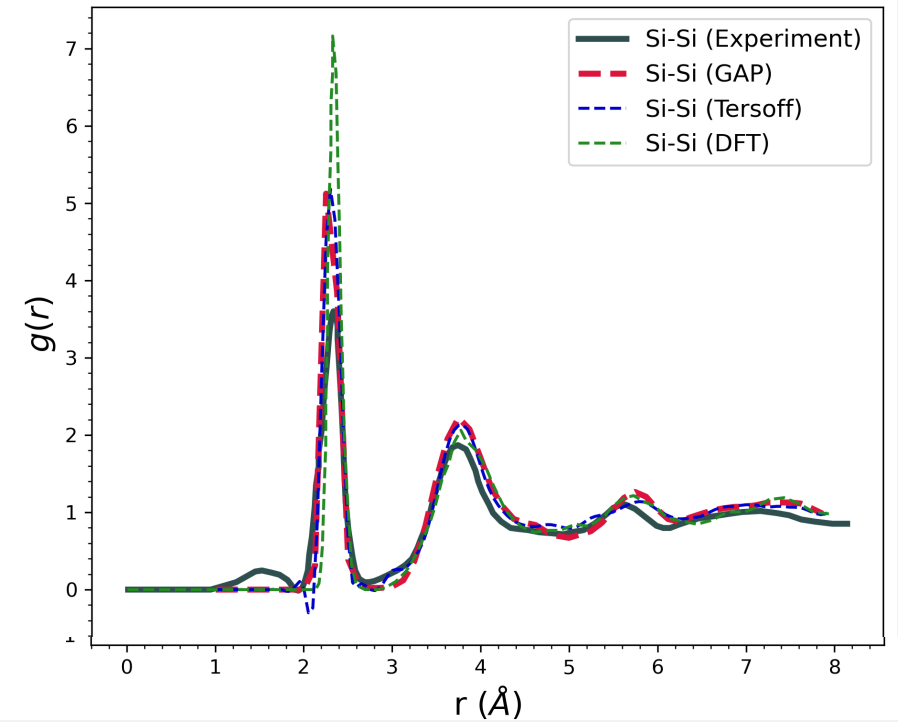
Bond angle distribution function – liquid Si-H



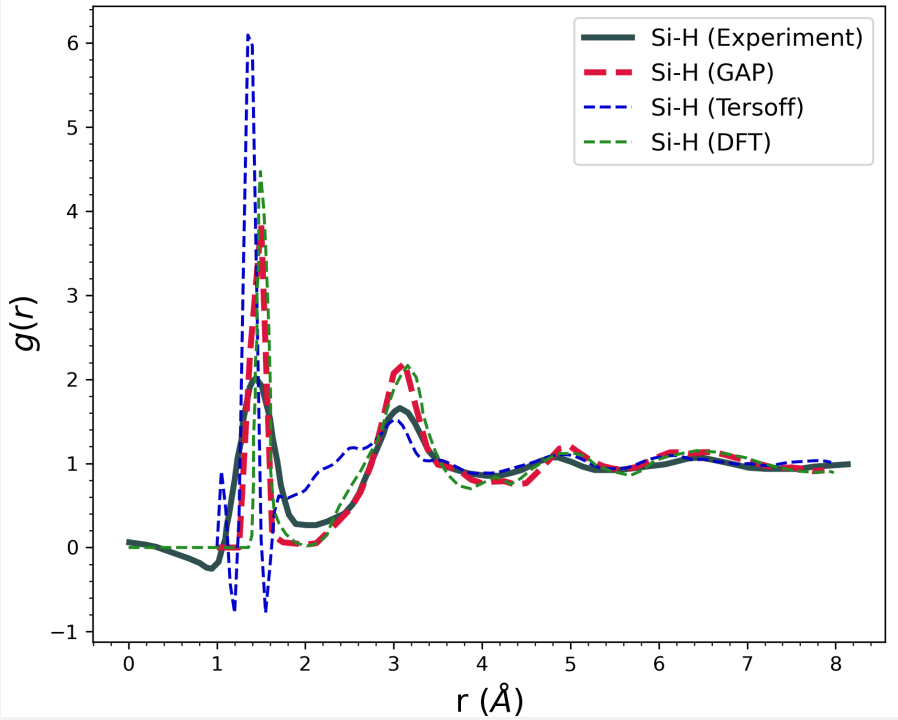
Our Si-H GAP reproduces DFT correlator qualitatively better than Tersoff

Machine-Learning based Si-H GAP: Validation, comparison

Si-Si radial correlation function in a-Si



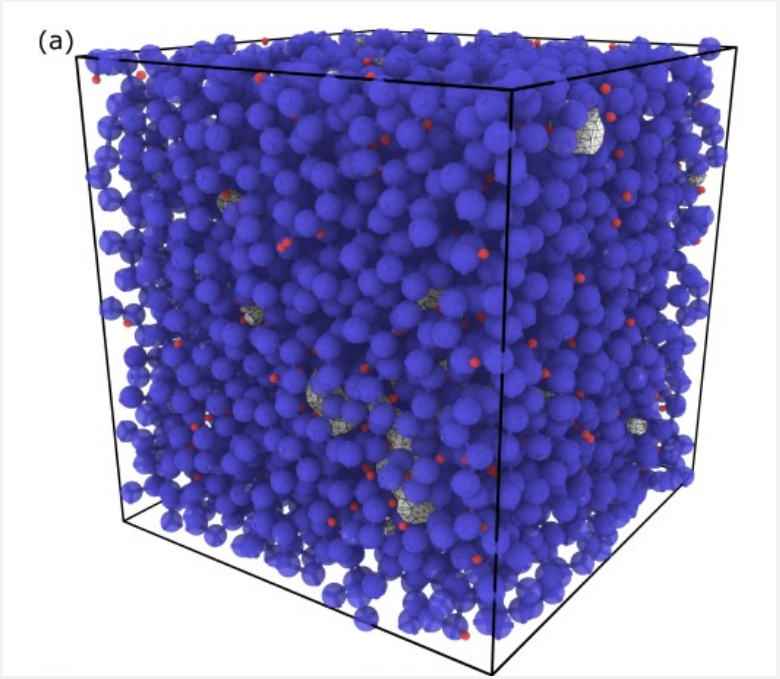
Si-H radial correlation function in a-Si

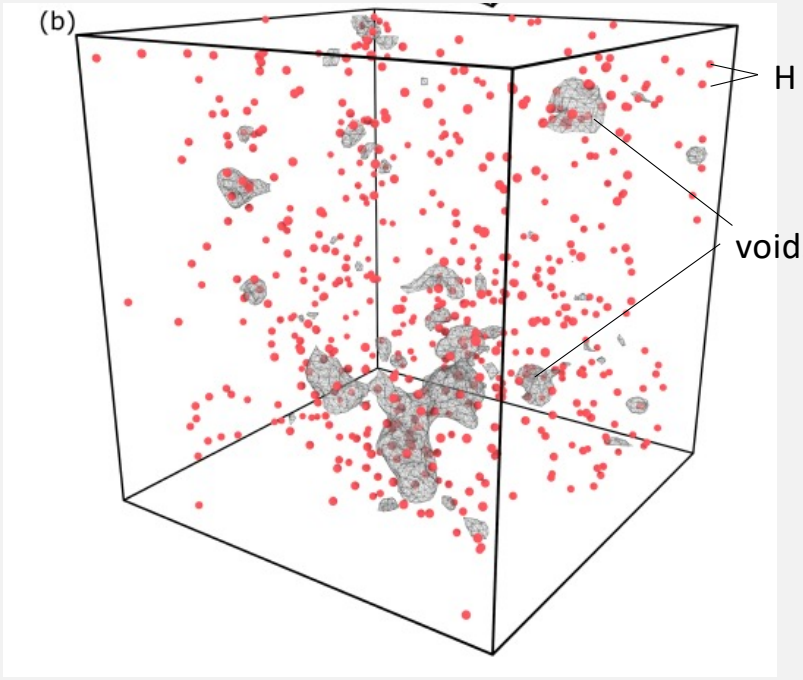


Our Si-H GAP is closer to experiments than DFT or Tersoff

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





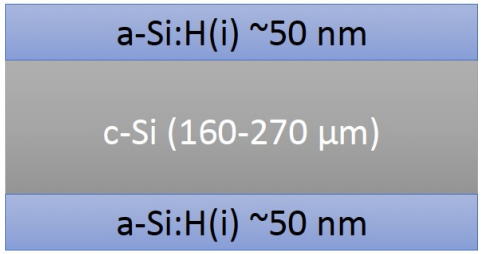
SW5

Si:H GAP Molecular Dynamics simulations can reach unparalleled sizes and number of realizations

III. Experimental analysis of SHJ degradation: samples, stressors

Bertoni, Manzoor (ASU)

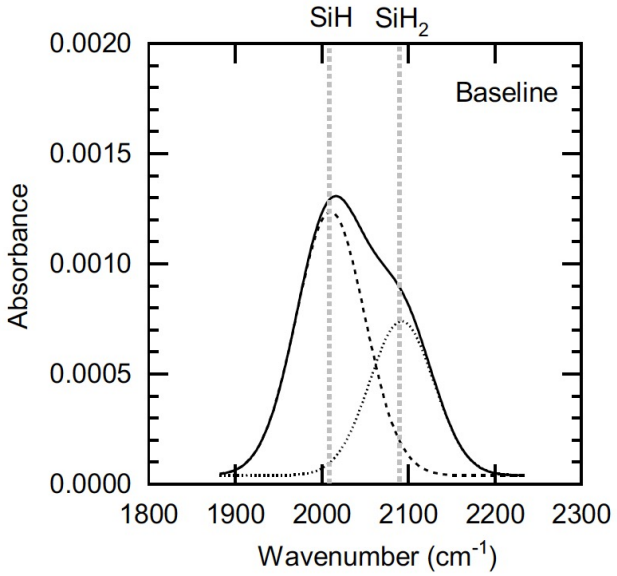
Samples



Deposition Conditions

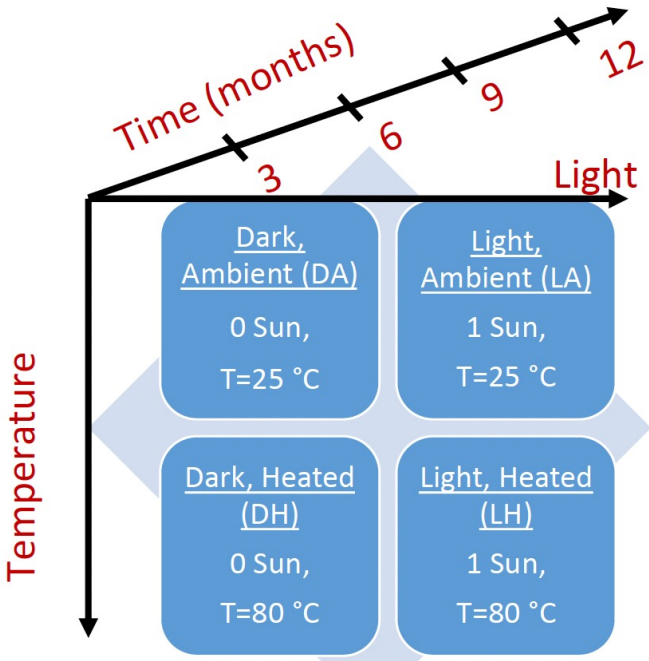
Name	Value
Frequency	13.56 MHz
Pressure	3.2 Torr
Power	200 W
H_2	200 sccm
SiH_4	40 sccm
Temperature	220 °C
Deposition rate	0.5 nm/sec

Characterization

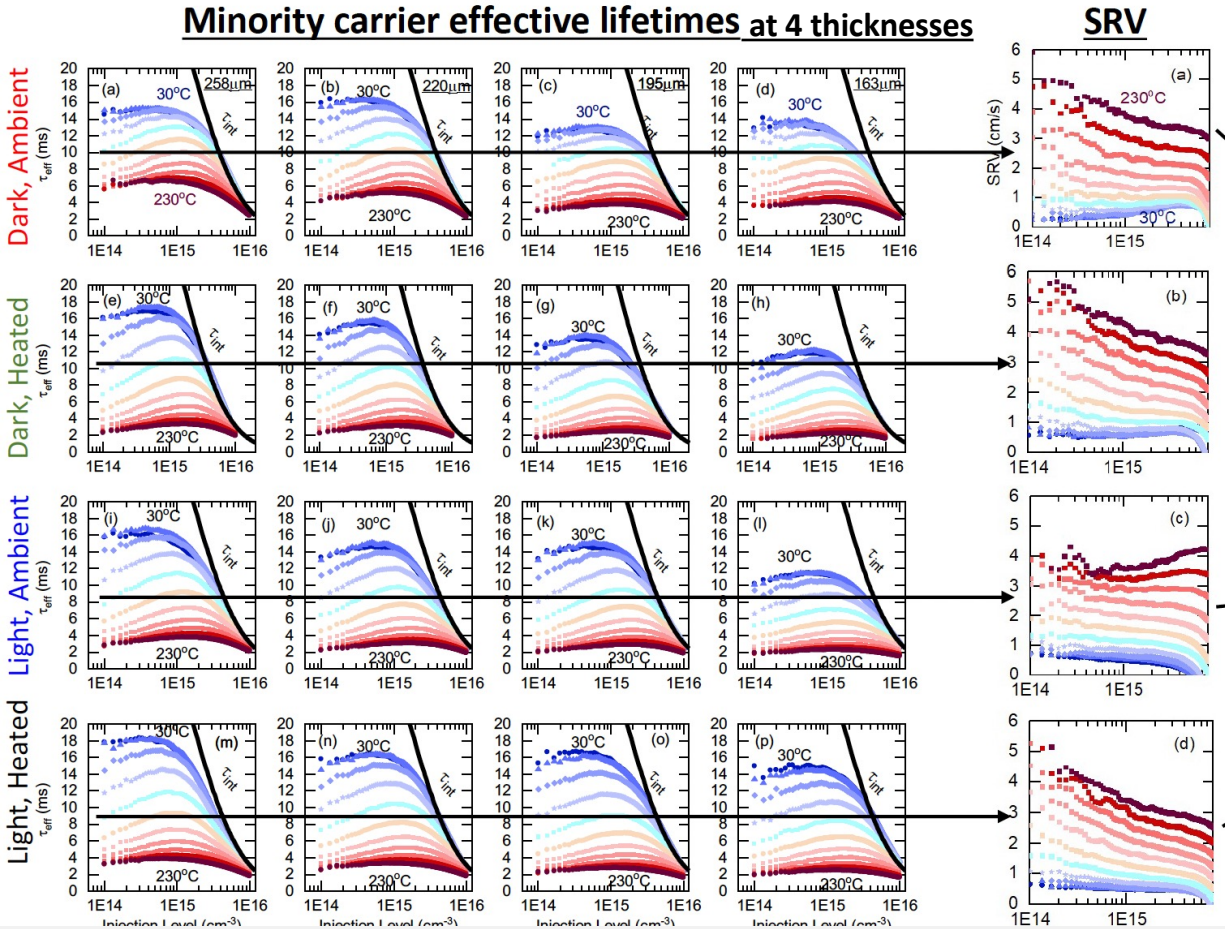


Bandgap	H conc.	ρ (g/cm^3)	E_u (meV)
1.68 eV	15 at.%	2.25	48

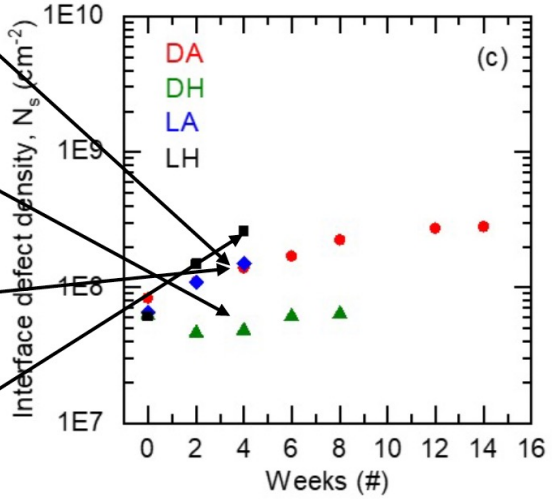
Ageing conditions



Data collection, processing



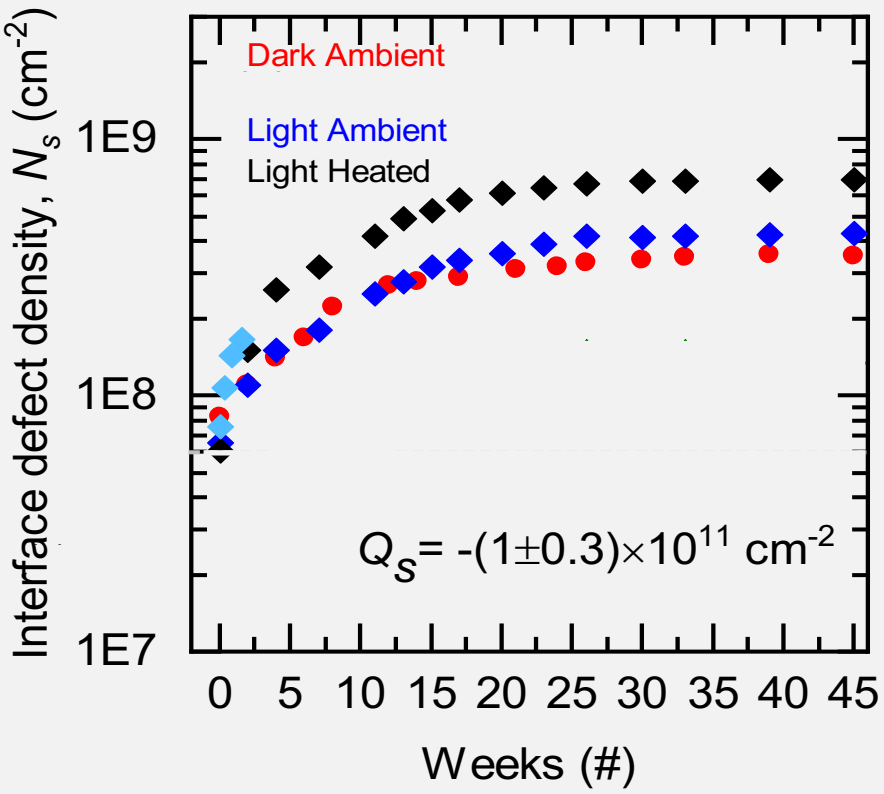
$$\frac{1}{\tau_{eff}} = \left(\frac{1}{\tau_{rad}} + \frac{1}{\tau_{aug}} + \frac{1}{\tau_{SRH}}\right) + \frac{2 \times SRV}{W}$$



III. Experimental analysis of SHJ degradation

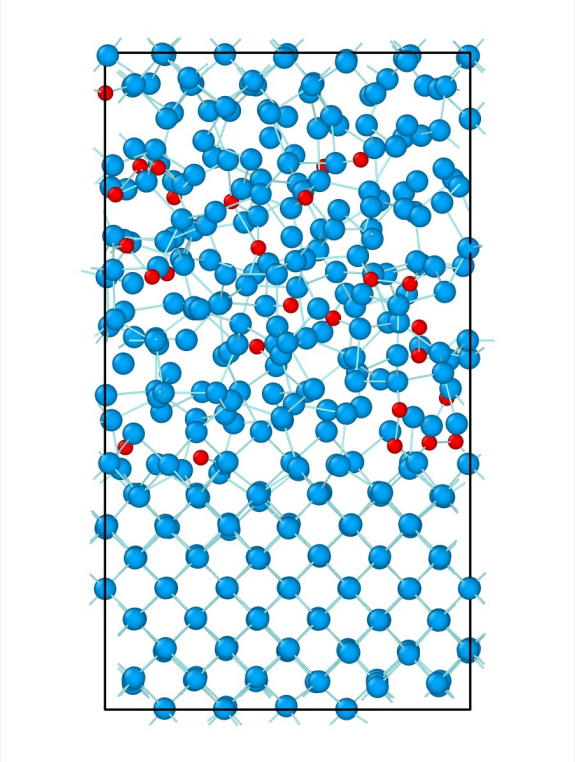
$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{aug}} + \frac{1}{\tau_{rad}} + \frac{1}{\tau_{SRH}} + \frac{2\times SRV}{W}$$

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

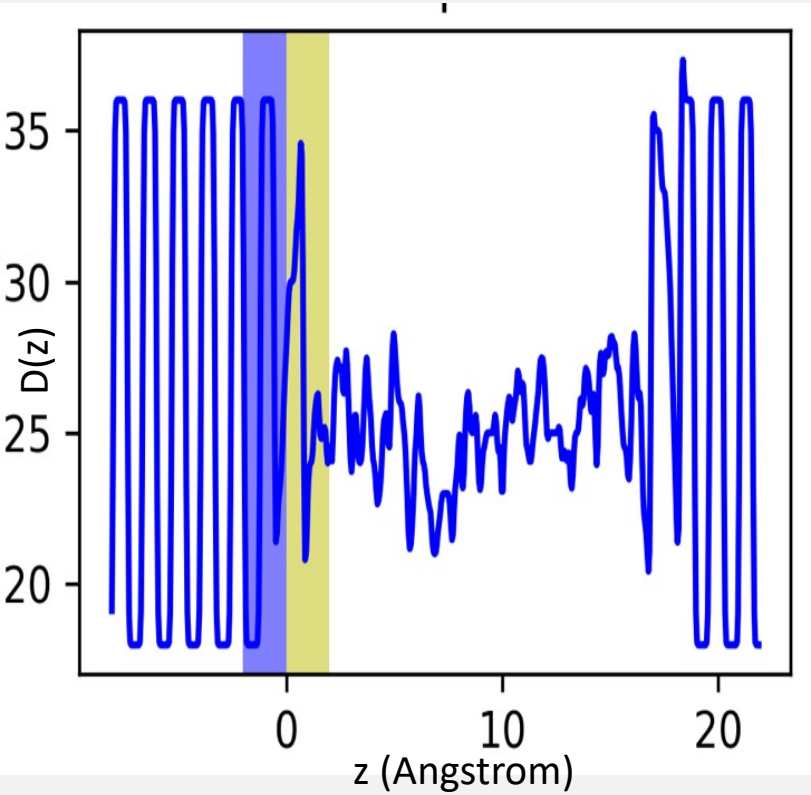


IV. Repeat SolDeg for c-Si/a-Si:H with Si-H GAP

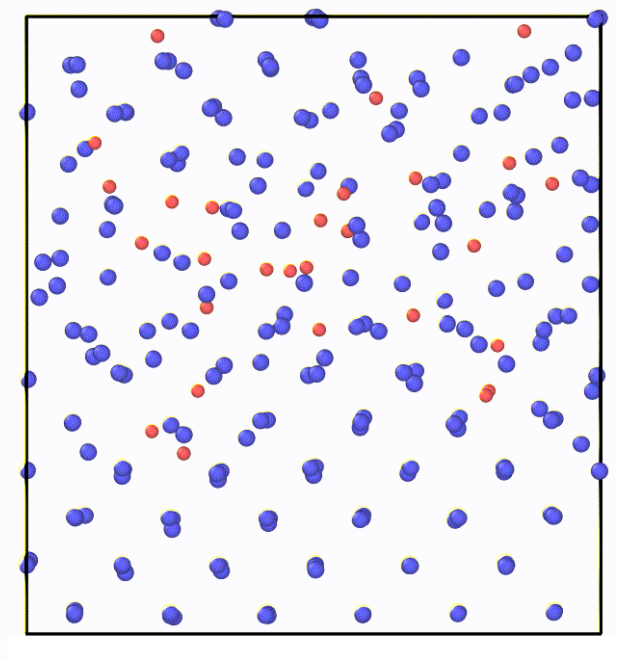
Created 60 c-Si/a-Si:H stacks.
H content: 12%, 15%



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

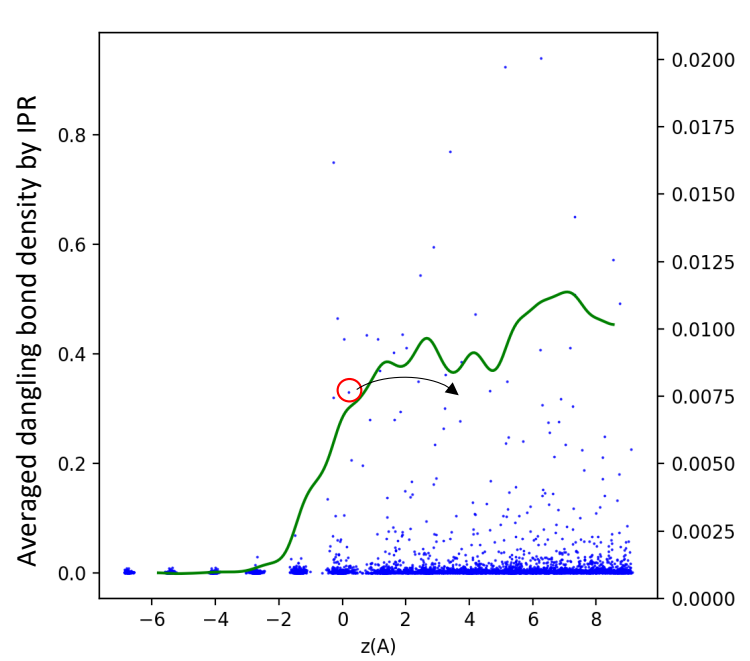


Observe: Defects are generated by hydrogen drifting from interface



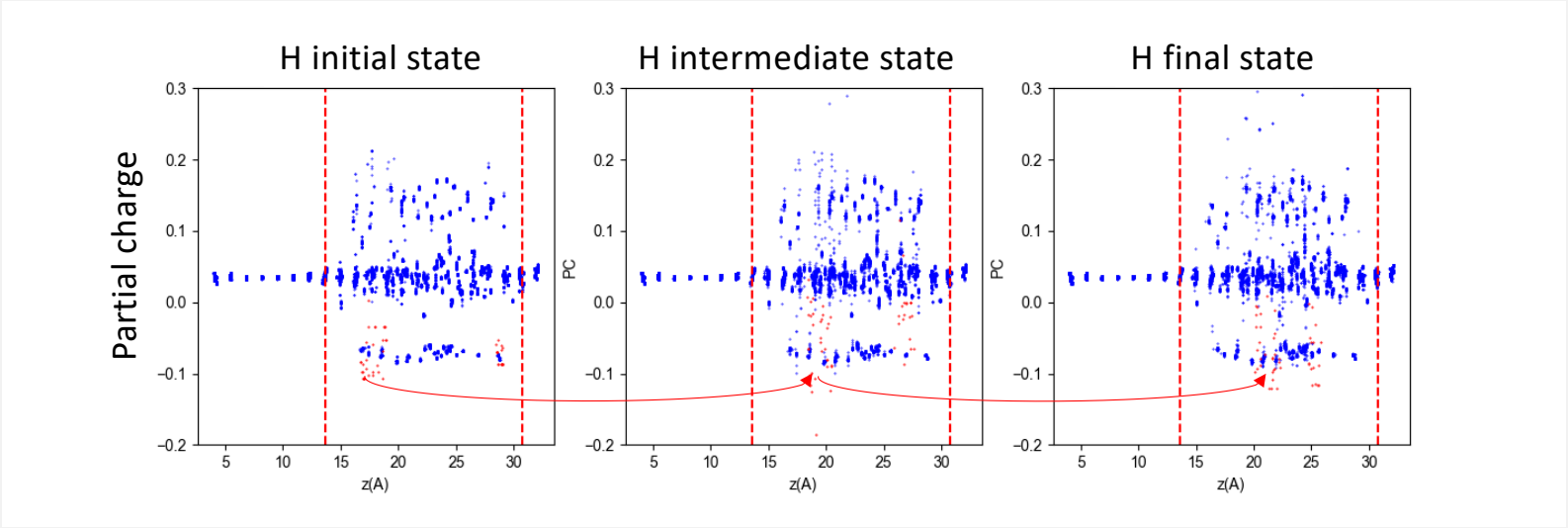
Movement of one H induces the collective motion of 10-20 atoms

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"

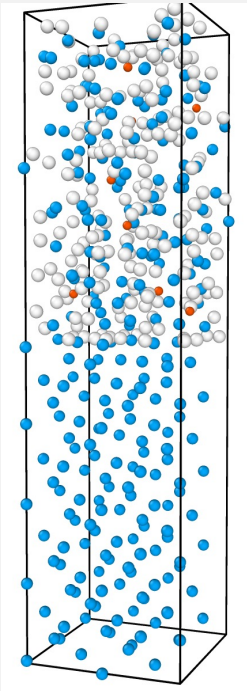
As H drifts, with DFT we track partial charge of all ~500 atoms: Si-blue, H-red
Partial charges remain in -0.2…+0.2 range: generated defects are approximately neutral

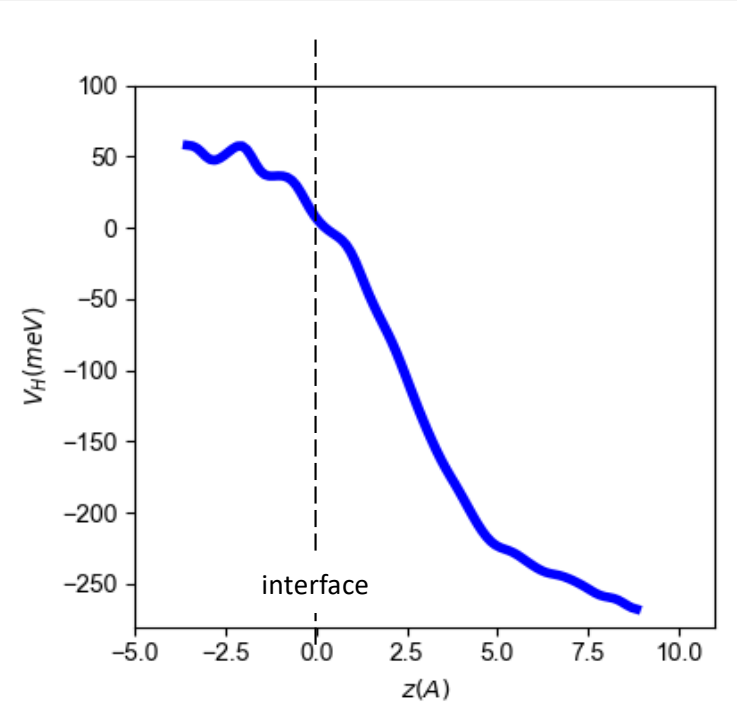


Why is hydrogen drifting? H energy is measured to exhibit gradient

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

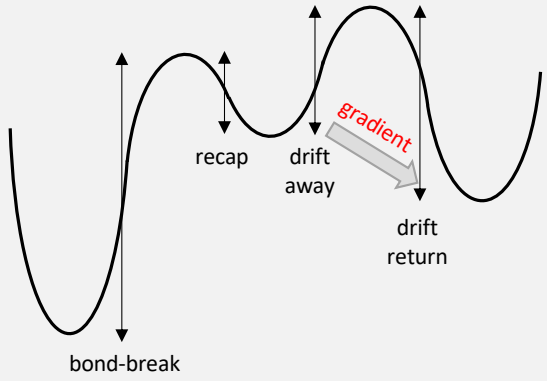
The hydrogen energy exhibits a gradient across interface
This creates a force that drives H atoms away from interface

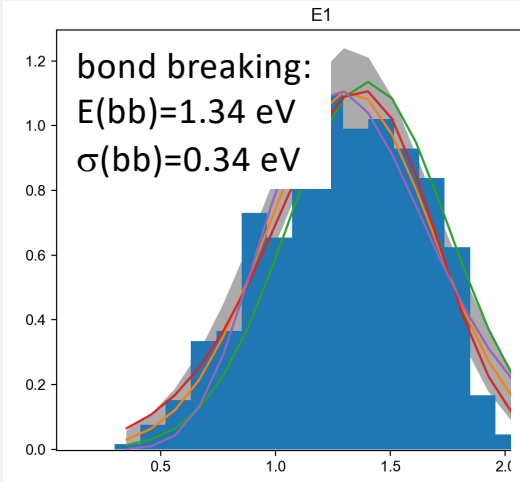


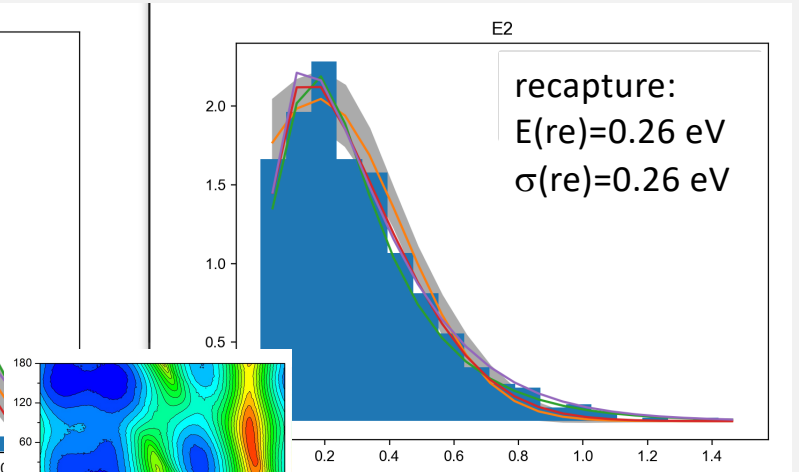


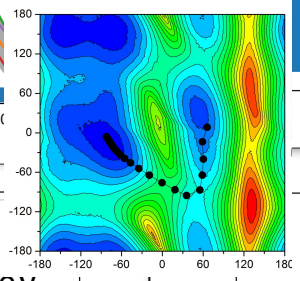
hydrogen energy

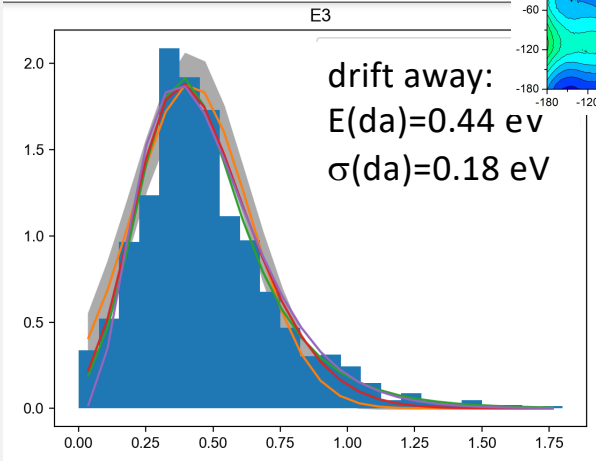
Energy barrier distributions of main processes

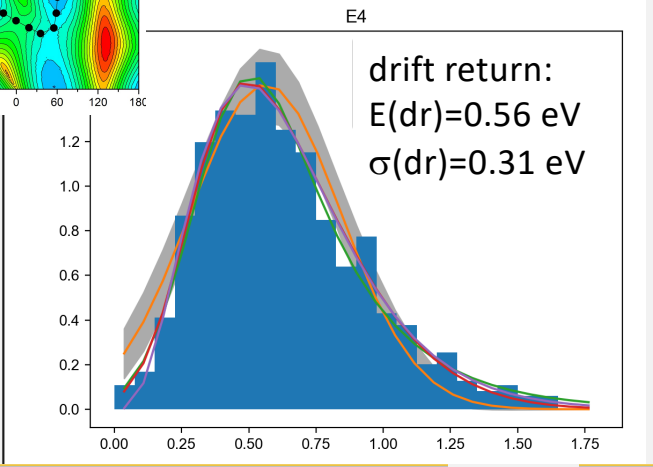










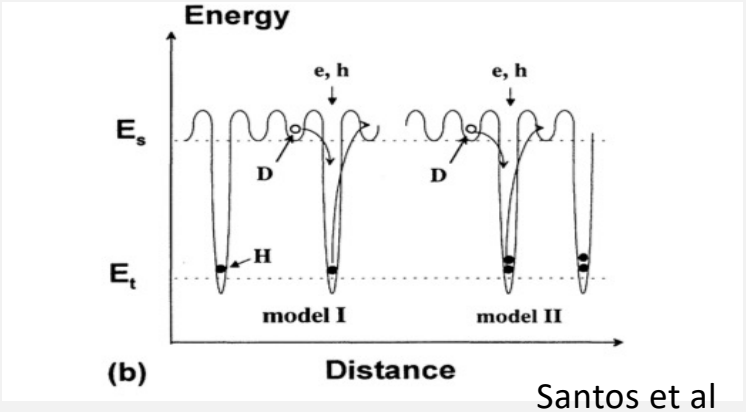


Novelty: Distributions from collective dynamics; H energy gradient

Matching up with previous work

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

Novelty:
Distribution of barrier energies from collective dynamics
Hydrogen energy gradient

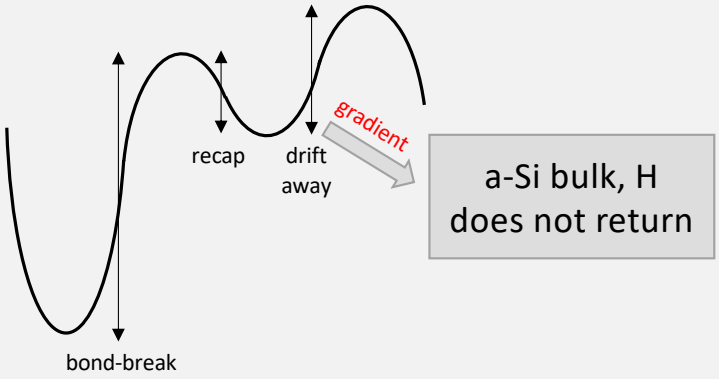


Santos et al

TABLE I. Parameters used in the simulations.

Parameter	Description	Model I
$C_H + C_D$	Total H+D density	7×10^{21} cm^{-3}
$E_m - E_s$	Shallow trap depth	0.5 eV
N_s	Maximum shallow trap density	1×10^{23} cm^{-3}
$E_m - E_t$	Deep trap depth	1.3 eV

Gradient allows simplifying model to three barriers



a-Si bulk, H does not return

$$\frac{\partial}{\partial t}N_1 = -k_1 N_1 + k_2 N_2$$
$$\frac{\partial}{\partial t}N_2 = -k_2 N_2 - k_3 N_2 + k_1 N_1$$
$$\frac{\partial}{\partial t}N_3 = k_3 N_2$$

$$N_1(t) = N_0 e^{-\frac{\alpha t}{2}}\left(\cosh(\frac{\beta}{2}\mathrm{t}) - \frac{\mathrm{k_1 - k_2 - k_3}}{\beta}\sinh(\frac{\beta}{2}\mathrm{t})\right)$$

$$\alpha = k_1 + k_2 + k_3$$

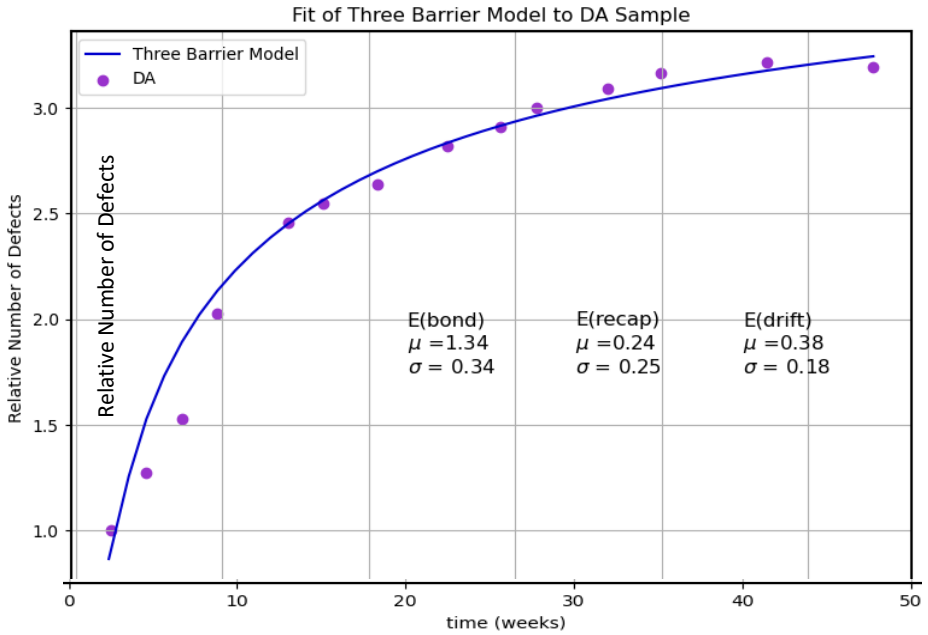
$$\beta \equiv \sqrt{\alpha^2 - 4k_1 k_3}$$

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

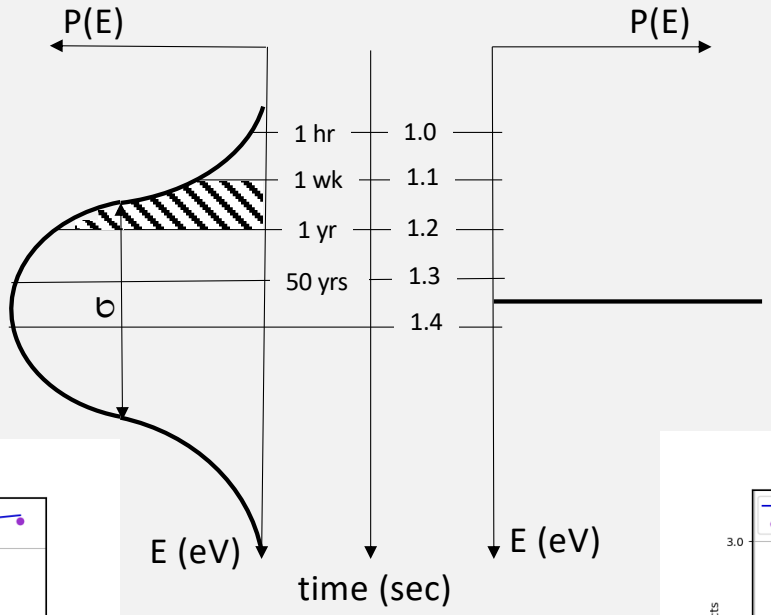
* Modelled N(t) with SolDeg-determined energies, averaged over SolDeg-determined distributions (line)
* Correspondence with experimental values (dots) is remarkable
* Not a fit – adjusted only within our narrow error bars

N(t) from AS-KMC without analytics or model truncation validates three barriers model

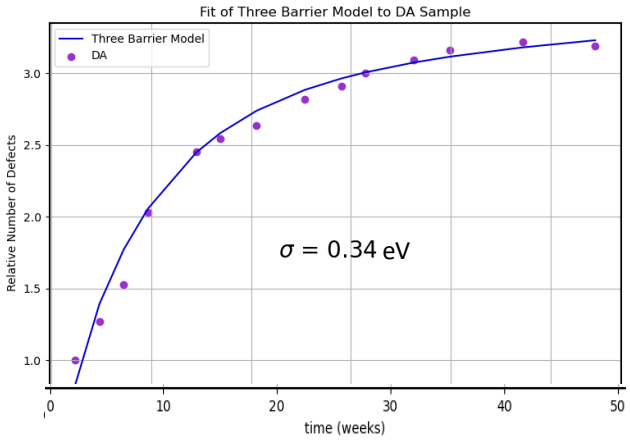


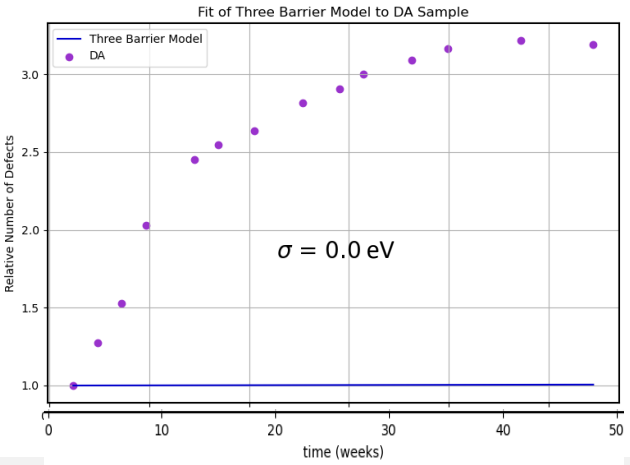
Broadened barrier distribution needed to provide active barriers

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



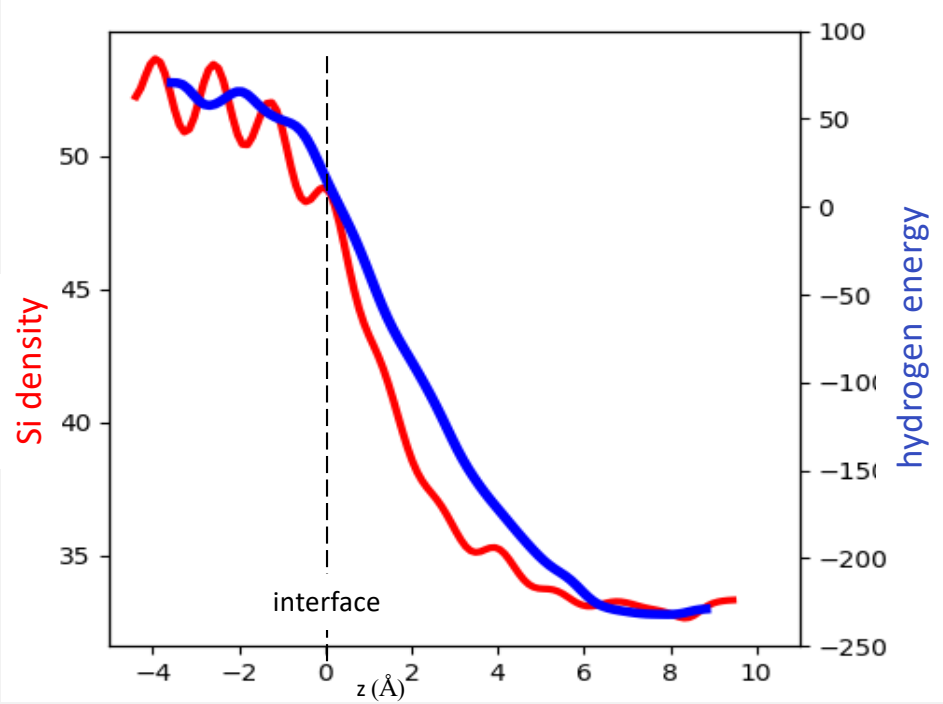
The 1.34 eV barriers are completely frozen between 1 week and 1 year. Broadening of P(E) around 1.34 eV provides barriers that are active in 1wk-1yr time window, and thus drive the time evolution of N(t).





Cause of H energy gradient? Si density gradient

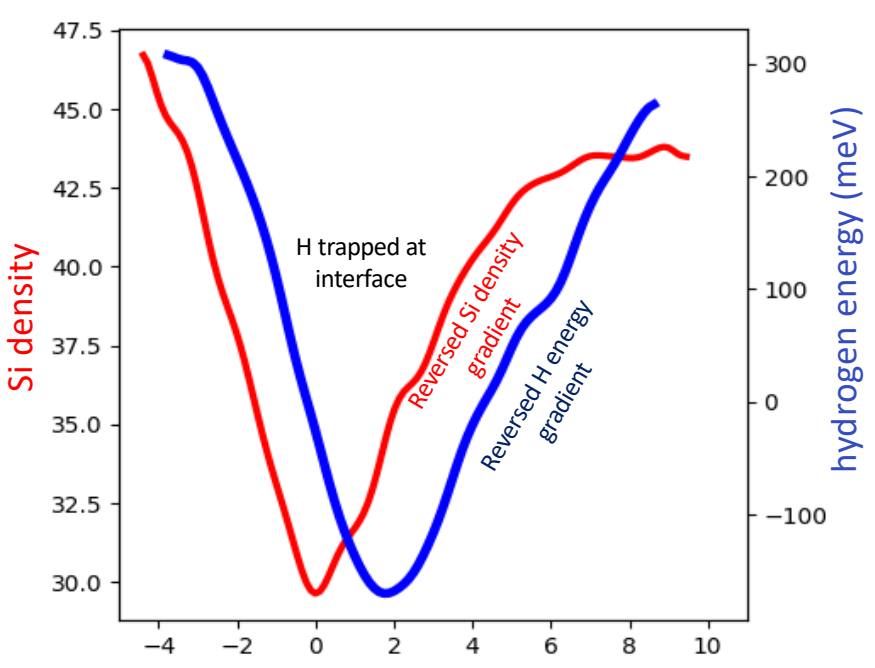
Hydrogen energy gradient is in blue. Measured Si density is in red. The Si density gradient correlates with, and likely causes, the hydrogen energy gradient. The increasingly porous a-Si offers more room/lower energy spots for H.



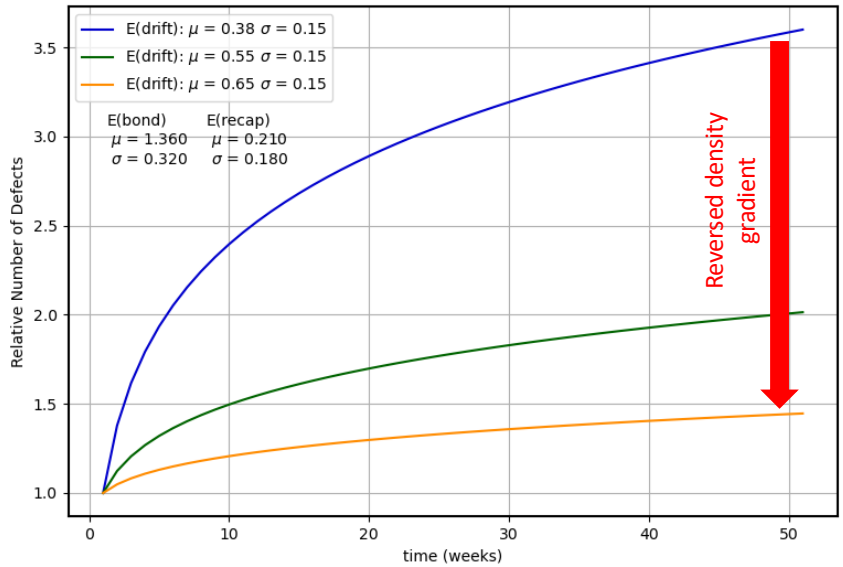
How to stop H-driven degradation? Reverse Si density gradient!

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!

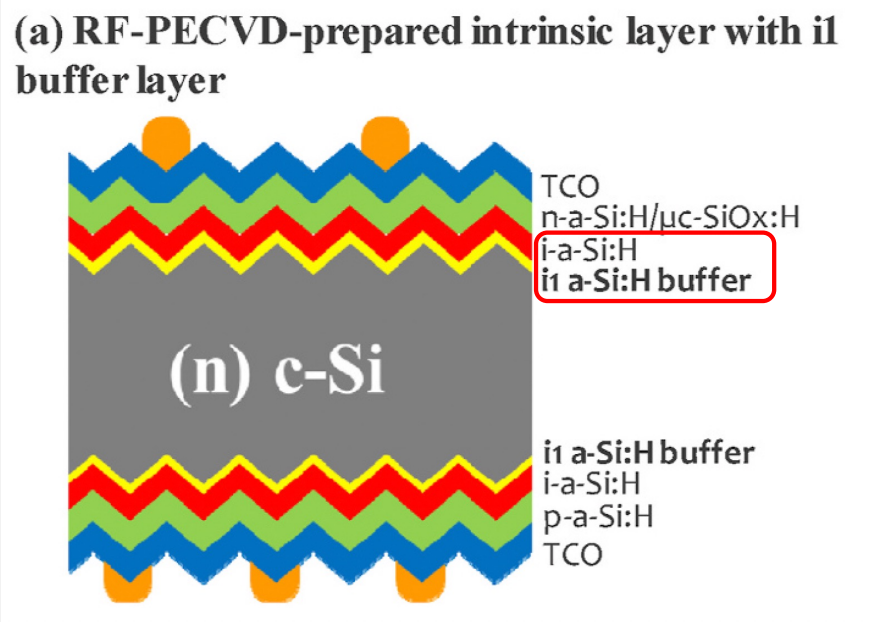


ΔN reduced by 5: ΔVoc reduced 0.5 %/yr ➡ 0.1%/yr



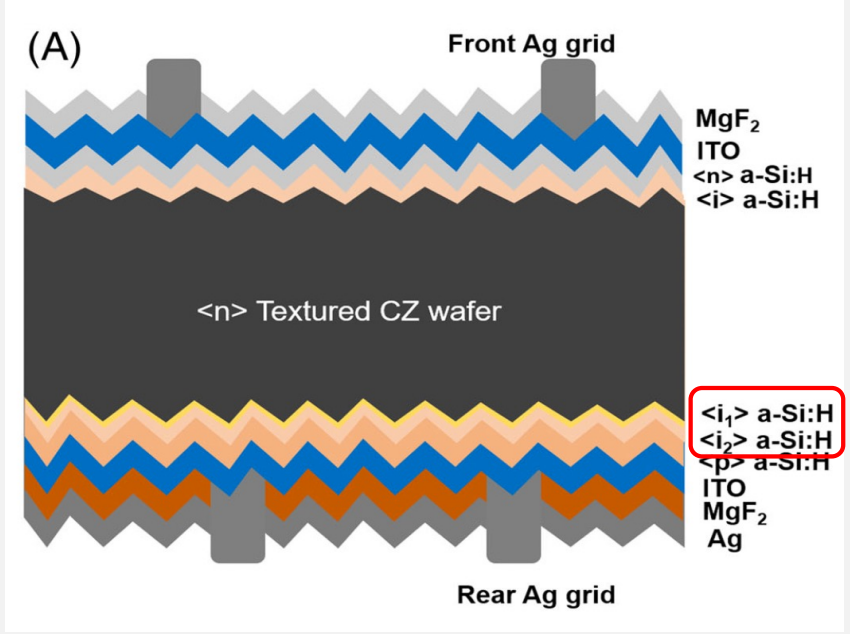
Related experiments

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)

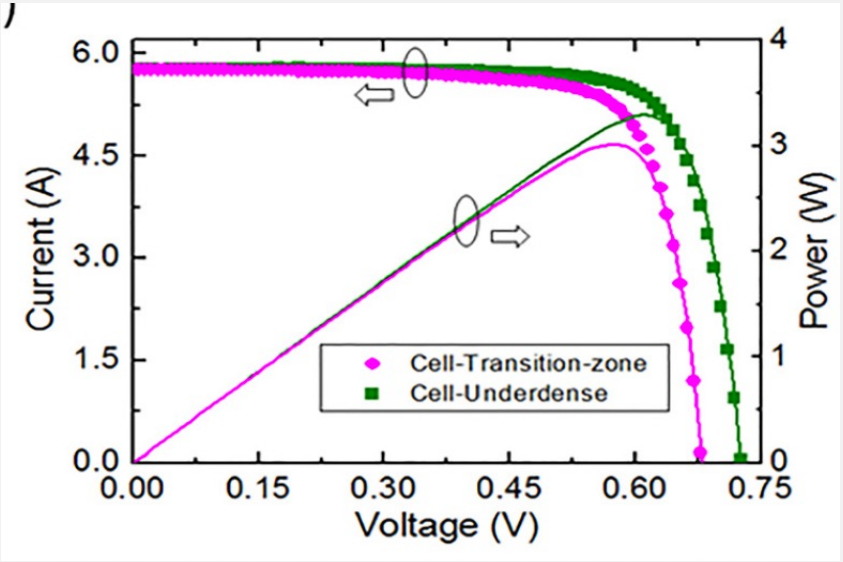


By using a denser and thinner second part of the intrinsic a-Si:H layer, a reduced vertical rear resistance loss was achieved. This favored vertical carrier transport and led to a higher *FF*.

Related experiments

Liu et al. J. Ap. Phys. (2016)

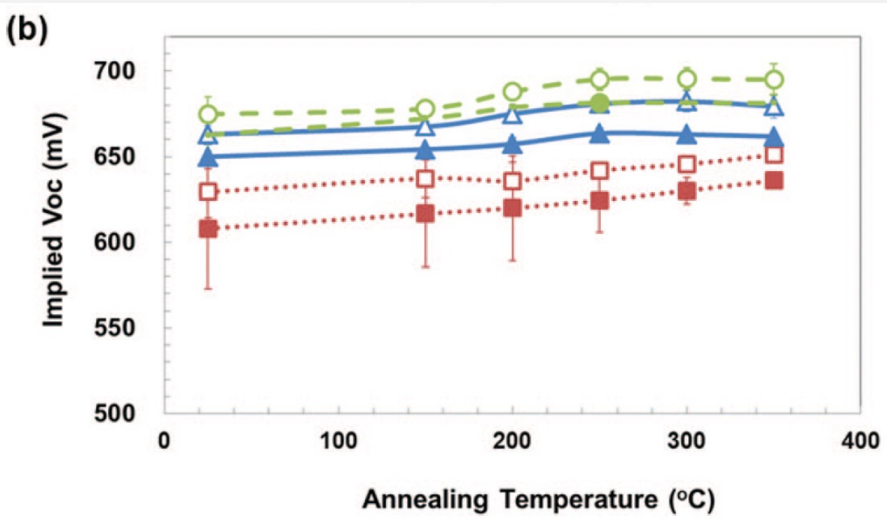
Underdense a-Si:H film capped by a dense film as the passivation layer of a silicon heterojunction solar cell



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 τ_{eff} of

Lee et al. ECS Solid State letters (2014)

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

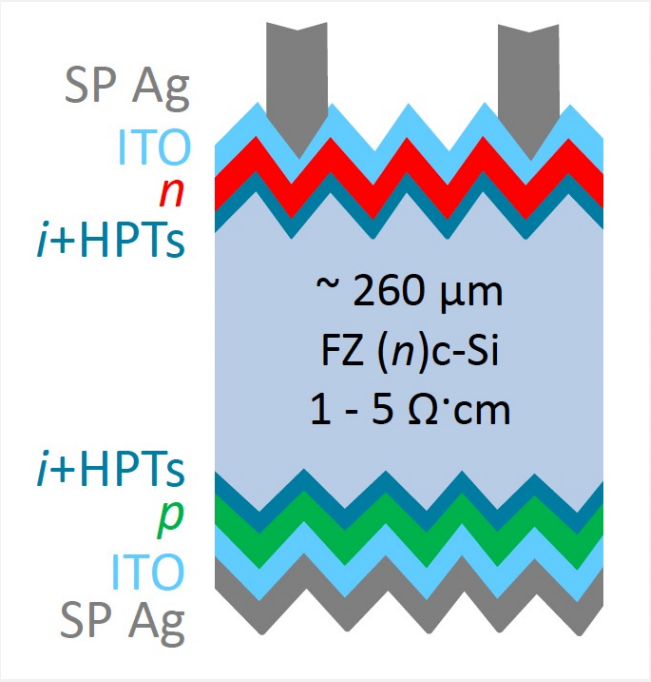


Empty symbols: second, underdense i-a-Si layer added

Related experiments

Arno Smets, Y. Zhao

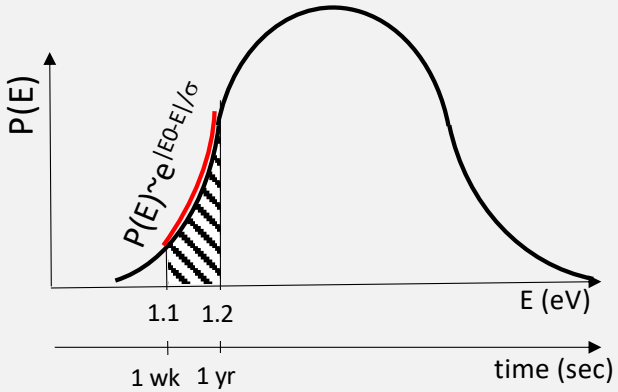
(*i*)a-Si:H monolayer vs bilayer



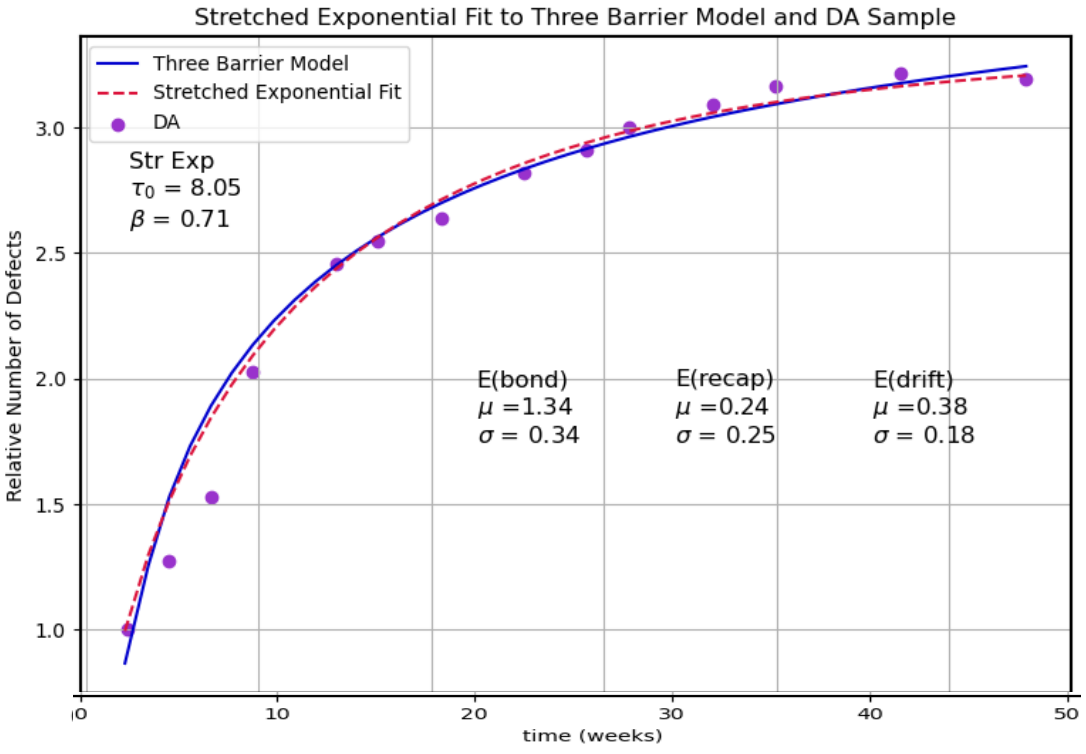
i2	8 or 9 nm (*i*)a-Si:H-2*
i1 + i2	1 nm (*i*)a-Si:H-1 + 7 or 8 nm (*i*)a-Si:H-2**

(*i*)-layers on (*n*)-/(*p*)-side	V_{OC} (mV)	J_{SC} (mA/cm^2)	*FF* (%)	η (%)
i2/*i2*	694.40 ± 4.67	36.92 ± 0.08	79.72 ± 0.46	20.44 ± 0.20
i2/*i1*+*i2*	698.60 ± 5.27	37.01 ± 0.17	80.26 ± 0.29	20.75 ± 0.14
i1+*i2*/*i1*+*i2*	704.20 ± 2.28	37.15 ± 0.05	80.55 ± 0.33	21.07 ± 0.03

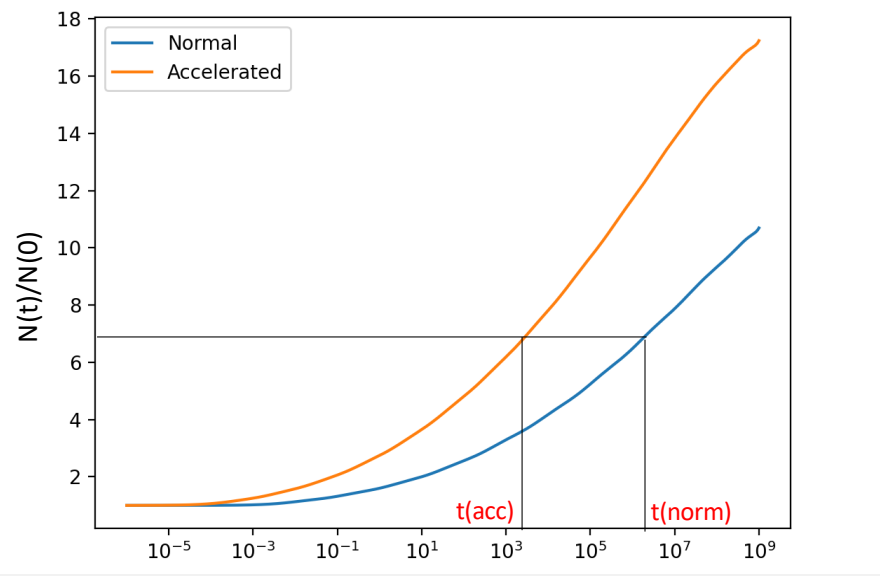
Can N(t) be fitted with stretched exponential?

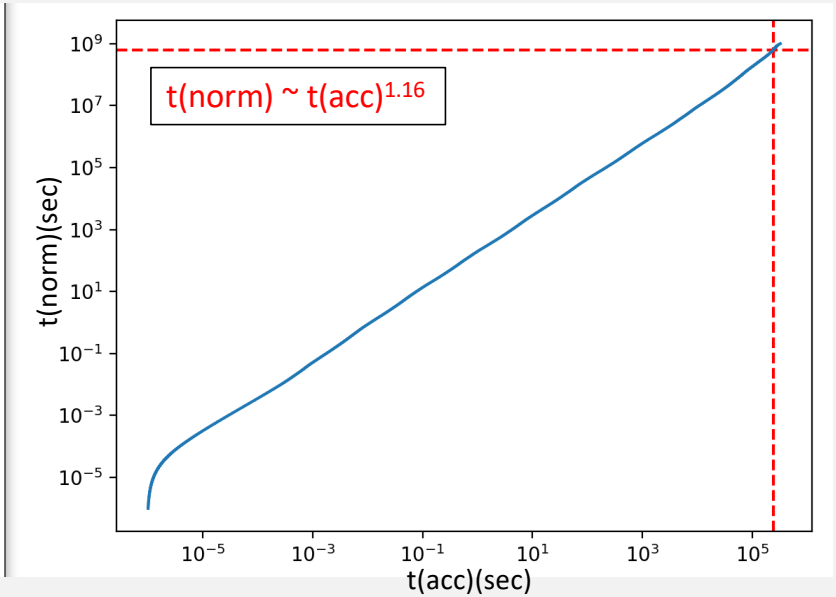


The 1 week-1 year time interval probes the P(E) barrier distribution only in the narrow range of 1.1-1.2eV. In this range P(E) can be well approximated with a simple exponential $P(E) \sim e^{|E0-E|/\sigma'}$.



Time correspondence curve for accelerated testing

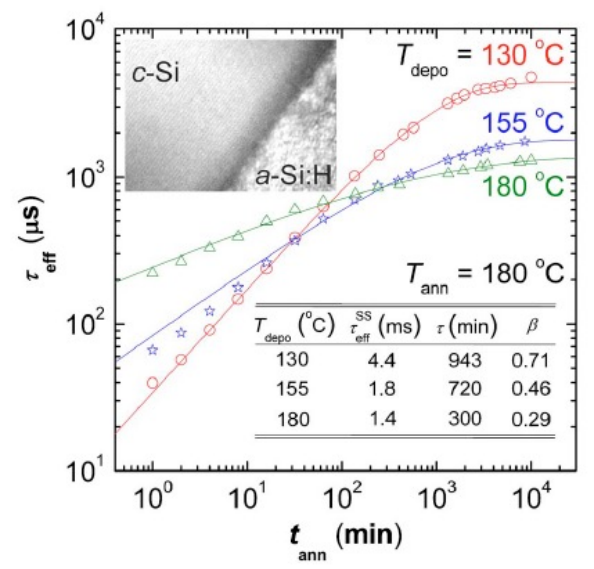




Stretched exponential N(t) unavoidably predicts:
$t(norm) \sim t(acc)^{(T(acc)/T(norm)}$, T(acc)/T(norm=1.17

Consistent with stretched exponential behavior
Exponent s = ratio of temperatures 350/300=1.17
Delayed start modifies this relationship.

Related theories and stretched exponentials



T_{depo} (°C)	τ_{eff}^{SS} (ms)	τ (min)	β
130	4.4	943	0.71
155	1.8	720	0.46
180	1.4	300	0.29

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

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

Stabler-Wronskii	Stabler, Wronskii 1977
Divacancies + nanovoids	Smets, Melskens 2000-2016
Anomalous diffusion with distribution of time scales	Street, Kakalios, Johnson 1993
Hydrogen collision	Brantz 1999
Stretched exp. in opposite direction	de Wolf, Ballif 2008; Edholm Blomberg 2000;
Anomalous diffusion with hierarchy of time scales:	Anderson, Palmer, Stein

SUMMARY

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

3. Scaling law of accelerated testing: $t(norm) \sim t(acc)^{(T(acc)/T(norm)}$

4. Developed Machine-Learning-based Si-H GAP potential for most accurate Molecular Dynamics simulation of c-Si/a-Si:H heterojunctions.

5. Reported experimental analysis: Neutral defect generation at interface drives degradation

6. Performed SolDeg simulation of c-Si/a-Si:H HJs to analyze neutral defect generation

7. H energy gradient drives H drift from HJ interface. This degrades the cell passivation

8. Computed N(t) with Soldeg energies & distributions: it was consistent with experimental data

Key: H energy gradient at interface; Wide distribution of barrier energies

9. 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 ➡ 0.1%/yr

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

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

submitted to SolMat

This talk, PVSC proceedings

Collaborators

Davis Unruh
UCD – Argonne

Reza Vatan
ASU

He is handsome too

Zitong Zhao
UCD

Salman Manzoor
ASU

Andrew Diggs
UCD

Stephen Goodnick
ASU

Mariana Bertoni
ASU

Gabor Csanyi
Cambridge, UK

THANK YOU