Heterojunction Si solar cells exhibit notable performance degradation. This is a substantial challenge for their market acceptance and for basic science. In order to shed light to the underlying causes, we studied this problem by layering several techniques on top of each other in order to determine the dynamics of electronic defect generation. The first layer of our method is adapting LAMMPS Molecular Dynamics simulations to create aSi/cSi stacks. Our simulations use femtosecond time-steps. For the interatomic potential, we used the Artificial-Intelligence-based GAP interatomic potential. Next, we optimized these stacks with Density Functional calculations. This was followed by creating localized structural defects in the stacks by local heat blasting. We then analyzed the just-generated structural defects by the Inverse Participation Ratio (IPR) method to identify which structural defects induced and supported electronic defects. Next, we adapted the Nudged Elastic Band (NEB) method to determine the energy barriers that control the formation of these electronic defects. We performed the NEB method for thousands of electronic defects to determine the distributions of these energy barriers. Finally, we developed an Accelerated Superbasin Kinetic Monte Carlo approach to determine the time dependence of the electronic defect generation, as controlled by this energy barrier distribution. The determination of the energy barriers out to 4 eV enabled us to determine the defect generation out to Gigaseconds, or of the order of 10 years. Our method is thus capable of connecting physical processes from femtoseconds to Gigaseconds.

Our main conclusions are that even in dark conditions, thermal activation processes lead to a substantial increase of the electronic defect density. Further, we also simulated the same processes at the accelerated testing temperature of 350K, and established a quantitative relationship between the regular and accelerated defect generation, thus making accelerated testing a more quantitative assessment tool.

I. INTRODUCTION

A. Solar Cell Degradation

Heterojunction (HJ) Si solar cells have world record efficiencies approaching 27%, due to the excellent surface passivation by their a-Si layer that leads to low surface recombination velocity and high open circuit voltage $V_{OC}$. In spite of the impressive efficiency records, HJ Si cells have not yet been widely adopted because of the perceived challenge that HJ cells may exhibit enhanced performance degradation, possibly related to their a-Si layer. Traditional c-Si modules typically exhibit about a 0.5%/yr efficiency degradation, primarily via $I_{sc}$ and the fill factor FF, typically attributed to external factors, such as moisture ingress and contacts. In contrast, in 2018 two papers reported studies of the degradation of fielded Si HJ modules over 5-10 $I_{sc}$.

They reported degradation rates close to 1%/yr, about twice the rate of traditional cells. They attributed this to a new, internal degradation channel, the decay of $V_{OC}$, at a rate of about 0.5% /yr. The decay of $V_{OC}$ suggests degradation processes possibly due to an increased recombination at the a-Si/c-Si interface, or in the a-Si layer. Either way, the degradation is suspected to be caused by the increase of the electronic defect density.

These initial reports on fielded panels were followed up by in-laboratory analysis. The Bertoni group has studied the surface recombination velocity at the c-Si/a-Si interface in HJ stacks. By applying a model for the recombination at the a-Si:H/c-Si interface to temperature- and injection-dependent SRV data, they analyzed the lifetime decay and were able to attribute it to a loss of chemical passivation. More recently, Holovsky et al. investigated ultrathin layers of hydrogenated amorphous silicon (a-Si:H), passivating the surface of crystalline silicon (c-Si). The authors applied highly sensitive attenuated total reflectance Fourier-transform infrared spectroscopy, combined with carrier-lifetime measurements. They manipulated the a-Si/c-Si interface by applying different surface, annealing and ageing treatments. Electronic interfacial properties were discussed from the perspective of hydrogen mono-layer passivation.
of the c-Si surface and from the perspective of a-Si:H bulk properties. They concluded that both models have severe limitations and called for a better physical model of the interface.\cite{4}

Understanding the degradation of the passivated c-Si surface is important not only for understanding aSi/cSi heterojunction solar cells. The PV industry roadmap shows that among newly installed modules, the fraction of advanced Passivated Emitter/Rear Contact (PERC) modules will rapidly rise above 50% in the next 3 years. On of the advanced features of these PERC cells is the improved interface passivation with the application of elevated levels of hydrogen. However, the increased efficiency was accompanied by notable levels of degradation. \cite{5,6,7} By experiments and modeling the hydrogen charge state fractions, the authors speculated that the PERC cell degradation both in the dark and under illumination could be explained by the migration of and interactions between different charged hydrogen species in Si.

To summarize, the accelerated degradation of $V_{OC}$ is slowing the market acceptance of the world-efficiency-record holder Si HJ modules, and impacts the introduction of the advanced PERC cells, thereby impacting the PV industry roadmap. Thus, analyzing and mitigating these degradation processes is of crucial importance.

B. Defects in Amorphous Si

Photoinduced degradation of a-Si under prolonged exposure to intense light was first studied, measured and modeled by D. L. Staebler and C. R. Wronski, so this phenomena is referred as Staebler-Wronski Effect (SWE) \cite{8}. The SWE manifests itself in the celebrated $t^{1/3}$ power-law temporal growth of the defect density. Recently, Wronski argued that three distinct defect states, A/B/C, are needed to account for all the data, instead of the standard single “midgap dangling bond” defect.\cite{9} The A/B states are efficient electron recombination centers, the C states recombine holes efficiently. The importance of three distinct states was recently confirmed by the Bertoni group \cite{3}, and the Wenham group \cite{6}. Wronski also speculated that these defects are differentiated by their different structures: dangling bonds, mono- and divacancies, as also advocated by Smets. The Wenham group proposed the intriguing alternative that the defect states may be the H+, H0, and H- charge states of hydrogen \cite{6}.

The Staebler-Wronski proposal was tested by different methods. Some groups performed electron spin resonance (ESR) measurement on a-Si (a-Si:H) to experimentally detect the increase of the density of dangling bonds induced by light exposure.\cite{10,11,12} Some of these papers also developed a phenomenological model to predict the SW defect-increase as a function of exposure time and light intensity. Other groups used the photocurrent method (PCM) to detect the change of defect density of a-Si under light exposure. In agreement with ESR experiments, PCM also revealed the increase of defect density under light exposure. While the ESR and PCM defect density measurements yielded analogous results, it is recalled here that they capture different type of defect states \cite{13,14}. ESR detects all neutral defect states that only include dangling bonds (DBs), while PCM detects both neutral and charged defect states that include DBs and other types of defect states. Therefore PCM measurements revealed that the origin of defect states might be a result of different type of general structural disorders beyond DBs.\cite{15,16} In addition to experimental work, several recent theoretical and computational work have shown highly strained bonds significantly contributing to midgap states and DBs\cite{17,18}.

To summarize, while a fair amount of progress has been achieved in characterizing defect generation in aSi, its underlying mechanism and connection to the different types of structural disorder is not fully understood. The problem is still open to question.

In our paper, we address the above twin problems of defect generation in aSi/cSi heterojunction solar cells, with a focus on defects in the aSi layer and at the interface.

II. METHODS AND RESULTS

A. Creating the Amorphous/Crystalline Stacks: Machine-Learning Driven Molecular Dynamics

To create a-Si/c-Si heterojunction structures, we adopted a two-fold approach. First, we created pure a-Si structures, which were carefully optimized in order to match lab-grown a-Si as closely as possible. Second, we placed these optimized a-Si structures on top of slabs of c-Si, and then annealed the interface region to create unified heterojunctions. This approach was chosen in order to create the most realistic a-Si atomic structures possible, while still yielding reasonable aSi/cSi interface regions. The details of this approach are as follows.

To create pure amorphous Si structures, we performed melt-quench MD simulations. In a melt-quench simulation, a crystalline Si structure is heated to its melting point to give liquid Si, which is then slowly quenched down to near-room temperature. This method is widely used for generating amorphous Si networks, though it is noted that the choice of the interatomic potential used for these simulations has a substantial effect on the results. These interatomic
potentials have limited numbers of parameters/descriptors, and are typically fitted against experimental structural data under a specific set of conditions such as material composition and temperature range. As such, their accuracy in reproducing a wider variety of structural properties of the specific material, or simulating a different temperature range or material structure than they were fitted on, often leaves something to be desired. Standard interatomic potentials for Si include Tersoff [19] and Stillinger-Weber (SW) [20].

Historically, adopting a melt-quench method to create a-Si, using the above mentioned standard interatomic potentials has been able to create structures which reasonably match various key characteristics of lab-grown a-Si. However, as to be expected from the above cautionary message, they have a few failings. The excess energy (energy compared to diamond-type Si) of the a-Si which is produced from these interatomic potentials is typically > 0.20eV/atom, falling outside of the lab-grown a-Si excess energy range of 0.09 – 0.16eV/atom. The defect densities, e.g. the density of dangling and floating bonds, also vary compared to typical low-grown a-Si. Additionally, these interatomic potentials are unable to reach DFT-level accuracy in measuring features such as the elastic constants and defect formation energies. Thus, the creation of accurate melt-quench a-Si requires significant DFT input. Even then, reaching experimental-level accuracy is still difficult, and this process can only yield structures on the edge of acceptability [18].

To improve the accuracy of our MD simulations in all aspects compared to using these standard interatomic potentials, we instead adopted a Machine-Learning driven general-purpose interatomic potential which has been created for Si [21]. This Machine-Learning driven approach uses the framework of the Gaussian Approximation Potential (GAP) with a Smooth Overlap of Atomic Positions (SOAP) kernel, and has been specifically developed to yield DFT-level MD accuracy while being a factor of 10x more efficient [22, 23]. Hereafter, we will refer to this potential simply as the Si GAP. It has been shown that the Si GAP is (significantly) better across the board than any other interatomic potential available [21]. As discussed down below, in combination with a minimum level of DFT optimization, adopting this potential for our MD simulations yielded a-Si structures that accurately reflect high quality experiments. Now we proceed with the technical simulation details.

Our melt-quench simulations were carried by starting with crystalline Si cubic supercells containing 216 Si atoms, with three dimensional (3D) periodic boundary conditions. The lattice constant $a_0$ was chosen to be 5.43 Å, and the dimensions of the supercell $a = b = c = 3a_0$. This lattice constant was chosen to ensure that the mass density of the resulting a-Si structures was 1-3% lower than the mass density of corresponding c-Si structures, consistent with the mass density measured by experiments.

The MD simulations were carried out using the LAMMPS software package [24]. The simulation time step was 1 fs. Simulations started with liquid Si at 1800K, which was cooled down to 1500K at a rate of $10^{13}$ K/s before being equilibrated at 1500K for 100 ps. This was followed by a quench down to 500K at a rate of $10^{12}$ K/s. This cooling rate is consistent with previous studies [21, 23, 27]. The first quench was performed in the constant-volume and variable-pressure (NVT) ensemble, while the second quench was performed in the variable-volume and constant-pressure (NPT) ensemble with fixed $x$ and $y$ dimensions (to match the dimensions of the c-Si unit cell in the later steps), both using a Nose-Hoover thermostat and barostat. The resulting structures were then minimized using a GAP-driven Hessian-free truncated Newton (HFTN) algorithm to relax all atomic positions into local minima.

These minimized structures were then further optimized at the DFT-level as implemented in the Quantum Espresso 5.2.1 software package [28, 29]. The BFGS quasi-newton algorithm, based on the trust radius procedure, was employed as the optimization algorithm for the relaxed structures.

The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [30] was used in both the ionic relaxation and the electronic structure calculations using periodic boundary conditions. The core and valence electron interactions were described by the Norm-Conserving Pseudopotential function. Unless otherwise stated, an energy cutoff of 12Ry was employed for the plane-wave basis set and a $2 \times 2 \times 2$ k-point mesh was used with the Monkhorst-Pack grid method for the Brillouin-zone sampling in all the calculations. Methfessel-Paxton smearing [31] of width 0.05Ry was applied to determine the band occupations and electronic density of states.

Motivated by Pedersen et al, using the radial distribution function (RDF), excess energy and bond angle distribution are the most compelling criteria with which to validate our generated a-Si structures against experimental counterparts [32]. Improvement of these criteria was what led us to employing the machine-learning driven Gaussian Approximation Potential instead of a classical interatomic potential in our MD simulations. In our resulting structures, the typical excess energies (energies measured relative to crystalline-Si) were around $0.13 – 0.14$ eV/atom, well within the experimentally acceptable range of $0.09 – 0.16$ eV/atom. The average bond-angle distribution was $109.1^\circ \pm 10.5^\circ$, which is also consistent with typical experimental values [33]. The average Si-Si bond length was $2.38 \pm 0.04$ Å. Assuming a Si-Si bond-length cutoff of $2.58$ Å, slightly less than 10% longer than the average bond-length, the average number of dangling bonds in each supercell was 2.2, and the average number of floating bonds was 0.8. Dangling (floating) bonds are missing (extra) chemical bonds of a Si atom from ideally four chemical bounds. The structures were further validated against experiment by calculating and comparing the RDF (cf. Fig. 1). The RDF, also known as the pair correlation function, measures the probability of finding the center of an atom at a given
distance from the center of another atom. For a-Si, the typical RDF exhibits a strong peak centered at 2.3 Å, and two weak peaks centered around 3.8 Å and 5.4 Å (the next-nearest and next-next-nearest neighbor distances in c-Si).

Figure 1. Radial distribution function $g(r)$ characterizing a typical melt-quench MD a-Si structure, plotted against the experimental values of ref. [34]

Si-heterojunction structures were created by placing the DFT-optimized a-Si on top of c-Si slabs (of the same dimensions and number of atoms as the a-Si structures). See Fig. 2. Note that maintaining periodic boundary conditions results in structures with two a-Si/c-Si interfaces. At both interfaces, the a-Si was placed 1.36 Å ($a_0/4$) away from the edge of the c-Si slab. This distance was chosen by calculating the total energy of a series of structures where this distance was systematically varied, and choosing the distance which yielded the lowest total energy. These calculations were performed primarily with one representative a-Si structure, but were coarsely checked against a few others as well.

The difficulty in adopting this method of creating heterojunctions is that, while the bulk a-Si layer is favorably comparable to lab-grown a-Si, the resulting c-Si/a-Si interfaces are highly strained and less characteristic of PCVD grown heterojunctions. Alleviating this problem requires that we go one step further, and relax each interface via thermal annealing. To avoid altering the structure of the carefully optimized a-Si layers, we only annealed strips of width $a_0$ centered between the a-Si and c-Si layers at both interface locations. The annealing was performed at 450K for 25 ps, and was followed by cooling down to 270K at a rate of $10^3$ K/s. Both steps were performed in the NVT ensemble with a timestep of 1 fs.

B. Creating and Identifying Structural Defects

In amorphous silicon, which contains many structural defects in the atomic structure, the mobility of holes and electrons in localized states close to the valence and conduction band edges are much lower in comparison to non-localized extended states that are above/below the mobility edge of the conduction and valence bands, respectively. The energy difference between the valence-band mobility edge and the conduction-band mobility edge is the so-called mobility gap. Electronic transport and carrier recombination in a a-Si/c-Si heterostructure is strongly affected by the carriers residing in these localized states within the mobility gap. In this section, we will discuss our method of creating structural defects in the a-Si/c-Si heterostructures, and how we further investigate the orbital localization of these heterostructures in order to determine the electronic defect states.
To create structural defects, we employ the idea of localized heating. Using LAMMPS and the ML-based Silicon Gaussian Approximation Potential (GAP) described in the previous section, we heat our structure in a small volume containing about 5 atoms at the crystalline/amorphous interface to a temperature of 5000K while leaving the rest of the system frozen. It was found that temperatures significantly below 5000K were not efficient at generating defect states. We allow the system to evolve at this elevated temperature for 20ns in order to allow the small sub-system time to explore configuration space. After these 20ns, the sub-system is frozen very quickly, so that it cannot easily escape whatever metastable configuration it is nearest to. We then perform Conjugate Gradient minimization of the frozen structure, again using the Si GAP. This process is repeated for all of our structures at many different points on the interface in order to get a broad distribution of initial and final states.

This localized heating method allows us to create a final state which differs very slightly from the initial state. In some cases, these final states will have created (or destroyed) a structural defect at the site of the localized heating, which can be identified geometrically. Common structural defects include dangling bonds, which is a 3-fold coordinated Si atom, and floating bonds, which are 5-fold coordinated Si atoms. However, not all of these structural defects will create localized electronic states. To identify which of these structural defects correspond to electronic defects, we need to go one step farther and measure the orbital localization of the a-Si/c-Si heterostructures using DFT.

C. Identifying Electronic Defects Induced by Structural Defects

The localization of Kohn-Sham orbitals was computed in detail for computer generated a-Si/c-Si structures using the inverse participation ratio (IPR) method. The IPR for an eigenstate $\Psi_n$ is given as:

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

Where $a_{ni}$ is the coefficient of ith basis set orbital in nth Kohn-Sham orbital $\Psi_n$ ($\Psi_n = \sum_{i=1}^{I} a_{ni}\phi_i$) and I is the total number of basis set orbitals used in DFT calculations. The higher the IPR, the higher the degree of localization.
The IPR for a completely extended state (extended equally on all the atoms) is close to zero, and for a completely localized state (located on only one atom) is one.

Fig. 3(a) indicates the calculated IPR of all the Kohn-Sham orbitals obtained from DFT versus their energy for a typical a-Si/c-Si. In agreement with our previous discussion, it’s clear that the localization of the orbitals inside the mobility gap is much higher than that of its outside. The mobility gap is assigned from 5.5 to 7 eV based on the observed relatively sharp transition between localized and extended states identifying the valence/conduction mobility edge.

In order to define localized structural defects, we rearrange Eq. 1 as follow:

\[ IPR(\Psi_n) = \frac{\sum_{k=1}^{K} \sum_{j=1}^{J} a_{nkj}^4}{(\sum_{k=1}^{K} \sum_{j=1}^{J} a_{nkj}^2)^2} \]  

Where \( a_{nkj} \) is the coefficient of jth atomic orbital belonging to the kth atom in the nth Kohn-Sham orbital. J is the total number of atomic orbitals used in DFT calculations which belong only to the kth atom in the supercell. Eq. 1 and 2 are basically the same and give exactly the same IPR values versus energy with the difference being that Eq. 2 enables us to calculate IPR values as a function of atoms by defining a quantity namely \( IPR_{nkj} \) as follow:

\[ IPR_{nkj} = \frac{a_{nkj}^4}{(\sum_{k=1}^{K} \sum_{j=1}^{J} a_{nkj}^2)^2} \]  

Here \( IPR_{nkj} \) is the contribution of the kth atom through its jth atomic orbital in the localization of the nth Kohn-Sham orbital. One can notice that the denominator of Eq. 3 is the same for the all \( IPR_{nki} \) as long as n is the same.
Thus, there are $J$ numbers of $IPR_{nkj}$ values for each Kohn-Sham orbital. If there are $N$ numbers of Kohn-Sham orbitals, we will have $NJ$ number of $IPR_{nkj}$ values for each atom present in the supercell. In order to assign only one $IPR$ value to each atom, we determine the maximum value of $IPR_{nkj}$ between all the $NJ$ possible values. We name this maximum value as $IPR_k$ and describe it as follows:

$$IPR_k = \text{MAX}_{n,j}^k \{ IPR_{nkj} \}$$  \hspace{1cm} (4)

Where $\text{MAX}_{n,j}^k$ means the maximum value among the list of $IPR_{nkj}$ values when $k$ is constant and $n$ and $j$ have all the possible values. Fig.3 shows $IPR_k$ values for a typical a-Si/c-Si heterostructure. As seen and expected, almost all of the localized states are located at the interfaces. There is no localized state in the c-Si counterpart and only one localized state in the a-Si. This localized states distribution is reasonable in terms of the presence of high degree of strain at the interface and low(no) strain in the a-Si(c-Si) counterpart. In order to define a defect state, we need to assign a cutoff $IPR_k$ value. Here we assume that a defect state is a state that is localized mostly on only one atom. With this assumption, the atoms with $IPR_k$ value greater than 0.5 are defects. Therefore, there is only one defect for each interface in Fig. 3.

Once the $IPR$ calculation has been completed, we can identify whether defects were created or annihilated by comparing the defect numbers of the initial and final states. To do this, we choose a threshold $IPR_k$ value that defines an electronic defect and determine which initial-final state pairs differ by exactly one defect. We keep all barriers calculated through NEB that connect initial and final states that differ by exactly one defect, separating the processes that result in defect creation and defect annihilation into two separate distributions, shown in Fig.1, above. We note here a few things regarding our choices about defect definition and selection criteria. First, we choose to use $IPR$ to identify defects rather than structural criteria because structural defects do not always lead to localized electronic states, which we see as the defects of relevance in solar cell degradation. Second, we choose to only track initial-final state pairs that differ by a single defect to avoid any possible defect-defect interactions that may affect our results. Third, our $IPR$ threshold definition is such that any site that contributes more than half to an electron’s wave function is considered to be a localization site and therefore a defect.

D. Determining Energy Barriers and Their Distribution with the Nudged Elastic Band Method

Once pairs of initial and final states have been identified where a single defect is either created or annihilated, we employ the nudged elastic band (NEB) method [35–38] to determine barrier heights between initial and final states. The nudged elastic band method connects two different local energy minima with several intermediate replica states, each connected to its nearest state neighbor with a spring that is nudged perpendicular to the path through state space to allow the "band" to find a saddle point. The NEB method is a standard tool for determining minimum energy paths between states in some fields, but to our knowledge, this tool is not common in the solar field, so we will describe the method in some detail here.

The NEB method uses a two component force to determine the minimum energy path (MEP). First, it uses a spring force that connects adjacent replica states with the slight modification that component of the spring force that is perpendicular to the MEP is projected out.

$$F^S_i = k(R_{i+1} - R_i) - k(R_i - R_{i-1}) \cdot \hat{\tau}$$ \hspace{1cm} (5)

Where $R_i$ represents the position in the energy landscape of the $i$th replica, $k$ is the spring constant, and $\hat{\tau}$ is the unit vector parallel to the MEP at replica $i$.

The second force used in NEB is the force on the replica due to the potential, with the component parallel to the MEP projected out, so it just acts to nudge the chain of states closer to the MEP.

$$F^V_i = -\nabla V(R_i) + \nabla V(R_i) \cdot \hat{\tau} \hat{\tau}$$ \hspace{1cm} (6)

Where $V$ is the potential energy landscape. The advantage to the NEB method over a standard elastic band method is that artifacts involved with the band cutting corners off the MEP are not a problem for the NEB method.

Our NEB simulations were performed in LAMMPS using the Si GAP [21]. We used 32 replicas for each simulation. In our simulations we kept the non-heated atoms fixed, e.g. only the heated atoms are allowed to move replica-by-replica. The energy stopping tolerance was $10^{-6}$ (unitless), and the force stopping tolerance was $10^{-6}$ eV/Å. The simulation timestep was 10 fs. We used the fire minimization algorithm, a damped dynamics method with a variable time step [39].
Figure 4. (a) Defect creation; and (b) Defect annihilation barrier distributions

The results of our NEB calculation are shown in Fig. 4. The barriers for defect creation processes are shown in panel (a), while the barriers for defect annihilation processes (a reverse transition across the defect creation barrier) are shown in panel (b). The matching energy scales of the two sets of transition processes ensures that the processes will be equally relevant to the time evolution of defect generation in the simulated heterostructures. We now move to our determination of the defect density in these heterostructures over long time scales (months to years).

E. Determining the Time Evolution of the Defect Density $N(t)$ From the Barrier Distribution

In order to extract the defect density as a function of time, we turn to kinetic Monte Carlo methods. We begin by creating a large bath of potential defect sites, and randomly choosing a small percentage of them to be defected. Each site is also given an energy barrier chosen from our barrier distributions determined by the method of the previous section. Crossing a barrier of energy $E$ corresponds to an event that changes the defect status of a site with an associated rate of

$$\Gamma = \Gamma_0 e^{-\frac{E}{kT}}$$  \hspace{1cm} (7)

Where $\Gamma_0$ is the attempt frequency of the system to overcome the barrier, taken here to be $10^{-10}$ Hz. These rates are calculated for each site and summed to determine the so called total rate, $\Gamma_{\text{tot}}$, and then an event is randomly selected from the possible events, with the probability of selecting event $i$ being equal to $P(i) = \frac{\Gamma_i}{\Gamma_{\text{tot}}}$. The time is then moved forward according to $\Delta t = \frac{-\ln(r)}{\Gamma_{\text{tot}}}$, where $r$ is a random number. This is equivalent to sampling a Poisson waiting time distribution.
The above described method becomes computationally prohibitive when the phenomenon of interest are rare events, with rates of occurrence that are several orders of magnitude smaller than typical events. Not only are these rare events exceptionally unlikely to be chosen by the algorithm, but the number of simulation steps needed to evolve the simulation time far enough to see the rare events will be impossibly large. Using our base kinetic Monte Carlo algorithm, without any acceleration efforts, a million simulation steps only evolves the simulation time by one-hundredth of a second. This is not feasible when we are trying to observe degradation that occurs on the scales of months or years.

Our solution to this problem is to implement what is known as an accelerated super-basin kinetic Monte Carlo (AS-KMC)\cite{40}. This method adds the extra algorithmic step of checking to see if any events which are part of a "super-basin" have been observed a set number of times, and increasing the activation energies of such events accordingly in order to lower their rate of occurrence. In the conventional terms, a super-basin consists of events which are linked to each other by high-frequency processes but are separated from the surrounding energy landscape by a low-frequency process barrier. As such, a standard kinetic Monte Carlo algorithm gets stuck in these super-basins, unable to escape, and this algorithm solves this issue by boosting them over the surrounding barrier. In our implementation, as each defect site is independent from all others, we consider each pair of defect transition rates (defect creation and defect annihilation) to be a superbasin. Leaving the superbasin in this sense means allowing the algorithm to evolve infrequently-transitioning defects. There are free parameters in the AS-KMC method that deal with how much the barriers should be raised and after how many repeated processes the barriers should be raised, but our results are largely insensitive to changes in these parameters.

Figure 5. N(t) results for AS-KMC with initial defect density of 20% of defect saturation at two different temperatures.

The results of this AS-KMC method are shown in Figure 5, the vertical axis is shown in units of the maximum number of defect candidate sites. We note here that the initial number of defects doesn’t affect the shapes of the curves significantly within this time range, as long as the initial conditions are well below saturation. One useful takeaway from this plot is how accelerated aging is related to standard temperature dark aging. From this plot, one can see that after $10^6$ seconds, the time scale of weeks, of accelerated aging at 350K, the expected number of defects generated is about the same as the number of defects generated over $10^9$ seconds, the time scale of years, for standard temperature dark aging. Most importantly, the highest level message of this plot, taken in the context of this work, is that we were successful in relating the time scale of molecular dynamics, to the time scale of solar cell lifetimes, tens of years.
III. DISCUSSION AND CONCLUSIONS

In this paper we studied the problem of heterojunction solar cell degradation by layering several techniques on top of each other in order to determine the dynamics of electronic defect generation. The first layer of our method was to adapt LAMMPS Molecular Dynamics simulations to create aSi/cSi stacks. Our simulations used femtosecond time-steps. For the interatomic potential, we used the Artificial-Intelligence-based GAP interatomic potential. Next, we optimized these stacks with Density Functional calculations. This was followed by creating localized structural defects in the stacks by local heat blasting. We then analyzed the just-generated structural defects by the Inverse Participation Ratio (IPR) method to identify which structural defects induced and supported electronic defects. Next, we adapted the Nudged Elastic Band (NEB) method to determine the energy barriers that control the formation of these electronic defects. We performed the NEB method for thousands of electronic defects to determine the distributions of these energy barriers. Finally, we developed an Accelerated Superbasin Kinetic Monte Carlo (AS-KMC) approach to determine the time dependence of the electronic defect generation, as controlled by this energy barrier distribution. The determination of the energy barriers out to 4 eV enabled us to determine the defect generation out to Gigaseconds, or of the order of 10 years. Our method was thus capable of connecting physical processes from femtoseconds to Gigaseconds. Our main conclusions were that even in dark conditions, thermal activation processes lead to a substantial increase of the electronic defect density. Further, we also simulated the same defect generation processes at the accelerated testing temperature of 350K, and established a quantitative relationship between the regular and accelerated defect generation. This correspondence makes accelerated testing a more quantitative assessment tool.

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Software Availability
The GAP suite of programs is freely available for non-commercial use from www.libatoms.org. The Quantum Espresso software package is freely available from www.quantum-espresso.org. The LAMMPS software package is freely available from lammps.sandia.gov.

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