

NON-EQUILIBRIUM GREEN FUNCTIONS APPROACH TO STUDY TRANSPORT THROUGH A-SI:H/C-SI INTERFACES

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ABSTRACT

The microscopic mechanisms of transport and recombination mechanisms in silicon heterojunction solar cells are still poorly understood. The purpose of the present work is to understand the transport mechanisms underlying photovoltaic devices based on silicon heterojunction technology by simulating at atomistic resolution amorphous-crystalline heterointerfaces. We have used classic molecular dynamics simulations to build up realistic c-Si/a-Si:H/c-Si interface at different temperatures. The ab initio characterization has been executed on selected configurations to monitor the electronic properties of the c-Si/a-Si:H/c-Si interface. The electron transmission is calculated at different temperatures based on the non-equilibrium Green functions approach and its behavior is correlated to the evolution of the intragap states. The whole outlined process will allow designing more efficient silicon solar cells belonging to the silicon heterojunction technology.

1 INTRODUCTION

The amorphous-crystalline heterointerfaces play a crucial role in the photovoltaic operation of silicon heterojunction (SHJ) technology, but the microscopic mechanisms of transport and recombination mechanisms at the interface are still poorly understood. The purpose of the present work is to understand the transport mechanisms underlying photovoltaic devices based on SHJ technology by simulating at atomistic resolution amorphous-crystalline heterointerfaces. In recent years, the SHJ solar cells reached the highest efficiency of 26.6% (Yoshikawa 2017), mainly due to the passivation contacts. In these devices, intrinsic hydrogenated amorphous silicon (a-Si:H) was used to passivate the Si surface and the p/n-type doped hydrogenated amorphous silicon was employed to select the transport carriers. The application of SHJs offers several advantages: first, a-Si:H provides efficient passivation of Si dangling bonds at the interface; second, field-effect passivation can produce a significant inversion effect at the a-Si:H/c-Si

interface that is able to increase the carrier lifetime. Moreover, fewer process steps are required to build-up the solar cells (SCs), and the low-temperature (< 200 °C) processing allows the use of very thin wafers without any substrate damage.

Understanding the influence of the density of defects at the a-Si:H/c-Si interface is pivotal in the design of amorphous/crystalline silicon heterojunction solar cells. In order to conceive a predictive ab initio simulation of the a-Si:H/c-Si interface, it is essential to build up an atomic-scale model of the interface that exhibits the experimentally observed features and at the same time it is almost free of defects. Indeed, due to the limited number of atoms in an ab initio calculation, already few defects lead to a strong overestimation of the gap-state density, possibly even resulting in metallic behavior. In our previous work we combined classic molecular dynamics (MD) simulations and ab initio characterization to investigate realistic c-Si/a-Si:H/c-Si heterojunction constituted by 1,152 atoms at different temperatures properly taking into account defect related intragap states (Buonocore 2020). We performed the ab initio characterization on selected MD snapshots to monitor the electronic properties of the c-Si/a-Si:H interface. The evolution of the intragap states was monitored by analyzing density of states and charge density. An analogous study has been performed in a full ab initio approach by some of us (Czaja 2018a) for a smaller a-Si:H/c-Si interface formed by 336 atoms. A similar interface formed by 334 atoms was used to study the band offsets (Jarolimek 2017). In the present work we consider the same configurations of our previous work and correlate the electron transmission at different temperatures of thermalisation to the different distribution of the intragap states in a realistic c-Si/a-Si:H/c-Si interface. The model we adopt allows us to reduce the undesired effects of the limited size of the a-Si:H/c-Si interface in the previous models,

2 METHODS

The c-Si/a-Si:H/c-Si interface is made of hydrogenated amorphous silicon (a-Si:H) between two crystalline silicon (c-Si) slabs. The relaxed $p(2 \times 1)$ symmetric reconstruction of the Si(001) surface constitutes the c-Si side of the interface. It is formed by 576 Si atoms, 16 layers of silicon with 36 atoms each. The a-Si:H side of the system is generated by cutting the a-Si:H structure, built as in reference (Czaja 2018b), such that the surface area is equal to the c-Si side and the thickness is about 16 Å. The hydrogenated amorphous silicon structure is composed of 512 Si atoms and 64 H atoms and it was previously analyzed and characterized. In particular, the calculated the radial pair correlation function $g(r)$ reveals good agreement with other computational and experimental results (see Figures 3b and 4 of reference Czaja 2018b). In the c-Si/a-Si:H/c-Si interface system, periodic boundary conditions (PBC) are imposed in all directions.

Classical MD analysis has been carried out by means of LAMMPS (Plimpton 1995) using the ReaxFF training set parametrization previously employed for the simulation of H bombardment of Si, Ge, and SiGe (100) surfaces (Psogiannakis 2016; Fogarty 2010). The complete MD analysis starts with $T = 0$ K minimization: at first, we fix all cell dimensions $L_x = L_y = 23.22$ Å and $L_z = 2 \cdot L_x$ Å, then later we still keep $L_x = L_y$ fixed and vary L_z as an additional degree of freedom. The resulting geometry is used as the initial condition for a subsequent quenching-thermalisation process. Initially, the system is heated up to 1100 K at zero pressure with a NPT (Nose-Hoover thermostat and barostat) (Hoover 1996) for 325 ps and next it is cooled down to the desired final temperatures of 300, 500, 700, and 900 K in 325 ps. A final thermalisation procedure is applied during 10 ns keeping a constant temperature with a csld (Bussi 2007) thermostat to avoid the flying ice cube artifact. A constant 1 fs integration time step is employed in the 300 and 500 K cases whereas at 700 and 900 K a smaller 0.5 fs time step was used to maintain the numerical stability of the simulations. The pressure is controlled along the z coordinate exclusively, keeping L_x and L_y box sizes fixed and allowing L_z to evolve isobarically ($P = 0$). The configurations of the system at the end of the thermalisation process at 300, 500, 700 and 900 K are shown in Figure 1.

We used first principles calculations based the density functional theory (DFT) to characterize the change of the electronic properties during the equilibration process simulated by MD simulations. Snapshots of the thermodynamic properties of the system as well as per atom dynamic values (coordinates, velocities, forces, etc.) are taken at 1 ps intervals for DFT DOS post-processing. The high value of first principles calculations is to derive the physical properties directly from the basic interactions without

introducing adjusting parameters. We use the PWscf (Plane-Wave Self-Consistent Field) code of the [Quantum ESPRESSO](#) suite (Giannozzi 2017; Giannozzi 2009) to relax the c-Si/a-Si:H/c-Si interface. Si and H ultrasoft pseudopotentials with Perdew-Burke-Ernzerhof (PBE) (Perdew 1996) approximant GGA exchange-correlation potential, available in the Quantum ESPRESSO library. The electronic wave functions were expanded in a plane-wave basis set with a kinetic energy cut-off equal to 40 Ry (the charge density cut-off was 240 Ry). The Brillouin zone integration for the self-consistent calculation is restricted to the Γ -point, which is justified by the sufficiently large super cell. Gaussian smearing of 0.08 Ry is needed to reach convergence due to defect states at the Fermi level.

To obviate to the intrinsic difficulty to calculate transport in the non-equilibrium Green functions approach for the large structures, we calculated the Hamiltonians which are the input for the quantum transport simulation using the Density Functional Tight Binding (DFTB) semi-empirical approach by the [DFTB+](#) code (Hourahine 2020) based on the [libNEGF](#) library. More details about the simulation algorithm can be found in (Pecchia 2018). In DFTB all Hamiltonian matrix elements between atomic orbitals are computed from first principles DFT, however neglecting the three center integrals allows for a very simple compilation of look-up tables making the Hamiltonian generation as fast as in empirical tight binding. Yet the accuracy of the approach has been proven over several decades of developments. For the calculations shown below a specifically tuned parametrization of Si has been developed that well reproduce the full bulk band structure (Markov 2015).

3 RESULTS AND DISCUSSION

In Figure 1 the configurations of the c-Si/a-Si:H/c-Si interface at the end of the thermalisation process at 300, 500, 700, and 900 K are shown. The distribution of the hydrogen atoms along the z direction is reported for comparison. We found that the number of hydrogen atoms present at the interface is 22 at $T = 300$ K and 23 at $T = 500, 700$, and 900 K, so that it is almost constant at all the temperatures investigated. The states within the energy gap of c-Si are found to be related to a-Si(p) orbitals. Therefore, it is useful to focus on the PDOS of a-Si(p) states to study the evolution of the intra-gap states. In order to monitor how intra-gap states change after the quenching, we show in Figures 2-5 the PDOS of the p-states of a-Si at $t = 0, 1, 4$, and 10 ns snapshots during the equilibration process. We observe a dense concentration of band tail and intra-gap peaks at the start of the equilibration ($t = 0$ ns). As the equilibration progresses, the PDOS peaks are narrowed and the corresponding intensity changes too. Overall, after the ReaxFF MD annealing, quenching, and equilibration, we have a decrease of the number of peaks. We found that the PDOS of the a-Si layers is modified in different ways by changing the thermalisation process. Narrowed peaks are evident for $T = 300$ K, and increasing the T of thermalisation the number of the peaks decreases. Increasing T to 700 and 900 K the intensity of the intragap states decreases too. However, intense peaks are always found nearby the Fermi energy level at 0 eV. In order to understand the behaviour observed in Figure 2, a coordination analysis of the Si atoms is performed. A geometrical criterion is used to identify the nearest neighbors in the coordination analysis, applying a distance cutoff of 2.85 Å and 1.7 Å for Si-Si pairs and for Si-H pairs, respectively. Concerning the $T = 300$ K at $t = 10$ ns snapshot, we found that 16 Si atoms have threefold coordination (1.4%), 1044 Si atoms have fourfold coordination (96.0%) and the remaining 28 Si atoms have fivefold coordination (2.6%). By increasing the thermalisation temperature the number of fourfold coordinated Si has a monotonous increase until to 1054 atoms (96.9%) at 900 K. In conclusion, after the thermalisation process the system is quite ordered with a high percentage of fourfold coordinated Si atoms, and this number increases by increasing the temperature. This is reflected by the decrease of the intensity of the peaks in the energy gap observed in Figures 2-5.

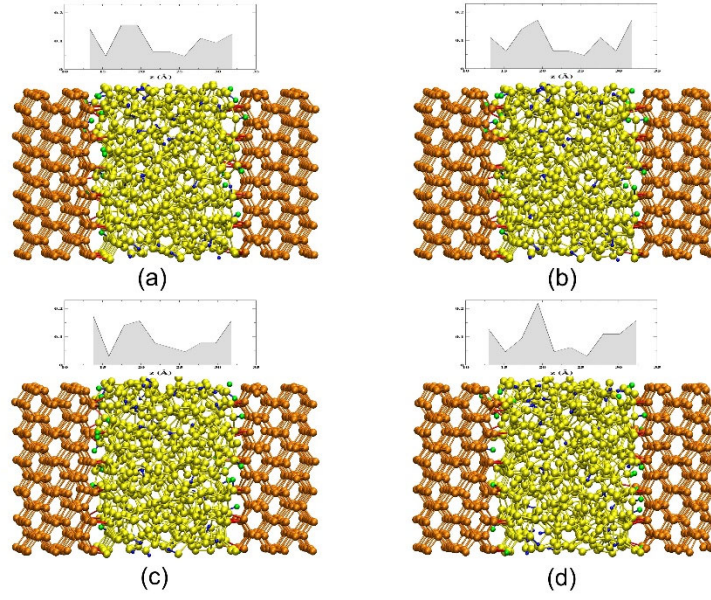


Figure 1: Snapshots of the c-Si/a-Si:H/c-Si interface at a) $T=300$ K; b) $T=500$ K; c) $T=700$ K; and d) $T=900$ K. Above the configurations, the distribution of the hydrogen atoms along the z direction are reported.

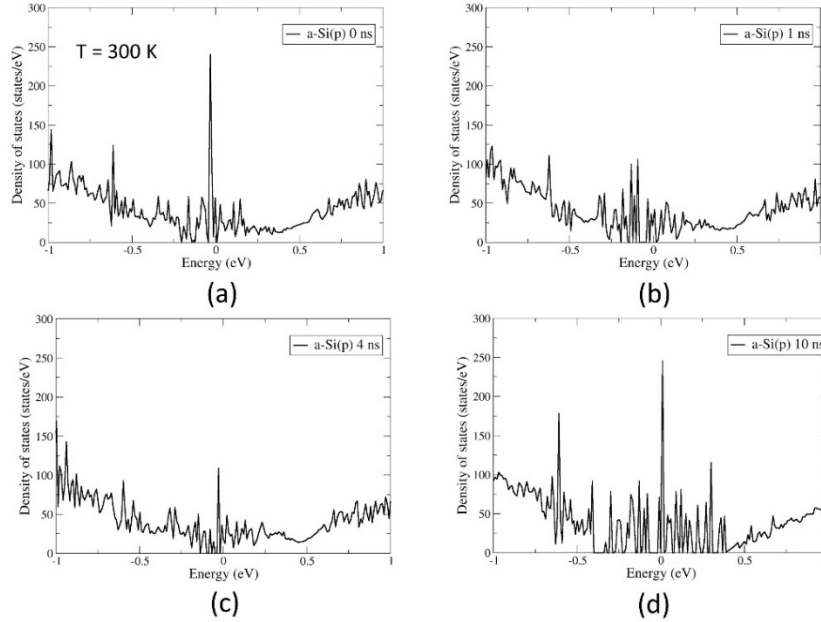


Figure 2: Projected density of states of amorphous silicon in the c-Si/a-Si:H/c-Si interface at a) 0, b) 1, c) 4 and d) 10 ns for $T=300$ K. The Fermi energy is at 0 eV.

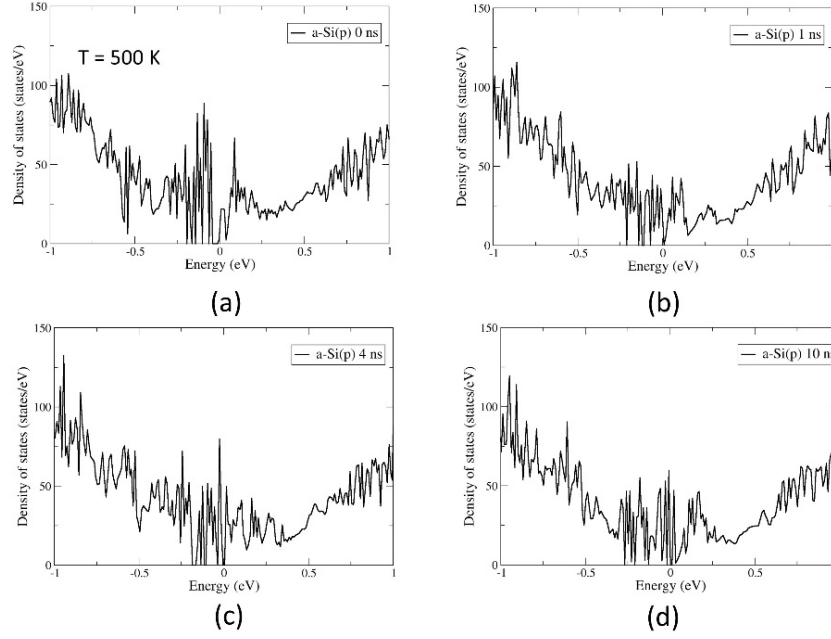


Figure 3: Projected density of states of amorphous silicon in the c-Si/a-Si:H/c-Si interface at a) 0, b) 1, c) 4 and d) 10 ns for $T = 500$ K. The Fermi energy is at 0 eV.

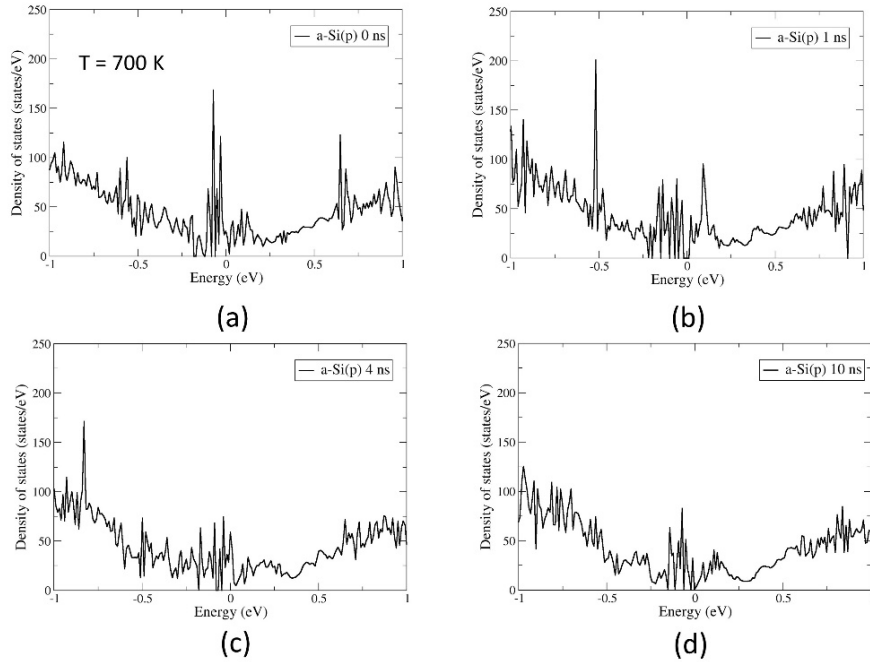


Figure 4: Projected density of states of amorphous silicon in the c-Si/a-Si:H/c-Si interface at a) 0, b) 1, c) 4 and d) 10 ns for $T = 700$ K. The Fermi energy is at 0 eV.

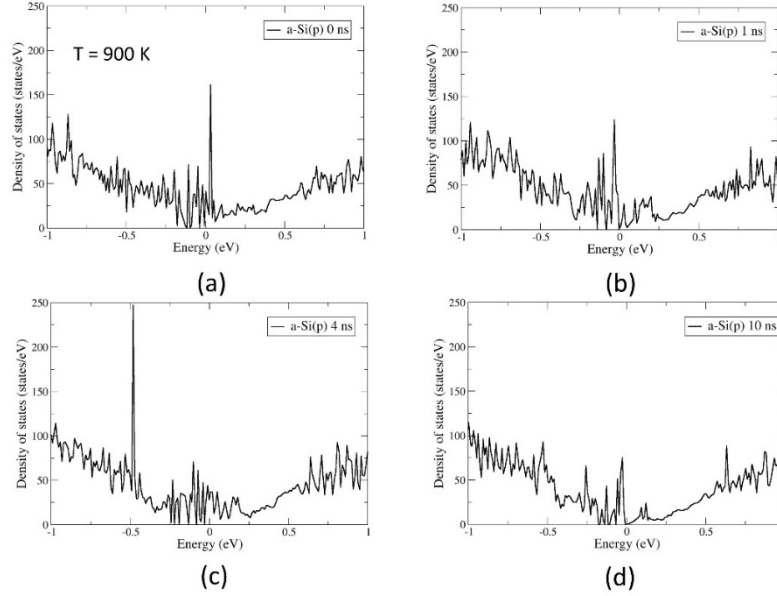


Figure 5: Projected density of states of amorphous silicon in the c-Si/a-Si:H/c-Si interface at a) 0, b) 1, c) 4 and d) 10 ns for T= 900 K. The Fermi energy is at 0 eV.

We plot the cumulative sum of the intragap p-states in Figure 6. We observe that the total number of the states in the energy gap decreases faster during the thermal annealing process by increasing the temperature. This finding, being in agreement with the observation of the decrease of the coordination defects, allows a quantitative evaluation of the reduction of defects. For example, the number of the intragap states has a 17% decrease during the T= 300 K thermalization and a 36% decrease during the T= 900 K thermalization.

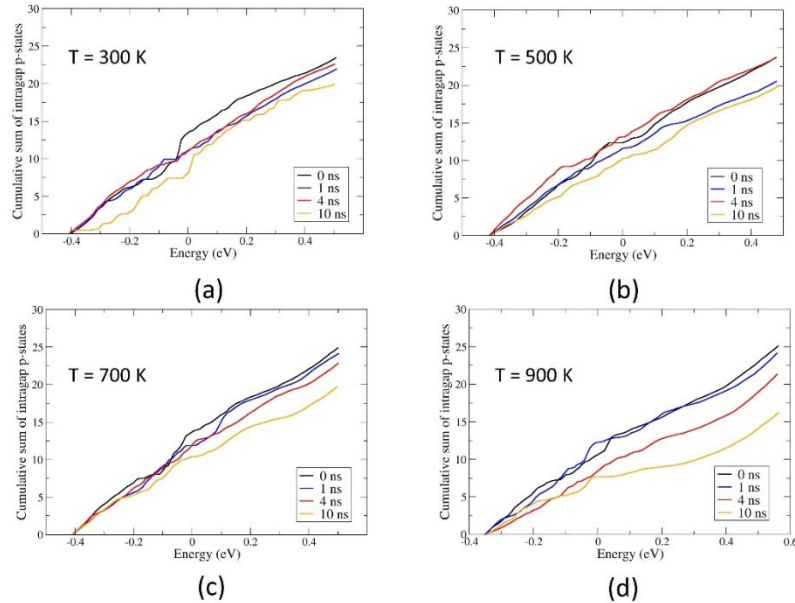


Figure 6: Cumulative sum of intragap p-states of the c-Si/a-Si:H/c-Si interface for a) T= 300 K, b) T= 500 K, c) T= 700 K and d) T= 900 K.

In Figure 7 we report the transmission function computed at temperature $T = 0$ K for the c-Si/a-Si:H/c-Si interface. The calculation is obtained with a 4×4 k-point sampling mesh in the direction transverse to transport. A sharp drop of transmission can be observed within the Si bandgap and is due to the gap of the ideal Si crystal. The sharp peaks within the gap are connected to the local density of states in the a-Si layer. This plot should be compared to the temperature dependent transmissions shown in Figure 8. For each line in the graph, we have considered the frozen geometry given by the last step obtained in the MD simulations at different temperatures, hence at $t = 10$ ns. Thermal noise in the atomic positions considerably increases the gap density of states, leading to a clear increase of transmission, compared to the more ordered c-Si phase obtained at 0 K. This increase is likely to be connected to the disorder in the c-Si contacting leads. On the other hand, also the amorphous layer sees an increase of PDOS with temperatures, but a decrease of PDOS at midgap. This well correlates with the decrease of transmission around the Fermi energy (-3.5 eV) that can be observed at 900 K and after 10 ns of annealing.

The disorder is also responsible for a sizeable increase of transmission both in the conduction and in the valence bands, albeit the latter is certainly less pronounced. This increase of transmission is directly related to an increase of percolation pathways in the a-Si that could be related to an increase of PDOS (see Figures 2-5), since disorder in the leads always reduces the transmission probability of the perfect crystal.

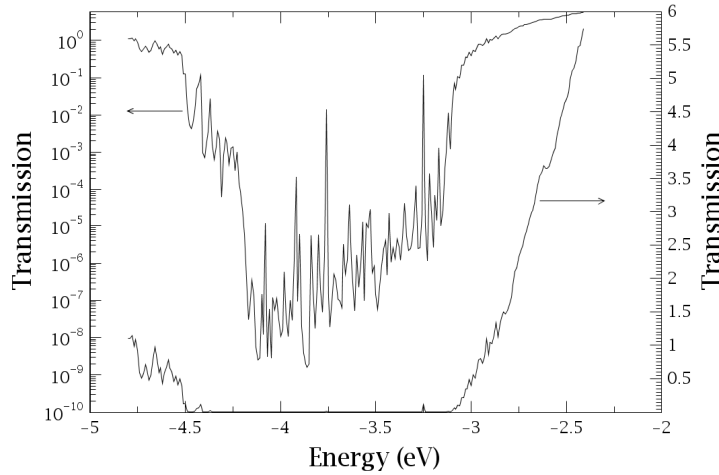


Figure 7: Transmission plot for the c-Si/a-Si:H/c-Si interface at $T = 0$ K (transmission is dimensionless).

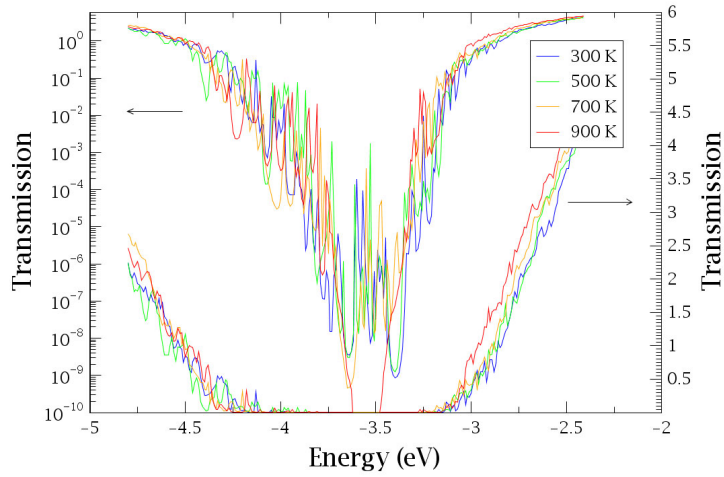


Figure 8: Transmission plot for the c-Si/a-Si:H/c-Si interface at increasing temperatures from $T= 300$ to 900 K (transmission is dimensionless).

4 CONCLUSIONS

In conclusion we apply transmission calculations to individual snapshots of ReaxFF MD simulations in order to investigate how intra-gap states of a large c-Si/a-Si:H/c-Si interface couple to bulk Si and how coherent states travel across the amorphous layer. These states have a crucial impact on the device performance due to their role as recombination centers. Throughout the annealing process, we monitor the evolution of the relevant structural and electronic properties and found that during the annealing process the PDOS in the gap decreases.

This work is a demonstration example of the capability of the combined MD/DFT/NEGF tools. The future goal is to include electron-photon and electron-phonon coupling via the related self-energies in the Green's functions. In the current status libNEGF can include elastic electron-phonon scattering and simple corrections to the transmission probability due to absorptions/emissions of photons. On the other hand, the implementation of inelastic electron/phonon scattering (e.g., optical phonons) will require important code improvements in the parallel communications in order to tackle problems of realistic size. This study paves the way to more accurate studies of the transport mechanisms in order to design more efficient silicon solar cells based on the SHJ technology.

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