

# Photo-Excited Charge Transfer Between A-Si:H/C-Si

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**Abstract** - Electron flow in hydrogenated amorphous silicon/crystalline silicon (a-Si:H/c-Si) heterojunctions under optical excitation is a key step in photovoltaic conversion. To date, the ability to visualize quantum kinetic changes and track the evolution of excited states over time has been limited by computational costs. In this work, we present the real-time time-dependent density functional tight-binding (TD-DFTB) method for the first time applied to a-Si:H/c-Si heterojunction systems of microscopic dimensions. The key role of phosphorus in the charge transfer process between heterojunctions is further confirmed by undoped and phosphorus-doped c-Si systems. The important role of hydrogen in the charge transfer process is also highlighted by the variation of hydrogen concentration, which drives the amount of charge transfer throughout the process, and the enhancement-decrease-enhancement pattern of charge separation and transfer throughout the process, indicating the importance of coherent vibrational coupling in the process.

**Keywords:** hydrogenated amorphous silicon, heterojunction, photo-excited, charge transfer, absorption spectrum, quantum simulation

## 1. Introduction

Despite advances in thin-film and various emerging solar cells, silicon-based solar cells still hold a very high market share (~95%) in the world PV market in 2019 **Error! Reference source not found.** due to many advantages such as abundant resources and high power conversion efficiency. In the beginning, Sanyo Corporation pioneered the development of a-Si:H/c-Si heterojunction solar cells [2] **Error! Reference source not found.**[3], after that, the utilization of interdigitated back contact (IBC) structure reduced the optical loss and made it possible to achieve a high conversion efficiency of 25.6% in 2014 [5]. Following continuous efforts, the efficiency of Si heterojunction cells have been continuously improved **Error! Reference source not found.****Error! Reference source not found.**, the high efficiency back contact hetero-structure has been improved in recent years to reach 26.7% **Error! Reference source not found.****Admittedly, these studies have greatly demonstrated the great potential of a-Si:H/c-Si heterojunction solar cells [8].**

However, it has been found in both homojunction [9] and a-Si:H/c-Si heterojunction [10] solar cells that apart from the effect of a-Si:H intrinsic defects, the interfacial defect states also strongly affect the stability and efficiency. Ahmad et al. [9] also confirmed that the photo-induced degradation (SWE) phenomenon of a-Si:H solar cell is not only a purely bulk phenomenon, but also the interface in which has a great influence on the instability and performance degradation of solar cells, and they experimented with the addition of a buffer layer at the p/i interface as a way to improve the stability and performance of thin film. Current studies basically believe that the most important role of a-Si:H is to passivate silicon surface or interfacial defects **Error! Reference source not found.****Error! Reference source not found.** and to selectively transfer photo-generated carriers and reduce electron and hole recombination to improve solar cell efficiency. However, photo-degradation effects of a-Si:H have so far remained to be solved. Photogenerated carriers and transport as the key to these studies to visualize the charge transfer between two semiconductors or at the interface will be expected.

Therefore, in this work, a novel research method is used to visualize the absorption spectra and the charge transfer between interfaces of a-Si:H/c-Si, including the amount and direction of charge transfer between heterojunctions. This method is a quantum dynamics approach using real-time time-dependent self-consistent charge density functional tight binding with the semi-classical Ehrenfest dynamics of nuclear-electron. This method has more reliable accuracy and acceptable computational resources than the widely used density generalized function theory (DFT) calculations and has been successfully applied in a large number of studies **Error! Reference source not found.****Error! Reference source not found.****Error! Reference source not found.****Error! Reference source not found.**

These studies stress the need to consider the nucleus motion in order to accurately describe the charge transfer processes in the system. whereas further understanding is needed for the a-Si:H related charge transfer quantum dynamics mechanism starting from the nuclear and electron motion promoting charge vibrational separation. To this end, we investigated the photo-induced charge transfer process with time evolution between a-Si:H/c-Si with different hydrogen concentrations to make a reference for further resolution of the photo-degradation effect.

## 2. Methods

We investigated the ground state of the a-Si:H/c-Si system based on the self-consistent charge density functional theory (DFT) combined with the tight binding (TB) models **Error! Reference source not found..** All DFTB quantum simulation calculations in this work are performed through DFTB+ code [19] , by utilizing the DFTB+ package with the matsci-0-3 parameter set [21] in the second-order SCC-DFTB.

### 2.1. Preparation of Sample

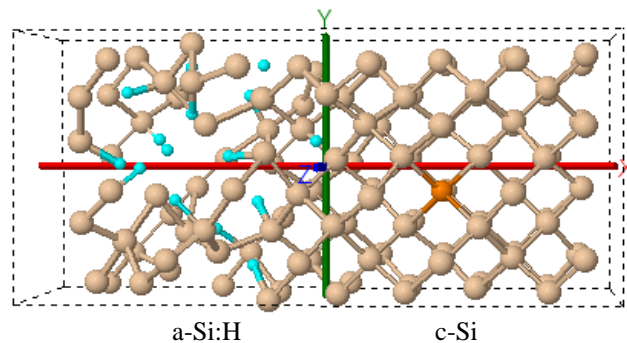
We focus on fairly small systems of a-Si:H/c-Si with various hydrogen concentrations (Fig. 1), the total number of atoms is 128. The preparation and structural configuration of the a-Si:H model is the same as in previous studies **Error! Reference source not found.**The c-Si model investigates both intrinsic crystalline silicon (c-Si(i)) and n-type crystalline silicon (c-Si(n)). The c-Si(n) is obtained by arbitrarily replacing one silicon atom with one phosphorus atom in the structure and then performing molecular dynamics (MD) calculations together with a-Si:H. The cell size is fixed to be  $21.724 \times 10.862 \times 10.862 \text{ \AA}^3$ . The periodic boundary conditions are assumed for all directions. The equations of motion were integrated using the Velocity Verlet algorithm with a time step of 0.5 fs. Using NoseHoover thermostat to control the temperature to 300 K and 500 steps MD calculation.

### 2.2. Optical Absorption and Charge Transfer Dynamics

Optical absorption and charge transfer dynamics are calculated by the real-time time-dependence DFTB method in combination with the semiclassical Ehrenfest method of nuclear-electron dynamics. Absorption spectroscopy is investigated by introducing a Dirac delta pulse for single-electron density matrix propagation in the linear response regime. After applying the pulse, the density matrix evolves with time **Error! Reference source not found.****Error! Reference source not found.** Applying a very small electric field, in the linear response region, the absorption spectrum of the system and the dipole moment will be obtained:

$$\mu(t) = \int_{-\infty}^{\infty} \sigma(t - \tau) E(\tau) d\tau \quad (1)$$

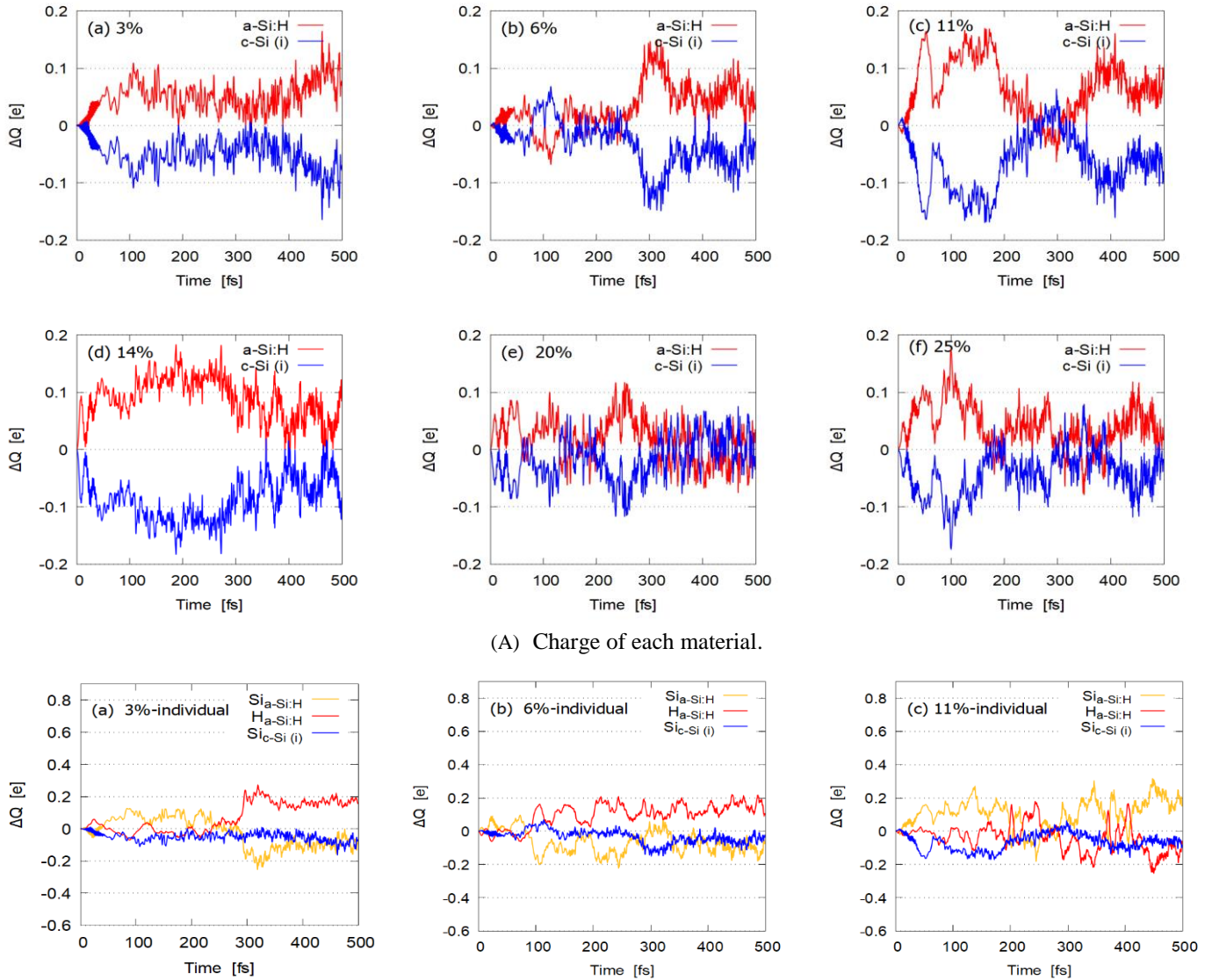
where  $\sigma(t - \tau)$  is the polarizability along the axis over which the external field  $E(t)$  is applied. or in the frequency domain. In the present work, in the linear response regime, we applied an electric field strength of  $0.001 \text{ V/\AA}$  and propagated 400 fs with the time step set to 0.01 fs. and applied an exponential damping with a time constant of 5 fs to convert it to frequency space after the propagation was completed.

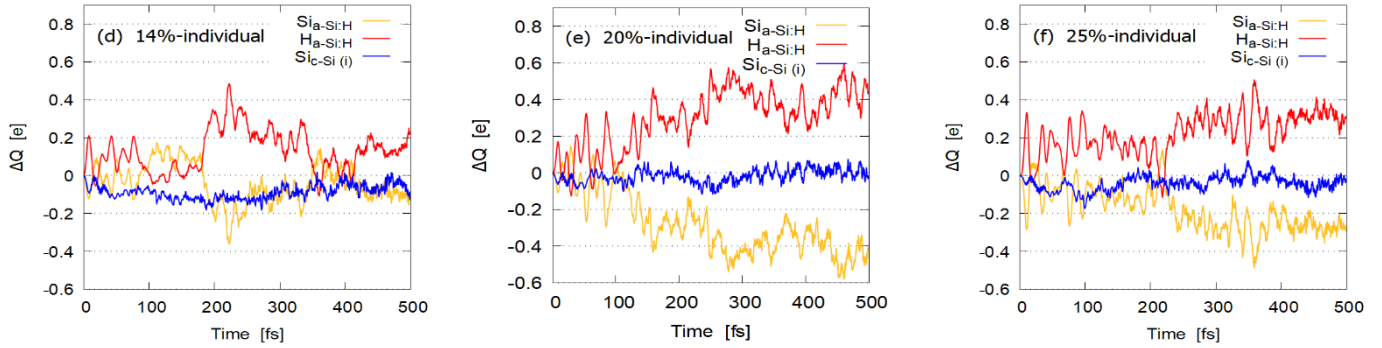


Moreover, in order to investigate the photo-excited charge transfer process between heterojunctions, the nucleus motion was emphasized **Error! Reference source not found.****Error! Reference source not found.**[19] . In this work, a sinusoidal  $\sin^2$  pulse shape perturbation is added to the Hamiltonian quantities to simulate the experimental laser pulse.

And the vector associated with the excitation resonance to produce the maximum absorption was used. For the hydrogen concentration investigations, a laser energy of 670 nm (1.85 eV) was chosen. In all cases, an electric field intensity of 0.01 V/Å and a time step of 0.2065 fs were set. The initial temperature of 300 K, pulse duration of 50 fs, and total 500 fs time range for charge transfer were evaluated.

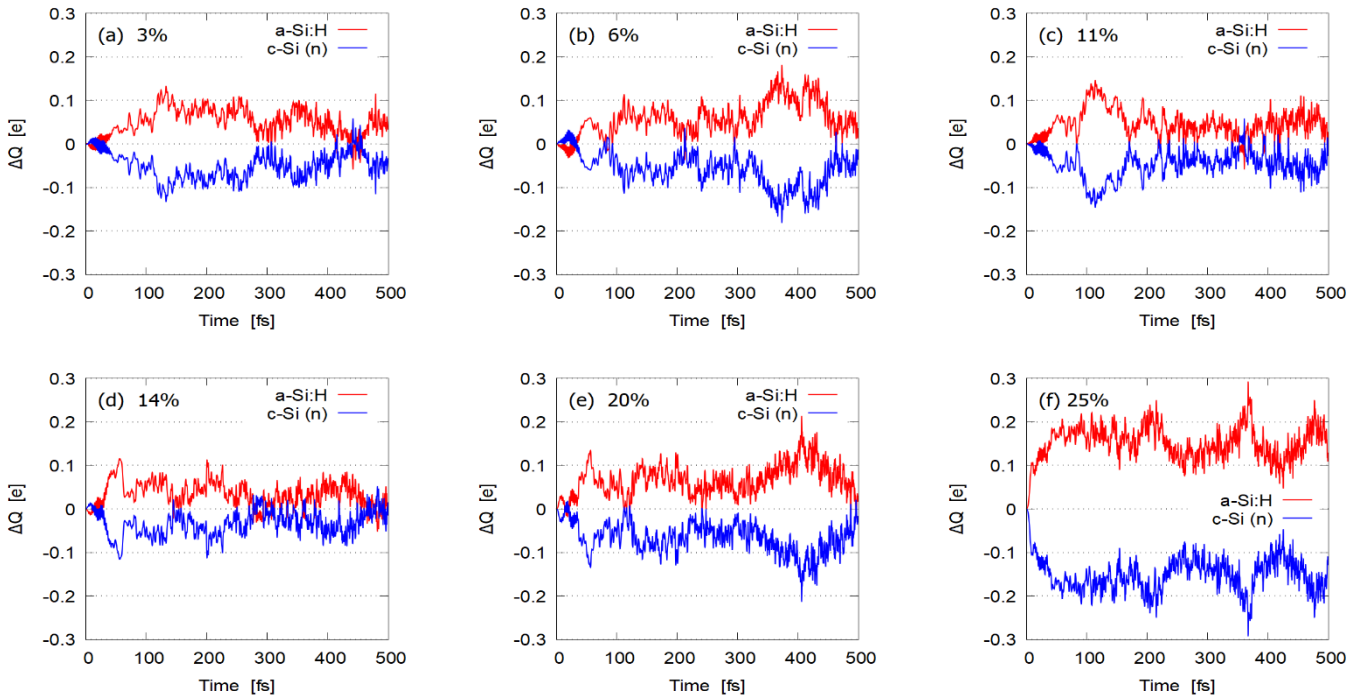
Fig. 1: Example of a-Si:H/c-Si system. The beige, cyan, and orange represent the Si, H, and P atoms, respectively.



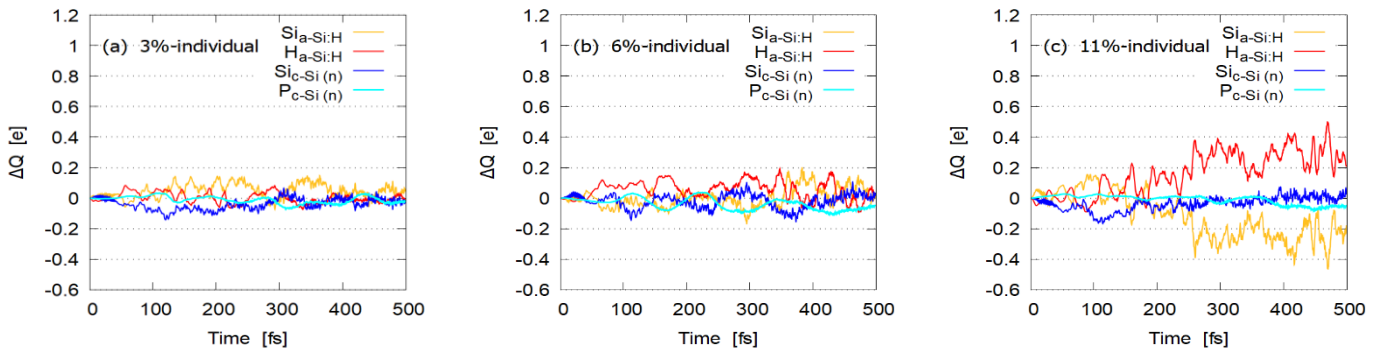


(B) Charge of each element.

Fig. 2: Charge as a function of time for a-Si:H/c-Si (i) system with various hydrogen concentrations.



(A) Charge of each material.



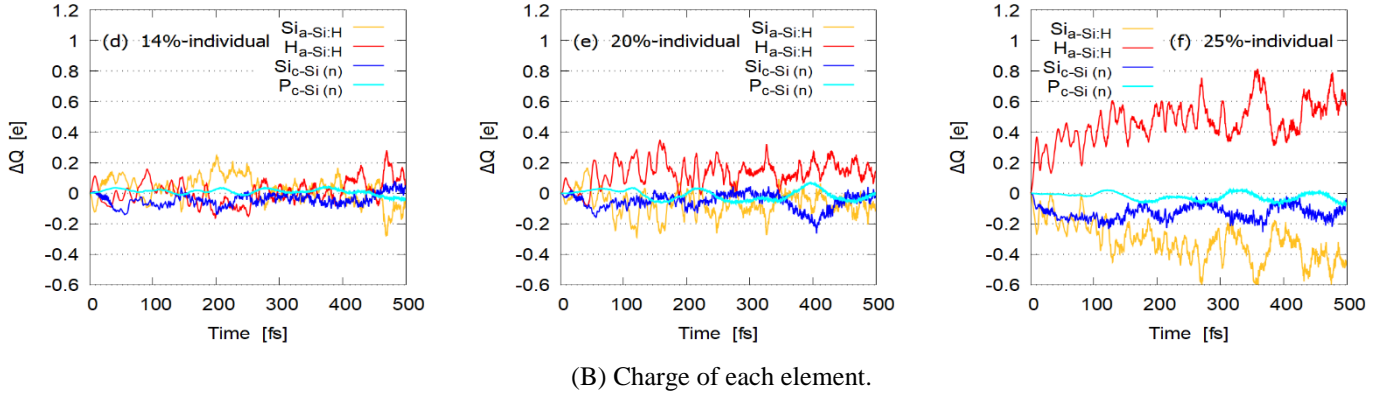


Fig. 3: Charge as a function of time for a-Si:H/ c-Si (n) system with various hydrogen concentrations.

### 3. Results and Discussion

#### 3.1 Effect of hydrogen concentration on charge transfer mechanism

Intrinsic a-Si:H is generally used as a passivation layer for silicon heterojunctions, which can effectively reduce the defect states on the surface of c-Si. Thus, we describe in detail the potential electron transfer that occurs after light irradiation by a real-time TD-DFTB electron dynamics method, which visualizes the amount and direction of charge transfer and reveals the role of hydrogen concentration on the photogenerated charge separation and transfer between a-Si:H/c-Si (Fig. 2).

Since the bandgap of a-Si:H is about 1.85 eV, we focused on the hydrogen concentration dependence of the a-Si:H/c-Si system at this photon energy. Fig. 2 shows the evolution of the Mulliken charge distribution generated by the photoexcitation of the a-Si:H/ intrinsic c-Si system under the perturbation of a 50 fs width pulsed electric field. The overall a-Si:H  $\Delta Q$  curve shows a positive value (i.e. the loss of electrons), while the intrinsic c-Si has a negative value (i.e. the gain of electrons). The charge separation and transfer between a-Si:H and c-Si are extremely unstable within the examined time window in Fig. 2(A), especially in the case of samples with increasing hydrogen concentration, the charges are separated and then recombined again, a-Si:H and c-Si keep switching between the roles of gain and loss of electrons, and the charges have failed to reach a complete separation. The result indicates that the electron-nucleus interactions, vibrational coupling between the two materials, and charge separation evolve with time in an enhanced-diminished interaction pattern, which also implies interatomic interactions and energy transfer.

It is also evident from the detailed charge transfer of individual atomic species in Fig. 2(B) that the charge transfer of hydrogen increases significantly with increasing hydrogen concentration and the charge transfer changes are large, demonstrating that hydrogen concentration plays an important role in the charge transfer mechanism.

Next, in view of the less desirable charge transfer behavior between a-Si:H and intrinsic c-Si, we attempted the more applicable n-type c-Si system. Fig. 3 shows the evolution of the Mulliken charge distribution generated by photoexcitation of the a-Si:H/ n-type c-Si system. The results show (Fig. 3(A)) that although there are also strong fluctuations in charge separation and transfer between a-Si:H and n-type c-Si within the investigated time window, the n-type c-Si system demonstrates a slightly better charge separation performance compared to the intrinsic c-Si, indicating that phosphorus plays an important role in the photo-excited charge separation and transfer process. which is associated with more efficient charge separation and transfer.

In addition, it is observed in combination with a more detailed contribution of individual atomic species (Fig. 3(B)) that an increase in hydrogen concentration increases the charge transfer of hydrogen, driving an increase in the charge transfer of the whole system, a more stable charge transfer from a-Si:H to n-type c-Si, and rapid and complete charge separation in the 25% system.

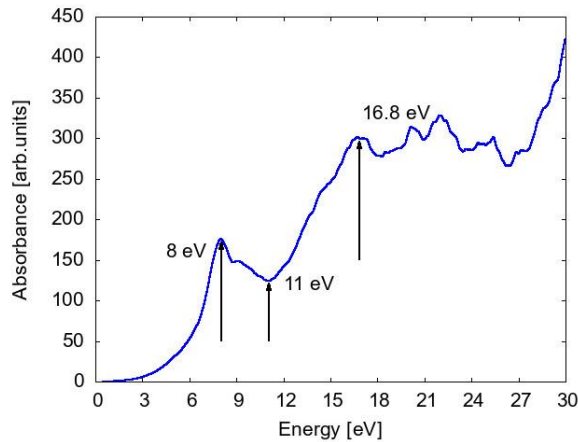
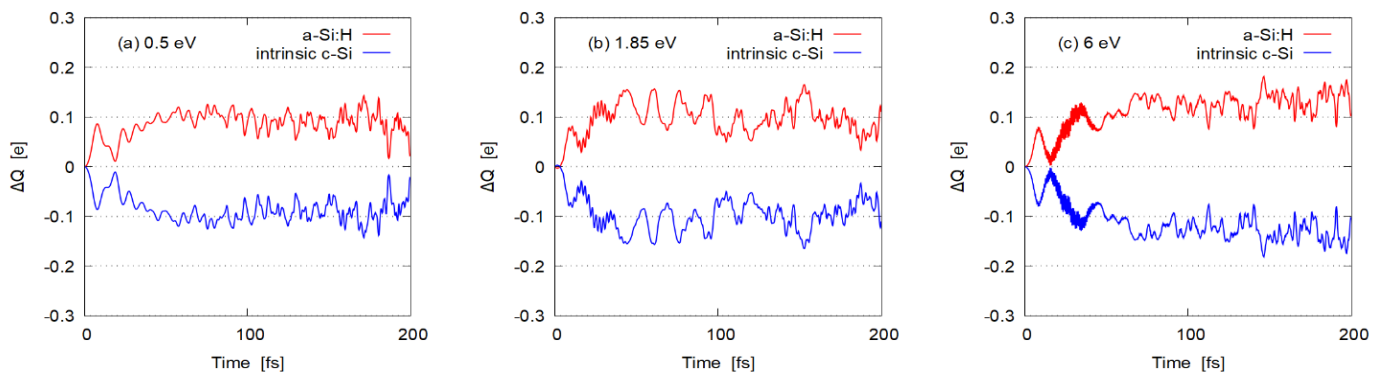


Fig. 4: Absorption spectrum for a-Si:H/c-Si (i) system with 14% hydrogen concentration.

### 3.2 Charge transfer at different photon energies

Fig. 4 shows the absorption spectrum of the a-Si:H/intrinsic c-Si system with 14% hydrogen concentration. In the wide energy range investigated, the absorbance of the system increases with increasing energy. However, it is observed that there are clear absorption peaks at 8 eV and 16.8 eV, with an absorption valley at 11 eV. Consequently, we investigated the charge separation of the system at different photon energies (Fig. 5). It can be noted that at less than 8eV, it is most obvious that the energy magnitude affects the frequency of the laser pulse and that the charge transfer is relatively stable after the end of the pulse (50fs). However, the charge separation transfer fluctuations become relatively strong at 8 eV energy, and the charge transfer increases significantly at 16.8 eV. Moreover, at the 11 eV absorption valley, the charge separation and transfer appear very large fluctuations, and after the charge transfer rapidly reaches the maximum at the end of the pulse, the charge transfer amount rapidly decreases to 0 e. During the transfer of energy, there is again a gradual increase in charge separation and transfer, showing a large vibrational coupling effect. Therefore, photon energy also plays a role in charge separation and transfer.



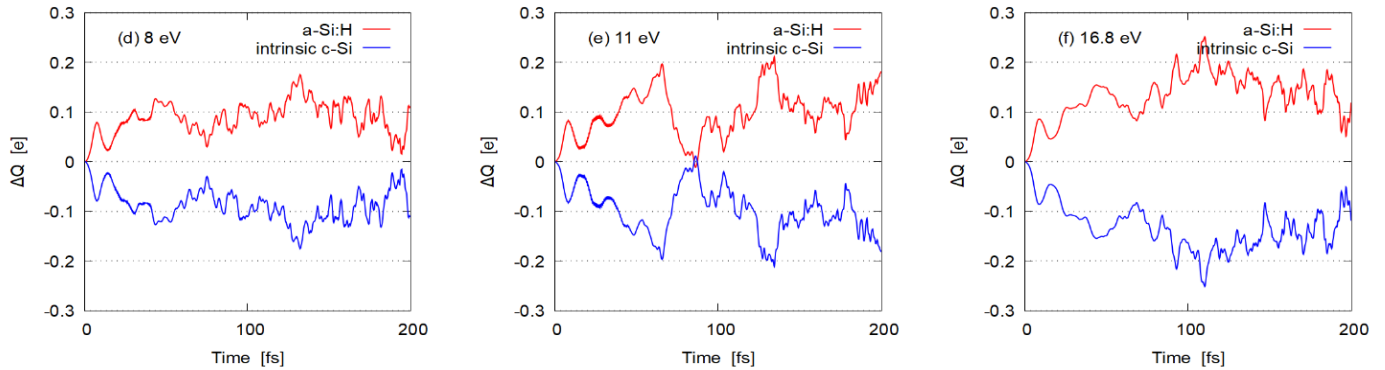


Fig. 5: Charge as a function of time for a-Si:H/c-Si (i) system with various energy for 14% hydrogen concentration.

#### 4. Conclusion

In this work, a fast and economical Ehrenfest dynamic method based on real-time TD-DFTB is presented to investigate the photo-excited charge separation and transfer between a-Si:H/c-Si heterojunctions. The whole process is divided into a three-step mechanism: (i) the initial stage, where electrons are excited after light irradiation. (ii) Charge separation, where a small amount of charge is transferred from a-Si:H to c-Si, or continuously converted to each other. (iii) Complete charge separation, with relatively stable charge transfer from a-Si:H to c-Si. In conclusion, the results illustrated intuitively the ultrafast charge separation and transfer process under excitation. The charge in the system as a whole was transferred from a-Si:H to c-Si with relatively large fluctuations throughout the process, but the n-type c-Si heterojunction system showed slightly better performance than the intrinsic c-Si system, demonstrating that the phosphorus doping effectively promoted the charge separation and transfer process. On the other hand, hydrogen concentration plays an important role in the heterojunction system, driving the increase in the amount of charge transfer in the system as the hydrogen concentration increases. The negative effect of structural disorder is slightly reflected in the charge transfer process of the intrinsic c-Si heterojunction system, but the effect is small in the n-type c-Si system. Photon energy also has an important role in charge separation and transfer; the importance of coherent vibrational coupling in the enhancement-diminution-enhancement process of charge separation and transfer is evident. The calculation method used in this work shows the microscopic changes between heterojunctions in a very intuitive way, which can be useful for further improvement of efficiency.

#### References

- [1] Y. Liu, Y. Li, Y. Wu, G. Yang, L. Mazzarella, P. Procel-Moya, A. C. Tamboli, K. Weber, M. Boccard, O. Isabella, X. Yang, and B. Sun, "High-Efficiency Silicon Heterojunction Solar Cells: Materials, Devices and Applications", *Materials Science and Engineering: R: Reports*, vol. 142, p. 100579, 2020.
- [2] T. Sawada, N. Terada, S. Tsuge, T. Baba, T. Takahama, K. Wakisaka, S. Tsuda, and S. Nakano, "High-Efficiency a-Si/c-Si heterojunction solar cell," in *Proceedings of 1994 IEEE 1st World Conference on Photovoltaic Energy Conversion - WCPEC (A Joint Conference of PVSC, PVSEC and PSEC)*, vol.2, pp. 1219-1226, 1994.
- [3] M. Taguchi, A. Terakawa, E. Maruyama, and M. Tanaka, "Obtaining a higher Voc in HIT cells", *Progress in Photovoltaics: Research and Applications*, vol. 13, no. 6, pp. 481-488, 2005.
- [4] M. Taguchi, A. Yano, S. Tohoda, K. Matsuyama, Y. Nakamura, T. Nishiwaki, K. Fujita, and E. Maruyama, "24.7% Record Efficiency HIT Solar Cell on Thin Silicon Wafer", *IEEE Journal of Photovoltaics*, vol. 4, no. 1, pp. 96-99, 2014.
- [5] K. Masuko, M. Shigematsu, T. Hashiguchi, D. Fujishima, M. Kai, N. Yoshimura, T. Yamaguchi, Y. Ichihashi, T. Mishima, N. Matsubara, T. Yamanishi, T. Takahama, M. Taguchi, E. Maruyama, and S. Okamoto, "Achievement of More Than 25% Conversion Efficiency With Crystalline Silicon Heterojunction Solar Cell", *IEEE Journal of Photovoltaics*, vol. 4, no. 6, pp. 1433-1435, 2014.

- [6] K. Yoshikawa, H. Kawasaki, W. Yoshida, T. Irie, K. Konishi, K. Nakano, T. Uto, D. Adachi, M. Kanematsu, H. Uzu, and K. Yamamoto, “Silicon heterojunction solar cell with interdigitated back contacts for a photoconversion efficiency over 26%”, *Nature Energy*, vol. 2, no. 5, p. 17032, 2017.
- [7] D. Adachi, J. L. Hernández, and K. Yamamoto, “Impact of carrier recombination on fill factor for large area heterojunction crystalline silicon solar cell with 25.1% efficiency”, *Applied Physics Letters*, vol. 107, no. 23, p. 233506, 2015.
- [8] K. Yamamoto, K. Yoshikawa, H. Uzu, and D. Adachi, “High-efficiency heterojunction crystalline Si solar cells”, *Japanese Journal of Applied Physics*, vol. 57, no. 8S3, pp. 08RB20, 2018.
- [9] M. Taguchi, “Review—Development History of High Efficiency Silicon Heterojunction Solar Cell: From Discovery to Practical Use”, *ECS Journal of Solid State Science and Technology*, vol. 10, no. 2, p. 025002, 2021.
- [10] G. Ahmad, G. Das, and J. N. Roy, “Performance and stability improvement of single junction a-Si:H solar cell by interface engineering”, *Journal of Materials Science: Materials in Electronics*, vol. 30, no. 13, pp. 12406–12415, 2019.
- [11] Z. P. Ling, J. Ge, R. Stangl, A. G. Aberle, and T. Mueller, “Detailed Micro Raman Spectroscopy Analysis of Doped Silicon Thin Film Layers and Its Feasibility for Heterojunction Silicon Wafer Solar Cells”, *Journal of Materials Science and Chemical Engineering*, vol. 1, no. 5, pp. 1–14, 2013.
- [12] M. Z. Burrows, U. K. Das, R. L. Opila, S. De Wolf, and R. W. Birkmire, “Role of hydrogen bonding environment in a-Si:H films for c-Si surface passivation”, *Journal of Vacuum Science & Technology A*, vol. 26, no. 4, pp. 683–687, 2008.
- [13] J. Panigrahi and V. K. Komarala, “Progress on the intrinsic a-Si:H films for interface passivation of silicon heterojunction solar cells: A review”, *Journal of Non-Crystalline Solids*, vol. 574, p. 121166, 2021.
- [14] F. P. Bonafé, B. Aradi, B. Hourahine, C. R. Medrano, F. J. Hernández, T. Frauenheim, and C. G. Sánchez, “A Real-Time Time-Dependent Density Functional Tight-Binding Implementation for Semiclassical Excited State Electron–Nuclear Dynamics and Pump–Probe Spectroscopy Simulations”, *Journal of Chemical Theory and Computation*, vol. 16, no. 7, pp. 4454–4469, 2020.
- [15] M. B. Oviedo, C. F. A. Negre, and C. G. Sánchez, “Dynamical simulation of the optical response of photosynthetic pigments”, *Physical Chemistry Chemical Physics*, vol. 12, no. 25, p. 6706, 2010.
- [16] D. M. Marquez and C. G. Sánchez, “Quantum efficiency of the photo-induced electronic transfer in dye–TiO<sub>2</sub> complexes”, *Physical Chemistry Chemical Physics*, vol. 20, no. 41, pp. 26280–26287, 2018.
- [17] A. Domínguez-Castro, C. R. Lien-Medrano, K. Maghrebi, S. Messaoudi, T. Frauenheim, and A. Fihey, “Photoinduced charge-transfer in chromophore-labeled gold nanoclusters: quantum evidence of the critical role of ligands and vibronic couplings”, *Nanoscale*, vol. 13, no. 14, pp. 6786–6797, 2021.
- [18] C. R. Medrano, M. B. Oviedo, and C. G. Sánchez, “Photoinduced charge-transfer dynamics simulations in noncovalently bonded molecular aggregates”, *Physical Chemistry Chemical Physics*, vol. 18, no. 22, pp. 14840–14849, 2016.
- [19] A. S. Christensen, T. Kubař, Q. Cui, and M. Elstner, “Semiempirical Quantum Mechanical Methods for Noncovalent Interactions for Chemical and Biochemical Applications”, *Chemical Reviews*, vol. 116, no. 9, pp. 5301–5337, 2016.
- [20] B. Hourahine, B. Aradi, V. Blum, F. Bonafé, A. Buccheri, C. Camacho, C. Cevallos, M. Y. Deshayé, T. Dumitrică, A. Domínguez, S. Ehlert, M. Elstner, T. Van Der Heide, J. Hermann, S. Irle, J. J. Kranz, C. Köhler, T. Kowalczyk, T. Kubař, I. S. Lee, V. Lutsker, R. J. Maurer, S. K. Min, I. Mitchell, C. Negre, T. A. Niehaus, A. M. N. Niklasson, A. J. Page, A. Pecchia, G. Penazzi, M. P. Persson, J. Řezáč, C. G. Sánchez, M. Sternberg, M. Stöhr, F. Stuckenberg, A. Tkatchenko, V. W.-Z. Yu, and T. Frauenheim, “DFTB+, a software package for efficient approximate density functional theory based atomistic simulations”, *The Journal of Chemical Physics*, vol. 152, no. 12, p. 124101, 2020.
- [21] <https://www.dftb.org/parameters/>
- [22] H. Li and M. Matsumoto, “Electronic transport properties of a-Si:H”, *AIP Advances*, vol. 12, no. 3, p. 035309, 2022.