

Singlet exciton fission-enhanced silicon photovoltaics: Interfacial engineering, device design and spectroscopic technique development

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The growing global energy demand combined with resource and space limitations necessitate enhancements in crystalline silicon solar cells, which are the current dominant solar technology. However, their efficiencies have only increased incrementally over the recent 20 years, as they are starting to approach the theoretical efficiency limit. The main source of loss is thermalization, where energy in excess of the bandgap absorbed by silicon is lost as heat. Singlet exciton fission in organic molecules has been proposed to reduce these losses. By having the organic layer absorb the high energy light and transferring the triplet excitons generated from the singlet fission process to silicon, the photocurrent in this spectral region can be doubled, with the potential of raising the efficiency from the traditional limit of 29.4 % to up to 42 %.

The greatest challenge with these devices has been to demonstrate an increase in the silicon photocurrent, a necessary condition to show that the technology is viable. Scientifically, there are three main components to this problem. The first is to successfully couple the triplet excitons to silicon. The second is that not much is understood regarding the exciton and charge carrier dynamics at this interface. Finally, the silicon solar cell architecture should also be considered to extract transferred carriers effectively.

We tackle these three parts from an interfacial materials, device architecture and spectroscopy approach. From an interfacial materials standpoint, we follow up on previously reported hafnium oxynitride (HfO_xN_y) thin films which enabled triplet exciton sensitization of silicon by tetracene, but the mechanism for the transfer process was not well understood. We show that the composition of this layer affects the sensitization process, and through a combination of density functional theory calculations and magnetic field-dependent silicon photoluminescence measurements, identify that defect-induced states that lie near the band edge of silicon are beneficial for the triplet exciton transfer process, potentially mediating a sequential charge transfer process. However, our studies also reveal that the HfO_xN_y layer can introduce a variety of mid-gap states that quench the silicon photoluminescence, acting detrimentally to the overall silicon performance. We also identify that electric field-effect passivation is beneficial for the triplet sensitization process, preventing transferred carriers from recombining at the interface – as a result, we design a bilayer interface between the tetracene and silicon layers consisting of a donor layer which introduces an energy level near the valence band edge of n-doped silicon such that charge separation is energetically supported from the triplet exciton state in tetracene, and an ultra-thin passivating layer that chemically passivates dangling bonds on the silicon surface. Using zinc phthalocyanine as the donor layer and either aluminum oxide as the passivating layer, we observe evidence for triplet excitons generating electric field-effect passivation, benefiting the silicon photoluminescence.

From a device architecture standpoint, we use our donor-passivation interface and apply it to various silicon solar cell architectures. We find that the silicon-tetracene heterojunction cells face challenges related to morphology of the tetracene layer, resulting in suboptimal device performance. We observe no evidence of enhancements from singlet fission in interdigitated-back-contact cells, suggesting that this device structure is not sensitive to surface carriers in silicon. Indeed, when we switch to microwire and shallow junction planar solar cells with pyramidal surface texturing, both devices designed to efficiently extract silicon surface charge carriers, we

observe enhancements in the silicon device external quantum efficiencies and photocurrent from tetracene. Additionally, we perform silicon doping dependence studies and interlayer knockout controls, confirming the importance of the interfacial energy alignment and the donor layer, as well as the device architecture.

From a spectroscopy standpoint, we work on techniques that can be used to better understand the exciton and carrier dynamics of the singlet fission-donor-passivation-silicon structure. To better understand carrier transport in bulk materials, we detail a numerical framework for robust estimation of carrier diffusivity. To better understand interfacial charge transport, we build a transient second harmonic generation spectroscopy setup. Finally, we probe early timescale dynamics of excitonic processes in tetracene using transient absorption and reflection, confirming that the singlet fission process in tetracene is not affected by the addition of the various donor, passivation and silicon layers. Our studies also reveal that the triplet transfer and electric field-effect passivation is occurring at timescales beyond the first 10 ns of excitation, opening up the studying of these interfaces to slower spectroscopy experiments, not limited to ultrafast time scales.

These results have shown that singlet fission-sensitized silicon solar cells are a viable technology for enhancing silicon solar cell efficiencies beyond the conventional single junction limit. This interface remains a rich area for fundamental scientific studies, involving coupling between molecular dark states to bulk silicon. We hope that the key findings can help direct research efforts towards scalable implementation of this technology, and stress that the fundamental understanding of the interface also has broad implications to other silicon technologies that can benefit from enhanced quantum yields, including photodetectors.

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