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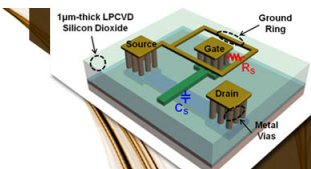
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# Hybrid pentacene/a-silicon solar cells utilizing multiple carrier generation via singlet exciton fission

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Silicon dominates the solar cell market because of its abundance, mature production processes, and high efficiencies, with the best solar cells approaching the Shockley-Queisser limit. Multiple exciton photogeneration provides a route to solar cells that surpass the Shockley-Queisser limit, and we report the use of pentacene, for which photogenerated singlet excitons rapidly convert into two lower-energy spin-triplet excitons. We report solar cells that couple amorphous silicon to pentacene. We show that a thin layer of nanocrystals between silicon and pentacene allows simultaneously harnessing low-energy photons absorbed in silicon and high-energy photons absorbed in pentacene, generating two excitons via singlet fission. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4757612>]

Five decades of research have taken silicon solar cell efficiencies<sup>1</sup> close to the Shockley-Queisser limit<sup>2</sup> for single-junction solar cells. This limitation occurs primarily because the energy extracted per photon is limited by the semiconductor bandgap. Strategies to overcome this limitation are called for. Tandem solar cells are well-established and reach efficiencies exceeding 30% (40% under concentrated sunlight).<sup>1</sup> A tandem solar cell consists of two individual cells that need to be current-matched. Hence, they are expensive to produce, limiting them to niche applications such as concentrator systems and space applications. A single-junction solar cell that incorporates a material producing more than one low-energy carrier per absorbed high-energy photon can, in principle, exceed the Shockley-Queisser limit when this is coupled to a semiconductor that makes use of the low-energy photons.<sup>3–5</sup> Semiconductor nanocrystals have been shown to generate multiple carriers from high-energy photons.<sup>6–9</sup> A parallel development is the use of singlet exciton fission to produce pairs of triplet excitons in organic semiconductors.<sup>3,10</sup> We use pentacene as an example of an organic semiconductor with efficient, fast, and spontaneous singlet exciton fission.<sup>11–13</sup> We have demonstrated infrared nanocrystal solar cells sensitized with pentacene,<sup>14</sup> and we report here how we can couple such structures to silicon, demonstrating the scope to improve on a well-established silicon solar cell technology.

Amorphous silicon (a-Si) solar cells have made good progress though efficiencies of 9–10% (Ref. 15) (and 13% in a silicon-germanium triple junction<sup>16</sup>) still lag behind crystalline silicon.<sup>17,18</sup> Here we use a-Si because of its large absorption coefficient and low-cost deposition. The bandgap of a-Si cannot be described with a simple energy band picture as the non-periodic structure results in tailing of the energy bands. In addition, defect states within the bandgap due to dangling bonds impose further uncertainty on the band structure.<sup>19</sup> Therefore, a rational design for solar cell behavior in a heterojunction between a-Si and other

semiconductors is difficult. Empirically, however, Klimov and co-workers have shown that a solar cell with a bilayer heterojunction between a-Si and lead sulfide (PbS) nanocrystals of bandgap 1.1 eV shows efficiencies less than 0.5%.<sup>20</sup> A similar approach has been used to fabricate solar cells from *n*-doped crystalline silicon nanotips and PbS nanocrystals with efficiencies approaching 2%.<sup>21</sup> Crystalline silicon has also been used with organic semiconductors such as P3HT (Ref. 22) or PEDOT:PSS,<sup>23</sup> yielding promising efficiencies. We note however that the organic semiconductors used so far are not capable of singlet exciton fission. We have shown previously that triplet excitons from pentacene can be harvested using lead selenide nanocrystals with a bandgap as high as 1.1 eV.<sup>24</sup> Here we use the 1.1 eV PbSe nanocrystals as an interlayer to extract the electrons from triplet excitons in pentacene and the holes from a-Si. These trilayer solar cells were produced by evaporating 50 nm pentacene on ITO/glass substrates followed by deposition of a 25–50 nm nanocrystal layer by successive cycles of spin-coating and crosslinking with 1,3-benzenedithiol. A layer of 100 nm amorphous silicon was then DC-magnetron sputter coated on top of the nanocrystal layer followed by thermal evaporation of an aluminum top electrode. Full experimental details are given as supplementary information.<sup>25</sup> From the good performance of the PV devices reported below, we consider that the PbSe nanocrystals protect pentacene during a-silicon deposition. Figure 1 shows the device structure and proposed working mechanism.

Singlet excitons in pentacene have been shown to undergo fission within 80 fs.<sup>13</sup> The fission process in pentacene is hence expected to show efficiencies close to unity due to the lack of competing loss processes at this time-scale.<sup>3</sup> This is consistent with high external quantum efficiencies from pentacene<sup>26–30</sup> and the energy available from the pentacene excitation.<sup>24</sup> We can hence attribute any photocurrent observed from pentacene absorption to dissociation of triplet excitons generated via singlet fission.

Figure 2(a) shows the external quantum efficiency (EQE) spectrum of the trilayer solar cell in comparison to a solar cell that does not contain silicon and one that does not

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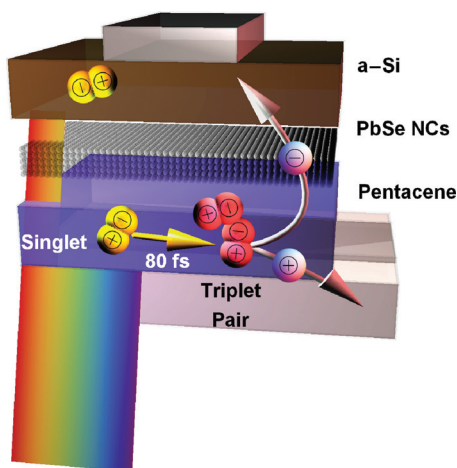


FIG. 1. Pentacene/PbSe/a-Si device structure and proposed working mechanism. Visible range photons are absorbed by pentacene and split into pairs of low energy triplet excitons. IR photons are absorbed in silicon and the thin PbSe layer.

contain pentacene. The absorption spectra of a-Si, pentacene, and PbSe nanocrystals are also shown. The EQE of the solar cell that contains silicon, pentacene, and PbSe nanocrystals displays features attributable to absorption in all three materials: pentacene, nanocrystals, and silicon. This is most clearly seen in Figure 2(b), which shows the spectral region of strong pentacene absorption. The difference in EQE between a solar cell with and without pentacene is also shown, clearly demonstrating an enhancement that follows the pentacene absorption spectrum. In addition, the solar cell that lacks silicon produces significantly less photocurrent in the spectral region where silicon absorbs most strongly. This indicates that all three active materials contribute to the photocurrent. It implies further that pentacene triplet excitons were harvested and the electrons transferred to the silicon. At the same time, current generation in the silicon layer was facilitated by hole extraction through the pentacene layer. The fact that the photocurrent is enhanced in the region of the pentacene absorption is particularly significant, since if the pentacene were acting simply as a passive absorber one would expect to see a dip in the EQE spectrum as light is prevented from reaching the a-Si layer.

We note that, in addition to the photocurrent enhancement due to absorption followed by singlet exciton fission in the pentacene, the device incorporating the pentacene layer

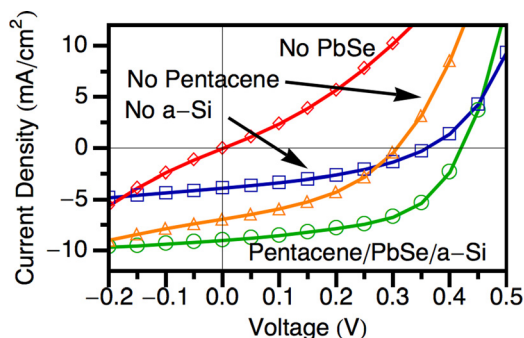


FIG. 3. Solar cell performance of the pentacene/PbSe/a-Si solar cell (○) in comparison to a solar cell without a-Si (□), without pentacene (Δ), and without PbSe (◇).

shows a small increase in photocurrent at higher energies, in the region where absorption is dominated by the a-Si. This indicates that the pentacene layer improves hole collection compared with a device where the PbSe nanocrystals are in direct contact with the ITO. This is a beneficial effect, but is independent of the effects of singlet exciton fission that we consider to be of more general importance.

Figure 3 shows the current-voltage behavior under one sun illumination (AM1.5G), comparing a device with all three layers to one without silicon, one without pentacene and one without PbSe. The solar cell without nanocrystals shows no photocurrent, probably because the pentacene is harmed during the sputtering process. Both the silicon and the pentacene increase the photocurrent as compared to solar cells without these layers, indicating photocurrent generation from both silicon and pentacene. The strong increase in photovoltage upon insertion of the pentacene layer is presumably due to superior hole extraction properties of pentacene as discussed above. The overall power conversion efficiency for the device with all three layers was 2.0%. Note that the efficiencies of our solar cells are lower than those of state-of-the-art amorphous silicon solar cells as we are using undoped silicon and hence no p-i-n junction is formed.

In conclusion, we have demonstrated that we are able to deposit a-Si on top of an organic semiconductor to form a working cell, to collect holes generated in the a-Si through the organic layer, and to generate photocurrent arising from singlet exciton fission following absorption in the organic layer. We have therefore shown the potential for singlet

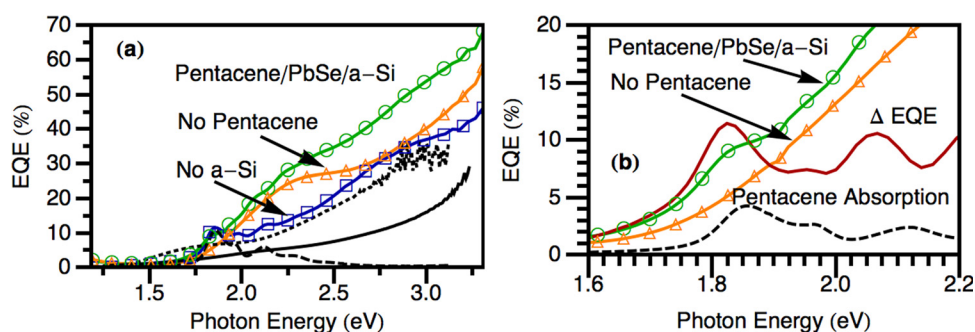


FIG. 2. External quantum efficiency (a) of the pentacene/PbSe/a-Si solar cell under short-circuit conditions (○) compared to a solar cell without silicon (□) and without pentacene (Δ). The absorption spectra of a-Si (dotted line) pentacene (dashed line) and PbSe nanocrystals (solid line) are shown for comparison. (b) The same spectra in the spectral range where pentacene absorbs strongly. The difference in EQE between the device with pentacene and the device without pentacene ( $\Delta$ EQE) is shown with a scaling factor of three, for comparison with the pentacene absorption spectrum (dashed line).

fission to improve the efficiency of conventional solar cell technologies. We expect further improvements in efficiency through optimization of device design, and we note the potential of this approach to be extended to overcome current efficiency limitations in crystalline silicon solar cells.

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