Double-Heterojunction Crystalline Silicon Solar Cell Fabricated at 250ºC with 12.9 % Efficiency

Sushobhan Avasthi[1], Ken A. Nagamatsu[1,2], Janam Jhaveri[1,2], William E. McClain[1,3], Gabriel Man[1], Antoine Kahn[1], Jeffrey Schwartz[1,3], Sigurd Wagner[1], and James C. Sturm[1,2]

[1]Princeton Institute for the Science and Technology of Materials (PRISM), Princeton University, NJ, 08544, USA

[2]Department of Electrical Engineering, Princeton University, NJ, 08544, USA

[3]Department of Chemistry, Princeton University, NJ, 08544, USA

***Abstract* —Double-heterojunction crystalline silicon solar cells were fabricated at temperatures of <250ºC using Si/organic and Si/metal-oxide heterojunctions, but no p-n junction in silicon. The first heterojunction, formed by spin-coating organic PEDOT:PSS on n-type silicon, functions as a front surface field that separates the photogenerated carriers and blocks electron dark-current while allowing hole photo-current to pass though. The second heterojunction, formed via metal-organic chemical vapor deposition of titanium dioxide on n-type silicon, functions as a back surface field that reduces hole dark-current while allowing electron photocurrent to pass through. Compared to a single heterojunction solar cell with only a Si/PEDOT heterojunction, the double-heterojunction device is more efficient with a power conversion efficiency of 12.9% under AM1.5.**

***Index Terms*—Silicon, Photovoltaics, Solar, Hybrid, Organic, Metal-oxide, Heterojunction, PEDOT:PSS, Titanium dioxide.**

I. INTRODUCTION

Silicon heterojunction solar cells represent a new approach towards next-generation low-cost high-efficiency photovoltaics. While conventional crystalline silicon (c-Si) solar cells are efficient (up to 25%), they are expensive, partly because they require diffused doped junctions – p^+/n, n/n^+, etc – fabricated at high temperatures (>800ºC)in ultra-clean furnaces[1]. An alternative to diffused junctions is the amorphous-silicon(a-Si)/c-Si heterojunction, used in the Heterojunction with Intrinsic thin layer (HIT) solar cells [2]. However, deposition of a-Si uses a plasma enhanced chemical vapor deposition (PECVD) process and it is difficult to independently tune the valence and conduction band offsets at the a-Si/c-Si interface [3]. Recently there has been considerable interest in Si/organic and Si/metal-oxide heterojunctions to fabricate low-cost Si solar cells [4].For example, a Si/organic heterojunction using the organic polymer Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) that blocks electrons but passes holes [5], and a Si/titanium-dioxide (TiO_2) heterojunction that blocks holes but passes electrons [6-7].

In this paper we describe a novel double-heterojunction silicon (DHS) solar cell, where the electron-blocking Si/PEDOT heterojunction and hole-blocking Si/TiO_2 heterojunction are integrated on the opposite faces of the same n-Si wafer with a maximum process temperature of < 250 ºC. Light absorption and charge separation in the DHS cell still occur in silicon, so the short-circuit current is high (~ 30 mA/cm^{2}for an un-textured silicon cell without an AR coating). The Si/PEDOT and Si/TiO_2interfaces selectively block the dark-current contribution of electrons and holes, respectively, thereby increasing the V_{OC} and achieving a power conversion efficiency of 12.9% under AM1.5 illumination.

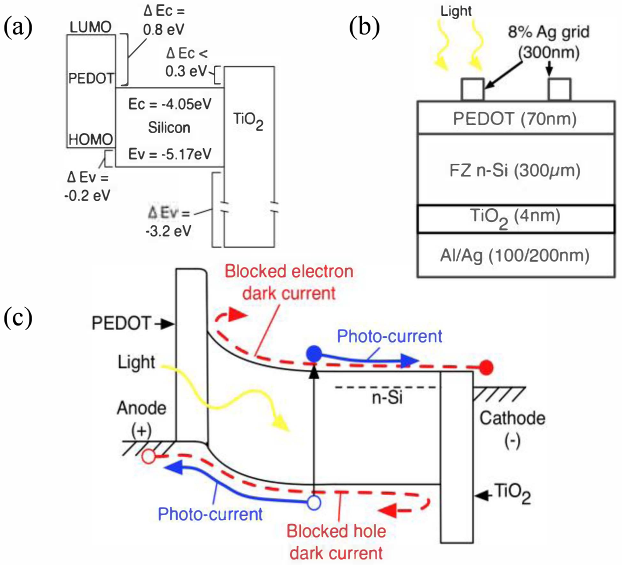

Fig. 1. (a) Band-alignment at PEDOT/Si and Si/TiO_2 interface as measured by photoelectron spectroscopy. (b) Structure and (b) band-diagram of the double-heterojunction solar cell under illumination and forward-bias. The solid lines represent photocurrent, and the dashed lines represent dark-current.

II. RESULTS AND ANALYSIS

A. Band-Offset Measurements

PEDOT:PSS has been reported to have the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels at 4.9 eV and 3.3 eV below the vacuum level, so the PEDOT/Si interface is expected to have a negligible valence-band offset ($\Delta E_V \approx$-0.2 eV) and a large conduction-band offset ($\Delta E_C \approx$ 0.8 eV), making PEDOT/Si interface suitable for selectively blocking electrons(Fig 1 (a)) [8].

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In contrast, the TiO_2/p-type-Si interface has been shown to have a large valence-band offset ($\Delta E_v \approx$ 3.4 eV) but a negligible conduction-band offset ($\Delta E_C \approx$ 0.1 eV), making it suitable for selectively blocking holes [7]. To measure the band-alignment of n-type-Si/TiO_2 interface, ultraviolet photoelectron spectroscopy (UPS) and inverse photo-emission spectroscopy (IPES) were used. Spectra measured on highly-doped n^+-Si/TiO_2 interface reveal that at the n-Si/TiO_2 interface, values of ΔE_v and ΔE_C are 3.2 ± 0.1 eV and 0.3 ± 0.2 eV, respectively (Fig 1 (a)).Therefore, the n-Si/TiO_2 interface is also expected to selectively block holes.

B. Device Principle

Fig. 1(b) shows the device structure and Fig. 1(c) shows the band structure of the DHS device under illumination and forward bias. Due to the high work-function of the heavily-p-type doped PEDOT layer (~5.0 eV [8]), there exists a depletion region in n-type silicon at the Si/PEDOT interface (~1 μm for $N_D = 10^{15}$ cm^{-3}). Light enters from the top of the cell, near the PEDOT:PSS/Si interface. The top metal grid is sparse (8% of the device area) and the PEDOT:PSS layer is more than 90% transparent at such thicknesses (~ 70 nm), so most of the light goes through the top-electrode/PEDOT stack and is absorbed in silicon. The depletion region separates the photogenerated carriers in silicon, causing a photocurrent. Due to the band-offsets at the PEDOT/Si interface, electrons in Si are blocked from flowing through the PEDOT to the top electrode, while holes are allowed to go through the PEDOT to the top electrode unimpeded. So the PEDOT/Si heterojunction is functionally similar to the p^+/n junction. The band-offsets at the Si/TiO_2 interface have a complementary behavior – the holes in Si are blocked from flowing though the TiO_2 layer, while allowing the electrons to pass though unimpeded. So the n-Si/TiO_2 heterojunction is functionally similar to the n/n^+ back surface field. Together, the two heterojunctions reduce both electron and hole dark-current (as shown by the dotted red lines in Fig. 1(c)), enabling the DHS solar cell to have a higher V_{OC} and a higher efficiency than the single heterojunction PEDOT/Si device of ref. [5].

C. Effect of Surface Recombination at Si/TiO_2 interface

Since the deposition of PEDOT and TiO_2 layers is not epitaxial, it is possible that Si dangling bonds at the Si surface cause interface defects, where carriers can recombine. If present, these recombination centers can adversely degrade the efficacy of carrier blocking at the Si heterojunctions.

This issue of interface recombination is not very severe at the PEDOT/Si interface because of the large built-in field in Si at the interface (a consequence of difference in work-function of PEDOT and n-Si, see Fig. 1(c)). The large electric field of the depletion region exponentially reduces the density of electrons at the Si surface (n_s), while increasing the density of holes at the Si surface (p_s), i.e. $n_s \ll p_s$. Since the rate of recombination at the PEDOT/Si interface ($U_{PEDOT/Si}$) is:

$$U_{PEDOT/Si} = IRV_{PEDOT/Si}\frac{(p_s n_s - n_i^2)}{p_s + n_s + 2n_i} \approx n_s IRV_{PEDOT/Si}$$

where $IRV_{PEDOT/Si}$ is the interface recombination velocity at the PEDOT/Si interface. Since $n_s \rightarrow 0$, even a large $IRV_{PEDOT/Si}$ does not lead to high recombination at the PEDOT/Si interface.

Unlike PEDOT/Si, the Si/TiO_2 interface does not have the advantage of a built-in field in Si to reduce the interface recombination. Ideally the bands are flat at the interface and thus the carrier profile in Si is a strong function of the interface recombination velocity at the Si/TiO_2 interface ($IRV_{Si/TiO2}$). Fig 2 shows the simulated hole-density profile of a DSH solar cell in dark at 0.65V forward-bias. Since the gradient of minority carrier density is proportional to dark-current, lower $IRV_{Si/TiO2}$ corresponds to lower J_0 and higher V_{OC}. Based on the simulations we need the $IRV_{Si/TiO2} <$ 1000 cm/s for ~10x decrease in dark-current.

Using photoconductance decay, the recombination velocity at the n-Si/TiO_2 interface was measured. The defect density at the as-deposited n-Si/TiO_2 interface was found to be high, with an $IRV_{Si/TiO2} \approx$1900 cm/s. However, annealing the n-Si/TiO_2 interface at just 250ºC dramatically improved the interface and the $IRV_{Si/TiO2}$ reduced to ≈70 cm/s (Table 1).

D. Device Fabrication and AM1.5Characteristics

Fabrication of the DSH cell begins with an RCA cleaned double-side polished 2-4 Ohm-cm float-zone n-Si wafer (~1.5×10^{15} cm^{-3} phosphorus doped). 4 nm thick TiO_2 and 70 nm thick PEDOT are deposited on to the bottom and top faces

Table 1: Effect of TiO_2 deposition and annealing on the interface recombination velocity (IRV) at the n-Si/TiO_2 interface

Structure	**IRV (cm/s)**
Bare Si	$> 10^6$
As-deposited Si/TiO_2	1900
Annealed Si/TiO_2	70

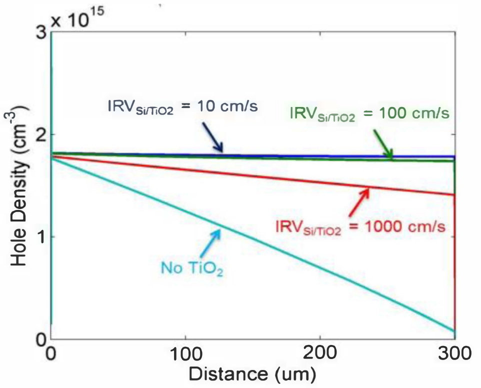

Fig. 2. Simulated hole density in the Si wafer for the DSH solar cell in dark at 0.65 V forward-bias, for different values of IRV at Si/TiO_2 interface. For comparison, the baseline case of 'No TiO_2' is also shown.

of the Si. Details of the deposition process have been published elsewhere [5-7]. The wafer is annealed at 250 °C for 120 s to improve the Si/TiO_2 interface.The back-side electrode is formed by thermally evaporating 100 nm of Al and 200 nm of Ag on the TiO_2 layer. Finally, 250 nm thick Ag is thermally evaporated on top of PEDOT, through a shadow-mask, to form an 8% metal-covered front-side electrode. The device area is 4 mm x 4 mm. The maximum process temperature was 250 °C. Note that the DSH solar cell does not have any diffused p/n or n/n$^+$ junctions.

AM 1.5 characterization was performed using a 4 x 4 mm^2 aperture to prevent over-estimation of photocurrent due to lateral collection of carrier generated outside the device area.

J-V characteristics of DHS device show well-behaved solar cell characteristics, with a J_{SC} of 29 mA/cm^2 and V_{OC} of 0.62 V (blue curve, Fig.3). The lack of an ‘S-shaped’ characteristic confirms the absence of an electron barrier at the n-Si/TiO2 interface and a hole barrier at the n-Si/PEDOT interface. For comparison, the J-V characteristics of a DHS device fabricated with as-deposited TiO_2 (red-curve, Fig 3) and a single heterojunction device without the Si/TiO_2 heterojunction (black-curve, Fig 3) were also measured. The ‘No-TiO_2’device has a PEDOT/Si heterojunction with a structure similar to the device of [5]. The V_{OC} of the ‘as-deposited TiO_2’ and ‘no TiO_2’ device were 0.59V and 0.54 V, respectively. Clearly, the addition of the Si/TiO_2 heterojunction at the back interface improves V_{OC}, although we note that some portion of this may be due to the TiO_2 removing a parasitic barrier for photocurrent (electrons) at the Al/Si interface. Annealing improves the V_{OC} even further to 0.62 V, arguably due to the reduced interface recombination velocity at the Si/TiO_2 interface (Table 1). Extracted solar cell parameters of these devices are summarized in Table 2.

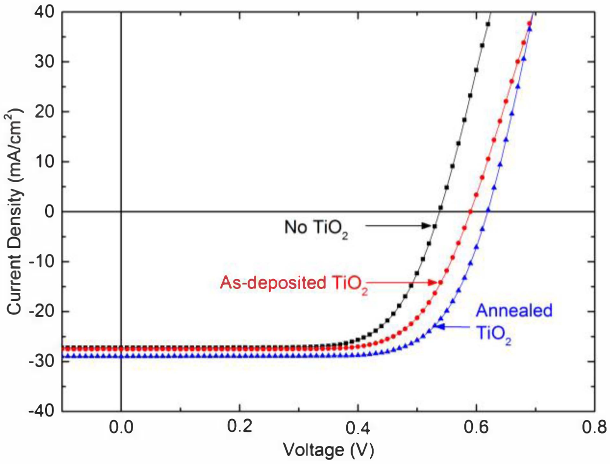

Fig. 3. J-V characteristics of a double heterojunction Si solar cell with ‘Annealed TiO_2’ (blue), ‘As-deposited TiO_2’ (red) and ‘No-TiO_2’ (black), under AM1.5

Table 2.Solar cell parameters of the three devices of Fig 3.

	No TiO_2	As-deposited TiO_2	AnnealedTiO_2
V_{OC} (V)	0.54	0.59	0.62
J_{SC} (mA/cm^2)	27.2	27.6	29.0
FF (%)	70.4	70.8	72.1
PCE (%)	10.3	11.5	12.9

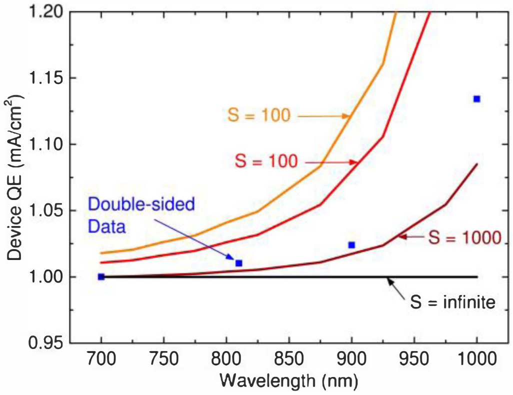

Fig. 4. External quantum efficiency of the double-sided device normalized to the single sided, compared to modeled S

Further evidence of the beneficial effect of the Si/TiO_2 heterojunction can be implied in the relative quantum efficiencies (Fig. 4). The relative EQE of the device with TiO_2 is larger the device without the TiO_2 at long wavelengths (>900 nm). Since longer wavelength photons are absorbed closer to the back interface, the higher EQE indicates reduced recombination near the Si/TiO_2. For comparison, a model of the expected gain in normalized EQE is shown for various values of surface recombination velocity.

III. CONCLUSIONS

We have demonstrated the concept of a double heterojunction silicon solar cell junction without any doped junctions. One heterojunction (PEDOT/Si) replaces the p-n junction, and the other (Si/TiO_2) replaces the n/n$^+$ back surface field at the substrate contact. The DHS solar cell was fabricated via spin-coating (PEDOT) and CVD (TiO_2) at a maximum process temperature of 250 °C. Simulations reveal that device efficiency is very sensitive to the interface recombination at the back interface, in this case Si/TiO_2. Under AM1.5, DHS solar cells with PEDOT/Si/TiO_2 structure yield V_{OC} of 0.62V and power-conversion efficiency (PCE) of 12.9 %.

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