A 12% Efficient Silicon/PEDOT:PSS Heterojunction Solar Cell Fabricated at < 100 °C

Ken Nagamatsu[1,2], Sushobhan Avasthi[1], Janam Jhaveri[1,2], James C. Sturm[1,2]

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

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

***Abstract* — Solar cells based on a heterojunction between crystalline silicon and the organic polymer PEDOT:PSS were fabricated at temperatures < 100ºC by spin-coating. The Si/PEDOT interface blocks electrons in n-type silicon from moving to an anode and functions as a low-temperature alternative to diffused p-n junctions. Reverse recovery measurements were used to show that current in the device is primarily due to holes injected from the anode into the silicon. At AM1.5, Si/PEDOT heterojunction solar cells achieve power conversion efficiency (PCE) of 11.7%, which is among the highest reported values for this class of devices.**

I. INTRODUCTION

Hybrid photovoltaic devices, which combine inorganic and organic materials, offer potential for high-efficiency, low-cost photovoltaics. The Silicon/Organic Heterojunction (SOH), for example, can be fabricated at <100ºC using spin-coating as opposed to conventional pn junctions, which require temperatures >800ºC [1-3]. SOH devices can substantially reduce the cost of silicon photovoltaics while still reaching high efficiency [4,5]. Previously a Si/P3HT heterojunction solar cell was demonstrated with 10% power conversion efficiency [1]. In this paper we report an investigation of the origin of dark current in Si/PEDOT:PSS devices, and demonstrate a Si/PEDOT:PSS solar cell with an AM1.5 power conversion efficiency of 11.7%.

Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate), or PEDOT:PSS is a commonly used organic which acts as a heavily doped p-type semiconductor with a large bandgap of ~1.6 eV [6-12]. The structure of Si/PEDOT heterojunction solar cell is shown in Fig. 1(a), and the electronic band structure is shown in Fig. 1(b). Light enters from the top of the cell, where the PEDOT:PSS is coated. As shown in Fig. 1(b), the LUMO level of PEDOT is offset from the conduction band of silicon. This forms a barrier to electron dark current (shown by dashed red line in conduction band of Fig. 1(c)). Fig. 1(b) also shows the HOMO level of PEDOT closely aligned with the valence band of silicon, which allows holes in silicon to flow into PEDOT unimpeded (shown by blue line in valence band in Fig. 1(c)). The high work-function of the heavily-doped PEDOT layer (~5.0 eV) creates a depletion region in the n-type silicon which seperates photogenerated carriers. These properties of the heterojunction lead to efficient collection of photogenerated carriers and a reduced electron dark current or J_0, which leads to higher V_{OC}.

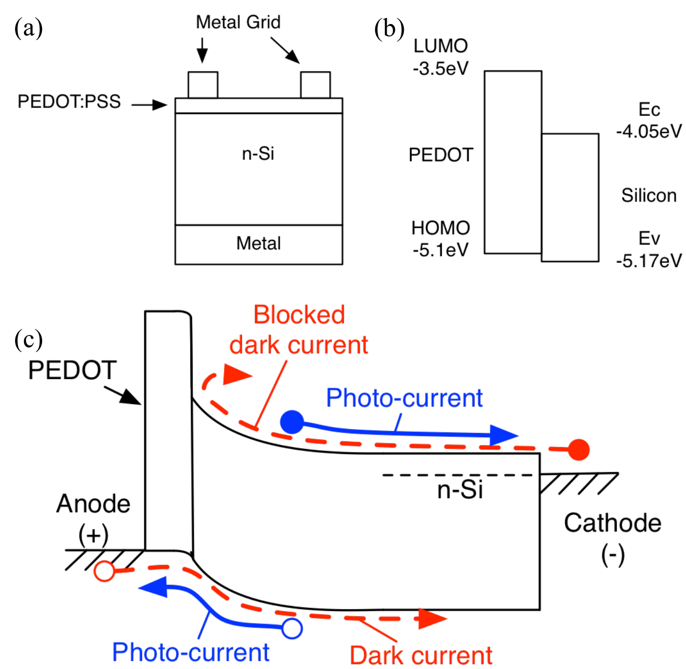

Fig. 1. (a) Physical structure and (b) electronic band alignment of SOH device. (c) Band diagram of device under illumination with positive bias. Dashed red lines indicate dark current, solid blue lines represent photocurrent.

II. EXPERIMENTAL

PEDOT:PSS was purchased (Clevios PH1000) and 10% w/w dimethyl sulfoxide (DMSO) was added for enhanced conductivity [12]. The silicon wafers were cleaned using standard RCA cleaning procedure. Si/PEDOT devices were fabricated by spin-coating a 70-nm layer of PEDOT on 10^{15}-cm^{-3}-doped n-type silicon wafers. Thermally evaporated silver and aluminum contacts were deposited on the front and backside of the wafer to form anode and cathode, respectively. The anode (front side contact) was patterned by a shadow mask to allow light to be absorbed in silicon (Fig. 1(a)). The top metal grid covers ~ 10 % of the surface. The device size was 4 mm x 4 mm.

Electrical measurement of the devices was performed with an Agilent/Hewlett-Packard 4155 parameter analyzer. AM1.5 illumination from a xenon lamp solar simulator was used for testing and was calibrated to $1000 W/m^2$ using a silicon reference cell. A 4x4mm aperture was used to prevent collection of laterally diffusing carriers.

II. Results and Analysis

A. Current-Voltage Measurements

Figure 2 (a) presents the J-V characteristics for a Si/PEDOT heterojunction cell under dark conditions. At 1.3 mA/cm^2 forward current, and using an ideality factor of 1 we can extract a saturation current J_0 to be 3.8 x 10^{-12}. For comparison Fig. 2(a) also presents the current expected for a metal/Si Schottky barrier with a barrier height of ϕ_B = 0.8 eV, with a saturation current given by:

$$J_{0,\,electrons} = A^{*}T^{2}\left(e^{-\frac{\phi B}{kT}}\right) \quad (1)$$

Where A^* is the Richardson constant, T is temperature, ϕ_B is the Schottky barrier height, and k is the Boltzmann constant. Figure 2 (a) clearly shows the dark current in the SOH device is lower than that of Eq. 1 by over four orders of magnitude, suggesting that the PEDOT:PSS blocks electron current.

Figure 2(b) shows that under AM1.5 illumination, an open circuit voltage of 0.57 Volts was achieved along with a short circuit current of 27.8 mA/cm^2 and fill factor of 73%. The overall power conversion efficiency of this device was 11.7%, which is among the best reported for this class of devices.

B. Reverse Recovery

The open circuit voltage of a solar cell is limited by the amount of dark current in the device. The V_{OC} ideally depends on by the dark-current, characterized by the saturation current (J_0), as:

$$V_{OC} \equiv \frac{kT}{q}\ln\left(1+\frac{J_{SC}}{J_0}\right) \quad (2)$$

where q is the elementary charge and J_{SC} is the short-circuit current. It has previously shown that current in Si/P3HT devices is mostly caused by holes (minority carriers) because electrons (majority carriers) are blocked [1]. Si/PEDOT devices operate under the same electron blocking principle. To investigate this we tested the device for stored minority carriers using the diode reverse recovery method [13-15].

In steady-state forward-bias, minority carriers will be injected from the anode into the quasi-neutral region, forming a stored charge of holes will be built up in the n-type silicon. Other possible current mechanisms such as thermionic emission of electrons over the PEDOT barrier or recombination at the interface will not contribute to stored charge. Therefore, the stored charges can be used to estimate the properties of the injected minority carriers.

The extracted minority carrier charge can be measured by switching the diode from forward to reverse bias. The circuit used to measure the transient along with the voltage and current waveforms is shown in the Fig. 3(a) and 3(b). The area under the curve until the beginning of the decay point in reverse bias is defined as the extracted charge ($Q_{extracted}$). For a given forward-bias current (I_F), $Q_{extracted}$ depends on the reverse bias current (I_R) by the equation [14]:

$$Q_{extracted} = I_R\tau\left[\mathrm{erfc}^{-1}\left(\frac{1}{1+\frac{I_R}{\alpha I_F}}\right)\right]^2 \quad (3)$$

where τ_{bulk} is the bulk recombination lifetime and α is the ratio of minority-carrier current to the total current. If the dark current is composed only of holes injected into silicon, α=1.

Fig. 3 (c) shows the measured value of $Q_{extracted}$ as a function of I_R, for an I_F = 1.3 mA/cm^2. At low I_R the holes are not extracted fast enough, so most of them recombine in silicon,

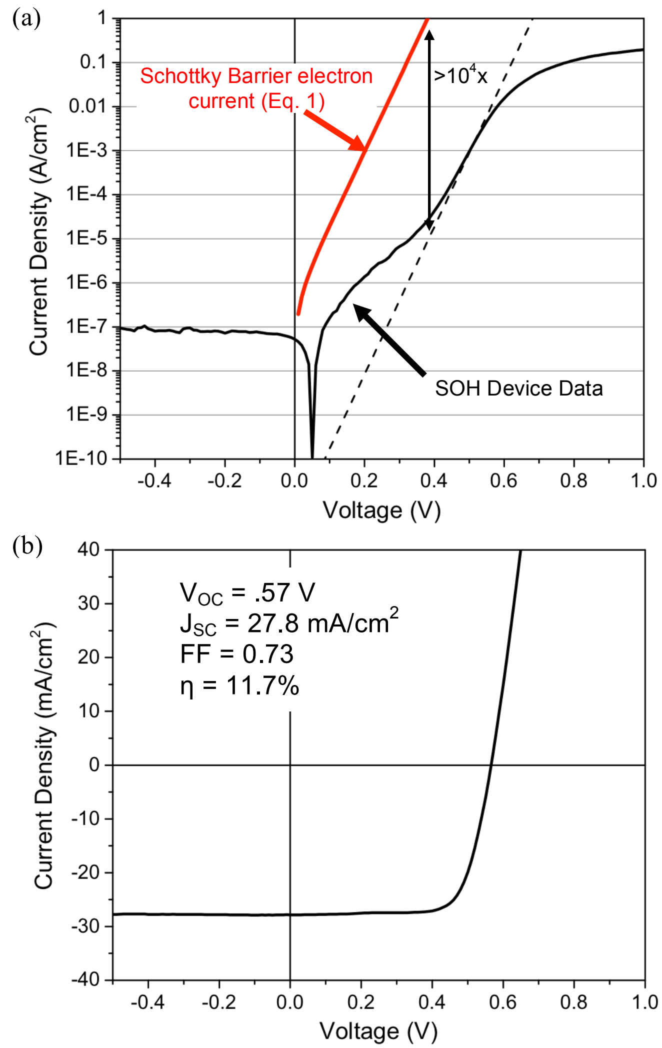

Fig. 2. (a) J-V characteristic of the SOH solar cell in dark and that calculated from a Schottky barrier (Eq. 1). 2. (b) J-V characteristic and parameters of SOH solar cell under AM1.5 illumination.

leading to low value of $Q_{extracted}$. At higher I_R the holes are sucked out before they can recombine so $Q_{extracted}$ is large. Fitting the data with Eq. (3) provides values of α and τ_{bulk} that are 1.0 and 114 us, respectively.

The value of $\alpha \approx 1$ proves that the barrier is effective at blocking electrons. The τ_{bulk} can be further used to estimate the value of minority carrier current ($J_{0,\,hole}$), using the equation:

$$J_{0,hole} \equiv q \frac{n_i^2}{N_D} \sqrt{\frac{D_{hole}}{\tau_{bulk}}} \qquad (4)$$

where N_D is the silicon doping level, D_{hole} is the hole diffusion coefficient, and n_i is the intrinsic carrier concentration of silicon. From the extracted value of τ_{bulk}, we estimate the $J_{0,\,hole}$ to be 6.64 x 10^{-12} A/cm^2.

Fig 4 plots the J-V characteristics of the SOH device measured with the reverse recovery experiment, along with the contribution of holes (minority carriers) to the dark current calculated from Eq. (4) (blue line).

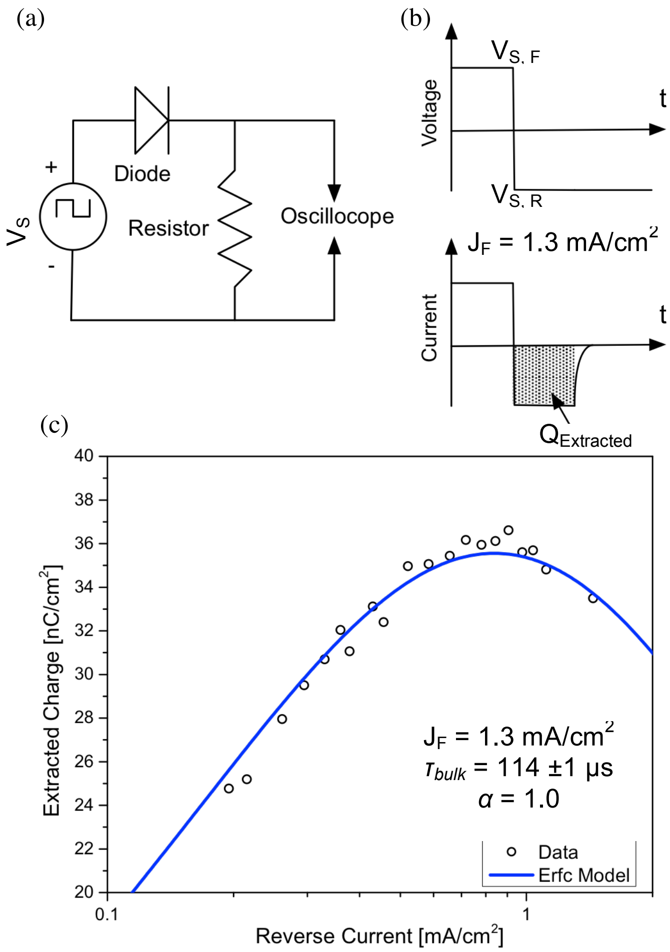

Fig. 3. (a) Circuit used for the reverse recovery experiment to measure effective injected hole lifetime τ_{bulk} and hole injection ratio α. (b) Typical waveforms for a device which has substantial minority carrier current, showing the $Q_{extracted}$. (c) $Q_{extracted}$ as a function of I_R. Black circles represent measured data and red line shows best fit to the data for τ_{bulk} = 114 us and α = 1.0.

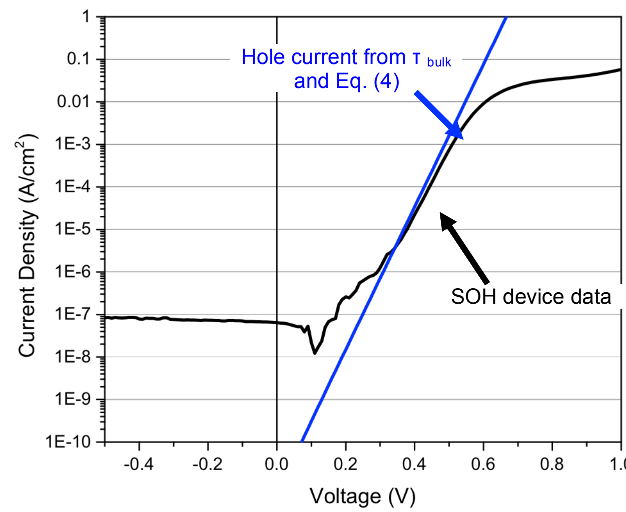

Fig. 4. J-V characteristic of SOH device measured with reverse recovery and hole current calculated from the measured τ_{bulk} and Eq. (4).

Furthermore, by using measured values of J_{SC} (~25 mA/cm^2) and the calculated $J_{0,hole}$ from Eq. (4), one can calculate an *expected* value of V_{OC} using Eq. (1). The expected V_{OC} is 0.57 V, which agrees with the experimentally measured value of 0.57 V. These results suggest that in Si/PEDOT devices, dark-current is predominantly composed of hole (minority) carriers and not electrons (majority) carriers.

IV. Conclusions

We have demonstrated an electron-blocking Si/PEDOT heterojunction that is fabricated by a room-temperature spin-coating process. Reverse recovery experiments provide a measurement of the stored charge provided by injection of minority carriers in forward bias. This provides a measurement of the current in the Si/PEDOT device that is carried by minority carrier hole injection from the anode. The data shows that the Si/PEDOT interface is very effective at blocking electrons, to the extent that dark-current in heterojunction devices on n-Si is not limited by electrons, but by the minority-carrier hole injection from anode into silicon. The best Si/PEDOT solar cells yield a high open-circuit voltage of 0.57V and an efficiency of 11.7%, which is among the highest reported for this class of devices.

Acknowledgements

This work was funded by the NSF MRSEC grant #DMR-0819860, and the DOE Sunshot grant #DE-EE0005315.

References

[1] S. Avasthi, S. Lee, Y. Loo, J. C. Sturm, "Role of Majority and Minority Carrier Barriers Silicon/Organic Hybrid Heterojunction Solar Cells" *Adv. Mater.* Vol. 23, pp 5762–5766 (2011)

[2] S. Avasthi, J.C. Sturm, "Charge Seperation and Minority Carrier Injection in P3HT-Silicon Heterojunction Solar Cells" *37th Photovoltaics Spec. Conf. (PVSC)* pp 002487-001685 June 19-24 (2009)

[3] A. Wang , J. Zhao , M. A. Green, "24% efficient silicon solar cells" *Appl. Phys. Lett.* Vol. 57, 602 (1990)

[4] J. Zhao, A. Wang, M. A. Green, F. Ferrazza, "19.8% efficient 'honeycomb' textured multicrystalline and 24.4% monocrystalline silicon solar cells" *Appl. Phys. Lett.* Vol.73, 1991 (1998)

[5] T.G. Chen, B.Y. Huang, E.C. Chen, P. Yu, H.F. Meng, "Micro-textured conductive polymer/silicon heterojunction photovoltaic devices with high efficiency" *Appl. Phys. Lett.* Vol. 101, 033301 (2012)

[6] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, J. R. Reynolds, "Poly(3,4=ethylenedioxythiophene) and Its Derivatives: Past, Present, and Future" *Adv. Mater.* Vol. 12, No. 7 pp 481-494 (2000)

[7] Y. Xia, K. Sun, J. Ouyang, "Solution-Processed Metallic Conducting Polymer Films as Transparent Electrode of Optoelectronic Devices" *Adv. Mater.* Vol. 24, pp. 2436-2440 (2012)

[8] T. Stocker, A. Kohler, R. Moos, "Why does the electrical conductivity in PEDOT:PSS decrease with PSS content? A study combining thermoelectric measurements with impedance spectroscopy" *Journal of Polym. Sci. Part B: Polym. Phys.* Vol. 50, pp 967-983 (2012)

[9] A.M. Nardes, M. Kemerink, M.M. de Kok, E. Vinken, K. Maturova, R.A.J. Janssen, "Conductivity, work function, and environmental stability of PEDOT:PSS thin films treated with sorbitol" *Org. Elec.* Vol. 9, pp 727-734 (2008)

[10] J. Hwang, F. Amy, A. Kahn, "Spectroscopic study on sputtered PEDOT:PSS: role of surface PSS layer" *Org. Elec.* Vol. 7, pp 387–396 (2006)

[11] E. L. Ratcliff, J. Meyer, K. X. Steirer, N. R. Armstrong, D. Olson, A. Khan, "Energy level alignment in PCDTBT:PC70BM solar cells: Solution processed NiOx for improved hole collection and efficiency" *Org. Elec.* Vol. 13, pp 744-749 (2012)

[12] H. Do, M. Reinhard, H. Vogeler, A. Puetz, M. F.G. Klein, W. Schabel, A. Colsmann, U. Lemmer, "Polymeric anodes from poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) for 3.5% efficient organic solar cells" *Thin Solid Films,* Vol. 517, pp 5900-5902 (2009)

[13] D. K. Schroder, "Ch. 8.5 Recombination Lifetime – Electrical Measurement Techniques" in *Semiconductor Material and Device Characterization,* USA, Wiley pp 394 (1990)

[14] S.M.Sze, *Physics of Semiconductor Devices*, USA, Wiley, pp 128 (1969)

[15] B. Lax and S. F. Neustadter, "Transient Response of a pn Junction" *Journal of Appl. Phys.* Vol. 25 pp 1148-1154 (1954