

High efficiency planar Si/organic heterojunction hybrid solar cells

Lining He, Changyun Jiang, Hao Wang, Donny Lai, and Rusli

Citation: [Applied Physics Letters](#) **100**, 073503 (2012); doi: 10.1063/1.3684872

View online: <http://dx.doi.org/10.1063/1.3684872>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/100/7?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[High efficiency silicon nanohole/organic heterojunction hybrid solar cell](#)

Appl. Phys. Lett. **104**, 053104 (2014); 10.1063/1.4863965

[Amorphous silicon oxide window layers for high-efficiency silicon heterojunction solar cells](#)

J. Appl. Phys. **115**, 024502 (2014); 10.1063/1.4861404

[Nanoimprinting-induced efficiency enhancement in organic solar cells](#)

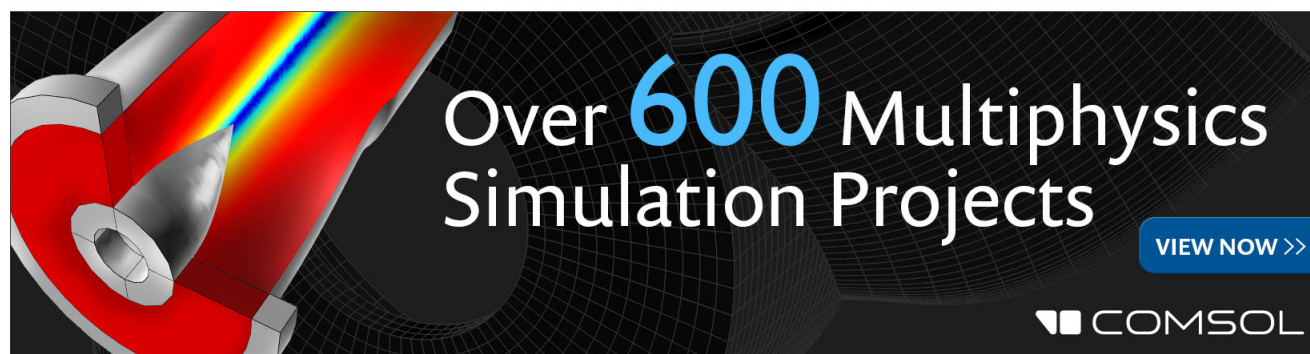
Appl. Phys. Lett. **99**, 183108 (2011); 10.1063/1.3659471

[Energy level alignments and photocurrents in crystalline Si/organic semiconductor heterojunction diodes](#)

J. Appl. Phys. **106**, 113704 (2009); 10.1063/1.3264945

[Efficient laser textured nanocrystalline silicon-polymer bilayer solar cells](#)

Appl. Phys. Lett. **90**, 203514 (2007); 10.1063/1.2739365

The advertisement for COMSOL Multiphysics features a dark background with a grid pattern. On the left, there is a 3D rendering of a mechanical part with a red and yellow color gradient. To the right of the rendering, the text "Over 600 Multiphysics Simulation Projects" is displayed in a large, white, sans-serif font. Below this text, there is a blue button with the text "VIEW NOW >>". In the bottom right corner, the COMSOL logo is visible, consisting of a small square icon followed by the word "COMSOL" in a white, sans-serif font.

High efficiency planar Si/organic heterojunction hybrid solar cells

Lining He,^{1,2,3,a)} Changyun Jiang,² Hao Wang,^{1,3} Donny Lai,^{1,3} and Rusli^{1,3,b)}

¹Nanofabrication Center, School of Electrical and Electronic Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798

²Institute of Materials Research and Engineering, A*STAR, 3 Research Link, Singapore 117602

³CINTRA UMI CNRS/NTU/THALES 3288, Research Techno Plaza, 50 Nanyang Drive, Border X Block, Level 6, Singapore 637553

(Received 9 November 2011; accepted 26 January 2012; published online 13 February 2012)

We present an efficient hybrid solar cell based on poly(3,4-ethylene-dioxythiophene):polystyrenesulfonate and planar Si with (100) and (111) orientations. The effect of Si surface native oxide on cell performance is studied. Compared to cell with hydrogen-terminated Si surface, the cell with oxygen-terminated Si surface reveals a 530-fold increase in power conversion efficiency (PCE) from 0.02% to 10.6%. The formation of SiO_x-Si bonds poses a net positive surface dipole which leads to a favorable band alignment for charge separation. However, thicker oxide degrades cell performance due to higher series resistance. This study demonstrates the highest PCE reported to-date in this field. © 2012 American Institute of Physics. [doi:10.1063/1.3684872]

Increasing solar cell efficiency in itself without considering the cost issue is insufficient to encourage wider use of photovoltaics. This has motivated extensive research on developing more cost-effective Si nanostructure hybrid solar cells incorporating liquid electrolyte^{1,2} or organic semiconductors,^{3–7} which benefit from their low temperature and solution based process capability. Until now, power conversion efficiency (PCE) of ~10% has been obtained from hybrid cells based on Si/poly(3-hexylthiophene) (P3HT)⁶ or Si/2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD)^{4,7} heterojunction. Recently, a transparent p-type polymer, poly(3,4-ethylene-dioxythiophene):polystyrenesulfonate (PEDOT:PSS), has been incorporated with Si nanowires (SiNWs) to fabricate hybrid cells,^{3,8,9} and we have reported the highest PCE of 9%.⁸ In that work, an efficient planar Si/PEDOT hybrid cell with a PCE of ~6.2% was also demonstrated.⁸ It was also found that the Si-substrate has contributed substantially to the photocurrent generated. In contrast, several studies have reported an extremely low PCE of 0.7%⁹ or 0.08%³ from cells based on similar planar Si/PEDOT structure. Apart from Si/PEDOT, other planar Si/organic hybrid solar cells such as poly((CH₃)₃Si-cyclooctatetraene/n-Si,¹⁰ polyaniline/n-Si,¹¹ and 4-tricyanovinyl-N,N-diethylaniline/p-Si¹² have been investigated and shown PCE up to 3.5%. Recently, Zhang *et al.* has reported that as compared to cells with hydrogen-terminated Si surface, the PCE of a planar Si/P3HT hybrid cell with oxide-terminated Si surface increased greatly from 0.006% to 0.9% with a 200-fold enhancement in the short circuit current. This was attributed to the formation of a thin native SiO_x layer leading to the generation of a favorable internal electric field at the interface.⁵ Similarly, the interface between Si and PEDOT could have played a critical role in determining the performance of the planar Si/PEDOT hybrid cells and accounted for the large differences in the PCE reported.^{3,8,9} It is important to clarify the source of the variation and maxi-

mize the PCE obtainable for planar Si/PEDOT cells before the advantages of incorporating SiNWs in such cells can be properly quantified.

In this work, planar Si/PEDOT hybrid cells are fabricated using Si wafers with (100) and (111) orientations. The effects of the Si surface termination conditions, hydrogen-terminated (H-Si), or oxide-terminated (SiO_x-Si) on the cell performance are investigated systematically. It is found that the H-Si surface results in an extremely poor PCE, attributed to a blocking internal electrical field induced at the interface. On the other hand, the SiO_x-Si surface significantly boosts the PCE of the cell owing to a favorable band alignment between SiO_x-Si and PEDOT. We have fabricated four planar SiO_x-Si (111)/PEDOT cells. An average PCE of 10.1%, a maximum PCE of 10.6%, and a minimum PCE of 9.3% have been obtained. This maximum PCE of 10.6% obtained here is the highest to-date among all the reported Si/organic based hybrid cells. It is also found that when the native SiO_x is too thick, it forms a barrier for charge transfer and thus reduces the open circuit voltage and fill factor of the cells.

Figure 1(a) shows the architecture of our planar Si/PEDOT hybrid solar cells. The starting wafers were single-crystal N-type Si (100) and Si (111) with the same resistivity of 0.6–1 Ω cm and thickness of 575 μm. The wafers were

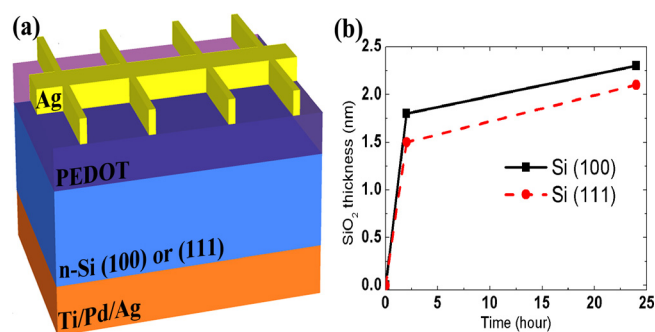


FIG. 1. (Color online) (a) Architecture of the planar Si/PEDOT hybrid solar cell. (b) Thickness of native oxide formed on H-terminated Si (100) and (111) surfaces versus exposure time in air.

^{a)}Electronic mail: heli0003@e.ntu.edu.sg.

^{b)}Electronic mail: erusli@ntu.edu.sg.

sequentially cleaned in acetone, ethanol, and deionized water for 10 min each at room temperature. Following that they were dipped in 5% hydrofluoric (HF) acid to remove any native oxide. Ti/Pd/Ag was deposited onto the backside of the Si wafer by e-beam evaporation to form the rear contact. Both the Si (100) and (111) samples were divided into three groups. Group 1 samples were dipped in 5% HF acid to remove any oxide and form a fresh H-Si surface, while group 2 and group 3 samples were exposed in air for 2 h and 24 h, respectively. Highly conductive PEDOT:PSS (Baytron PH500) mixed with dimethyl sulfoxide (DMSO), and a wetting agent Triton X-100 was then spin coated onto all the samples. The samples were then annealed on a hotplate at 100 °C for 8 min. Finally, silver metal grids were deposited on the PEDOT layer by e-beam evaporation to complete the cells each with a device area of 0.95 cm².

Figure 1(b) shows the native oxide thickness (d_{ox}) on an initially H-terminated Si (111) and (100) substrates after they were exposed in air for 2 h and 24 h. The d_{ox} was investigated using spectroscopic ellipsometry. The ellipsometric data have been acquired using a J. A. Woollam spectroscopic ellipsometer in the wavelength range of 300–1200 nm under an angle of incidence of 75°. It is seen that the resulting native d_{ox} reaches 1.8–2.3 nm on Si (100) substrate and 1.5–2.1 nm on Si (111) substrate. The slower oxide growth rate on the Si (111) surface is attributed to the fact that the atoms on the (111) surface are more densely packed, which leads to a lower oxidation rate.¹³

Figure 2 shows the current density-voltage (J - V) characteristics of the hybrid cells with Si (111) and Si (100) surfaces under 100 mW/cm² illumination (AM 1.5G) from a solar simulator (San-EI electric). The intensity of the light source was calibrated using a Si reference cell. The photovoltaic parameters of short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF), and PCE are summarized in Table I. It is seen that the H-Si (111) cell reveals an extremely low PCE of 0.02%, which is similar to that of the previously reported H-Si/P3HT hybrid cell.⁵ The PCE is noted to improve tremendously by 530-fold from 0.02% to

TABLE I. Summary of the photovoltaic parameters of the hybrid cells.

Sample	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)
H-Si (111)	0.28	0.27	19.3	0.02
SiO _x -Si (111) d_{ox} 1.5 nm	26.4	0.61	65.9	10.6
SiO _x -Si (111) d_{ox} 2.1 nm	26.3	0.57	34.6	5.2
H-Si (100)	0.46	0.29	16.9	0.02
SiO _x -Si (100) d_{ox} 1.8 nm	25.8	0.58	62.4	9.4
SiO _x -Si (100) d_{ox} 2.3 nm	24.7	0.53	25.5	3.4

10.6% for the SiO_x-Si (111) d_{ox} = 1.5 nm cell, as a result of the increase in J_{sc} , V_{oc} , and FF from 0.28 to 26.4 mA/cm², 0.27 to 0.61 V, and 19.3% to 65.9%, respectively. As the d_{ox} increases from 1.5 to 2.1 nm, the PCE of SiO_x-Si (111) cell drops substantially from 10.6% to 5.2% mainly due to its lower V_{oc} and FF. For the cells with Si (100) surface, similarly the H-Si (100) cell has a very low PCE of only 0.02% while the SiO_x-Si (100) cells achieved a much improved PCE of 9.4%. The relatively lower PCE of the SiO_x-Si (100) cells as compared to the corresponding SiO_x-Si (111) cells is attributed to the thicker oxide formed. Figure 3 shows the reflectance spectra of the planar Si before and after coated with PEDOT layer as well as the external quantum efficiency (EQE) spectrum of the SiO_x-Si (111) d_{ox} = 1.5 nm cell. It is seen that PEDOT serves as an antireflection layer which suppresses the reflectance of the planar Si down to 7.4% at ~660 nm. Accordingly, the SiO_x-Si (111) d_{ox} = 1.5 nm cell exhibits a broad EQE spectrum over 350–1100 nm and accounts for the high J_{sc} observed.

A kink is noted between −1 to 0 V in the J - V curve of the H-Si cells shown in Fig. 2. Such a feature is usually referred to as S-shape,¹⁴ and it is a characteristic occasionally observed in organic solar cells.^{15,16} The origin of such S-shape is generally proposed to be due to the presence of interfacial dipoles or carrier injection barriers.^{14,17} Figures 4(a) and 4(b) show the energy band diagrams of the H-Si/PEDOT and SiO_x-Si/PEDOT hybrid heterojunction,

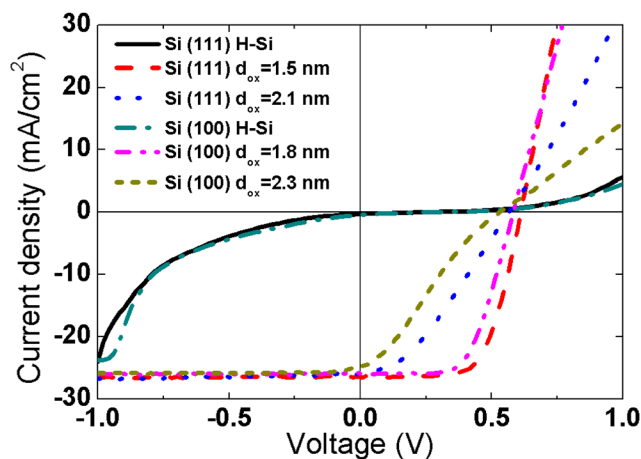


FIG. 2. (Color online) The current density-voltage (J - V) curve of the planar Si hybrid cells with Si (111) and (100) orientations under 100 mW/cm² illumination (AM 1.5G).

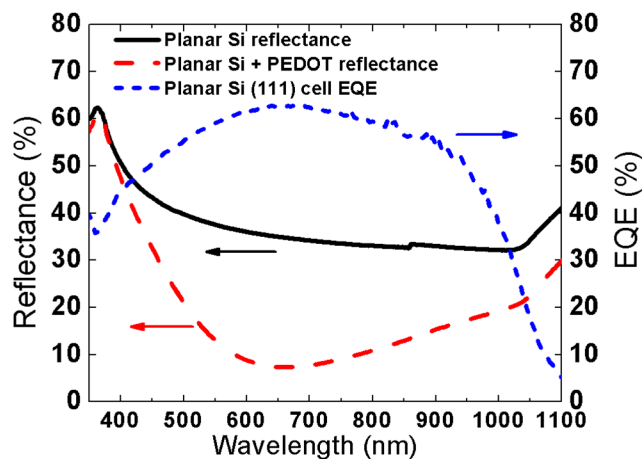


FIG. 3. (Color online) Reflectance spectra of the planar Si before and after coated with PEDOT layer; EQE spectrum of the SiO_x-Si (111) d_{ox} = 1.5 nm cell.

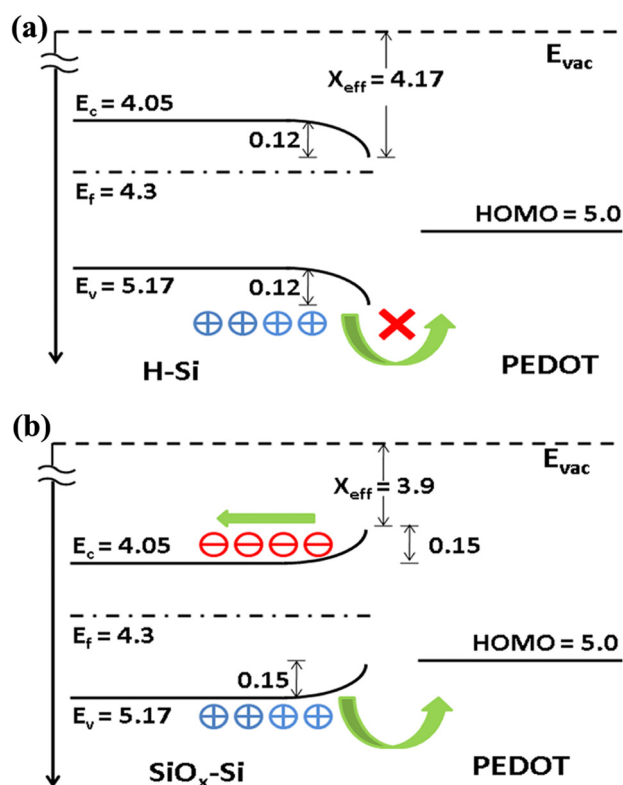


FIG. 4. (Color online) The energy band diagrams of the (a) H-Si/PEDOT and (b) SiO_x-Si/PEDOT hybrid heterojunctions.

respectively. The electron affinity (X_{Si}) of bulk Si is 4.05 eV.¹⁸ However, a covalently bonded passivating layer on the Si surface can either increase or decrease the effective electron affinity (X_{eff}) at the Si surface relative to that in the bulk Si, depending on the polarity of the associated dipole.^{5,19} Synchrotron photoemission study has demonstrated that the H-Si surface would pose a net negative surface dipole of 0.12 eV upon the formation of the covalent H-Si surface bonding.¹⁸ This leads to an increase in X_{eff} up to 4.17 eV at the Si surface and thus a bending down of Si energy band by 0.12 eV near the Si/PEDOT junction interface, as shown in Fig. 4(a). As a result, a blocking internal electrical field exists and prevents the photoexcited holes in the Si from injecting into PEDOT, resulting in higher carrier recombination at the interface. The hole blocking is also supported by the observation that the current density is almost zero in the vicinity of zero applied bias. It is also noted that the reverse current density of the H-Si cells increases sharply to $\sim 24 \text{ mA/cm}^2$ at -1 V , reaching a similar current level as the SiO_x-Si cells at this voltage point. This could be ascribed to the tunneling of holes against the blocking internal electrical field under high reversed bias.¹⁴ Figure 4(b) reveals that the X_{eff} at the SiO_x-Si surface drops to 3.9 eV owing to the formation of covalent SiO_x-Si bonding, which has been reported to pose a net positive surface dipole of 0.15 eV.⁵ Accordingly, the Si energy band will bend up and give rise to a favorable band alignment between SiO_x-Si and PEDOT to promote carrier separation. Moreover, the SiO_x layer helps in suppressing the Si surface recombination velocity, just as

for the conventional Si solar cells,²⁰ down to as low as 3 cm/s.²¹ Therefore, a lower carrier recombination at the SiO_x-Si/PEDOT interface and higher J_{sc} is expected. Though a thin native SiO_x is beneficial for charge separation at the interface, a thicker SiO_x would become a barrier for charge transport in the cells, leading to a higher series resistance. This accounts for the lower FF and PCE of the SiO_x-Si (100) cells as compared to the SiO_x-Si (111) cells, due to their thicker SiO_x layer.

In conclusion, we have studied the effects of surface native oxide on the performance of the planar Si/PEDOT hybrid solar cells. The cells with SiO_x-Si surface obtain an excellent PCE of 10.6%, which is 530-fold higher than that of cells terminated with a H-Si surface. The PCE is the highest reported for Si/organic hybrid cells to-date. The remarkable improvement seen for the SiO_x-Si/PEDOT cells is ascribed to their favorable band alignment and internal electric field at the junction interface that results in an efficient charge separation. With a 10.6% PCE achieved for the planar Si cell, an even higher PCE is expected if Si-nanostructures are incorporated to enhance light trapping. Therefore, with a proper surface termination and light trapping, such Si/organic hybrid cells can potentially deliver very high PCE to render them suitable for practical application.

The research is supported by A*STAR, Singapore under Grant No. 092 101 0055.

- ¹A. P. Goodey, S. M. Eichfeld, K.-K. Lew, J. M. Redwing, and T. E. Mal-louk, *J. Am. Chem. Soc.* **129**, 12344 (2007).
- ²X. Shen, B. Sun, F. Yan, J. Zhao, F. Zhang, S. Wang, X. Zhu, and S. Lee, *ACS Nano* **4**, 5869 (2010).
- ³S.-C. Shiu, J.-J. Chao, S.-C. Hung, C.-L. Yeh, and C.-F. Lin, *Chem. Mater.* **22**, 3108 (2010).
- ⁴L. He, C. Jiang, Rusli, D. Lai, and H. Wang, *Appl. Phys. Lett.* **99**, 021104 (2011).
- ⁵F. Zhang, B. Sun, T. Song, X. Zhu, and S. Lee, *Chem. Mater.* **23**, 2084 (2011).
- ⁶S. Avasthi, S. Lee, Y.-L. Loo, and J. C. Sturm, *Adv. Mater.* **23**, 5762 (2011).
- ⁷X. Shen, B. Sun, D. Liu, and S.-T. Lee, *J. Am. Chem. Soc.* **133**, 19408 (2011).
- ⁸L. He, Rusli, C. Jiang, H. Wang, and D. Lai, *IEEE Electron Device Lett.* **32**, 1406 (2011).
- ⁹B. Ozdemir, M. Kulakci, R. Turan, and H. E. Unalan, *Appl. Phys. Lett.* **99**, 113510 (2011).
- ¹⁰M. J. Sailor, E. J. Ginsburg, C. B. Gorman, A. Kumar, R. H. Grubbs, and N. S. Lewis, *Science* **249**, 1146 (1990).
- ¹¹W. Weining and E. A. Schiff, *Appl. Phys. Lett.* **91**, 1 (2007).
- ¹²A. A. Darwish, M. M. El-Nahass, H. M. Zeyada, and K. F. Abd-El-Rah-man, *Sol. Energy Mater. Sol. Cells* **91**, 1120 (2007).
- ¹³H. Angermann, W. Henrion, A. Roseler, and M. Rebien, *Mater. Sci. Eng.* **73**, 178 (2000).
- ¹⁴A. Kumar, S. Sista, and Y. Yang, *J. Appl. Phys.* **105**, 094512 (2009).
- ¹⁵K. Norrman, M. V. Madsen, S. A. Gevorgyan, and F. C. Krebs, *J. Am. Chem. Soc.* **132**, 16883 (2010).
- ¹⁶A. Wagenpfahl, D. Rauh, M. Binder, C. Deibel, and V. Dyakonov, *Phys. Rev. B* **82**, 115306 (2010).
- ¹⁷K. Schulze, C. Uhrich, R. Schuppel, K. Leo, M. Pfeiffer, E. Brier, E. Rein-old, and P. Bauerle, *Adv. Mater.* **18**, 2872 (2006).
- ¹⁸R. Hunger, R. Fritsche, B. Jaeckel, W. Jaegermann, L. J. Webb, and N. S. Lewis, *Phys. Rev. B* **72**, 45317 (2005).
- ¹⁹S. Maldonado, K. E. Plass, D. Knapp, and N. S. Lewis, *J. Phys. Chem. C* **111**, 17690 (2007).
- ²⁰J. Zhao, A. Wang, and M. A. Green, *Prog. Photovoltaics* **7**, 471 (1999).
- ²¹W. D. Eades, and R. M. Swanson, *J. Appl. Phys.* **58**, 4267 (1985).