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Efficiency improvement in silicon nanowires/ conductive polymer hybrid solar cells based on formic acid treatment

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Abstract

We investigated the mechanisms causing the power conversion efficiency (PCE) improvement in hybrid silicon nanowires/ poly(3,4-ethylenedioxythiophene): poly(styrenesulfonate) (PEDOT:PSS) solar cells by formic acid treatment. After the five minutes of formic acid treatment at elevated temperature (140 °C), the averaged PCE of the device can be improved from 8.00 % to 9.22 %. Through the formic acid treatment, the conductivity of the PEDOT:PSS film increases from 683 S/cm to 1582 S/cm and the averaged built-in voltage also increased from 0.43 V to 0.48 V. The larger built-in voltage value can suppress the recombination of photogenerated charges in the hybrid solar cells and turn the silicon nanowires/PEDOT:PSS junction barrier more close to ideal mott-schottky barrier. Through XPS and trap state density calculation, we confirmed such improvement is attributed to the decreases of interface states density in the hybrid solar cells after the formic acid treatment. Our findings indicate the critical roles of polymer conductivity and the

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interface quality of organic/inorganic interface in the performance of hybrid silicon nanowires/PEDOT:PSS solar cells.

Keywords:

silicon nanowires, PEDOT:PSS, hybrid solar cell, efficiency improvement, interface states

1. Introduction

Being one of the important alternative energy sources to fossil fuel, solar energy can be used to produce electricity through solar cells directly. To date, although silicon based solar cell is still dominating the market, a number of novel photovoltaic devices based on other materials system such as organic and perovskite materials have been developed. One kind of solar cell which also draws a lot of attentions from the research community is the hybrid cells which combining the advantages of both organic and inorganic devices. [1,2]. For example in the silicon/organic photovoltaics, the high temperature diffusion process can be eliminated and it reduces the energy consumption during the solar cell production process by 35% [3]. As a result, the manufacturing cost of the hybrid solar cells can be significantly lower than the silicon counterparts [4,5]. Among different organic semiconductors which have been utilized in hybrid silicon solar cells such as graphene [6,7], poly(3-hexylthiophene) (P3HT) [8], carbon nanotubes [9,10,11] and poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) [12,13]. PEDOT:PSS is one of the promising candidates due to its high optical

transparency [14], good thermal stability [15] and solution processability [16]. However, at the same time, the pristine PEDOT:PSS also suffered from the issue of low electrical conductivity (less than 1S/cm) [17].

The low conductivity of the PEDOT:PSS would suppress the carriers collection, promote joule heating and lower the device efficiency. To overcome this challenge, dimethyl sulfoxide (DMSO) has been added to PEDOT:PSS as a co-solvent to increase the conductivity of the pristine PEDOT:PSS film and thus the power conversion efficiency (PCE) of planar silicon/PEDOT:PSS solar cells [18,19,20]. By adding 2.5% by weight DMSO to the PEDOT:PSS solution, the conductivity of PEDOT:PSS film can be enhanced extensively from less than 1 to around 99 S/cm and PCE was increase from 2.8% to 8.5% [20]. The PCE improvement is attributed to more interconnected conduction paths in the DMSO-added PEDOT:PSS films so that better charge carrier transportation and separation in the solar cell can be achieved [20]. The conductivity can be further enhanced by using the nitric acid vapor post-treatment. Zhao et al. demonstrated the conductivity of the DMSO-added PEDOT:PSS film can be increased from 300 to 1000 S/cm and PCE of the planar silicon/PEDOT:PSS solar cell can improves from 4.52% to 8.81% by exposing the device under nitric acid vapor environment for around ten seconds [21]. Similarly, formic acid formic acid treated PEDOT:PSS films were also utilized to replace tin doped indium oxide (ITO) layer in the flexible poly(3-hexylthiophene)/[6,6]-phenyl-C₆₁-butyric acid methyl ester (P3HT/PCBM)

polymer solar cells [22]. Actually, other than the post-treatment process on the PEDOT:PSS, the performance of silicon/PEDOT:PSS hybrid solar cells can also be improved by modifying the surface morphologies of the organic/inorganic interface and one effective way to do this is to convert the planar silicon into the nanowires (NWs) form. The increase of junction area by nanowires can enhance photon absorption and charge separation in the device [23,24]. In this work, other than the increases in the PEDOT:PSS conductivity, we are focusing on investigating what are the other possible factors causes the increases of PCE in the formic acid treated SiNWs/PEDOT:PSS solar cells with a special focus on the quality of the interface. The treatment was carried out by dropping formic acid onto the PEDOT:PSS thin film which has been annealed with 5 wt% DMSO. The formic acid treated device shows a PCE improvement in the open circuit voltage (V_{oc}) and fill factor (FF) of the device and thus the PCE of the device can reach 9.22%. The reverse saturation current and ideality factor of the hybrid solar cell are also analyzed from the C-V measurements and the fitting of J-V curves to Lambert's W-function. From the x-ray photoemission spectroscopy (XPS) and atomic force microscopy (AFM) characterizations, we found a drop in the ratio of PSS to PEDOT surface composition of the formic acid treated devices such that the PEDOT is aggregated at the surface layer. We further compared the SiNWs/PEDOT:PSS interface quality in the hybrid solar cells before and after the formic acid treatment by evaluating the density of interface states. It was found that the density of the interface states is ten times

smaller in the formic acid treated device.

2. Experimental details

The n-type silicon (100) wafers with resistivity of 1-10 $\Omega\cdot\text{cm}$ and thickness of 525 μm were cleaned and underwent the electroless etching process to develop silicon nanowires array with a length of around 400 nm. The details of the electroless etching process has been reported elsewhere and will not repeat here [22]. After the formation of the nanowires, the silicon wafers were immersed in dilute hydrofluoric acid to remove the native oxide and followed by twenty minutes of ambient air exposure to improve the surface wetting property. Pristine PEDOT:PSS solution (Clevios PH1000 mixed with 5 wt% DMSO) was filtered via a 0.45 μm pore size membrane and spin-coated on the nanowires textured silicon wafers at 3000rpm for 30s. The wet PEDOT:PSS films were annealed under 140°C for 5 minutes. In our formic acid treatment, 100 μl of 98wt% formic acid is dropped onto the annealed PEDOT:PSS film and then dried at 140°C for another 5 minutes. Finally, the devices were finished by depositing silver anode fingers by screen-printing silver paste on top of PEDOT:PSS and gallium indium eutectic on the backside of the silicon wafers as cathode. The schematic diagram of the silicon/PEDOT:PSS hybrid solar cell is shown in Fig. 1(a).

3. Results and discussion

The average performance of totally 50 devices with and without formic acid treatment were shown in Table I. The optical transmittance and the current density-voltage (J-V) curves

of the pristine and treated films were shown in Fig. 1(b) and (c), respectively. Although a mild decrease in transmittance can be observed for wavelength larger than 600nm, the devices go through the formic acid treatment in general show a higher open circuit voltage than the pristine devices. From the statistical study plot in Fig. 2, it can be noticed that the device to device variation in the formic acid treated solar cells are smaller, and the averaged PCE increases from 8.00% (pristine) to 9.22% (treated), corresponding to a 15.3% PCE improvement. The solar cell characteristic parameters including light generation current density (J_L), reverse saturation current density (J_0), ideality factor (n), series resistance (R_s) and the shunt resistance (R_{sh}) can be further obtained by fitting experimental J-V data with the Lambert's W-function [25] and the results are summarized in table II:

$$J = n \cdot \frac{(k_B T / q)}{R_s} \cdot \text{lambertw} \left(\frac{J_0 R_s}{n \cdot (k_B T / q) \cdot (1 + R_s / R_{sh})} \exp \left(\frac{V + R_s (J_0 + J_L)}{n (k_B T / q) (1 + R_s / R_{sh})} \right) \right) + \frac{V / R_{sh} - (J_0 + J_L)}{1 + R_s / R_{sh}} \quad (1)$$

The R_s of the device decreases from 1.77 to 1.53 Ωcm^2 after formic acid treatment which agrees with the four probe conductivity measurements of the PEDOT:PSS films (683 S/cm for pristine and 1582 S/cm for treated). On the other hand, the ideality factor, reverse saturation current density and shunt resistance all show a decrease in the formic acid treated devices. To confirm the origin of the conductivity increases, we utilized XPS to examine the chemical composition at the surface the PEDOT:PSS films (Fig. 3(a)). In the Sulphur (2p) spectra of the films, the binding energy peaks at 169 and 167.8eV are referring to the sulphur

atoms in PSS and those at 164.6 and 163.4eV are referring to the sulphur atoms in PEDOT [26]. Based on the area of the energy peaks in Fig. 3(a), the composition ratio of PSS to PEDOT can be evaluated and the composition ratio decreased from 2.94 (pristine) to 1.22 (treated). ~~which is comparable with the observation from Mengistic et al [22].~~ The reduction in the PSS ratio suggests more hole transporting PEDOT is able to connected with the silver grid anode which can reduce R_s of the device. From the atomic force microscopy (AFM) height in Fig. 3(b-c), it can be noticed that aggregation of the PEDOT is occurred in the treated PEDOT:PSS film. The brighter area and darker area of the phase image in Fig. 3(d-e) represent the aggregated PEDOT and PSS matrix respectively. The separation distance between the hole conductive PEDOT phase is decreased after formic acid treatment and thus better interconnection of PEDOT clusters is expected. The smaller value of R_s value also contributed to the improvement in FF in the formic acid treated devices. The averaged FF of the SiNWs/PEDOT:PSS hybrid solar cells improved from 55.8% to 60.1% after formic acid treatment.

The build in-voltage (V_{bi}) of a diode actually provides important information on the quality of the junction. One way to evaluate the value of V_{bi} is by using the x-axis intercept of the $1/C^2$ -V plot as shown in Fig. 4(a-b). From the figures, it can be noticed that the values of V_{bi} are quite similar for the pristine and formic acid treated device and maintained at 0.6V.

However, such V_{bi} values does not match that obtained from J-V method, where the V_{bi} values were calculated via the equation [27]:

$$V_{bi} = (-k_B T / q) \ln(J_0 / (A^{**} T^2)) - V_n \quad (2)$$

here A^{**} is the effective Richardson constant ($110 \text{ Acm}^{-2}\text{K}^{-2}$ for n-type silicon) [27], and $V_n = (k_B T / q) \ln(N_c / N_d)$ where N_c is the effective density of states in the conduction band of silicon ($=3 \times 10^{19} \text{ cm}^{-3}$) and N_d is the doping level of silicon ($=6 \times 10^{14} \text{ cm}^{-3}$). By using the equation to perform fitting, the averaged built-in voltage are 0.43V and 0.48V for pristine and after formic acid treatment device respectively. Based on fitting the J-V curves of the twenty five devices into Eq (1) and Eq. (2), we noticed a the built-in voltage and the ideality factor the silicon/PEDOT:PSS hybrid solar cells is linear correlated. It can be observed from Fig. 4(c) that when $n=1$, the V_{bi} value is around 0.60V, which agree with the finding by using the C-V measurements. The deviation of the V_{bi} values between the C-V and J-V method is actually related with the non-ideal ($n>1$) behavior of the SiNWs/PEDOT:PSS hybrid solar cells. It is due to the schottky-mott relationship in the $1/C^2$ -V plot predicts the built-in voltage in the absence of interface states by assuming $n=1$. As mentioned before, the fitted n values were equal to 2.56 and 2.11 for the pristine and formic acid treated PEDOT:PSS respectively. The deviation of the ideality factor and built in voltage suggests the junction between SiNWs/PEDOT:PSS is non-ideal and interface states in the hybrid solar cells cannot be ignored in determining the actual V_{bi} .

The origin and the density of the interface states are worth to further study as they are directly related to the performance of the hybrid solar cell. After the preparation of silicon surface by diluted hydrofluoric acid etching, the routine de-ionized water rinsing and drying procedure could unavoidably grow a thin insulating oxide film on the silicon surface. The thickness of the interfacial oxide layer presented at the freshly prepared Si/PEDOT:PSS interface can reach around 1.5 nanometers [28]. The relationship between the interface states (D_s) and the ideality factor is given by [29]:

$$n = 1 + \frac{(\delta / \varepsilon_i)(\varepsilon_s / W + qD_{s,Si})}{1 + (\delta / \varepsilon_i)qD_{s,P}} \quad (3)$$

where δ is the interface layer thickness, ε_i and ε_s is the permittivity of the interfacial layer ($\approx 3.5\varepsilon_0$) and the semiconductor ($\approx 11.7\varepsilon_0$) respectively. W is the space charge width which can be evaluated by $W = \sqrt{(2\varepsilon_s V_{bi}) / (qN_d)}$. By using V_{bi} values of 0.43V for the pristine device and 0.48V for the formic acid treated device, W are around 0.89 μm (pristine) and 0.94 μm (treated). The interface states are contributed from two parts, partly on the PEDOT:PSS ($D_{s,P}$) and partly on the silicon ($D_{s,Si}$). The two curves (open circle and open triangle) in Fig. 5 show the relationship between $D_{s,P}$ and $D_{s,Si}$ for the value $n = 2.56$ and 2.11 respectively. When the device is under zero bias, the two components ($D_{s,P}$ and $D_{s,Si}$) constitute an interface-state charge density Q_{GS} [30]: $Q_{GS} = qD_s(qV_{bi} + qV_n - E_g + \phi_{CNL})$ where $D_s = D_{s,P} + D_{s,Si}$. They are represented in the energy band diagram in Fig. 6. On the other hand, by charge neutrality, Q_{GS} is also equal and opposite to the total charges developed on the PEDOT:PSS surface (Q_P)

and space charge layer (Q_{sc}) in silicon, which can be written as [27]:

$$Q_{GS} = (\epsilon_i / \delta)(\phi_P - (\chi - V_{bi} + V_n)) - \sqrt{2q\epsilon_s N_d (V_{bi} - kT/q)}$$
 where ϕ_P is work function of

PEDOT:PSS and χ is electron affinity of silicon. By using the values in table III, we can

obtain D_s for the devices before ($3.03 \times 10^{14} \text{ eV}^{-1}\text{cm}^{-2}$) and after ($3.97 \times 10^{13} \text{ eV}^{-1}\text{cm}^{-2}$)

treatment as shown by the two curves (black star and red cross, respectively) in Fig 5. By

locating these D_s and n values in Fig.5, $D_{s,P}$ and $D_{s,Si}$ are 1.1×10^{14} and $1.9 \times 10^{14} \text{ eV}^{-1}\text{cm}^{-2}$ for

pristine devices respectively and 1.2×10^{13} and $2.7 \times 10^{13} \text{ eV}^{-1}\text{cm}^{-2}$ for formic acid treated

devices respectively. Both $D_{s,P}$ and $D_{s,Si}$ decreased after formic acid treatment. The decrease

of the total interface states after formic acid treatment would result in a larger built-in voltage

and barrier height ($V_{bi} + V_n$). The larger barrier height suggested that recombination in the

junction between the treated PEDOT:PSS and silicon could be smaller than the pristine

PEDOT:PSS and silicon, thus the overall power conversion efficiency was increased.

4. Conclusions

The improvement of the PCE of SiNWs/ PEDOT:PSS hybrid solar cells by formic acid treatment is investigated. The average performance of devices shows a significant enhancement from 8% to 9.22%. The four point probe measurement showed the conductivity of the PEDOT:PSS film after formic acid treatment is increased by two times. Moreover, the XPS results indicates that the formic acid treatment led to larger PEDOT domain in the PEDOT:PSS film which can benefit the charge separation and collection. We further

confirmed the improvement of the PCE by evaluating the density of interface states in the pre-treated and after treated devices. We noticed that one order of magnitude drop in the interface states would occur for the device after formic acid treatment. These findings not only quantify the interface states level in the hybrid solar cell, but also provide direct evidences that formic acid treatment is very suitable to improve the efficient of SiNWs/PEDOT:PSS hybrid solar cell.

References

- [1] J.Y. Jeng, Y.F. Chiang, M.H. Lee, S.R. Peng, T.F. Guo, P. Chen, T.C. Wen, CH₃NH₃PbI₃ Perovskite/Fullerene Planar-Heterojunction Hybrid Solar Cells, *Adv. Mater.* **25** (2013) 3727-3732.
- [2] M. Wright, A. Uddin, Organic-inorganic hybrid solar cells: A comparative review, *Sol. Energy Mater. Sol. Cells* **107** (2012) 87-111.
- [3] R. Hezel, Recent Progress in MIS Solar Cells, *Prog. Photovolt. Res. Appl.* **5** (1997) 109-120.
- [4] J. Kalowekamo, E. Baker, Estimating the manufacturing cost of purely organic solar cells, *Sol. Energy* **83** (2009) 1224-1231.
- [5] R.G. Little, M.J. Nowlan, Crystalline Silicon Photovoltaics: the hurdle for thin films, *Prog. in Photovolt. Res. and Applications* **5** (1997) 309-315.
- [6] L. Yang, X. Wu, X. Shen, X. Yu, D. Yang, Investigating the Effect of Thermal Annealing Process on the Photovoltaic Performance of the Graphene-Silicon Solar Cell, *International J. of Photoenergy* **2015** (2015) 626201.
- [7] T. Feng, D. Xie, Y. Lin, Y. Zang, T Ren, R. Song, H. Zhao, H. Tian, X. Li, H. Zhu, L. Liu, Graphene based Schottky junction solar cells on patterned silicon-pillar-array substrate, *Appl. Phys. Lett.*, **99** (2011) 233505-1-233505-3.
- [8] V.V. Brus, M.Zellmeier, X.Zhang, S.M. Greil, M.Gluba, A.J. Tofflinger, J. Rappich, N.H. Nickel, Electrical and photoelectrical properties of P3HT/n-Si hybrid organic-inorganic heterojunction solar cells, *Org. Electronics* **14** (2013) 3109-3116.
- [9] J. Wei, Y. Jia, Q. Shu, Z. Gu, K. Wang, D. Zhuang, G. Zhang, Z. Wang, J. Luo, A. Cao, D. Wu, Double-Walled Carbon Nanotube Solar Cells, *Nano Lett.* **7** (2007) 2317-2321.
- [10] Z. Li, V.P. Kunets, V. Saini, Y. Xu, E. Dervishi, G.J. Salamo, A.R. Biris and A.S. Biris, Light-Harvesting Using High Density p-type Single Wall Carbon Nanotube/n-type Silicon Heterojunctions, *ACS Nano* **3**, (2009) 1407-1414.
- [11] Y. Jia, J. Wei, K. Wang, A. Cao, Q. Shu, X. Gui, Y. Zhu, D. Zhuang, G. Zhang, B. Ma, L. Wang, W. Liu, Z. Wang, J. Luo and D. Wu, Nanotube-Silicon Heterojunction Solar Cells, *Adv. Mater.* **20** (2008) 4594-4598.
- [12] J. Ouyang, C.W. Chu, F.C. Chen, Q. Xu, and Y. Yang, Polymer Optoelectronic

-
- Devices with High Conductivity PEDOT Anodes, *J. Macromolecular science, Part A Pure and Appl. Chem.* **41** (2004) 1497-1511.
- [13] D. Alemu, H.Y. Wei, K.C. Ho, C.W. Chu, Highly conductive PEDOTPSS electrode by simple film treatment with methanol for ITO free polymer solar cells, *Energy Environ. Sci.* **5** (2012) 9662-9671.
- [14] J. Zhang, L. Gao, J. Sun, Y. Liu, Y. Wang, and J. Wang, Incorporation of single-walled carbon nanotubes with PEDOTPSS in DMSO for the production of transparent conducting films, *Diamond and Related Materials* **22** (2012) 82-87.
- [15] C.H. Chiang, and C.G. Wu, High-efficient dye-sensitized solar cell based on highly conducting and thermally stable PEDOT:PSS glass counter electrode, *Org. Electronics* **14** (2013) 1769-1776.
- [16] K. Sun , S. Zhang, P. Li, Y. Xia, X. Zhang, D. Du, F. H. Isikgor, and J. Ouyang, Review on application of PEDOTs and PEDOTPSS in energy conversion and storage devices, *J. Mater. Sci: Mater Electron* **26** (2015) 4438-4462 .
- [17] J.Y. Ouyang, C.W. Chu, F.C. Chen, Q.F. Xu and Y. Yang, Polymer Optoelectronic Devices with High-Conductivity Poly(3,4-Ethylenedioxythiophene) Anodes, *J. of Macromolecular Sci.* **41** (2004) 1497-1511.
- [18] N.K. Unsworth, I.Hancox, C. Argent Dearden, P. Sullivan, M. Walker, R.S. Lilley, J. Sharp, T.S. Jones, Comparison of dimethyl sulfoxide treated highly conductive PEDOT PSS electrodes for use in indium tin oxide-free organic electronic photovoltaic devices, *Org. Electronics* **15** (2014) 2624-2631.
- [19] J. Ouyang, Secondary doping methods to significantly enhance the conductivity of PEDOTPSS for its application as transparent electrode of optoelectronic devices, *Displays* **34** (2013) 423-436.
- [20] M. Pietsch, M. Y. Bashouti, and S. Christiansen, The Role of Hole Transport in Hybrid Inorganic Organic silicon PEDOTPSS Heterojunction Solar Cells, *J. Phys. Chem. C* **117** (2013) 9049-9055.
- [21] H. Zhao, D. Xie, T. Feng, Y. Zhao, J. Xu, X. Li, H. Zhu, and T. Ren, Enhanced performance of PEDOT PSS n-Si hybrid solar cell by HNO₃ treatment, *Appl. Phys. Express* **7** (2014) 031603-1-031603-3.
- [22] D.A. Mengistie, M.A. Ibrahim, P.C. Wang, and C.W. Chu, High conductive PEDOT PSS treated with formic acid for ITO-free polymer solar cells, *ACS Appl. Mater. Interfaces* **6** (2014) 2292-2299.
- [23] H.J. Syu, S.C. Shiu, C.F. Lin, Silicon nanowire/organic hybrid solar cell with efficiency of 8.4%, *Sol. Energy Mater. Sol. Cells* **98** (2012) 267-272.
- [24] S.C. Shiu, J.J. Chao, S.C. Hung, C.L. Yeh, C.F. Lin, Morphology dependence of silicon nanowire/ Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) Heterojunction solar cells, *Chem. Mater.* **22** (2010) 3108-3113.
- [25] A. O. Conde, F. J. G. Sanchez, J. Muci, New method to extract the model parameters of solar cells from the explicit analytic solutions of their illuminated I-V characteristics, *Sol. Energy Mater. Sol. Cells* **90** (2006) 352-361.
- [26] S. I. Na, G. Wang, S. S. Kim, T.W. Kim, S. H. Oh, B. K. Yu, T. Lee, D.Y. Kim, Evolution of nanomorphology and anisotropic conductivity in solvent-modified PEDOTPSS films for polymeric anodes of polymer solar cells, *J. Mater. Chem.* **19**, (2009) 9045-9053.
- [27] S.M. Sze, K.K. Ng, *Physics of Semiconductor Devices* (Wiley, 2006), p. 161, 373-376.
- [28] S. Jackle, M. Liebhaber, J. Niederhausen, M. Buchele, R. Felix, R. G. Wilks, M. Bar,

- K. Lips, S. Christiansen, Unveiling the Hybrid n-Si/PEDOT:PSS interface, ACS Appl. Mater. Interfaces **8** (2016) 8841-8848.
- [29] H. C. Card, E. H. Rhoderick, Studies of tunnel MOS diodes I Interface effects in silicon schottky diodes, J. Phys. D: Appl. Phys. **4** (1971) 1589-1601.
- [30] T. Tung, Recent advances in Schottky barrier concepts, Mat. Sci. Eng. R **35** (2001) 1-138.
- [32] H. Luth, *Solid Surfaces, Interfaces and Thin films*, (Springer, 2015), p. 337, 358.

TABLE I. The average photovoltaic performances of the SiNWs /PEDOT:PSS hybrid solar cells with and without formic acid treatment.

Treatment	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
Pristine	0.491	29.22	55.77	8.00
FA treated	0.527	29.14	60.13	9.22

TABLE II. The average values of the characteristic parameters of the SiNWs /PEDOT:PSS hybrid solar cells with and without formic acid treatment calculated by equation (1).

Treatment	J_0 (A/cm ²)	n	R_s (Ω cm ²)	R_{sh} (Ω cm ²)
Pristine	2.59×10^{-5}	2.56	1.77	5.37×10^5
FA treated	2.56×10^{-6}	2.11	1.53	2.24×10^5

Table III. Values for the calculation.

Items	<i>Symbol</i>	Values
Band gap of silicon	E_g	1.1 eV

Work function of PEDOT:PSS	ϕ_P	5 eV
Electron affinity of silicon	χ	4.05 eV
Energy at charges neutrality level [32]	ϕ_{CNL}	0.4 eV

- Fig. 1 (a) Schematic diagram of the SiNWs/PEDOT:PSS hybrid solar cell. (b) The transmittance curves of the pristine and formic acid (FA) treated film. (c) The current density-voltage (J-V) curves of totally 50 hybrid solar cells with and without FA treatment under AM1.5G 1000W/m² illumination.
- Fig. 2 The distribution of open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF) and power conversion efficiency (PCE) of the pristine and formic acid (FA) treated devices.
- Fig. 3 (a) XPS Sulphur 2p spectra of the PEDOT:PSS film showed the decrease of PSS to PEDOT composition ratio after FA treatment. AFM height and phase images of (b,d) pristine and (c,e) formic acid treated PEDOT:PSS film. The upper are the height images and the bottom are the phase images. All images are 1 μm x 1 μm size.
- Fig. 4 The x-intercept of the extrapolation of the $1/C^2$ -V plot at 100kHz showed the fundamental built-in voltage at the SiNWs/PEDOT:PSS interface of the (a) pristine and (b) formic acid treated devices. (c) The relationship between ideality factor and the built-in voltage of the SiNWs/PEDOT:PSS hybrid solar cells.
- Fig. 5 The relationship between interface states partly equilibrium to PEDOT:PSS ($D_{s,P}$) and those partly equilibrium to silicon ($D_{s,Si}$) before and after formic acid treatment.
- Fig. 6 Energy band diagram of a SiNWs/PEDOT:PSS contact with an thin interfacial layer.