

Defect-Minimized PEDOT:PSS/Planar-Si Solar Cell with Very High Efficiency

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Hybrid solar cells made of a p-type conducting polymer, poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS), on Si have gained considerable interest in the fabrication of cost-effective high-efficiency devices. However, most of the high power conversion efficiency (PCE) performances have been obtained from solar cells fabricated on surface-structured Si substrates. High-performance planar single-junction solar cells have considerable advantages in terms of processing and cost, because they do not require the complex surface texturing processes. The interface of single-junction solar cells can critically influence the performance. Here, we demonstrate the effect of adding different surfactants in a co-solvent-optimized PEDOT:PSS polymer, which, in addition to acting as a p-layer and as an anti-reflective coating, also enhances the device performance of a hybrid planar-Si solar cell. Using time-of-flight secondary ion mass spectrometry, we conduct three-dimensional chemical imaging of the interface, which enables us to characterize the micropore defects found to limit the PCE. Upon minimizing these micropore defects with the addition of optimized amounts of fluorosurfactant and co-solvent, we achieve a PEDOT:PSS/planar-Si cell with a record high PCE of 13.3% for the first time. Our present approach of micropore defect reduction can also be used to improve the performance of other organic electronic devices based on PEDOT:PSS.

would have additional advantages of elimination of the complex surface texturing steps and reduction in the manufacturing cost, assuming of course that similarly high PCE could be achieved. The performance of PEDOT:PSS/planar-Si solar cells are affected by a number of factors, including conductivity and thickness of the active layers, chemical affinities of the two materials, nature of the surfactant used to increase the wettability of PEDOT:PSS on Si, interface effects (particularly the thickness of the native SiO_x layer and the associated interface defects), spin speed and time used to regulate the thickness of PEDOT:PSS films, annealing temperature and time after the spin-coating process, and top and bottom electrode configurations.^[5,6] Though there has been much effort to understand the influence of all these factors with the goal to improve the performance, the highest reported PCE is well below that of crystalline-Si-based solar cells and the Shockley–Queisser efficiency limit for a single-junction optimized photovoltaic device.^[7] Further understanding of the factors influencing the heterojunction

1. Introduction

Hybrid solar cells (HSC) based on an inorganic semiconductor and an organic conducting polymer are currently attracting a lot of attention because of their potential to produce highly efficient solar cells at a greatly reduced cost.^[1,2] In particular, solar cells made of a p-type polymer, poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS), on a n-type Si substrate are gaining strong interest mainly due to the simple fabrication processes and the high achievable power conversion efficiency (PCE) of above 10%.^[1–4] However, these high PCE solar cells have been obtained largely on surface-structured Si substrates.^[1,2] Indeed, solar cells based on planar substrates

will be helpful in producing HSCs competitive with crystalline-Si solar cells.

The conductivity of PEDOT:PSS has a great effect on the solar cell performance, and it depends on both the percentage of PSS, which has insulating properties, and the relative amount of co-solvent used to increase the conductivity.^[5,8,9] Ethylene glycol (EG) and dimethyl sulfoxide (DMSO) are often used as co-solvents to improve the conductivity of PEDOT:PSS. The addition of EG has recently been found to be more effective in improving the conductivity of the highly conducting grade PEDOT:PSS (PH1000, Clevios) than DMSO.^[10,11] We found that the addition of 7 wt% EG in PEDOT:PSS (referred here as EG7-PEDOT:PSS) provides a higher conductivity and consequently a higher PCE than additions of other EG or DMSO amounts.^[12] Along with PSS chain rearrangement, the polar groups in the co-solvent stabilize the PEDOT nanocrystals, which results in size enhancement and realignment of the PEDOT nanocrystals and enhances the conductivity and the solar cell performance.^[9,12]

The solar cell performance is also critically influenced by the nature of its interface. A recent report by Canesi et al. showed the importance of an interfacial layer to improve the efficiency

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in a polymer-oxide non-Si-based cell.^[13] Similarly, for the HSC with a Si substrate, a thin SiO_x layer at the interface acts as a passivation layer thus reducing the interface carrier recombination.^[14,15] The thickness of this oxide layer is important, because an insulating layer at the interface that is too thick will cause a charge transport barrier that degrades the performance. We have recently reported that the exposure of H-terminated Si in an ambient atmosphere for 1–3 h is optimal in producing a thin oxide layer^[14] with just the right thickness (1.5–1.8 nm) that enhances the solar cell performance.^[15] In addition, during the spin-coating process, the hydrophilic nature of the oxide layer can improve the wettability of PEDOT:PSS allowing the polymer to better disperse on the Si substrate. The amount of surfactant added into PEDOT:PSS therefore further enhances the wettability of the substrate surface. Consequently, a non-ionic surfactant, such as Triton-X100 (TX), is often added into PEDOT:PSS prior to the spin-coating process.^[14,15] Earlier reports indicated that the properties of PEDOT:PSS can also be modified by adding a cationic or anionic surfactant.^[16] However, there has been limited information about their effects on the interface and the solar cell performance. Further investigation is therefore needed on the influence of different surfactants on the properties of co-solvent optimized PEDOT:PSS and on the polymer interface with Si. To date, this type of studies are hindered by the fact that most of the presently available tools can only provide two-dimensional localized information of the device interface, thus missing the crucial depth information in the near surface and at the interface itself.^[14]

A three-dimensional (3D) view of the interface will indeed be beneficial to understanding the nature of the heterojunction that is so crucially important to device fabrication. Secondary ion mass spectrometry (SIMS) has been used, for more than 30 years, as an effective technique for probing detailed information of materials and devices.^[17,18] With the advancement of ion sputtering technology that employs a gas cluster ion source to sputter polymer or organic materials without creating a large surface disruption region, detailed 3D chemical imaging can be achieved with a depth resolution of 1–2 nm.^[18–20] Here we show that the interface properties of a PEDOT:PSS/planar-Si cell can be optimized by controlling the relative amount of a suitable surfactant present in the EG-optimized PEDOT:PSS solution. Furthermore, we compare the solar cell performances after the addition of different surfactants to EG7-PEDOT:PSS and to pristine PEDOT:PSS. We demonstrate that by adding 0.25 wt% fluorosurfactant (FS) into EG7-PEDOT:PSS, we achieve a record high PCE of 13.3%. Based on our TOF-SIMS 3D chemical imaging studies, we conclude that “minimal-defect” interfaces have been obtained by our procedure and the reductions in the number and size of the micropore defects present at the interface are responsible for the observed record high PCE.

2. Results and Discussion

In order to investigate the influence of the surfactant on the interface and device performance, two different surfactants, TX and FS (0.10 to 0.50 wt%), were added to EG7-PEDOT:PSS to reduce the surface tension and increase the wettability of the solution. Figure 1 shows the current density vs voltage curves

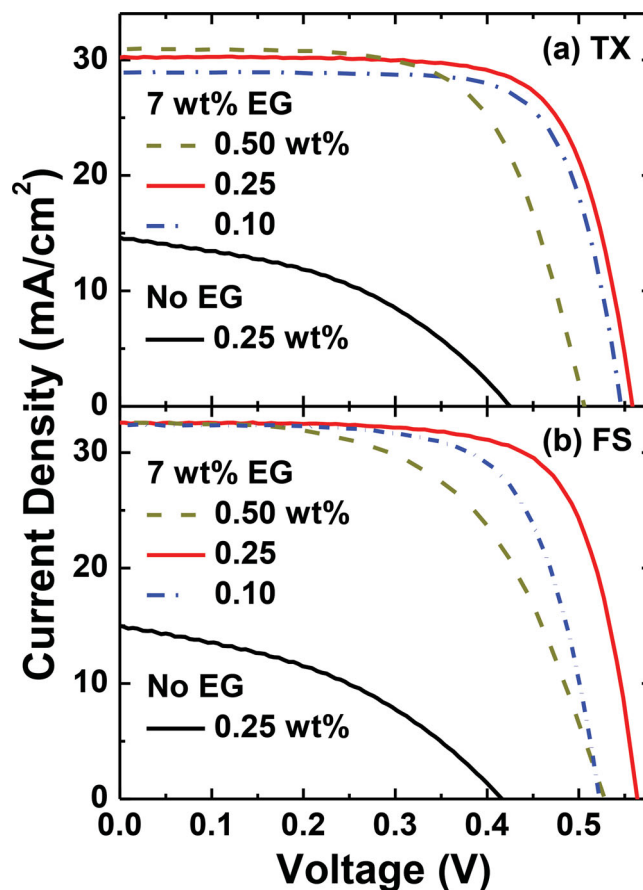


Figure 1. Current density vs voltage curves of PEDOT:PSS/planar-Si solar cells prepared with the addition of 7 wt% EG and of 0.10, 0.25 and 0.50 wt% a) TX and b) FS. They are compared with planar-Si solar cells made from pristine PEDOT:PSS (i.e., without EG) added with 0.25 wt% of the respective surfactant.

for PEDOT:PSS/planar-Si HSCs obtained with the addition of 7 wt% EG and different wt% of TX and FS to the polymer solution. It should be noted that all the HSCs in the present work were fabricated with SiO_x layers naturally grown to a carefully chosen thickness on the planar-Si substrates. The corresponding photovoltaic properties, including short-circuit current density (J_{sc}), open-circuit potential (V_{oc}), fill factor (FF), and PCE, are plotted in Figure 2 and summarized in Table 1. To demonstrate the influence of EG on the solar cell performance, we also fabricated a “TX-reference” and a “FS-reference” cells with just 0.25 wt% of the respective surfactants in the pristine PEDOT:PSS solution (i.e., without any EG added). Interestingly, the highest PCE of 13.3% was achieved for 0.25 wt% FS in EG7-PEDOT:PSS, which was 1.0% higher than the corresponding TX-added sample with the same surfactant wt%. Slightly lower PCE values were obtained for 0.10 wt% TX (11.6%) and FS (11.7%). The PCE decreased to 9.7% for 0.50 wt% surfactant addition. The J_{sc} value was found to increase significantly with increasing TX wt%, from 28.9 mA cm^{-2} for 0.10 wt% to 30.2 mA cm^{-2} for 0.25 wt%, and to 31.8 mA cm^{-2} for 0.50 wt%. On the other hand, the J_{sc} value remained essentially unchanged at $\approx 32.5 \text{ mA cm}^{-2}$ for all three FS wt%. For both surfactant additions, the highest V_{oc} values were obtained

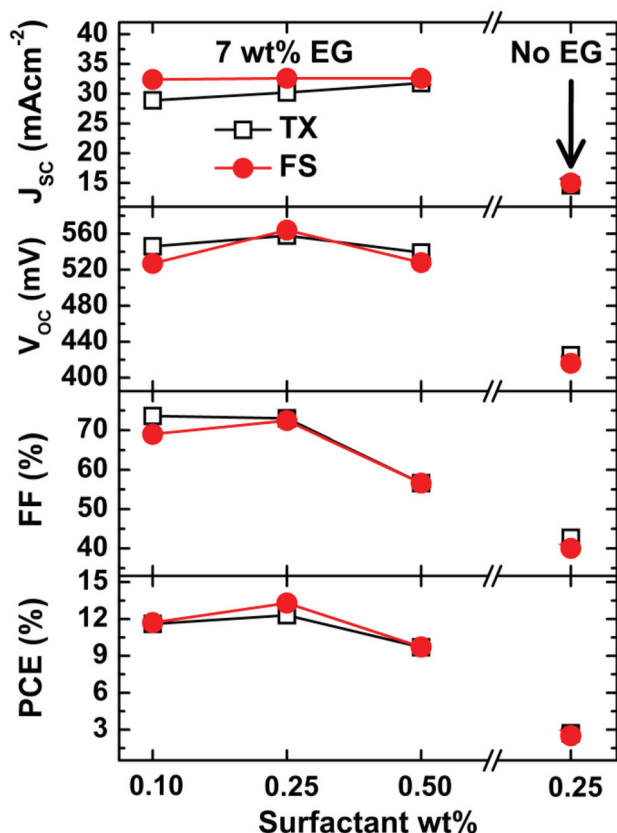


Figure 2. Photovoltaic properties including short-circuit current density (J_{sc}), open-circuit potential (V_{oc}), fill factor (FF), and power conversion efficiency (PCE) of PEDOT:PSS/planar-Si hybrid solar cells obtained with the addition of 0.10, 0.25, and 0.50 wt% of TX (open squares) and of FS (solid circles) in EG7-PEDOT:PSS and of 0.25 wt% of the respective surfactant in pristine PEDOT:PSS.

for 0.25 wt%, with 558 mV for TX and 564 mV for FS. High FF values of over 69% were achieved for surfactant additions of 0.10 and 0.25 wt%, with a lower FF value (56.6%) obtained with 0.50 wt%. Evidently, the addition of 0.25 wt% TX or FS was remarkably effective in improving the PCE performance, and a higher or lower amount of surfactant addition appeared to only

Table 1. Photovoltaic properties of PEDOT:PSS/planar-Si hybrid solar cells obtained with PEDOT:PSS added with 7 wt% EG and 0.10, 0.25, and 0.50 wt% of surfactant (TX or FS) and with pristine PEDOT:PSS added with no EG and 0.25 wt% surfactant.

Co-solvent	Surfactant [wt%]		J_{sc} [mA cm ⁻²]	V_{oc} [mV]	FF [%]	PCE [%]
7 w% EG	TX	0.10	28.9	546	73.6	11.6
		0.25	30.2	558	73.0	12.3
		0.50	31.8	539	56.6	9.7
	FS	0.10	32.4	527	69.0	11.7
		0.25	32.6	564	72.4	13.3
		0.50	32.6	528	56.6	9.7
No EG	TX	0.25	14.6	425	42.7	2.7
	FS	0.25	15.0	416	40.0	2.5

reduce the PCE slightly. The reference solar cells fabricated without EG addition to PEDOT:PSS exhibited very low PCE values of just 2.7% and 2.5% for 0.25 wt% additions of TX and FS, respectively. These samples showed FF values of 42.7% for TX and 40.0% for FS, with lower values for J_{sc} (14.6 mA cm⁻² for TX and 15.0 mA cm⁻² for FS) and V_{oc} (0.425 mV for TX and 0.416 mV for FS). These results indicate that the solar cell performance is greatly improved by the addition of the EG co-solvent and it can be further optimized by a 0.25 wt% FS addition to PEDOT:PSS. In separate experiments, we also prepared solar cells without adding any surfactant to EG7-PEDOT:PSS and to pristine PEDOT:PSS. These experiments showed that a continuous film could not be formed on the Si substrate. It is therefore extremely important to add a surfactant, albeit a small wt% (e.g. 0.25 wt% employed here), in PEDOT:PSS in order to produce a continuous film on the Si substrate.

To investigate the influence of a sulfur-based cationic surfactant in PEDOT:PSS on the solar cell performance, we prepared a separate cell with the addition of 0.25 wt% sodium dodecyl sulfate (SDS) in EG7-PEDOT:PSS. It has been reported in the literature that the addition of SDS can improve the conductivity of PEDOT:PSS and therefore the solar cell performance.^[16] However, our solar cell fabricated with the 0.25 wt% SDS addition showed a less impressive PCE of only 10.2% (Figure S1 and Table S1, Supporting Information). Addition of higher wt% SDS resulted in the formation of non-uniform films with very rough surfaces and they are omitted from further studies. The PCE of 13.3% obtained with the 0.25 wt% FS addition in the present work is therefore the highest efficiency ever reported for this type of hybrid solar cells. This is a remarkable result particularly in view of the fact that the record PCE was obtained on planar-Si substrates (and not on nanostructured Si substrates). Moreover, the reproducibility in the fabrication of this super high-efficiency HSC is excellent and has been verified by preparing multiple cells with 0.25 wt% FS addition to EG7-PEDOT:PSS (Table S2, Supporting Information).

It should be noted that contact angle measurements (not shown) could not show any significant difference with the slight variation in the surfactant wt% in PEDOT:PSS with or without EG. A detailed study is therefore carried out to elucidate the mechanism behind the high-efficiency performance of these hybrid solar cells. The effects of surfactant and EG additions on the optical properties have been examined by measuring the reflectance spectra of PEDOT:PSS on Si (Figure 3). For comparison, the reflectance spectrum of the Si substrate (dotted line) is also included in the figure. Evidently, the PEDOT:PSS layer acts as an anti-reflection coating on Si substrates and reduces the reflection to below 10% in the region of 620 to 745 nm. Slight blue-shifts in the reflection minima for the 0.10 and 0.25 wt% TX (Figure 3a) and red-shift for the 0.25 wt% FS (no EG) samples (Figure 3b) relative to the other samples are observed. On the other hand, the transmittance spectra of the films on glass for TX (Figure S2a, Supporting Information) and FS (Figure S2b, Supporting Information) with or without the addition of 7 wt% EG in PEDOT:PSS all show very high transmittance, similar to that of the glass substrate (top lines with the highest transmittance). As shown in the magnified views between 330 and 800 nm (Figure S2, Supporting Information, insets), addition of co-solvent and surfactant could introduce

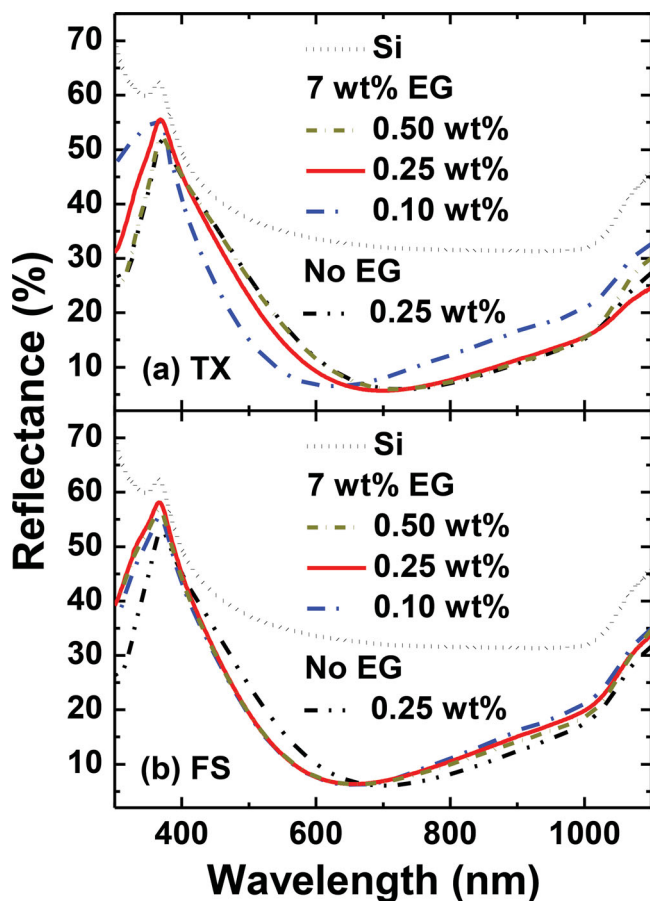


Figure 3. Reflectance spectra of Si substrate and of PEDOT:PSS layer on Si substrates obtained with the addition of 7 wt% of EG and of 0.10, 0.25, and 0.50 wt% surfactant, and of no EG but 0.25 wt% surfactant a) TX or b) FS.

minor changes in the spectra, with the highest transmittance found for surfactant addition of 0.25 wt%. These results therefore indicate that the addition of co-solvent and surfactant can only affect the optical properties of the PEDOT:PSS films slightly, but the layer acts as an anti-reflection coating that contributes to the observed large improvement in the solar cell performance. It is also clear that the transmittance as well as the anti-reflection properties of the PEDOT:PSS films can be maximized by optimizing the wt% of the added co-solvent and surfactant, which is essential to achieving the highest PCE performance for the planar-Si-based HSC reported here.

To evaluate the co-solvent and surfactant influence on the conductivity and structural properties of PEDOT:PSS, we conducted sheet resistance (R_s) measurement, and Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) studies. The very low observed R_s values (Figure 4a) demonstrate the highly conducting nature of EG7-PEDOT:PSS. The R_s values for TX-added EG7-PEDOT:PSS ($239 \Omega \text{ sq}^{-1}$ for 0.10 wt%, $272 \Omega \text{ sq}^{-1}$ for 0.25 wt%, and $252 \Omega \text{ sq}^{-1}$ for 0.50 wt%) are found to be generally higher than those for FS-added samples with the corresponding amounts ($212 \Omega \text{ sq}^{-1}$ for 0.10 wt%, $264 \Omega \text{ sq}^{-1}$ for 0.25 wt%, and $225 \Omega \text{ sq}^{-1}$ for 0.5 wt%). These R_s values are also lower than those of the PEDOT:PSS films

post-treated in different solvents reported in the literature.^[10] By contrast, the reference samples of pristine PEDOT:PSS with no EG but with 0.25 wt% TX or FS added exhibit very high R_s values ($4 \times 10^6 \Omega \text{ sq}^{-1}$ for TX and $3 \times 10^6 \Omega \text{ sq}^{-1}$ for FS, i.e., four orders of magnitude higher). Further study will be required to investigate why the higher R_s values are obtained for EG7-PEDOT:PSS films with TX or FS addition of 0.25 wt% in comparison to other wt%. Under the optimized conditions, PSS accumulation appears to be occurring largely on the top surface, which would result in a higher sheet resistance.^[9,21] However, interface effects and internal arrangement of the film with a compact PEDOT ordering could also enhance charge transport from the top electrode to the bottom electrode during the solar cell operation.

It is well known that in the highly conducting form of PEDOT:PSS, transformation in the PEDOT structure arising from the addition of co-solvents can be observed in their Raman spectra.^[9,22,23] Most of the major Raman peaks for PEDOT are observed between 1150 and 1610 cm^{-1} . Figure 4b compares the Raman spectra of 0.25 wt% TX and FS added EG7-PEDOT:PSS samples to those of 0.25 wt% TX and FS added pristine PEDOT:PSS samples. The features at 1425 and 1453 cm^{-1} (marked by vertical lines in the figure) correspond to the symmetric stretching modes of quinoid $\text{C}_\alpha\text{--C}_\beta$ and benzoid $\text{C}_\alpha = \text{C}_\beta$ components, respectively.^[22,23] Other major peaks at 1530 and 1568 cm^{-1} are attributed to the asymmetric $\text{C}_\alpha\text{--C}_\beta$ stretching modes. A discernible peak at 1366 cm^{-1} can be assigned to $\text{C}_\beta = \text{C}_\beta$ stretching vibrations while the features between 1100 and 1300 cm^{-1} correspond to $\text{C}_\alpha = \text{C}_\alpha$ stretching modes.^[22] The shifts in the peak positions from 1400 to 1460 cm^{-1} provide evidence for the rearrangement of the PEDOT chains, from the coil-like benzoid structure to a more linear or extended quinoid structure, as a result of the co-solvent addition.^[9,22,23] We also collected Raman spectra of TX and FS added EG7-PEDOT:PSS samples. These spectra (not shown) indicate that the addition of different amounts of surfactants in the co-solvent optimized PEDOT:PSS does not significantly change the spectra.

To examine the extent of how the addition of co-solvents in PEDOT:PSS affects the surface structure and sheet resistance, we employ XPS to determine the ratio of PEDOT to PSS at the sample surface (Figure 4c). A typical spectrum of the 0.25 wt% FS added EG7-PEDOT:PSS sample is shown in Figure 4d. The spectrum reveals two S 2p bands, each corresponding to a doublet of S $2p_{3/2}$ and S $2p_{1/2}$ components with a 1.2 eV spin-orbit splitting and a 2:1 intensity ratio. The weaker S $2p_{3/2}$ ($2p_{1/2}$) peak at 163.7 (164.9) eV and the stronger S $2p_{3/2}$ ($2p_{1/2}$) peak at 167.7 (168.9) eV correspond to the sulfur atoms of PEDOT and PSS, respectively.^[24] The S 2p spectra of the EG7-PEDOT:PSS and pristine PEDOT:PSS films after the addition of different amounts of surfactants do not show any discernible spectral difference (Figure S3). However, the ratio of the S $2p_{3/2}$ peak areas for PEDOT and PSS (used here to estimate the relative surface composition of PEDOT to PSS) shows variation with the amount of added co-solvents (Figure 4c). The highest PEDOT-to-PSS surface composition ratio (0.37) is found for the sample with 0.25 wt% FS-added to EG7-PEDOT:PSS. The 0.10 and 0.50 wt% additions of either TX or FS reduce the PEDOT-to-PSS surface composition ratio to less than 0.31. Interestingly, the composition ratios of the 0.25 wt% TX and FS added pristine

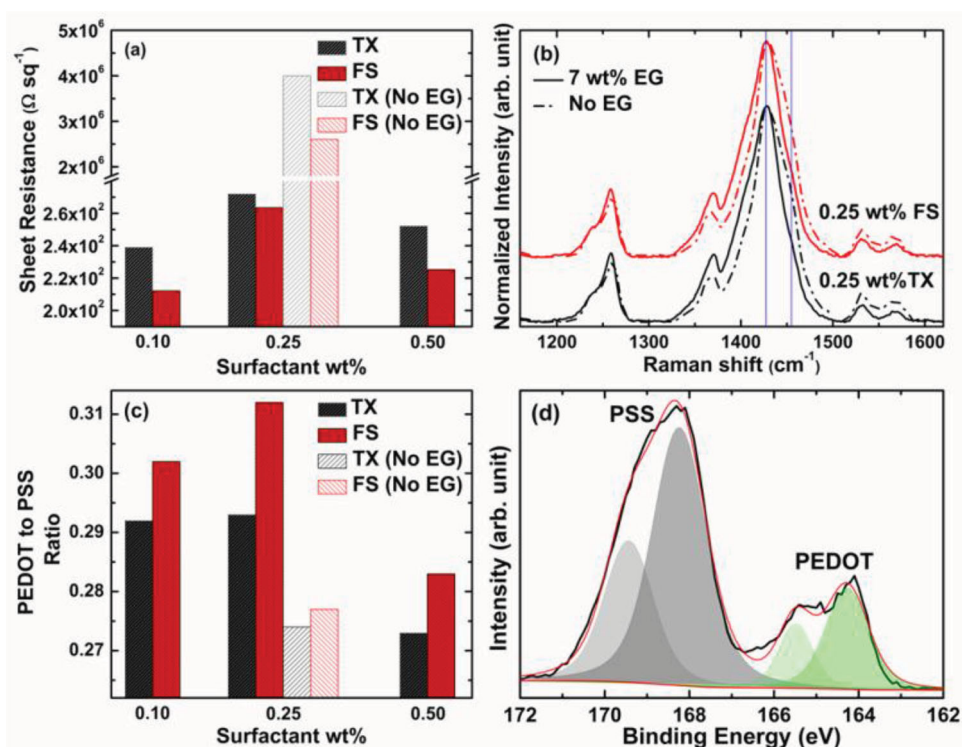


Figure 4. a) Sheet resistance of PEDOT:PSS layer on glass substrates obtained with the addition of 7 wt% of EG and of 0.10, 0.25, and 0.50 wt% of surfactant (TX or FS) and with just 0.25 wt% surfactant (TX or FS) and no EG. b) Raman spectra for PEDOT:PSS added with 0.25 wt% surfactant (TX or FS) with and without the addition of 7 wt% EG. c) Intensity ratios of the S 2p peak for the PEDOT feature to that for the PSS feature for the respective samples shown in (a). d) Typical XPS spectra of the S 2p region for PEDOT:PSS added with 0.25 wt% surfactant [TX (black) or FS (red)] and 7 wt% EG.

PEDOT:PSS samples are found to be similar to those of the 0.50 wt% added EG7-PEDOT:PSS samples. This latter result undermines the importance of reducing the PSS content at the surface with co-solvent addition in enhancing the conductivity, as suggested in the literature.^[21,25] Instead, it supports the mechanism of nanostructural reordering with PEDOT nanocluster formation and PSS aggregation to grain boundaries.^[12]

The influence of interface on solar cell performance is further evaluated by TOF-SIMS depth profiling and 3D chemical imaging studies. This was achieved by sputtering the sample with Ar₁₀₀₀⁺ ions to minimize the structural damage to the polymer layer while analysing the secondary ions using Bi₃⁺ ions (Figure S4, Supporting Information). The depth profiles of PEDOT (with its characteristic C₈H₇SO₃⁻ ions), interface SiO_x, and Si substrate components for EG7-PEDOT:PSS samples with the addition of 0.10, 0.25 and 0.50 wt% TX or FS and for pristine PEDOT:PSS added with 0.25 wt% TX or FS are shown in Figure 5. For the FS-added samples, the fluorine (F) component of the surfactant is also shown in the figure. The reduction in the sputtering time to completely remove PEDOT:PSS after the addition of EG is evident in the profiles. This indicates the formation of a thicker film for the pristine PEDOT:PSS sample without any EG added than that for the EG7-PEDOT:PSS sample (i.e. with 7 wt% EG added). For all the TX-added EG7-PEDOT:PSS samples, the corresponding PEDOT profiles show essentially the same sputtering time to reach the interface (Figure 5a). Similar behaviour is also observed for 0.25 and 0.50 wt% FS-added samples (Figure 5b).

However, the 0.10 wt% FS added EG7-PEDOT:PSS sample apparently requires a longer sputtering time to reach the interface. For the FS-added samples, the F depth profiles suggest a largely uniform distribution throughout the film with slightly higher accumulation on the top and bottom surfaces. The 3D chemical images of the total ions show similarly smooth surfaces for all the samples. A representative top-view of such an image for the 0.25 wt% FS-added EG7-PEDOT:PSS sample is shown in Figure S5, Supporting Information. The 3D chemical images of the PEDOT components for the interface regions of 0.10, 0.25, and 0.5 wt% TX (FS) added EG7-PEDOT:PSS samples and of 0.25 wt% TX (FS) added PEDOT:PSS are shown in Figure 5c–f (g–j). The dark circular regions with diameter of 10–20 μm indicate the presence of micropore defects in the PEDOT:PSS layer, and these micropore defects are evidently present at the interfaces for all the samples. Discernibly fewer micropore defects are observed in the 3D chemical images of both the TX and FS added EG7-PEDOT:PSS samples (Figure 5c–e and g–i). Together with the smaller thickness of the micropores, the few number of micropore defects in the EG7-PEDOT:PSS samples result in a larger interface contact area. In contrast, the corresponding 3D chemical images of the PEDOT:PSS samples (without EG addition) show more micropore defects at the interfaces (Figure 5f,j). The larger thickness of the micropores found for the pristine PEDOT:PSS films causes a higher barrier for charge transport, resulting in poor solar cell performance. On the other hand, for an optimized amount of surfactant (0.25 wt% FS), a “minimal-defect”

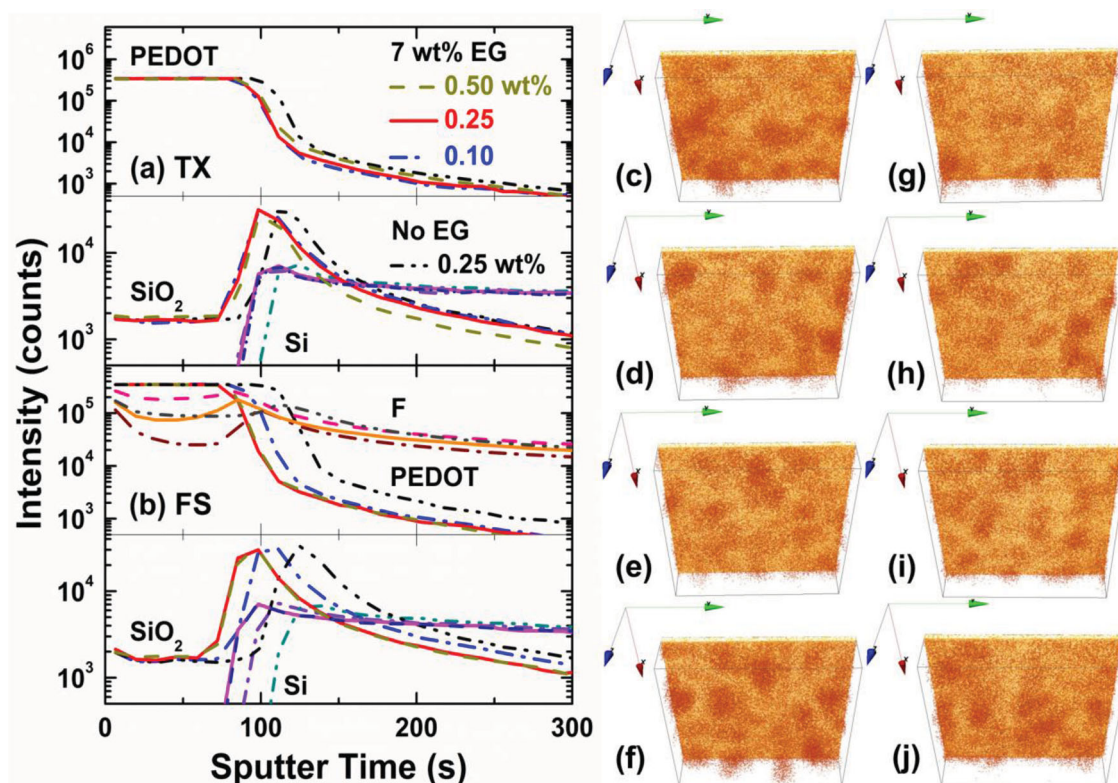


Figure 5. TOF-SIMS depth profiles of PEDOT:PSS/planar-Si hybrid solar cells obtained with the addition of 7 wt% EG and of 0.10, 0.25 and 0.50 wt% surfactant and with the addition of no EG and just 0.25 wt% surfactant of a) TX and b) FS. Interface view of the corresponding 3D chemical images ($150 \times 150 \mu\text{m}^2$) of PEDOT ($\text{C}_8\text{H}_7\text{SO}_3^-$ ions) component for the cells obtained with PEDOT:PSS added with 7 wt% EG and c,g) 0.50, d,h) 0.25, and e,i) 0.10 wt% surfactant, and f,j) for the cells obtained with pristine PEDOT:PSS added with 0.25 wt% surfactant c–f) TX and g–j) FS.

interface with maximum contact area between the co-solvent-added PEDOT:PSS polymer and the Si substrate is achieved. The schematic models in **Figure 6** illustrate the observed differences in the nature of the interfaces between surfactant-added PEDOT:PSS with and without the addition of co-solvent, with the charge transfer processes during the cell operation marked by arrows. The reduction in charge transport at the interface for low-efficiency devices due to micropore formation is mainly responsible for poor solar cell performance.

Our results differ from the earlier finding about HSCs fabricated on Si nanowires, the high PCE of which was obtained by increasing the contact area by creating a nanostructured substrate.^[1,2] Here, we demonstrate that it is possible to achieve

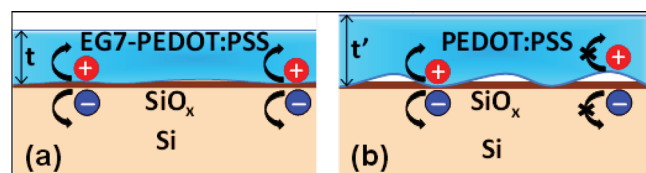


Figure 6. Schematic models of the PEDOT:PSS layer formation on SiO_x/Si for a) EG7-PEDOT:PSS and b) pristine PEDOT:PSS, added with 0.25 wt% surfactant (FS or TX). Accumulation of PSS on the top polymer surface and at the interface, along with micropore-pronounced formation at the interface of the pristine PEDOT:PSS polymer layer, are responsible for the less efficient charge transfer processes (shown with arrows) during solar cell operation.

record high PCE with just planar substrates by eliminating micropore defect formation with careful tuning of the co-solvent and surfactant addition. Addition of suitable wt% of the surfactant is found to be particularly important in the structural rearrangement of PEDOT:PSS and in the improvement of the interface characteristics during its layer formation on the substrates. A less optimal wt% (higher or lower than 0.25 wt%) of surfactant can lead to formation of a large number of micropore defects at the interface that restrict the charge transport and lower the solar cell performance. The similarity in the PEDOT-to-PSS ratios found for the 0.50 wt% TX or FS added EG7-PEDOT:PSS and the 0.25 wt% FS or TX added pristine PEDOT:PSS suggests that the conductivity increase observed for surfactant addition is not exclusively related to the variation of the PSS content at the top surface. The TOF-SIMS depth profiles provide evidence for the accumulation of F content on the top and bottom surfaces of FS-added samples. It is possible that PSS molecules are also aggregating in a similar manner on the top surface of the polymer layer and at the interface (Figure 6). This PSS accumulation can be minimized with optimized amounts of co-solvent and surfactant, which augmented by the internal rearrangement leads to the formation of thinner films ($t < t'$ in Figure 6) and further improvement in the conductivity of PEDOT:PSS films. It should be noted that the variations in the solar cell performance, especially V_{oc} and J_{sc} , are related to the recombination levels and to the front carrier collection efficiency in the co-solvent-modified and surfactant-added

PEDOT:PSS. Addition of appropriate amounts of co-solvent and surfactant causes internal rearrangement of PEDOT and PSS in an effective manner by maximizing the conducting channels in the PEDOT:PSS layer and by increasing the contact area with the substrate surface that enhances the solar cell performance. Our results therefore demonstrate that HSC with a very high PCE can indeed be obtained even on planar substrates using the above approach, and the PCE achieved thus far could obviously be further improved by introducing nanostructures to the substrate surface (as already shown by earlier work^[1,2] and/or by refining the top electrode configuration.

3. Conclusion

Planar-Si HSCs with record high PCE exceeding 13% are achieved for the first time by addition of a carefully chosen amount of a suitable surfactant to a co-solvent optimized PEDOT:PSS polymer. The TOF-SIMS 3D chemical images of the interface reveal that the high PCE is likely resulted from the minimal-defect interface so obtained between PEDOT:PSS and the planar Si substrate. The solar cell performance could be further improved by fabricating the device on surface-structured substrates, by incorporating plasmonic nanoparticles, and by refining the electrode configuration. The very low sheet resistance value achieved for 0.25 wt% FS-added EG7-PEDOT:PSS indicates that these procedures can also be very useful for improvement in the properties of other electronic devices based on PEDOT:PSS.

4. Experimental Section

The HSCs were fabricated on one-side-polished, n-type Si(100) substrates (Phosphorus doped), with resistivity of 1–2 Ω cm and thickness of 250 μ m (Virginia Semiconductor Inc.). The substrates were ultrasonically cleaned for 10 min successively in acetone and isopropyl alcohol and rinsed with Millipore water. After cleaning, the substrates were immersed in 2% hydrofluoric acid (HF) for 10 min to remove the native oxide and then thoroughly cleaned in Millipore water. The unpolished side of the Si substrate was deposited with Al metal (200 nm thick) in a dual-target magnetron sputtering system (EMS575X) immediately after the HF cleaning. After the Al deposition, the substrates were kept in an ambient air atmosphere for 1 h to facilitate the formation of a naturally grown SiO_x layer, which was used to provide a favourable internal electrical field to enhance the solar cell performance.^[14,15]

PEDOT:PSS (Clevios, PH-1000) was mixed with 7 wt% EG, which is designated here as EG7-PEDOT:PSS. All other chemicals were purchased from Sigma-Aldrich. Three sets of EG7-PEDOT:PSS were prepared by adding three different types of surfactants to investigate the influence of surfactants on the co-solvent-optimized PEDOT:PSS and their solar cell performance. They include a non-ionic surfactant (Triton-X100, designated as TX), a fluorosurfactant (FS-300, designated as FS) and a cationic surfactant (sodium dodecyl sulfate, SDS). For the first two sets, three different wt% of TX and FS (0.10, 0.25, and 0.50 wt%) were added to EG7-PEDOT:PSS. The third EG7-PEDOT:PSS solution was prepared with 0.25 wt% SDS addition in order to compare with the solutions obtained with the same wt% TX and FS addition. We also prepared two reference solutions by adding 0.25 wt% of TX and FS to as-received PEDOT:PSS without any EG added, in order to facilitate comparison of the improvement of solar cell performance with EG-added PEDOT:PSS. These five sets of PEDOT:PSS solutions were

spin-coated on planar-Si substrates at a spin rate of 6,000 rpm for 1 min, and followed by annealing at 108 ± 2 °C on a hot plate for 10 min in air. A comb-type Ag metal grid with a thickness of 50 nm was sputter-deposited on the polymer layer through a shadow mask, and it was used as the top electrode for solar cell property measurement. The solar cells performances (*I*–*V*) were measured using a solar cell characterization system (PV Measurements IV5). The *I*–*V* measurements were performed under 100 mW cm^{-2} illumination using a class ABA solar simulator (AM 1.5G) in air with a typical device area of 6.3×6.3 mm^2 . Prior to the *I*–*V* measurement, a Si reference cell (PVM782 with a BK7 window) was used to calibrate the light source intensity.

The reflectance spectra of PEDOT:PSS layer on Si (without the Ag top electrodes) and transmittance spectra of PEDOT:PSS layer spin-coated on glass substrates were collected in an ultra-violet-visible spectrometer (PerkinElmer, Lambda 35 and 1050, respectively). The samples on glass substrates were also used for sheet resistance measurement using the four-point probe method in a van der Pauw configuration (Ecopia HMS-5300). Ag paste was applied to the corners of the PEDOT:PSS layer on glass and used to provide contact points for the sheet resistance measurement. Raman spectra were collected at room temperature with a laser wavelength of 785 nm and laser power of 50 mW in a Bruker Senterra spectrometer. X-ray photoelectron spectroscopy studies were performed in a Thermo-VG Scientific ESCALab 250 microprobe equipped with a monochromatic Al $K\alpha$ source (1486.6 eV). TOF-SIMS measurements were conducted in an ION-TOF 5 system (IONTOF GmbH), equipped with a 2 m long reflectron time-of-flight analyzer operated in the negative polarity mode, and a Bi_3^+ analysis ion source (30 kV) and an Ar cluster ion (Ar_{1000}^+) sputtering source (5 kV). Depth profiling was performed in the spectrometry mode (non-interlaced) with a cycle time of 200 μ s, a sampling area of 150×150 μm^2 and sputtering area of 400×400 μm^2 . The TOF-SIMS spectra were mass-calibrated on the C_x fragments.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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