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Citation: *Appl. Phys. Lett.* **100**, 183901 (2012); doi: 10.1063/1.4709615

View online: <http://dx.doi.org/10.1063/1.4709615>

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Highly efficient crystalline silicon/Zonyl fluorosurfactant-treated organic heterojunction solar cells

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(Received 27 February 2012; accepted 15 April 2012; published online 1 May 2012)

We demonstrate a highly efficient hybrid crystalline silicon (c-Si) based photovoltaic devices with hole-transporting transparent conductive poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonic acid) (PEDOT:PSS) films, incorporating a Zonyl fluorosurfactant as an additive, compared to non additive devices. The usage of a 0.1% Zonyl treated PEDOT:PSS improved the adhesion of precursor solution on hydrophobic c-Si wafer without any oxidation process. The average power conversion efficiency η value was 10.8%–11.3%, which was superior to those of non-treated devices. Consequently, c-Si/Zonyl-treated PEDOT:PSS heterojunction devices exhibited the highest η of 11.34%. The Zonyl-treated soluble PEDOT:PSS composite is promising as a hole-transporting transparent conducting layer for c-Si/organic photovoltaic applications. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4709615>]

Crystalline Si (c-Si) heterojunction solar cells with intrinsic hydrogenated amorphous silicon (a-Si:H) thin-film (HIT) have also been extensively studied for high performance devices with a power conversion efficiency η of 22%–23%.^{1,2} The a-Si:H and transparent conductive oxide (TCO) layer, in general, are fabricated by plasma-enhanced chemical vapor deposition (PE-CVD) and sputtering. The alternative approach using organic solar cells is potentially cheaper due to low-temperature processing such as spin-coating and spray deposition, but the organic devices are not very efficient. To this aim, we have demonstrated the c-Si(100)/organic hybrid photovoltaic devices using spin-coated poly(ethylenedioxy thiophene):poly(styrenesulfonate) (PEDOT:PSS):Graphene oxide (GO) composite with a high efficiency of 10.7%.³ The alternate spin coating was attempted to improve the film uniformity on hydrophobic c-Si(100) wafer. But these products were still inhomogeneous frequently. The usage of the electrospray deposition (ESD) made possible the uniform coating, although the film deposition rate was very slow of 0.2 nm/s.⁴ Simple coating technique with high film uniformity, therefore, is strongly required on hydrophobic c-Si wafer. Recently, Vosgueritchian *et al.* revealed that the Zonyl fluorosurfactant-treated PEDOT:PSS film showed lower sheet resistance compared to untreated films, and it is a possible material for indium tin oxide (ITO)-free organic photovoltaics as stretchable and flexible transparent electrodes.^{5,6} These findings will be also expected for the uniform spin coating of PEDOT:PSS on hydrophobic c-Si wafer without any complicate processes.

In this paper, we demonstrate the highly efficient c-Si/Zonyl-treated PEDOT:PSS heterojunction solar cells showing a high efficiency of 10%–11%.

Figure 1 shows the schematic of the c-Si/PEDOT:PSS hybrid solar cells. One-side-polished with N-type CZ Si(100) with resistivity of 3–5 Ω -cm and thickness of 300 μ m was used as a substrate. The c-Si wafers were cleaned in ace-

tone, ethanol, and deionized water for 10 min each. Following that they were dipped in 5% hydrofluoric (HF) acid to remove any native oxide. Highly conductive 5% by weight dimethyl sulfoxide (DMSO) added PEDOT:PSS (CLEVIOS1000) mixed with different amounts of Zonyl fluorosurfactant was then spin coated onto the RCA H-terminated c-Si wafer with 1000 rpm for 60 s followed by thermal annealing at 140 °C for 30 min. Finally, the top ring electrode (5 mm \times 5 mm in inner size, 0.1 mm width) was formed using silver paste by pattern printer. The outer area of the silver electrode was covered with an opaque mask to eliminate the incident light. The silver electrode has resulted in a power loss of 5%–7% of the incident light due to shadowing. The PEDOT:PSS composite films were characterized by atomic force microscopy (AFM; Seiko Instruments SPA-300/SPI-3800), spectroscopic ellipsometry (SE), current density-voltage (J - V) in the dark and under illumination of AM1.5G, 100 mW/cm² simulated solar light (Bunkoukeiki CEP-25BX), and capacitance-voltage (C - V) measurements.

In Fig. 2, the AFM and photo images of 100 nm-thick PEDOT:PSS films on flat c-Si(100) wafer are shown with and without adding a 0.1% Zonyl fluorosurfactant. The former was prepared by alternate spin coating with 1000 and 2000 rpm after dropping few shots of pure PEDOT:PSS solution to improve the film uniformity rather than the single spin coating. The latter was prepared by the spin coating with 1000 rpm for 60 s and subsequent dry at 140 °C for 30 min. Both film thicknesses were around 100 nm. It is clear that the surface uniformity of spin-coated PEDOT:PSS

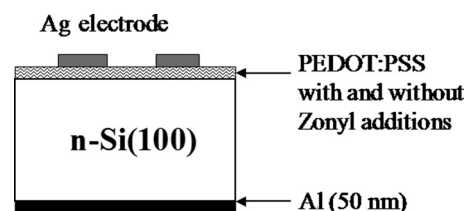


FIG. 1. Schematic of c-Si/PEDOT:PSS heterojunction photovoltaic device.

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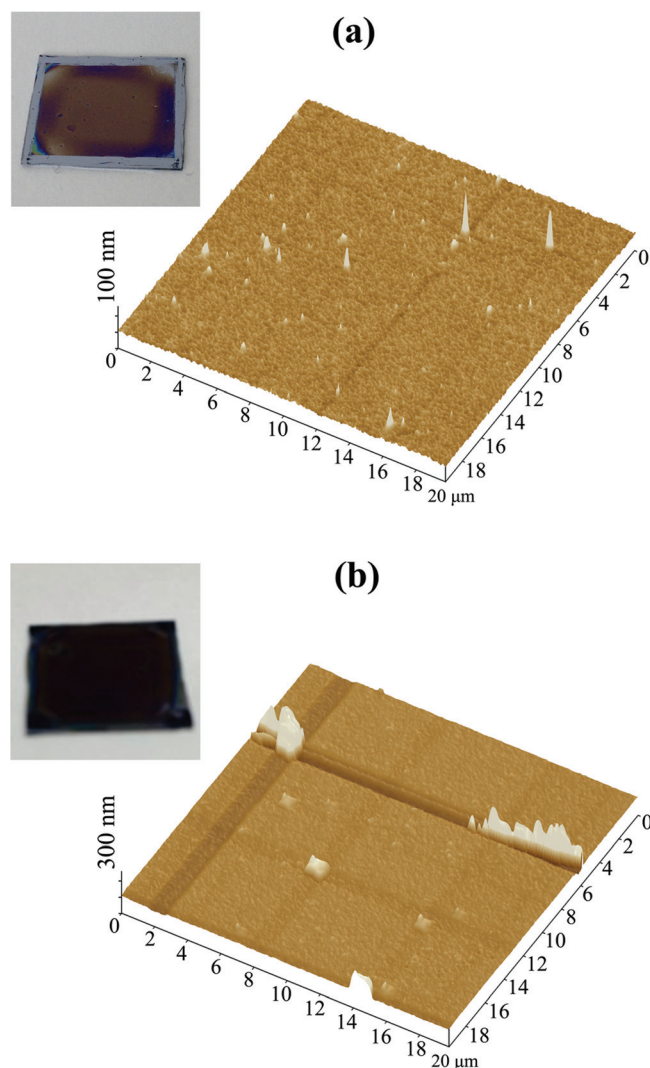


FIG. 2. AFM and photo images of (a) pristine and (b) 0.1% Zonyl added PEDOT:PSS films on c-Si wafer. The former was for the alternate spin coating with 1000 and 2000 rpm after dropping few shots of pure PEDOT:PSS solution. The latter was prepared by spin coating with 1000 rpm for 60 s and subsequent dry at 140 °C for 30 min. Both film thicknesses were around 100 nm.

composite is improved markedly despite of the 0.1% Zonyl addition. The root-mean-square roughness (RMS) values were 2.6 and 3.3 nm for the films with and without a 0.1% Zonyl addition, respectively, in the $20 \times 20 \mu\text{m}^2$ area.

Figure 3 shows the J - V characteristics in the dark and under illumination of AM1.5G 100 mW/cm^2 simulated solar light, and external quantum efficiency (EQE) spectra for the PEDOT:PSS/c-Si hybrid devices with and without a 0.1% Zonyl addition. The photovoltaic parameters, i.e., open circuit voltage V_{oc} , short circuit current density J_{sc} , fill factor FF , and η , are summarized for the devices with different Zonyl weight percents in Table I. It is seen that dark current density J_d is suppressed significantly for the 0.1% Zonyl added device [Fig. 3(a)]. The calculated series resistance R_s showed a minimum of $0.75 \Omega\text{-cm}^2$ with a highest shunt resistance R_{sh} of $1.2 \times 10^4 \Omega\text{-cm}^2$ for the 0.1% Zonyl added PEDOT:PSS diode. The reduction in the dark current is clear evidence for reduced electron current and the suppression of electron recombination. These imply that the junction property is improved by the 0.1%

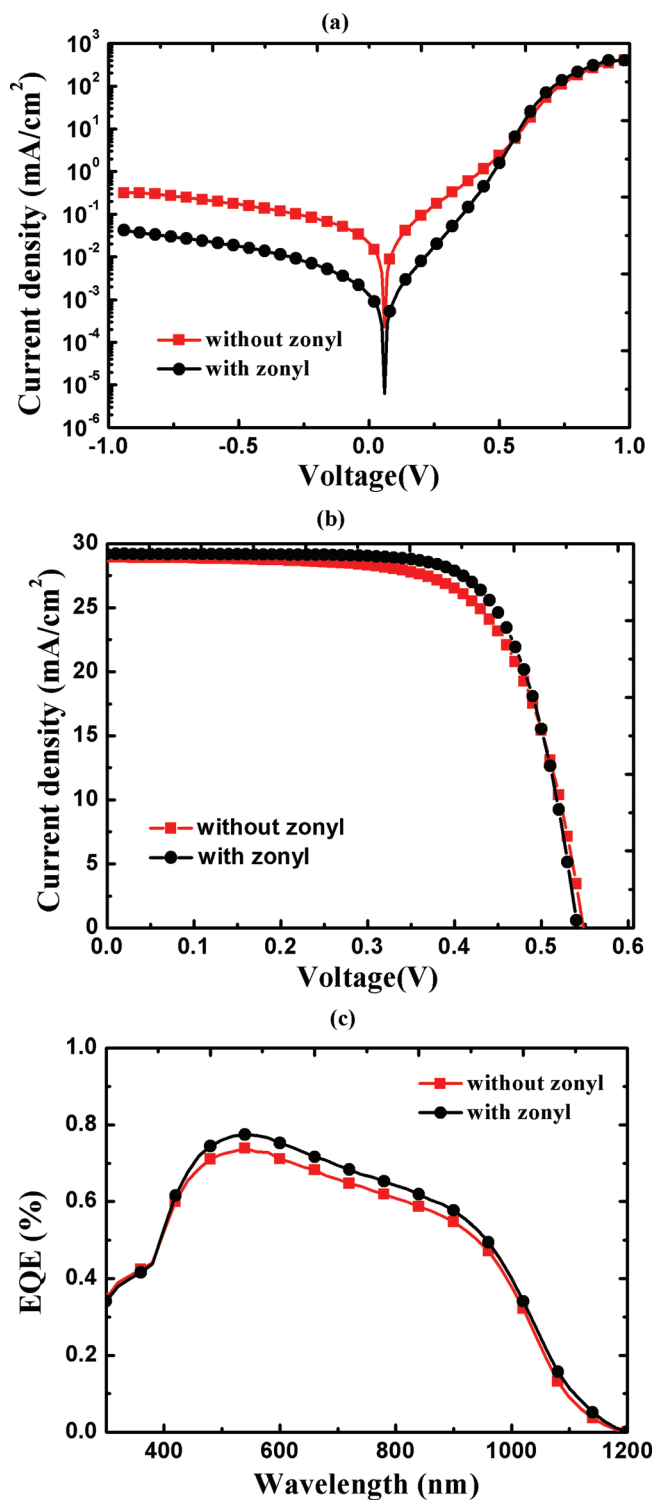


FIG. 3. J - V curves of c-Si heterojunction solar cells for PEDOT:PSS composite buffer layers with and without an addition of a 0.1% Zonyl fluorosurfactant (a) in the dark and (b) under illumination of a simulated AM1.5G 100 mW/cm^2 light. (c) EQE spectra of corresponding c-Si hybrid solar cells.

Zonyl treatment without creating additional defects at the junction interface.

The devices for the pristine PEDOT:PSS buffer layer exhibited an average η of 9.5%–10.2%. This maximum η value was achieved of a η of 10.2% with a J_{sc} of 29.0 mA/cm^2 , a V_{oc} of 0.527 V, and a FF of 0.669. Once 0.1% Zonyl was added in conductive PEDOT:PSS, the average η value increased to 10.8%–11.34%. The best performance was

TABLE I. Performance details (V_{oc} , J_{sc} , FF , η , and R_s) of the c-Si/PEDOT:PSS hybrid cells with different Zonyl concentrations.

Zonyl concentrations	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	Eff (%)	R_s (Ω cm ²)	R_{sh} (Ω cm ²)
Pristine	29.02	0.527	0.669	10.23	0.99	6829.4
0.1%	29.20	0.541	0.718	11.34	0.75	12050.1
0.5%	31.10	0.550	0.631	10.80	1.46	7184.6
1%	30.10	0.539	0.545	8.85	3.89	4891.5
10%	3.65	0.235	0.162	0.148	8.54	34.7

achieved with a η of 11.34%, a J_{sc} of 29.2 mA/cm², a V_{oc} of 0.541 V, and a FF of 0.718 [Fig. 3(b)]. Obviously, the improvement in the device performance can be attributed to the usage of the 0.1% Zonyl addition. In particular, the FF value improved from 0.669 to 0.718 by the 0.1% Zonyl addition. The EQE improved markedly in the visible and near-infrared region for the 0.1% Zonyl added devices compared to that of pristine PEDOT:PSS [Fig. 3(c)]. Further increases of the Zonyl content deteriorated the cell performance (Table I).

Figure 4 shows the $1/C^2$ - V plot at 1 MHz and C - f (f : measurement frequency) characteristics of c-Si/PEDOT:PSS composite junction solar cells with and without a 0.1% Zonyl addition. The built-in potential V_b and donor density N_d were 0.87–0.94 V and 5.82×10^{15} cm⁻³ for the pristine PEDOT:PSS diode, whereas V_b and N_d were 0.88–0.96 V

and 7.99×10^{15} cm⁻³, respectively, for the 0.1% Zonyl added diode [Fig. 4(a)]. The slope of the $1/C^2$ - V plot relating to $(1/N_d + 1/N_a)$: N_a acceptor density) was lower for the 0.1% Zonyl added PEDOT:PSS diode than that of pristine PEDOT:PSS, suggesting that the N_a in the organic increased. In addition, the junction capacitance was almost independent of f , and it was suppressed to be lower for the lower measurement-frequency range in the 0.1% Zonyl added PEDOT:PSS [Fig. 4(b)]. These imply the lower interface defect density.⁷ Thus, the role of the 0.1% Zonyl addition into conductive PEDOT:PSS is considered as the suppression of electron recombination, and/or promote the hole current by enhancing the carrier mobility.⁸ This is achieved by inserting PEDOT:PSS with wider energy gap than 1.1 eV such that the lowest unoccupied molecular orbital (LUMO) of the organic is higher than the conduction minimum (E_c) of c-Si, the lower space charge density at the interface and/or the enhanced hole mobility by the lowering the highest occupied molecular orbital (HOMO) of the organic-valence band maximum (E_v) offset. In general, the V_{oc} is described through the relation $V_{oc} = \frac{nkT}{q} \ln(\frac{J_{sc}}{J_0})$.⁹ Thus, large LUMO- E_c offset result in a lower J_0 and, hence, a larger V_{oc} . However, the SE characterization revealed that the HOMO-LUMO gap energy in PEDOT:PSS was almost same for both samples. Both V_{oc} and J_{sc} were 0.52–0.54 V and 28–30 mA/cm², respectively, and they were almost independent of the Zonyl content up to 0.5% by weight. Thus, the improvement of FF value by the 0.1% Zonyl treatment can be attributed to the lowering of space charge layer at the c-Si/PEDOT:PSS interface. It is also well known that the spin-coated PEDOT:PSS exhibit the prominent anisotropic optical property, i.e., the ordinary optical component showing the metallic property and the extraordinary component exhibiting a dielectric behavior.¹⁰ This property also promotes the role of the hole-transporting layer as well as the highly transparent conductive layer by adding the 0.1% Zonyl. Thus, the improved adhesion of PEDOT:PSS conjugated polymer on hydrophobic c-Si wafer results in the efficient suppression of defect generation at the c-Si/organic interface, resulting in the higher device performance in addition to a native SiO_x layer.^{11–14}

In conclusion, we have studied the role of Zonyl fluoro-surfactant addition to conductive PEDOT:PSS on the performance of c-Si/PEDOT:PSS hybrid heterojunction devices. The 0.1% Zonyl addition to conductive PEDOT:PSS improved significantly the adhesion on hydrophobic c-Si wafer. As a consequence, a highly efficient c-Si/organic hybrid solar cell was obtained with the highest power conversion efficiency of 11.34% with a J_{sc} of 29.2 mA/cm², a V_{oc} of 0.541 V, and a FF of 0.718. Such Si/organic hybrid cells can potentially further deliver high conversion efficiency combining with the

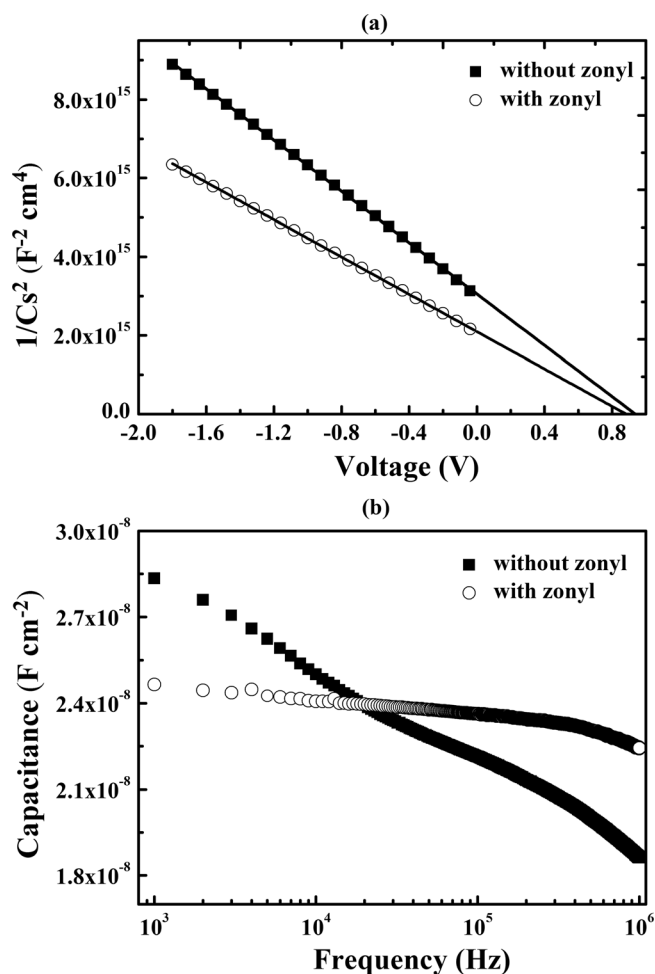


FIG. 4. (a) $1/C^2$ - V and (b) C - f plots of c-Si/PEDOT:PSS composite heterojunction diodes with and without an addition of a 0.1% Zonyl fluoro-surfactant.

textured structure and the creation of ohmic junction at the rear surface.

This research was partially supported by a Japan Science and Technology (JST) Agency (A-step) grant and a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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