Efficient organic/polycrystalline silicon hybrid solar cells

Qiming Liu ^{a,1}, Tatsuya Ohki^a, Dequan Liu^b, Hiromitsu Sugawara^a, Ryo Ishikawa^a, Keiji Ueno^a,
and Hajime Shirai ^{a,*}

^a Graduate School of Science and Engineering, Saitama University, Saitama, 338-8570 Japan.

^b International Center for Materials Nanoarchitectonics (MANA), National Institute for Materials Science, Tsukuba, 305-0047 Japan

Abstract

We firstly investigated efficient poly(3,4-ethylenedioxythiophene): poly(styrenesulfonic acid) (PEDOT:PSS)/n-type polycrystalline silicon (p-Si) heterojunction solar cells fabricated by chemical mist deposition (CMD) using a high-pressure H₂O-vapor-treated p-Si prior to organic film deposition. High-pressure H₂O vapor treatment of the p-Si efficiently suppressed grain boundary defects and improved carrier transport at the PEDOT:PSS/p-Si interface. Furthermore, compared to spin coated devices, the CMD devices demonstrated a more uniform photovoltaic

¹ Corresponding author at Graduate School of Science and Engineering, Saitama University. Saitama, 338-8570 Japan.

Phone: +81-048-858-3676

Email address: Liuqm670@gmail.com (Q. Liu), Shirai@fms.saitama-u.ac.jp (H. Shirai).

performance. The power conversion efficiency of the PEDOT:PSS/p-Si heterojunction solar cells was 9.7% with a short-circuit current density of 33.5 mA/cm², an open-circuit voltage of 0.54V, and a fill factor of 0.53. These findings suggest that CMD with a negatively charged mist precursor provides uniform adhesion of PEDOT:PSS on p-Si, resulting in increased photovoltaic performance.

Keywords

Polycrystalline silicon; Hybrid solar cells, Surface passivations, Conjugated polymers, Bulk heterojunctions

Introduction

Conjugated polymer-silicon heterojunction solar cells composed of an n-type crystalline silicon (c-Si) and organic poly(ethylene dioxythiophene):poly(styrene sulfonate acid)(PEDOT:PSS) layers provide the unique possibility of combining the high energy conversion efficiency of c-Si solar cells with the potentially low fabrication cost of organic solar cells. Promising efficiencies of ~12% have already been reported [1-10], and the highest efficiencies were realized by either passivating the organic-silicon interface using an ultrathin interface-passivating tunneling silicon oxide (SiO_x) layer containing carbon nanotubes, molybdenum tri-oxide (MoO₃), and ferroelectric polymer poly(vinylidene fluoride-tetrafluoroethylene) P(VDF-TeFE), graphene, graphene oxide, and metal nanowires at the c-Si/PEDOT:PSS interface [11-15]. The passivation layers can be fabricated by a simple solution process such as spin coating (SC), and its work function can be easily tuned as desired to optimize the device performance. These findings suggest that the

organic films could be used as a surface passivation layer for c-Si, similar to SiO_2 and SiN_x , although the optical and carrier transport properties depend on the solvent and preparation method [16].

To date, most research efforts have predominantly focused on the effects of the c-Si surface morphology, passivation, and the optical and carrier transport properties of PEDOT:PSS [16,17]. To further improve device performance, the usage of textured c-Si can increase the effective optical path of incident light inside absorbing materials by light trapping or scattering. However, for spin coating (SC), the uniformity of the organic layer on textured c-Si is insufficient, and causes performance variation [7, 18]. Therefore, we attempted organic deposition by chemical mist deposition (CMD) using a negatively charged mist precursor. The optical properties and hole mobility of PEDOT:PSS can be controlled during film growth by CMD using a negative DC bias to charge the mist precursor [19]. Better uniformity of PEDOT:PSS on textured c-Si(100) and an average η of 12.7% were obtained with a short-circuit density J_{sc} of 35 mA/cm^2 , an open-circuit voltage V_{oc} of 0.54 V, and a fill factor FF of 0.68 due to enhanced light trapping. Thus, CMD is also expected to provide a uniform organic coating on micro-roughened substrates such as a p-Si board using the cast method to provide low-cost photovoltaic devices.

In the present paper, we demonstrate for the first time the efficient photovoltaic performance of conductive PEDOT:PSS/n-type p-Si heterojunction solar cells. We observed a relatively high η of 9.7% after combining defect passivation of the p-Si with a uniform organic layer deposited by CMD using a charged mist precursor.

Experimental section

High pressure water vapor treatment

Polycrystalline silicon substrates with a size of $2 \times 2 \text{ cm}^2$ were ultrasonically cleaned in methanol, acetone and deionized(DI) water for 10min each. Samples were subsequently immersed in 5% HF solution to remove native oxide layer, followed by placing in a 100mL size Teflon-lined stainless autoclave with 10mL DI water. Inside-chamber is Teflon made container for setting the samples, outside is stainless made frame for high pressure prevention. The closed reactor was then contained in the thermostat at $100^\circ\text{C}/200^\circ\text{C}$ for hours and stay overnight for cooling down. Saturation vapor pressure of water under 200°C is $16P_0$.

Solar cells Fabrication

The devices were fabricated use polycrystalline silicon wafer with a thickness around $200 \mu\text{m}$, resistivity of $1\text{-}3 \Omega \cdot \text{cm}$, with and without high pressure treatment. The native oxide was removed by dipping the samples in 5% HF solution for 3 min. Then, the wafers were cleaned by RCA cleaning and left in air for 6h. Highly conductive PEDOT:PSS (Clevios™ PH 1000) solution mixed with 5wt% dimethyl sulfoxide (DMSO) and 0.01wt% Zonyl fluorosurfactant (Sigma Aldrich) was spin-coated at 3000 rpm for 1min, followed by annealing at 140°C for 20 min. In the case of CMD deposition, process is described in more detail in refs.19 and 24. The apparatus consists of an ultrasonic atomization reactor, a glass tube with a 20 mm outer diameter, a mesh electrode to supply a DC bias for charging the mist deposition precursor, and substrate stage. Commercialized PEDOT:PSS (CLEVIOS PH1000) was used as a starting material. An aqueous solution of 5wt% DMSO added conductive PEDOT:PSS diluted in DI water and EG(10 wt%) cosolvents was placed in an ultrasonic vibrator with a working frequency of 3 MHz for mist

generation followed by thermal annealing at 140°C for 20 min to remove any residual solvent. After that, a top Ag grid electrode (finger electrode: 1 mm in width, bus bar: 2 mm in width and 18 mm in length) was formed from a silver paste using a screen printer (Newlong Seimitsu Kogyo Co., Ltd. DP-320). Finally, an InGa alloy was used to form ohmic contact as a rear electrode.

Samples characteristic

The samples were characterized by Scanning Electron Microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and imaging Raman spectroscopy (Renishaw: inVia Raman microscope: 532 nm). The carrier mobility μ and acceptor concentration N_a of n-type p-Si before and after high-pressure H₂O vapor treatment was determined for poly-Si with an 1×1 cm² area from Hall measurements in a van der Pauw configuration. The capacitance-voltage (*C-V*) and *C-f* (*f*: measurement frequency) characteristics were also measured with a 1 mm² Ag top electrode to understand the carrier transport properties at the PEDOT:PSS/p-Si interface. The current density-voltage (*J-V*) characteristics of solar cell device structure in the dark and under AM1.5G, 100 mW/cm² simulated solar light illumination (Bunkoukeiki CEP-25BX) were measured. A 2-dimensional map of the photovoltaic parameters, J_{sc} , V_{oc} , FF , η , and the external quantum efficiency (EQE) of the devices (2×2 cm²) were also measured using a line-illumination scan combined with computer tomography calculations (MAP: MP50, Lasertec Co., Ltd.).

Results and discussions

Figure 1(a) shows the molecular structure of PEDOT:PSS and a schematic of a PEDOT:PSS/p-Si heterojunction solar cells. An n-type p-Si wafer with a resistivity of 1-3 $\Omega\cdot\text{cm}$ and a thickness of $\sim 200\ \mu\text{m}$ was used in this study. The p-Si wafer was pre-treated with a high-pressure H_2O vapor at 1.6 GPa and 200 $^\circ\text{C}$ for 2h to terminate dangling bond defects at the grain boundaries [20, 21]. Following that, the wafer was dipped in 5% hydrofluoric (HF) acid to remove the surface oxidized layer. Then, the wafers were cleaned by RCA cleaning and left in air for 6 h [6, 22, 23].

Figure. 1 (a) Schematic of a PEDOT:PSS/p-Si heterojunction photovoltaic device and the molecular structure of PEDOT:PSS. (b) Schematic of the CMD apparatus used in this study.

Figure 1(b) shows a schematic of the CMD apparatus. The PEDOT:PSS mist was transported through a glass tube using a N_2 as a carrier gas at 0.5 SLM and then, passed through a mesh electrode 3 cm from the substrate stage. The film deposition was performed with a mesh DC bias of +5 kV and a substrate temperature T_s of 40 $^\circ\text{C}$. The film deposition rate was $\sim 10\ \text{nm/min}$ and

the resulting film thickness was 100~120 nm. For comparison, an SC device was also fabricated using an identical aqueous solution of 5 wt% DMSO added PEDOT:PSS at 3000 rpm for 60 s followed by drying at 140°C for 30 min.

Figure 2(a) shows an FTIR spectrum of a p-Si wafer after a high-pressure H₂O vapor treatment and a subsequent 5% HF rinse for 30 s. The spectrum is shown referred to that of an un-treated poly-Si wafer. Si-O-Si and SiO related absorption peaks appeared in the 800-1250 cm⁻¹ regions with CH (2990 cm⁻¹) and SiOH (3000~3500 cm⁻¹) peaks, suggesting that oxygen atoms were incorporated into the p-Si and that some of these oxygen atoms contributed to the termination of dangling bonds at grain boundaries. Figure 2(b) shows a 1/C²-V plot at 1 MHz and the C-f (f: measurement frequency) characteristics of SC and CMD Ag(1 mm²)/PEDOT:PSS(100 nm thick)/p-Si diodes with and without a high-pressure H₂O vapor treatment. For reference, the results for an untreated p-Si device with SC PEDOT:PSS is also shown as a reference. N_d of the p-Si was determined from the slope of the 1/C²-V plot relating to 1/N_a+1/N_d (N_a, charge carrier density of PEDOT:PSS). Here, the N_a value of 1.1×10²¹ cm⁻³ obtained from our previous C-V and spectroscopy ellipsometry (SE) studies was used for PEDOT:PSS [5, 24]. The 1/C²-V plot for the untreated p-Si diode showed a non-linear relationship, suggesting that space charge was accumulated at grain boundaries and/or the PEDOT:PSS/p-Si interface. Additionally, the N_d for non-treated p-Si was ~4×10¹⁷ cm⁻³, nearly two orders of magnitude higher than the doping concentration (0.5-1×10¹⁶ cm⁻³). On the other hand, 1/C²-V plots for SC and CMD diodes on treated p-Si showed linear relationships, suggesting that the depletion region widened to p-Si. The calculated N_d value was suppressed to 2×10¹⁶ cm⁻³, which was consistent with the doping density of the p-Si. Hall measurements of the p-Si also revealed that N_d decreased from 7.8×10¹⁶

to $1.9 \times 10^{15} \text{ cm}^{-3}$ with increasing Hall mobility μ_H from ~ 2 to $\sim 15 \text{ cm}^2/\text{Vs}$ after the treatment, which was a similar tendency to that for the $1/C^2$ -V measurements. On the other hand, the slope

Figure. 2 (a) FTIR spectrum of p-Si treated by high-pressure H₂O vapor at 200°C for 2 h. (b) $1/C^2$ -V and (c) C - f plots of SC and CMD PEDOT:PSS/p-Si diodes after high-pressure H₂O vapor treatment. The results for an SC PEDOT:PSS diode on untreated p-Si are also shown for comparison.

of the $1/C^2$ -V plot was lower for the CMD diode on high-pressure H₂O vapor treated p-Si than for SC, implying an enhanced N_d and/or carrier mobility in the PEDOT:PSS. The built-in potential V_b was ~ 0.7 V for the SC diode, whereas V_b was ~ 1 V for the CMD diode. Furthermore, the junction capacitance was almost independent of f and was lower, for both SC and CMD devices on treated p-Si substrates than on untreated p-Si wafers: in the lower measurement-frequency region, implying a suppressed interface defect density in treated p-Si substrates [25].

Figure 3(a) shows photocurrent density J_p -V curves for SC PEDOT:PSS/p-Si heterojunction solar cells with high-pressure H₂O vapor treatment under different conditions. The results for untreated p-Si device are also shown for reference. η increased markedly from $\sim 4\%$ for a pristine organic/p-Si device to $\sim 7\%$ for one treated at 200°C for 2 h. Figure 3(b) shows a 2-dimensional map of J_{sc} and EQE at 950 nm for PEDOT:PSS/p-Si heterojunction solar cells (2×2 cm²) with and without the treatment. Fine structures attributed to defects in the p-Si such as twin boundaries, dislocation, and screw transition were clearly observed in the J_{sc} and EQE maps of the untreated device, whereas these fine structures almost disappeared from the treated device. These findings suggest that high-pressure H₂O vapor treatment can suppress dangling bond defects in entire p-Si regions.

Figure. 3 (a) J - V curves of corresponding PEDOT:PSS/p-Si solar cells shown in Fig. 2. (b) 2D map of J_{sc} and EQE at 950 nm of a $2 \times 2 \text{ cm}^2$ area before and after high-pressure H_2O vapor treatment at 200 °C for 2 h.

Figure 4(a) shows optical microscopy images of SC and CMD 100-nm-thick PEDOT:PSS on p-Si along with a 2D map of the imaging Raman peak intensity at 1350-1500 cm^{-1} corresponding to the C=C bond of PEDOT. The typical Raman spectra of corresponding sample measured at two different positions are also shown [26]. Spotted distribution of PEDOT:PSS was observed for the SC film, whereas the imaging Raman intensity was more uniform for the CMD film. SEM images of SC and CMD PEDOT:PSS on p-Si are also shown in Fig. 4(b). Several separated regions were observed in the SC film, whereas a uniform coating was observed for the CMD film, although this depended on the choice of solvent and the mesh bias.

In Fig. 4(c), the J - V characteristics measured at four different positions ($5 \times 5 \text{ mm}^2$) are shown for SC and CMD PEDOT:PSS/p-Si heterojunction devices under illumination by AM1.5G 100 mW/cm^2 simulated solar light. The average photovoltaic parameters, i.e., V_{oc} , J_{sc} , FF , and η are summarized for the devices in Table I. The performance was uneven and the devices for the SC PEDOT:PSS buffer layer exhibited an average η of 6-8%, although a maximum η was achieved of a η of 9.8% with a J_{sc} of 30.5 mA/cm^2 , a V_{oc} of 0.52 V, and a FF of 0.62. On the other hand, uniform performance was provided relatively with an average η value of $\sim 9\%$. The best performance was obtained with a η of 9.7%, a J_{sc} of 33.5 mA/cm^2 , a V_{oc} of 0.54 V, and a FF of 0.53. Obviously, larger variation in data of J_p - V curve was observed for SC devices, whereas it was suppressed relatively for the CMD device. The improvement in the device performance can be attributed to the use of CMD with a charged mist precursor. In particular, J_{sc} improved from 29 to 33 mA/cm^2 with a V_{oc} of 0.53-0.54 V by the CMD rather than the SC, although a FF value was still 0.5. These findings imply that the carrier transport at the PEDOT:PSS/p-Si interface is improved by the combination of a high-pressure H_2O vapor treatment of p-Si prior to the film

Table 1. Performance details (V_{oc} , J_{sc} , FF , and η) of CMD and SC PEDOT:PSS/p-Si heterojunction solar cells measured at four different positions, a, b, c, and d ($5 \times 5 \text{ mm}^2$).

Device	$J_{sc}(\text{mA/cm}^2)$	$V_{oc}(\text{V})$	FF	η (%)
CMD	33.6	0.53	0.48	8.5
CMD	33.5	0.54	0.53	9.7
CMD	33.0	0.54	0.54	9.6
CMD	32.4	0.54	0.51	8.8
SC a	27.2	0.48	0.46	5.9
SC b	28.4	0.45	0.46	5.9
SC c	29.5	0.49	0.58	8.4
SC d	30.5	0.52	0.62	9.8

Figure. 4 (a) Microscope images of SC and CMD PEDOT:PSS on high-pressure H₂O vapor treated p-Si with a 2D map of the imaging Raman intensity at 1400-1500 cm⁻¹ corresponding to the C=C bond of PEDOT at two different positions. Scanning area was 0.1×0.1mm² (b) SEM image of SC and CMD PEDOT:PSS on p-Si. (c) *J-V* curves of

corresponding PEDOT:PSS/p-Si heterojunction solar cells measured at four different positions under simulated AM1.5G solar light illumination. The active area was $5 \times 5 \text{ mm}^2$.

deposition of organic and an use of CMD. Thus, the role of these procedures is considered as the suppression of grain boundary defect of p-Si and PEDOT:PSS/p-Si interface. As far as the SC is concerned, the variation of J - V characteristics is larger at each measurement position due to the inhomogeneous coating, whereas it was suppressed relatively for the CMD device with increased J_{sc} and V_{oc} values. These findings are mainly due to the improved uniformity and adhesion of organic on p-Si, which lower defect at the organic/p-Si interface, resulting in the increased PV performance.

Figure. 5 Schematic of the band potential of PEDOT:PSS/p-Si interface and the density of states of p-Si before and after high-pressure H_2O vapor treatment.

Figure 5 shows a schematic of the band diagram of PEDOT:PSS/p-Si interface region and the density-of-states distribution for p-Si before and after high-pressure H₂O vapor treatment. The pristine p-Si included many defects at grain boundaries, and these were passivated by oxygen, forming Si-O-Si during the high-pressure H₂O vapor treatment. Hall measurements also revealed that the μ value for the p-Si increased markedly with decreasing N_a after the treatment. Therefore, the density of tail states near the valence and conduction bands suppressed to be lower with decreasing the defect density at mid gap by the treatment. As a result, Fermi level shifted toward mid gap, resulting in an increase in V_b . Furthermore, CMD with a negatively charged mist precursor promoted the adhesion of PEDOT:PSS to the p-Si. In fact, higher V_{oc} and J_{sc} values were obtained compared with those of SC, although further improvement of FF values is required. The highest occupied molecular orbital (HOMO) of the organic -valence band maximum (E_v) of the c-Si offset was negligibly small, implying that the photogenerated holes can pass from p-Si to PEDOT:PSS with no resistive loss. In addition, the CMD PEDOT:PSS film with a mesh bias V_m used to charge the mist precursor exhibited more prominent uniaxial optical anisotropy. Thus, the SE study revealed that the extraordinary refractive index and hole mobility of PEDOT:PSS increased with increasing V_m , resulting in improved photovoltaic performance [5, 11, 24]. Improved adhesion of PEDOT:PSS to p-Si and the hole mobility of PEDOT:PSS using CMD with a charged mist precursor results in the efficient suppression of defect generation at the organic/p-Si interface, leading to increased photovoltaic performance.

Conclusions

In summary, we investigated the photovoltaic performance of PEDOT:PSS/n-type p-Si heterojunction solar cell devices. High-pressure H₂O vapor treatment of p-Si efficiently passivated dangling bond defects at the grain boundaries. Chemical mist deposition of conductive PEDOT:PSS using a negatively charged mist precursor significantly improved the adhesion of PEDOT:PSS to p-Si, resulting in enhanced carrier collection efficiency in the 850-1000 nm region. As a consequence, efficient PEDOT:PSS/p-Si heterojunction solar cell were obtained with the highest η of 9.7%, a J_{sc} of 33.5 mA/cm², a V_{oc} of 0.54 V, and a FF of 0.53. Such organic/p-Si heterojunction cells can potentially further deliver a high FF and a high conversion efficiency along with sufficient passivation of dangling bonds and the organic adhesion on the p-Si.

Acknowledgments

This research was supported in part by a Japan Science and Technology (JST) Agency (A-step) grant and a Leading-edge Industry Design Project of Saitama prefecture. The authors thank Drs. S. Wakamatsu and M. Azuma of Tokuyama Co., Ltd. for supplying n-type poly-Si wafers.

References

- [1] S. Avasthi, S. Lee, Y. -L. Loo, and J. C. Sturm, *Adv. Mater.* 23 (2011), 5672.
- [2] T. Song, S. T. Lee, B. Sun, *Nano Energy* 1 (2012) 654–673
- [3] L. He, D. Lai, H. Wang, C. Jiang, and Rusli, *Small* 8 (2012), 1664.
- [4] Q. Liu, I. Khatri, R. Ishikawa, K. Ueno, and H. Shirai, *Appl. Phys. Lett.* 102 (2013), 183503.
- [5] Q. Liu, T. Imamura, T. Hiata, I. Khatri, Z. Tang, R. Ishikawa, K. Ueno, and H. Shirai, *Appl. Phys. Lett.* 102 (2013), 243902.
- [6] Y. Zhu, T. Song, F. Zhang, S. -T. Lee, and B. Sun, *Appl. Phys. Lett.* 102 (2013), 113504.
- [7] J. Schmidt, V. Titova, and D. Zielke, *Appl. Phys. Lett.* 103 (2013), 83901.
- [8] A. S. M. Pietsch, M. Bashouti, and S. Christiansen, *J. Phys. Chm. C* 118 (2013), 9049.
- [9] M. Y. Bashouti, M. Pietsch, G. Brönstrup, V. Sivakov, J. Ristein, S. Christiansen, *Prog. Photovoltaics* 22 (2013), 1050.
- [10] M. Pietsch, S. Jäcke, and S. Christiansen, *Appl. Phys. A* 115 (2014), 1109.

- [11] M. Ono, Z. Tang, R. Ishikawa, T. Gotou, Z. Tang, K. Ueno, and H. Shirai, *Appl. Phys. Express* 50 (2012), 032301.
- [12] I. Khatri, Z. Tang, Q. Liu, R. Ishikawa, K. Ueno, and H. Shirai, *Appl. Phys. Lett.* 102 (2013), 063508.
- [13] Y. Zhang, F. Zu, S-T. Lee, L. Liao, N. Zhao, and B. Sun, *Adv. Energy. Mater.* 4 (2014), 201300923.
- [14] I. Khatri, Z. Tang, T. Hiata, Q. Liu, R. Ishikawa, K. Ueno, and H. Shirai, *Thin Solid Films* 558C (2014), 306.
- [15] Q. Liu, I. Khatri, R. Ishikawa, A. Fujimori, K. Ueno, K. Manabe, H. Nishino, and H. Shirai, *Appl. Phys. Lett.* 103 (2013), 163503.
- [16] Q. Liu, M. Ono, Z. Tang, R. Ishikawa, K. Ueno, and H. Shirai, *Appl. Phys. Lett.* 100 (2013), 183901.
- [17] Y. Dan, K. Seo, K. Takei, J. H. Meza, A. Javey, and K. B. Crozier, *Nano Lett.* 11 (2011), 2527.
- [18] T.-G Chen, B.-Y Huang, E.-C Chen, P. Yu, and H.-F Meng, *Appl. Phys. Lett.* 101 (2012), 033301.
- [19] I. Khatri, T. Imamura, A. Uehara, R. Ishikawa, K. Ueno, and H. Shirai, *Phys. Sta. Sol. C* 9 (2012), 2134.
- [20] T. Sameshima, M. Satoh, K. Sakamoto, K. Ozaki, and K. Saitou, *Jpn. J. Appl. Phys.* 37 (1998), 4254.
- [21] T. Sameshima, K. Sakamoto, and K. Asada, *Appl. Phys. A* 69 (1999), 221.
- [22] Y. Ding, R. Gresback, Q. Liu, S. Zhou, X. Pi and T. Nozaki, *Nano Energy* 9 (2014), 25.
- [23] H. Fujiwara and M. Kondo, *J. Appl. Phys.* 101 (2007), 054516.
- [24] T. Hiata, N. Miyauchi, Q. Liu, R. Ishikawa, K. Ueno, and H. Shirai, *J. Appl. Phys.* 115 (2014), 123514.
- [25] T. Unold, M. Rösch, and G. H. Bauer, *J. Non-Cryst. Solids* 1033 (2000), 266.
- [26] A. Farah, S. Rutledge, A. Schaarschmidt, R. Lai, J. Freedman, and A. Helmy, *J. Appl. Phys.* 112 (2012), 113709.

Graphical abstract: