

Efficient Crystalline Si/Poly(ethylene dioxythiophene):Poly(styrene sulfonate):Graphene Oxide Composite Heterojunction Solar Cells

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Efficient crystalline silicon (c-Si) heterojunction solar cells with conductive poly(ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) and graphene oxide (GO) composite are demonstrated using a structure of Ag/PEDOT:PSS/PEDOT:PSS:GO composite/c-Si (100) (ρ : 3–5 $\Omega\cdot\text{cm}$)/Al. The power-conversion efficiency η increased to 10.7% under illumination of AM1.5 100 mW/cm² simulated solar light by adjusting the PEDOT:PSS and GO mixing concentration ratio. The GO addition to conductive PEDOT:PSS suppressed electron recombination and/or promoted the hole current at the anode. The soluble PEDOT:PSS:GO composite is promising as a hole-transporting transparent conducting layer for c-Si photovoltaic applications. © 2012 The Japan Society of Applied Physics

To date, crystalline silicon (c-Si) based heterojunction solar cells with an intrinsic hydrogenated amorphous silicon (a-Si:H) thin layers (HIT) offer high efficiency with an efficiency of 22–23%.¹⁾ The a-Si:H layers, in general, is fabricated by a low-pressure plasma-enhanced chemical vapor deposition (PE-CVD) of a SiH₄ and H₂ mixture. Indium tin oxide (ITO) films as the transparent conductive oxide (TCO) layer are also prepared by low-pressure rf magnetron sputtering.

As an alternate approach using organic solar cells (OSCs) is potentially cheaper due to low-temperature processing. Among them, OSCs with organic photoconversion layers such as poly(3-hexylthiophene-2,5-dily):[6,6]-phenyl-C₆₁-butyric acid methyl ester (P3HT:PCBM) mixture have been extensively studied due to their potential as a renewable, alternative source of electricity and their preference in low cost, light weight, mechanical flexibility, and easy processing conditions.^{2–4)} In addition, for the hole collection in common solar cells, poly(ethylene dioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) is often used to modify the ITO electrode in view of the superior injection/collection properties of the PEDOT:PSS/active layer compared with those of the ITO/active layer interface. So far, several approaches have been developed to improve the conductivity of PEDOT:PSS including thermal treatment, secondary doping of inert solvents such as glycerol, sorbitol, dimethyl sulfoxide (DMSO), *N,N'*-dimethyl formamide (DMF), tetrahydrofuran (THF), graphene oxide (GO), and polymers.^{5–8)} However, the organic photovoltaic devices are still not very efficient.

Here, we demonstrate a hybrid approach to crystalline Si heterojunction solar cells showing a high power-conversion efficiency η of 10.7% with spin-coated PEDOT:PSS:GO composite as the hole-collecting and conductive buffer layer. Thus, a hybrid device exploits the advantageous properties of both organic and silicon to enable potentially low-cost and efficient solar cells.

A functionalized graphene (graphene oxide, GO) used in this study was prepared by a modified Hummers method, a chemical oxidation method.^{9,10)} The average size of GO flake sheets was 1–3 μm . GO is highly soluble in an aqueous solution, and therefore, is expected to be well dispersed in the PEDOT:PSS (CLEVIOS PH1000). In order to remove ionic impurities in GO originating from the graphite source

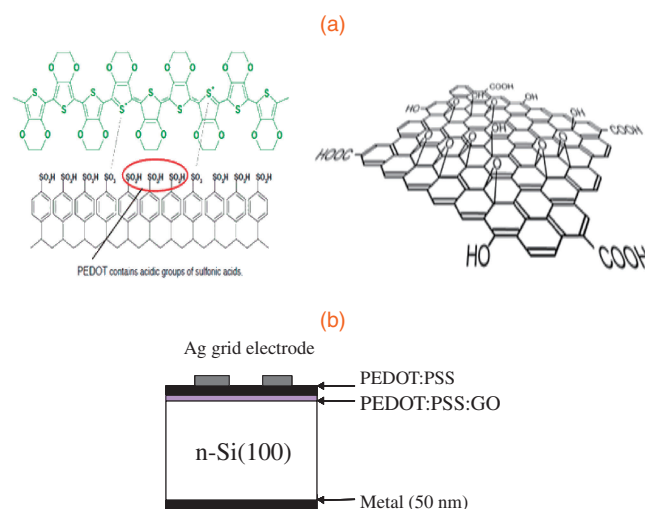


Fig. 1. (a) Chemical structures of PEDOT:PSS and graphene oxide (GO). (b) Schematic of c-Si/PEDOT:PSS:GO/PEDOT:PSS heterojunction photovoltaic device.

and oxidizing agents, especially Li, B, and Mn ions, the resultant GO solution was purified by dialysis. The chemical structures of PEDOT:PSS and GO are shown in Fig. 1(a). The schematic of the photovoltaic devices used in this study is shown in Fig. 1(b), which has a structure of Ag grid/conductive PEDOT:PSS(5% DMSO)/PEDOT:PSS:GO/c-Si/Al. The PEDOT:PSS:GO composite diluted in methanol was spin-coated on an RCA-cleaned CZ c-Si(100) wafer (resistivity ρ : 3–5 $\Omega\cdot\text{cm}$). For comparison, photovoltaic devices based on a buffer layer of pristine PEDOT:PSS junction having a similar device structure were also prepared. After spin coating of the PEDOT:PSS or PEDOT:PSS:GO films, thermal annealing at 200 °C for 1 h was conducted to remove the residual solvent. The thickness of PEDOT:PSS:GO composite was 55 nm. The active area of the device, as defined by the top electrode, was 5 × 5 mm². The current density vs voltage (*J*–*V*) characteristics were measured in air with and without light illumination using simulated solar light (AM1.5G, 100 mW/cm², Bunkoukeiki CEP-25BX). The power conversion efficiency η was calculated as $\eta = V_{oc} J_{sc} FF / P_{in}$, where V_{oc} is the open circuit voltage, J_{sc} is the short circuit current density, *FF* is the fill factor, and P_{in} is the incident light power. *FF* is

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determined as $FF = (V_m J_m)/(V_{oc} J_{sc})$, where V_m and J_m are voltage and current density in the maximum power point of the J - V curves in the fourth quadrant. The PEDOT:PSS:GO composite films were characterized by atomic force microscopy (AFM: Seiko Instruments SPA-300/SPI-3800). The c-Si/PEDOT:PSS:GO interface property was also studied using spectroscopic ellipsometry (SE, UVISSEL HORIBA Jobin Yvon) and capacitance-voltage (C - V) measurements.

The J - V curves for the c-Si/PEDOT:PSS:GO heterojunction photovoltaic devices with different GO mixing concentration ratios are shown under dark and illumination of AM1.5G 100 mW/cm² light exposure in Figs. 2(a) and 2(b), respectively. The quantum efficiency (QE) spectra are also shown in Fig. 2(c). The solar cell performance details are listed in Table I. The dark currents in forward and reverse bias were lower for the PEDOT:PSS:GO composite films than those of pristine PEDOT:PSS. In particular, the reverse saturated dark current J_0 is suppressed for the PEDOT:PSS:GO composite rather than that of pristine PEDOT:PSS. In addition, the forward and reverse dark currents are almost the same and the relationship between $\log J$ and $\log V$ shows linear relationship. This indicates the presence of a parallel current path due to a shunt resistance R_{sh} . The calculated R_{sh} increased from 2.55×10^4 to $6.78 \times 10^4 \Omega\cdot\text{cm}^2$ with the increase of GO content, thus, enhances the insulating property. The reduction in the dark current is clear evidence for reduced electron current and the suppression of electron recombination. The series resistance R_s of the corresponding PEDOT:PSS:GO devices was 5–7.7 Ω , which was slightly larger than that of pristine PEDOT:PSS. These imply that the junction property is improved by the GO addition without creating additional defects at the junction interface.

The device for the pristine PEDOT:PSS buffer layer gives η of 6.62%, J_{sc} of 21.5 mA/cm², V_{oc} of 0.508 V, and FF of 0.606. Once small amount of GO was mixed in PEDOT:PSS, the η value was enhanced. It became up to 8.53% with J_{sc} of 27.36 mA/cm², V_{oc} of 0.532 V, and FF of 0.6 for the 12.5% GO-mixed PEDOT:PSS cell. Obviously, the improvement in the device performance can be attributed to the usage of the PEDOT:PSS:GO composite. The QE was improved markedly in the visible and near-infrared region for the PEDOT:PSS:GO composite devices compared with those of pristine PEDOT:PSS. These suggest an improved charge collection ability of the buffer layer, although the QE at 300–450 nm region reduced significantly at GO content above 50% due to the optical absorption of GO.¹¹⁾ Thus, there exists an appropriate GO mixing concentration for improving QE in the wide wavelength region. The high optical transmittance over 90% is still maintained in the 350–900 nm region for the 12.5 wt % GO-mixed PEDOT:PSS.

Figure 3 shows the $1/C^2$ - V plot at 1 MHz and C - f (f : measurement frequency) characteristics of c-Si/PEDOT:PSS:GO composite junction solar cells with different GO concentrations. The $1/C^2$ - V plot showed a straight line with the increase of the slope with GO concentration [Fig. 3(a)]. Once the small amounts of GO was mixed, the built-in potential V_b increased from 1.02 for pristine PEDOT:PSS to 1.18 V for PEDOT:PSS:GO (12.5%), although its change was not systematic. In addition, the

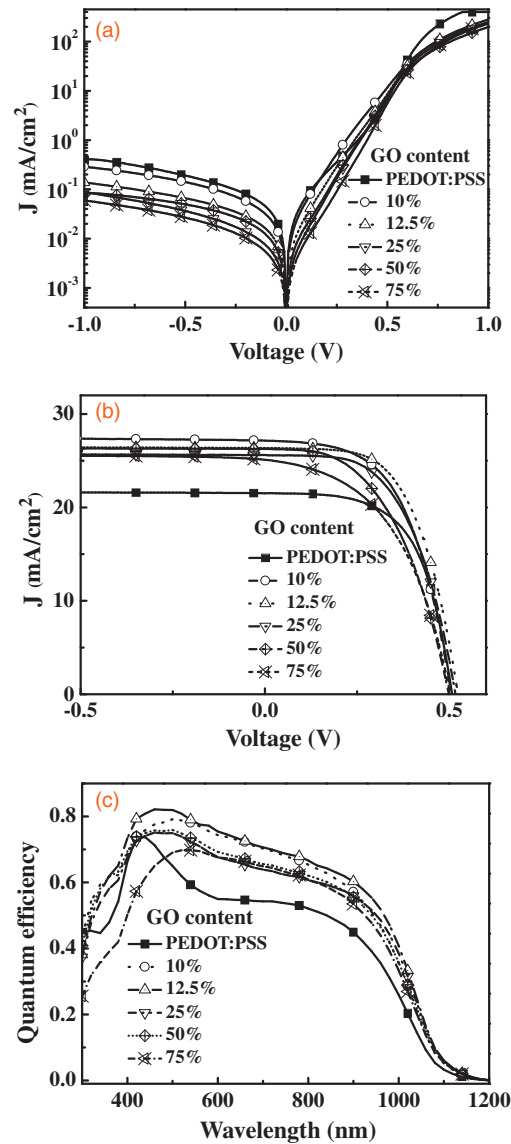


Fig. 2. (a) J - V curves of c-Si heterojunction solar cells with PEDOT:PSS:GO composite buffer layers with different GO concentrations in the dark, and (b) under illumination of a simulated AM1.5G 100 mW/cm² light. (c) QE spectra of corresponding solar cells.

Table I. Performance details (V_{oc} , J_{sc} , FF , η , and R_s) of the c-Si photovoltaic devices having different buffer layers.

GO content (%)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	η (%)	R_s (Ω)
PEDOT:PSS	0.508	21.52	0.606	6.62	4.65
10	0.506	27.15	0.556	7.64	5.01
12.5	0.532	27.36	0.6	8.53	5.48
25	0.517	25.61	0.559	7.41	6.86
50	0.499	26.25	0.499	6.54	7.70
75	0.503	25.10	0.483	6.10	8.02

increase in the $1/C^2$ - V slope with GO content suggests the reduction of acceptor carrier density in PEDOT:PSS layer, i.e., insulating characteristics. In addition, the junction capacitance for the wide measurement-frequency range is suppressed to be lower rather than the pristine PEDOT:PSS [Fig. 3(b)], implying the lower interface defect density.

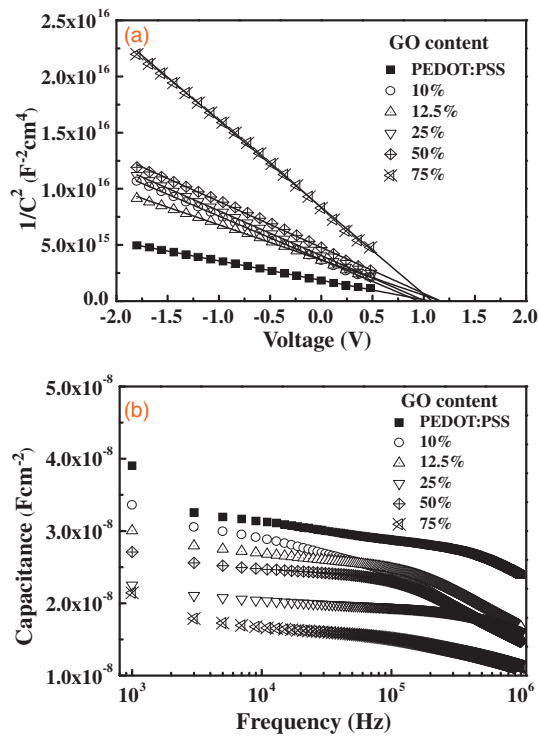


Fig. 3. (a) $1/C^2$ - V and (b) C - f plots of c-Si/PEDOT:PSS:GO composite heterojunction solar cells with different GO mixing concentration ratios.

Thus, the role of GO addition into conductive PEDOT:PSS is considered as follows, i.e., the suppression of electron recombination, and/or promote the hole current by enhancing the carrier mobility.⁷⁾ This is achieved by inserting PEDOT:PSS:GO with wider energy gap than 1.1 eV such that the lowest unoccupied molecular orbital (LUMO) of the organic is much higher than the conduction minimum (E_c) of Si. In general, the V_{oc} is determined from J_0 and J_{sc} through the relation: $V_{oc} = nkT/q \ln(J_{sc}/J_0)$. Thus, large LUMO- E_c offset result in a lower saturation dark current density and hence a larger V_{oc} . These contributions suppress the recombination efficiency of electrons and holes near the c-Si/PEDOT:PSS/Ag interface by adding GO (Fig. 4).

Here, the carrier transport property is mainly determined by the fine structure of host PEDOT:PSS polymer because the guest GO content is as low as $\sim 12.5\%$. It is also reported that the GO addition into PEDOT:PSS or P3HT:PCBM conjugated polymers promote the hole mobility.⁷⁾ As the result, the charge transfer efficiency could be enhanced due to the larger drift driving force, leading to an improved J_{sc} and V_{oc} . They promote the hole collecting ability due to block of electron recombination at the Ag metal anode. In other words, the LUMO- E_c , and/or the highest occupied molecular orbital (HOMO)-valence band maximum, E_v , offsets block electron recombination and/or enhance the photogenerated hole current collection.

Further improvements of the cell performance were performed by adjusting the thickness of PEDOT:PSS:GO layer and its adhesion on c-Si wafer. The efficiency has been enhanced up to 10.7% with J_{sc} of 28.9 mA/cm², V_{oc} of 0.548 V, and FF of 0.675 (Fig. 5). These findings imply that the silicon/spin-coated PEDOT:PSS:GO composite junctions are new approach towards photovoltaic devices that

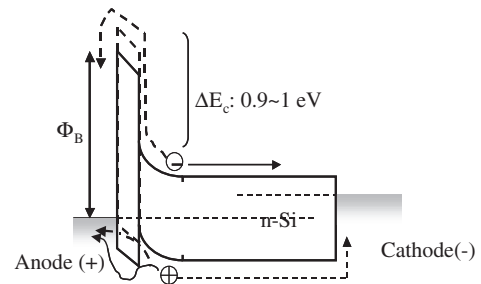


Fig. 4. Band diagrams of Si/PEDOT:PSS:GO composite heterojunction photovoltaic devices under small forward bias.

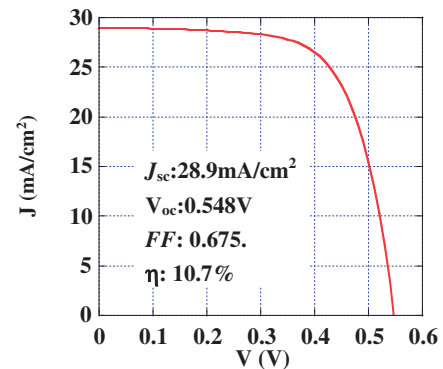


Fig. 5. J - V curves of c-Si/PEDOT:PSS:GO composite junction solar cell with optimized PEDOT:PSS layer under AM1.5G 100 mW/cm² light.

harness the advantageous properties of both organic and inorganic materials.

In summary, we have demonstrated a hybrid silicon/spin-coated PEDOT:PSS:GO (55 nm thickness) composite solar cells showing a high energy conversion efficiency of 8.75% with J_{sc} of 26.7 mA/cm², V_{oc} of 0.5 V, and FF of 0.62 for the 12.5% GO-added conductive PEDOT:PSS. Further high efficiency was obtained up to 10.7% with J_{sc} of 28.9 mA/cm², V_{oc} of 0.548 V, and FF of 0.675. These findings imply that the silicon/conjugate polymer heterojunctions are new approach towards photovoltaic devices. In particular, PEDOT:PSS:GO composite is a promising material as the hole-collecting transparent conductive layer in place of inorganic material such as p-layer and TCO, because of its easy processing capability.

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