



# Crystalline-Si heterojunction with organic thin-layer (HOT) solar cell module using poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS)

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## ABSTRACT

We represent the photovoltaic performance of n-type crystalline silicon (n-Si) heterojunction with organic thin-layer (HOT) solar cell module using poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)(PEDOT:PSS) together with 4,4'-cyclohexylidenebis [N,N-bis(4-methylphenyl) benzenamine] (TAPC) as a protecting layer of PEDOT:PSS for air storage and barium hydroxide, Ba(OH)<sub>2</sub> as a hole blocking layer at the rear c-Si/cathode interface, respectively. PEDOT:PSS/n-Si front-junction solar cell showed a power conversion efficiency (PCE) of 13–14% (11–12%) with a short-circuit density,  $J_{SC}$  of 29–31 mA/cm<sup>2</sup> (25–26 mA/cm<sup>2</sup>), an open-circuit voltage,  $V_{OC}$  of 0.62 V (0.625 V), and a fill factor,  $FF$  of 0.72 (0.704) for a  $2 \times 2$  cm<sup>2</sup> (4 in.) size device. Solar cell module consisting of ten-units of series-connected  $2 \times 2$  cm<sup>2</sup> (4 in.) sized cells exhibited a output power of 0.37 W (7.3 W) with a  $V_{OC}$  of 6.1 V (6.2 V), a  $J_{SC}$  of 0.084 A (1.78 A), and a  $FF$  of 0.712 (0.71). We also confirmed that it worked as a stand-alone photovoltaic system for remote monitoring of wireless camera drive.

## 1. Introduction

Recently, n-type crystalline silicon (n-Si) heterojunction with solution-processed conductive polymer such as poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) has been extensively studied, since a single junction of PEDOT:PSS/n-Si acts as a photovoltaic device without using traditional p-n junction and transparent conductive layer such as indium tin oxide (ITO) [1,2]. It is also compatible to the well-established crystalline-Si(c-Si) photovoltaic process. Promising power conversion efficiency (PCE) of PEDOT:PSS/n-Si front-junction solar cell has been reached to 12–15% by adjusting a type of solvent, thickness of PEDOT:PSS film, resistivity of silicon wafer, and without any light harvesting technique [3–6]. Thus, we named this type of solar cell as c-Si heterojunction with organic thin-layer “HOT” solar cell.

For further increase in photovoltaic (PV) performance of the HOT solar cells, however, several technological schemes should be taken into account, e.g., the lowering work function (WF) of cathode electrode to enhance the electron injection capability, the suppression of oxidation of PEDOT:PSS for air storage and light soaking, and the reduction of contact resistance of between n-Si and Al cathode electrode. In general,

a local enhancement of back-surface field (BSF) underneath cathode grid electrode has been adopted in sophisticated c-Si p-n junction solar cells to increase the PV performance by local phosphorus diffusion, i.e., passivated emitter and rear contact (PERC) [7]. So far, several materials such as polyethylene oxide (PEO), poly[(9,9-dioctyl-2,7-fluorene)-*alt*-(9,9-bis(3'(N,N-dimethylamino) propyl)-2,7-fluorene)] (PFN), Perylene diimide (PDIN), Cs<sub>2</sub>CO<sub>3</sub>, and [6,6]-phenyl-C61-butyric acid methylester (PCBM) have extensively been studied as interfacial layer to lower contact resistance in the Si/organic and polymer solar cells [8–18]. Lowering resistivity of Ag grid electrode has been also attempted using several types of silver or copper paste by screen print, plating, and ink-jet at a lower sintering temperature of 80–200 °C to suppress the thermal damage of conducting organic polymer.

Furthermore, back-PEDOT and back-contact n-Si/PEDOT:PSS solar cell device structures have also been investigated to protect the ultraviolet (UV) damage of front PEDOT:PSS face and to remove the optical loss of front metal grid electrode. J. Schmidt et al. have simulated a back-contact and back-junction solar cell with a limiting PCE of 25.1% with a  $V_{oc}$  of 708 mV using printed hole-collecting layer of PEDOT:PSS and electron-collecting layers [19,20]. More recently, dopant-free back-contact n-Si solar cells using evaporated MoO<sub>x</sub> and LiF as a hole- and

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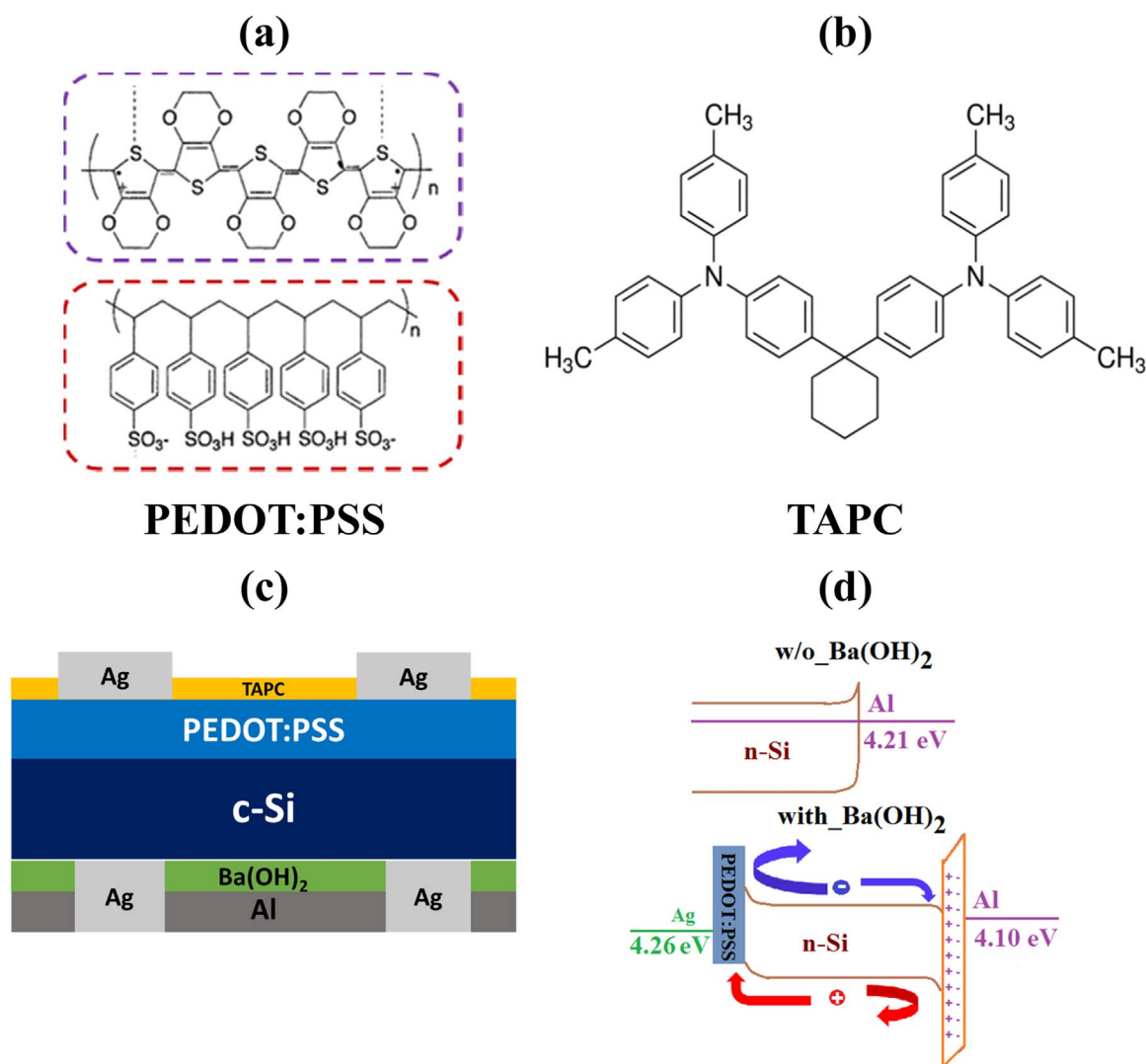


Fig. 1. Molecular structure of (a) PEDOT:PSS and (b) TAPC, (c) Schematic of the device structure of PEDOT:PSS/n-Si front-junction HOT solar cell, and (d) Schematic energy diagram of device structure of PEDOT:PSS/n-Si front-junction HOT solar cell (not to scale).

electron-transporting layer, respectively, combined with photolithographic patterning have also reported with a PCE of 15.4% [21]. However, most of the studies on solution-processed PEDOT:PSS/c-Si heterojunction solar cells have been performed on several milli- and centimeter sized c-Si substrates. Very few studies on solution-processed PEDOT:PSS/c-Si heterojunction HOT solar cell module have been performed.

In the present paper, we reveal for the first time the photovoltaic performance of PEDOT:PSS/c-Si front-junction HOT solar cell module employing several techniques, i.e., the suppression of oxidation of PEDOT:PSS using organic protection layer, the reduction of contact resistance of screen-printed Ag grid electrode and enhanced hole blocking capability at the rear n-Si/cathode interface as well as the uniform deposition of PEDOT:PSS layer by consecutive reeled-wired bar-coating.

## 2. Experimental section

### 2.1. Solar cell and module fabrication

Fig. 1 shows the molecular structure of PEDOT:PSS and 4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine] (TAPC) together with device structure used in this study. The device structure consists of PEDOT:PSS/c-Si front-junction with TAPC as a protection layer of

PEDOT:PSS for oxidation and  $\text{Ba}(\text{OH})_2$  as a hole blocking layer at the rear c-Si/cathode interface. Solar cell devices were fabricated on both-side-polished plane CZ N-type c-Si(100) wafers with a nominal resistivity of 0.1–0.3  $\Omega$  cm and a thickness of 250  $\mu\text{m}$ . Silicon wafers were cleaned in acetone for 10 min, followed by isopropyl alcohol (IPA) and deionized (DI) water cleaning for 10 min each in ultrasonic bath. Then, they were cleaned in 40%  $\text{NH}_4\text{F}$  solution for 3 min followed by DI water cleaning twice and dried by nitrogen ( $\text{N}_2$ ) gas. PEDOT:PSS (Clevios 1000) with zonyl-surfactant of 0.1 wt% and ethylene glycol (EG) of 7 wt% cosolvent was used as a precursor. PEDOT:PSS emitter was fabricated by spin coat (SC) and bar coat on a  $2 \times 2 \text{ cm}^2$  sized n-Si(100) substrates followed by thermal annealing at 140  $^\circ\text{C}$  for 30 min to remove residual solvent.

The total quality control (TQC) bar coater was also used for the deposition of PEDOT:PSS thin film on flat 4-in. sized n-Si substrate (COTEC. Co., Ltd.). The bar coating method is briefly discussed in Section 3.1. First, the bar-coat deposition of PEDOT:PSS was performed with same precursor as used for the SC [22]. The film thickness was precisely controlled within 80–90 nm, which showed a relatively high photovoltaic performance for SC and bar-coated devices, by adjusting the diameter of reeled-metal wire on the bar, and bar traveling speed, followed by thermal annealing at 140  $^\circ\text{C}$  for 30 min to remove residual solvent. Second, front- and rear-Ag finger grid electrodes were formed by screen print (Newlong Seimitsu Kogyo, DP-320S) using Ag paste

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