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RAPID COMMUNICATION

Efficient organic/polycrystalline silicon hybrid solar cells

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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 H_2O-vapor-treated p-Si prior to organic film deposition. High-pressure H_2O 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 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/cm^2, an open-circuit voltage of 0.54 V, 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.

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 (MoO_3), and ferroelectric polymer poly(vinylidene fluoride-tetrafluoroethylene) P(VDF-TeFE), graphene, graphene oxide,

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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(1 0 0) 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 article, 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*2 cm^2 were ultrasonically cleaned in methanol, acetone and deionized (DI) water for 10 min each. Samples were subsequently immersed in 5% HF solution to remove native oxide layer, followed by placing in a 100 mL size Teflon-lined stainless autoclave with 10 mL 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 °C/200 °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 μm, resistivity of 1–3 Ω 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 6 h. Highly conductive PEDOT:PSS (Clevios^{TM} PH 1000) solution mixed with 5 wt% dimethyl sulfoxide (DMSO) and 0.01 wt% Zonyl fluorosurfactant (Sigma Aldrich) was spin-coated at 3000 rpm for 1 min, followed by annealing at 140 °C for 20 min. In the case of CMD deposition, process is described in more detail in refs. [19,24]. 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 5 wt% 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 accepter concentration N_a of n-type p-Si before and after high-pressure H_2O vapor treatment was determined for poly-Si with an 1×1 cm^2 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 mm^2 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 AM1.5 G, 100 mW/cm^2 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 cm^2) were also measured using a line-illumination scan combined with computer tomography calculations (MAP: MP50, Lasertec Co., Ltd.).

Results and discussions

Fig. 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 Ω cm and a thickness of ~200 μm 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 °C for 2 h 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].

Fig. 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