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Highly efficient back-junction PEDOT:PSS/n-Si hybrid solar cell with omnidirectional antireflection structures

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ABSTRACT

Hybrid planar solar cells based on bulk n-doped Si wafers and poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) with a back-junction geometry demonstrated an excellent power conversion efficiency of more than 11%. When a random pyramid or a Si nanowire antireflection structure was incorporated into the front of the cell surface, the power conversion efficiencies were further enhanced to 13.9% or 14.5%, respectively. Moreover, the cells with the Si nanowire antireflection structure displayed omnidirectional light-trapping characteristics over the random pyramid structures. These cells also maintained a constant power conversion efficiency even at an incident angle of 60°.

1. Introduction

The costly processes and materials for fabricating crystalline Si solar cells hinder the wide application of photovoltaics. The fabrication of p-n junctions for Si involves furnace diffusion, which is an expensive technique that requires considerably high temperatures (approximately 1000 °C). Although the use of low-temperature processable organic semiconductors is a potentially inexpensive alternative, such approach produces less efficient organic solar cells. Therefore, hybrid solar cells that combine semiconductors and conjugated polymers at low temperatures provide a possible alternative that can simplify the fabrication processes and reduce costs [1–14]. One such conjugated polymer is poly (3,4-ethylenedioxythiophene): poly (styrenesulfonate) (PEDOT:PSS), which is the most widely used organic material for hybrid solar cell devices. PEDOT:PSS is transparent and conductive (over 1000 S/cm), and it can produce a hybrid heterojunction with silicon [15]. The film-forming properties of polymers can be processed under low temperature with low cost and in a large area. Illuminative light is absorbed mostly by the n-type semiconductor substrate, and a hole transport layer in the PEDOT:PSS can extract the holes generated in the substrate out of the device. Thus, the efficiency of hybrid PEDOT:PSS/semiconductor solar cells is comparable to that of conventional semiconductor p-n junction solar cells.

Several recent studies on organic/semiconductor heterojunction solar cells have been designed to augment the power conversion efficiency (PCE) by spin coating a thin PEDOT:PSS polymer layer onto silicon/gallium arsenide wafers. Investigations on techniques that can improve the performance of hybrid PEDOT:PSS/semiconductor solar cells have been widely conducted; such studies include studies those on surface structure [4–8], surface passivation [6,12], surface field [12], and additive use [9–12]. These techniques improve the device efficiency by more than 15%. The limited efficiency of current PEDOT:PSS/Si solar cells is due to the location of the heterojunction at the front side, which results in a parasitic light absorption within the organic material and a shading loss from the front contacts. In addition, the rear surface of these front-junction solar cells is commonly poorly passivated. Recently, the “BackPEDOT” heterojunction solar cell is established; in this solar cell, the PEDOT:PSS (junction side) is placed on the rear side, instead of the front surface, to avoid parasitic light absorption in the PEDOT:PSS [16]. With the combination of a realistic maximum short-circuit current density (J_{sc}) of 41.1 mA/cm^2, a reachable open-circuit voltage (V_{oc}) of 0.668 V, and a fill factor of 0.83, an efficiency of more than 22% is predicted for this type of solar cell.

Hybrid PEDOT:PSS/Si solar cells with nanostructures have been extensively investigated. Various nanostructures can be fabricated on silicon substrates through different methods [17–22], of which the most cost-effective approach is the metal-assisted chemical etching (MACE) [23–25]. MACE uses a thin metal layer to etch the Si surface at room temperature, and the etched morphology can be easily controlled. Although the MACE-fabricated nanowire (NW) structure can enhance the antireflective effect and improve the light trapping, this structure can also produce surface defects, which results in high surface recombination in NWs and ultimately, compromises the device performance. Moreover, the efficiency of front-junction PEDOT:PSS/Si solar cells

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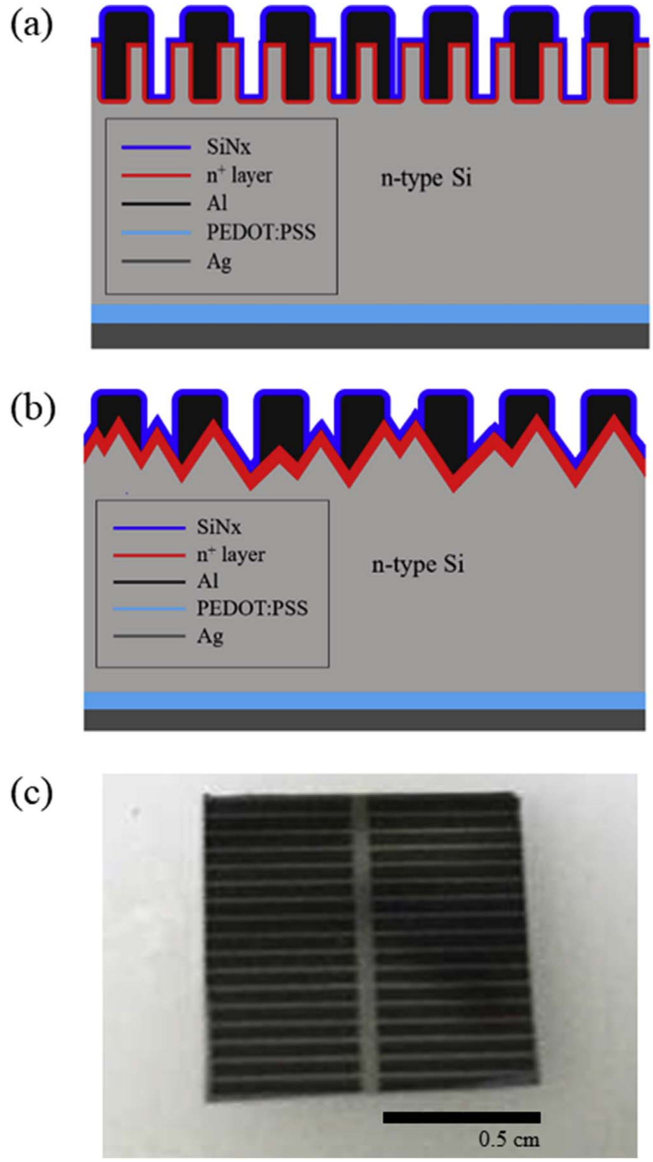

Fig. 1. Schematic of the hybrid BackPEDOT cell cross-section with front surface modified with (a) Si NWs and (b) RPs and (c) Optical image of the device with an active area of ~1 cm × 1 cm.

with NW antireflection (AR) structures is limited due to the poor contact at the PEDOT:PSS/Si NW interface [26–28].

In the present study, we investigated the hybrid solar cells based on the BackPEDOT concept. BackPEDOT cells with Si NWs and those with random pyramid (RP) AR structures were compared. The BackPEDOT solar cells with Si NW AR structures in front of the device were fabricated using the MACE method. These cells demonstrated an optimum PCE of 14.5%. The proposed back-contact solar cell structure can minimize the parasitic absorption in PEDOT:PSS and avoid the poor contact at the PEDOT:PSS/Si NWs/anode interfaces. Cells with Si NW AR structures also showed omnidirectional light-trapping characteristics over those with RP structures. These cells also maintained a constant PCE with the increase of incident angles to approximately 60°.

2. Materials and methods

The schematic cross-section of the proposed BackPEDOT solar cell with front Si NWs/RPs and SiN_x AR structures and photo image of the fabricated cell are displayed in Fig. 1(a)-1(c). We used n-type single-crystalline (100)-oriented 150 μm-thick silicon wafers (Jin Hua International Co., Ltd.) with a resistivity of 1–10 Ω-cm for all the hybrid solar cells. Fig. 2 shows the flowchart for fabricating BackPEDOT solar cells with Si NW/SiNx AR structures. A thin layer of photoresist was coated on the rear side of the wafers as a protective layer after RCA cleaning. The wafers were dipped in $AgNO_3$ (0.01 M)/HF (4.8 M) solution at room temperature for 1 min to deposit silver nanoparticles (Ag NPs). Ag NP-coated wafers were immersed into the H_2O_2 (0.4 M)/HF (4.8 M) solution for chemical etching and formation of Si NW structures. The wafers were subsequently soaked in HNO_3 solution, acetone, and isopropyl alcohol (IPA) to remove the Ag NP residue and the photoresist. Following the RCA cleaning process, a 100 nm-thick SiN_X layer was deposited as the surface protection layer on the polished side (rear side) of the wafers through plasma-enhanced chemical vapor deposition (PECVD). Afterward, the front surface was passivated with a shallow phosphorus n^+ front-surface-field (FSF) diffusion at 850 °C. The 100 nm-thick SiN_X protection layer was removed with phosphoric acid at 160 °C. The wafer was cleaned with IPA, acetone, and diluted HF (1 wt%) to remove the organic residues and oxides. The front contacts (cathodes) were fabricated by depositing a 100 nm-thick Al finger electrodes with the use of a thermal evaporator followed by an 80 nm-thick SiN_X AR layer deposition through PECVD. A 70 nm-thick PEDOT:PSS layer was formed on the Si wafer rear surface by spin coating a highly conductive polymer solution with a mixture of PEDOT:PSS (PH1000 from Clevios) solution, 5 wt% dimethyl sulfoxide (DMSO) as a secondary dopant to increase conductivity, and a surfactant (Dupont Capstone FS-31) and subsequently thermal annealing at 120 °C for 10 min. Finally, a rear anode contact was fabricated by thermally evaporating a 100 nm-thick silver grid through a steel foil shadow mask.

A key element in this device is the n^+ layer that provides FSF. The presence of FSF is beneficial for reducing the concentration of the minority carriers at the interface, enhancing the current transport of lateral majority carriers, and decreasing the series resistance losses [29–32]. The samples were first RCA-cleaned and, subsequently, a phosphorus diffusion was performed from a $POCl_3$ source in a quartz-tube furnace at 850 °C followed by an annealing at 950 °C to from a FSF. The sheet resistance of the samples after the phosphorus diffusion was measured by using a four-point probe. Samples with different sheet resistance (phosphorus concentrations), as shown in Table 1, were prepared by varying the diffusion time from 4 min to 10 min. The diffusion depth at an annealing temperature of 950 °C was ~1 μm determined by secondary ion mass spectrometry (SIMS). From Table 1, one can see that the sheet resistance decreased from 212.7 Ohm/sq to 11.4 Ohm/sq as the diffusion time was increased from 4 min to 10 min. To determine the optimum FSF diffusion profile and minimize surface recombination, BackPEDOT cells without any front surface structure were fabricated with six different diffusion profiles. Fig. 3 shows the schematic of the BackPEDOT cell and the fabrication flowchart. Fig. 4 illustrates the photovoltaic response of the BackPEDOT cells prepared with different diffusion profiles by an AM1.5G sun simulator. Relevant solar cell photovoltaic parameters extracted from the current density–voltage (J-V) curves are summarized in Table 1. Results indicated that the diffusion profile with a sheet resistance of 26.9 Ohm/sq delivers the optimum FSF, thereby obtaining the most remarkable cell efficiency. Therefore, this particular diffusion profile was used in fabrication all BackPEDOT cells with AR structures in this study.

The cell performance deteriorated at a sheet resistance lower than 11.4 Ohm/sq, which was attributed to the increased surface recombination velocity (or decreased minority carrier lifetime) [33]. This was confirmed by the microwave detected photoconductivity measurement, which showed that the minority carrier lifetime increased from 1.61 μs to 9.7 μs with decreased sheet resistance from 212.7 Ohm/sq to 26.9 Ohm/sq. However, at a sheet resistance of 11.4 Ohm/sq, the minority carrier lifetime reduced to 5.6 μs□ The influence of the FSF on the internal quantum efficiency and power conversion efficiency of the solar cells has been discussed in Refs. [33,34]. It was noted that only