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14.1% efficiency hybrid planar-Si/organic heterojunction solar cells with SnO_2 insertion layer

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ABSTRACT

Hybrid planar-Si/organic heterojunction solar cells have gained considerable interest in the fabrication of costeffective and high-efficiency devices. However, most of high power conversion efficiency (PCE) performances have been obtained with particular structures, front surface texture or rear surface field layer. In this paper, we provide a simple method without complex structures, and demonstrate the superiority and the mechanism of using stannic oxide (SnO₂) as an insertion layer. The SnO₂ insertion layer takes the place of the Schottky barrier, which reduces barrier height of rear Si to enhance charge transfer. And the effect of the insertion layer reduces contact resistance and enhances contact quality of rear Si side. Meanwhile, it has been indicated that the Si-O-Sn bonds were formed by SnO₂ and Si dangling bond (Si-), which have a passivation effect on the Si surface to effectively suppress the recombination losses. Furthermore, simulations using density functional theory (DFT) confirm that the electrostatic potential can improve electronic transmission from Si to Sn between Si-O-Sn bonds. Finally, for the hybrid planar-Si/PEDOT:PSS heterojunction solar cells without any special structures, the highest PCE of 14.1% was achieved, up 10.8% compared with that without SnO₂ insertion layer. These findings provide an effective way of improving Si/metal contact via a simple, room temperature process for other photovoltaic devices.

1. Introduction

Silicon (Si)/organic heterojunction solar cells made of a poly (3,4ethylenedioxythiophene); poly(-styrenesulfonate) (PEDOT:PSS), on Si have gained considerable interest in the fabrication of cost-effective and high-efficiency devices (He et al., 2012; Thomas and Leung, 2014). The heterojunction between Si surface and PEDOT:PSS film separates and extracts photogenerated electrons-holes, which were formed by a simple spin-coating method in room temperature. In order to improve the performance of Si/PEDOT:PSS heterojunction solar cells, lightharvest texture, surface passivation, modification of PEDOT:PSS solution and ultrathin Si substrate were studied (Bai et al., 2012a, 2013, 2012b; Ding et al., 2014; Duan et al., 2014; Geng et al., 2012; Li et al., 2016; Tecedor et al., 2018). At present, the power conversion efficiency (PCE) of Si/PEDOT:PSS heterojunction solar cells is up to ~16%, which has not surpassed that of the traditional homojunction Si solar cells (He et al., 2017a, 2018). However, the traditional homojunction Si solar cells have the inborn disadvantages of pollution and energy consumption. The advantages of Si/PEDOT:PSS heterojunction solar cells can compensate for the shortage of its PCE, and it has significance to be researched in the future.

Although PCE of Si/PEDOT:PSS heterojunction solar cells has been greatly improved, there are many problems between rear Si and electrode still to be solved (Han et al., 2017). The Schottky barrier reduces the collection of electrons and increases the surface carrier recombination in rear Si to jeopardize the performance of the solar cell (Huang et al., 2007). This matter draws many research groups' attention who have achieved fruitful results (Devkota et al., 2016; Han et al., 2017; He et al., 2017b; J. Liu et al., 2017; Y. Liu et al., 2017; Liu et al., 2016; Tong et al., 2018; Xia et al., 2017). A traditional method of Ohmic contact between Al and Si via high doping in Si side is generally used to improve the electrical contact properties. However, this process requires high temperature (~800 °C) as well as toxic gases, such as diborane or phosphine, which are similar to the disadvantages in

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Fig. 1. (a) scheme of Hybrid planar-Si/PEDOT:PSS heterojunction solar cell with SnO_2 layer. (b) AFM of SnO_2 film under the Si substrate with scan size of $6 \times 6 \mu m$. (c) I-V curves of photodetector devices based on SnO_2 , SiO₂ and without both in the dark and under AM 1.5G illumination. (d) The device structure diagram and equivalent circuit diagram of current-voltage (I-V) testing.

traditional homojunction Si solar cell (He et al., 2017a). As an alternative, n-type polymers (PCBM, N2200 and F-N2200) and alkali metal salts (LiF, Cs₂CO₃) have been used to improve contact quality between rear Si and electrode (Devkota et al., 2016; Han et al., 2017; Lee et al., 1998; J. Liu et al., 2017; Zhang et al., 2015). These materials can be deposited between rear Si and electrode by solution method that has a simple process with low temperature (< 120 °C). Solution method is better than that with toxic gases. Although the problem of rear Si has been solved through these materials as insertion layer, these materials are not perfect due to a matter of band structure or stability. Metal oxide materials with wide band gaps are suitable insertion layer materials to transmit of electrons and block holes. Stannic oxide (SnO₂) is a typical metal oxide with wide band gap as an intercalation layer, which has suitable energy levels with the conduction band (Ec) of 4.30 eV and valence band (Ev) of 8.09 eV. And the chemical bonds are produced between this material and Si surface to reduce the dangling bonds and surface recombination.

In this paper, we deposited SnO₂ insertion layer between rear Si and electrode by a solution method which takes the place of the Schottky barrier to reduce contact resistance. The band structure of SnO₂ is measured by ultraviolet photoelectron spectroscopy (UPS) and suitable for selective transmission of electrons and holes. The simulations using density functional theory (DFT) confirm that the electrostatic potential can improve electronic transmission by Si-O-Sn bonds. It has been found that, those bonds enhance Si surface passivation and suppress the recombination losses to improve short-circuit current (I_{sc}). The opencircuit voltage (V_{oc}) of 593 mV with a highest PCE of 14.1% was achieved from planar-Si/PEDOT:PSS heterojunction solar cells just by

adding SnO₂ insertion layer.

2. Experimental section

2.1. Materials and devices fabrication

The planar-Si/PEDOT:PSS heterojunction solar cells were fabricated on one side polishing n-type Si (100) substrates (Phosphorus doped), with resistivity of 2–4 Ω ·cm and thickness of 500 µm (Tianjin Upward Technology Development Co., Ltd). The substrates were cut into $1.5 \times 1.5 \text{ cm}^2$ and ultrasonically cleaned for 10 min successively in acetone, ethanol and deionized (DI) water. After cleaning, the substrates were immersed in 5% hydrofluoric acid (HF) for 3 min to remove the native oxide and then thoroughly cleaned in DI water. We diluted raw SnO₂ solution (alfa) with DI water which was mixed with 0.1 wt% Triton (Alfa, TX-100). The diluted SnO₂ solution was spincoated onto rear silicon surface at 3000 rpm and then annealed at 120 °C for 8 min, and 100 nm thick Ag film was deposited onto the rear silicon by magnetron sputtering. PEDOT:PSS (Heraeus, PH1000) solution was mixed with 5 wt% dimethyl sulfoxide (innochem, DMSO) and 0.25 wt% TX-100, and then stirred for several hours with magnetic force. The processed PEDOT:PSS solution was spin-coated onto front silicon surface at 5000 rpm and then annealed at 120 °C for 15 min, and 200 nm thick Ag grid electrode was deposited onto the PEDOT:PSS layer through a shadow mask by magnetron sputtering. Finally, the cell was cut into $0.7 \times 0.4 \text{ cm}^2$ for testing, whose active area was about 0.20 cm^2 after subtracting Ag grid electrode from it.

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