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Enhanced photovoltaic performance of PEDOT:PSS/Si solar cells using hierarchical light trapping scheme

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ABSTRACT

Organic-inorganic hybrid solar cells have attracted tremendous research attention in recent years owing to their low fabrication cost and potentially high performance. In the present study, hierarchical structures consisting of nanostructures made over micro-textured pyramidal (MPs) silicon surface are used in PEDOT:PSS/Si heterojunction solar cells to achieve a power conversion efficiency (PCE) up to 10.26%. The combined micro-nanostructuring concept provides a superior light trapping ability (compared to only micro-textured Si), mechanical stability (compared to only Si nanowire arrays concept), increased junction area and hence improved photovoltaic (PV) characteristics including short-circuit photocurrent and PCE. Silver assisted electroless wet chemical etching is used to produce nanostructures of different length over the micro-pyramidal Si. The hierarchically structured surfaces have one-fourth reflectance in broad spectral range (300–1100 nm) as compared to micro-pyramidal Si (~13%) arising from the enhanced light trapping properties of nanostructures owing to multiple interaction of incident light and dimensions equivalent to sub-wavelength structures. Moreover, the hierarchical structures exhibit excellent omnidirectional light trapping ability at wide range of angle of incidence of light and spectral wavelength, which is essential for practical PV applications. This has been demonstrated using solar weighted reflectance corresponding to AM 1.5G solar flux and compared with that of MPs surface. Influence of nanostructuring time on reflectance and PV performance of the solar cell has been investigated. A significant enhancement in PCE up to 0.78% (absolute) and over 8.0% (relative) could be achieved as compared to MPs-Si based hybrid solar cell (control cell) for an optimized hierarchically structured Si surfaces. It is established that an optimal trade-off between reduced reflectance of such surfaces and solar cell performance parameters is essential. Longer nano-structuring despite exhibiting a better light trapping properties results in poor cell efficiency as the nano-structuring also leads to increased surface area and non-conformal coating of the polymer. Hence, increase in photocurrent is also accompanied by a simultaneous deterioration of other cell parameters such as open circuit voltage and fill factor of the device. Nevertheless, a properly designed hierarchical-structured device paves a promising way for developing low-cost and efficient PV applications in the future.

1. Introduction

Perhaps, climate change is the biggest threat to organized human life and planetary biodiversity. It has been generated and is being generated by emission of carbon dioxide, among others. Consumption of traditional sources of energy is among the principal factors responsible for the emission of carbon dioxide. This has created immense interest in renewable energy resources. Solar radiation is the finest source of everlasting, non-conventional forms of energy. It provides an estimated 1.4×10^5 TW amount of energy to earth of which 3.6×10^4 TW is usable whose only ~0.05% was global energy consumption in 2012 (Hosenuzzaman et al., 2015). Solar photovoltaic (SPV) is one of the most reliable technologies for harvesting solar energy. At present, SPV landscape is dominated by silicon (Si) based homojunction solar cells (Technology Roadmaps, Solar Photovoltaic Energy, IEA). These devices are based on dopant diffusion or ion implantation and annealing processes. In such devices, junction is fabricated through heating of Si wafers at high temperature, ≥850 °C, in atmosphere of phosphorus or boron, depending upon type of impurity in Si wafer (Srivastava et al., 2015; Lin et al., 2015). Naturally, these processes have high thermal budget and are also time consuming. The process complexity in turn increases per unit power cost of the SPV devices. Decreased energy cost can not only outwit dirty energy sources but also provide solution to some pressing problems such as scarcity of

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potable water, low agricultural productivity etc. This has driven recent interests in combining the best of both organic and inorganic systems. Organic-inorganic hybrid solar cells have attracted tremendous research attention in recent years owing to their low fabrication cost and potentially high performance. Most commonly, an inexpensive highly conducting polymer based on poly(3,4-ethylenedioxythiophene)-poly (styrene sulfonate) (PEDOT:PSS), which acts as a p-layer (hole transport) is coated over n-type crystalline Si (Yameen et al., 2015; Nagamatsu et al., 2014; Wang et al., 2016a, 2016b; Singh et al., 2018) resulting into a Schottky junction at PEDOT:PSS/Si interface. The PEDOT:PSS is a conducting polymer and is widely used as a hole transporting layer or metal-free electrode in organic electronic devices. It has been proven to be commendable to act as a hole transporting layer in hybrid solar cells (Alemu et al., 2012; Kirchmeyer and Reuter, 2005; Xia and Ouyang, 2011; Zhang et al., 2015). Generally, in a PEDOT:PSS/Si heterojunction-based solar device, the incoming light is mostly absorbed by Si. Light-induced charge carriers (electron-hole pairs) are generated and then separated under the built-in electric field of the Schottky junction at PEDOT:PSS/Si interface. It is because of the built-in field at the junction, electrons are blocked in the n-Si and are transported towards the rear electrode and the holes which are minority carriers in n-Si are pushed towards the PEDOT:PSS (p-layer) which are finally transported to top electrode. The role of PEDOT:PSS as hole transport layer and electron blocking layer is schematically illustrated in the simplified energy band diagram of the heterojunction cell structure of Ag/PEDOT:PSS/n-Si/In-Ga shown in our earlier work (Yameen et al., 2015). The PEDOT:PSS in particular, is highly stable (Elschner et al., 2011) and its conductivity can also be enhanced (as high as $1000\,S\,cm^{-1}$) by adding suitable additives e.g., dimethyl sulfoxide (DMSO), N,N-dimethyl formamide, glycerol, sorbitol, ethylene glycol etc. (Gasiorowski et al., 2013; Pietsch et al., 2014; Huang et al., 2009). Moreover, as Si is the base material in such devices and light absorption and photo carriers generation take place in Si only, theoretically it is possible for these devices to achieve the power conversion efficiency (PCE) comparable to now dominant dopant diffusion based Si solar cells (Jeong et al., 2012). Heterojunction solar cells made of PEDOT:PSS on Si have attracted a lot of attention towards low-cost and efficient PV devices. The PEDOT:PSS/Si solar cells employing different Si surfaces like planar Si, micro-pyramidal Si (MPs-Si) or silicon nanowires (Si NWs) array have been reported extensively (Yu et al., 2013; Wu et al., 2016; Wang et al., 2015a, 2015b; Syu et al., 2013; He et al., 2011a, 2011b, 2012a, 2012b, 2015, 2016, 2017; Chen et al., 2012; Liu et al., 2012a, 2012b, 2014a, 2014b, 2015; Nam et al., 2017; Jeong et al., 2012; Wei et al., 2013; Thiyagu et al., 2014; Dai et al., 2016; Gasiorowski et al., 2013; Pietsch et al., 2013, 2014; Huang et al., 2009; Schmidt et al., 2013; Bashouti et al., 2014; Yameen et al., 2015) (see Table S1 in supplementary data for details). Over the past few years, considerable progress towards high-efficiency PEDOT:PSS/n-Si hybrid solar cells has been achieved leading to PCE over 10%. There have been several reports with PCE between 10 and 13% (Wang et al., 2015a, 2015b; He et al., 2011a, 2011b, 2016; Chen et al., 2012; Liu et al., 2012a, 2012b; Nam et al., 2017; Jeong et al., 2012; Wei et al., 2013; Thiyagu et al., 2014) and in few cases reaching between 13 and 16% (Yu et al., 2013; Wu et al., 2016; Liu et al., 2014a, 2014b, 2015; He et al., 2015, 2017; Dai et al., 2016) employing planar Si, MPs-Si or Si nanostructures (NSs) (see Table S1 for details). A comprehensive review on PEDOT:PSS/Si based solar cells employing the planar Si, micro-pyramid structured Si, nanostructured Si (like SiNWs array, Si nanoholes, nanocones etc.) and hierarchical structures (consisting of Si NSs and MPs-Si) with respect to the best cell parameters, their device structures and special features/parameters/materials/process employed to achieve the best performances are presented in Table S1 in the supplementary data. However, it may be noted that over 10% PCE in the hybrid cells has been achieved only by adjusting major factors such as electrical conductivity, chemical affinity, interfacial layers, thickness of the materials, also employing some other advance approaches like, back surface field, antireflection coating, different kinds of surfactant in PEDOT:PSS, different surface treatments, and front/back passivation schemes for better polymer–Si contact and improved electrical response leading to the high efficiency (Yu et al., 2013; Wu et al., 2016; Wang et al., 2015a, 2015b; Syu et al., 2013; He et al., 2011a, 2011b, 2012a, 2012b, 2015, 2016, 2017; Chen et al., 2012; Liu et al., 2012a, 2012b, 2014a, 2014b, 2015; Nam et al., 2017; Jeong et al., 2012; Wei et al., 2013; Thiyagu et al., 2014; Dai et al., 2016). It is also to be noted that with the simple device structure without any advanced surface engineering, antireflection coating, passivation or back surface field, the highest efficiency achieved is always been under 10% (see Table S1) irrespective of nature of Si surface (planar, micro-textured, or nanostructured).

Reflectance loss is one of the primary losses in any Si based solar cells (homo- or hetero-junction). Planar Si surface has reflectivity of > 35% in the spectral range useful for Si solar cell and it can be reduced to ∼11–14% after alkaline (KOH/NaOH) micro-texturing of the Si (μT-Si) which has random micro-pyramids on the surface. The arrays of Si nanowires (NWs) by metal assisted chemical etching (MACE) method, on the other hand, can suppress the reflection losses to a minimum (∼2% in broad spectral range) without anti-reflection coatings for sufficiently long (≥5 μm) NWs (Peng et al., 2005; Srivastava et al., 2010, 2014; Guo et al., 2010, 2015). However, in view of the application of SiNW arrays for photovoltaic (PV) devices, longer NWs have several limitations such as (i) bunching of longer NWs, (ii) mechanical fragility/unstability leading to shunting of junction, (iii) processing (such as metal electrodes formation, non-conformal polymer coating) related difficulties that requires improvisation in solar cell fabrication protocol and therefore the cost (Kumar et al., 2011; Singh et al., 2015) etc. In addition, enhanced electronic surface recombination (for longer NWs) may be dominant and thus the gain on optical front is lost. This is one of the basic reasons why solar cells based on Si NWs surfaces have not been able to surpass PCE of conventionally micro-textured silicon based devices, despite the fact that Si NWs have much better optical performance, both in homojunctions as well as organic/Si heterojunction cells without an effective passivation layer (Srivastava et al., 2016; Syu et al., 2012; Wang et al., 2015a, 2015b, 2016a, 2016b). Therefore, there is need for suitably structured surfaces which not only minimize the refection but also the electronic losses and have compatibility with solar cell processing protocol.

Recently, a lot of attention is being paid to combine both Si nanostructures (Si NSs) fabricated by metal assisted chemical etching (MACE) method and alkaline (KOH/NaOH) textured micro-pyramid structures leading to SiNSs/μT-Si hierarchical structures for efficient light harvesting. Such binary structures have threefold benefits, (i) increased light absorption, (ii) increased junction area, and (iii) mechanically robust surfaces (as compared to Si NWs). There have been few successful examples of such binary structures in conventional homojunction silicon solar cells applications (Lee et al., 2013; Chen et al., 2014; Liu et al., 2014a, 2014b; Jiang et al., 2014; Yang et al., 2014). The application of hierarchically structured Si for PEDOT:PSS/Si heterojunction solar cell has been very limited to the best of our knowledge. Its application was first reported by He et al. (2012b) in 2012 who first proposed the concept of hierarchical structure for PEDOT:PSS/Si solar cell using device structure of Ag/PEDOT:PSS/SiNWs-MPs/Al wherein SiNWs of length 0.4 μm and 0.8 μm were used on MPs-Si surface. They fabricated hierarchical surface by a two-step chemical etching process on highly doped 0.7–0.9 Ω cm n-Si(1 0 0) wafer by anisotropic etching using KOH and isopropanol (IPA) solution followed by SiNW arrays fabrication (0.4 and 0.8 μm lengths) on the MPs substrate by Ag assisted MACE process in a solution of HF and $AgNO_3$. Reflectance < 5% was achieved in 350–1100 nm spectral range. However, they did not investigate angle dependent light trapping property of the hierarchical structures. They could achieve maximum PCE of 9.9% (J_{sc} of $31.4\,mA/cm^2$) corresponding to hierarchical structures with Si NWs of 0.4 μm. The group also used highly doped n-Si