



Graphene/porous silicon Schottky-junction solar cells



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ABSTRACT

Porous silicon (PSi) is highly attractive for the solar cell applications due to its unique properties such as efficient antireflection, band gap widening, broad range of optical absorption/transmission, and surface passivation/texturization effect. We first report PSi Schottky-type heterojunction solar cells by employing graphene transparent conductive electrodes doped with silver nanowires (Ag NWs). The PSi is formed based on metal-assisted chemical etching process, and its porosity is controlled by varying the deposition time (t_d) of Ag nanoparticles used for the etching. The Ag NWs-doped graphene/PSi solar cells show a maximum power-conversion efficiency (PCE) of 4.03% at $t_d = 3$ s/concentration (n_A) of Ag NWs = 0.1 wt percent (wt%). As t_d increases, the diode ideality factor and the light absorption increase. As n_A increases, the work function (thus the open circuit voltage) and the transmittance decrease whilst the light absorption increases/the sheet resistance decreases. These trade-offs explain why the PCE is maximized at $t_d = 3$ s/ $n_A = 0.1$ wt%.

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1. Introduction

Since the reflection of light from the surface of solar cells is one of the main obstacles limiting their performance, it should be minimized to maximize the power-conversion efficiency (PCE) of solar cells. The reflectance of a material is closely related to its refractive index. Currently, Si is a principal material used for commercial solar cells due to its low cost and compatibility with conventional semiconductor device processes. However, high refractive index (~3.5) of Si prevents electron-hole pairs from being efficiently generated, thereby limiting the PCE of Si solar cells. Therefore, it is very important to reduce the reflection of Si. Anti-reflection (AR) coating is used to reduce the surface reflection because it increases the PCE by extending the carrier lifetime and improves the electrophysical properties of photovoltaic cells [1,2]. The AR coating is currently studied mainly by using organic materials, whose properties are very changeable [3,4]. So, it is necessary to find the AR material compatible for Si-based solar cells. Among several candidate materials, porous silicon (PSi) is attractive for the solar cell applications due to its efficient AR effect and additional benefits such as band gap widening, broad optical

absorption/transmission range, and surface passivation/texturization effects [1,5]. The high AR effect of PSi originates fundamentally from its large magnitude of the surface to volume ratio [6], which can be controlled by varying the porosity. PSi is also useful for transforming high-energy solar radiation into low-energy light, which can be absorbed more efficiently into bulk silicon [7–9].

Graphene is one of the fascinating two-dimensional materials that are promising for its applications in possible post-CMOS and other novel optoelectronic devices [10,11]. Graphene-semiconductor Schottky junctions have been intensively studied for their possible applications in photodetectors [12], solar cells [13–17], barristers [18], and chemical/biological sensors [19]. Among various semiconducting materials, nanostructured Si is recognized as a leading candidate for the graphene-based Schottky junctions due to its compatibility with the existing Si CMOS processes. Recently, graphene/PSi Schottky junctions [9] have been shown to be very useful for their application in high-responsivity photodetectors. Here, we first successfully fabricate graphene/PSi heterostructure solar cells in a typical Schottky diode configuration, where PSi acts as a photoexcitation layer that exhibits large absorption and high efficiency in the generation of electron-hole pairs in the near-UV range, compared to bulk Si. We vary the deposition time (t_d) of Ag nanoparticles (NPs) for the etching of Si to control the porosity of PSi, necessary for the optimization of the solar cells. We also employ silver nanowires (Ag NWs) as a dopant to enhance

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the conducting properties of the graphene as a transparent conducting electrode (TCE). The photovoltaic properties are strongly affected by t_d and concentration (n_A) of Ag NWs, and highest PCE (4.03%) is achieved at $t_d = 3$ s and $n_A = 0.1$ wt percent (wt%). The performance of the solar cells is discussed based on their systematic structural, electrical, and optical characterizations.

2. Experimental

525- μm -thick 10- $\Omega\text{-cm}$ n-type (100) Si wafers were used as substrates. For the fabrication of PSi by metal-assisted chemical etching (MacEtch) [9] (Supporting Information Fig. S1), Ag NPs as catalyst were firstly deposited on the Si surface in the AgNO_3 solution. Secondly, MacEtch of Si was performed in the HF and H_2O_2 mixture solution. During this process, the Si part attached with Ag NPs was selectively etched down, thereby generating pores on the Si surface. The porosity of Si was controlled by varying t_d of Ag NPs from 1 to 5 s in the AgNO_3 (5 mM) and HF (5 M) mixed deposition solution. Immediately, each Si substrate with Ag NPs was immersed in a mixed etchant of HF, H_2O_2 , and H_2O ($[\text{HF}]:[\text{H}_2\text{O}_2]:[\text{H}_2\text{O}] = [2.4]:[0.1]:[50.0]$) for 5 s at room temperature. Finally, the remnant Ag NPs were removed in HNO_3 for 1 min.

Transfer of graphene was done following conventional three essential steps [20] of (i) adhesion of polymer supports to the graphene/Cu foil; (ii) etching of the Cu foil; and (iii) transfer onto target substrates. PSi/Si, Si, and quartz target substrates were used in this work. Ag NWs powder was dissolved in isopropyl alcohol to prepare Ag NWs solution, whose n_A was varied from 0.05 to 0.3 wt %. For the fabrication of the solar cells (Supporting Information Fig. S1), the solution was coated on graphene/PSi/Si at 1500 rpm for 1 min, and then was dried on a hot plate at 100 °C for 2 min. Al and InGa films were deposited on the top of graphene and the bottom of Si substrate as the electrodes by using a shadow mask to open 14 mm² windows as the illumination area of solar cells.

The morphologies on the surface of the samples were analyzed by field emission scanning electron microscopy (FE-SEM) (Carl Zeiss, model LEO SUPRA 55) with energy dispersive x-ray spectroscopy (EDX) facilities. The reflectance/transmittance, sheet resistance, and work function of the TCEs were measured by ultraviolet–visible–near-infrared optical spectrometer (Varian, model Cary 5000), 4 probe measurement (Dasol eng, model FPP-HS8-40K), and Kelvin probe force microscopy (Park systems, model XE 100), respectively. To confirm the charge transfer between graphene and dopants, the sample was analyzed by Raman spectroscopy with a laser excitation energy of 532 nm (2.33 eV).

The photovoltaic properties of the cells were measured using a solar simulator (McScience, K201) under illumination of 1 Sun (100 mWcm⁻² AM 1.5G) and a calibrated Si reference cell certified by Korea Industrial Standards (LG company). The external quantum efficiency (EQE) was measured by a power source (ABET 150 W xenon lamp, 13014) with a monochromator (Dong Woo Optron, MonoRa-500i).

3. Results and discussion

Fig. 1 (a) shows a schematic diagram of graphene/PSi/n-Si solar cell. The PSi was prepared by conventional MacEtch of lightly-doped n-type Si substrate [9]. The high porosity of the PSi surfaces was confirmed by FE-SEM images for various t_d (Supporting Information Fig. S2). The pore depth was estimated to be ~20 nm by cross-sectional FE-SEM (Supporting Information Fig. S2). Raman spectra were measured with increasing t_d to check whether the porosity is well controlled depending on t_d . As t_d increases, the Raman peak is blue-shifted (Supporting Information Fig. S3), as expected, consistent with the previous reports [21]. The chemical-

vapor-deposition-grown graphene of $1 \times 1 \text{ cm}^2$ area was transferred on Si wafer as well as on PSi/Si substrates. Clear separation between graphene-covered/bare PSi regions was also confirmed by a FE-SEM image (Supporting Information Fig. S4).

Fig. 1 (b) illustrates the energy band diagram of the graphene/PSi/n-Si junction. We assume that the Fermi level of PSi is located almost at the center of the band gap, regardless of the doping level of the starting Si wafer, based on the fact that the pores are formed dominantly at defect and dopant sites of Si in MacEtch [22], thereby considerably reducing the doping concentration of Si. The band gap energy of PSi is widened compared to that of solid Si wafer, due to the quantum confinement effect of Si nanostructures, and the surface defects of PSi can generate additional accessible states trapping carriers [23,24]. To check whether the PSi is available for high-efficiency Si-based solar cells, it is necessary to analyze its reflectance. With increasing t_d , the reflection measured in a diffuse manner is significantly reduced over full range of wavelength (Supporting Information Fig. S5a). In particular, the reflectance in the UV region (300–400 nm) is lowered to about 60% of its original value of Si wafer at $t_d = 5$ s. The refractive index is directly related to the porosity of PSi. As the porosity increases, the reflectance decreases due to the larger void space [25,26]. The transmittance (T) of PSi/Si can be set to 0 because the Si substrate is opaque. Then, the absorbance (A) can be expressed by the equation: $A (\%) = 100 - R$, where R is the reflectance. As a result, the absorption is maximized at $t_d = 5$ s (Supporting Information Fig. S5b). These results suggest that the generation efficiency of the electron/hole pairs can be improved in PSi/Si compared to Si wafer.

The J - V curves of the solar cells were measured for various t_d under air mass 1.5 global (AM 1.5G) one sun illumination at 100 mW cm⁻². Fig. 1 (c) shows typical J - V curves under dark and illumination for $t_d = 0$ and 3, respectively. (see Supporting Information Fig. S6 for the J - V curves at other t_d). All the photovoltaic parameters as functions of t_d are summarized in Table 1. The graphene/bare-Si Schottky diode ($t_d = 0$) exhibits the lowest PCE due to its relatively high reflectance. The PCE gradually increases with increasing t_d from 1 to 3 s due to the decrease of reflectance and the increase of absorption at the same time. However, the PCE is slightly reduced at $t_d = 5$ s due to the large trap density and low mobility caused by the high porosity of the PSi despite the continued decrease/increase of reflectance/absorption. The photovoltaic parameters: open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and PCE for the best device ($t_d = 3$ s) are 0.331 V, 15.83 mA/cm², 44.38%, and 2.32%.

Fig. 1(d) shows the external quantum efficiency (EQE) of the solar cells for various t_d . The EQE is greatly enhanced over almost full range of wavelength with increasing t_d up to 3 s, but at $t_d = 5$ s, it decreases. The J_{sc} values calculated by the integration of the EQE spectra are 11.47, 13.42, 15.46, and 14.16 mA/cm² at $t_d = 0, 1, 3,$ and 5s, respectively, consistent with the experimental J_{sc} ones, as shown in Table 1, which demonstrates the well-known strong correlation of J_{sc} with EQE [27].

To understand why the solar cell exhibits best PCE and J_{sc} at $t_d = 3$ s, we extracted the leakage (shunt) current and the ideality factor from the J - V curves, as shown in Fig. 2. The regions I, II, and III illustrate how the different components of the solar cell equivalent circuit dominate the J - V response of the cell at different voltages. At low voltages (region I), the J - V characteristics are primarily determined by shunt resistance (R_{sh}), at intermediate voltages (region II) by ideal factor (n), and at high voltages (region III) by series resistance [28]. At low voltages (region I, $V < 0.1$ V), the R_{sh} is calculated to be 2423, 2061, 1675, and 889 $\Omega \text{ cm}^2$ for $t_d = 0, 1, 3,$ and 5 s, respectively, indicating smaller R_{sh} at longer t_d . The J - V characteristics of the nonideal diode based on the thermionic emission model can be expressed by the equation $J = J_s [\exp (eV/nkT) - 1]$

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