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Effect of alkali treatment on the spectral response of silicon-nanowire solar cells

Yurong Jiang*, Ruiping Qin, Meng Li, Guangna Wang, Heng Ma, Fanggao Chang*

College of Physics & Electrics Engineering, Henan Normal University, Henan Key Laboratory of Photovoltaic Materials, Xinxiang 453007, PR China

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ABSTRACT

The effect of alkali treatment of Si nanowires (SiNWs) on the spectral response of solar cells was investigated using monochromatic incident photon-to-electron conversion efficiency spectroscopy. SiNWs were prepared on a substrate by metal-assisted etching and were then treated with NaOH/isopropanol. The results show that alkali treatment of SiNWs for 30 s obviously improved the cell conversion efficiency. This was attributed to enhancement of the red light response and a decrease in surface reflectivity from 6% to ~2%. However, SiNW alkali treatment led to poor blue light response, which is a major limiting factor for efficient SiNW solar cells. To improve the photovoltaic properties of SiNW cells, a near-complete response over the whole solar spectrum is essential.

1. Introduction

Silicon nanowires (SiNWs) are attractive because of their unique electrical and optical properties compared to bulk silicon, so they are potential candidates for cost-effective, third-generation, high-efficiency solar cells [1–4]. In particular, SiNWs vertically aligned to the substrate demonstrate excellent broadband antireflection owing to strong light trapping by multiple scattering of incident light [5–10] and the optical antenna effect [11]. As a simple and low-cost process for silicon photovoltaic applications, metal-assisted chemical etching for SiNW fabrication has attracted much attention [10,12–15]. SiNWs can form in various crystallographic orientations on silicon surfaces [16–19].

Surface pretreatment of silicon wafers causes an increase in SiNW density and improves the uniformity of SiNW arrays [20]. KOH dipping is a simple and cost-effective process that can be used to separate NWs from bundles by tapering them; this improve the antireflection and photovoltaic characteristics of NWs [21]. Surface treatment plays an important role in SiNW morphology and in suppressing reflection. A micrometer-scale texture forms a thin reflecting film and enhances photon absorption, mainly via a geometric optical effect. However, there has been no investigation into the effect of alkali treatment of SiNWs as an absorber layer on planar components using monochromatic incident photon-to-electron conversion efficiency (IPCE) spectroscopy to date.

We investigated the effect of alkali treatment on the spectral response of SiNW cells using IPCE spectroscopy. We found that 30 s treatment improved the light response of SiNW solar cells over the range 450–1100 nm. However, alkali-treated SiNW solar cells showed a poor blue light response, which is a major limiting factor for efficient SiNW cells.

2. Experimental

Polished p-type Si (100) wafers (0.1–1 Ω/cm, 5 cm in diameter) were ultrasonically cleaned in acetone and in ethanol at room temperature for 10 min to remove organic

* Corresponding authors.
E-mail addresses: jiangyurong@whut.edu.cn (Y. Jiang), chfg@henannu.edu.cn (F. Chang).

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contaminants. The clean wafers were immediately immersed in an aqueous solution of 5 M HF and 0.02 M $AgNO_3$ for 30 min for growth of vertically aligned SiNWs in a simple Teflon vessel. After etching, the samples were wrapped with a thick dendritic Ag structure [22]. Silver nanoparticles were easily removed after electroless etching by dipping the samples in nitric acid (68 wt%) for 120 min. The samples were then rinsed with deionized water, dipped in 10 wt% HF solution to remove native oxide, rinsed with deionized water again, and dipped in a solution of 30 wt% NaOH and 10 wt% isopropyl alcohol (IPA) at 25 °C. IPA increases the wettability of crystalline silicon surfaces in alkaline etching solutions [23].

A control sample was prepared by dipping a Si (100) wafer into a solution of 30 wt% NaOH and 10 wt% IPA for 30 min at 80 °C; this led to a silicon etch depth of approximately 5–10 μm.

Solar cells were fabricated using SiNWs according to the following steps. (1) The substrate was heated in a 3:1 mixture of 97% H_2SO_4 and 30% H_2O_2 for 10 min to remove organic residues and heavy metals. (2) Cleaned wafers were rinsed thoroughly with deionized water and then 1% HF solution to remove native oxide. (3) Phosphorus oxychloride was spin-coated onto SiNWs on a wafer. (4) Phosphorus-coated wafers were heated in a tube furnace at 930 °C for 10 min. This led to phosphorus ion doping of the NW wafer surface via thermal diffusion to form a bulk p–n junction on the samples. SiNWs ought to be n-type after phosphorus diffusion [9].

The depth of the diffusion layer on the underlying wafer was estimated as ~300–500 nm according to a chemical coloration method. The sheet resistance was controlled at approximately 46.3 Ω/□ as measured using a four-point probe. To assess the effect of light absorption by SiNWs on the photovoltaic response, we printed silver paste as the front and rear electrodes of the p–n junction over an area of 0.5 cm^2.

Fig. 1 shows a schematic of the fabrication process for SiNW solar cells. The as-synthesized SiNWs were characterized using a scanning electron microscope (SEM; Jeol 6301F). SiNWs-based solar cells with an area of 1×1 cm^2 were cut out. Reflectivity and transmittance measurements were carried out on a UV-3600 spectrophotometer equipped with an integrating sphere and a photomultiplier tube and PbS for detection over the wavelength range 300–1300 nm. The light source was a halogen lamp. The internal quantum efficiency (IQE) of the cells was characterized using a Newport 1000-W halogen lamp and a grating monochromator (Acton Spectra Pro 2300i) with an SR540 optical chopper and a lock-in amplifier (SR-830) to avoid electrical and optical interference. A calibrated Newport 818-UV sensor was used to measure the absolute IQE of the solar cells under AM 1.5 illumination.

3. Results and discussion

The cross-sectional SEM image in Fig. 2a shows NWs of ~8 μm in length with excellent vertical alignment to the substrate. The tilted SEM image in Fig. 2b demonstrates the overall morphology of the electroless etched SiNWs and reveals a bunched morphology between the top ends of the as-etched NWs. NW bundles were observed due to agglomeration at their tops ends [21]. This agglomeration can be attributed to van der Waals forces between the NWs. The tilted SEM images in Fig. 2c,d illustrate the effect of the NaOH/IPA etching time on the NW array morphology. Agglomerated top ends of the NWs were easily separated by even short (30 s) treatment with NaOH/IPA (Fig. 2c).

The wet etching rate of single-crystal Si depends heavily on the bond strength of surface atoms [24]. Top corner edges in a square microstructure have weak bond strength owing to the drastic transition in surface atom density at the corners. This results in a faster etching rate at the corners than over flat regions, so convex undercutting is clearly visible and a sharp tip and tapered shape form on the top [21].

Therefore, we used an anisotropic etching process after metal-assisted etching to decrease van der Waals forces between NWs and separate NW bundles. When the etching time was increased to 60 s, the NWs almost disappeared (Fig. 2d), exposing the rugged surface morphology. It is clear from the SEM images that alkali treatment significantly changed the NW morphology. Etching led to separation of tapered single NWs, in accordance with previous research [21].

The morphology of the textured wafer used as a control shows uneven pyramid structures on the sample surface (Fig. 2e). This confirms that alkali etching of Si (100) leads to a textured surface because of the anisotropic etching behavior of crystalline Si [25].

After removal of the silver layer, etched silicon wafers were dark black in appearance, which is indicative of low surface reflectivity. Photons reflected from a photovoltaic cell surface are neither absorbed nor converted to electricity. This motivated us to investigate the reflectivity of our samples. Total reflectance spectra were measured on a UV-3600 spectrophotometer (Fig. 3a). Compared to SiNWs and the random pyramid structure formed on the textured

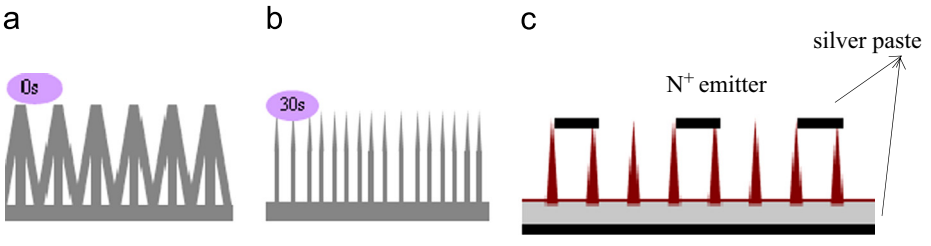

Fig. 1. Schematic illustration of the fabrication process for SiNW-array solar cells. (a) Formation of bundled SiNW arrays on the wafer. (b) Alkali treatment of SiNWs for 30 s. (c) Formation of an n-type emitter by phosphorus diffusion and electrode on the rear and front surfaces.