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Core-shell structured Si/ZnO photovoltaics

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ABSTRACT

Periodic Si pillar arrays synthesized by metal assisted chemical etching method exhibit an excellent light harvesting capability, ideal for core-shell structured solar cell applications. To investigate the photovoltaic prospective, a radial heterojunction device is fabricated by conformal coating a layer of Al doped ZnO film on the *p*-Si pillar array. This core-shell structure has achieved low reflectance ($<12\%$) over a broad wavelength range, and has demonstrated more than doubled enhancement of the short-circuit current as compared to the traditional planar architecture. Although reverse recovery transient measurement shows that this device with no surface passivation has shorter minority carrier life time than the planar structure, the overall efficiency is enhanced. It suggests that device efficiency could be much improved through proper surface treatment. This renders a promising path for core-shell structured solar cell with higher efficiency yet reduced material per device element.

1. Introduction

Solar energy is one of the abundant, clean, and sustainable energy sources. In recent years, much research effort has been directed to develop cost-effective photovoltaic devices through configuration and material innovations. To build a high efficient solar cell, all three essential processes in photoelectric energy conversion should be concurrently optimized, that is, light absorption, charge separation, and charge collection. However, light absorption and charge separation are difficult to be fulfilled simultaneously in traditional planar structured solar cells. Thick absorption layer results in better light harvest but less efficient charge collection, limited by the minority diffusion length in the material. Core-shell photovoltaic structure provides a viable solution to this issue and has attracted considerable interest because it orthogonalizes the light absorption and charge collection direction. In addition, it possesses many advantages including reduced reflection, enhanced light trapping capability, increased defect tolerance, reduced material cost, and large area scalability [1–6].

Inspired by the three dimensional pillar structures, we have constructed a prototype of *p*-Si/*n*-ZnO heterojuntion solar cell. Si is extensively utilized because of its abundance, stability, low toxicity, and high efficiency-to-cost ratio. Yet, as one knows, most of the energy ($>70\%$) in the UV region is lost in Si through lattice thermalization due to its narrow energy bandgap (1.12 eV), resulting in increased operation temperature and degrading device performance. In order to promote more efficient UV light absorption, ZnO with a direct wide bandgap (3.37 eV) is selected as the complementary material for its high absorption in the UV region [7]. In addition, ZnO has high transmittance in the visible region and relatively high electric conductivity, and is often utilized as the anti-reflective window layer in solar cells [7–9]. Moreover, Si/ZnO heterojunction solar cell is theoretically predicted to have a conversion efficiency as high as 25% [10]. In this work, periodic Si pillar array is used to form *p*-Si/*n*-ZnO photovoltaic, not only because it reduces the active material volume, but more importantly, it also maximizes the optical absorption in contrast to Si thin film planar configuration [11,12]. This study aims to evaluate the core-shell structured geometry on the performance of the radial heterojunction photovoltaic device. The electrical, optical, and photovoltaic properties of the prototype are investigated. Comparison is made to its planar structured counterpart in order to address the fundamental property differences between perpendicular and periodic radial junctions.

2. Experiments

Periodic *p*-Si pillar arrays were fabricated by a simple metal-assisted chemical etching method [13], and the periodicity was

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controlled by pre–patterning of metal catalyst through optical lithography. *p*-Si wafer (boron-doped (1 1 0) thickness ~400 μm) substrate was first cleaned by acetone, ethanol and DI water, and then quickly dipped in HF solution for 30 seconds to remove the native oxide on the surface. Photoresist coating with periodic dot structure was patterned through photolithography on the Si substrate, followed by a bi-layer catalyst (Ag/Au, 20 nm/5 nm) deposition. After removing the unwanted part of the metal layer, (those on the top of dot structured photoresist) Si wafers were etched in the etchant solution (0.02 M H_2O_2, 5 M HF) at room temperature. During the etching, Ag served as a local cathode to promote the reduction of oxidant (H_2O_2) and the generation of holes at the metal-semiconductor interface, followed by the reaction with anode (Si) [14]. The top Au layer was to protect the Ag film from dissolving in etchant [13,15]. Thus, the region with metal coating is etched down faster than dot region and a pillar structure is formed. Then the samples were cleaned by DI water, and the residual metal was removed by H_2SO_4 and H_2O_2 mixture.

To form core-shell structures, the as-synthesized Si pillar arrays were coated with ZnO: Al film (highly *n*-doped) by RF magnetron sputtering. Meanwhile, a bare Si wafer was coated in the same process batch to fabricate planar structured solar cells for comparison study. Before ZnO deposition, Ar^+ plasma was applied to the samples to remove the native oxide and to reduce the contact serial resistance. The RF power was set at 150 W during the sputtering process while the deposition time was 1.5 hours. To improve the crystal quality of the ZnO layer, a post annealing process was carried out in Ar ambience at 500 °C for 1 hour.

The morphology of the samples was characterized by a field-emission scanning electron microscope (FESEM, JEOL JSM-7001 F). Reflection spectra were obtained by a UV/Vis/NIR Spectrophotometer (LAMBDA 950) with an integrating sphere. The photocurrent density versus voltage (J–V) characteristics measurements were performed by a semiconductor parameter analyzer (HP 4156c) under simulated sunlight (AM 1.5 G, 100 mW/cm^2 produced by an Oriel Solar Simulator). The metal contacts were selected to be Ni/Au for *p*-Si and Ti/Au for *n*-ZnO in order to minimize the work function mismatch. Minority carrier life time of the *p*-Si/*n*-ZnO heterojunction was investigated by reverse recovery transient method, where voltage was applied by a digital delay/pulse generator (DG535) and current response was monitored by an oscilloscope (Agilent MSO8104A).

3. Result and discussion

3.1. Morphology of Si micro pillar arrays and Si/ZnO heterojunction

Fig. 1 shows the SEM images of well-ordered Si pillar arrays. The diameter of each pillar is ~2 μm with a pitch size of ~5 μm between adjacent pillars. The dimensions can be adjusted for optimization of light scattering and absorption. And the height of pillars can be controlled by adjusting the etching time. As shown in Fig. 1b-d, the height of Si pillars is 0.68 μm, 1.15 μm, and 2.8 μm, corresponding respectively to different etching time of 7 min, 15 min, and 30 min. In this prototype evaluation, Si pillar arrays with a height of 0.68 μm have been selected to construct *p*-Si/*n*-ZnO core-shell structures. The conceptual comparison between the radial junction core-shell structure and the planar structure is illustrated in Fig. 2a. Fig. 2b shows the cross-section SEM images of core-shell structure in contrast with the planar structure *p*-Si/*n*-ZnO heterojunctions (Fig. 2c), illustrating a large area conformal coating of ZnO film (thickness ~600 nm) on the Si pillar arrays.

3.2. Reflectance measurement

Fig. 3 shows the total reflectance spectra of Si wafer and periodic Si pillar array with and without ZnO film coating at a wavelength range of 300–800 nm. Note that the transmission is negligible for the thickness of Si substrate (~400 μm). Compared with the planar Si wafer, Si pillar array shows ~30% lower reflectance over the whole spectrum. The vertically aligned pillar array fosters the resonant trapping of light in the periodic structure [16]. In addition, it facilitates

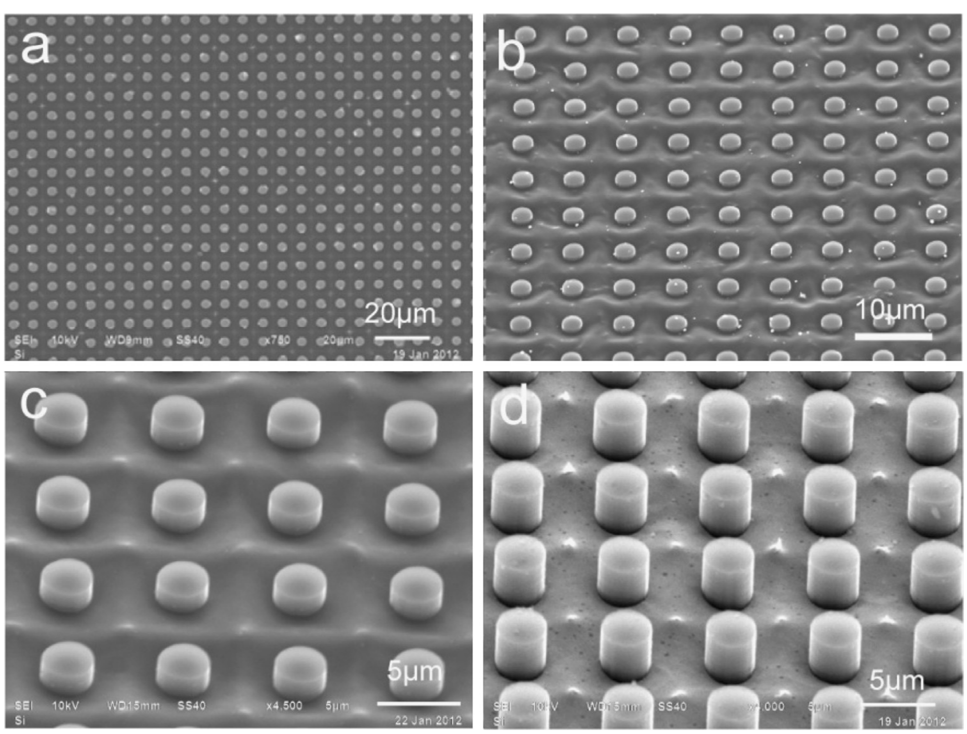

Fig. 1. SEM images of periodic Si pillar arrays synthesized by metal-assisted chemical etching method. (a) Top view of a large area Si pillar array. (b-d) 45° tilted view of Si pillar arrays. The height of Si pillars is 0.68, 1.15, and 2.8 μm, respectively after etching for 7, 15, and 30 min.