Silicon nanowire array solar cell prepared by metal-induced electroless etching with a novel processing technology

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1. Introduction

There has been a significant interest in renewable energy, especially for solar energy. The use of nanostructured materials represents a general approach to reduce cost and to enhance photovoltaic efficiency. Among them, Si nanowire (NW)-based solar cells are one of the promising candidates for the next-generation photovoltaic devices. Several methods have been used to fabricate the Si NW-based solar cell [1-3]. Although substantial works have been devoted for the development of the efficient Si NW solar cell, but high cost, small cell size and complex process are still challenging.

Here, we employed an electroless etching technique with a simultaneous doping using spin-on dopants (SODs) for the fabrication of Si NW array solar cells. Arial densities of a Si NW array were precisely controlled by a simple electroless etching for enhancing the anti-reflection effects. The novel technique for simultaneous doping of boron and phosphorous SOD was developed for the first time while providing less thermal damages to a Si NW array.

2. Experimental

Si NW arrays were fabricated by electroless etching on Si (100) substrate (*p*-type, $1 \sim 10 \ \Omega \text{cm}$) as shown in Fig. 1 (a)-(c). The detailed information about the fabrication process can be found from the literature [4].

The doping process is illustrated in Fig. 1 (d)-(f). The phosphorous SOD wafer and the front side of Si NW array substrate were kept at a closely spaced distance. The NW array substrate-source stack was held at 1050 °C for 5 min in a conventional quartz-tube furnace. The phosphorous compound (P_2O_5) from the floating phosphorus SOD wafer was transferred via gas-phase transport process to the Si NW array (proximity diffusion). It reacted with the NW surfaces and released phosphorous. On the other hand, the boron compound (B_2O_3) was directly transferred from boron SOD to backside of the Si substrate (direct diffusion).



Fig. 1. Schematic diagram of the process for Si NW array solar cell : (a)-(c) formation of Si NW array on the wafer; (d)-(f) formation of uniform n-type and p^+ -type junction.

After simultaneous diffusion, the doped Si NW array substrate was cleaned in a 2% HF solution to remove both SOD and oxide formed during the doping process.

The morphology of as-prepared Si NW arrays was characterized by a Hitachi S-4800 scanning electron microscope (SEM). Optical reflectance spectra were measured with the help of Varian Cary 5000 UV–VIS–NIR spectrophotometer. Si NW array solar cell was investigated under the illumination of air mass 1.5 (AM 1.5, 1000 W m⁻²) from a solar simulator (Peccel PEC-L11).

3. Results and discussion

To optimize optical property of Si NW array for solar cell, the size of the Ag nanoparticles (NPs) was modified. SEM images in Fig. 2 (a)-(f) show different morphologies of the deposited Ag NPs with NPs with different sizes and the corresponding electroless etching results. When galvanic process time was 10 sec, the NPs were island-like, with wide gaps and little interconnection among them. With increasing time, the deposited NPs tended to increase



Fig. 2. (a)-(f) Morphologies of deposited Ag NPs with different sizes and the corresponding electroless etching results; (a)-(c) planar SEM images of Ag NPs formed by galvanic displacement for 10sec, 60sec and 120 sec, respectively; (d)-(f) cross-sectional SEM images of etched substrate corresponding to (a), (b) and (c), respectively. (g) reflectance spectra of various morphologies of Si NW array.

the size of NPs, resulting in interconnected NPs networks and shrinkage of the interspaces. When process time reached about 60 sec or more, the surface of the substrate was almost overlaid by NPs with few gaps. There is a relationship between the NPs size and structure of etched substrate. Small NPs (diameter: < 62 nm) with wide gaps between NPs leaded to the formation of porous Si (Fig. 2 (d)). On the other hand, thin NWs were fabricated by large NPs (> 97 nm) and agglomerated as shown in Fig. 2 (f). So, we optimized the proper size (60~90 nm) of NPs for the fabrication of vertically aligned Si NW array (Fig. 2 (e)). Fig. 2 (g) shows the optical reflectance spectra of Si NW arrays with different size of gap between NWs. The reflectance of vertically aligned Si NW array was lower than that of agglomerated Si NW array over the range of 300~1000 nm. Therefore, the highly dense and vertical Si NW array with proper size (60~90 nm) of NPs shows a small optical loss of the incoming light, which make them suitable for anti reflection coating.

To measure an approximate dopants concentration, secondary ion mass spectroscopy (SIMS) analysis was performed on the bulk Si substrate (both direct and proximity diffusion). In case of direct boron diffusion, the surface concentration was in the range of 7~8 x 10^{20} cm⁻³. Fig. 3 clearly shows that boron profile is flat under $1\mu m$ (>10²⁰ cm⁻³), resulting from a higher diffusion coefficient at higher concentration [5]. This highly doped region was acted as back surface field (BSF) by direct diffusion. However, for doping of Si NWs, direct diffusion was limited due to difficult process of spin-coating on Si NW array. Therefore, proximity diffusion appeared to be particularly promising for the controlled introduction of dopants without the defect or morphological changes. After proximity diffusion at 1050 °C for 5 min, the surface concentration was in the range of 1×10^{20} cm⁻³ and junction depth was in the range of approximately 1µm, resulting in the formation of fully doped Si NWs.

Si NW array solar cells with an area of $1 \times 1 \text{ cm}^2$ were taken to perform the electrical and photovoltaic characterization. Fig. 4 shows the current-voltage (I-V) characteristic of Si NW solar cell with BSF. The devices exhibited rectifying behavior in darkness. Upon illumination of the front surface, a clear photovoltaic response was observed. When the photovoltaic cell was characterized in the simulated sunlight, a power conversion efficiency of 5.94 %,



Fig. 3. SIMS analysis for boron by direct diffusion and phosphorous by proximity diffusion at 1050 $^{\circ}$ C for 5 min.

short circuit current of 17.04 mA/cm², open circuit voltage of 521 mV, and fill factor of 66.92 were obtained for Si NW solar cell. The conversion efficiency was not as high as expected. We thought that the low conversion efficiency may be due to the low current-collection efficiency of the front grid electrodes. To improve the main photovoltaic parameters such as short-circuit current and open-circuit voltage, some technological regimes including phosphorus diffusion and contacts fabrication should be optimized.



Fig. 4. I-V characteristic of Si NW solar cell. The inset shows schematic of top and rear electrode. For ohmic contact, Ga-In alloy was used.

4. Conclusions

In summary, we have fabricated Si NW arrays by a simple electroless etching technique with Ag NPs, and also investigated the application of Si NW array as a solar cell. We have found that the highly dense Si NW array with a low reflectivity could be obtained with a optimal size (60~90 nm) of Ag NPs. These Si NW arrays were used as an efficient anti-reflection coating for a solar cell application. We have also presented a simultaneous doping method for boron and phosphorous co-diffusions by using a SOD for the emitter and the BSF in a one-step thermal process. We could confirm ~6% conversion efficiency. Generally, NW-photovoltaic cells offer rather lower conversion efficiencies compared to the well-developed conventional Si solar cell, which may be estimated to stem from the low current-collection efficiency at the front-grid electrodes. For further boosting the cell efficiencies, the optimal integration of front metal electrodes with a NW array is critically required.

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