Facile Fabrication of Si Nanowire Arrays for Solar Cell Application

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Large-area Si nanowire arrays have been fabricated on phosphorus doped Si surface by a facile silver-catalyzed chemical etching process. The solar cell incorporated with Si nanowire arrays shows a power conversion efficiency of 6.69% with an open circuit voltage of 558 mV and a short circuit current density of 25.13 mA/cm² under AM 1.5 G illumination without using any extra antireflection layer and surface passivation technique. The high power conversion efficiency of Si nanowires based-solar cell is attributed to the low reflectance loss of Si nanowire arrays for incident sunlight. Optimization of electrical contact and phosphorus diffusion process will be critical to improve the performance of Si nanowires-based solar cell in the future.

Keywords: Si Nanowire, Solar Cell, Antireflection, Chemical Etching, Power Conversion Efficiency, Silver.

1. INTRODUCTION

Among the various energy projects in progress, solar photovoltaic power generation is an almost maintenance-free and renewable clean-energy technique and considered as the most promising candidate for the future energy resource. Si, the most important semiconductor material in micro-electronics, and Si-based photovoltaic devices, including single-crystalline Si, multi-crystalline Si, and amorphous Si, still play the dominant role in today’s photovoltaic market due to their high power conversion efficiency. Recently, nanostructured materials provide a new approach to reduce the cost and improve efficiency in photovoltaics. Si nanowires (SiNWs), Si nanopillar (SiNPs) and Si nanotips (SiNTs) have been theoretically demonstrated their good ability for improving the charge collection efficiency and increasing the absorption for incident sunlight. However, the experimental report on this area is relatively rare.

During the past few years, SiNW arrays were fabricated by various methods, such as the chemical vapor deposition (CVD),7 Molecular beam epitaxy,8 and Cl₂ plasma based reactive ion etching.9 However, rigorous experimental conditions and complex instruments are often required for these methods. Recently, a wet chemical etching method has been developed to fabricate single-crystalline SiNW arrays by immersing Si wafer into the mixture solution of AgNO₃ and HF.10–12 This technique is actually an electrochemical deposition of silver plus a chemical etching process. In this study, we reported a facile process to fabricate large-area SiNW arrays by using a dry deposition of silver film plus a chemical etching process. Based on this chemical etching process, SiNWs-based solar cell with a conversion efficiency of 6.69% is achieved. We hope this fabrication process has a potential application in Si-based solar cell.

2. EXPERIMENTAL DETAILS

In the author’s experiments, a 0.6 mm-thick single-crystal (100) p-type Si wafers with a specified surface roughness of Ra 5~10 nm and resistivity of 1–30 Ω·cm were used. Before experiment, Si wafers were washed with deionized water and acetone sequentially, and then immersed into Piranha solution (H₂SO₄/H₂O₂ = 3:1, v:v) for 1 h to entirely remove the surface contamination compounds. Then a thin layer of silver film with thickness of 25 nm was coated on Si wafer by using a sputtering system with argon flow rate of 30 sccm. Next, the silver coated Si wafers were immersed into a Teflon vessel containing the mixture solution of HF and H₂O₂ at room temperature. The concentration of HF and H₂O₂ is 0.44 M and 4.6 M, respectively. The etching duration depends on the desired length of SiNWs. After chemical etching process, the Si wafers were thoroughly rinsed by deionized water for several times.

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Scheme 1. Diagram of fabrication process for SiNWs-based solar cell: (a) pre-cleaning of Si wafer; (b) formation of Si p-n junction wafer by a phosphorus diffusion process; (c) fabrication of SiNW arrays; (d) deposition of rear and front side electrode and fabrication of SiNWs-based solar cell.

The residual silver particles were removed by AMP solution (NH4OH/H2O2/H2O = 2:1:5, v:v) and HPM solution (HCl/H2O2/H2O = 2:1:8) sequentially. Finally, the samples were rinsed by deionized water and dry in N2 atmosphere.

The detailed processing sequence for SiNWs-based solar cell is schematically depicted in Scheme 1. In general, it involves the following steps:
(a) fabrication of planar Si p-n junction wafer with doping depth of ~0.7 μm and doping concentration of 2 × 10^{18}/cm^3 by a POCl3 diffusion process at 930 °C for 50 min;
(b) removal of the parasitic p-n junction on back side of Si wafer by a CMP process;
(c) deposition of silver film with thickness of 25 nm on Si substrate;
(d) fabrication of SiNW arrays on planar Si p-n junction wafer and removal of residual silver particles by aforementioned chemical solutions;
(e) deposition of aluminum film with thickness of 250 nm on rear side of Si wafer and annealing at 550 °C for 50 sec via a rapid thermal process to form the rear side electrode;
(f) deposition of Ti/Pd/Ag films (60/60/100 nm) on SiNWs surface via a shadow mask evaporation process to form the front side electrode.

After annealing in N2 atmosphere at 200 °C for 6 h and cooling down to room temperature, the samples were finally cut into 1 × 1 cm^2 to remove the circumferential p-n junction and yield a standard solar cell.

The morphologies and structures of samples were examined by using LEO 1550 field emission scanning electron microscopy (FESEM) and Raman microspectroscopy (WITEC CRM200 confocal system with exciting wavelength of 532 nm). Optical reflectance spectra were recorded by a PerkinElmer LAMBDA 950 UV/Vis/NIR spectrophotometer. The power conversion efficiency of the as-prepared SiNWs-based solar cells was performed by a simulated Air Mass (AM) 1.5 G solar illumination with intensity of 100 mW/cm^2.

3. RESULTS AND DISCUSSION

In this study, SiNW arrays are fabricated by a dry silver film deposition plus a wet chemical etching process. When immersing into the chemical etching solution, the color of Si wafer changes from gray to straw yellow, and finally turn into the black. Figure 1 shows the SEM images of fabricated SiNW arrays with chemical etching duration of 40 sec. From the top-view SEM image, as shown in Figure 1(a), it can be seen that SiNWs with diameters...
ranges from 50 nm to 200 nm are uniformly distributed over large-area, indicating a facile process for fabricating wafer-scale of uniform SiNW arrays with low cost and high throughput. This wafer-scale fabrication process thus offers a great convenience for exploring their potential application in solar cell. Cross-sectional SEM image, as shown in Figure 1(b), indicated that all SiNWs with length of ca. 450 nm are vertically aligned on Si wafer, implying that the etching process is preferred along the direction perpendicular to Si surface. Linear etching traces and track cavity could also be easily observed on SiNWs surface. The morphology on top side of SiNWs is coarser than that of bottom side, which may be related to the longer etching duration it suffered. The silver film, which actually consists of nanoclusters, plays the role of catalyst during chemical etching process. The silicon under the silver nanoclusters is preferentially etched away and finally going into chemical solution in form of \(H_2SiF_4\), while the Si surface without silver nanoclusters covered remain unchanged. With the continuous dissolution of silicon and the simultaneous sinking of silver nanoclusters, the silicon surface without silver nanoclusters covered protrudes out from the network of silver nanocluster, and consequently SiNW arrays forms along the direction perpendicular to the surface of Si substrate. During the chemical etching process, some silver particles also intrude into SiNWs and leave some cavities on the sidewall of SiNWs after the silver catalyst was removed. This maybe related with the undulation of solution or the produced bubbles during chemical etching process. Figure 1(c) shows the cross-sectional SEM image of SiNWs with etching duration of 80 sec. It can be seen that the length of SiNWs increases remarkably, and reaches 1.1 \(\mu m\) with the prolonged chemical etching duration. Some SiNW bundles or clumps could also be found on sample surface. Figure 2 shows the Raman spectra recorded from pristine Si wafer and SiNW arrays. The typical Raman band at 520.2 \(cm^{-1}\) corresponds to the first-order transverse optical phonon mode of Si surface. Compared with that of pristine Si wafer, the first-order Raman peak of SiNWs at 518.9 \(cm^{-1}\) shows a dramatic asymmetric broadening and lower downshift, implying that SiNWs still remain its original crystalline structure. The asymmetry and lower downshift is mainly attributed to the phonon quantum confinement effect and the possible strain resulted from chemical etching process.\(^{13}\) According to quantum theory, when the crystalline size decreases, momentum conservation will be relaxed (\(q \neq 0\)) and Raman-active mode will not be limited to being at the center of the Brillouin zone. The smaller the crystalline grain, the larger the frequency shift and the more asymmetric and the broader the peak becomes. This phenomenon has been confirmed by previous report.\(^{13}\)

The reduction of reflectance loss is one of the most important factors for high efficiency solar cell. The nanoporous structure and black color of the as-prepared samples imply their possible antireflection properties and applications in solar cell. Figure 3 demonstrates the reflectance spectra recorded from the Si wafer covered with different lengths of SiNW arrays. Compare with that of pristine Si wafer, the presence of SiNW arrays effectively reduces the optical reflection loss of Si wafer. The average reflectance loss of SiNW arrays with length of \(\sim 450 \text{ nm}\) is \(\sim 4.01\%\) over the range of 200–1000 \(\text{nm}\) wavelength, which is far lower than that of pristine Si wafer and also the Si pyramidal structure, as well as the porous Si nanostructures.\(^{14–16}\) The reflectance loss of Si surface could be further decrease to 2.98\% as the length of SiNWs increase to 1.1 \(\mu m\). The remarkable low reflectance loss of SiNWs covered Si wafer may be related with the ultrahigh specific surface area and the typical subwavelength structure of SiNW arrays.

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**Fig. 2.** Raman spectra recorded from the pristine Si wafer surface and SiNW arrays.

**Fig. 3.** Reflectance spectra of Si wafer and SiNW arrays with different lengths.

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According to the aforementioned results, the as-synthesized SiNW arrays demonstrate the excellent antireflection property and possess several advantages over the other surface texture structures. This facial process enables us to fabricate wafer-scale SiNW arrays at room temperature with low cost and high throughput. No rigorous experimental conditions, such as high temperature, hazardous silicon precursor, or complex instrument are required in our experiment. This will pave the way to explore the possible application of SiNWs in high efficiency solar cell. With this in mind, here we integrate this SiNW arrays into planar Si p-n junction wafer and explore the possible photovoltaic applications of SiNWs on conventional solar cell. The main fabrication process of SiNWs-based solar cell is shown in Scheme 1 and described in experimental section. To prevent the possible chemical contamination to diffusion furnace, in this strategy, p-n junction is generated on Si wafer prior to chemical etching process. By synthetically considering the diffusion depth of phosphorous and the impact of the length of SiNWs on reflectance loss, the length of SiNWs is selected as 450 nm and corresponding chemical etching duration is ca. 40 sec. Figure 4(a) shows the optical image of the as-prepared SiNWs-based solar cell recorded by a digital camera. The black areas consist of SiNW arrays, while the block lines stand for Ti/Pd/Ag films front grid electrode. The morphology of the black region is same as that in Figure 1(a). Figure 4(b) demonstrates the cross-sectional SEM image of the block line area. As can be seen that Ti/Pd/Ag films tightly compact on the top of SiNWs. Some parts of Ti/Pd/Ag films intrude the interspace of SiNWs and paste on the side wall of SiNWs. This is believed to be beneficial for increasing the contact area between SiNWs and electrode to some extent and improving the electron collection efficiency. Figure 5 shows the current density–voltage (J–V) characteristic curves of the as-prepared SiNWs-based solar cell in darkness and under AM 1.5 G illumination condition. The solar cell exhibits a clear diode behavior in darkness, with turn-on voltage of ~0.3 V and rectification ratio on the order of 10² at 0.2 V. Only a negligible reverse leakage current was found at reverse voltage, implying the good quality of the SiNWs-based device and good controllability of our fabrication process. When illuminated under AM 1.5 G conditions, SiNWs-based solar cell (filled circle) exhibits an open circuit voltage (V_{oc}) of ~558 mV and a short circuit current density (J_{sc}) of ~23.51 mA/cm² without using any extra antireflection layer and surface passivation technique. Filled factor (FF) and power conversion efficiency (η) of the SiNWs-based solar cell were calculate to be 0.51 and 6.69%, respectively. Compared with that of pristine Si wafer-based solar cell (unfilled circle), the conversion efficiency of SiNWs-based solar cell increases remarkably, which is closely related with the excellent antireflection and trapping effect of SiNWs for incident sunlight, and thus the high short circuit current density of fabricated solar cell. It should be noted
that both the $V_{OC}$ and $FF$ of SiNWs-based solar cell is still lower than that of standard single-crystalline Si-based solar cell, indicating that the optimization of phosphorus diffusion and contact between electrodes and SiNWs is still needed. Some surface passivation technologies, such as the indium-tin oxide and silicon nitride film should be used to annihilate the surface defects and dangling bonds resulted from chemical etching process, reduce the surface recombination velocity, and finally improve the $V_{OC}$ and $FF$ of the solar cell. After these treatments, the high performance SiNWs-based solar cell could be expected in the future.

4. CONCLUSION

In summary, large-area SiNW arrays were fabricated on Si surface by a facile silver-catalyzed chemical etching process. The as-synthesized SiNW arrays show excellent antireflection property with average reflection loss lower than 4.01% within range of 200–1000 nm wavelength. The SiNWs-based solar cell shows a high conversion efficiency of 6.69% with $V_{OC}$ of $\sim 558$ mV and $J_{SC}$ of $\sim 23.51$ mA/cm$^2$ under 1.5 G illumination. The high conversion efficiency of SiNWs-based solar cell is attributed to the low reflectance loss and excellent trapping effect of SiNWs for incident sunlight. The optimization of phosphorus diffusion and contact between the electrodes and SiNWs is still needed and high power conversion efficiency of SiNWs-based solar cell could be expected in the future.

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References and Notes


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