Effect of nanowire length on the performance of silicon nanowires based solar cell

Van Trinh Pham\textsuperscript{1,2}, Mrinal Dutta\textsuperscript{2}, Hung Thang Bui\textsuperscript{1} and Naoki Fukata\textsuperscript{2}

\textsuperscript{1} Institute of Materials Science, Vietnam Academy of Science and Technology, 18 Hoang Quoc Viet Road, Cau Giay District, Hanoi, Vietnam
\textsuperscript{2} International Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

E-mail: trinhvp@ims.vast.ac.vn and FUKATA.Naoki@nims.go.jp

Received 6 October 2014
Accepted for publication 21 October 2014
Published 14 November 2014

Abstract
Currently, silicon nanowires (SiNWs) are attracting attention as promising candidate materials for developing the next-generation solar cells to realize both low cost and high efficiency due to their unique structural, electrical, and optical properties. In this paper, a vertical-aligned SiNWs array has been prepared by metal-assistant chemical etching technique and implemented on SiNW array textured solar cells for photovoltaic application. The shape and size of SiNWs were controlled by etching time of 30 min, 45 min and 60 min with the length of SiNWs of 4 $\mu$m, 6 $\mu$m and 8 $\mu$m, respectively. The etching rate was estimated to be about 133 nm per minute. The optical properties of a SiNWs array with different lengths were investigated in terms of optical reflection property. Less than 6% reflection ratio from 300 nm to 800 nm wavelength was achieved. In addition, $I$–$V$ characteristic was used to estimate the dependence of the SiNWs length on the performance of SiNWs based solar cell. Conservation efficiencies were achieved of 1.71%, 2.19%, and 2.39% corresponding to 4 $\mu$m, 6 $\mu$m and 8 $\mu$m SiNWs in length, respectively.

Keywords: silicon nanowires, SiNW array, solar cells, SiNWs based solar cell

Mathematics Subject Classification: 4.08, 6.03

1. Introduction

There is great demand for the development of the next generations of solar cell with higher efficiency, cheaper price and longer life. Nanomaterials and nanostructures based solar cells hold promising potency to enhance the performance of solar cells by improving both light trapping and photo-carrier collection. Many approaches have been taken to lower the production cost of Si photovoltaics, among which thin-film Si solar cells offer a promising low-cost solution [1, 2], however, thin-film Si solar cells have lower efficiencies than bulk Si, due to their limited absorption thickness. Si nanowires (SiNWs) have been considered as novel class of nanostructured materials for high-performance devices [3, 4] due to their unique structural, electrical, optical, and thermoelectric properties. Recently, SiNWs have been widely investigated for developing next-generation solar cells to realize both low cost and high efficiency [5–9].
such as VLS process [15, 16] and wet diffusion process [17, 18] have been used for this goal. Therein, wet diffusion process using dopant solution has become a promising approach for lowering the cost manufacturing of solar cells.

Therefore, in this paper, we present the results of the investigation of using SiNWs for low cost solar cell with the combination of metal-assisted chemical etching for preparing SiNWs and wet diffusion process for fabricating the radial pn junction. The optical property and $I-V$ characteristics of SiNWs based solar cell are also presented in this paper.

2. Experimental procedure

2.1. Materials

Acetone, ethanol, sulfuric acid (H$_2$SO$_4$), hydrogen peroxide (H$_2$O$_2$), hydro fluoric (HF) acid and nitric acid (HNO$_3$) were supplied by Wako Pure Chemical Industries Co. Silver nitrate (AgNO$_3$) were purchased from Sigma-Aldrich. The p-type Si (100) wafers were produced by Ferrotec Silicon Co. Ohka coating diffusion-source (OCD) solution containing phosphorus manufactured by Tokyo Chemical Industry Co. Ltd. Silver and aluminum targets were purchased from Kojundo Chemical Laboratory Co.

2.2. Preparation of SiNWs

SiNW arrays were prepared with Ag-assisted etching method. p-type (100) silicon wafers were cleaned with acetone (5 min) and ethanol (5 min), rinsed with deionized water (10 min) 3 times, then immersed in a 3:1 mixture of H$_2$SO$_4$ (97%) and H$_2$O$_2$ (30%) for 10 min, thoroughly rinsed with deionized water for 10 min, and then dipped in HF solution for 1 min. The cleaned silicon wafers were immersed into an aqueous HF solution (4.6 M) containing AgNO$_3$ (0.02 M) and treated for 30 min, 45 min and 60 min at room temperature. As-prepared SiNW samples were rinsed in deionized water and dried at room temperature. SiNW arrays were treated in HNO$_3$ (35%) for desired durations, and SiNW array of varied nanowire densities could be obtained.

2.3. Fabrication of solar cell

The fabrication process of SiNW radial pn junction arrays shown in figure 1 consists of two main steps: (a) spin-coating OCD solution onto the surface of synthesized SiNW arrays at a speed of 2000 rpm; (b) annealing of the samples by a thermal annealing system in argon atmosphere at 850 °C for 45 min followed by removal of remaining OCD solution in piranha solution for 4 min and SiO$_2$ film in 1% HF solution for 2 min. After radial pn junction structure was formed, a thin layer of aluminum film with thickness of 200 nm was deposited on the rear side of samples. Then a Ag film with thickness of 600 nm was deposited on the surface of SiNW radial pn junction arrays to form the front electrode via a shadow mask evaporation process in thermal evaporation system.

2.4. Characterization

The morphologies of the samples were characterized by Hitachi S4800 field emission scanning electron microscope (FESEM). Optical reflectance spectra were recorded by Jacob V-570 UV/Vis/NIR spectrophotometer. The $I-V$ characteristic measurement of based solar cell was performed using a solar simulator under Air Mass (AM) 1.5 G illumination with intensity of 100 mW cm$^{-2}$.

3. Results and discussion

Morphologic observation of SiNWs is shown in figure 2. figure 2(a) shows the top-view SEM image of SiNWs determining that the diameter of SiNWs is in the range of 50 to 180 nm. Cross-sectional SEM images of vertically aligned SiNW arrays with different lengths of 4 $\mu$m, 6 $\mu$m and 8 $\mu$m were prepared by Ag assistant etching method for 30 min, 45 min and 60 min, respectively. As a result, the lengths of SiNWs depended linearly on the etching time with the constant etching rate of 133 nm per minute. With the above constant etching rate, SiNWs of desired length could be prepared easily by controlling the etching time.
The doping diffusion profile of radial pn junction was estimated by the following equation [19]

\[ L = \sqrt{D \cdot t}, \]

where \( D \) is the diffusivity of P into Si, \( t \) is the diffusion time and \( L \) is the diffusion depth. Dopant diffusion process was carried out at 850 °C and diffusion time of 45 min with \( D = 1.5 \times 10^{-15} \text{ cm}^2 \text{ s}^{-1} \), the diffusion length was estimated about 20 nm. In addition, the diameter distributions of SiNWs are shown in figure 3 almost remaining from 50 to 180 nm. As a result, this indicated that the radial pn junction was formed on SiNWs with n-typed Si about 20 nm acting as shell layer coated p-typed Si core as shown in figure 3(d). Therefore, SiNWs not only acted as a non-reflecting electrode but also acted as radial pn junction array for solar cell structure.

Figure 4 shows the spectral reflectivity of SiNW arrays of planar silicon surface and SiNWs with different lengths in wavelength ranging from 200 to 1300 nm. Obtaining from reflective spectrum, the reflection of SiNWs sample decreases strongly compared with the planar Si substrate. The reflection of SiNW array remained on average about 10% for the wave length from 200 to 1300 nm. From this result it was demonstrated that the texture structure of SiNWs remained vitally important for reducing the light reflection on the surface of samples. The reflectance of an SiNW array is dependent on the length of SiNWs; the reflection becomes lower with higher length. The low reflectivity from an SiNW array’s surface has been attributed to the structural morphology of SiNW arrays, which closely resembles the sub-wavelength structured (SWS) surfaces. In addition, because of the unique morphology there is porosity variation from top to bottom in the arrays, which results in refractive index gradient with depth and, therefore, SiNW arrays effectively act as a multi-layer anti-reflection surface.

To analyze the electrical properties, the \( I-V \) curve of the fabricated SiNWs solar cell was measured by solar simulator under AM 1.5 (100 mA cm\(^{-2}\)) illumination. Figure 5 shows the typical light current–voltage curves of SiNWs along with planar Si based solar cell in the 1 cm\(^2\) effective area. Solar cell parameters consist of short circuit current density (\( J_{sc} \)), open circuit voltage (\( V_{oc} \)), fill factor (FF) and efficiency (\( \eta \)), presented in table 1. The measured results show that the performance of SiNWs based solar cell increases since greater length of SiNWs was used. Among these SiNW-based solar cells, the 8 \( \mu \)m SiNW-based solar cells had the highest efficiency of 2.39%, which is not only nearly twice higher than our planar Si solar cell but also is one of the highest efficiency compared with other SiNWs based solar cells. Additionally, in this case, the corresponding \( J_{sc} = 11.76 \) mA, approximating twice higher than that of the single-side polished short circuit controls (in \( J_{sc} \)).
Figure 3. Diameter distribution of SiNWs with different etching times (a) 30 min, (b) 45 min, (c) 60 min and (d) core–shell pn junction structure of individual SiNWs after using wet diffusion process.

Figure 4. Reflectance of planar Si and SiNWs with different lengths measured by UV–vis spectroscopy in wavelength ranging from 200 to 1300 nm.

Figure 5. Measured I–V characteristics of planar Si and different length SiNWs based solar cell.
Table 1. Solar cell parameters: short circuit current density ($J_{sc}$), open circuit voltage ($V_{oc}$), fill factor (FF), efficiency ($\eta$).

| Cell samples  | $J_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (V) | FF (%) | $\eta$ (%) |
|---------------|----------------------|-------------|--------|------------|
| Planar Si     | 5.8                  | 0.47        | 47.02  | 1.27       |
| SiNWs (4 $\mu$m) | 9.73               | 0.47        | 38.54  | 1.76       |
| SiNWs (6 $\mu$m) | 10.57              | 0.44        | 47.62  | 2.19       |
| SiNWs (8 $\mu$m) | 11.76              | 0.42        | 48.91  | 2.39       |

4. Conclusion

SiNWs synthesized by metal-assisted chemical etching method can easily be integrated into silicon solar cell fabrication technology and can be a key issue for improving the conversation efficiency by enhancing the light absorption with texture structures. The reflection is dependent on the length of SiNWs and decreases with higher lengths. The conversation efficiency of an SiNWs based solar cell was improved by reducing the light reflection, and achieved 1.71%, 2.19%, and 2.39% corresponding to 4 $\mu$m, 6 $\mu$m and 8 $\mu$m SiNWs in length, respectively, which is higher in comparison with the planar Si based solar cell. Wet diffusion process using dopant solution is a cost effective approach to reduce the cost of solar cell energy in future. However, the application of SiNWs to solar cell using wet diffusion for making pn junction still needs further optimization of various parameters related with SiNW formation, diffusion etc, to improve the performance of the SiNW based solar cell.

Acknowledgments

The author (VTP) would like to thank the support of National Institute for Materials Science, Japan for the opportunity to perform this research through NIMS internship fellow program.