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Bandgap Tuning of Silicon Nanowire Arrays for the Application to All Silicon Tandem Solar Cells

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Abstract

To reduce the diameter of silicon nanowire (SiNW) arrays for the purpose of bandgap tuning, diameter-reduction (DR) process of H_3PO_4 oxidation and HF etching were conducted for SiNWs with the diameter of 30 nm and the length of 15 µm. After 5-times DR process, the diameter of SiNWs around the tip part was successfully reduced below 10 nm. From the cathode luminescence measurement, the bandgap of SiNWs at the tip part was estimated at 1.2 eV, suggesting that bandgap widening occurred due to the quantum size effect.

1. Introduction

Silicon nanowires (SiNWs) have recently attracted much attention as one of novel photovoltaic materials. Since a SiNW embedded in a wide-gap material can confine electrons and holes, the bandgap can be tuned owing to the quantum size effect [1]. If the bottom cell in the tandem solar cell is crystalline silicon and the bandgap of the top cell should be in the range of 1.68 to 1.82 eV, a more than 30% efficient silicon-based tandem solar cell can be expected. Moreover, it is expected that SiNW solar cells [2] with a relatively thin absorber layer will have the potential to realize sufficient photocurrent [3].

Some researchers have prepared SiNW arrays by metal assisted chemical etching (MACE) [4], which is a redox reaction between silver and silicon, to prepare SiNW arrays covering a large area without a vacuum process. We have developed new fabrication method of metal assisted chemical etching using silica nanoparticles (MACES) [5] to control the shape and diameter. In this process, silica nanoparticles work as etching masks and the diameter of SiNWs can be controlled until around 30 nm. However, to control the bandgap of SiNWs using the quantum size effect, the diameter has to be less than 10 nm [1]. One of the ways to reduce the diameter of SiNWs further is surface oxidation. Kurstjens *et al.* fabricated 2.5~13-nm-diameter SiNW arrays by 193 nm deep ultraviolet (DUV) immersion lithography, dry etching, and postoxidation using dry O_2 or a mixture of O_2 and N_2 [6]. However, since dry O_2 oxidation needs high temperature around 1000 ºC, impurity diffusion is significant concern. In this study, diameter of SiNWs was reduced by oxidation using a H_3PO_4 solution and post-etching using a HF solution. Since this diameter reduction (DR) process can be carried out at the lower temperature of 160 ºC, it is not necessary to concern the contamination due to thermal diffusion. To confirm the bandgap widening, cathode-luminescence measurement was conducted for the diameter-reduced SiNW arrays.

2. Experimental

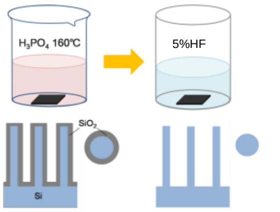
Si wafers (n-type, (100), 1-5 Ω·cm, thickness is 280 µm) were immersed for 1 hour at 2 ºC in a solution in which 30 nm-silica nanoparticle modified carboxyl group were dispersed. After that, 20 nm-thick silver film was deposited on the Si wafers with silica nanoparticles using a DC sputtering system. The silver film on silica nanoparticles were broken away by ultrasonication in deionized water. The wafers were chemically etched by using 4.8M HF and 0.15M H_2O_2 at room temperature and were subsequently put in HNO_3 solution to remove silver films. Finally, the oxide layer existing on the prepared SiNW array was removed with a 5% HF solution. SiNW arrays with the diameter of 30 nm and the length of 15 µm were arranged.

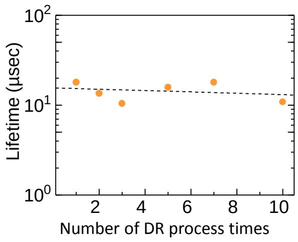
Figure 1 shows schematic diagram of the DR process using a H_3PO_4 solution. SiNW arrays were dipped into 85wt% H_3PO_4 solution at 160 ºC to oxidize the surface of SiNW arrays. (In the case of a Si wafer, SiO_2 thickness reached around 3 nm after oxidation for 60 minutes.) A SiO_2 layer on the SiNW arrays was removed using 5% HF solution. The process of oxidation and etching was repeated 10 times. To evaluate minority carrier lifetime in diameter-reduced SiNW arrays, Al_2O_3 passivation films were deposited by atomic layer deposition (ALD) and were post-annealed at 400 ºC for 30 minutes.

The structure of the diameter-reduced SiNW arrays was characterized by high-resolution transmission electron microscopy (HR-TEM) with HITACHI H-9000NAR. To evaluate the bandgap of SiNW arrays, cathode luminescence measurement was carried out using scanning electron microscopy (HITACHI, S-4300SE) equipped with a spectrometer (HORIBA, HR-320) and InGaAs CCD. Minority carrier lifetime was measured by µ-PCD method with KOBELCO LTE-1510EP.

3. Results and discussion

Figure 2 shows minority carrier lifetime as a function of cycle number of the DR process. Since surface of SiNWs was passivated by Al_2O_3, measured lifetime reflects bulk





(Left) Fig. 1. Diameter reduction (DR) process using H_3PO_4 oxidation and HF etching. (Right) Fig. 2. Minority carrier lifetime of SiNW arrays with Al_2O_3 passivation films after the DR process.

lifetime in the SiNW arrays. Even if the cycle number was increased, the lifetime was not changed so much and the value was kept around 10-20 μsec. This suggests that the DR process does not influence the quality of SiNW arrays. Cross-sectional TEM image of the SiNW array after 5-times DR process was shown in Figure 3. Fig. 3(a) shows the whole figure of the SiNW array. It was found that the length of SiNWs was around 15 μm and the tip part of SiNWs was aggregated. This is because the SiNW arrays were fabricated in the etching solution and after extraction from the solution, surface tension made SiNWs aggregated. Fig. 3(b) shows cross-sectional TEM image at bottom part of SiNWs. Diameter of SiNWs is around 70 nm. On the other hand, as shown in Fig. 3(c), the diameter of SiNWs around the tip part is less than 10 nm, suggesting that the diameter around the tip part was successfully reduced by the reduction process. The ununiformity of diameter is due to the MACE process. During the MACE process, Ag nanoparticles make c-Si etched. However, the size of Ag nanoparticles was gradually reduced during the etching process. Therefore, the diameter of SiNWs was increased at a deeper part. To avoid the ununiformity, it is needed to improve the MACE process.

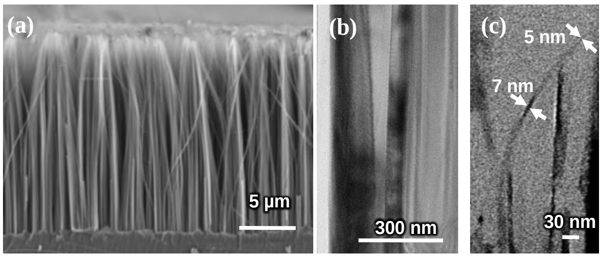


Fig. 3. (a) Cross-sectional TEM image of a SiNW array after 5-times DR process. (b) Magnified image at the bottom part and (c) tip part of the SiNW array.

Figure 4(a) shows cross-sectional SEM image of the SiNW after 10-times DR process for the cathode-luminescence measurement. Electron beam was irradiated normally from bulk c-Si region to the tip of SiNWs. During the measurement, the sample temperature was kept at 36 K. Fig. 4(b) shows cathode-luminescence spectra at each depth. At the depth of 20 μm, the sharp peak can be seen at 1130 nm, which is corresponding to the luminescence from band-to-band transition in bulk Si. As the measurement position became shallower, the peak position was shifted to shorter wavelength region. From the TEM images, SiNWs had a tapered shape. Since a diameter at bottom region is larger, the peak position was close to the bulk Si. On the other hand, around the tip region, the diameter was reduced below 10 nm. Therefore, the peak position was shifted due to the quantum size effect. At the depth of 8 μm, the bandgap of SiNWs was estimated at 1.2 eV. Since at more shallow depth than 8 μm, the intensity of the peak became smaller than noise, the evidence of the bandgap widening more than 1.2 eV could not be obtained in this measurement.

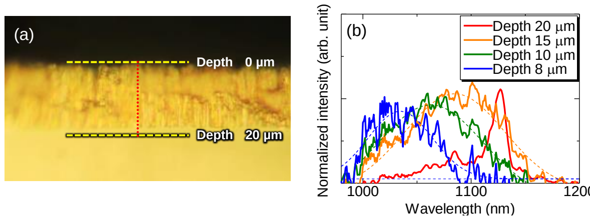


Fig. 4. (a) Cross-sectional SEM image of a SiNW array covered with Al_2O_3 after 10-times DR process. (b) Cathode luminescence spectra of a SiNW array at each depth.

4. Conclusions

To reduce the diameter of silicon nanowire (SiNW) arrays for the purpose of bandgap tuning, diameter-reduction (DR) process, where H_3PO_4 oxidation and HF etching were repeated several times, was conducted for SiNWs with the diameter of 30 nm and the length of 15 μm. Cross-sectional TEM image of the SiNW arrays after 5-times DR process showed the diameter of SiNWs around the tip part was reduced below 10 nm, suggesting that the diameter around the tip part was successfully reduced by the DR process. From the cathode luminescence measurement, the bandgap of SiNWs at the tip part was estimated at 1.2 eV. This result reflects bandgap widening due to the quantum size effect.

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