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Preparation of a Diameter-controlled Silicon Nanowire Array by Metal Assisted Chemical Etching using Silica Nanoparticles (MACES)

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Introduction

Silicon nanowires (SiNWs) have recently attracted great attention as one of the candidates of novel photovoltaic materials. Since a SiNW embedded in a wide-gap material can make electron and hole confined, the bandgap can be tuned due to the quantum size effect. Moreover, since the SiNW array has high light confinement effect, it is expected that SiNW solar cells with a relative thin absorber layer have a potential to obtain enough photocurrent.

Several methods to prepare SiNWs have been reported such as laser ablation [1], thermal evaporation [2], chemical vapor deposition [3], molecular beam epitaxy [4], chemical etching [5], and solution growth[6]. For solar cell application, SiNWs should be prepared on a large area and by a simple method. We have prepared SiNW arrays by metal assisted chemical etching (MAE)[7], which is redox reaction between silver and silicon, to prepare SiNW arrays covering large area without using vacuum process. Generally the silver was fabricated by electroless silver plating. However the shape and diameter of SiNWs cannot be controlled by the method due to depending on silver which has deregulated island shape. In this study, we prepared SiNW by metal assisted chemical etching using silica particle (MACES) to control the shape and diameter. We also investigated the difference of the optical property between SiNW arrays prepared by MAE after electroless silver plating and MACES.

Experimental

The surface of Si wafer (p-type, [100], 2-10 Ωcm, thickness is 500 μm) is hydrophilic and the wafer was immersed for 1 hour at 2 °C in solution in which 30 nm-silica particle modified carboxyl group were dispersed. After that, 20 nm-thick silver film was deposited on the Si wafer with silica particles 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 HF solution.

The morphology of silica nanoparticles and the structure of the prepared SiNW arrays were characterized by field emission scanning electron microscopy (FE-SEM) with HITACHI S-4500 and high-resolution transmission electron microscopy (HR-TEM) with HITACHI H-9000NAR. The optical properties were measured by UV-VIS-NIR spectrophotometers (SHIMADZU Co., Ltd., SolidSpec-3700).

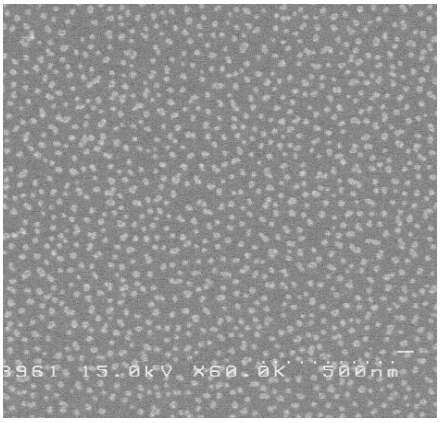

Fig..1. 30 nm-diametrical silica nanoparticles dispersed on a Si substrate at about 20 nm intervals.

Results and discussion

Figure 1 shows SEM image of two-dimensional arranged silica particle on a Si substrate. The average distance between these silica particles was about 20 nm. The silica particles did not pile each together, since these particles were repelled by negative charge of a carboxyl

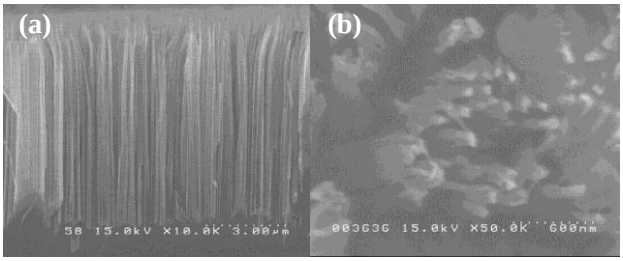

Fig..2. (a) Cross sectional SEM image of the SiNW array. (b) Top-view SEM image of the SiNW array

radical (COO^-). Although Brownian motion is more dominate than gravitation motion on these nanoparticles, the Brownian motion is very weak due to low temperature (2 ^oC). As shown in Figure 2 (a), vertically well aligned SiNWs were observed through the entire silicon substrate after etching.

The direction of SiNWs depended on the plane direction of Si wafer [7]. Figure 2 (b) shows the SEM image of the top of view of SiNWs. Some bound SiNWs by surface tension were observed. The diameter of SiNW was around 30 nm from the TEM image of Figure 3. However a few SiNWs whose diameter was 50nm were confirmed, since a few silica particles agglutinated due to van der Waals force. The force was stronger than electrostatic repulsion when both particles got very close by the Brownian motion. In Figure 4, the reflectance of Si wafer and 12.5 μm-long SiNWs array prepared by MAE after electroless silver plating and MACES are shown. The reflectance of both of SiNWs were drastically reduced by 60% compared to the bare silicon wafer. Especially, the reflectance of the SiNW array by MACES was lower than MAE and became lower than 0.5% below the wavelength of 1000 nm. It suggests that the SiNW arrays by MACES have stronger optical confinement than MAE after eletroless silver plating. Since in the case of MAE after electroless silver plating, it is difficult to control the shape of SiNWs precisely, larger non-etching area is remaining compared to MACES. Therefore, the reflectance of SiNWs prepared by MACES was reduced compared to MAE after the elctroless plating.

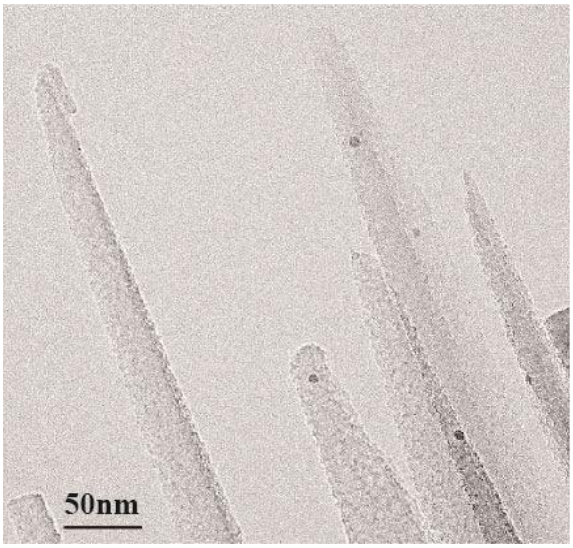

Fig..3. Cross-sectional TEM image of the tip of SiNWs.

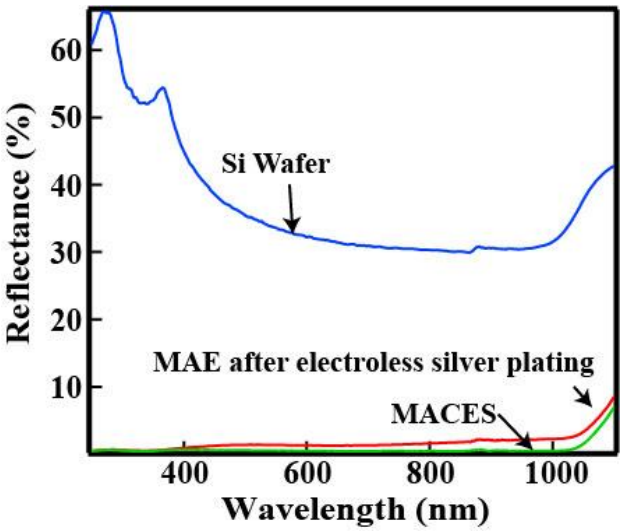

Fig..4. Optical reflectance of Si wafer and 12.5 μm-long SiNW arrays prepared by MAE after electroless silver plating and MACES.

Conclusion

30 nm-diametrical silica nanoparticles with a carboxyl radical (COO^-) were successfully dispersed on a silicon wafer at about 20 nm intervals due to the repulsion among the nanoparticles with negative charge. The dispersed silica nanoparticles were used as the mask for the preparation of silicon nanowire (SiNW) arrays by metal assisted chemical etching (MAE). The diameter of prepared SiNWs was around 30 nm from the TEM image. The reflectance of the SiNW array prepared by MAE using silica nanoparticles (MACES) was lower than MAE after electroless silver plating and became lower than 0.5% below the wavelength of 1000 nm. It suggests that the SiNW arrays by MACES have stronger optical confinement.

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