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Al-catalyzed Silicon Nanowire Formation and its Application for Photovoltaic Device

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Abstract

Silicon (Si) nanostructure formations using new promising Al catalyst with vapor-liquid-solid (VLS) growth were investigated. The effects of substrate temperature on the structure formation and surface transformation from nanodot (ND) to nanowire (NW)-surrounded structure were explored. Extremely low light reflectance was controlled for photovoltaic application. The complete removal of Al catalyst was successfully done by hydrofluoric acid (HF) etching, realizing the VLS-SiNW device fabrication. Our first Al-catalyzed SiNW-based solar cells were demonstrated and the efficiency could be enhanced upon 9 % with the optimization of SiNW length.

1. Introduction

Core-shell NW-based solar cells and gate-all-around NW field-effect transistors (FETs) are hot research topics for advanced technology at this moment. VLS mechanism using metal catalysts and chemical-vapor-deposition (CVD) technique is one of candidates to create NW structures on low cost substrates and to apply for a large scale manufacturing. Several NW formations and characterizations in our previous researches have already been reported [1-3]; however, high performance devices are remaining in progress to accomplish owing to catalyst contamination or NW surface damage. In this study, we would like to present Al which has been recently proposed as a new alternative catalyst [4-6] to form SiNWs. The binary Al-Si phase diagram suggests that SiNWs can be possibly grown by VLS mechanism at low eutectic temperature of 577 °C with Si composition of 12.6%. Moreover, the ease of Al-catalyst removal and the capability of Al existence as a p-dopant in Si are advantageous to overcome the recent problems of catalyst contamination. In this experiment, the effects of substrate temperature on Al-catalyst SiNW formation obtained by thermal CVD process were firstly investigated. Then, Al removal from the tip of SiNWs by diluted HF after VLS growth was continuously observed. Structural and optical properties of Al-catalyzed SiNWs were discussed for photovoltaic application. The solar cells were fabricated and the accomplishment of VLS-SiNW device was proved.

2. Experimental Details

All Al-catalyzed SiNW growth were carried out using Si(111) substrates with the thickness of 525 µm and the resistivity of 1-10 Ω·cm. The 50-nm-thick Al-catalyst films were prepared by sputtering. After Al_2O_3 removal by dipping into diluted HF for a few seconds, the samples were immediately loaded into CVD chamber. SiNWs were formed at various substrate temperatures of 550 °C, 600 °C, 650 °C, and 700 °C. The VLS mechanism was controlled under chamber pressure of 800 Pa with fixed deposition time of 30 min, SiH_4 and N_2 gas flows of 20 and 30 sccm, respectively. SEM, TEM, UV-Vis-NIR, Raman spectroscopy were used to characterize Al-catalyzed SiNW properties. To fabricate solar cells, SiNW surfaces were dipped into diluted HF for 5 min to remove Al catalyst and SiO_2. Then, p^+-Si shell layer was formed at 750 °C for 8 min with B doping concentration of ~4×10^{19} cm^{-3}. The flow rate of SiH_4, B_2H_6, and N_2 gases were set at 19, 0.5, and 30 sccm, respectively, under chamber pressure of 800 Pa. Next, the back surface field or n^+ layer was introduced at the back side of n-Si(111) substrates by spin coating of phosphorus containing solution (OCD P-59210) and N_2 annealing at 850 °C for 20 min. For solar cell front electrode preparations, 120-nm-thick indium tin oxide film was first sputtered and followed by 200-nm-thick Ag with finger-grid pattern. After that, 50-nm-thick Ti and 200-nm-thick Ag were deposited for the back contact. Al-catalyzed SiNW-based solar cells were examined with an active area of 1 cm^2.

3. Experimental Results and Discussions

Figure 1 shows SEM images of Al-catalyzed SiNWs formed at various substrate temperatures. SiNWs could be grown at 600 °C and good vertical taper-shaped SiNW structure was achieved at 650 °C. Adding of non-directional SiNW branch was more obvious at 700 °C. ND

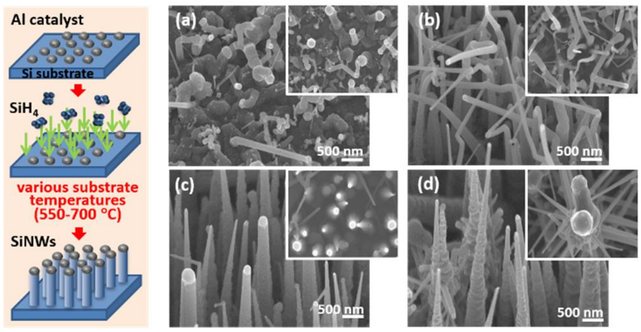


Fig. 1. Schematic and 30°-tilted SEM images of Al-catalyzed SiNWs formed at various substrate temperatures of (a) 550 °C, (b) 600 °C, (c) 650 °C, and (d) 700 °C. Insets are the top view SEM images.

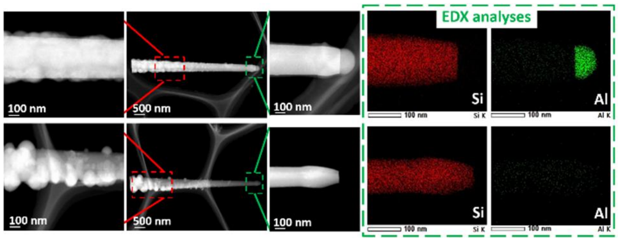
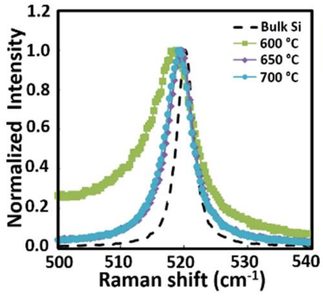


Fig. 2. STEM images and EDX analyses of Al-catalyzed SiNWs formed at 650 °C (a) before and (b) after Al catalyst removal.



	Peak position	Peak shift	FWHM
Bulk-Si	520.10	0.00	2.92
600 °C	518.75	- 1.35	6.36
650 °C	519.56	- 0.54	4.17
700 °C	519.29	- 0.81	4.77

Fig. 3. Raman spectra and characteristics of Al- catalyzed SiNWs formed at various substrate temperatures.

formation on surrounding surface of all SiNWs was observed. Figure 2 shows STEM images and EDX analyses of Al-catalyzed SiNWs formed at 650 °C before and after Al catalyst removal. The creation of amorphous- and poly-crystalline-Si NDs was confirmed at as-grown SiNW surface. Single-crystal Si growth was detected inside SiNW and SiNW formation was shown along [111] direction. EDX analyses showed that Al catalyst existed on the tip of SiNW and was completely removed with remained ND structures after diluted HF etching.

From Raman spectra in Fig. 3, SiNWs formed at 600 °C, 650 °C, and 700 °C were monitored. Mixed formation of amorphous and crystal structures in SiNWs at 600 °C was indicated by the large shift of Si optical phonon peak and broad full width at half maximum (FWHM). Good crystal uniformity of SiNWs grown at 650 °C and 700 °C was detected as the sharp peak with narrow FWHM.

The light reflectance of SiNWs grown at various substrate temperatures and various formation times were

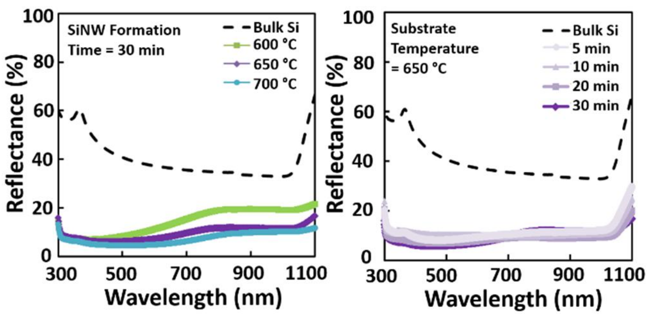


Fig. 4 Reflectance spectra of (a) Al-catalyzed SiNWs formed at various substrate temperatures of 600 °C, 650 °C, and 700 °C for 30 min compared to bulk-Si and (b) Al-catalyzed SiNWs formed at 650 °C with various SiNW formation times for 5 min, 10 min, 20 min, and 30 min.

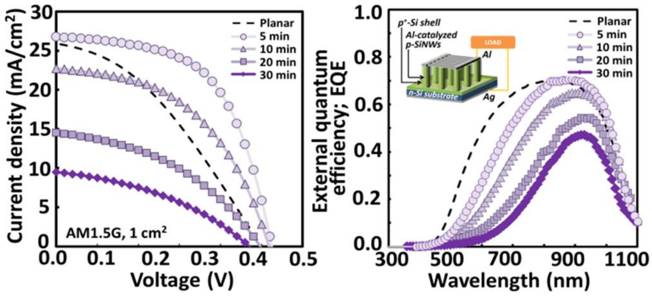


Fig. 5 J–V characteristics measured under AM1.5G at RT and EQE of solar cells fabricated using Al-catalyzed SiNWs formed at 650 °C with various SiNW formation times.

investigated as shown in Fig. 4(a) and (b), respectively. The reflectivity was decreased to lower than 20% with increasing of SiNWs formation temperature corresponding to their structures as shown in Fig. 1. The adjusting of SiNW formation time (from 30 min to 5 min) for controlling of SiNW length to the optimized condition [2-3] (from ~8 µm to ~1 µm) showed the unchanged light reflectance level.

In this study, the vertical SiNWs grown at 650 °C were applied for SiNW-based solar cell fabrication. Figure 5 shows J–V characteristics and EQE of their SiNW-based solar cells with various formation times compared to planer cell. The maximum efficiency of solar cells was achieved to 9.3 % with short circuit current (J_{sc}) of 26.79 mA/cm^2, open circuit voltage (V_{oc}) of 0.53 V, and fill factor (FF) of 0.57. The better light absorption by NW structures enhanced solar cell efficiency. However, EQE in the short wavelength range has to be further improved. The crystallinity of ND structures and the interface property between ND and NW structures possibly caused the defects. The surface passivation technique, the shell-layer thickness, and other parameters are in progress to optimize for the solar cell efficiency improvement.

4. Conclusions

The successful of Al-catalyzed SiNW formation including solar cell fabrication in this study indicated new promising SiNW-based material for future photovoltaic application. However, other parameters for improving of SiNW structures and device performances have to be further investigated.

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