

Hybrid Nanoimprint SiNW-based Solar cell Fabrication with Efficiency Enhancement by Hydrogen Annealing

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Abstract

Hybrid 3D-structure solar cell fabrication was achieved using n-Si nanowires synthesized by nanoimprint and Bosch process. Solar cell fabrication and efficiency improvement upon 6% for an active area of 1 cm² were simply modified by H₂ annealing technique and optimization of p-Si matrix coverage. H₂ annealing reduced defect densities on n-SiNW surface and inside p-Si layer, and improved p-Si crystallinity. Optimized p-Si matrix coverage enhanced solar cell performances by reducing of contact resistance and increasing of V_{oc} and I_{sc}.

1. Introduction

Conical or cylinder shape of nanowire (NW) structure gives them novel physical properties as compared to bulk material [1]. Extreme high surface area and light trapping are attracted a great deal of attention for next generation solar cells. Some NW synthesis methods are promising to provide opportunities for fabricating on low cost substrates and route to applying for a large scale. Metal-catalyzed electroless etching (MCEE), chemical vapor deposition (CVD), and nanoimprint and Bosch process have been proposed [2-4], and their application for high efficient three-dimensional structure solar cells has been intensively investigated [5]. However, appropriate NW-based solar cell materials and junction properties are important issues to realize these device targets. Several techniques of NW surface treatment for planar or NW-based solar cell efficiency improvement were reported such as O₃ annealing and various thin film passivations of Al₂O₃, a-Si:H, SiO₂/a-SiN_x:H, or alkali ion to minimize roughness and defect densities on NW surface [6-7].

In this work, hybrid nanoimprint SiNW-based solar cell fabrication was achieved and modified with hydrogen (H₂) annealing technique for efficiency enhancement. n-SiNW synthesized by nanoimprint and Bosch process were combined with p-Si matrix grown by CVD. The effect of H₂ annealing on both synthesized Si materials together with the improving of solar cell junctions and efficiencies were observed. This single pn-junction solar cell structure with different p-Si matrix coverage was also investigated.

2. Experimental Details

All experiments were carried out using n-type Si(100) wafer with resistivity of 1-10 Ω·cm and thickness of 525 μm as substrates. n-SiNW structures were prepared by

nanoimprint and Bosch process before combining with CVD p-Si matrix to fabricate hybrid single junction solar cells. Approximate 1-μm-length SiNWs were provided by nanoimprint patterning of 30-nm-thick Cr sputtering and mold stamping. Then, Bosch process of SF₆ and C₄F₈ plasma etching was performed. Prior to p-Si deposition, all n-SiNW surfaces were etched in 1.1M HF in 2.6M isopropanol for SiO₂ removal and immediately set into CVD chamber. p-Si matrix formation was conducted at 750 °C with B doping concentration of ~4×10¹⁹ cm⁻³. The flow rate of SiH₄, B₂H₆, and N₂ gases were controlled at 19, 0.5, and 30 sccm, respectively, under chamber pressure of 800 Pa. To provide solar cell electrodes, 200-nm-thick Al front electrode with finger-grid pattern and 150-nm Ag back contact were sputtered. The effects of H₂ annealing on both Si materials of nanoimprint n-SiNWs and CVD p-Si matrix were examined using annealing temperatures of 900 °C or 1000 °C for 10 min. The p-Si matrix coverage was optimized to improve the solar cell efficiency.

3. Experimental Results and Discussions

Figure 1 shows scanning electron microscopy (SEM) images of (a) n-SiNWs synthesized by nanoimprint and Bosch process, and (b) p-Si layer formed by CVD with and without H₂ annealing for 10 min at 900 °C and 1000 °C. n-SiNW structures were not significantly changed by H₂ annealing up to 1000 °C but the coalescence of Si islands and defects were obviously shown in case of p-Si layer after H₂ annealing at 900 °C and 1000 °C, respectively. The improvement of p-Si layer crystallinity could be obtained at 900 °C corresponding to Raman spectra as shown in Fig. 2. The effect of H₂ annealing was clearly revealed by electron spin resonance (ESR) measurements at 4.2 K with microwave power of 0.5 mW that defects at n-SiNW surface and

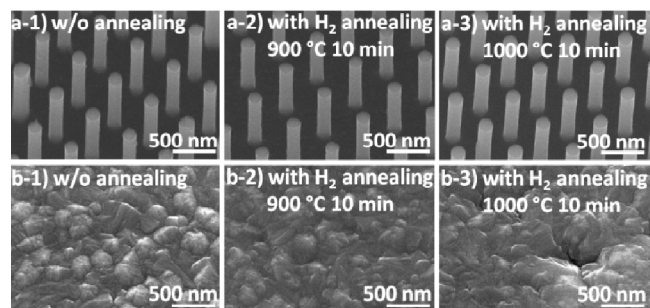


Fig. 1 SEM images of (a) SiNWs synthesized by nanoimprint and (b) CVD p-Si layer with and without H₂ annealing for 10 min at 900 °C and 1,000 °C.

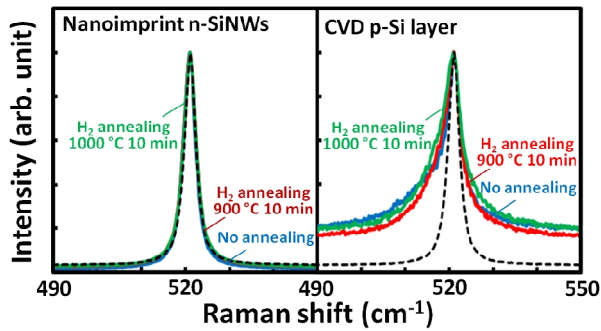


Fig. 2 RAMAN spectra of nanoimprint n-SiNWs and CVD p-Si layer with and without H₂ annealing for 10 min at 900 °C and 1000 °C.

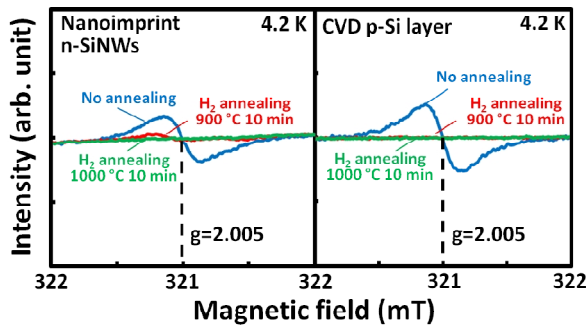


Fig. 3 ESR spectra of nanoimprint n-SiNWs and CVD p-Si layer with and without H₂ annealing for 10 min at 900 °C and 1000 °C measured at 4.2 K with microwave power of 0.5 mW.

in p-Si layer (g -value of 2.005) could be reduced as shown in Fig. 3. The defect intensities are similarly low at both annealing temperatures for both Si materials. After optimization of H₂ annealing condition, the highest solar cell efficiency was acquired by operating at 900 °C for 10 min after both of n-SiNW synthesis and p-Si matrix formation.

p-Si matrix coverage was verified by varying CVD deposition time of 3, 5, 8, and 10 min together with applying of H₂ annealing. SEM images of various p-Si deposition periods were shown in Fig. 4. After 8-min deposition, p-Si matrix coverage was fully formed as square close-packing structure. Current-voltage (I-V) characteristics and external quantum efficiency (EQE) of these nanoimprint

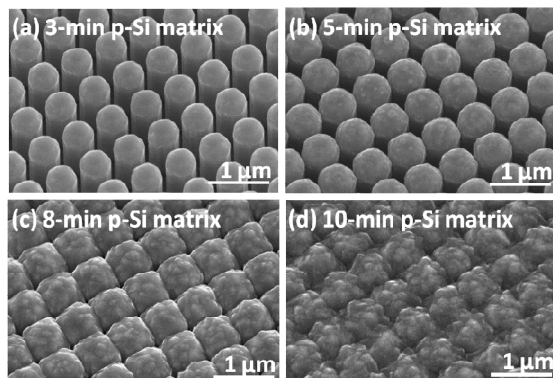


Fig. 4 SEM images of nanoimprint-SiNWs embedded in various p-Si matrix with different deposition times of (a) 3 min (b) 5 min (c) 8 min and (d) 10 min.

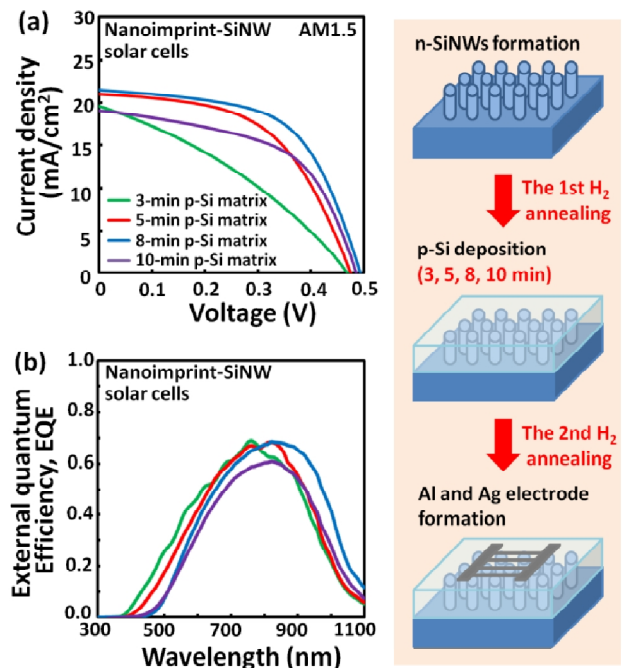


Fig. 5 (a) I-V characteristics and (b) EQE of nanoimprint SiNW-based solar cells with various p-Si matrix deposition times. Schematics of process flow with H₂ annealing are illustrated.

SiNW-based solar cells were examined. The best conversion efficiency approximately 6 % was obtained from 8-min p-Si matrix deposition with $I_{sc} = 21.57 \text{ mA/cm}^2$, $V_{oc} = 0.49 \text{ V}$ and $FF = 0.58$ as shown in Fig. 5(a). Increasing of p-Si deposition time led to more coalescence of p-Si matrix resulting in decreasing of contact resistance and increasing of V_{oc} . However, the current leakage increased when the deposition time was longer than 8 min. In addition, the recombination loss by defects in the vicinity of surface became more obvious indicated by degradation of EQE in short wavelength range as shown in Fig. 5(b). The generated carriers in the 10-min sample were not effectively extracted possibly due to short carrier diffusion length and thick p-Si matrix coverage.

4. Conclusions

Hybrid nanoimprint SiNW-based solar cells were fabricated using H₂ annealing technique and adjusting of p-Si matrix coverage to improve Si-based materials and solar cell performances.

References

- [1] G. Zhang, et. al., *Nanoscale* **3** (2013) 2403.
- [2] Z. Huang, et. al., *Adv. Mater.* **23** (2011) 285.
- [3] H.-J. Choi, *Nanowires Semiconductor Nanostructures for Optoelectronic Devices* (2012) 1.
- [4] K.J. Morton, et. al., *Nanotech.* **19** (2008) 345301.
- [5] M. Yao, et. al., *Nano. Lett.* **14** (2014) 3293.
- [6] M. Z. Rahman, and S. I. Khan, *Mater. Renew. Sustain. Energy*, **1** (2012) 1.
- [7] M. Dutta, and N. Fukata, *Nano Energy*, **11** (2015) 219.