Solar Energy 161 (2018) 180–186

Contents lists available at ScienceDirect

Solar Energy

journal homepage: www.elsevier.com/locate/solener

Wet-chemically etched silicon nanowire: Effect of etching parameters on the morphology and optical characterizations

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ARTICLE INFO

Keywords:
Metal-catalyzed electroless etching
Silicon nanowires
Optical properties
FDTD

ABSTRACT

A two-step metal-catalyzed electroless etching (MCEE) of silicon wafer in $HF/AgNO_3$ and HF/H_2O_2 subsequently has been reported. Since the mechanism of nanowires (SiNWs) growth in MCEE route depends highly on etching process, we investigated the role of HF concentration and the etching time. The morphology and the optical absorption of the as-fabricated Si-based micro/nanostructured nanowires has been thoroughly investigated. It has been observed that the optical absorption characteristics were influenced by the etching time as well. An improvement by 10 of the absorption was obtained by increasing the etching time. Through finite-difference time-domain simulations it was observed that absorption, energy distribution, electric profile and generation get enhanced in presence of silicon SiNWs grown on bulk silicon. The experimental results reveal that the SiNWs produced by MCEE are very promising due to their potential application in photovoltaic devices.

1. Introduction

Over the last few decades, advancements in silicon nanowire technology have shown promising potential in future-generation electronics, opto-electronics and chemical/biological sensing applications. Silicon nanowires (SiNWs) have been used to demonstrate nanoelectronic transistors (Cui et al., 2001, 2003; Cui and Lieber, 2001; Chung et al., 2000; Cui et al., 2001; Hahm and Lieber, 2004; Huang et al., 1897; McAlpine et al., 2003; Peng et al., 2004). Since the silicon is the basic material in microelectronics, SiNWs are promising. The high demand for powerful devices and the limitations of current approaches based on lithographic techniques to achieve some nanometer sized components require the development of new methods. The control of the synthesis and SiNWs surface properties can open up new possibilities in the field of silicon nanoelectronics and nanodevices using SiNWs like to build nanocircuits and biosensors. Due of their nanoscale size, and the possible quantum confinement effect, the NWs have attracting, optical, thermal, electronic, and chemical.

The most commonly used methods of producing silicon nanowires are bottom-up chemical vapor deposition (CVD) and top-down lithography-based techniques. However, these methods require complicated and expensive equipment. In 2002, Peng et al. produced nanowires at the large-scale using simple, cheap chemical etching methods. Their methods consisted of dipping silicon in an HF-$AgNO_3$ solution at room temperature. They fabricated SiNWs and nanostructures with a high degree of orientation. They also produced porous silicon and silicon nanoholes by metal-catalyzed electroless etching (MCEE), which involves etching silicon wafers in an aqueous HF/Fe $(NO_3)_3$ or H_2O_2 solution (Peng et al., 2002, 2008). The underlying mechanism suggested for MCEE was based on a local oxidation and dissolution-induced anisotropic silicon metal in the oxidizing aqueous solution of HF acid. They observed that the displaced metal preferentially to silicon orientation (1 0 0), which causes anisotropic etching. They also compared MCEE chemical vapor deposition and reactive ion etching and concluded that MCEE is, low temperature single, scalable and easy process. MCEE has been used to produce vertical SiNWs with diameters from 20 to 300 nm, which maintained the orientation of the starting substrate, and showed desirable electrical properties (Bailie et al., 2015). Due to its flexibility in wafer scale production and ability to fabricate vertically aligned SiNWs arrays, MCEE is considered a cheaper alternative to common top-down etching techniques. MCEE fabricated nanowires are homogeneous in terms of their shape, size, density, doping profile, crystal orientation, which are important for photovoltaic applications. For instance, by combining MCEE and nanospheres lithography, researchers obtained SiNWs of controlled diameters, densities, and lengths (Peng et al., 2008; Huang et al., 2007; Fang et al., 2006). MCEE-prepared

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https://doi.org/10.1016/j.solener.2017.12.038
Received 6 November 2017; Received in revised form 11 December 2017; Accepted 19 December 2017
0038-092X/

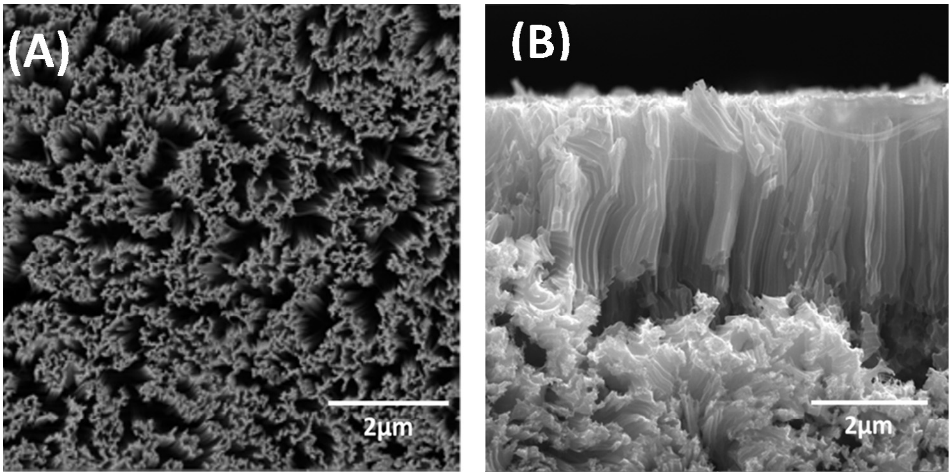

Fig. 1. SEM characterization of (A) top view (B) cross section of silicon nanowires produced by metal catalyzed electroless etching MCEE.

SiNWs are of great interest due to their electric conductivity and optical activity (Huang et al., 2007; Fang et al., 2006; Peng et al., 2009), which make them suitable for use in photovoltaic devices, chemical sensors (Garnett and Yang, 2008) and thermoelectric devices (Peng et al., 2005).

Tsakalakos et al. and Sivakov et al. have measured the absorption properties of silicon nanowires fabricated on glass substrates chemical etching. (Sivakov et al., 2009; Tsakalakos et al., 2007) they observed a low reflectance of the SiNW arrays (~10% at 300–800 nm), and strong broadband optical absorption (~90% at 500 nm), they show that the optical absorption are much higher than Si films of the equivalent thickness. The strong resonance among the aligned silicon nanowire film induces this high optical absorbance. The high density surface states in the SiNW are the origin of this observed absorption. Using an optical transmission and the measurement of photocurrent Garnet and Yang showed an increase of 73 times the path length of the solar radiation silicon nanowires films in the AM1.5G spectrum incident (Garnett and Yang, 2010). The interesting improvement factor of the trapping path length of the light is above the theoretical limit of a randomization scheme and superior to any traditional method of trapping light. The improvement is attributable to the development of photonic crystal effects in devices (Garnett and Yang, 2010). More recently Han-Don Um et al. are used MCEE to fabricate vertical silicon nanowires with several models by varying different parameters as thickness and morphology of the metal catalyst film. High quality vertical silicon μwires were obtained with length of 23, 2 μm, and these μwires was applied in solar cells, they achieve conversion efficiency up to 13%. An open circuit voltage of 547.7 mV, a short-circuit current density of 33.2 mA/cm^2, and a fill factors of 71.3%, this is due to the enhancement of light absorption and effective carrier collection by the silicon μwires (Um et al., 2015).

Based on the previous results obtained by several authors (Cui et al., 2001, 2003; Cui and Lieber, 2001; Chung et al., 2000; Hahm and Lieber, 2004; Huang et al., 1897; McAlpine et al., 2003; Peng et al., 2002, 2004, 2008a, 2008b, 2009; Bailie et al., 2015; Huang et al., 2007; Fang et al., 2006; Garnett and Yang, 2008; Peng et al., 2005; Sivakov et al., 2009; Tsakalakos et al., 2007; Garnett and Yang, 2010; Um et al., 2015), we propose a new combined mechanism and optimized process parameters for the formation of well-separated silicon nanowires. We believe that an improved performance can be achieved through further process optimization. Consequently, in the present study, we investigated MCEE process on silicon. The influence of the etching parameters (i.e., hydrofluoric acid concentration, and etching time) on the structure morphology, absorption, was studied.

2. Experimental details

2.1. Materials

Silver nitrate ($AgNO_3$ 99.8%), (H_2O_2 30% in water) H_2SO_4 98%, (HF 48%) were purchased from HACH, Scharlau, Applichem Panreac respectively and were used as received without any further purification, distilled water was used throughout the work, one side polished silicon wafer p type (1 0 0) electrical resistivity 1–10 ohm cm was chosen to prepare the silicon nanowires. The morphologies and microstructures of the as synthesized samples were characterized by field emission scanning electron microscope (FESEM) and SEM-aided energy dispersion X-ray spectroscopy (EDX), oxford. The optical characterization has been conducted by using the UV–vis spectrophotometer and optical simulation was conducted by using finite-difference time-domain (FDTD) package of lumerical solution.

2.2. Silicon nanowires preparation

SINWs are prepared by metal assisted chemical etching of p-Si (1 0 0) wafer having resistivity of 1–10 ohm-cm. The wafer is treated by several chemicals, for cleaning and etching to produce SINWs. Specifically, the silicon sample is cleansed by Acetone, isopropanol, H_2O 15 min each followed by piranha attack H_2O_2: H_2SO_4 (1: 1 v/v) for 10 min and then thoroughly rinsed and placed in the EDI (Deionized water) before drying with nitrogen. The sample is then directly introduced into the 5 M HF 0.02 N $AgNO_3$ at different concentration mixture for a 1 min after that the silicon wafer covered with Ag nanoparticles were immersed in a second etching solution of HF/H_2O_2 5 M/30% followed by EDI rinsing and drying with nitrogen.

To remove the residual Ag from the silicon nanowires, the sample is immersed for 1 h in a mixture H_20: HCl: HNO_3 (1:1:1 v/v/v), followed again by rinsing and drying EDI with nitrogen drying.

3. Results and discussion

The nanowires obtained have a length range from 15 to 20 μm. This length is homogeneous on the same substrate regardless of the sample size. Diameters between 10 nm and 100 nm and depending of the synthesis conditions the nanowires can be "linked" to each other and form rather 'nanosheets' or 'nanowalls' as shown in Fig. 1. In MCEE method, silicon is oxidized and etched preferentially by mixture solution of HF/H_2O_2 under thin layer of noble metal (e.g. Ag, Au, Pt, etc.), leaving bare non-etched silicon regions and the concentration of HF and H_2O_2 will have an effect on the structure and shape of the nanowires. The silver particles play a role of cathode, at which the reduction of the oxidant generates holes in these holes diffuse through the metal catalyst