



Silicon nanowires grown on metal substrates via self-catalyst mechanism



Vladislav Dřinec^{a,*}, Mariana Klementová^b, Radek Fajgar^a, Pavel Dytrych^a

^a Institute of Chemical Process Fundamentals of the AS CR, v. v. i., Rozvojová 135, 165 02 Prague 6, Czech Republic

^b Institute of Physics of the AS CR, v. v. i., Na Slovance 2, 182 21 Prague, Czech Republic

ARTICLE INFO

Article history:

Received 16 March 2015

Received in revised form

2 July 2015

Accepted 19 July 2015

Available online 20 July 2015

Keywords:

CVD

Silicon

Nanowire

Catalyst-free

Self-catalyzed

ABSTRACT

Low Pressure Chemical Vapor Deposition (LPCVD) was applied to grow Silicon Nanowires (SiNWs) without any heteroatom catalyst or special pretreatment of substrates used. Silane (SiH₄) as a precursor was pyrolyzed at 500 °C in an oven at molybdenum or iron substrates. NWs were several microns long, about 100 nm thick and possessed a core–jacket structure. The thin core was composed of crystalline silicon oriented in <110> direction whereas the jacket was formed by amorphous silicon. Unlike other approaches, this method avoids contamination caused by metal heteroatom seeds and/or applying special procedures for substrate pretreatment to initialize/support NW growth. The photocatalytical activity revealed that SiNW layers could be accredited with a relatively high rate of photocatalytical splitting of water into H₂/O₂.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Among other nanowires, silicon nanowires (SiNWs) make a significant body of the current study owing to two reasons: (i) unlike bulk silicon, SiNWs such as 1D objects possess quite different physico-chemical properties due to nanoscale dimensions and (ii) silicon is the most commonly used semiconductor material, and its usage, analysis and fabrication are a standard routine from the technological point of view. Some SiNWs applications such as solar cells, sensors, transistors, photodetectors have been reported [1–5].

Several techniques are applied to prepare SiNWs: lithographic methods, laser ablation, various CVD techniques, solution phase synthesis, chemical etching, molecular beam epitaxy, oxide assisted growth method [1–6]. Many of them incorporate VLS/VSS (Vapor–Liquid–Solid, Vapor–Solid–Solid) approaches in which nanoscale metal particles serve as initialization/growth agents. Silicon from gaseous silicon based precursor(s) is dissolved in liquid/solid metal particles which become supersaturated resulting in precipitation of silicon forming a nanowire. As a material for those particles/seeds, gold is used predominantly. However, Au atoms form deep trap states for charge carriers in a midgap [7] and it is not easy to remove them from nanowire tips. Despite some reports on successful removing of gold containing nanowire tips [8], standard chemical etching is not sufficient. Also, consecutive

thermal oxidation followed by HF deoxidation is not efficient to remove gold residues [9]. Thermal oxidation enhances gold diffusivity into nanowire bulk at elevated temperatures. This step followed by HF deoxidation results in a core–shell structure in a nanowire.

Therefore, substitution of Au with other metals (Fe, Ni, Ag, Ti, Pt, Cu, In, Zn, Al, Co, Ga, Sn) [2], as well as sulfur [10], was also attempted. Nevertheless, those elements may also have detrimental effects on technology due to side reactions, atom migration, contamination, parasitic reflection etc., and their removal anticipates using other technological processes e.g. HF dipping [9,11].

The main goal of our work was (i) to avoid the use of metal seeds during SiNWs growth and (ii) to exploit all the advantages of the broadly used standard CVD technique with a high application potential. Therefore, we prepared SiNWs via the catalyst-free Low Pressure Chemical Vapor Deposition (LPCVD) technique.

2. Experimental

SiNWs were grown on molybdenum (0.5 mm, 99.9+%, Aldrich) and iron substrates (0.5 mm, 99.9+%, Aldrich) in a quartz tube placed in an oven. First of all, the tube was evacuated using the turbo station unit (TC110 Pfeiffer Vacuum) to 5 · 10^{−4} Pa. Subsequently, the temperature in the oven was increased up to 500 °C and after reaching that value, silane SiH₄ was allowed to enter the tube to be decomposed over the substrates. The pressure in the

* Corresponding author.

E-mail address: dřinek@icpf.cas.cz (V. Dřinec).

tube was controlled by a needle valve integrated between the tube and the rotary pump. After the 60-min run, the silane flow was stopped and the temperature dropped to room temperature.

Consequently, the samples were analysed by a Scanning Electron Microscopy (SEM) setup (Vega 3 Tescan Indusem) equipped with an EDX modul (Bruker XFlash Detector 5010) for detecting the elemental composition. Raman spectra were performed by dispersive Raman Nicolet Almega XR with excitation wavelength of 473 nm, power of 10 mW and resolution of 2 cm^{-1} . Transmission electron microscopy (TEM) was performed on a Philips CM 120 (LaB₆, 120 kV) equipped with NanoMEGAS precession unit DigiStar, an Olympus SIS CCD camera Veleta (2048 × 2048), and an EDAX windowless EDS detector Apollo XLTW. The samples were prepared on holey-carbon coated Cu grids by brushing a grid against the substrate containing nanowires.

Photoinduced electrochemical properties of Si/Mo electrodes in 0.1 M Na₂SO₄ solution (unbuffered at pH 5 ± 0.05 , not stirred, no gas purging) as electrolyte were investigated in a three-electrode arrangement [12]. The pH value of the electrolyte solution was constant during the experiments. The prepared Si/Mo layer was always used as the working electrode and the area was fixed at 1 cm^2 . It was irradiated in a Pyrex cell with the light beam of AM1.5G at intensity of 1 Sun. The temperature was kept at 23 °C during the whole measurement. Open Circuit Potential (OCP) measurements were performed (30 s dark, 60 s illumination, 60 s dark).

3. Results and discussions

Deposition of silane on molybdenum and iron substrates yielded thick grown films (Fig. 1). According to Scanning Electron Microscopy (SEM) micrographs, some nanowires were more than 20 μm long. Raman analysis (not shown) revealed a sharp peak at 512 cm^{-1} for 30% of nominal power of the excitation Raman source. That was a shifted value in comparison with 527 cm^{-1} for bulk silicon. A larger shift to 505 cm^{-1} was found for 65% of the nominal power. No quantum effects were expected for SiNWs because the NW thickness was about 100 nm; therefore, this shift demonstrated a heating effect of the Raman excitation laser [13].

The Transmission Electron Microscopy (TEM) analysis of the same sample showed a uniform type of SiNWs. Only a small NW fraction was kinked and/or suffered from tapering. NWs had the length of several microns with the width of about 100 nm (Fig. 2a). The front tip was usually round whereas the bottom end was flat sharp as the NW was broken of (Vlášto, nemá tu být “on”?) the

substrate for the TEM study. EDX analyses from the tip and other parts of nanowire showed the same composition (Fig. 2d). There were only Si and O present.

SiNWs were composed of a core and a jacket. The crystalline core was very thin (sometimes barely visible as in Fig. 2b), usually only about 10 nm in diameter. However, it was clearly discernible in the electron diffraction (Fig. 2c). NWs grew in the $\langle 110 \rangle$ direction of the Si crystalline core. The composition of the amorphous jacket was not clear from the EDS analysis. It is obvious that there was a thin layer of silicon oxide on the surface of NW; however, to decide whether the rest of the NW jacket was composed of amorphous oxide or amorphous silicon, amorphous silica was added to the sample, and the electron diffraction of the NW was compared to the one of silica (Fig. 3). The Process Diffraction software was used to integrate diffraction patterns and produce diffraction profiles in Fig. 3c. The first broad maxima of silica and NW did not overlap, which suggests that the NW jacket was composed of amorphous silicon rather than amorphous silicon oxide. This fact is further corroborated by the fact that the maximum corresponded to the distance of (111) planes of Si.

One of the samples was tested by Open Circuit Potential (OCP) measurements. This analysis showed the instantaneous response of layers to the incident light (Fig. 4). The spikes at 30 s and 90 s could be attributed to switching on/off the light, which corresponded to highest rate of charging up/discharge of SiNW layer. The large amount of bubbles of gas was observed during that measurement on both electrodes (Pt, Si/Mo).

The presence of only amorphous Si in the NW tip proved that the growth mechanism was self-catalytic as there were no metal heteroatoms detected. As a growth mechanism, Oxide Assisted Growth (OAG) could be excluded since this mechanism proceeded at high temperatures at about 1000 °C, and grown NWs had a SiO₂ jacket around the silicon core [14]. Starting materials were then SiO₂/Si or SiO. The present or generated silicon oxide was highly reactive and induces initialization of SiNW growth. Although there were traces of oxygen in the tube during experiments, the oxygen amount and temperature were not sufficient to trigger this mechanism in our case.

Nevertheless, we speculate that a vapor–solid (VS) approach [15] could be responsible for the SiNW growth. Before the SiNW started to grow from the specific nucleation site, a nuclei at this site was formed on the surface during the initialization period. Those nucleation sites were prepared on Si substrates by etching of silicon oxide free surface by ultrapure deionized water to achieve a reactive SiO_x layer [15,16]. Thermodynamic conditions preferred an anisotropic Si growth from the nuclei. Silicon adatoms

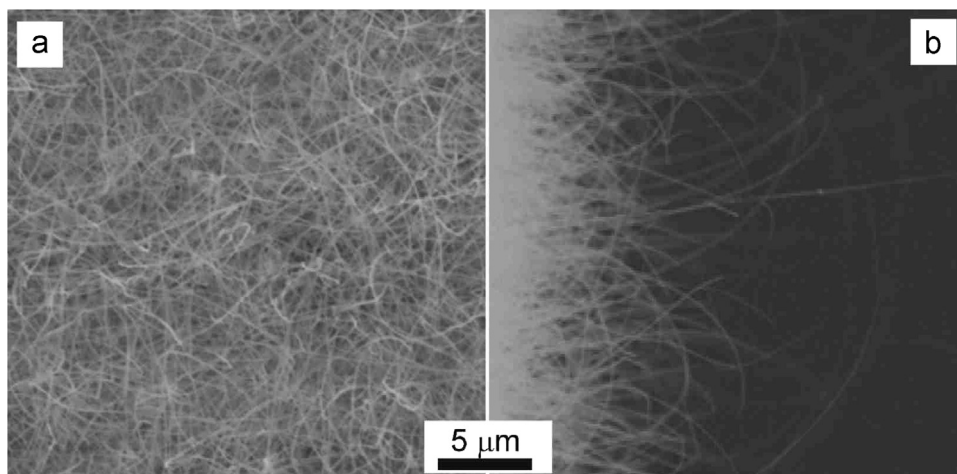


Fig. 1. SEM images of SiNWs grown at a molybdenum substrate at 500 °C. (a) Plan view, (b) side view.

Download English Version:

<https://daneshyari.com/en/article/1641986>

Download Persian Version:

<https://daneshyari.com/article/1641986>

[Daneshyari.com](https://daneshyari.com)