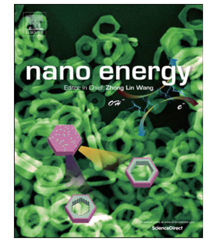
Nano Energy (2014) **5**, 20–27

Available online at www.sciencedirect.com

ScienceDirect

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



RAPID COMMUNICATION

Tuning silicon nanowires doping level and morphology for highly efficient micro-supercapacitors

F. Thissandier[a,b], P. Gentile[b,*], N. Pauc[b], T. Brousse[c,**], G. Bidan[a], S. Sadki[a,***]

[a]*CEA Grenoble, INAC-SPrAM (UMR 5819 (CEA,CNRS, UJF))-LEMOH, France*
[b]*CEA Grenoble, INAC-SP2M (UMR-E CEA-UJF)-SiNaPS Lab. 17, Rue des Martyrs, 38054 Grenoble, France*
[c]*Institut des Matériaux Jean Rouxel (IMN),Université de Nantes, CNRS, 2 Rue de la Houssinière, BP 32229, 44322 Nantes Cedex 3, France*

Received 16 October 2013; received in revised form 16 December 2013; accepted 26 January 2014
Available online 7 February 2014

KEYWORDS
Micro-supercapacitor;
Energy;
Silicon nanowires;
Doping;
CVD;
VLS

Abstract
Silicon nanowires (SiNWs) are grown by Chemical Vapor Deposition on highly doped silicon wafer via localized gold catalysis with monitored length, diameter, density and doping level. This work highlights the influence of SiNWs morphological characteristics on their electrochemical performances and analyses in details the key role of the doping level for exhibiting a typical double layer capacitive behavior. The electrochemical performances of silicon and SiNWs electrodes are evaluated in an organic electrolyte by electrochemical impedance spectroscopy and cyclic voltammetry. Electrode capacitance has been improved up to 440 $\mu F\,cm^{-2}$, i.e. about 75 fold that of bulk and about 10 fold that of the one previously reported.

Introduction

On-chip energy micro-devices are attractive solutions for powering various devices such as smartcards, RFID (Radio Frequency IDentification) tag, MEMs (MicroElectroMechanical systems), wireless sensors, etc. Currently, advanced rechargeable micro-batteries made via well-controlled thin film technologies are commercially available [1] but they suffer from the same limitations of their larger counterparts, namely limited cycle life, abrupt failure, poor low-temperature kinetics, and

*Corresponding author.
**Corresponding author.
***Corresponding author.
E-mail addresses: pascal.gentile@cea.fr (P. Gentile), thierry.brousse@univ-nantes.fr (T. Brousse), said.sadki@cea.fr (S. Sadki).

http://dx.doi.org/10.1016/j.nanoen.2014.01.005
2211-2855

safety concerns associated with using metallic lithium [2]. To associate or replace them by micro-supercapacitors, should overcome this cycle life and power issue [3]. Indeed, micro-supercapacitors [4], also named micro-electrochemical capacitors or micro-ultracapacitors, store less energy than micro-batteries but have a more impressive cycle life and higher power density [5]. Moreover, they exhibit volumetric energy density ~100 times higher than that of conventional dielectric capacitors.

For the last ten years, micro-supercapacitors have been designed with various carbon based materials [6-13] or pseudo-capacitive materials such as RuO_2 [14] or VN [15]. Such metal oxide electrodes are operated in aqueous based electrolytes, thus symmetrical device voltage is limited to less than 1.2 V. Most of the research efforts on micro-ECs are dedicated to carbon-based electrodes in organic electrolytes or ionic liquids [6-13]. However, they present some difficulties to be directly integrated on silicon based substrates commonly used in micro-electronic devices. This on-chip integration should be easier with silicon based electrodes. Recently, porous silicon nanowires (SiNWs) [16], porous silicon coated with gold [17,18], SiC nanowires [19] or SiNWs coated with NiO [20,21] or SiC [22] have been studied as potential materials for supercapacitor electrodes. Si/SiC core-shell nanowires-based electrodes show the most promising performances and cycling stability but the active material is SiC, not silicon. Our pioneer work on the field [23-25] has demonstrated that highly doped silicon nanowires based electrodes show a promising cycling stability in an organic electrolyte and a quasi-ideal capacitive behavior, i.e., the energy is stored thanks to electrolyte ions accumulation at the polarized electrode/electrolyte interface [23]. These similarities with carbon enable to envision the use of silicon based electrodes micro-supercapacitors with long lasting cycle life. The counterpart of capacitive charge storage is the surface limited capacitance. Indeed, the specific capacitance is proportional to the developed surface of the silicon electrode just like in carbon electrodes. We recently demonstrated that growing silicon nanowires leads to a large increase in the capacitance per surface of substrate compared to flat silicon wafer [23-25].

As in our previous work, SiNWs have been grown by CVD via a localized gold catalysis. SiNWs morphological and doping characteristics can be accurately monitored by the fine tuning of various growth parameters thanks to the Vapor-Liquid-Solid (VLS) mechanism [26-27] and the use of HCl during the growth [28-32]. SiNWs diameters and density is monitored by the catalyst. The use of gold colloids enables to get SiNWs with homogeneous diameters. In that case, SiNWs density is monitored by the number of successive gold colloids deposition. SiNWs with small diameters (<50 nm) from gold colloids catalyst can be obtained thanks to the use of HCl gas [28,30-32]. The use of a gold thin film enables to get denser SiNWs but with inhomogeneous diameters. The thickness of the thin film and the growth temperature enable to monitor the diameter range. SiNWs length is monitored by the growth duration. SiNWs doping type and level are monitored by the doping gas/silane ratio. n-Doped NWs are obtained by using PH_3 gas and p-doped NWs are obtained by using B_2H_6 gas. The use of HCl during the growth enables to precisely monitor the SiNWs doping level and to improve their morphology [29].

This work analyses in details the influence of the SiNWs morphology (length, diameter, density) and doping level on the electrodes electrochemical behavior and capacitance, in correlation with SiNWs growth parameters (gold catalyst deposition routes, growth temperature and time, CVD gas composition).

Materials and methods

SiNWs growth by CVD

SiNWs are grown in a Chemical Vapor Deposition reactor (CVD) via gold catalysis on highly doped n-Si (111) substrate (doping level (i.e. the number of doping atoms per cm^3 of materials) $N_d = 5 \times 10^{18}\ cm^{-3}$). H_2 is used as carrier gas, silane (SiH_4) as silicon precursor, phosphine (PH_3) as n-doping gas, diborane (B_2H_6) as p-doping gas and HCl as additive gas. As shown in our previous work [28-32], the use of HCl in our process enables to reduce the gold surface migration and improve the NWs morphology. Their roughness decrease and their diameters are constants from the bottom to the top, whatever the nanowires length. Gold colloids with homogeneous diameters or gold thin film have been used as catalyst. Only gold colloids lead to SiNWs with homogeneous diameters. Thanks to the growth Vapor-Liquid-Solid mechanism, SiNWs characteristics can be monitored: their length by the growth duration, their density by their number of gold colloids deposition, their doping type by the doping gas nature and their doping level by the doping gas/silane ratio. This ratio can vary from 10^{-6} to 10^{-2} leading to doping level from $N_d \approx 10^{16}$ to $\approx 10^{20}\ cm^{-3}$ [29].

Prior to the growth, wafer surface are cleaned by successive dipping in (i) Acetone, Isopropanol and Caro (H_2SO_4:H_2O_2, 3:1) to remove organics impurities, followed by (ii) HF, 10% and NH_4F solution to remove the native oxide layer. Then, gold catalyst is deposited on the surface. Gold colloids are deposited with HF, 10% from an aqueous gold colloid solution (BritishBioCell). Gold thin film is evaporated under UHV on the substrate. SiNWs density is estimated by counting the number of gold colloids or dewetted gold nanoparticles per cm^2 on several SEM pictures.

Several growths have been performed to get SiNWs with several lengths, diameters, densities and doping levels. Different SiNWs lengths are obtained by increasing the growth time.

SiNWs with different doping level are grown at 600 °C (for 50 nm and 100 nm gold colloids) or at 650 °C (for 200 nm gold colloids and gold thin films), under 3 Torr total pressure, with 100 sccm (standard cubic centimeters) of HCl gas, 700 sccm of H_2 as carrier gas and various silane/doping gas ratio [29]. For both temperatures, highly doped SiNWs growth rate is about 500 nm min^{-1}.

Highly doped SiNWs are obtained by using 40 sccm (standard cubic centimeters) of SiH_4 and 80 sccm of doping gas (0.2% PH_3 in H_2 or 0.2% B_2H_6 in H_2).

SiNWs growth from small diameter gold colloids (5 nm, 10 nm, 20 nm) is performed at 500 °C, under 8 Torr total pressure, with 60 sccm of SiH_4, a 3×10^{-3} phosphine/silane ratio, 50 sccm of HCl gas, 700 sccm of H_2 as carrier gas for 20 min [29].