SILICON CARBIDE NANOWIRES AS AN ELECTRODE MATERIAL FOR HIGH TEMPERATURE SUPERCAPACITORS

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ABSTRACT

Supercapacitors have attracted much attention for energy storage applications, owing to their long cycle life and high power densities. We report on the growth of silicon carbide (SiC) nanowires (NW) and the evaluation of their performance as electrode material for micro-supercapacitors. Their specific capacitance has been studied as a function of their morphology (size, diameter) and the optimal growth conditions have lead to a capacitance comparable to the state of the art. They exhibit an exceptional stability, with a lifetime exceeding 10^6 charge/discharge cycles. An excellent thermal stability is expected for SiC NWs, opening the way to the fabrication of high temperature micro-supercapacitors.

INTRODUCTION

With the development of wireless sensors networks, there is an urgent need for compact power sources. Standard rechargeable Li-ion batteries can be used in many cases, but some advanced applications require the development of new energy storage devices. This is particularly true for sensors operating in harsh environments like geothermal well logging, where batteries cannot operate. In this context, supercapacitors have attracted much interest in the past years, because of their increased lifetime and their wide temperature range of operation. Moreover, their energy storage mechanism, purely electrostatic, ensures very high charge/discharge rates, suitable for a use in combination with energy harvesting devices and wireless communication.

Some planar micro-supercapacitors have already been reported in the literature [1-4] with acceptable performances. The challenge to develop such planar devices is the integration of the electrodes' high surface area material necessary to ensure a high capacitance. Activated carbon, which is the common material used in standard supercapacitors, is difficult to integrate in planar technology [3]. Most of the studies have focused on nanomaterials like carbon nanotubes [1], nanowires [2, 5] or graphene [6], which are by nature high surface area materials and compatible with standard microfabrication techniques. Even if high capacitance and power density values have been reported so far, there is still a lack of a material robust enough to ensure a long lifetime and a stable operation at high temperature.

This paper reports on the performance of silicon carbide nanowires as electrode materials for micro-supercapacitors. SiC is known to be a material highly suitable for fabricating devices able to operate in harsh environment [7] and this work is the first step towards the fabrication of a high temperature micro-supercapacitor.

EXPERIMENTAL

SiC NWs have been grown by a chemical vapor deposition (CVD) process similar to that reported in ref. [8]. All NW growths presented in this paper have been performed on n-doped SiC thin films (2 µm) deposited by low pressure CVD [9] on oxidized silicon wafers. The performance of the SiC NWs as electrodes for supercapacitors has been evaluated in terms of specific capacitance, charge/discharge rate and lifetime as a function of their morphology by using an electrochemistry test station.

SiC nanowires growth and characterization

A thin layer of nickel is deposited by e-beam evaporation on previously cleaned $Si/SiO_2/SiC$ substrates. This layer acts as a catalyst for the NWs growth, most likely following a vapor-liquid-solid mechanism. Three thicknesses have been tested for the Ni layer (1.5, 2.2 and 3.1 nm) in order to vary the NW diameter. Growths are performed in a horizontal hot wall low pressure (5 Torr) furnace at 950°C. Samples are placed inside the furnace and temperature is increased to 950°C at a rate of 55°C/min under 10 sccm of H_2. When the growth temperature is reached, 0.5 sccm of methlytrichlorosilane (MTS, CH_3SiCl_3) are introduced in the tube and the H_2 flow rate is reduced to 5 sccm. To control the lengths of the NWs, growth time has been varied between 15 and 60 minutes. At the end of the growth, H_2 flow rate is increased to 10 sccm while MTS flow and heating are stopped. Samples are then cooled down to room temperature at a rate of 15°C/min.

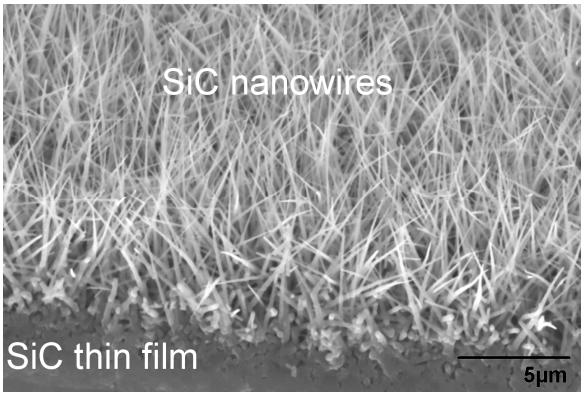

Figure 1: SEM image of the SiC nanowires grown on a SiC thin film.

Nanowire morphology is characterized by scanning electron microscopy (SEM) using a LEO 1550 (cf. figure 1). Their diameters are measured to be approximately 21, 43 and 82 nm for catalyst thicknesses of respectively 1.5, 2.2 and 3.1 nm. Nanowire lengths vary linearly from 4.2 to 7.8 µm when the growth time is increased from 15 to

60 minutes. Their crystal structure is determined using a Siemens D5000 automated diffractometer operated in θ-2θ geometry. X-ray diffraction (XRD) spectrum of nanowires grown on a Si(111) substrate are reported in figure 2. Only two peaks are noticeable in the range 20-90°: the Si(111) peak at 28.5° and the SiC(111) peak at 35.5°. This reveals the nanowires have a cubic structure (3C-SiC), with a growth along the <111> direction. The shoulder observable at 34° is related to the presence of stacking faults [10]. The full width at half maximum values for Si (111) and SiC (111) peaks, after stripping of the $K\alpha_2$ peak, are respectively 0.1° and 0.43°, with 0.1° being the minimum resolution of the XRD system. This is indicative of the good crystalline structure of the SiC nanowires.

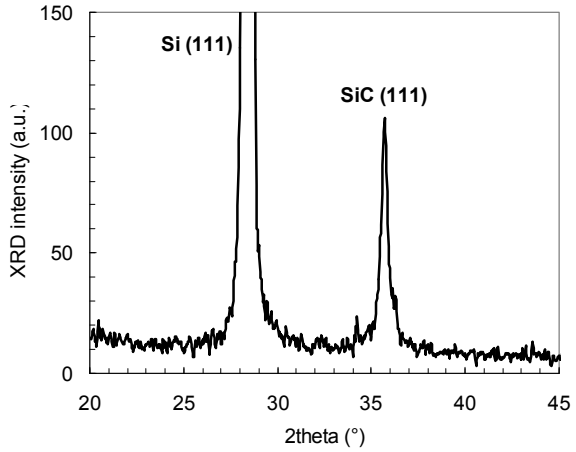

Figure 2: XRD spectrum of SiC nanowires grown on a Si(111) substrate.

Electrochemical measurements

Performance of the nanowires is evaluated using an electrochemical workstation (CH Instruments Inc., 660D) in a 3-electrode configuration. Electrical connection to the nanowire samples is made thanks to the doped SiC thin film (ρ=0.01 Ω.cm) on which the nanowires are grown. During catalyst evaporation a part of the sample is masked in order to create a nanowires-free area which is used for this connection. A platinum wire is used as counter electrode and an Ag/AgCl electrode is used as reference electrode. All measurements are performed in an electrolyte solution made of 3.5M KCl. Prior to acquisition samples are cycled ten times to ensure removal of any adsorbed contaminants.

RESULTS AND DISCUSSIONS

Supercapacitors store energy at the interface between the electrodes and the electrolyte, in what is called the electric double layer (EDL) [11]. The capacitance of such devices is then directly proportional to the surface area of the electrodes' material. By using high surface area materials like nanowires high capacitances values are thus expected. To evaluate the contribution of the nanowires to the total measured capacitance, we measured by cyclic voltammetry the specific capacitance of a sample with 5.7µm long and 43nm wide nanowires. Comparison of its capacitance with the SiC thin film alone and with the SiC thin film covered with 2.2nm of Ni annealed at 950°C under H_2 is presented in figure 3.

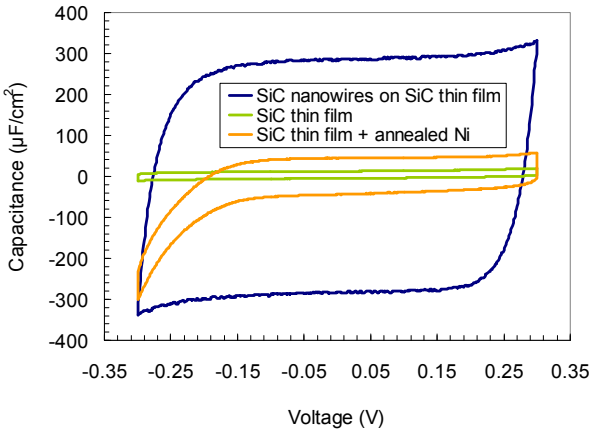

Figure 3: Specific capacitance of the SiC thin film (green), SiC thin film + Ni catalyst after annealing (orange) and SiC nanowires (blue) obtained at a scan rate of 100 mV/s in a solution of 3.5 M KCl.

The measured capacitance of the NWs sample is 26 times higher than the SiC thin film alone and 7 times higher than the SiC thin film covered with annealed Ni. As expected, SiC NWs, thanks to their high aspect ratio, exhibit a high specific capacitance around 400 µF/cm^2. This value is comparable to the results obtained using carbon nanotubes [1] or carbide-derived carbons [4]. The Ni covered sample exhibits a higher capacitance than the SiC thin film alone, revealing the possible formation of nano-droplets of Ni during the annealing step. The peak visible around -0.20V for this sample is attributed to the reduction of the oxygen present in the solution by the Ni [12]. This reaction being not reversible cannot be exploited to increase the specific capacitance, and care has to be taken not to confuse this with pseudo-capacitance [2, 11].

In order to maximize the capacitance, we proceeded to a series of NWs growths with different catalyst thicknesses and growth times. The catalyst thickness has a direct influence on the nanowires diameters while the growth time controls the nanowires length. Figure 4 presents the evolution of the specific capacitance as a function of the nanowires' morphology.

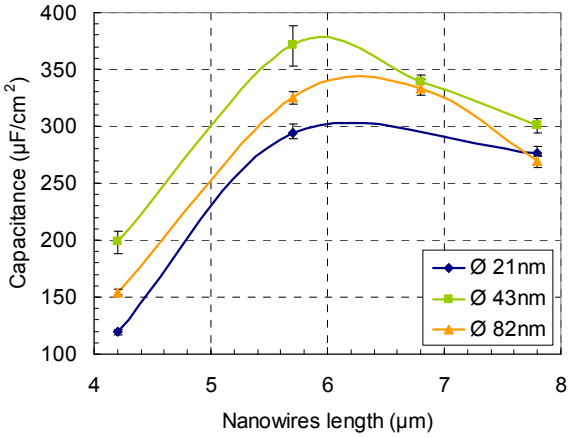

Figure 4: Specific capacitance of the SiC nanowires as a function of their morphology.

The errors bars correspond to the dispersion obtained when the scan rate is varied from 0.01 V/s to 0.1 V/s. The dispersion is very small, always below 5%, revealing good capacitance behavior. For all samples the capacitance increases slightly with lower scan rates, revealing the presence of faradaic reactions on the electrodes surfaces [13] probably due to the presence of Ni in the nanowires. For each diameter studied, the optimal nanowire length is determined to be around 5.7 µm, suggesting that the electrolyte cannot access the entire nanowire surface beyond this length. This transport limitation may be due to the non-vertical growth of the nanowires and needs to be improved upon in future work.

In order to evaluate the performance of the nanowires in terms of charging speed, charge/discharge cycles have been performed. Figure 5 reports the charge/discharge data obtained with the sample presented in figure 3.

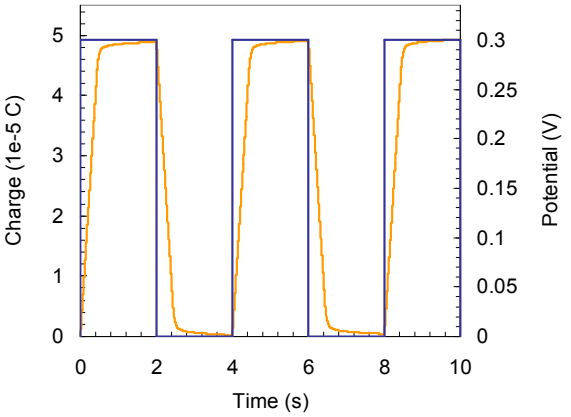

Figure 5: Charge/discharge rate of the SiC nanowires under a square-wave voltage toggling between 0 and 0.3V.

The data reveals a high charge/discharge rate of 300 ms, which leads to a power density of 50 µW/cm^2. This power is limited by the high contact resistance between the nanowires and the SiC thin film, which has been measured in the order of several hundreds of Ω.cm^2 by impedance spectroscopy. Efforts are ongoing to reduce this contact resistance by in-situ doping of the nanowires or graphitization of the SiC thin film prior to nanowire growth [14].

One million charge/discharge cycles have been performed with the same sample in order to evaluate the lifetime of the nanowires. Figure 6 reports the evolution of the relative capacitance (C/C_0) as a function of the cycle number.

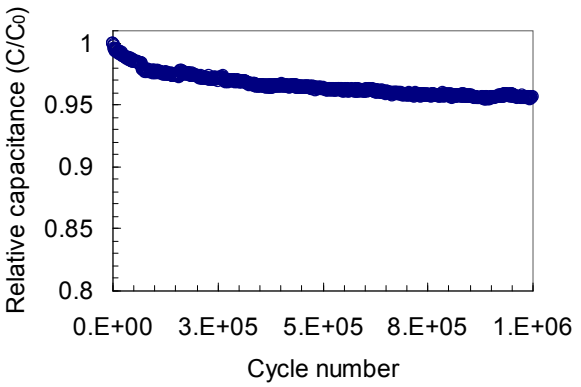

Figure 6: Lifetime testing of the SiC nanowires. 10^6 charge/discharge cycles have been performed at a scan rate of 5 V/s in a 3.5M KCl solution.

This test reveals an extremely stable behavior, with a capacitance loss smaller than 5% after a million charge/discharge cycles. This result confirms the advantage of supercapacitors over batteries, whose lifetime is limited to a few thousands of cycles. The excellent stability of SiC in harsh environments projects a stable behavior at high temperature and its investigation is ongoing.

CONCLUSIONS

We have studied the specific capacitance of SiC nanowires grown by catalytic CVD on SiC thin films. The nanowires exhibit a high aspect ratio and a good crystalline structure. Study of their specific capacitance as a function of their morphology allowed us to determine the optimal growth conditions and capacitance results we obtained are at the level of the state-of-the-art values. We have demonstrated a 1 million cycle lifetime without significant capacitance loss, confirming the potentiality of these nanowires as electrode material for reliable supercapacitors.

Efforts are ongoing to reduce the contact resistance between the nanowires and the substrate in order to increase the power density. Further work will focus on the fabrication of a high temperature micro-supercapacitor able to power SiC wireless sensors operating in harsh environment.

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