

From silicon nanowires to innovative silicon nanotrees for micro-supercapacitors

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In the race to competitiveness, micro-electronic devices have to be more and more efficient. One way to reach this goal is to integrate supercapacitors in their circuit [1]. However, their integration in micro-electronic circuit is still a challenge. Elaborate silicon based micro-supercapacitors should facilitate it.

We will present the elaboration and the electrochemical characterization of micro-supercapacitors electrodes made either with silicon nanowires (SiNWs) [2,5] or highly doped silicon nanotrees (SiNTrs), with a special focus on our recent advances on the SiNTrs growth, their characterization and their use as electrodes in micro-supercapacitor devices.

SiNWs and SiNTrs based electrodes are elaborated by Chemical Vapor Deposition (CVD) on highly doped silicon substrate via localized gold catalysis. Highly doped SiNTrs have been grown via two different methods: either with two CVD growths separated by a new gold catalyst deposition, or with only one growth [3, 4]. For this second method, the trunks and the branches growth are separated by an annealing which enables the gold catalyst to pour along the nanowires. Morphologies are checked after the growth by SEM. Their doping level can be monitored by the doping gas/silane ratio thanks to the Vapor Liquid Solid (VLS) mechanism. Electrochemical performances of these electrodes are evaluated with an organic electrolyte (NEt₄BF₄, PC, 1M) and an ionic liquid (EMI-TFSI) by Electrochemical Impedance Spectroscopy and dynamic electrochemistry (cyclic voltametry and galvanostatic charge/discharge).

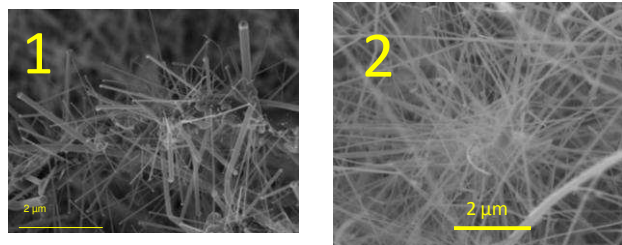


Fig. 1 : SEM image of SiNTrs grown by two CVD steps
Fig. 2 : SEM image of SiNTrs grown by one CVD step

First results highlight that increasing SiNWs length, density and doping level enable to enhance electrode capacity. A 440 $\mu\text{F}\cdot\text{cm}^{-2}$ capacity, i.e. about 75 fold bulk silicon capacity, has been obtained by using dense, highly doped, 50 μm long silicon nanowires. Moreover, when SiNWs doping level is increased, electrodes acquire a quasi-ideal supercapacitor behavior [2]. That's why highly doped silicon nanotrees have been grown. The HCl gas ratio during the trunk growth, the annealing time and temperature have been identified as key parameters to obtain hyperbranched SiNTrs. A 950 $\mu\text{F}\cdot\text{cm}^{-2}$ electrode capacity, i.e. about 158 fold bulk silicon capacity, has been reached by using highly doped, dense, hyperbranched ($L \approx 3 \mu\text{m}$, $\varnothing \approx 30 \text{ nm}$), 40 μm long silicon nanotrees. Devices built with two of these electrodes show highly stable cycle efficiency (97 %) and capacity over at least 100 000 cycles for current density ranging from 5 to 500 $\mu\text{A}\cdot\text{cm}^{-2}$. The use of ionic liquid as electrolyte enables to enlarge the potential window and thus improve devices performances.

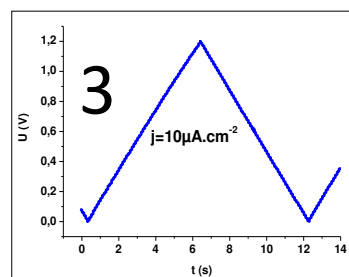


Fig. 3 : Galvanostatic charge/discharge of 50 μm -SiNWs/50 μm -SiNWs micro-supercapacitor with 1M, NEt₄BF₄, PC as electrolyte

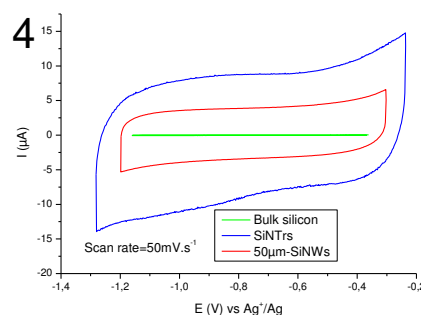


Fig. 4 : Cyclic voltametry curves of bulk silicon, 50 μm -SiNWs and SiNTrs electrodes with 1M, NEt₄BF₄, PC as electrolyte

- [1] J.R. Miller, P. Simon, Science, 2008, 321, 651
- [2] F. Thissandier, A. Le Comte, O. Crosnier, P. Gentile, G. Bidan, E. Hadji, T. Brousse, S. Sadki, Electrochem. Comm., 2012, 25, 109
- [3] P. Gentile, T. David, F. Dhalluin, D. Buttard, N. Pauc, M. Den Hertog, P. Ferret, T. Baron, Nanotechnol., 2008, 19, 125608
- [4] G.S. Doerk, N. Ferralis, C. Carraro, R. Maboudian, J. Mater. Chem., 2008, 18, 5376
- [5] F. Thissandier, N. Pauc, T. Brousse, P. Gentile, S. Sadki, Nanoscale Research Lett., 2012, accepted