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TITANIUM NITRIDE / POROUS SILICON ELECTRODE FOR MICROSUPERCAPACITOR APPLICATIONSR. DAILLEAU^{1,2}, T. DEFFORGE¹, F. TRAN VAN² AND G. GAUTIER^{1,*}¹GREMAN UMR-CNRS 7347, INSA Centre Val de Loire, Université de Tours, Tours, France²PCM2E Tours, EA 6289, Université de Tours, France*Corresponding author e-mail address: gael.gautier@univ-tours.fr**SUMMARY**

This abstract deals with the investigation of a tunable way to prepare integrated micro-supercapacitors made of coated porous silicon (pSi). pSi allows developing a large specific surface area of the electrode material. To overcome the insulating behavior of the pSi, we chose to use Atomic Layer Deposition (ALD) to deposit a 2 nm thin layer of Titanium Nitride (TiN), to cover the pore sidewalls. SEM characterizations have been realized to confirm the conformal deposition of the conductive layer inside the porosity and electrochemical characterizations were carried out to determine the performances of supercapacitors. Capacity around 500 $\mu\text{F}/\text{cm}^2$ were obtained in Na_2SO_4 1M aqueous media.

1. INTRODUCTION

A supercapacitor is an electrochemical energy storage device that can release more power than a battery and store more energy than a classic capacitor¹. Integrating this kind of device in the micro-electronic supply chain is challenging for the internet of things system emergence². An efficient micro-supercapacitor electrode must be chemically stable, have a low electrical resistance, and high specific surface area. All those characteristics can be reached by using pSi as substrate material but the silicon surface must be covered for instance by ALD³. This deposition technique is inspired from Chemical Vapor Deposition (CVD) consisting of alternatively saturating the whole surface developed by a substrate with a gas, and then with its co-reactant to form a thin layer, atomic layer by atomic layer. This technique is more and more used to deposit conformal ultrathin layers, which is coherent with global warming issues and matter consumption. TiN is a well-known electrode material in micro-electronics industry, used for its electrical conductivity and electrochemical stability⁴. Here, we have used TiCl_4 and NH_3 as co-reactants to cover the whole surface of the meso/macro pSi with TiN after optimization of the deposition conditions. Characterizations of the TiN ALD layer have been realized and preliminary electrochemical characterization have been carried out to confirm the storage capacity of the material to realize promising electrochemical storage microdevices.

2. EXPERIMENTAL RESULTS AND DISCUSSIONS

pSi was prepared by electrochemical etching of silicon wafer in hydrofluoric acid solution. Meso/macroporous silicon with an average pore size diameter of 60 nm and a porosity of 60%, evaluated by gravimetric measurements, was synthesized. The pSi sidewalls were covered with TiN by ALD in a TFS-200 reactor from Beneq[®]. The ALD deposition procedure was optimized to allow the chemicals to be adsorbed onto the high aspect ratio pore sidewalls and therefore enable a uniform deposition of TiN, even at the bottom of the pores. A pSi layer top view is presented on *Figure 1* showing the morphology of the porous layer before ALD deposition. The good uniformity after TiN deposition on pSi, even at the pSi/Si interface, is illustrated on *Figure 2*. The small particles on top of pSi that can be seen on *Figure 2a* are imputed to CVD nanoparticle growth that occurs when residual precursor species remain in the chamber. EDS analysis presented on *Figure 2f* confirms the presence of titanium covering the pore sidewalls. Finally, to verify the electrochemical behavior of the pSi/TiN layers, cyclic voltammetry using a three electrodes electrochemical cell immersed in Na_2SO_4 1M aqueous solution was carried out. The active electrode consisted in: pSi (60 nm pore diameter, 4 μm thick pSi) / TiN as working electrode (WE), overcapacitive carbon paste (activated carbon / carbon black / PTFE) as counter electrode, and saturated calomel electrode as reference electrode. Preliminary results showed a clear capacitive behavior (*Figure 3*) for the composite electrode and with a capacitance of about 500 $\mu\text{F}/\text{cm}^2$.

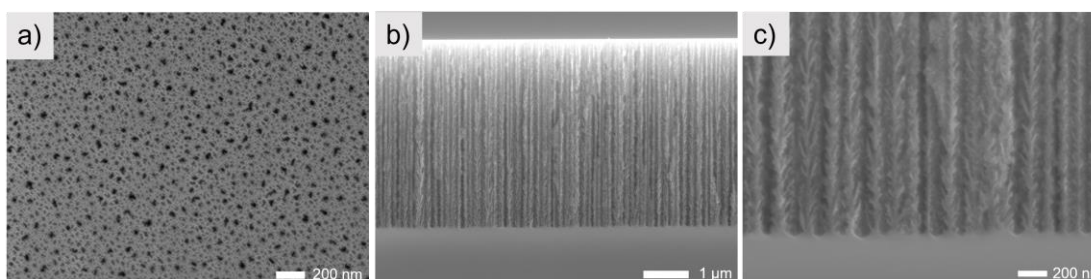


Figure 1 – SEM images of pSi before ALD deposition. a) Top view. b) Cross section. c) Cross section at pSi/Si interface.

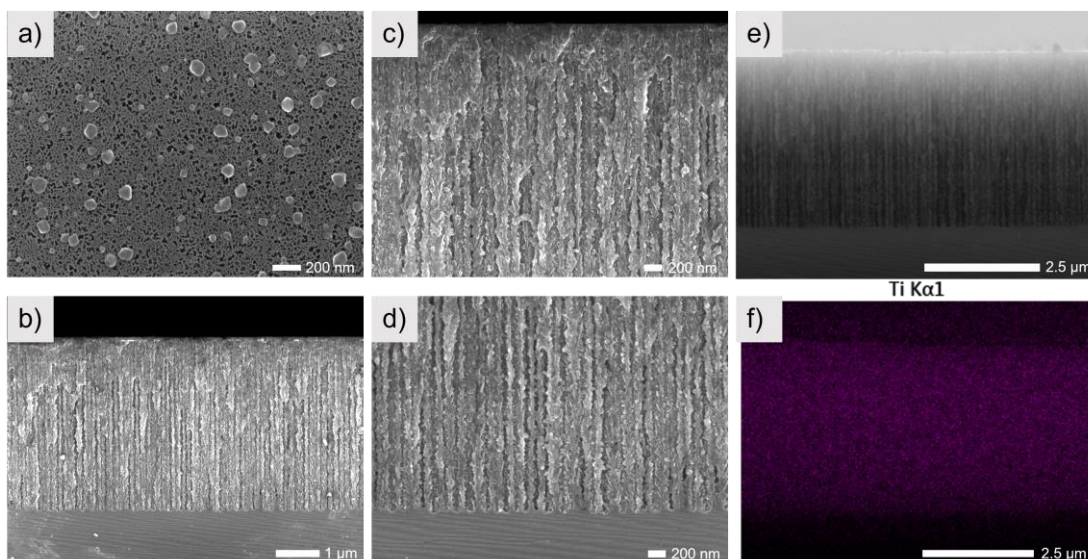


Figure 2 – SEM images of porous silicon with TiN deposited by ALD. a) Top view. b) Cross section view. c), d) Cross section view with higher magnification focused on the upper part of the cross section. d) Cross section view with higher magnification focused on the lower part of the cross section, interface pSi + TiN / Si. e) SEM image of the EDS analysed area. f) Titanium Ka signature on EDS analysed area.

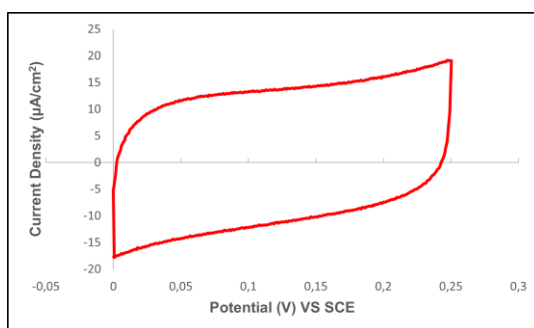


Figure 3 – Cyclic voltammetry at 20 mV/s of pSi + TiN material as WE in Na₂SO₄ (1M) aqueous solution.

3. CONCLUSIONS

Under optimized ALD deposition conditions, we have demonstrated the feasibility of fabricating micro-supercapacitor electrodes made from pSi and covered with TiN by ALD. Combining porous silicon formation and ALD deposition of a conductive layer, a specific capacity up to 500 $\mu\text{F}/\text{cm}^2$ was obtained. These results are promising for the next generation integrated micro-supercapacitors⁵.

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