

# Coated Porous Si for High Performance On-Chip Supercapacitors

**K. Grigoras, J. Keskinen, L. Grönberg, J. Ahopelto, and M. Prunnila**

VTT Technical Research Centre of Finland, P. O. Box 1000, FI-02044 VTT Espoo, Finland

Email: mika.prunnila@vtt.fi

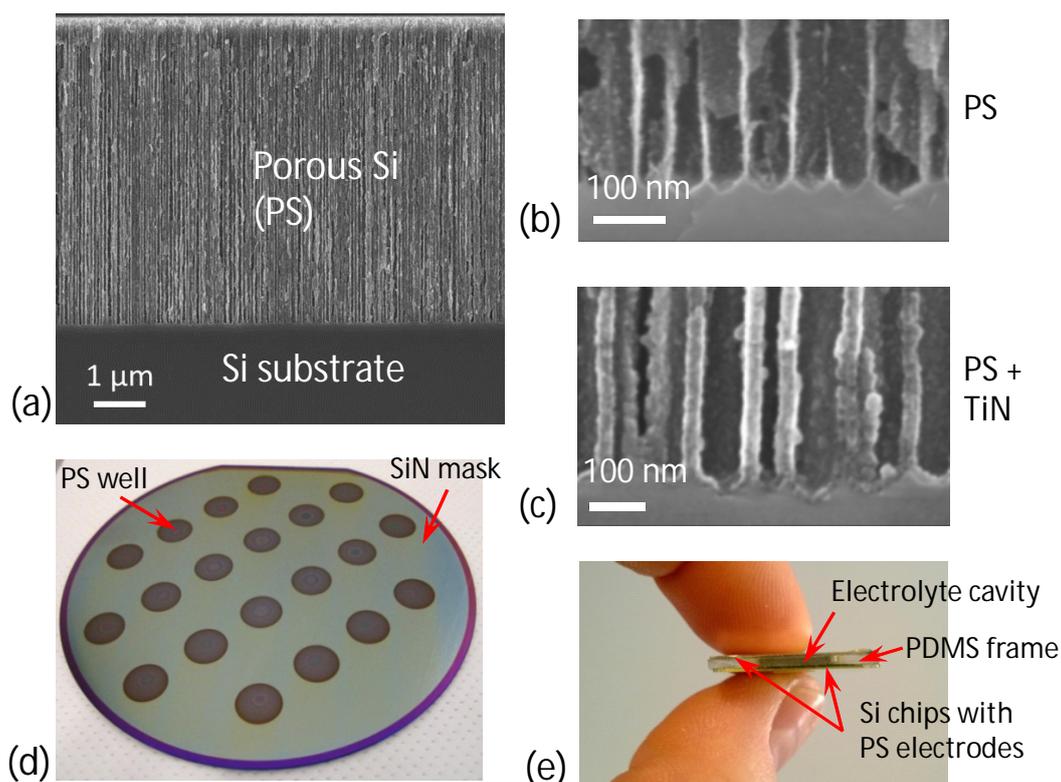
**Abstract.** High performance porous Si based supercapacitor electrodes are demonstrated. High power density and stability is provided by ultra-thin TiN coating of the porous Si matrix. The TiN layer is deposited by atomic layer deposition (ALD), which provides sufficient conformality to reach the bottom of the high aspect ratio pores. Our porous Si supercapacitor devices exhibit almost ideal double layer capacitor characteristic with electrode volumetric capacitance of  $7.3 \text{ F/cm}^3$ . Several orders of magnitude increase in power and energy density is obtained comparing to uncoated porous silicon electrodes. Good stability of devices is confirmed performing several thousands of charge/discharge cycles.

## 1. Introduction

Electrochemical double layer capacitors (EDLC), commonly called as supercapacitors, offer an option for short term high power storage [1, 2]. These energy storage elements could find many applications in the field of energy harvesting and MEMS if reliable integrated elements could be realized. High surface area carbon materials (as activated carbon) are typically used as supercapacitor electrodes, but those are challenging to integrate on chip with silicon devices. Supercapacitor elements based on Si nanostructures could be an optimal solution here, and there are numbers of reports dealing with silicon nanowires and similar structures [3], but these devices exhibit relatively low capacitance.

Porous silicon (PS) (see figures 1a and b) is an attractive candidate due to ease fabrication and integration possibility, but its resistance is relatively high and it suffers from high reactivity - features resulting in low power density and poor stability [4, 5]. Coating of PS has been recognized as a possible route to reduce the resistance and increase the stability [4-6], but even for coated electrodes the performance has still been several orders of magnitudes below that of carbon based supercapacitors. This is due to the fact that the power density is eventually limited by the resistance of the complex Si nanostructure and, therefore, in addition of the stability the coating has to provide high conductivity. In this work, we use atomic layer deposition (ALD) technique to get a conformal (see figure 1c), low resistance and stable coating on the complex porous silicon surface. Our results demonstrate that TiN coated PS is a promising material for micro supercapacitors.





**Figure 1.** (a) Cross-sectional SEM image of 7  $\mu\text{m}$  thick PS layer. (b) High magnification SEM image of PS. (c) Optical image of a 150 mm Si wafer with PS wells for supercapacitor electrodes. (d) High magnification SEM image of PS matrix with a  $\sim 10$  nm atomic layer deposited TiN layer. (e) Test bench device to characterise the properties of PS/TiN electrodes.

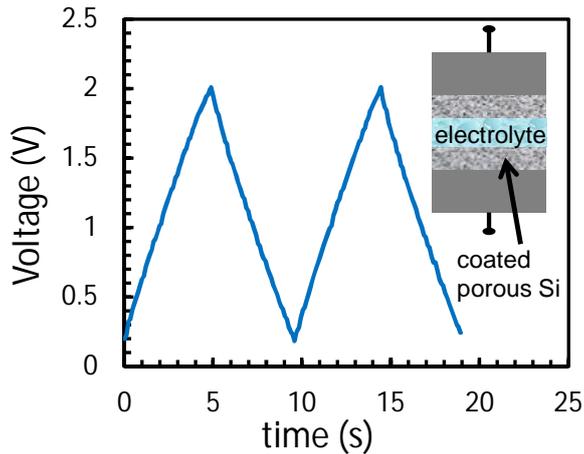
## 2. Experimental

Porous silicon was prepared by electrochemical etching of highly-boron-doped silicon wafers (1 - 4  $\text{m}\Omega\text{-cm}$ ) in a 1:4 solution of 50 % aqueous-HF and ethanol. A whole 150 mm diameter wafer with a patterned silicon nitride mask was processed resulting in 20 identical porous areas  $1.5 \text{ cm}^2$  each (see figure 1 d). Approximately 6  $\mu\text{m}$  thick porous layer was prepared during 30 minutes anodization step at 5.3  $\text{mA}/\text{cm}^2$  current density. Porosity of the layer was about 88% as evaluated from gravimetric measurements. Pore diameter was about 50 nm (see figure 1b). The TiN layer was deposited by ALD using  $\text{TiCl}_4$  and ammonia as precursors and nitrogen as carrier and purging gas. As can be observed from figure 1c, close to ideal conformality was achieved.

As a test bench for material study we have been using two PS/TiN electrodes with a PDMS frame that forms a cavity for the electrolyte, as shown in figure 1(e). The 2 mm thick PDMS frame served as a separator and as a reservoir for electrolyte, which was 0.5 M of tetraethyl-tetrafluoroborate in propylene carbonate (TEABF<sub>4</sub>/PC).

## 3. Results and discussion

Galvanostatic charge/discharge curves of coated porous Si supercapacitors at constant current are shown in figure 2. Almost symmetric triangular shape of voltage response indicates good performance as an EDL capacitor. The efficiency of the cell is about 82% and evaluated capacitance is 3.9 mF.

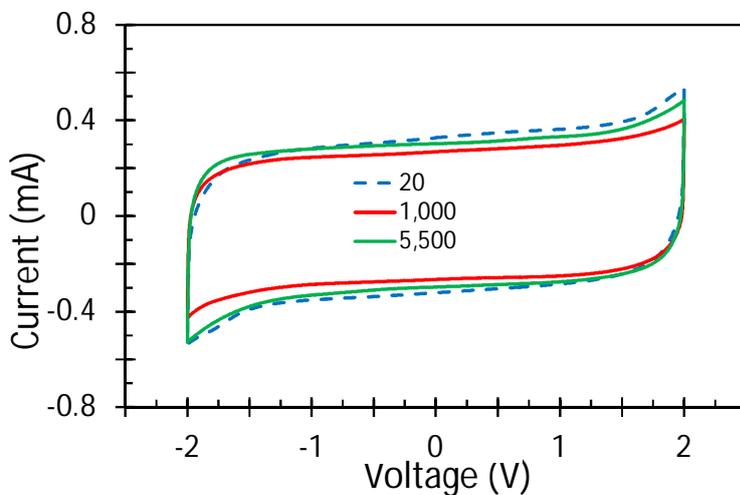


**Figure 2.** Galvanostatic charge/discharge of TiN coated porous Si supercapacitor structure at current of 1 mA. Current polarity changes at the instances where the time derivative of the measured voltage changes the polarity.

Electrochemical impedance spectroscopy (EIS) was used to examine the frequency characteristics and equivalent series resistance (ESR) of our devices. We found close to ideal capacitive behaviour and ESR value of  $18 \Omega$ , which is very close to the values obtained from galvanostatic measurements ( $17 \Omega$ ). The ESR mainly arises from the 2 mm thick electrolyte region in between the coated PS electrodes and only  $\sim 1 \Omega$  or less comes from the electrodes themselves.

Good performance as EDL capacitor was confirmed also by cyclic voltammetry (CV) measurements. The CV curves of figure 3 exhibit almost ideal rectangular shape – a feature that has not been observed for porous silicon based devices before [4, 5, 6]. Such shape is an indicator of a very low ESR of our electrodes due to the conductive coating. From figure 3 we also can observe that the capacitance retention behavior is excellent. During the 5500 scans the CV characteristics change very little. In fact, if we inspect only the capacitance (at 1 V) after first drop/transient during the first 200-300 cycles the capacitance slowly approaches the initial value.

To compare our devices with other results, the volumetric values of specific energy and specific power were calculated, taking into account total porous volume of both electrodes. Our obtained energy value of  $1 \text{ mWh/cm}^3$  is comparable with the best results for on-chip capacitors and power value of  $7.3 \text{ W/cm}^3$  is at least order of magnitude larger than other results for silicon (and porous silicon) based supercapacitors.



**Figure 3.** Cyclic voltammetry (CV) curves of TiN coated porous Si supercapacitor structure at 100 mV/s voltage scan rate. Few CV curves during 5500 cycles shown.

#### 4. Conclusions

Un-coated pristine porous silicon cannot be used as electrode material for supercapacitors due to large reactivity of the surface and poor overall conductivity. Even in highly doped material the resistivity of the porous Si nanostructures significantly reduce the power extraction. TiN coating by ALD greatly improves the electrode performance by increasing the conductivity and passivating the surface. ALD is the best method for the coating as it provides the required conformality and tuneability for the coating layer parameters. Fabricated TiN coated porous Si supercapacitor electrodes show good figures of merit: electrode volumetric capacitance up to 7.3 F/cm<sup>3</sup>, power density of 32 W/cm<sup>3</sup> and energy density of 1 mWh/cm<sup>3</sup>. Together with the demonstrated high stability these values pave the way for on-chip supercapacitor technologies that can be integrated with MEMS energy harvesters.

#### Acknowledgments

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#### References

- [1] P. Simon and Y. Gogotsi, "Materials for electrochemical capacitors", *Nature Materials*, Vol. 7 (2008), pp. 845-854
- [2] Y. Zhang et al, "Progress of electrochemical capacitor electrode material: A review", *Int. J. Hydrogen Energy*, Vol. 34 (2009), pp. 4889-4899
- [3] J. Alper, M. Vincen, C. Carraro, R. Maboudian, "Silicon carbide coated silicon nanowires as robust electrode material for aqueous micro-supercapacitor", *Appl. Phys. Lett.*, Vol. 100 (2012), pp. 163901-3
- [4] S. Desplombain, G. Gautier, J. Semai, L. Ventura, and M. Roy, "Investigation on porous silicon as electrode material in electrochemical capacitor", *Phys. Stat. Sol. C*, Vol. 4 (2007), pp. 2180-2184
- [5] L. Oakes *et al.*, "Surface engineered porous silicon for stable, high performance electrochemical supercapacitors", *Sci. Rep.*, Vol. 3 (2013), pp. 3020-7
- [6] S.E. Rowlands, R.J. Latham and W.S. Schlindwein, "Supercapacitor devices using porous silicon electrodes", *Ionics* Vol. 5 (1999) pp. 5 144-149.