High areal capacity Li-ion all solid state 3D microbattery based on anatase TiO_2 deposited by ALD on silicon microstructures

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Nowadays, nomadic electronic devices should have a sufficient autonomy owing to the high energy and power capabilities of embedded rechargeable batteries. Scaling the size of the electronic devices to follow the *"More Moore"* approach opens the road of numerous applications with high societal impact such as medical implants, air quality analysis for structural, homeland security, and environmental monitoring. Typically, wireless autonomous microsystems composed of additional values and diversified technologies as compared to classical microelectronic devices issued from the CMOS technology and following the *"More than Moore"* concept can fulfill the requirements of such applications. The small footprint area of a lithium microbattery (MB) and the compatibility with standard CMOS fabrication process should enable its monolithic integration with a wireless autonomous microsystem on a same chip to reach the energy autonomy. Commercially available planar thin films lithium microbatteries (MB) do not provide enough areal capacity to get autonomous a miniaturized microsystem. To reach this goal, the first solution consists in increasing the thickness of the electrode material till a critical limit (~ 5µm) that's limit the power capability of the microbattery.

The second way to improve the areal capacity consists in using a 3D topology. The 3D MB has been intensively studied in the past decade and several concepts (vertical rods[1-3], microcontainers [4], deep trenches[5, 6], Tobacco Mosaic Virus based [7]…) have been reported within the scientific community.

To achieve a high areal capacity 3D lithium ion MB while maintaining fast kinetics of the lithium ion in the electrode, our approach [8] consists in micromachining a silicon wafer and performing a conformal deposition of the anatase TiO_2 polymorph on these 3D microstructures. The 3D topology is firstly optimized and fabricated using photolithography and deep reactive ion etching processes. A tradeoff between performance, robustness and potential industrial technology transfer has been selected. The fabricated 3D silicon microstructures array on a 3 inches silicon substrate is depicted in fig. 1. Several topologies are realized, from micropillars up to microtubes array. The high density of the 3D microstructures array is clearly linked to the high areal capacity of the microbattery. The pillars/tube external diameter and the etched depth are respectively 3µm and 23µm. The spacing between two pillars/tubes is fixed to 1µm. Despite the small lateral dimension and high etched depth, no sticking of the 3D microstructures has been exhibited after a spin coating of photoresist contrary to 3D nanostructures as mostly developed [2] that's lead to potentially fabricate a full device and not to limit our research to a semi-electrode demonstration. To measure the area enlargement factor (AEF) of such 3D topology, a conformal deposition of platinum (current collector) and anatase TiO_2 made by atomic layer deposition facility at 350°C is performed on the 3D topologies as shown in the scanning electron microscope images of the cross-section (fig. 2- microribbon). The cyclic voltammetry of a planar and a 3D structured sample (pillars) exhibit several peaks corresponding to the lithium insertion/extraction reactions occurring in the TiO_2 anatase polymorph (confirmed by XRD measurement). The peaks intensity is effectively more pronounced for the 3D structured samples as compared to the planar one. The AEF (value~12), issued from GCPL measurement performed on 3D micropillars, demonstrates without any doubt the potential of the proposed 3D topology.

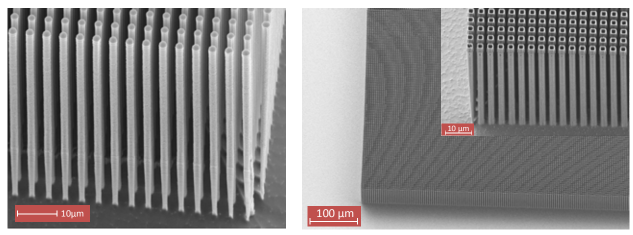

Fig. 1. Scanning Electron Microscope view of the 3D Si microstuctures

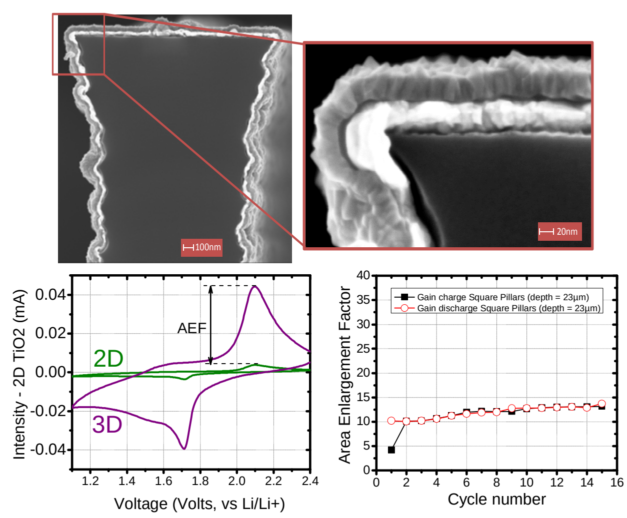

Fig. 2. Cross section of the TiO_2/Pt/Si deposited on 3D microribbons and electrochemical measurements

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References

1. C. Wang *et al*, *Electrochemical and Solid-State Letters* **7** (2004) (11) A435.
2. W. Wang *et al*, *Nano Letters* **12** (2012) (2) 655.
3. S.K Cheah *et al*, *Nano Letters* **9** (2009) (9) 3230.
4. M. Nathan et al, *IEEE JOURNAL OF MICROELECTROMECHANICAL SYSTEMS* **14** (2005) (5) 879.
5. H.C.M. Knoops *et al*, *ECS Transactions* **25** (2009) (4) 333.
6. P.H.L. Notten *et al*, *Advanced Materials* **19** (2007) (24) 4564.
7. K. Gerasopoulos *et al*, *ACS Nano* **6** (2012) (7) 6422.
8. C. Lethien *et al Microelectronic engineering* **88** (2011) (10) 3172.