Energy harvesting and storage with Si-based micro and nano structures

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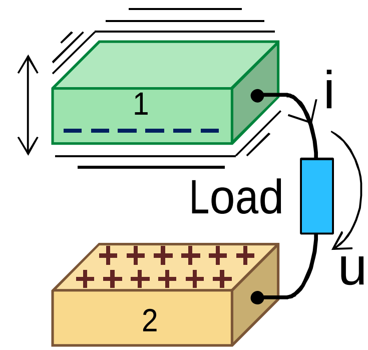
VTT Technical Research Centre of Finland Ltd

eMRS, Lille, May 6th 2016

Symposium: Materials and systems for micro-energy harvesting and storage

Outline & collaboration

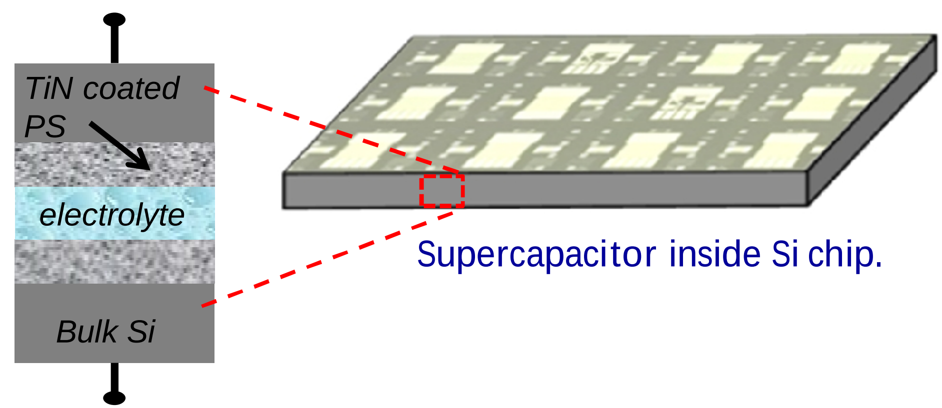
1. Work function energy harvester



Collaboration:
A. Varpula, S. J. Laakso, T. Havia, J. Kyynäräinen, M. Prunnila

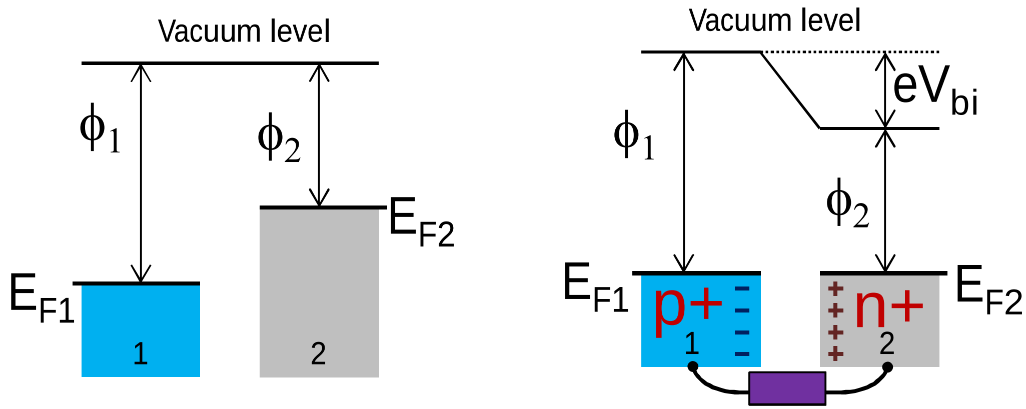
2. TiN coated porous Si electrodes for supercapacitors

- Material performance
- On-chip Integration

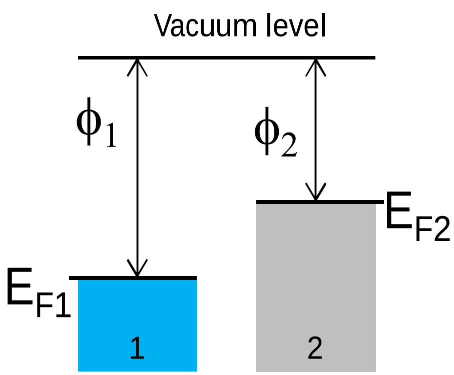


Collaboration:
K. Grigoras, J. Keskinen, L. Grönberg, E. Yli-Rantala, S. J. Laakso, H. Välimäki, P. Kauranen, J. Ahopelto, M. Prunnila

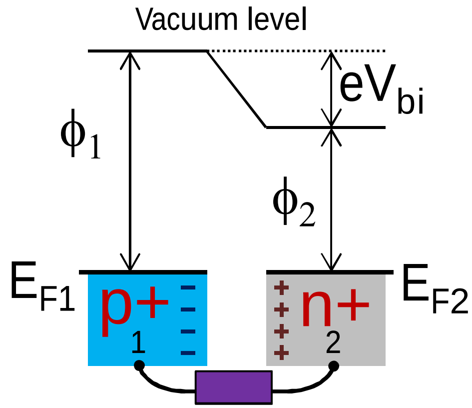
1. Work function energy harvester



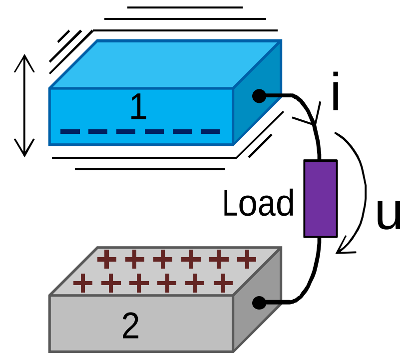
Work function e-harvester: operation principle



Electronic energy levels of electrode materials when electrodes are not in contact



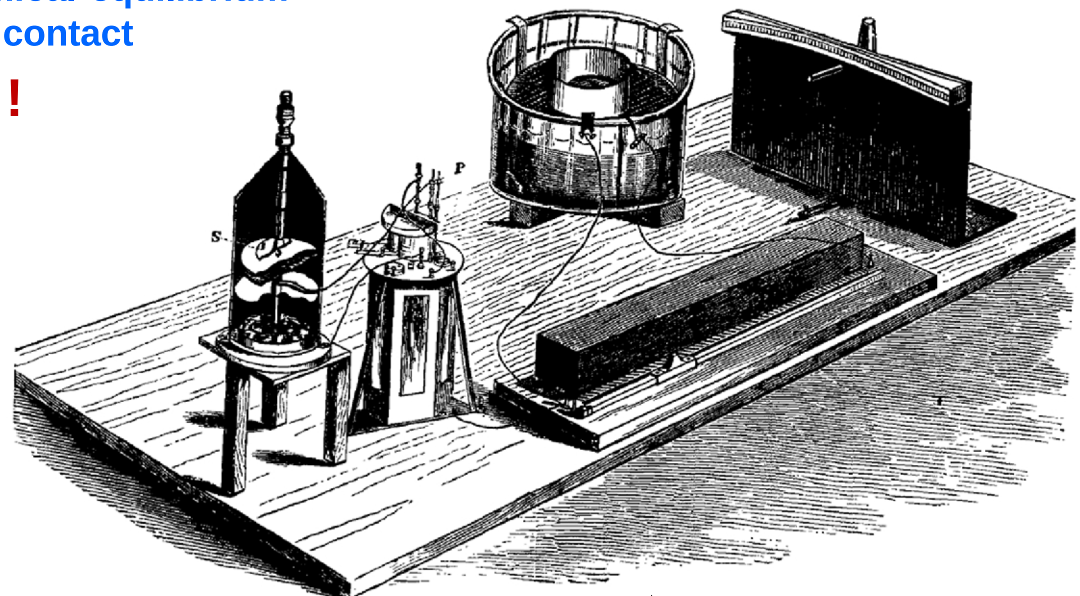
The energy levels in the thermodynamical equilibrium after making contact



Changing the distance between 1 and 2 creates current.

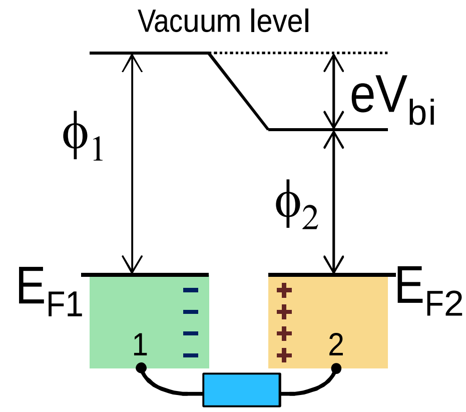
Doped semiconductors: $eV_{bi} = E_g$!

- The principle dates back to 19th century: see e.g. the experiments of Lord Kelvin [1]
- 2006: The harvesting idea was first considered by Ingo Kuehne and coworkers [2]
- 2014: Experimental investigations and comparison with comprehensive theory [3]



[1] Lord Kelvin, Nature 23, 567–568 (1881); Philos. Mag. Series 5 Vol. 46, 82–120 (1898).
[2] I. Kuehne et al., Solid-State Device Research Conference, 138 (2006).
[3] A. Varpula, S. J. Laakso, T. Havia, J. Kyynäräinen, M. Prunnila, Sci. Rep. 4, 6799 (2014).

Dynamics and power



$$V_{bi} = (\phi_1 - \phi_2)/e$$

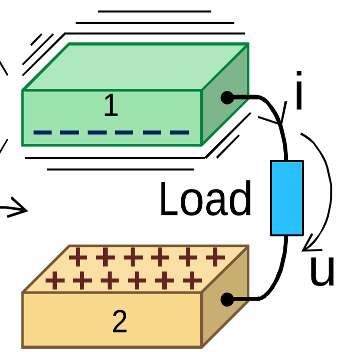
- Output current

$$i = \frac{d}{dt}(Cu) - V_{bi}\frac{dC}{dt}$$

- Power

$$P_{idealQ} = \frac{C_{max}V_{bi}^2}{2\Delta t}\left(1 - \frac{C_{min}}{C_{max}}\right)\left\{\frac{C_{max}}{C_{min}} + \frac{C_{min}}{C_{max}} + 2 - \frac{2C_{par}}{C_{min}}\left[1 + \left(\frac{C_{min}}{C_{max}}\right)^2\right]\right\}$$, frequency f = 1/Δt

$$P_{idealQ} = \frac{C_{max}V_{bi}^2}{2\Delta t}\frac{C_{max}}{C_{min}} \quad , \begin{cases} C_{max} >> C_{min} \\ C_{par} = 0 \end{cases}$$



gap capacitance

$$C(t) = C_{gap}(t) + C_{par}$$

total capacitance

parasitic capacitance

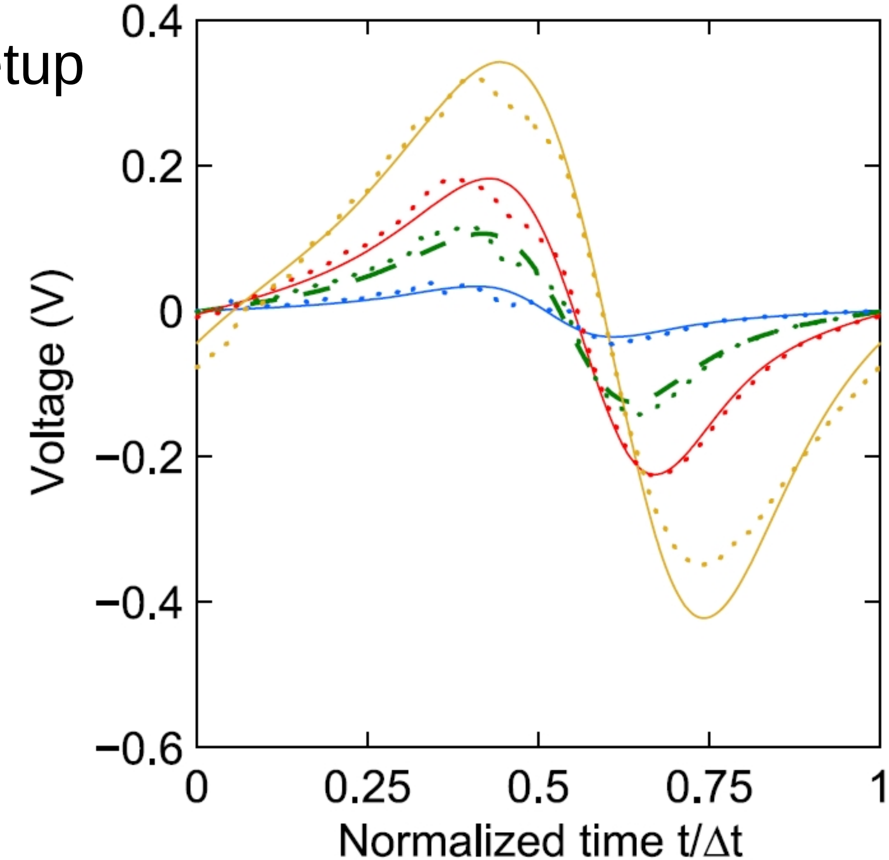
Example:
C_{max} = 200 pF; f = 100 Hz; V_{bi} = 3 V; C_{max}/C_{min} = 100;

→ P_{idealQ} ~ 50 uW

Experimental test

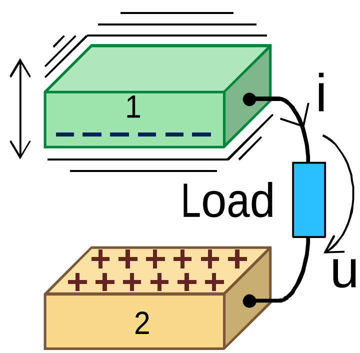
- Macroscopic variable capacitance setup
- Resistive load
- Driven with a motor
- V_{bi} = 1.03 V
- Metallic plates

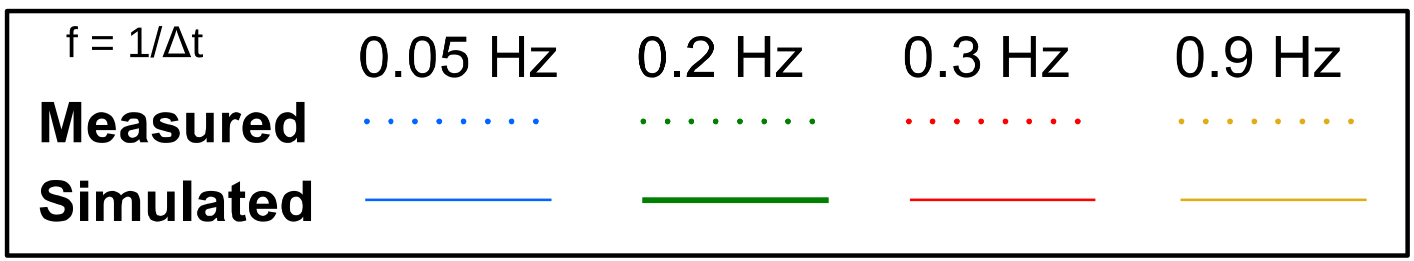
  (V_{bi} close to E_g of Si)



Dynamical equation with resistive load:

$$\frac{du}{dt}C + u\left(\frac{dC}{dt} + \frac{1}{R}\right) = V_{bi}\frac{dC}{dt}$$





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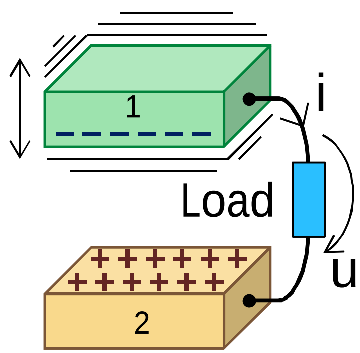
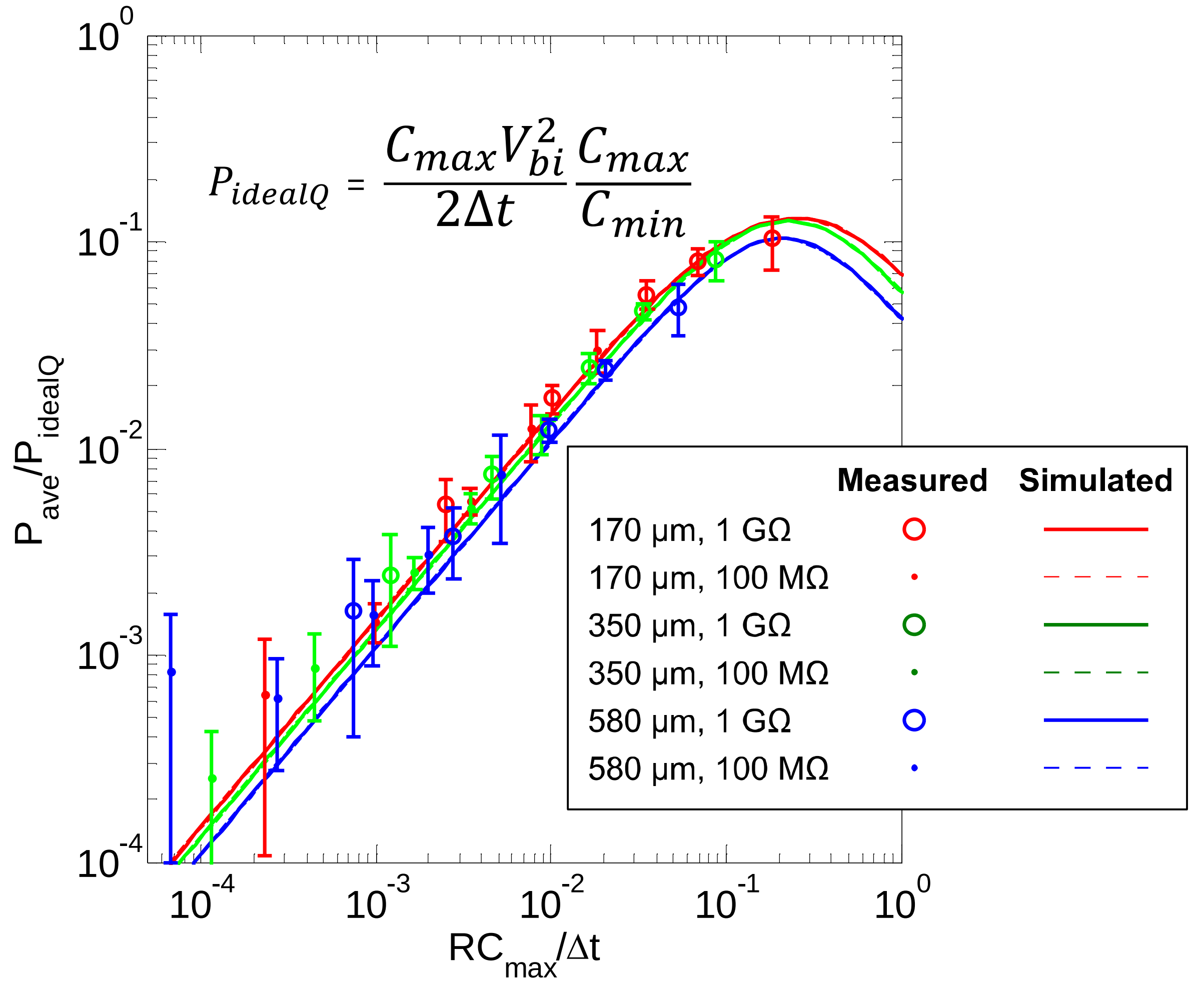


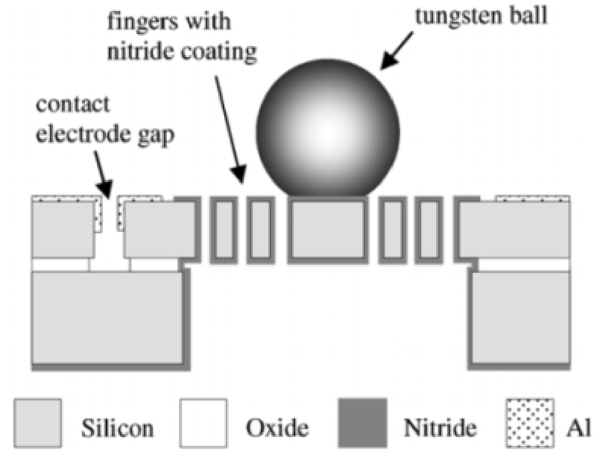


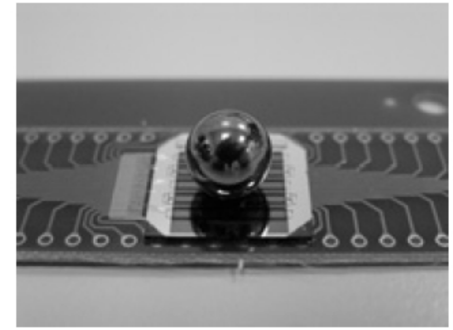
Normalized output power as a function of normalized frequency

A. Varpula, S. J. Laakso, T. Havia, J. Kyynäräinen, M. Prunnila, Sci. Rep. 4, 6799 (2014).

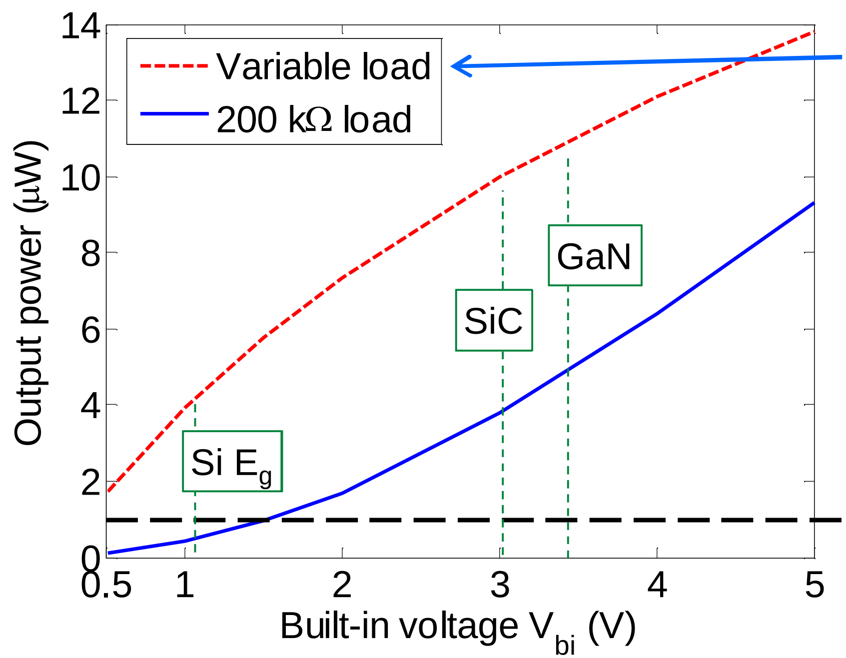
MEMS work-function energy harvester

- Performance of MEMS work-function energy harvester by simulations
- Device geometry and mechanical parameters from existing electrostatic MEMS harvester [1]





Excitation 32.5 m/s²
At 1868 Hz
(close to the resonance)



Switching Operation (off-state 50 GΩ, on-state 10 Ω)

Measured output power of the electrostatic MEMS device:
1.2 μW with 9 V voltage source [1]

Simulated output power of MEMS work-function energy harvester

[1] Y. Chiu, V. F. G. Tseng, J. Micromech. Microeng. 18, 104004 (2008)

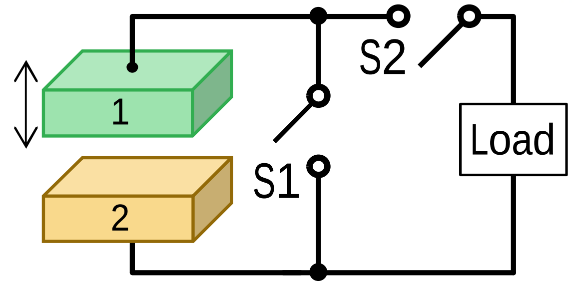
A. Varpula, S. J. Laakso, T. Havia, J. Kyynäräinen, M. Prunnila, Sci. Rep. 4, 6799 (2014).

Power enhancement by advanced device schemes

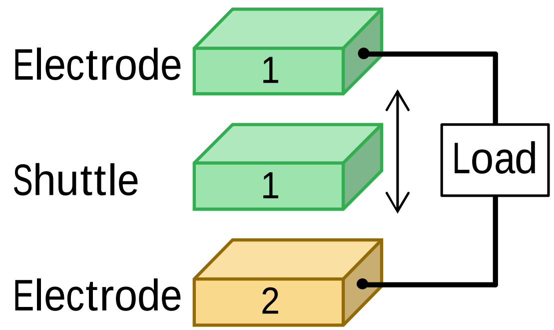
➢ **Output power can be enhanced by using**

1. External switches
2. Charge shuttle mode
3. Contacting mode operation

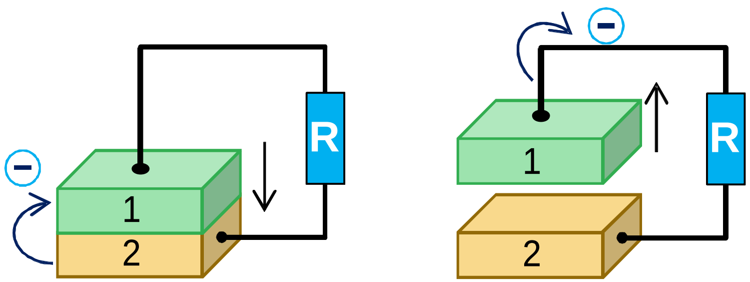
Note: 2 & 3 are impossible with battery driven electrostatic harvester



1. Work-function energy harvester using external switches



2. Work-function energy harvester using a charge shuttle



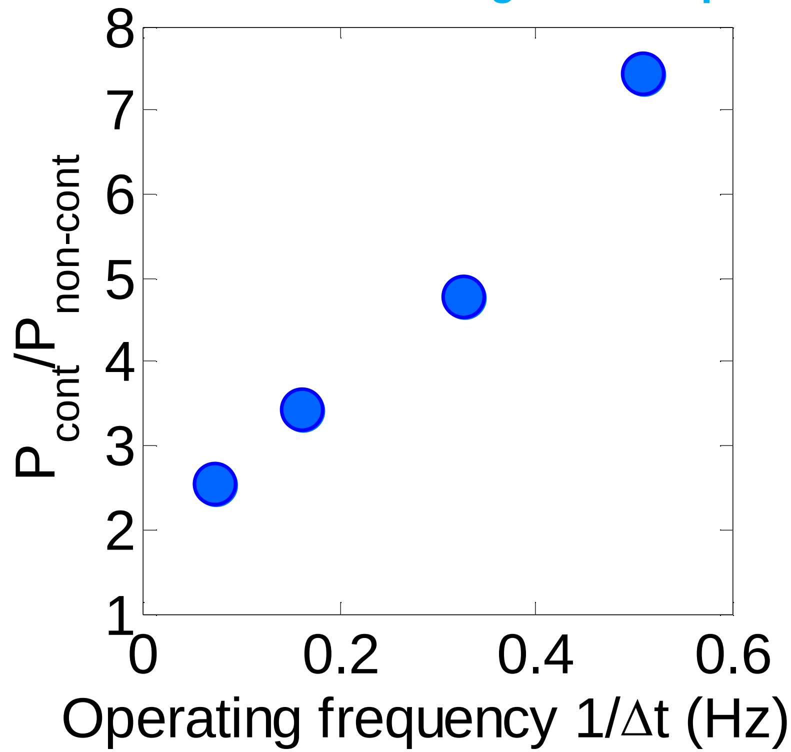
3. Work-function energy harvester operated in contacting mode

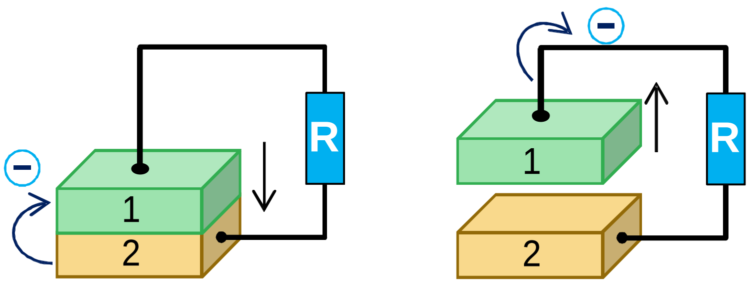
A. Varpula, S. J. Laakso, T. Havia, J. Kyynäräinen, M. Prunnila, Sci. Rep. 4, 6799 (2014).

Contacting mode operation

Macroscopic moving plate device

Over 7× enhancement in power
In the contacting mode experiment





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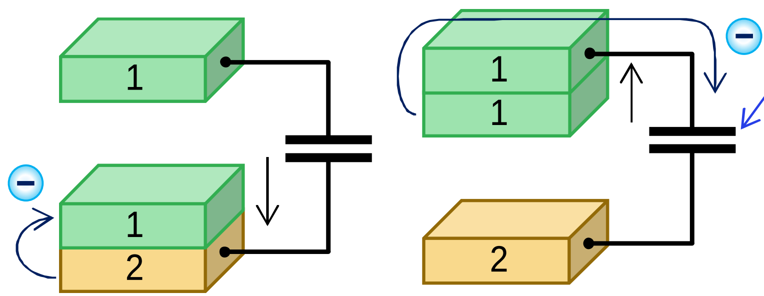
Contacting mode operation

Shuttle with a storage

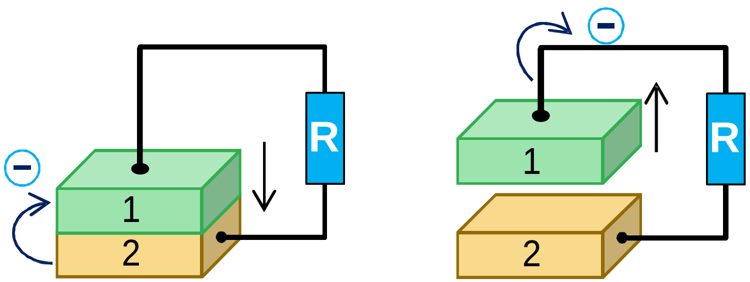
e.g. supercapacitor



Charging of shuttle

Charge flow to storage

A. Varpula, S. J. Laakso, T. Havia, J. Kyynäräinen, M. Prunnila, Sci. Rep. 4, 6799 (2014).



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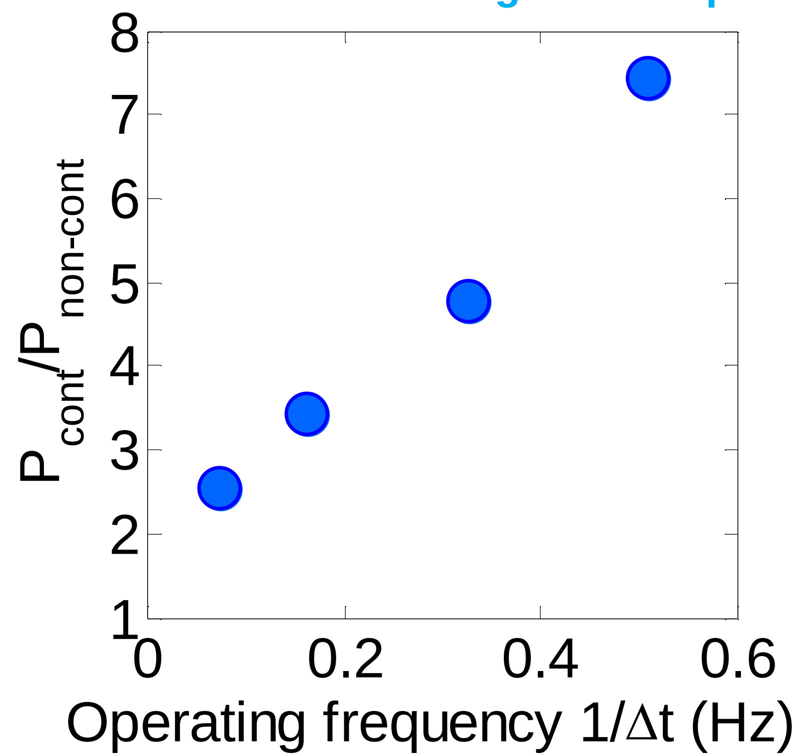

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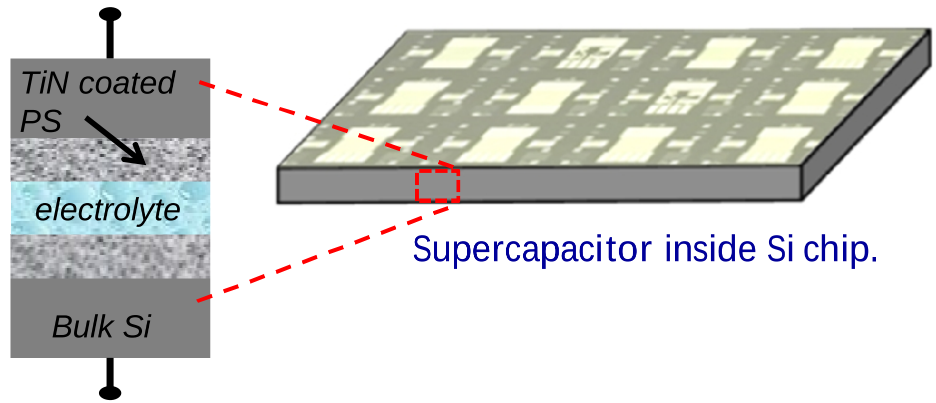
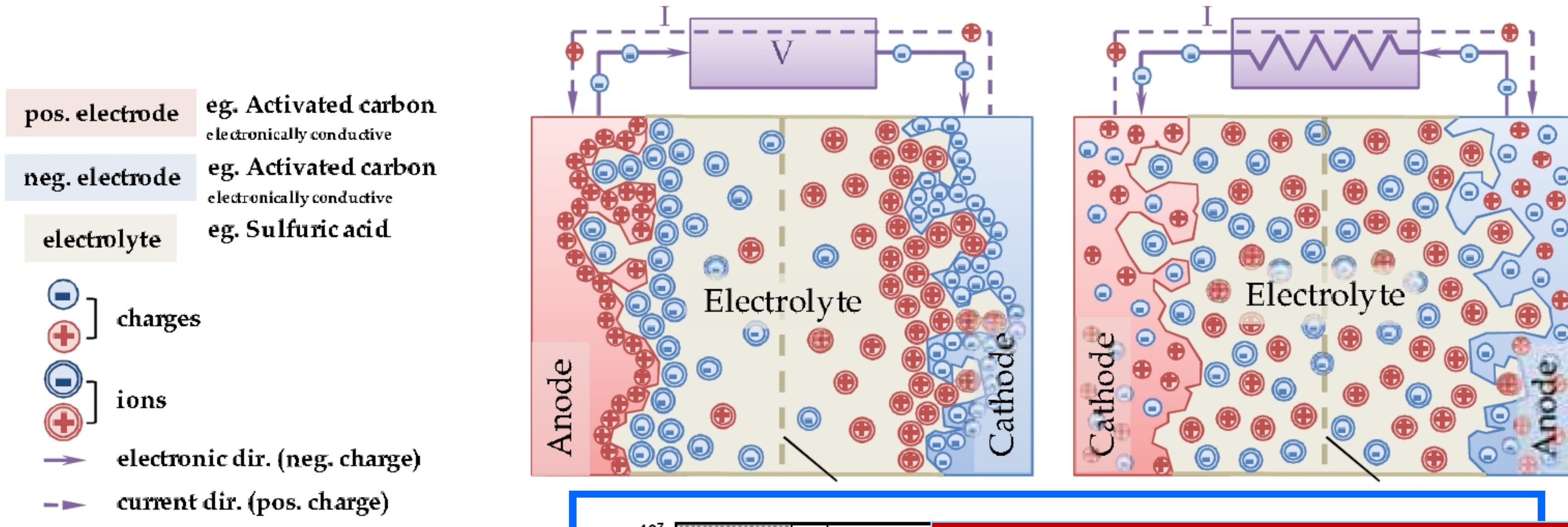
2. TiN coated porous silicon electrodes for supercapacitors

- Material performance
- On-chip Integration

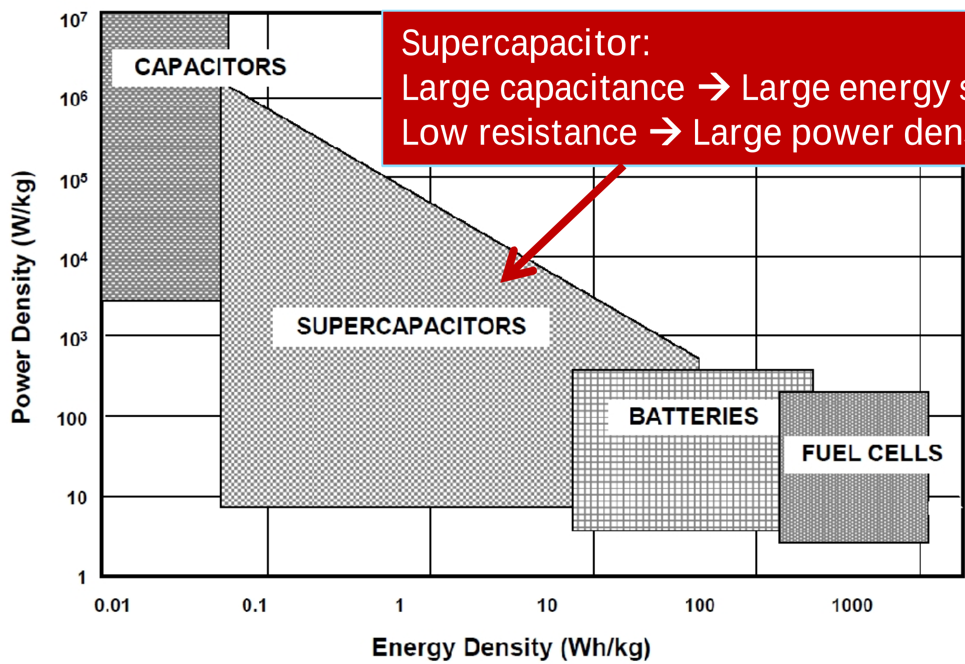


Supercapacitor inside Si chip.

Supercapacitor



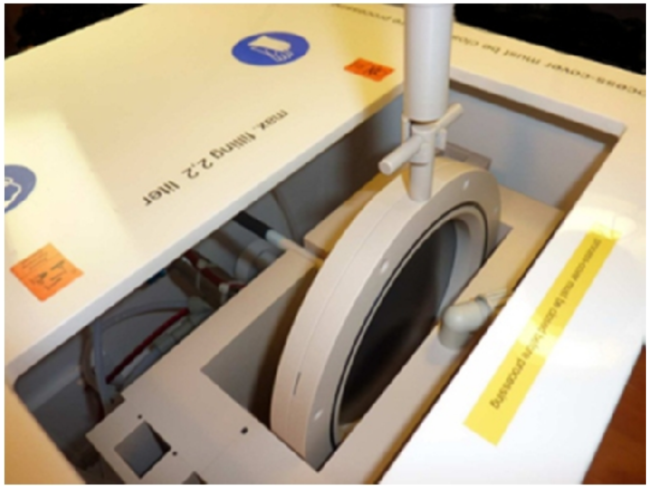
P. Jampani et al, Interface, Fall 2010, p.57



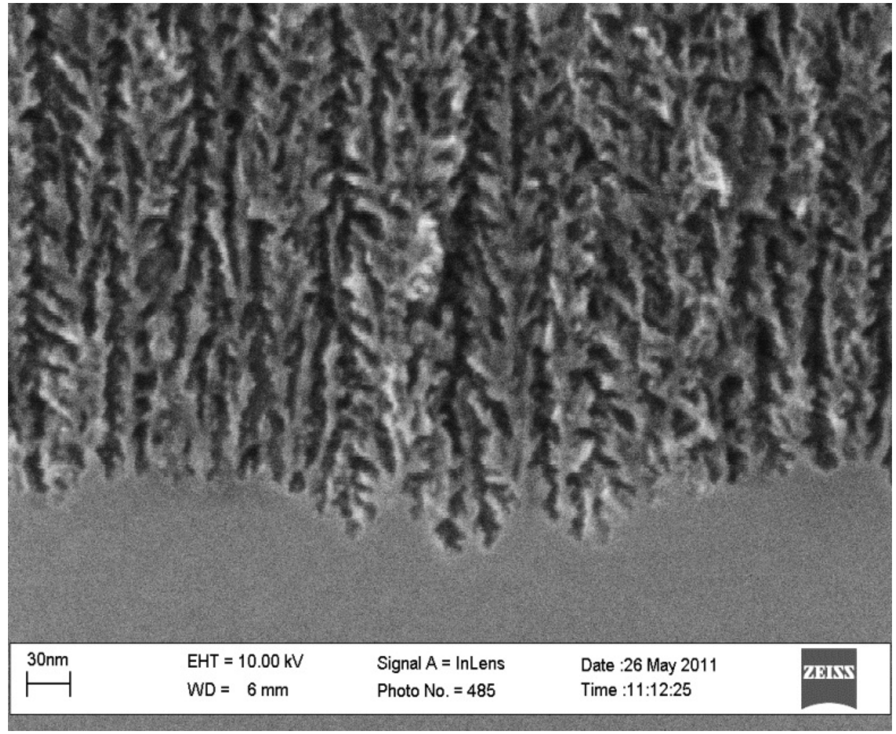
Supercapacitor:
Large capacitance → Large energy storage density!
Low resistance → Large power density!

Kotz, R. and M. Carlen Electrochimica Acta 45 2483-2498 (2000).

Porous silicon (PS)



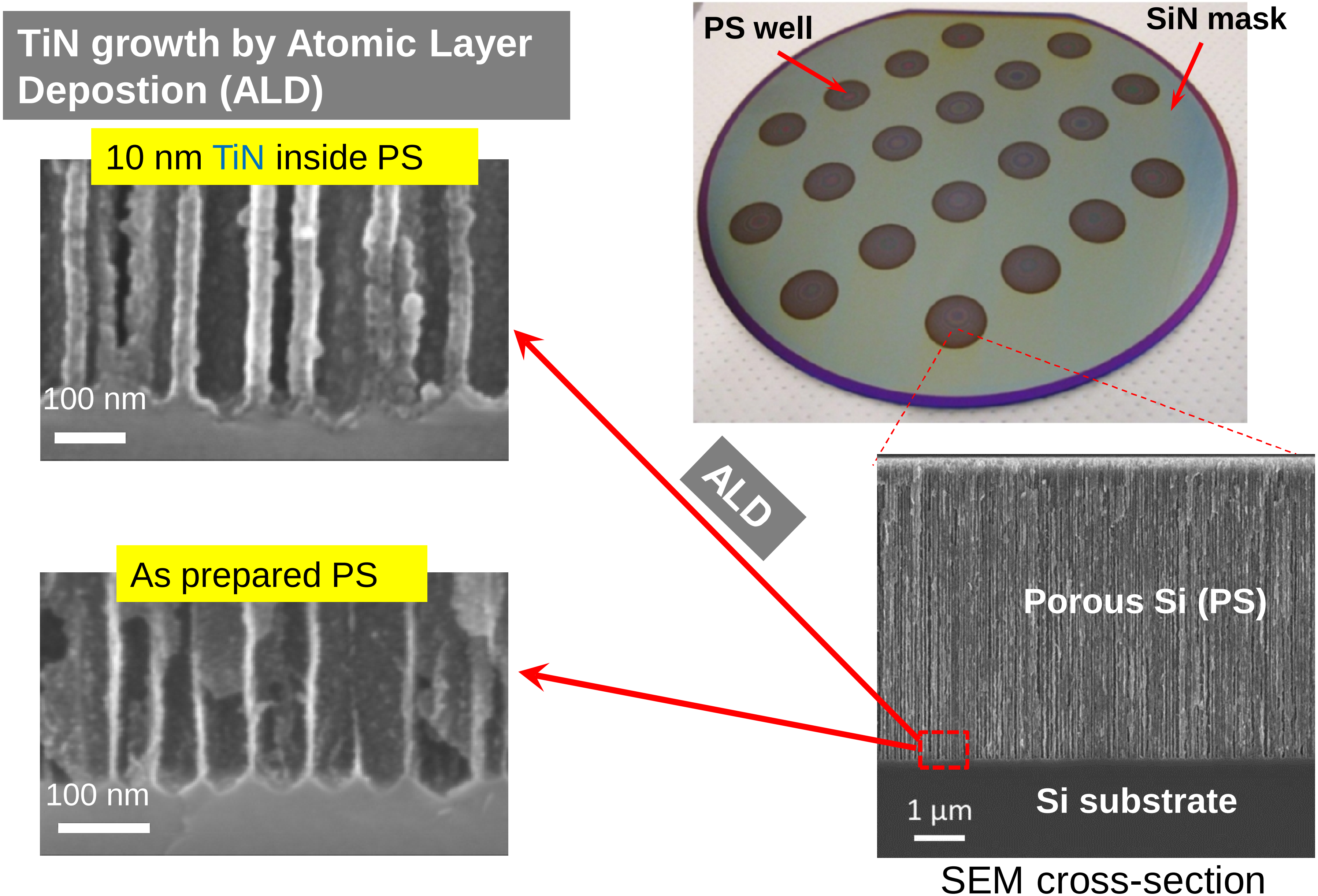
AMMT equipment.



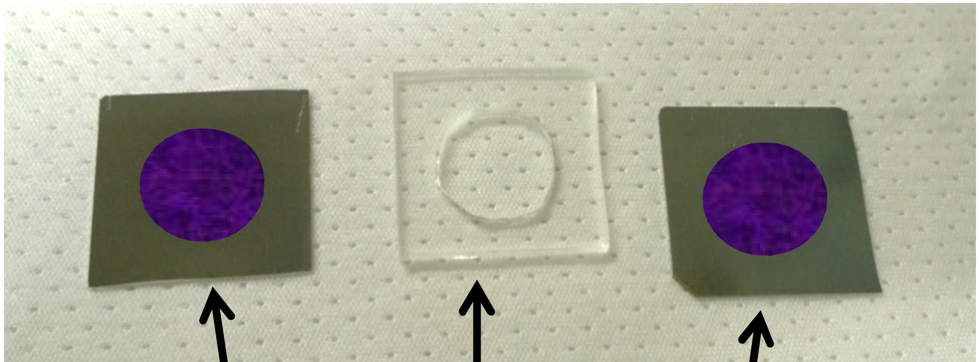
Electrochemical etching of bulk silicon

Big surface area: reaching 500 m^2/cm^3

Preparation of porous Si test structures

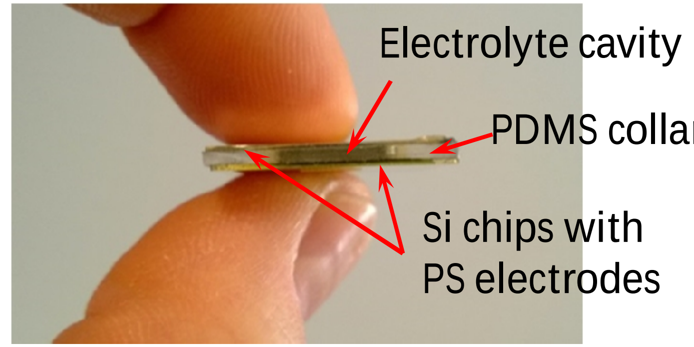


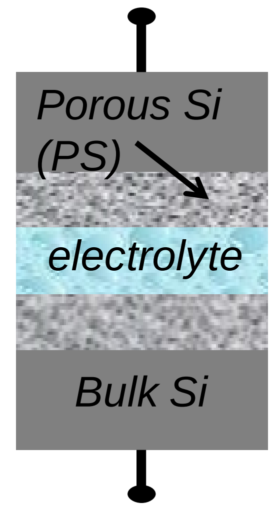
Material test bench for PS supercapacitors



PDMS collar

PS electrodes (with and without TiN coating)

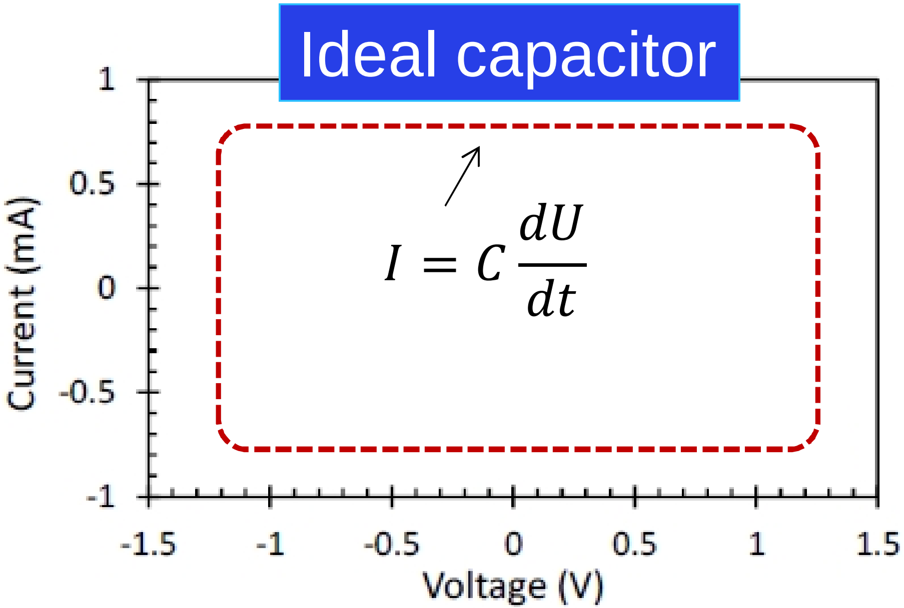


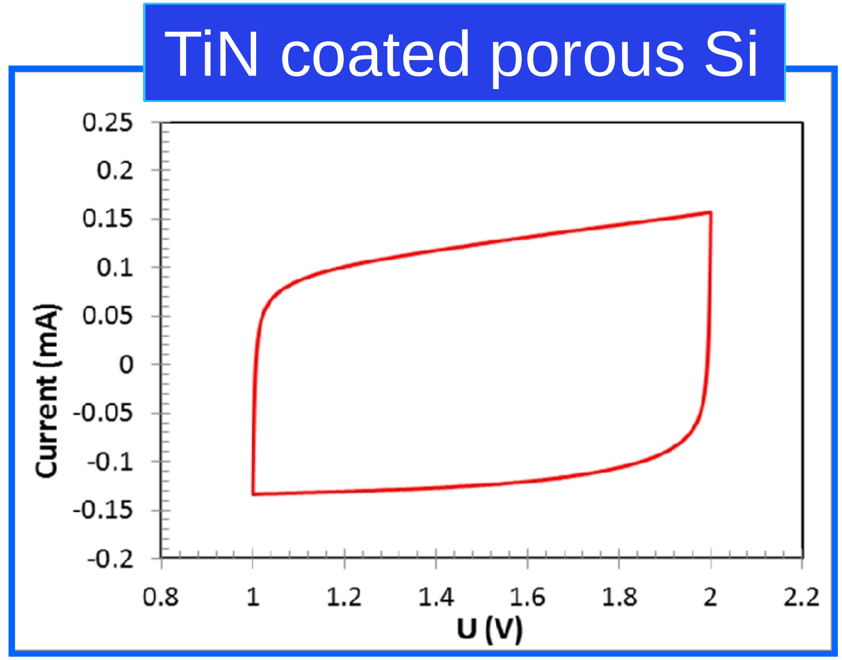


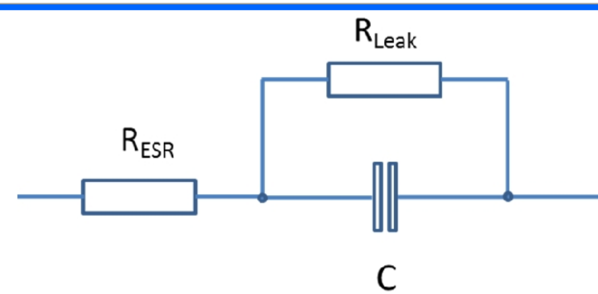
Electrolytes

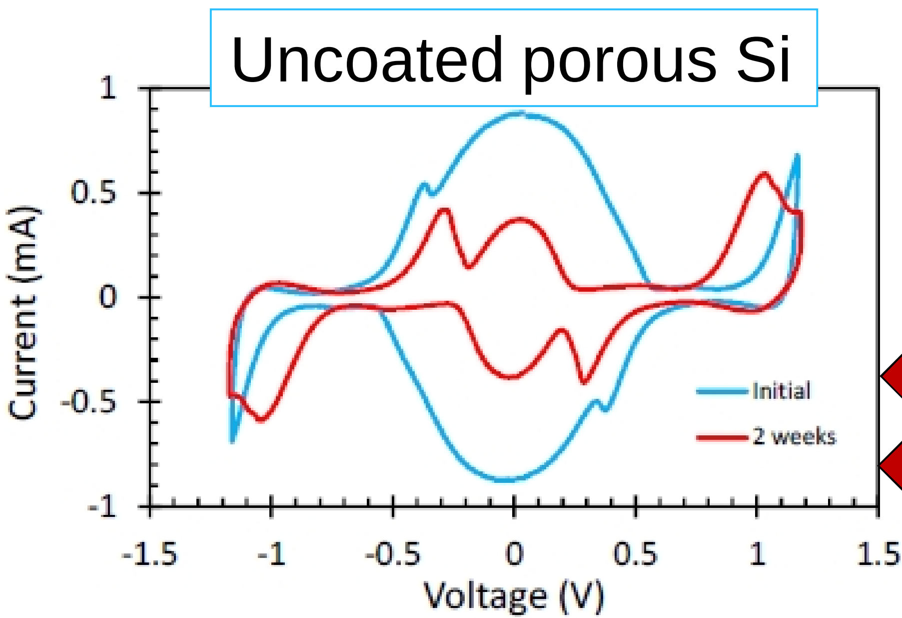
- Aqueous: 1 M NaCl water solution
- Organic: 0.5 M TEABF4 in PC (tetraethyl ammonium tetrafluoroborate in propylene carbonate)

Characterization: cyclic voltametry (CV)









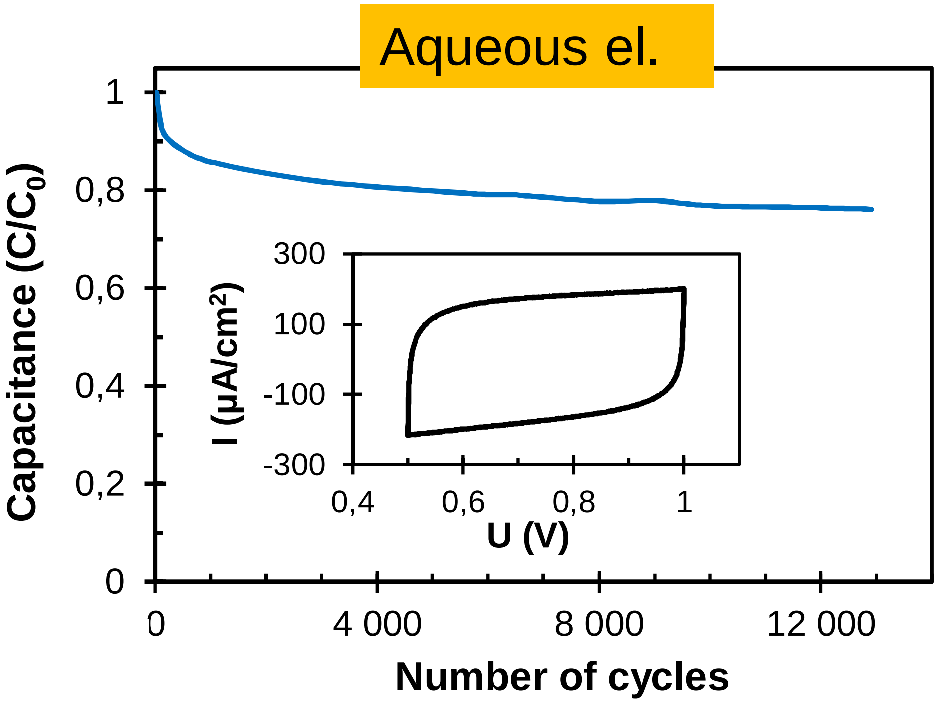
Problems due to:

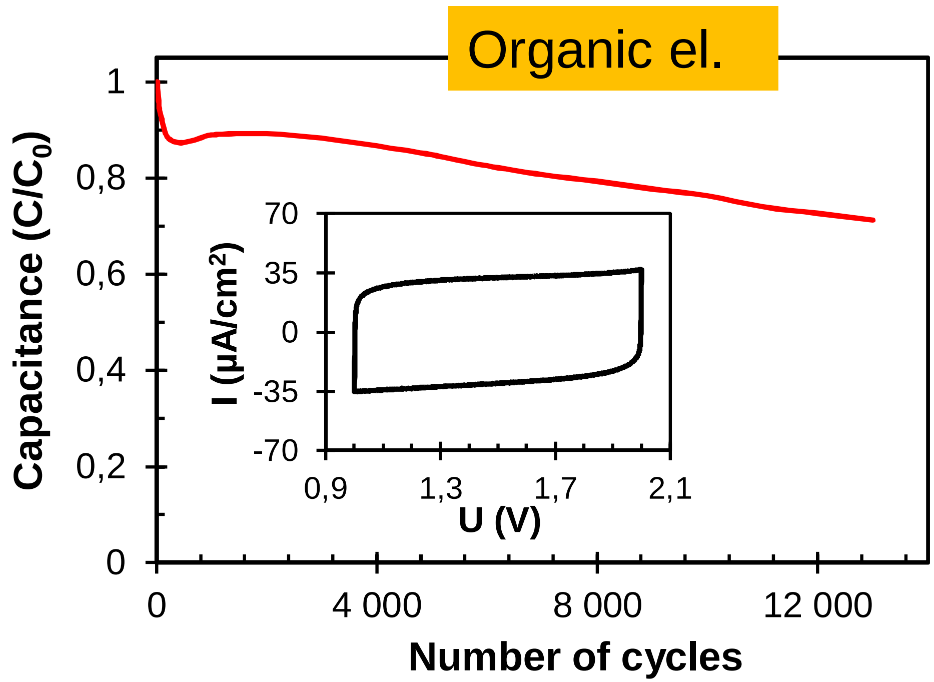
- High resistance of Si nanostrutures
- Chemical reactions

Characterization: cyclic voltametry (CV) & retention

TiN coated porous Si

Capacitance retention during 13 000 cycles

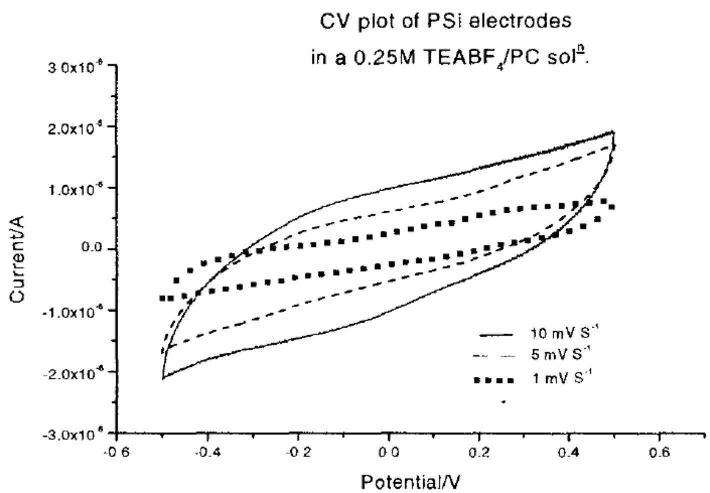




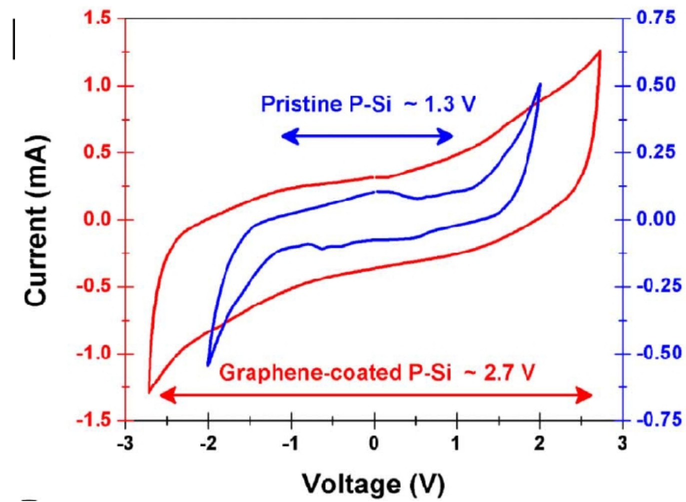
K. Grigoras, J. Keskinen, L. Grönberg, E. Yli-Rantala, S. J. Laakso, H. Välimäki, P. Kauranen, J. Ahopelto, M. Prunnila, arXiv:1603.00798 & Nano Energy, *in print* (2016).

Comparison with other results on porous Si

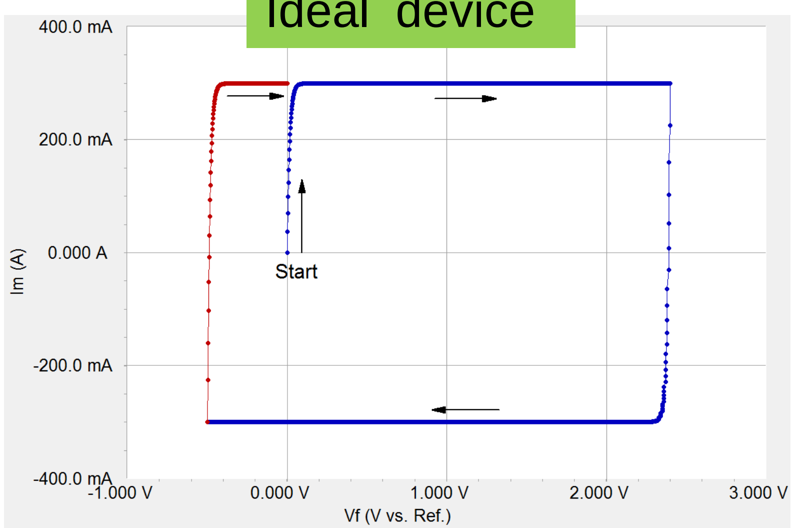
S. Rowlands et al, Ionics 5, p.144 (1999)



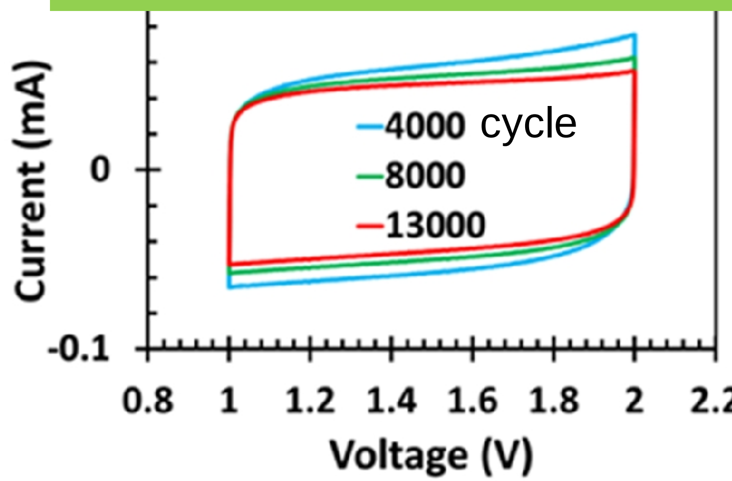
L.Oakes et al, Sci.Rep. **3** 3020 (2013)



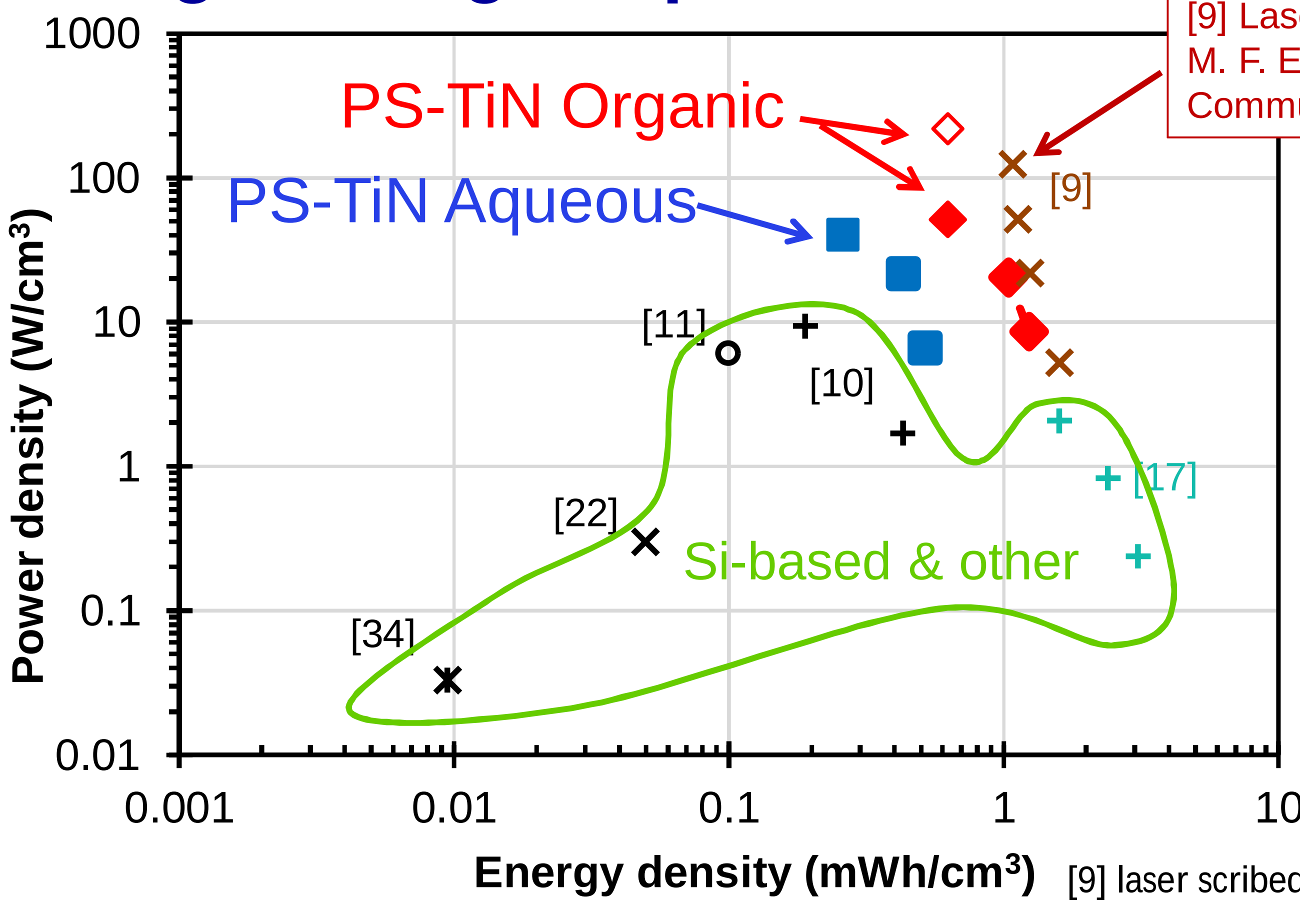
Ideal device



2014: Our TiN coated device



Comparison with other micro supercapacitor technologies: Ragone plot

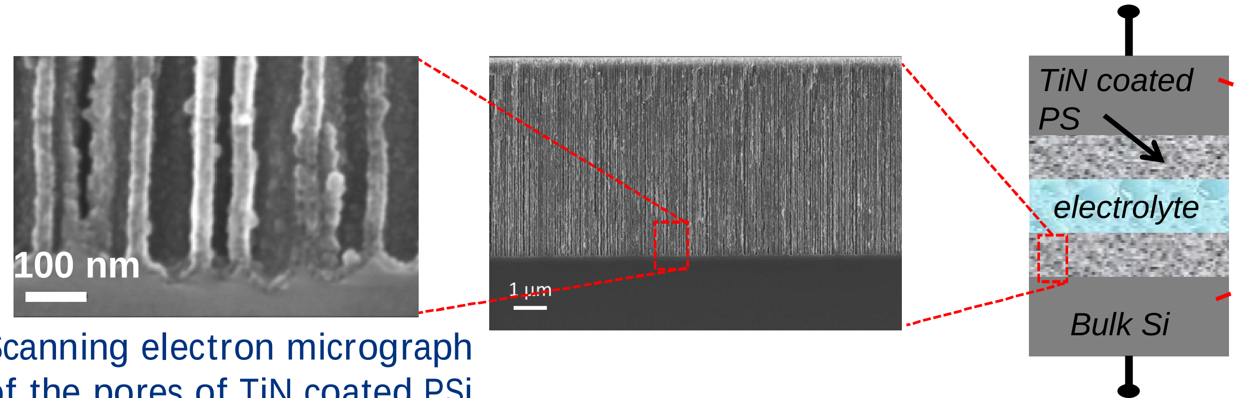


[9] Laser scribed graphene oxide: M. F. El-Kady, R. B. Kaner, Nat. Commun. 4 (2013) 1475.

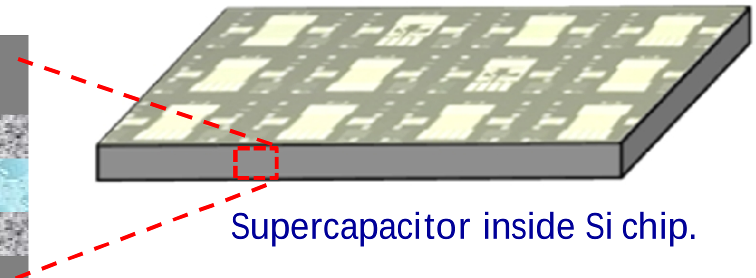
[9] laser scribed graphene oxide
[10] laser written hydrated graphene oxide
[11] graphitization of silicon carbide
[17] graphene coated porous silicon
[22] carbon fabrics with TiN nanowires
[34] silicon carbide nanowires

K. Grigoras, J. Keskinen, L. Grönberg, E. Yli-Rantala, S. J. Laakso, H. Välimäki, P. Kauranen, J. Ahopelto, M. Prunnila, arXiv:1603.00798 & Nano Energy, *in print* (2016).

Integration of TiN coated PS supercapacitors

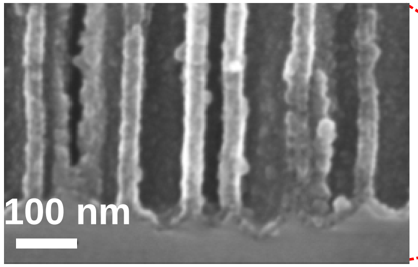


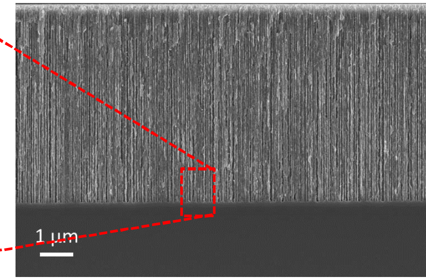
Scanning electron micrograph of the pores of TiN coated PSi supercapacitor.



Supercapacitor inside Si chip.

Integration of TiN coated PS supercapacitors





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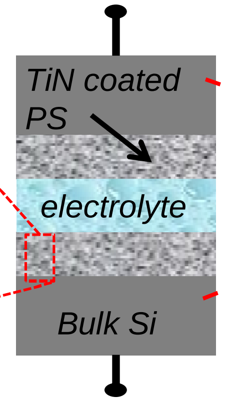
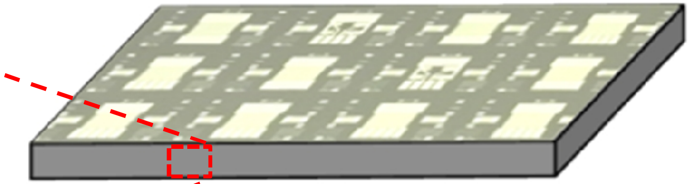
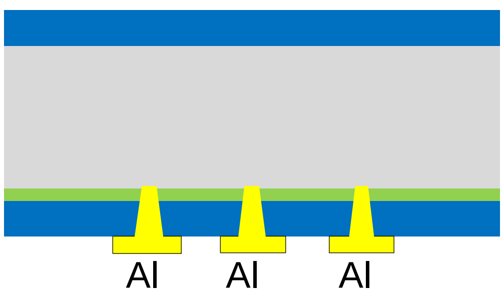
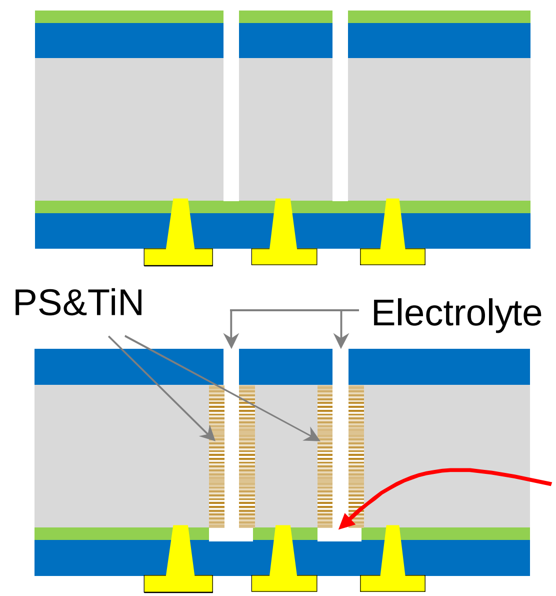




Supercapacitor inside Si chip.

The in-chip supercapacitor





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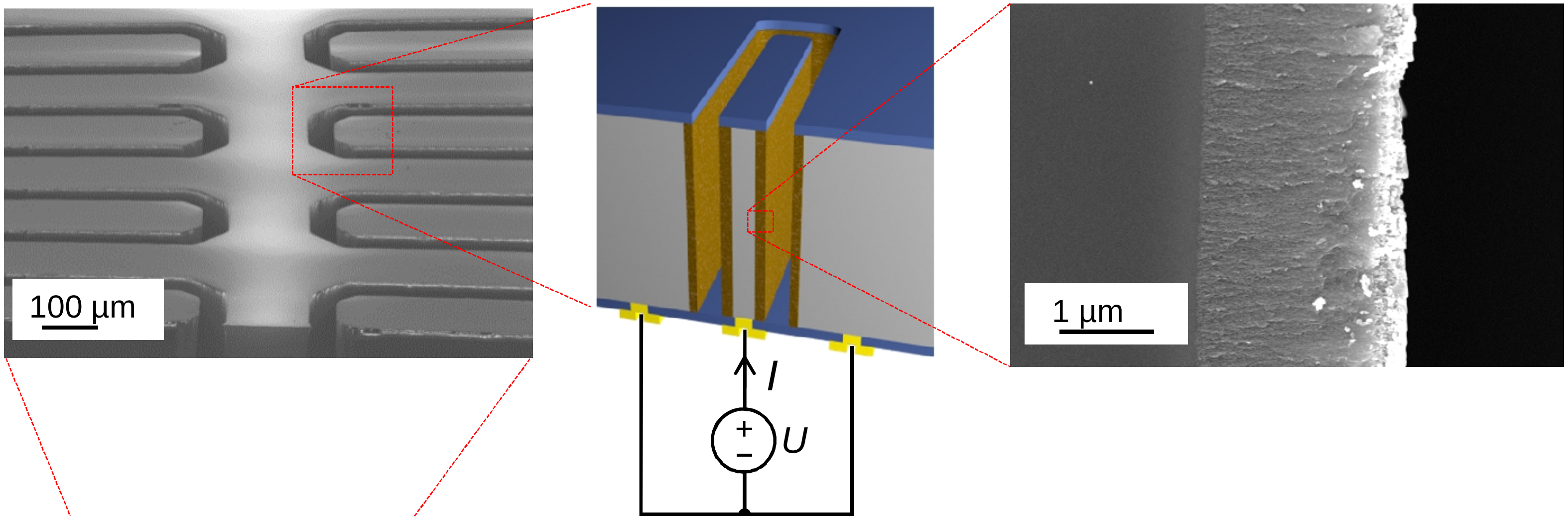
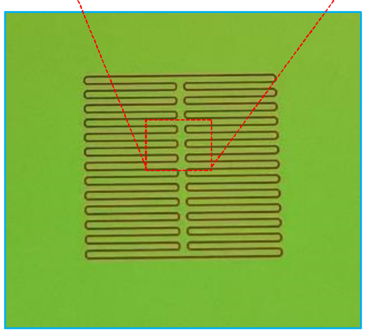
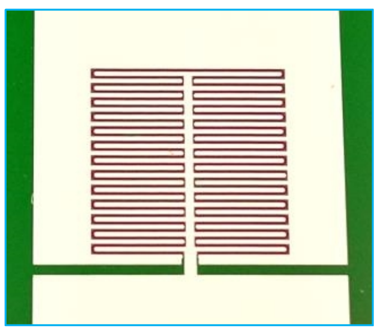
The in-chip supercapacitor





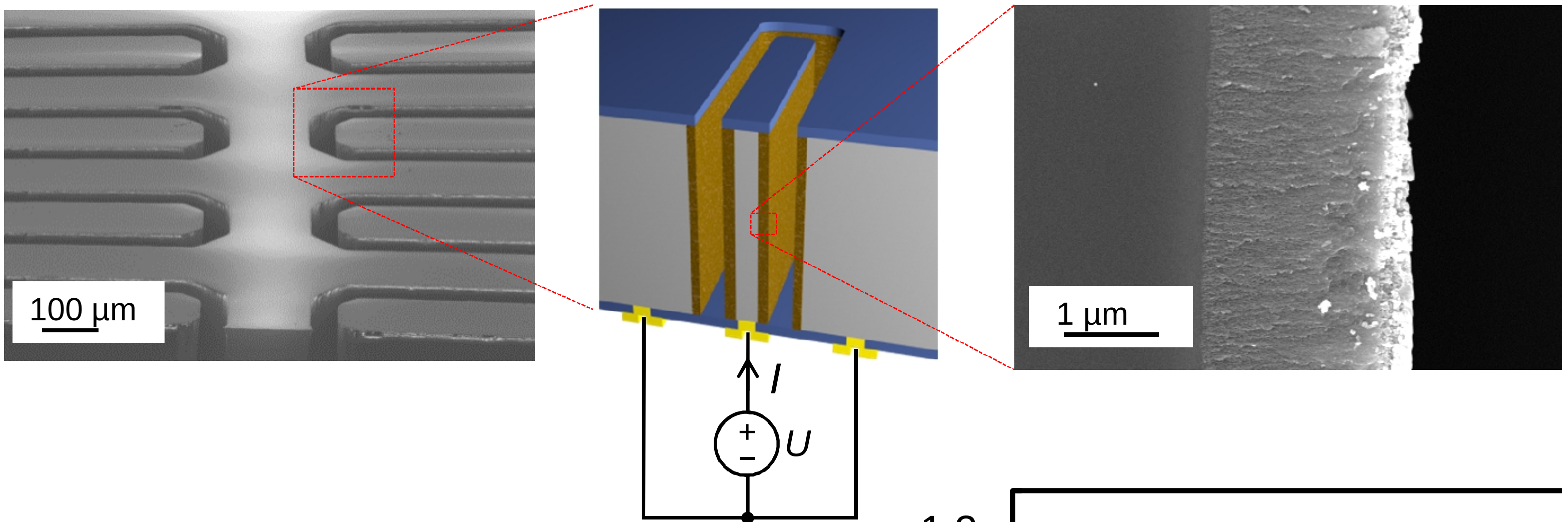
Electrolyte via side

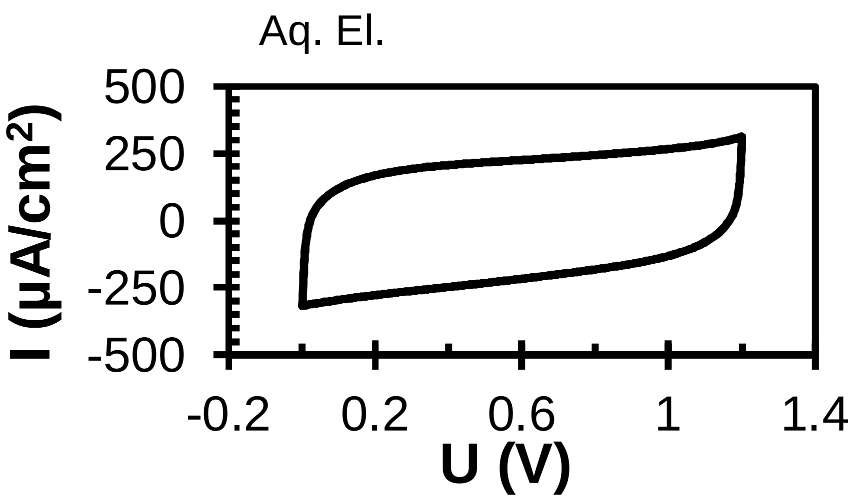


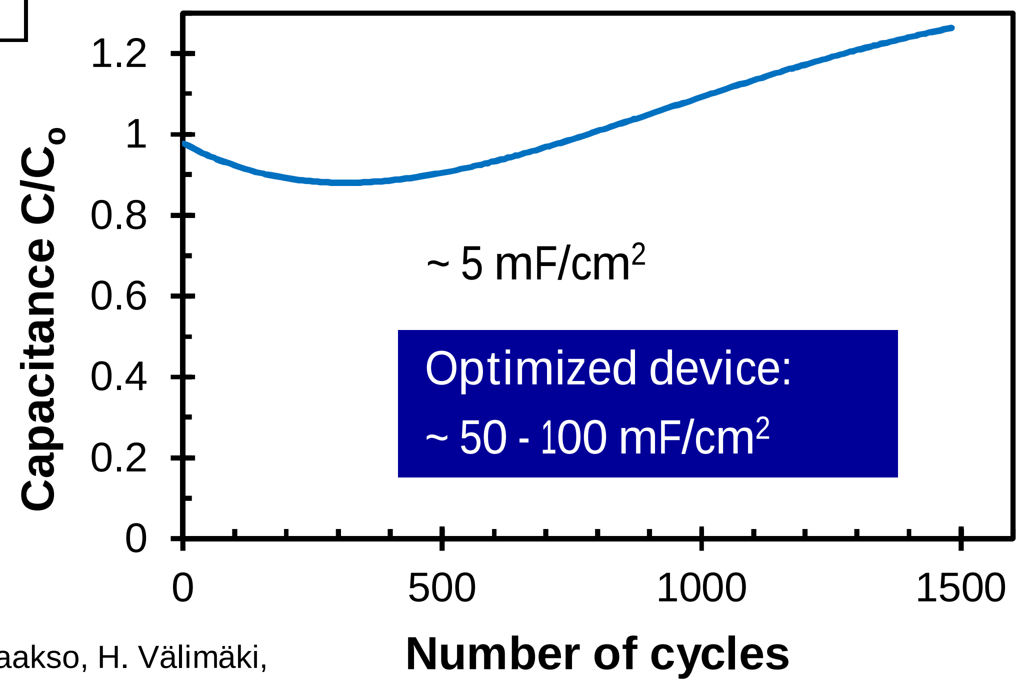
Metal side

K. Grigoras, J. Keskinen, L. Grönberg, E. Yli-Rantala, S. J. Laakso, H. Välimäki,
P. Kauranen, J. Ahopelto, M. Prunnila, arXiv:1603.00798 & Nano Energy, *in print* (2016).

The in-chip supercapacitor







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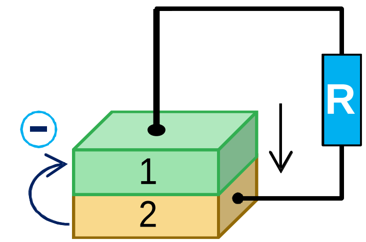
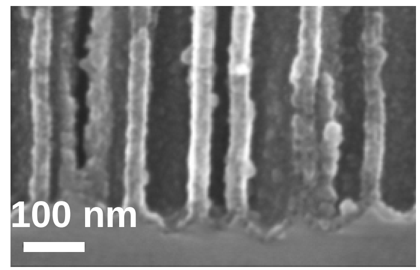
Summary

Work function energy harvester

- A capacitive vibration energy harvester which does not require battery or electrets
- Semiconductors can be directly used as the active electrodes
- Can outperform electrostatic harvesters

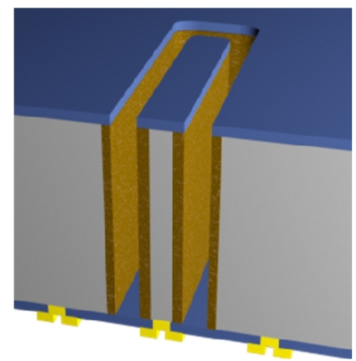


Further details:
A. Varpula, S. J. Laakso, T. Havia, J. Kyynäräinen, M. Prunnila, Sci. Rep. **4**, 6799 (2014).
A. Varpula, S. J. Laakso, T. Havia, J. Kyynäräinen, M. Prunnila, J. Phys: Conf. Series **557** 012010 (2014).



TiN coated porous Si supercapacitors

- TiN coating of porous Si by ALD enables high performance microsupercapacitor electrodes
- This technology has enabled the in-chip supercapacitor



Further details:
K. Grigoras, J. Keskinen, L. Grönberg, E. Yli-Rantala, S. J. Laakso, H. Välimäki, P. Kauranen, J. Ahopelto, M. Prunnila, arXiv:1603.00798 & Nano Energy, *in print* (2016).