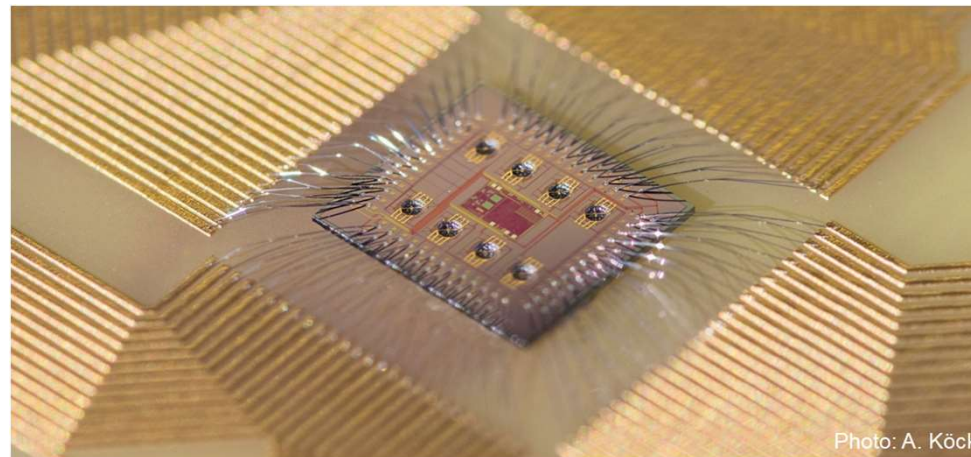


Materials-related challenges for autonomous sensor nodes



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**anton.koeck@mcl.at



- Wireless Sensor Networks for the Internet of Things (IoT)
- Autonomous sensor nodes
- Strategies to realise energy autonomy
 - Low-power gas sensors
 - Broadband piezoelectric harvesters
 - High-energy density dielectric capacitors
- Integration possibilities

Some definitions...



Digitalisation

converting information to a digital format and **making it available**

improving business procedures (*digital revolution*)

<https://workingmouse.com.au> <https://en.wikipedia.org>

Internet-of-Things (IoT)

network of physical devices that enables them to connect and exchange data

realising intelligent (smart) operation

Smart home

Smart cities

Smart vehicle

Smart industry
(*Industry 4.0*)

Sensors

Actuators

CPU

Network

Power supply



Smart device or system

system capable of analysing the environment and performing intelligent action on the environment.

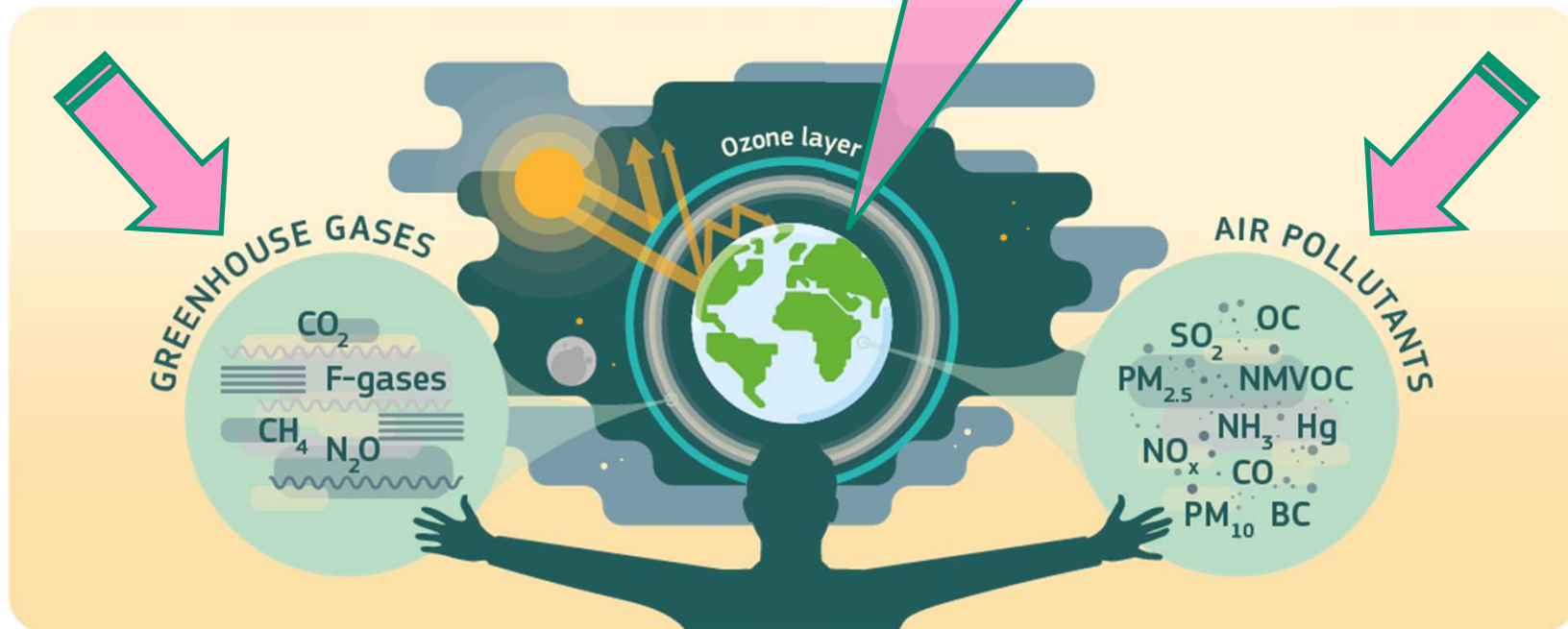
Environmental monitoring



EDGAR The Emissions Database
for Global Atmospheric Research

Mapping human emissions on Earth

We have to monitor
all emissions !

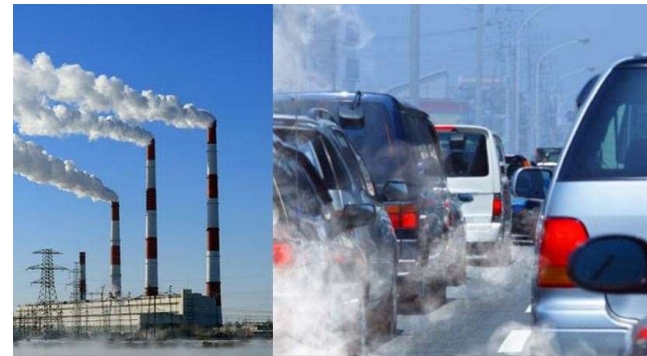


Source: The Emissions Database for Global Atmospheric Research (EDGAR):
<http://edgar.jrc.ec.europa.eu>

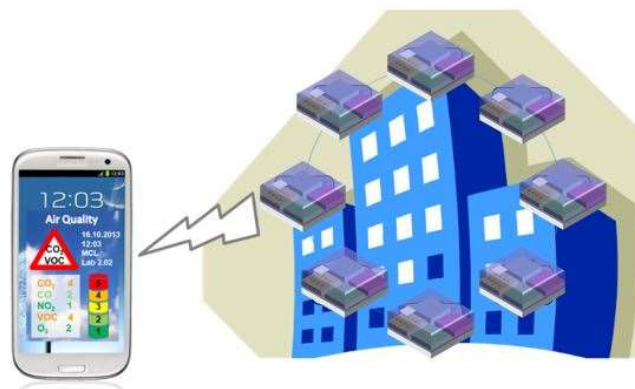
Indoor and outdoor air quality monitoring



Indoors
CO, CO₂, VOCs, PM



Outdoors
NO₂, O₃, CO, PM₁₀, PM_{2.5}, UFPs

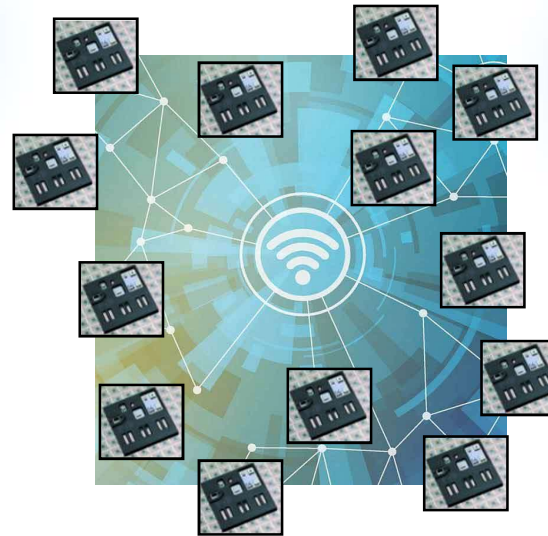


SENSOR NETWORKS
ENABLING AUTOMATIC
CONTROL AND
REGULATION

Wireless Sensor Networks



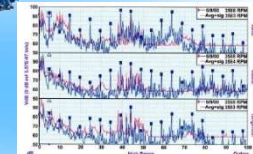
Air quality monitoring



Structural health monitoring



Condition monitoring



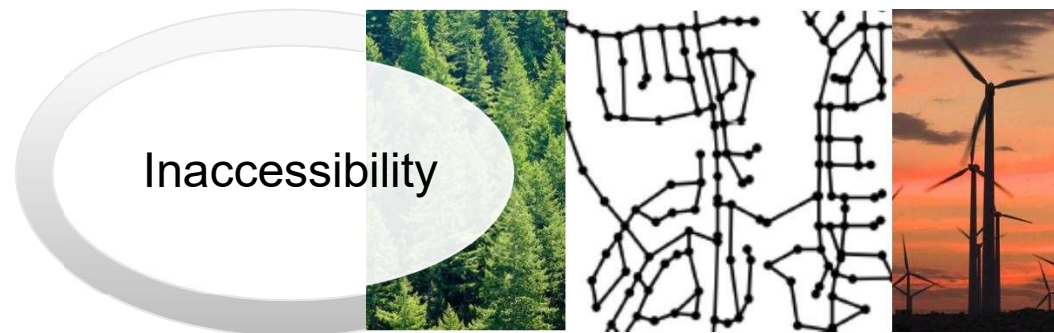
Predictive maintenance



Industry 4.0

Realising GHG emission reduction goals

Challenges for sensor networks

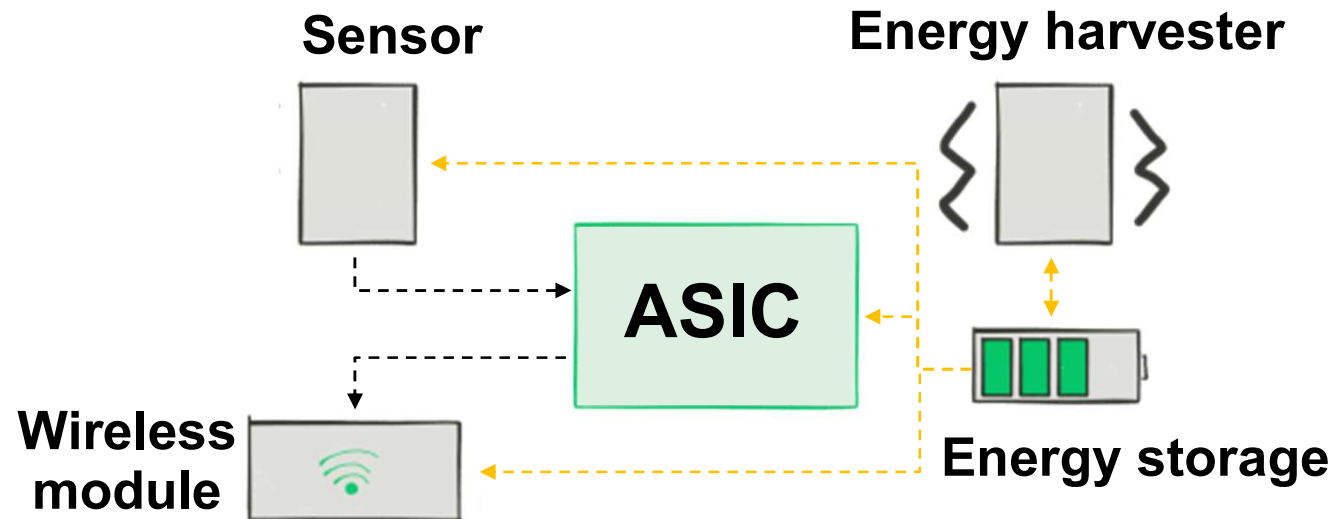


↓ Device footprint ↑ Energy efficiency

Miniaturised self-powered (energy autonomous) sensor nodes



Self-powered wireless sensor nodes



ENERGY CONSUMPTION	CMOS gas sensor: 144 J/d	Temperature sensor: 0.47 J/d
	Self-heating gas sensor: 0.14 J/d	Vibration sensor: 0.6 J/d
	ASIC/RFID (1 read/minute, ≤ 10 m transmission distance): < 0.1 J/d	

ENERGY GENERATION	Photovoltaic harvester: 2.9 kJ/d	Thermoelectric harvester: 5.2 J/d
	Piezoelectric vibration harvester: ~0.9 J/d	

ENERGY STORAGE	Ceramic multilayer capacitor: $2.5 \cdot 10^{-4}$ J/cycle	Supercapacitor: $2 \cdot 10^{-2}$ J/cycle
	Thin film multilayer capacitor: $2.5 \cdot 10^{-2}$ J/cycle	

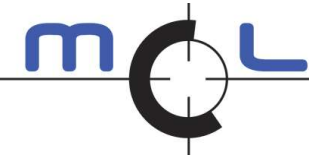
Q. Wang et al., IEEE Explore, DOI: [10.1109/SAHCN.2006.288433](https://doi.org/10.1109/SAHCN.2006.288433) (2007)

M. S. Mahmoud et al., Adv. Inter. Th. 6, 19-29 (2016)

A. Baranov et al., Sens. Act. A 233, 279-289 (2015)

A. L. Gesing et al., Scientific Reports 8, 3920 (2018)

Materials-related challenges



Low power consumption

- *sensor/harvester performance*

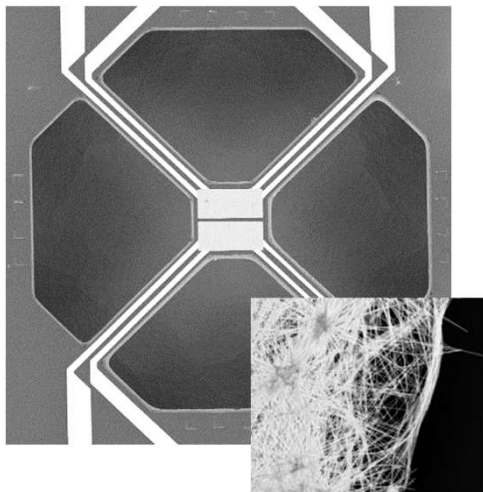
Variability of the energy source

- *harvester + storage unit perf.*

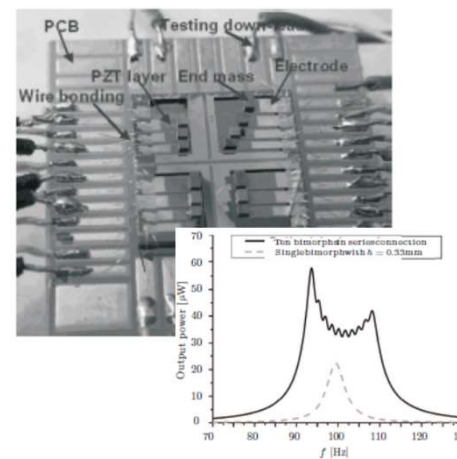
Low cost per unit

- *high-yield low-cost production*

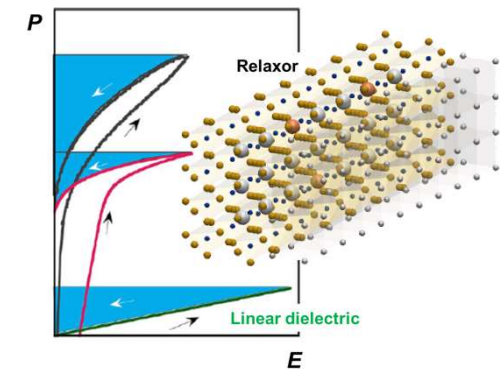
Low-power gas sensors



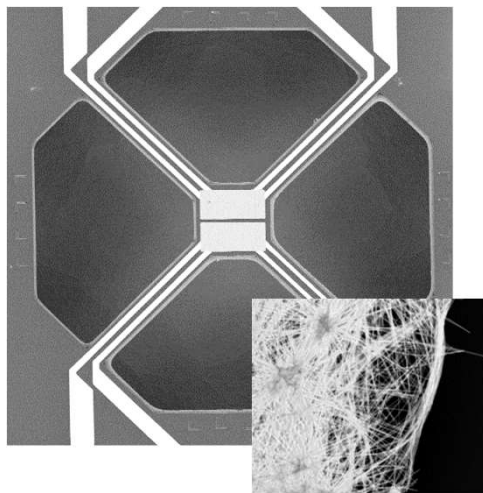
Broadband piezo-harvesters



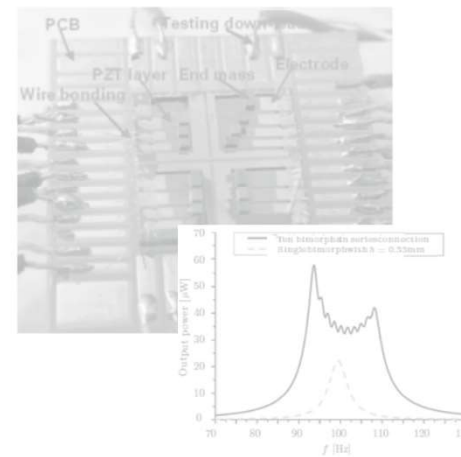
High energy-density capacitors



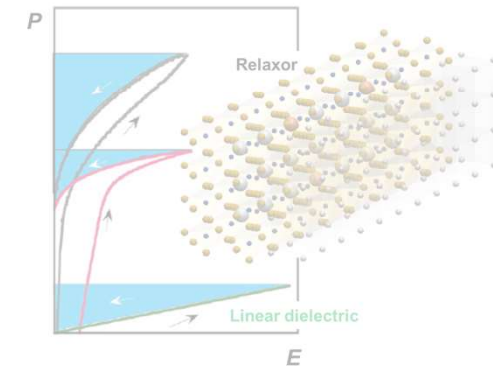
Low-power gas sensors



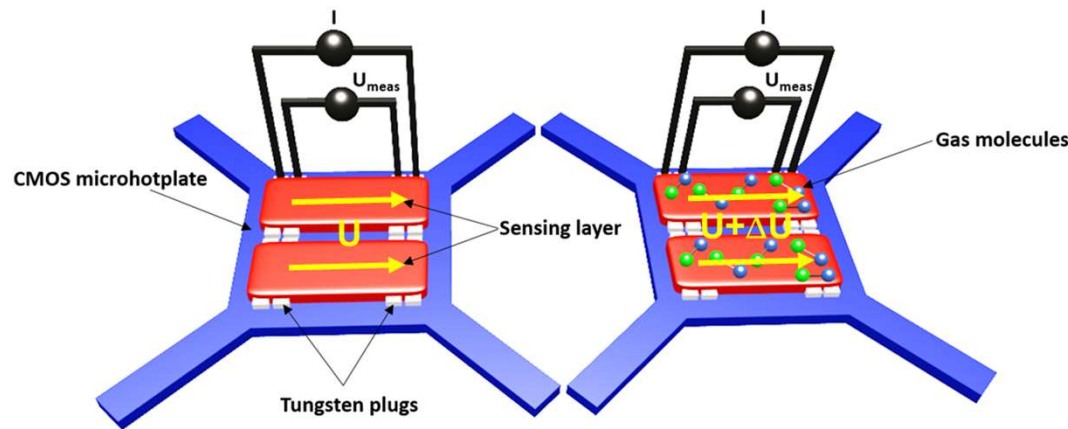
Broadband piezo-harvesters



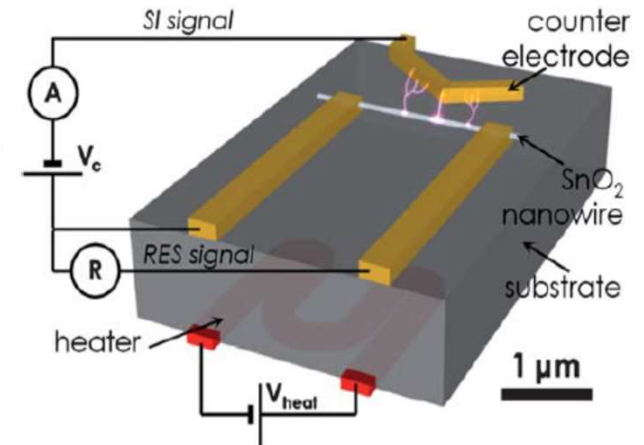
High energy-density capacitors



Conductometric (resistive)



Surface ionisation



Sensing Material

- SnO₂
- ZnO
- CuO
- WO₃

Thin films
Nanowires

Functionalising Nanoparticles

- Au, Pt, Pd
- AuPd, PdPt,...
- ZrO₂
- BaTiO₃

Target Gases

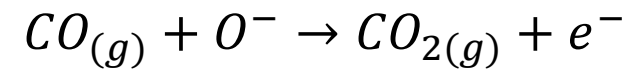
- CO
 - CO₂
 - VOCs
 - NO₂
 - H₂S
 - H₂, O₃
- Dry and humid air

Metal oxide gas sensors

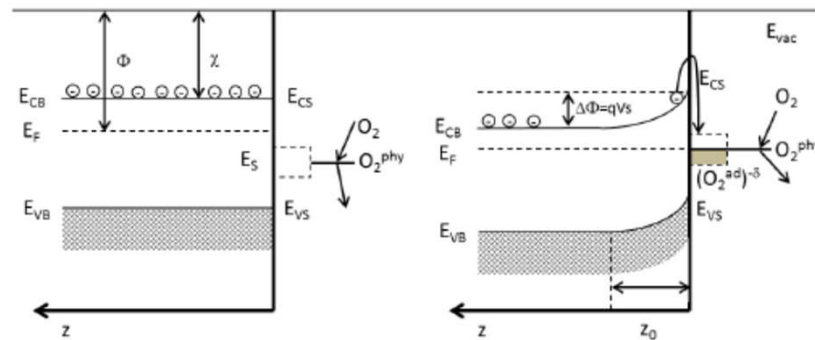


C. Wang et al., Sensors 10 (2010) 2088-2106

Conductometric Gas Sensor

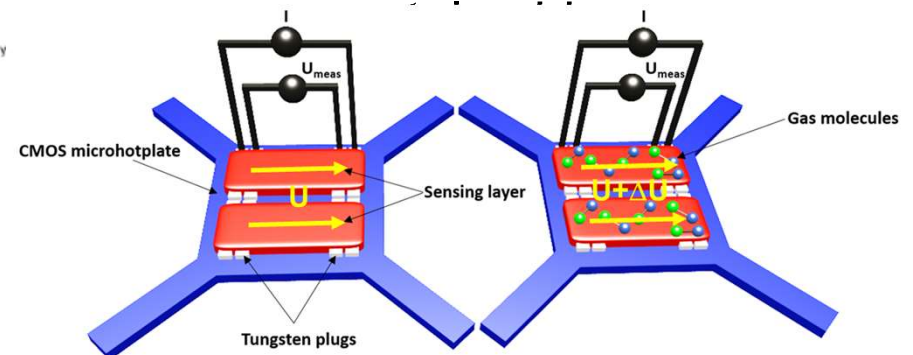


n-type



W. Göpel, Prog. Surf. Sci 20 (1985) 9-103

Reaction of gas with adsorbed O⁻ changes the resistance of the



- Optimal reaction T: 300° C – 450° C → Hotplate needed
- Decreasing particle size, surface/volume ratio of sensing surface layer increases

→ Nanocrystalline thin films and nanowires ↑ Sensitivity

- Doping with noble metal particles is beneficial

→ Catalyses the reaction with gas

→ Improves electron exchange in sensing layer

↑ Sensitivity

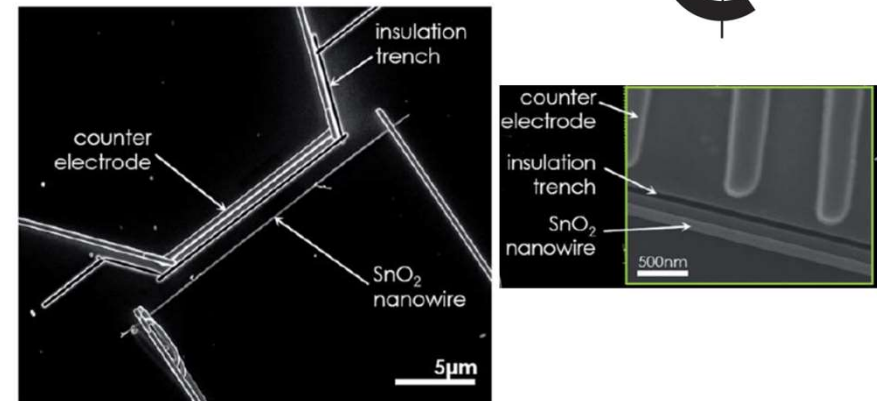
Metal oxide gas sensors



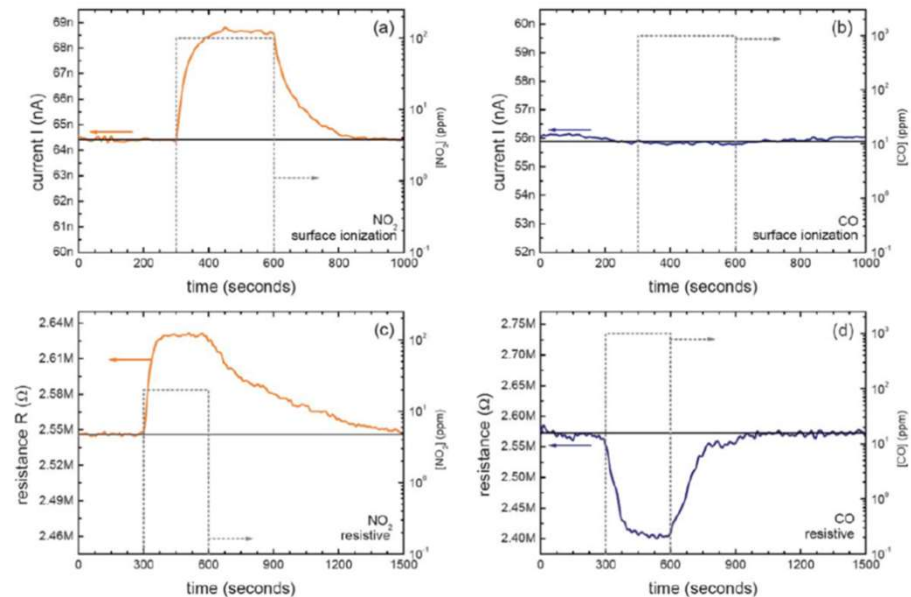
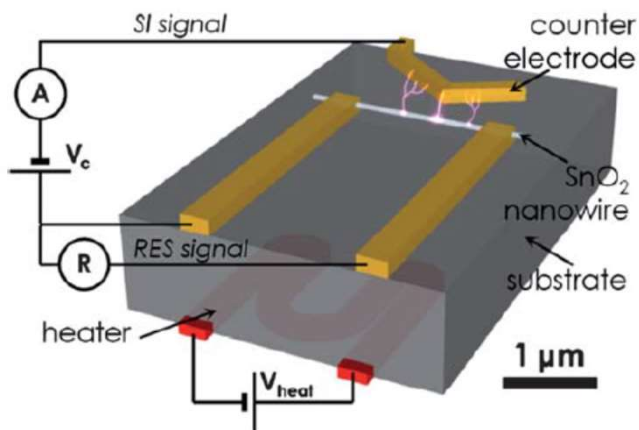
Ionisation Gas Sensor

Adsorbed gas on metal oxide extracted by ionisation applying voltage to a counter electrode

Gap: 400 nm Voltage < 1 V
E-Field > 15 kV/cm



F. Hernandez-Ramirez et al., Nanoscale 3 (2011) 630-634

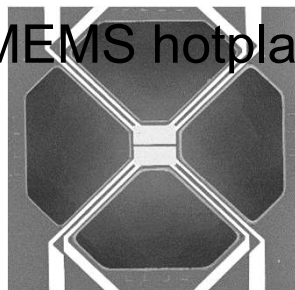


Sensitivity + Selectivity

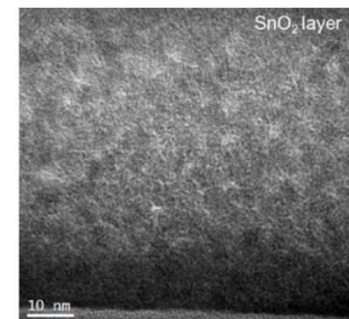
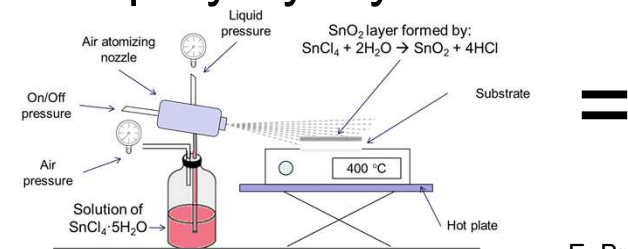
Simultaneous ionisation (current) and conductometric (resistance) measurements at very low operating power

Nanocrystalline Thin Films

MEMS hotplate



Spray Pyrolysis

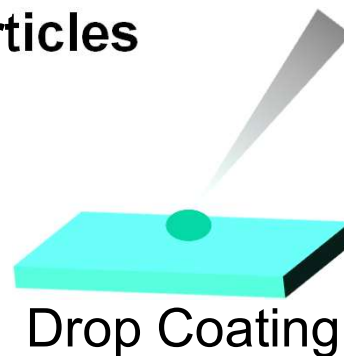


E. Brunet et al., Sens. Act. B 165 (2012) 110-118

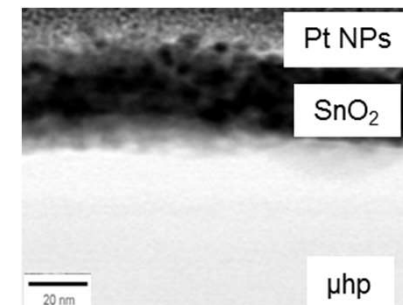
Functionalising Nanoparticles



+

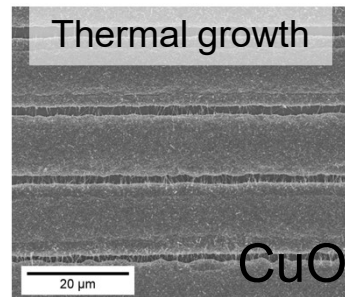
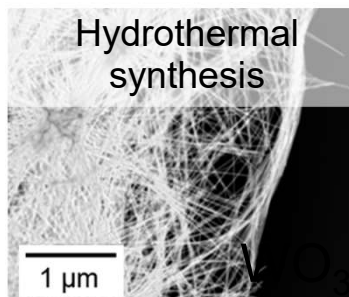


=



A. Köck, M. Deluca et al., Sensor+Test 2017

Nanowires

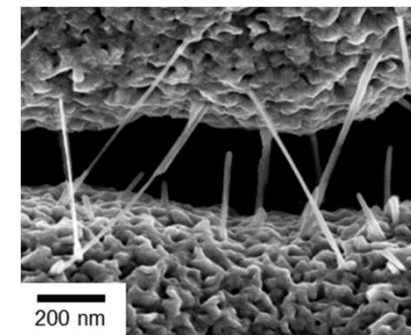


+

Transfer printing

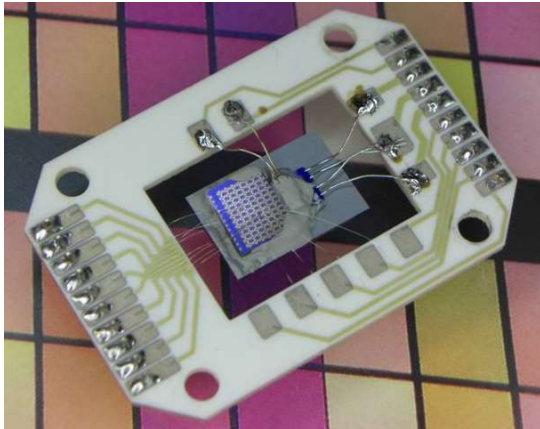


=



A. Carlson et al., Adv. Mater. 24 (2012) 5284-5318

Bulk Conductometric



Bulky Pt-heater

Large size ($> 15 \text{ cm}^2$)

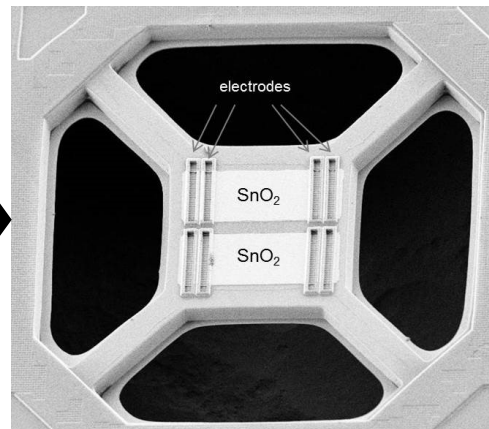
No CMOS-integration

Large power consumption

600 mW operation

4.3 kJ/day

CMOS Conductometric



MEMS polysilicon heater

Small size ($< 5 \text{ mm}^2$)

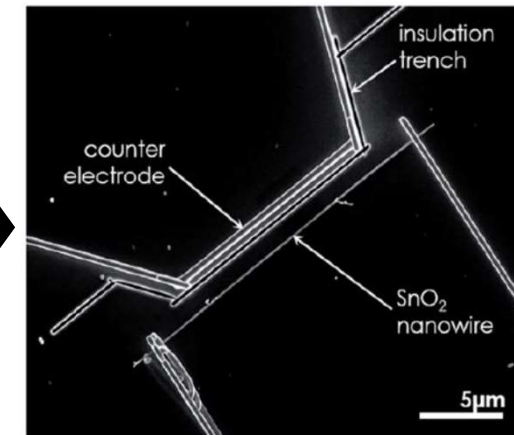
CMOS-integration

Medium power cons.

20 mW operation

144 J/day

Self-heating



Self-heating nanowires

Small size ($< 1 \text{ mm}^2$)

CMOS-integration

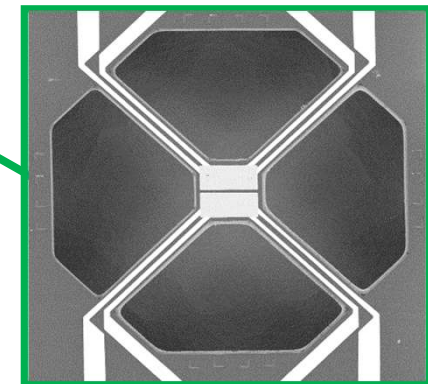
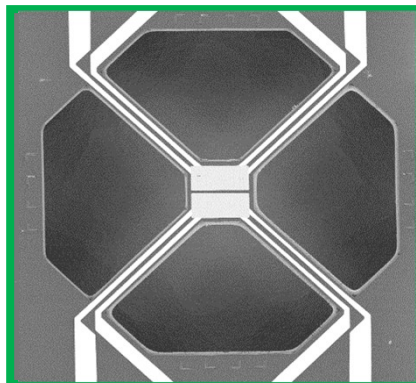
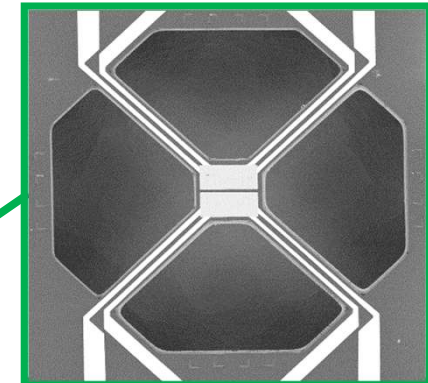
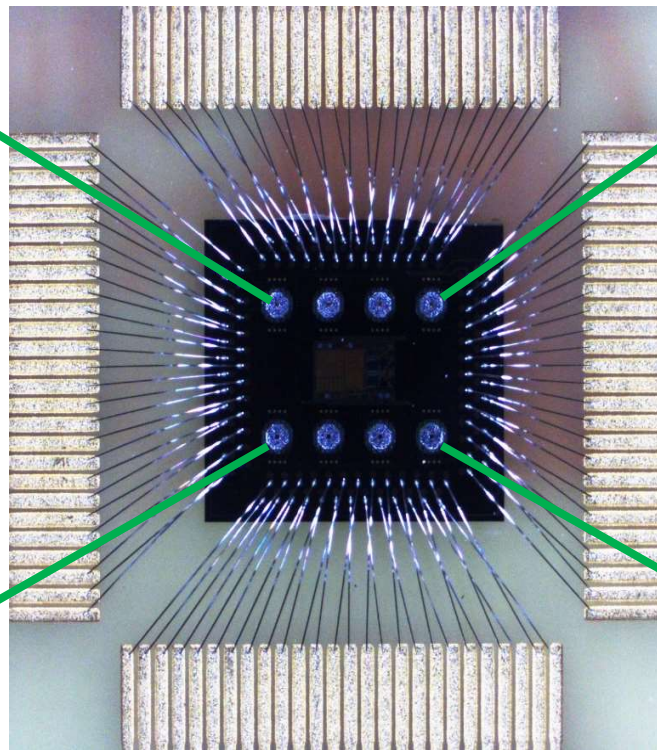
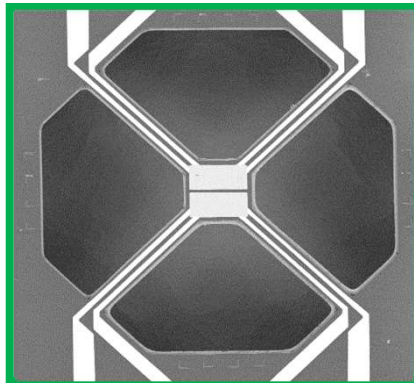
Low power consumption

20 μW operation

0.144 J/day

MEMS resistive arrays

Self-heating nanowires



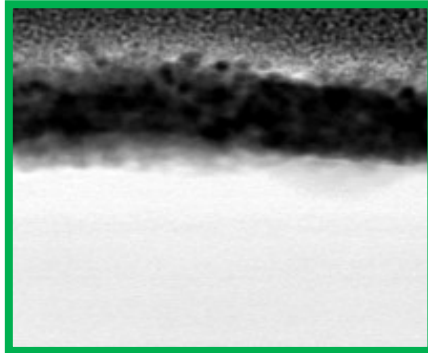
Power consumption: 20 μ W

0.144 J/d

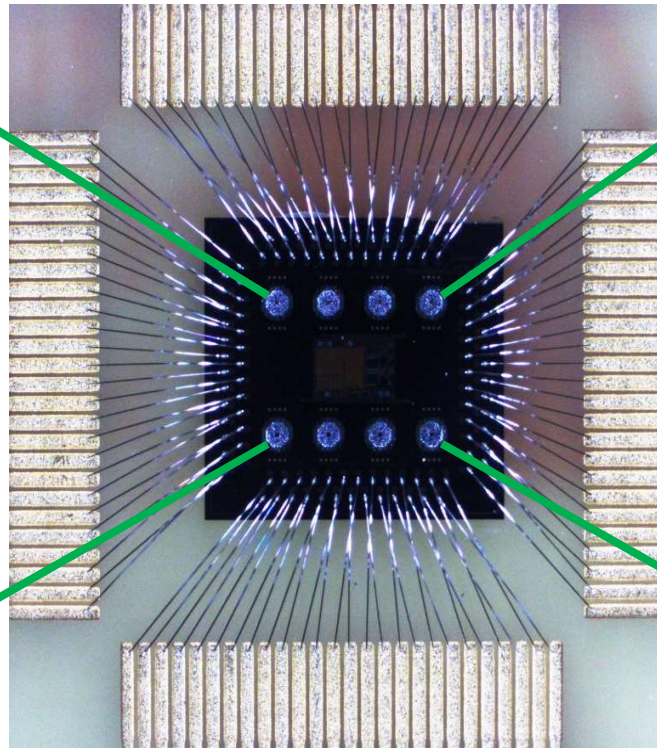
Highly selective gas sensor arrays



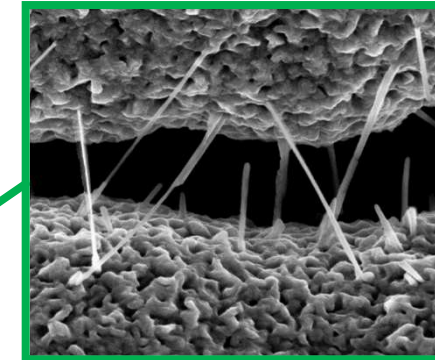
$\text{SnO}_2 + \text{Pt}$



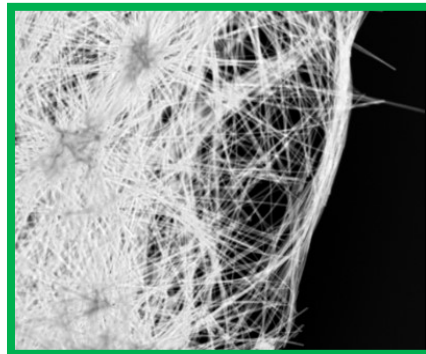
MEMS resistive arrays
Self-heating nanowires



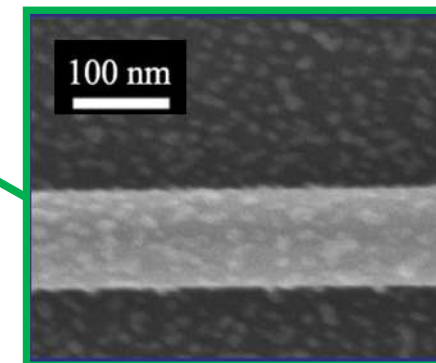
CuO-NWs



WO_3



CuO-NWs + Au

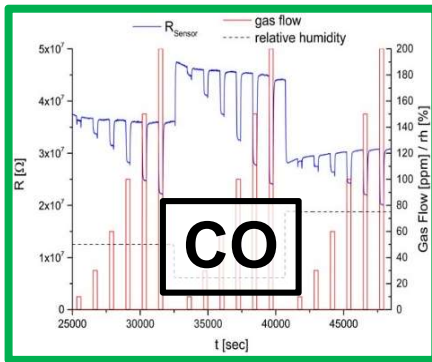


Functionalised with different materials
Selectivity to different gases

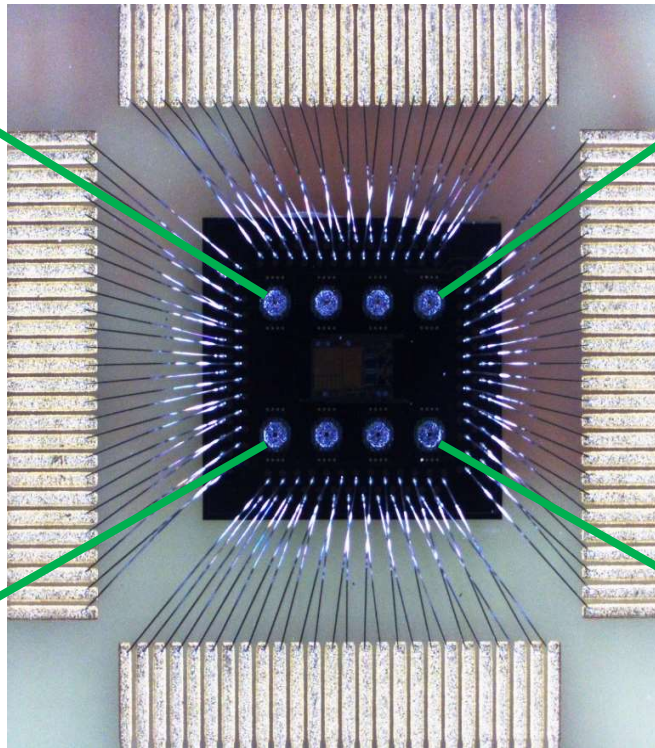
Highly selective gas sensor arrays



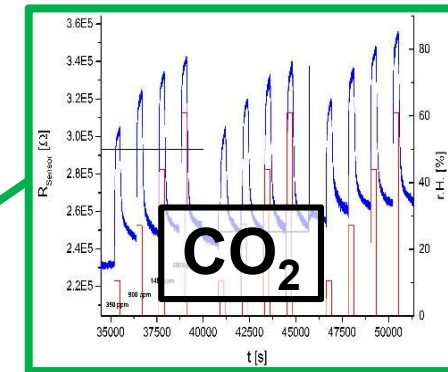
SnO₂ + Pt



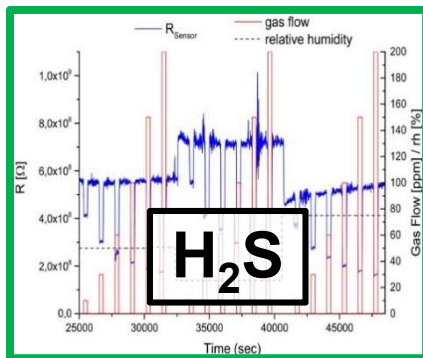
MEMS resistive arrays
Self-heating nanowires



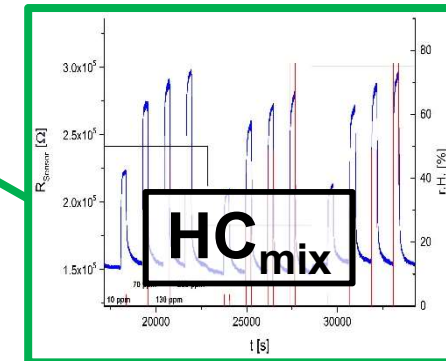
CuO-NWs



WO₃

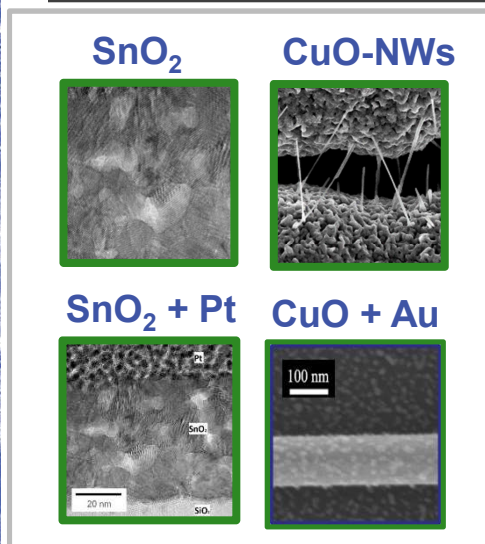


CuO-NWs + Au

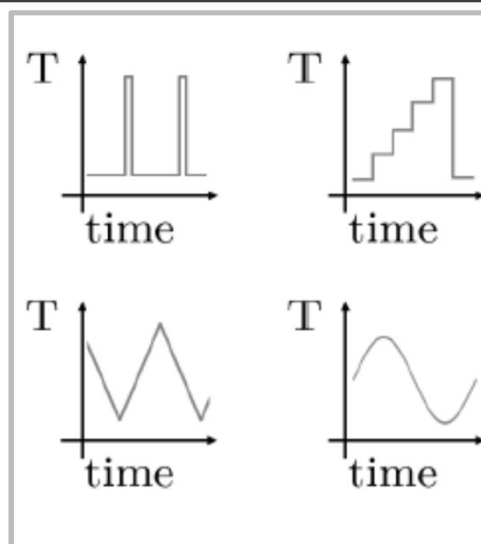


„Cross-Sensitivity“ problem

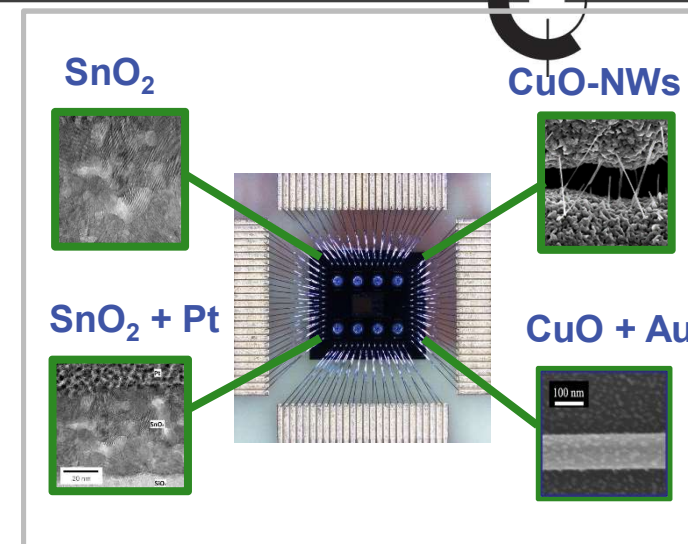
Multifunctional sensors



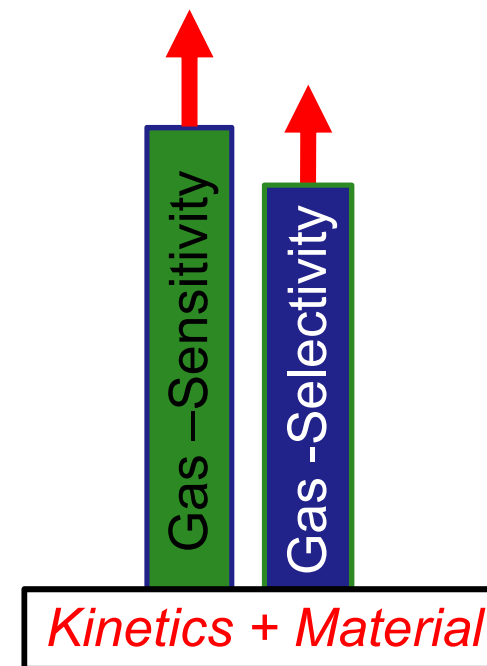
Single Sensors



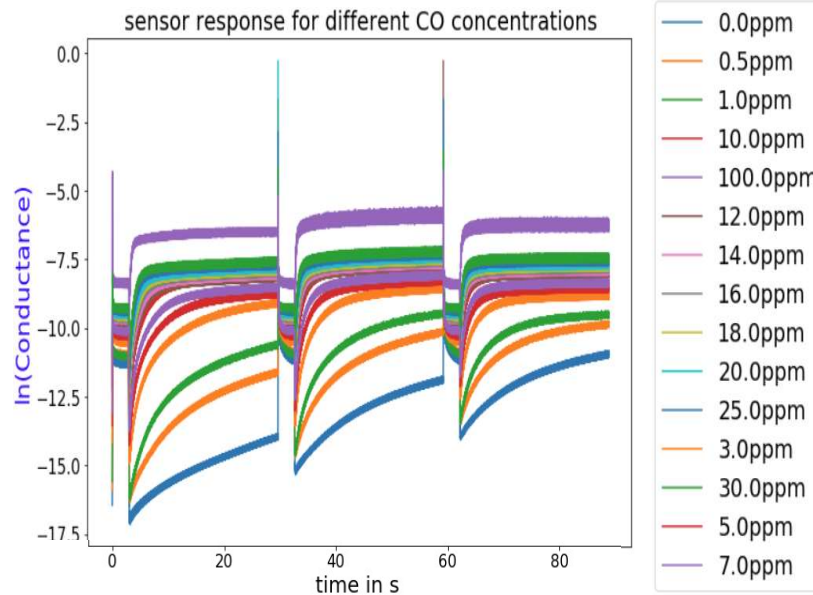
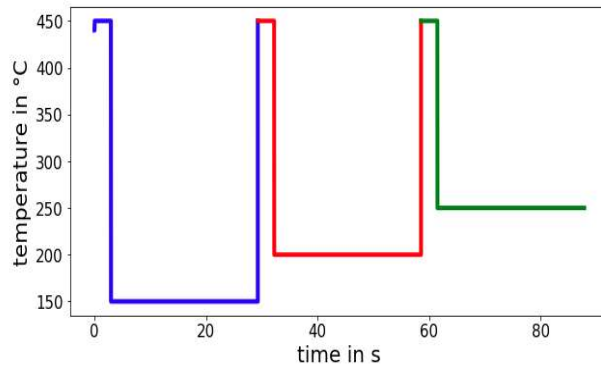
Temperature Cycles



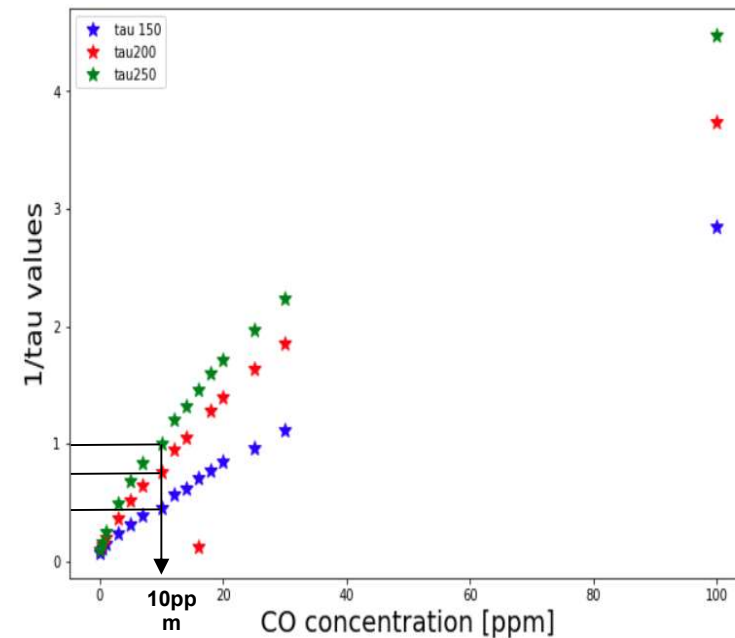
Sensor Arrays



Temperature cycles for gas quantification



τ -Evaluation for gas quantification



$$\tau = t(0.632(\ln(G_{max}) - \ln(G_{min}))) - t_{start}$$

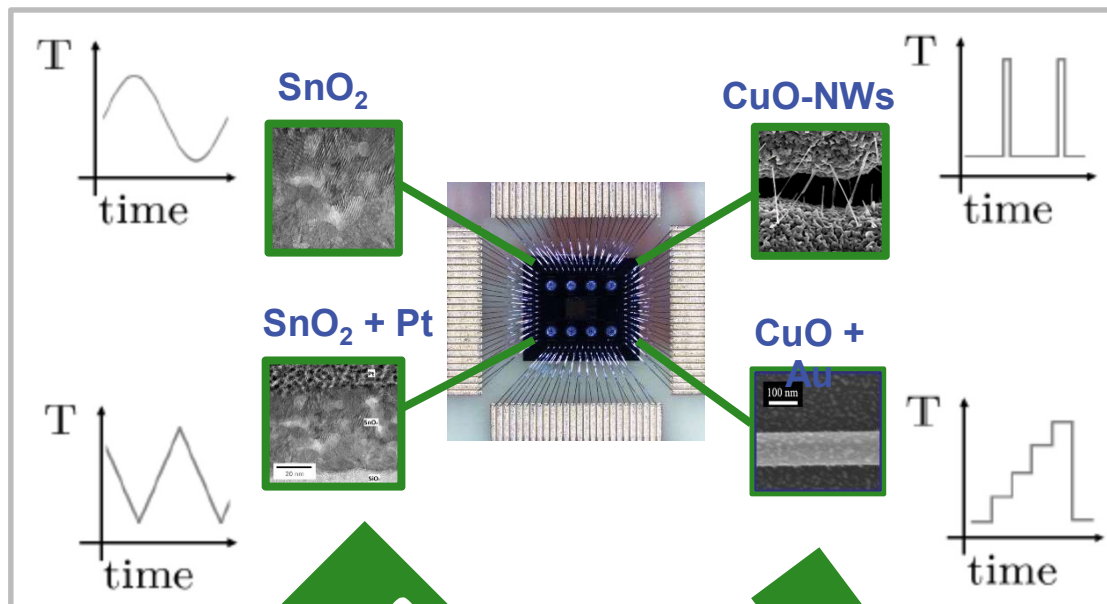
Faster measurement!

Kinetics: Slope change is dependent on gas concentration and temperature

Multifunctional sensors



Sensor arrays + Temperature cycles



**Feature
Extraction
+ Training**

Offline (Laboratory)

Classifier

Online (Sensor)

Gas -Sensitivity

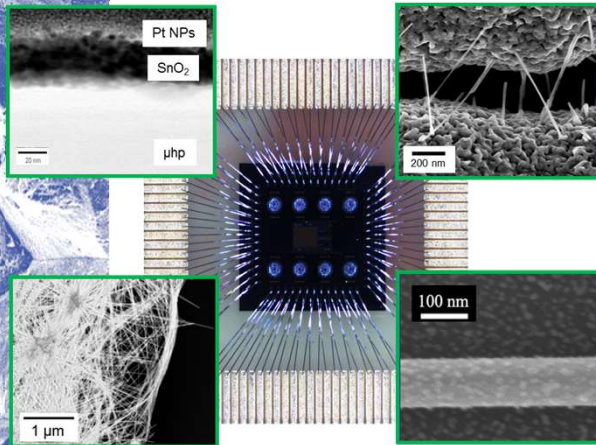
Gas -Selectivity



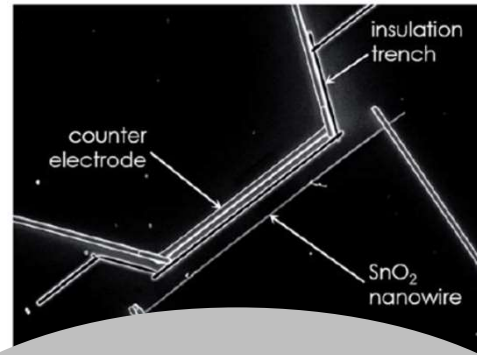
Highly selective gas sensor arrays



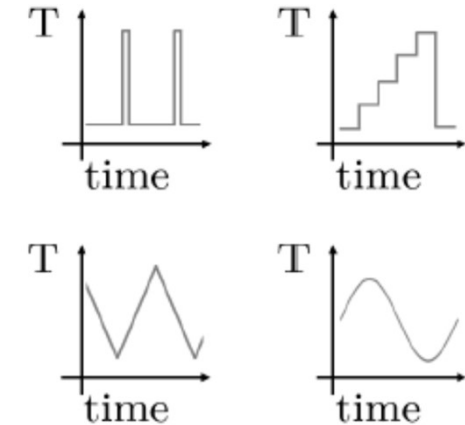
MEMS arrays



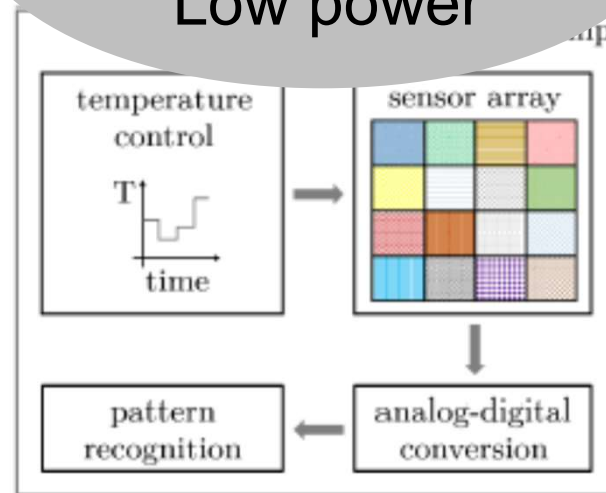
Ionisation sensor



Thermal profiles



High sensitivity
High selectivity
Low power

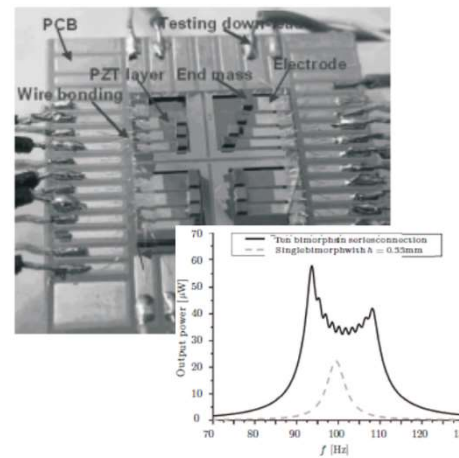


System-on-Chip
for gas detection

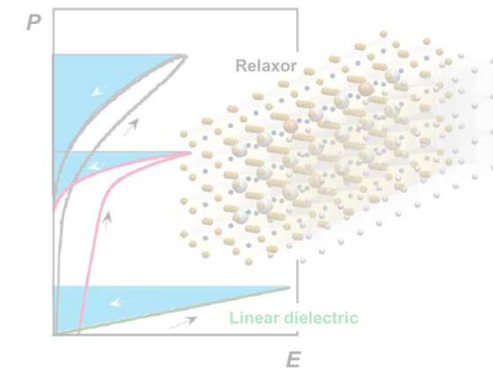
Low-power gas sensors



Broadband piezo-harvesters



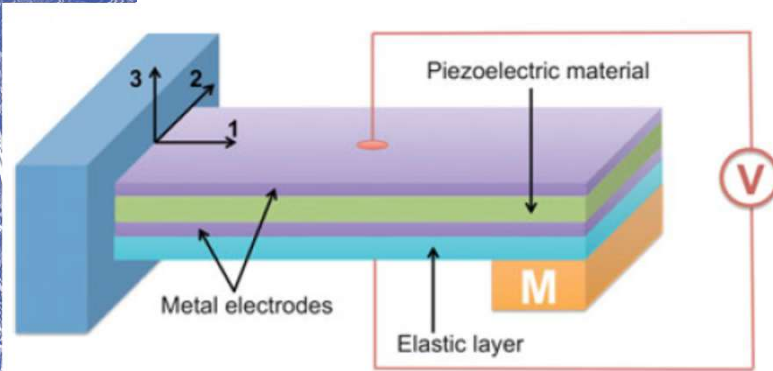
High energy-density capacitors



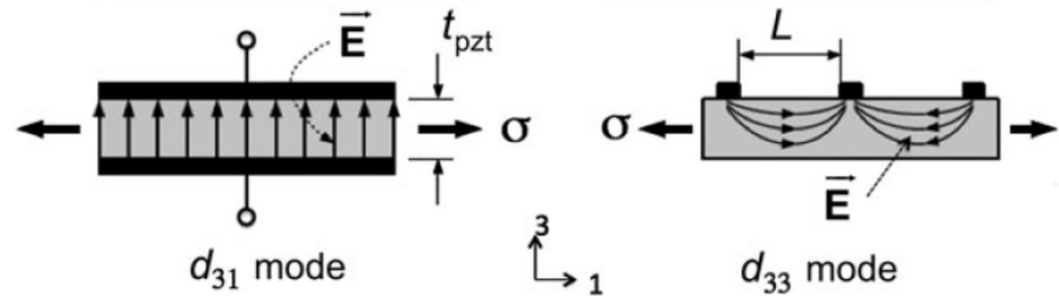
Piezoelectric energy harvesting



Linear piezoelectric energy harvesting



S.-G. Kim et al., MRS Bull. 37 (2012) 1039-1050



Mode of operation

Harvested energy

$$FOM = f \left(\frac{d_{ij}^2 E}{\epsilon_{33}^\sigma \tan \delta} \right)$$



d_{ij}



E (Young's modulus)



ϵ_{33}



$\tan \delta$ (mech. losses – $1/Q_m$)

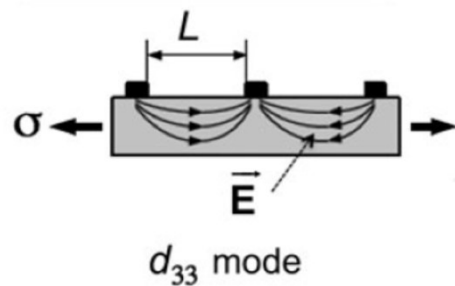
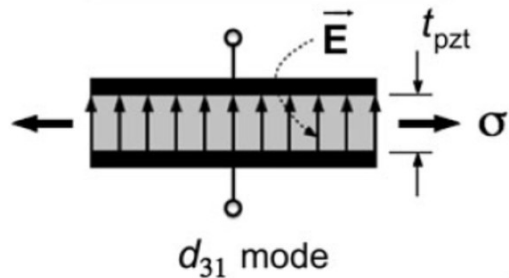
Material	d_{31} (pC/N)	ϵ_{33}	Frequency (Hz)	Power ($\mu\text{W}/\text{mm}^3$)
PZT	170	3000	126	20.5
KNN	100	900	1036	6.5
AlN	3	9	214	0.2

Vibration Source	Frequency (Hz)
Ship engine	12
Numeric control machine	70
Office building, 2 nd floor	100

Piezoelectric properties

Maximise d_{ij}

$$FOM = f \left(\frac{d_{ij}^2 E}{\epsilon_{33}^{\sigma} \tan \delta} \right)$$



Operational range

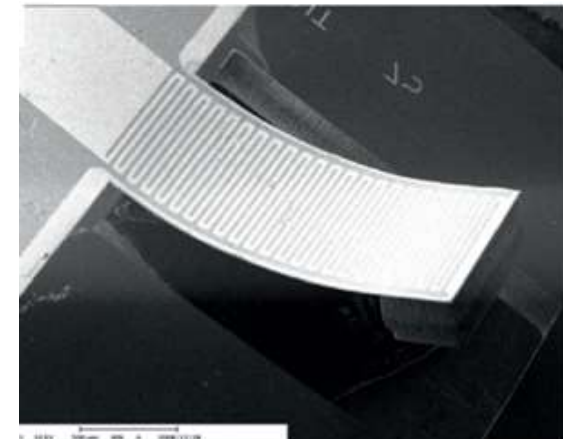
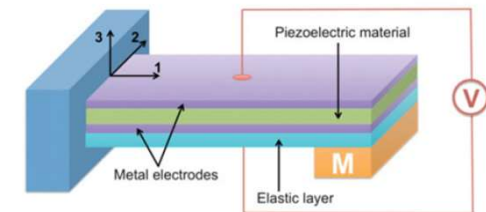
- Frequency matching
- Low-frequency operation
- Broadband operation



Trade-off ω_r , Q_m

Cost

- Thin film deposition
- MEMS structures



S. Priya et al., Energy Harvest. Syst. 4 (2017)

Low-frequency energy harvesting



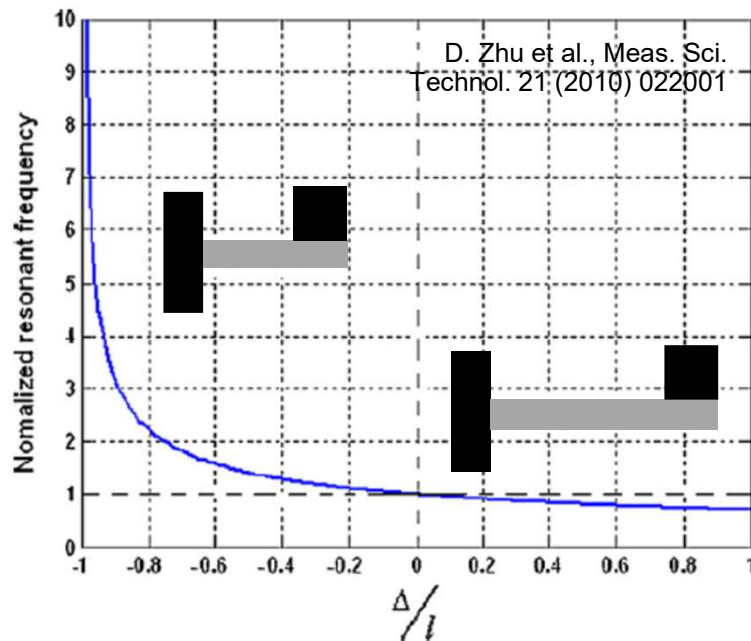
Resonance frequency of mass-cantilever system

$$f_r = \frac{1}{2\pi} \sqrt{\frac{Ewh^3}{4l^3(m + m_c)}}$$

w, h, l width, thickness, length of cantilever
 E Young's modulus of cantilever material
 m, m_c mass of proof mass and cantilever

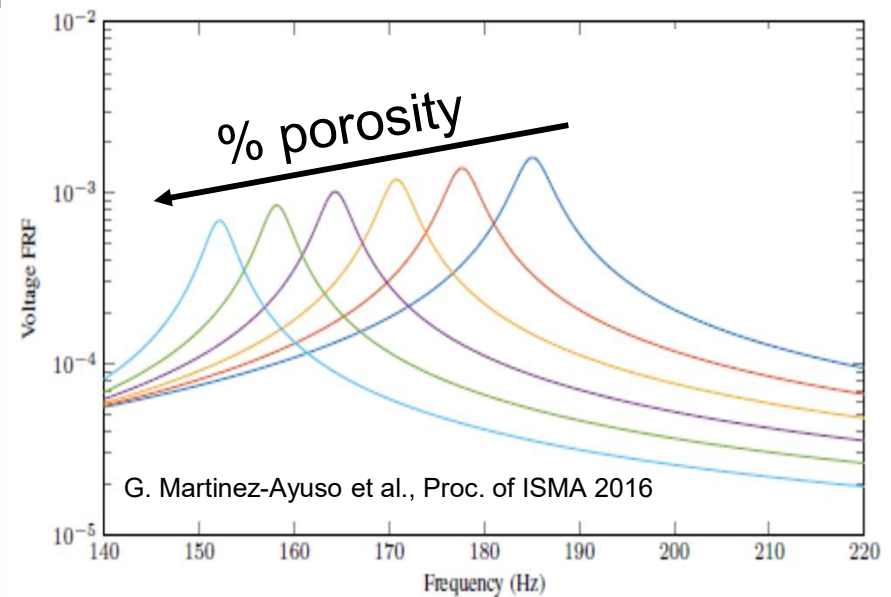
D. Zhu et al., Meas. Sci. Technol. 21 (2010) 022001

Modify cantilever geometry



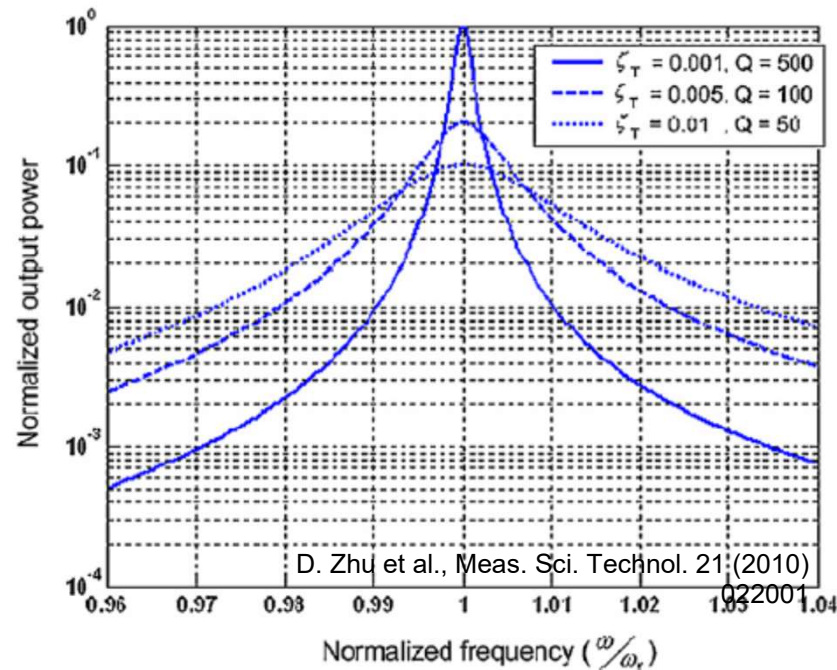
Q_m remains constant

Modify Young's modulus



Q_m decreases

Modify Q_m

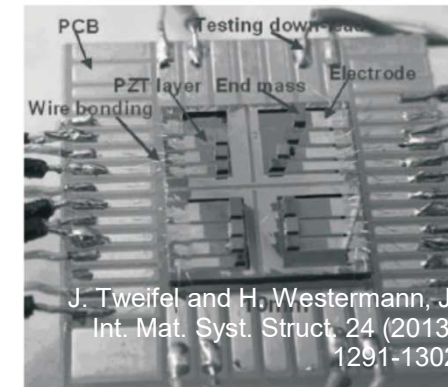


Suitable for low-power applications

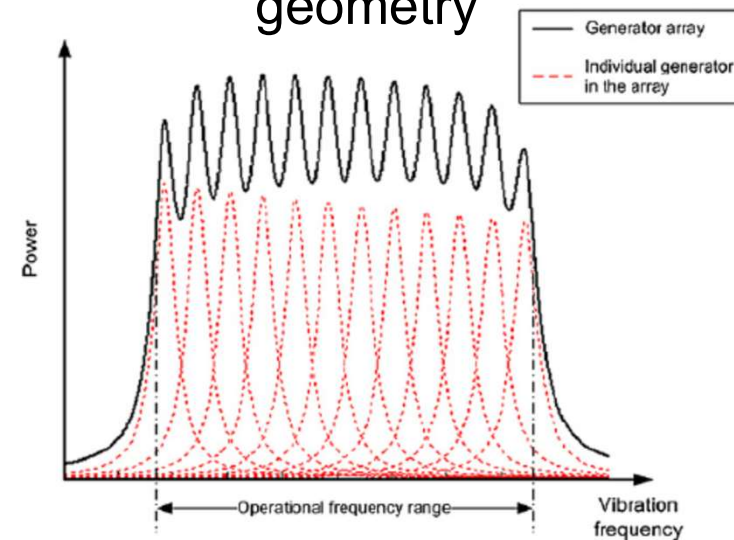
↓ $Q_m =$ ↓ Stiffness

- Increase porosity
- Choose „softer“ material (polymer)

Modify Geometry

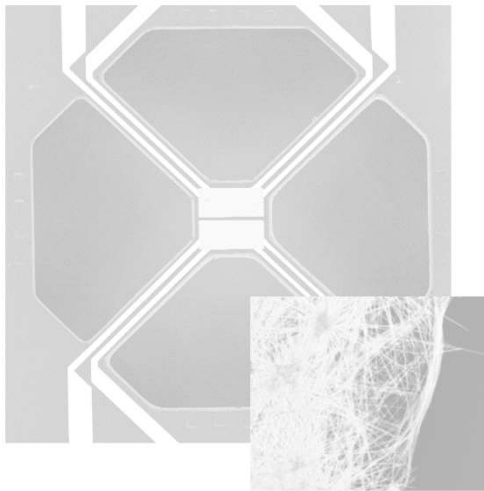


Cantilever array with variable geometry

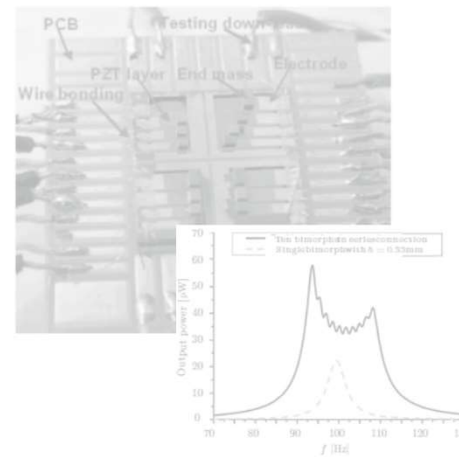


D. Zhu et al., Meas. Sci. Technol. 21 (2010) 022001

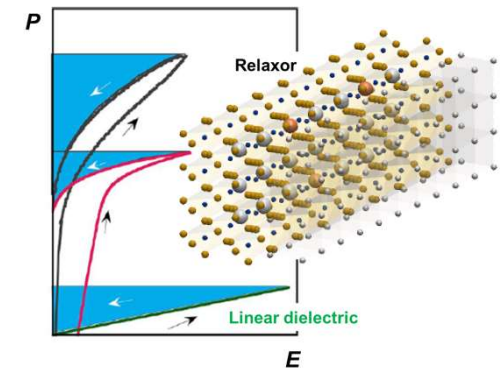
Low-power gas sensors



Broadband piezo-harvesters



High energy-density capacitors



Energy storage for wireless sensors



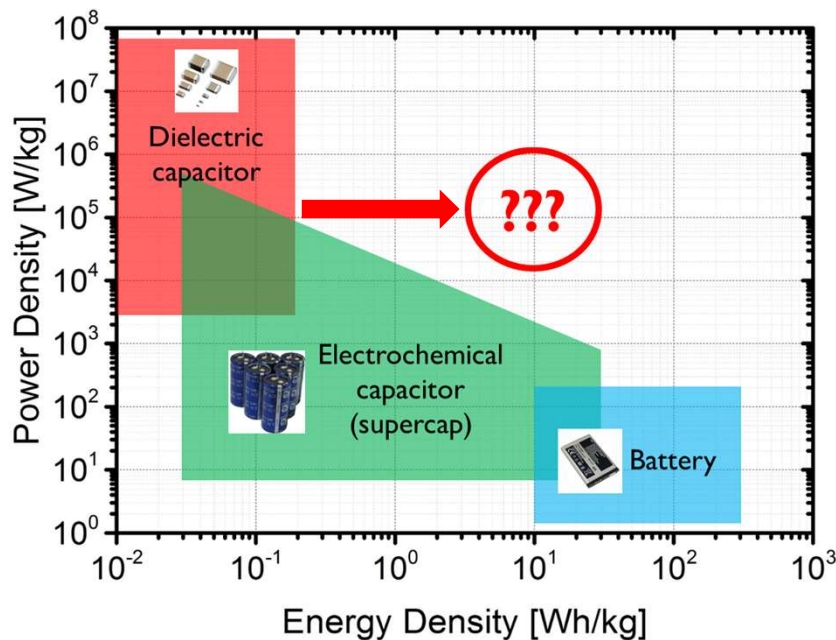
Energy sources change quickly
Need quick charge/discharge

High power density



Energy sources may be not available for long times
Need long-term energy supply

High energy density



Dielectric capacitors:

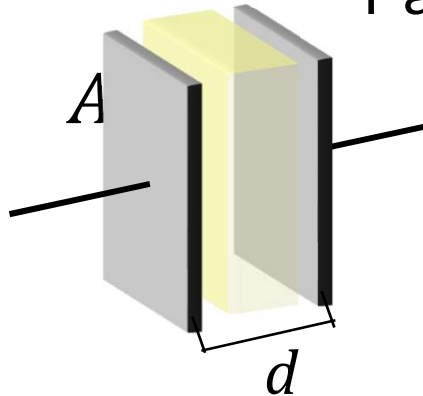
- High power density
- Temperature stability
- Cyclic stability

Need high energy density

Energy density of ceramic capacitors



Parallel plate capacitor with dielectric



$$U = \frac{1}{2} CV^2 \quad \text{El. potential energy}$$

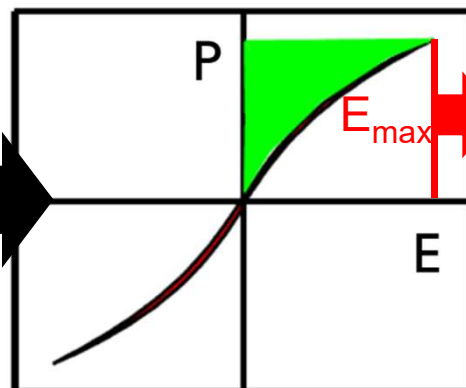
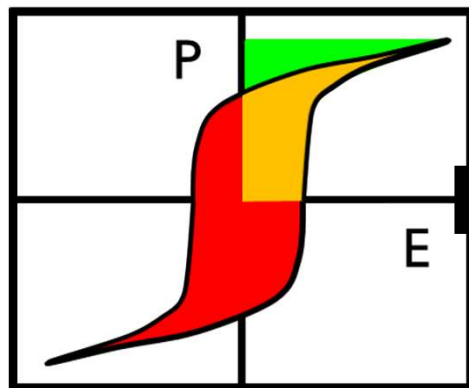
$$J = \frac{U}{Ad} \quad \text{Energy density}$$

$$J = \frac{1}{2} \epsilon_0 \epsilon_r E^2 = \int_{P_1}^{P_2} E dP$$

$$\begin{aligned} C &= \epsilon_0 \epsilon_r \frac{A}{d} \\ P &= \epsilon_0 \epsilon_r E \end{aligned}$$

Ferroelectric

Relaxor

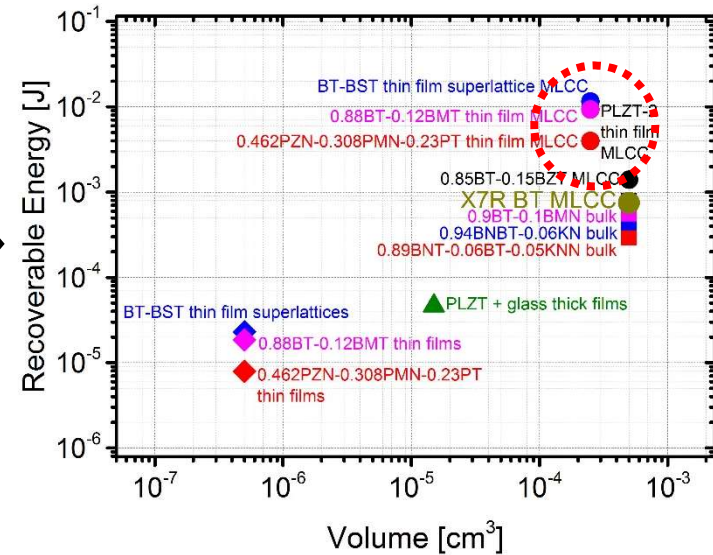
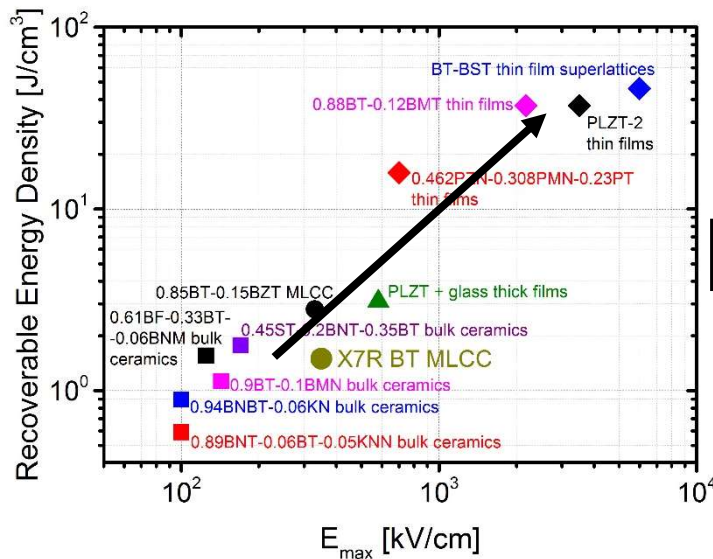


- + = Stored energy density
- = Recoverable energy density
- = Energy loss (hysteresis)

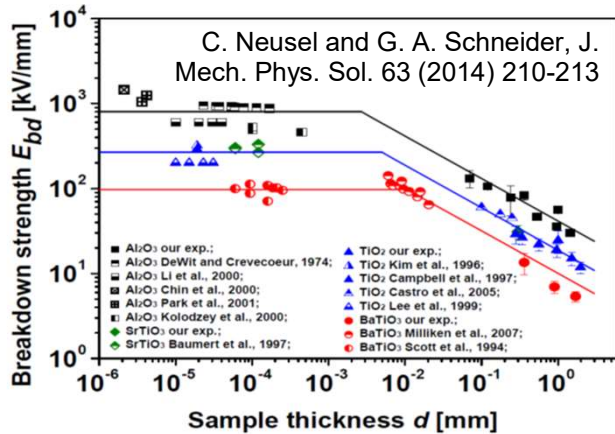
Ways to increase energy density:

1. Reducing hysteretic losses *while maintaining high permittivity (i.e. P)*
2. Increasing dielectric breakdown strength (DBS) – enhancing E_{\max}

Increasing the DBS: Thin film processing

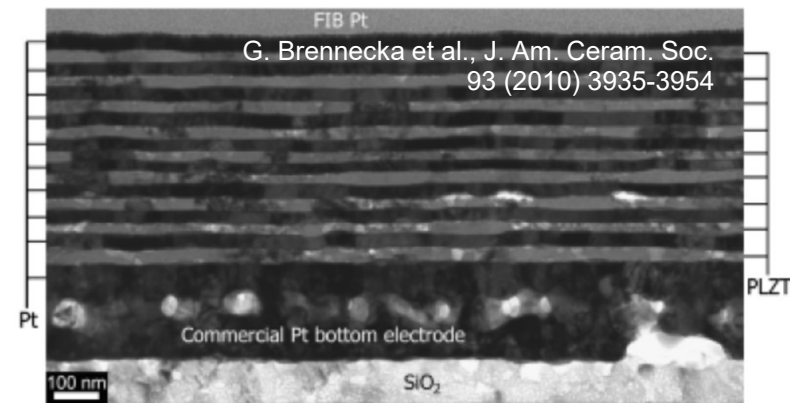


Reduced layer thickness



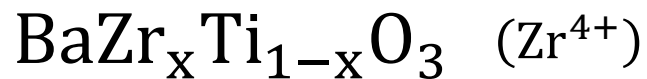
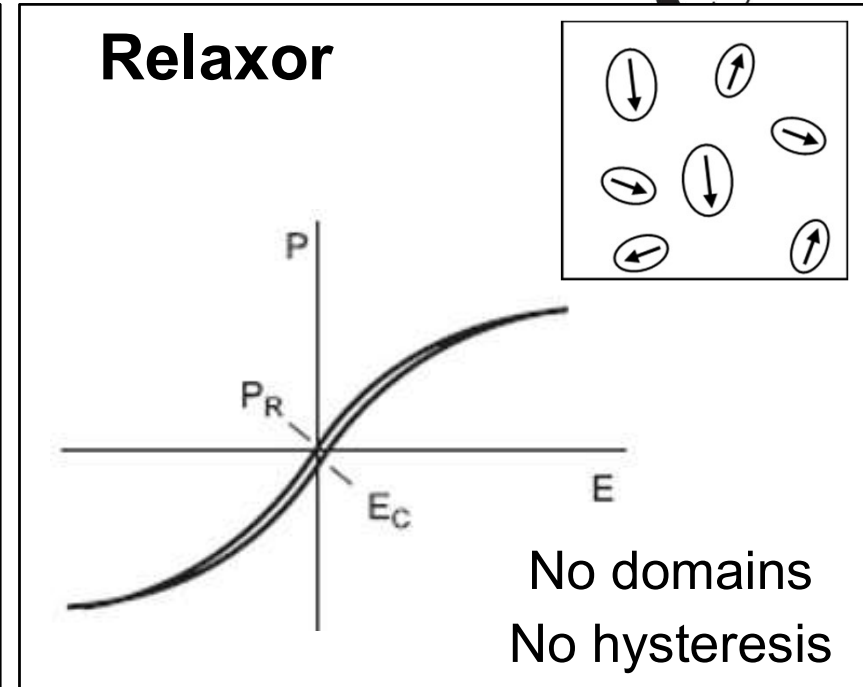
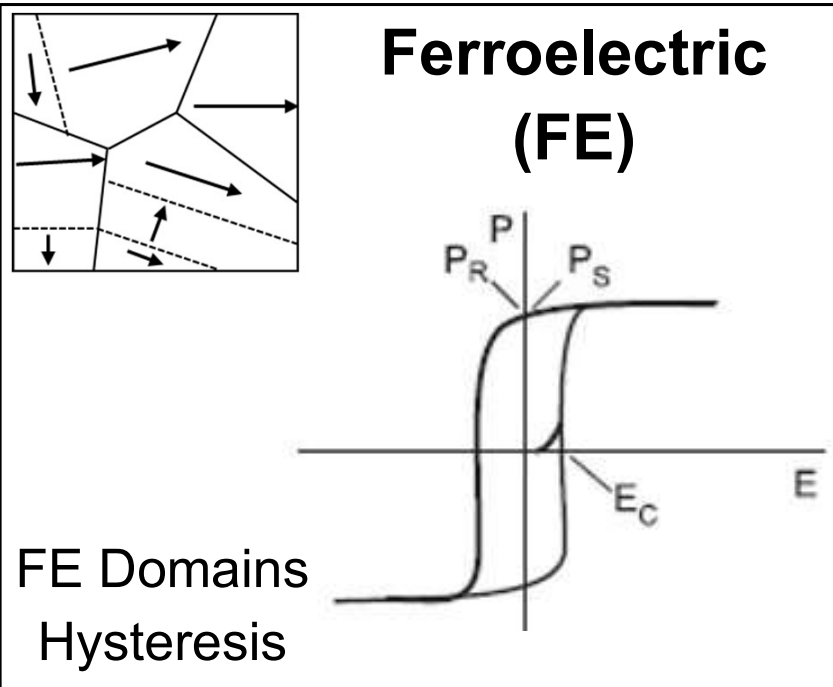
Less probability to find a critical defect

Chemical solution deposition

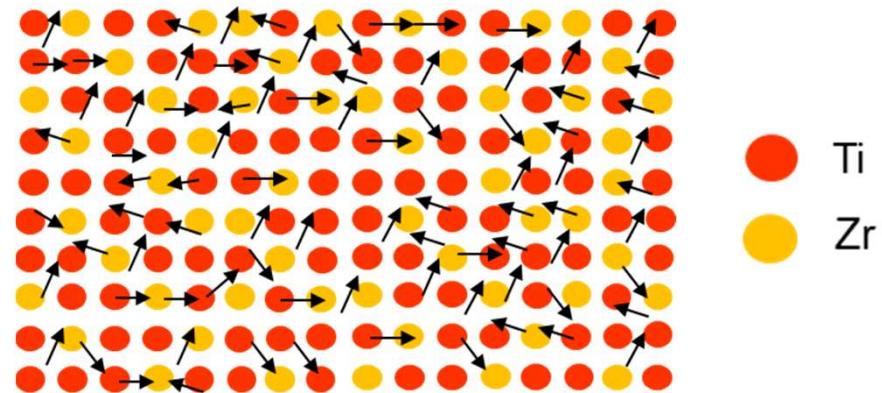


Low porosity and defect density compared to solid-state processing

Optimising the polarisation: Relaxors



relaxor for $x = 0.35$

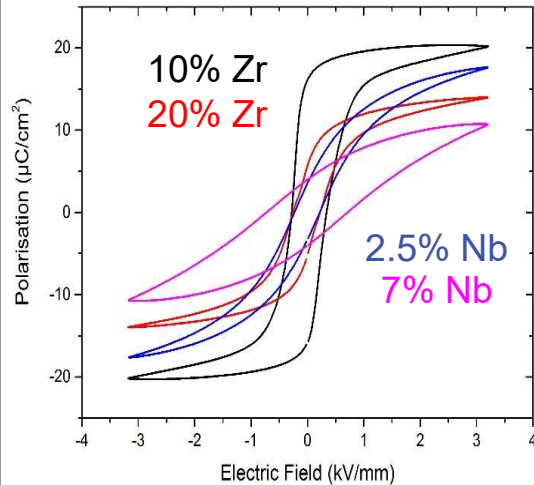


Relaxors: Chemical substitution breaks the long-range cooperative displacement of Ti cations and disrupts ferroelectricity

Optimising the polarisation: Relaxors



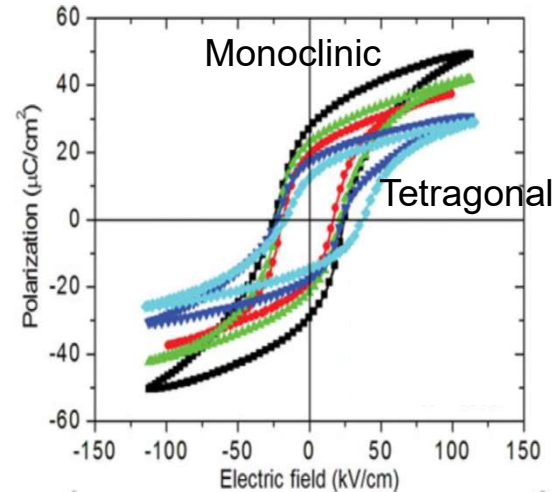
Composition



Substitution disrupts ferroelectricity

M. Deluca et al., unpublished (2019)

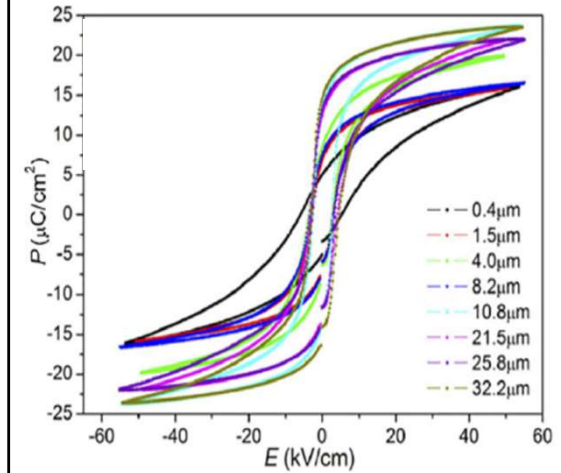
Symmetry



Monoclinic phase increases permittivity

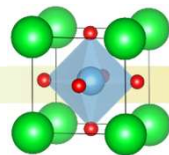
E. C. Lima et al., Ferroel. 465 (2014)

Grain size

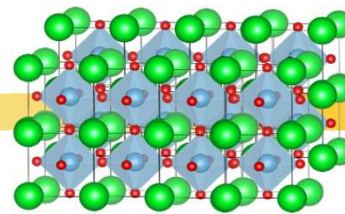


Small grain size suppresses ferroelectricity

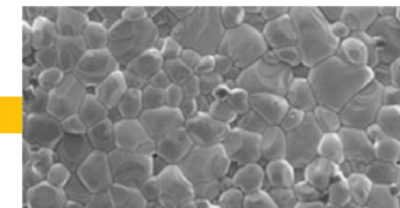
M. Acosta et al., Appl. Phys. Rev. 4 (2017) 041305



Atomic scale



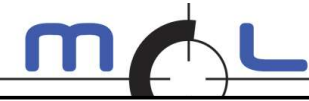
Nanoscale



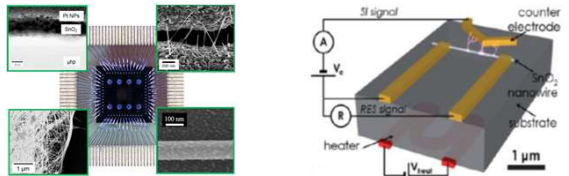
Mesoscale

Knowledge of relationship between chemical substitution and macroscopic polarisation is decisive for **optimising polarisation loops** in relaxors.

Self-powered wireless sensor nodes

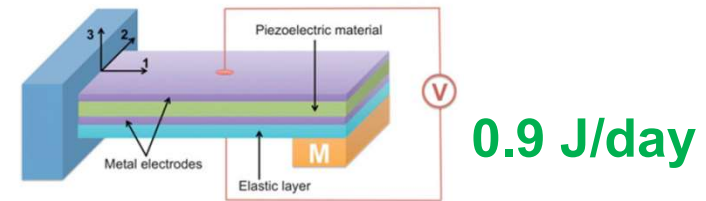


MEMS resistive + Ionisation gas sensor

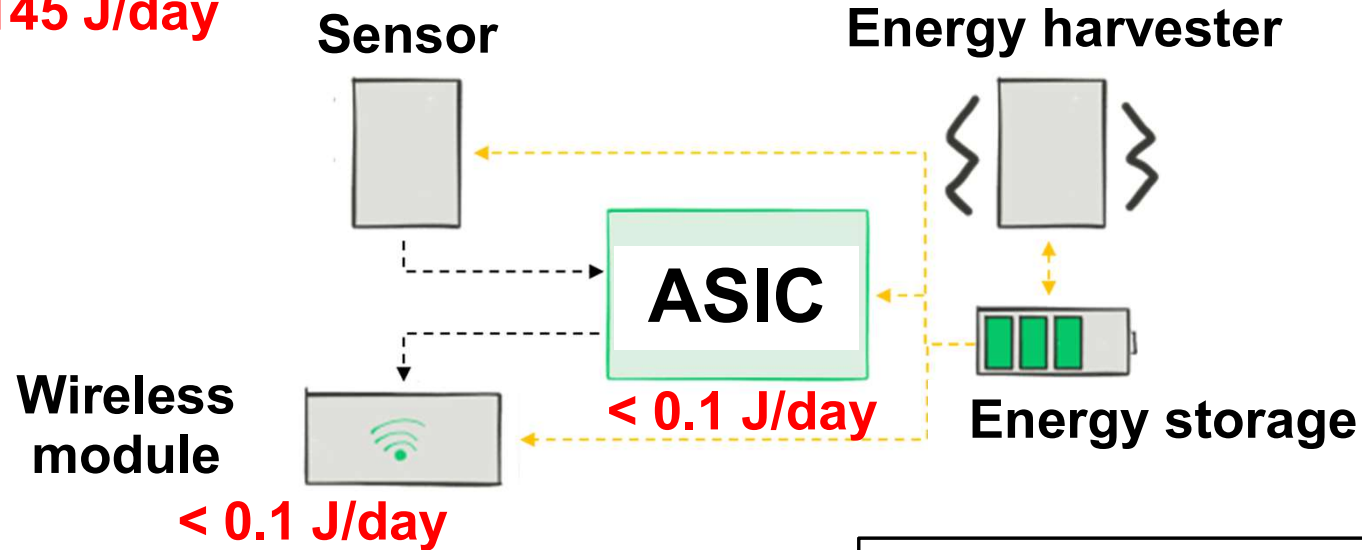


0.145 J/day

Piezoelectric energy harvester

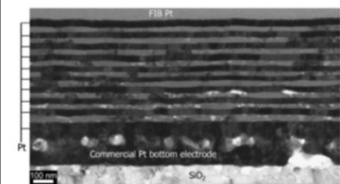


0.9 J/day



Energy autonomous operation possible!

Thin film ceramic MLCC



40 J/cm³
8 cycles/hour
0.9 J/day

Take-home messages:

Autonomous IoT sensor nodes must combine the following elements:

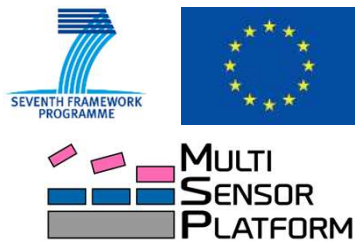
- **Low-power sensors** including ASIC and network element
- **Resilient** energy harvesters such as **broadband** and **low-frequency piezoelectric energy harvesters**.
- **High-power** and **high energy density** energy storage.

Ionization or **self-heating gas sensors** may be a viable way to reduce power consumption and to improve selectivity.

Piezoelectric energy harvesting is suitable to low-power sensor nodes and works 24/7, but need broadband technology

High storage energy density is attained in **dielectric capacitors** using **thin film** technology and **relaxor systems**

Acknowledgements



FP7-ICT-2013-10 – GA. 611887

MSP – Multi Sensor Platform for Smart Building Management



ERC-COG-2018 – GA. 817190

CITRES - Chemistry and Interface Tailored Relaxor thin films for Energy Storage capacitors

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement No 817190)



Der Wissenschaftsfonds.

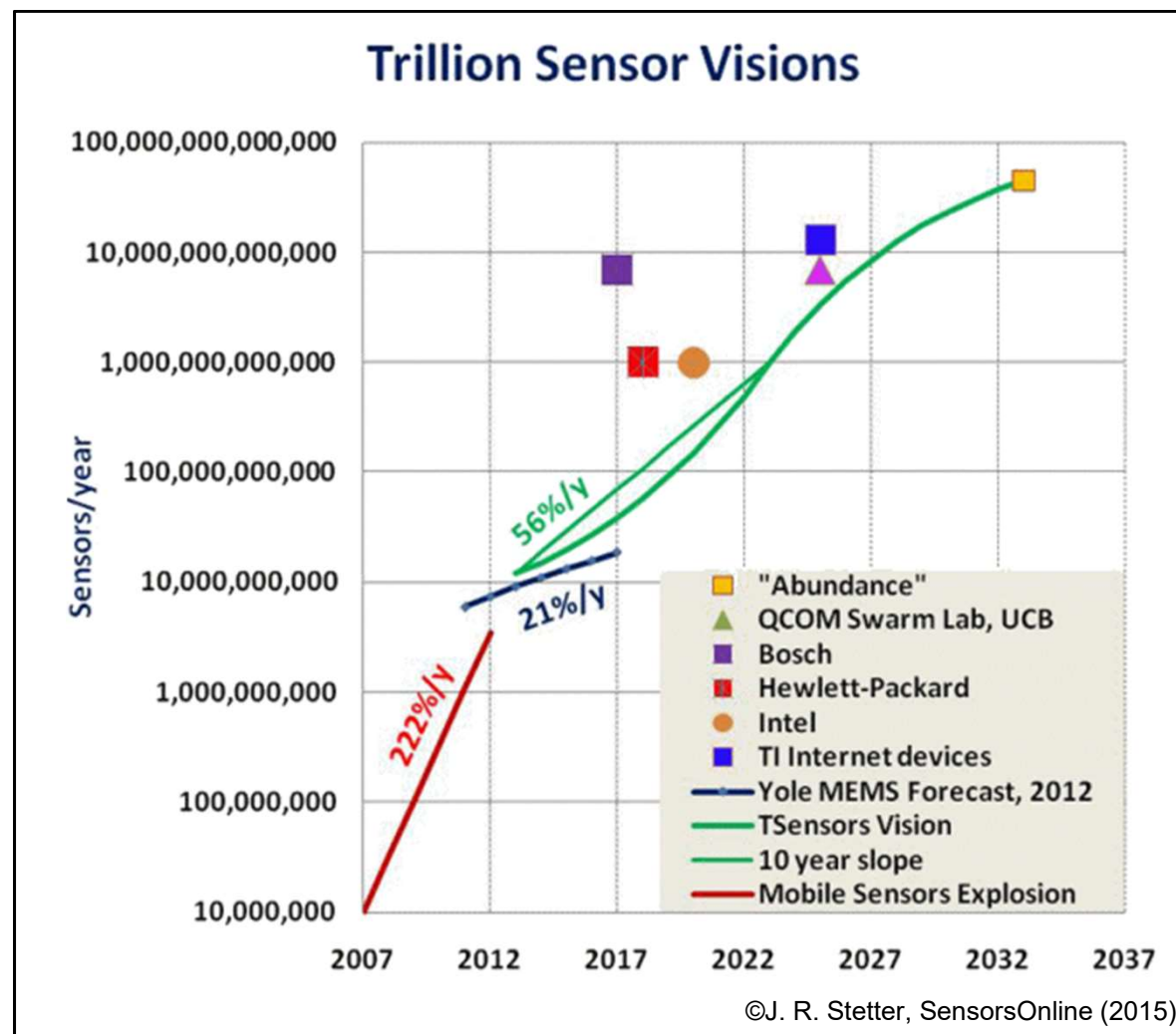
FWF Single Project – Nr. P29563-N36

Origin of relaxor behaviour in Ba-based lead-free perovskites



FFG „Production of the Future“ – Nr. 858637

FUNKYNANO – Optimized Functionalization of Nanosensors for Gas Detection by Screening of Hybrid Nanoparticles



Thank you for your attention!

