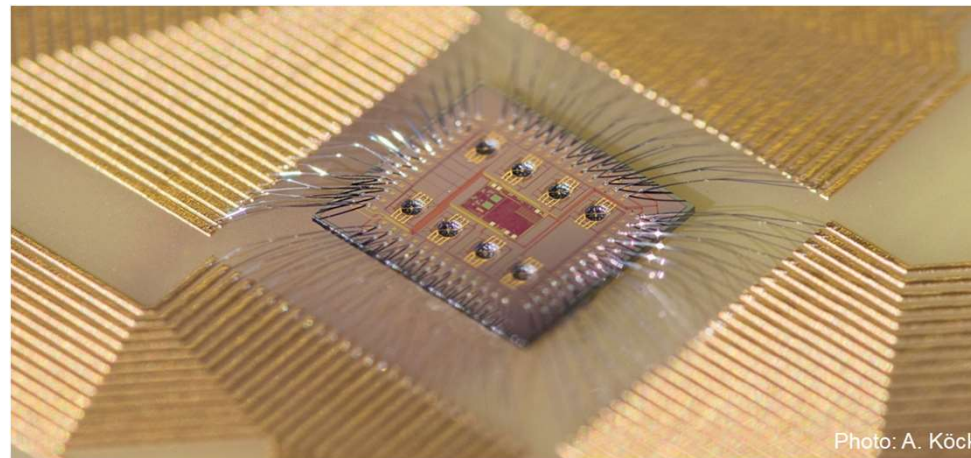


# Materials-related challenges for autonomous sensor nodes



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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.



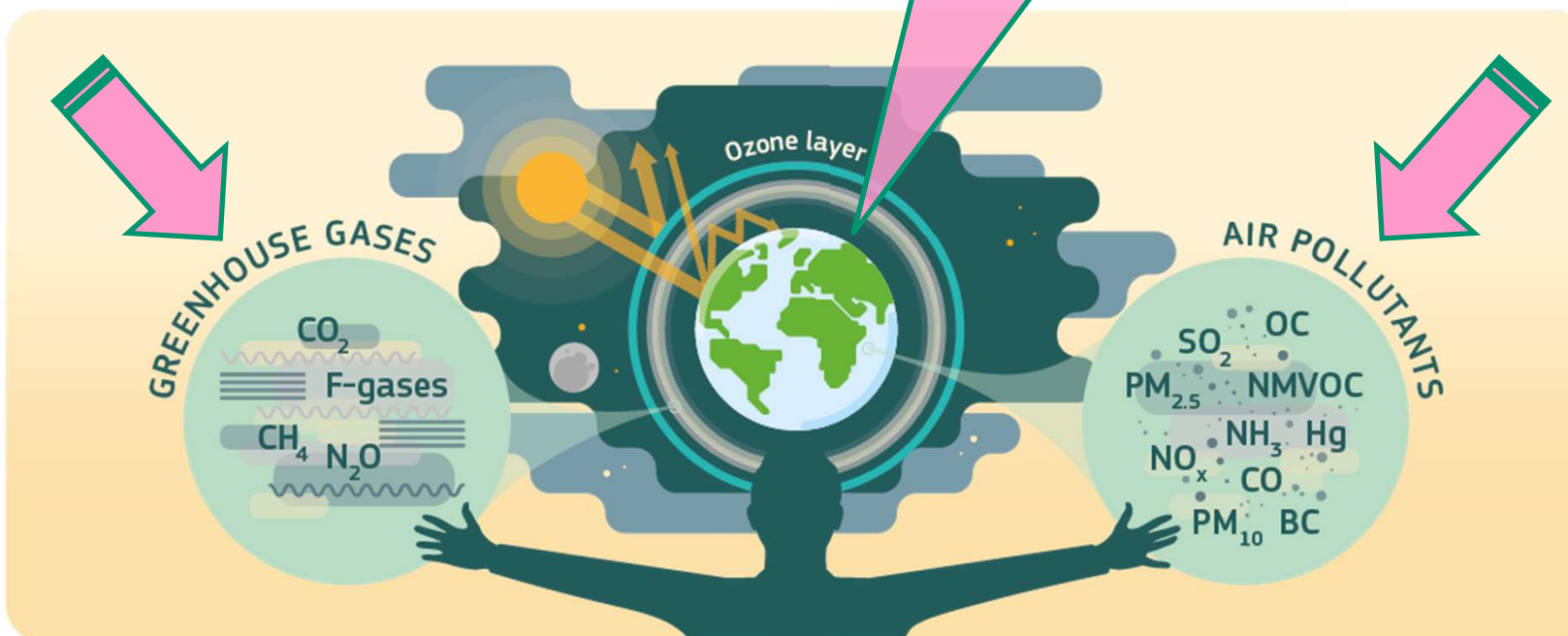
# Environmental monitoring



**EDGAR** The Emissions Database  
for Global Atmospheric Research

Mapping human emissions on Earth

We have to monitor  
all emissions !

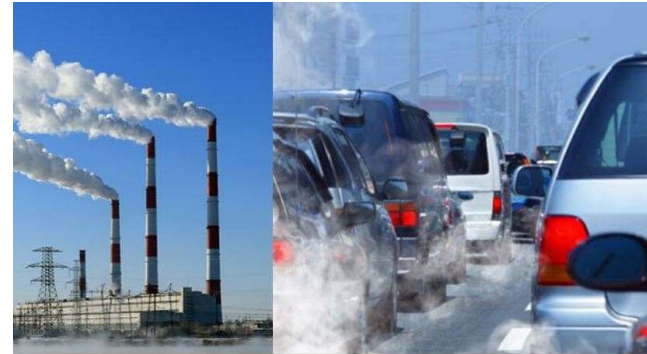


Source: The Emissions Database for Global Atmospheric Research (EDGAR):  
<http://edgar.jrc.ec.europa.eu>

## Indoor and outdoor air quality monitoring



Indoors  
CO, CO<sub>2</sub>, VOCs, PM



Outdoors  
NO<sub>2</sub>, O<sub>3</sub>, CO, PM<sub>10</sub>, PM<sub>2.5</sub>, UFPs



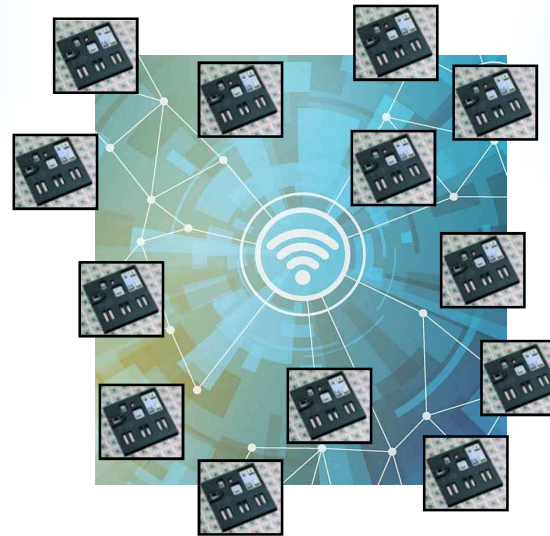
SENSOR NETWORKS  
ENABLING AUTOMATIC  
CONTROL AND  
REGULATION



# Wireless Sensor Networks



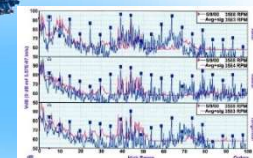
**Air quality monitoring**



**Structural health monitoring**



**Condition monitoring**



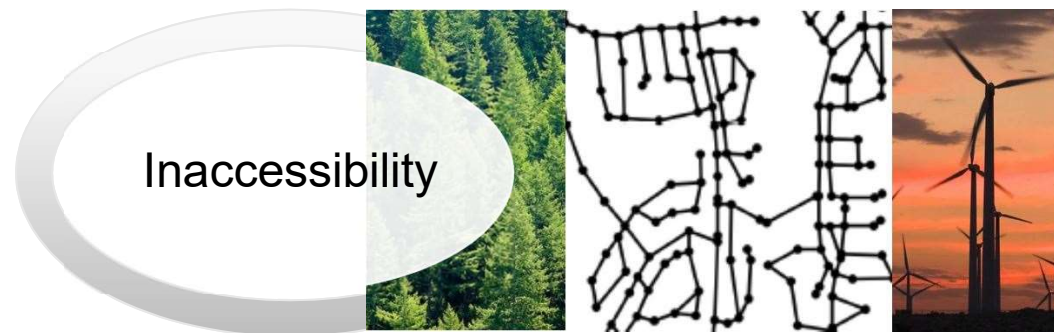
**Predictive maintenance**



**Industry 4.0**

***Realising GHG emission reduction goals***

# Challenges for sensor networks



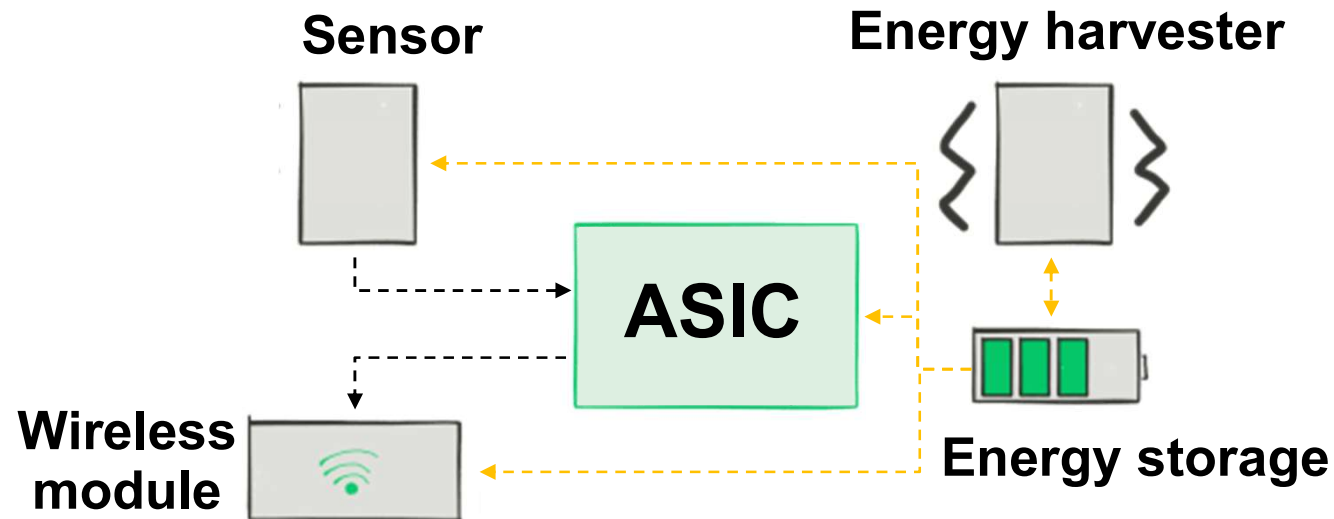
Device footprint



Energy efficiency

Miniaturised self-powered (energy autonomous) sensor nodes

# Self-powered wireless sensor nodes



ENERGY CONSUMPTION	CMOS gas sensor: <b>144 J/d</b>	Temperature sensor: <b>0.47 J/d</b>
	Self-heating gas sensor: <b>0.14 J/d</b>	Vibration sensor: <b>0.6 J/d</b>
	ASIC/RFID (1 read/minute, $\leq 10$ m transmission distance): <b>&lt; 0.1 J/d</b>	

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

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



# Materials-related challenges



Low power consumption

- *sensor/harvester performance*

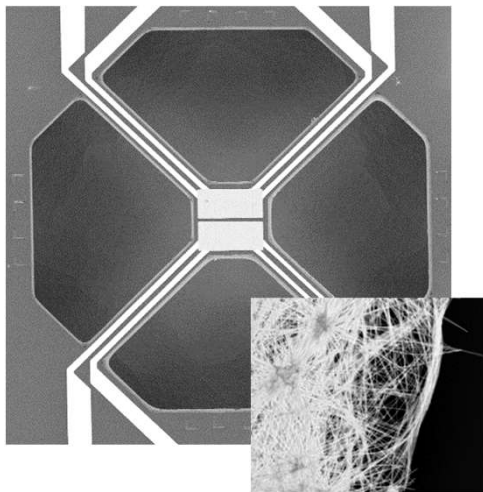
Variability of the energy source

- *harvester + storage unit perf.*

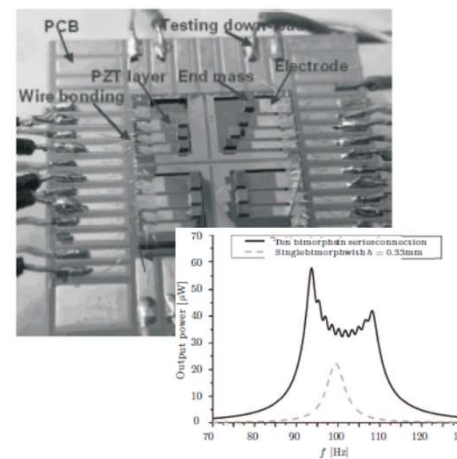
Low cost per unit

- *high-yield low-cost production*

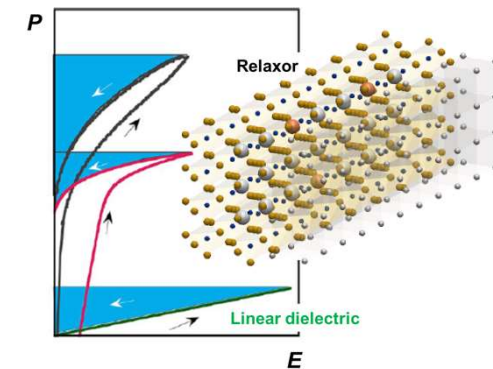
## Low-power gas sensors



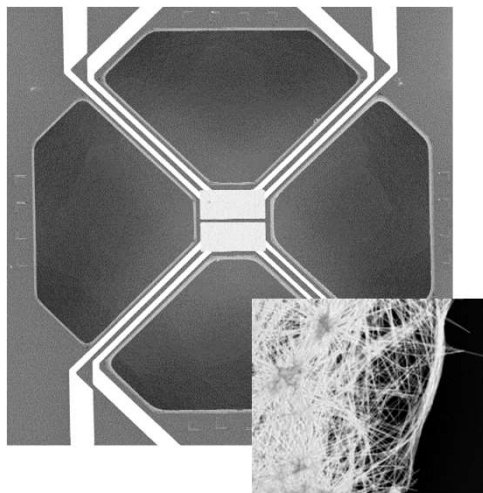
## Broadband piezo-harvesters



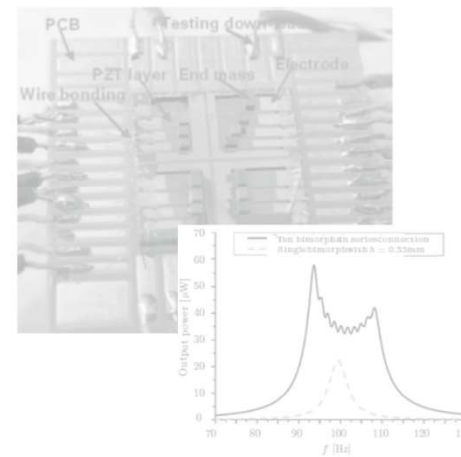
## High energy-density capacitors



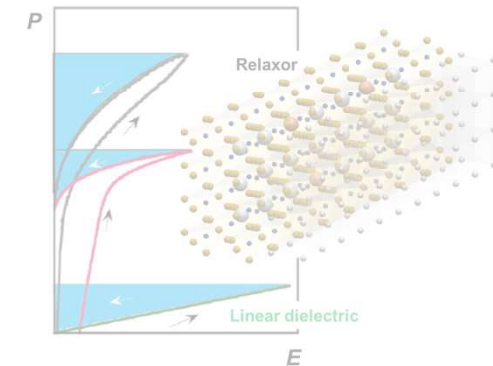
## Low-power gas sensors



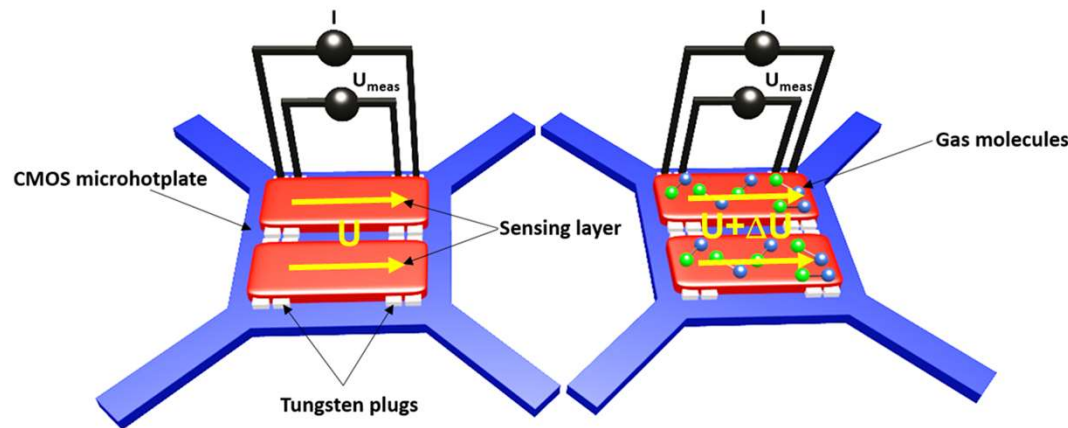
## Broadband piezo-harvesters



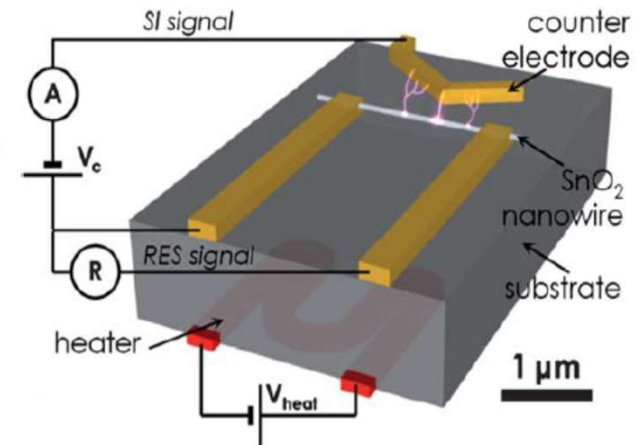
## High energy-density capacitors



## Conductometric (resistive)



## Surface ionisation



### Sensing Material

- $\text{SnO}_2$
- $\text{ZnO}$
- $\text{CuO}$
- $\text{WO}_3$

Thin films  
Nanowires

### Functionalising Nanoparticles

- Au, Pt, Pd
- AuPd, PdPt, ...
- $\text{ZrO}_2$
- $\text{BaTiO}_3$

### Target Gases

- CO
  - $\text{CO}_2$
  - VOCs
  - $\text{NO}_2$
  - $\text{H}_2\text{S}$
  - $\text{H}_2, \text{O}_3$
- Dry and humid air

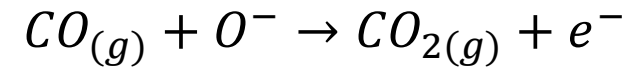


# Metal oxide gas sensors

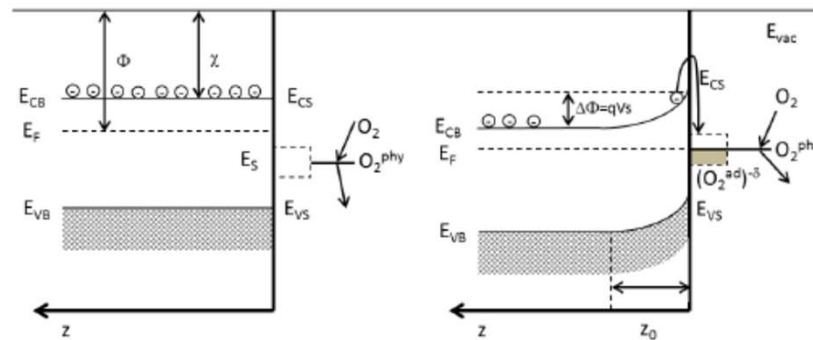


C. Wang et al., Sensors 10 (2010) 2088-2106

## Conductometric Gas Sensor

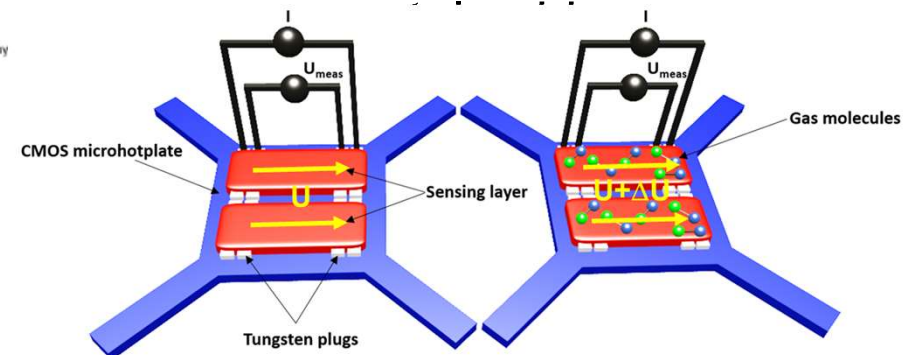


n-type



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

Reaction of gas with adsorbed O<sup>-</sup> 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

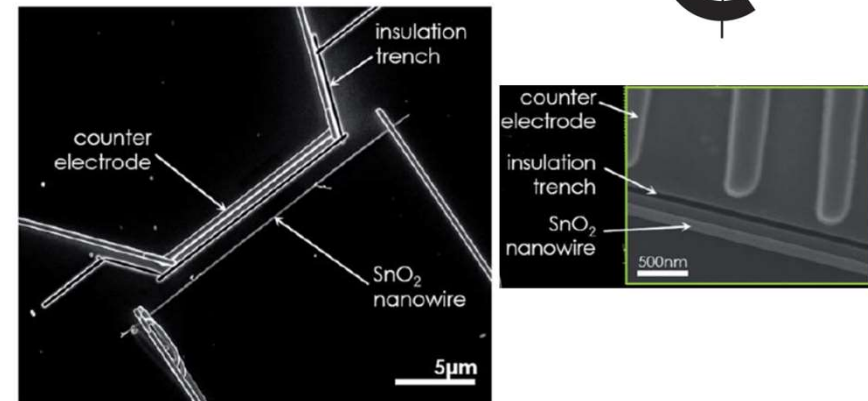
# Metal oxide gas sensors



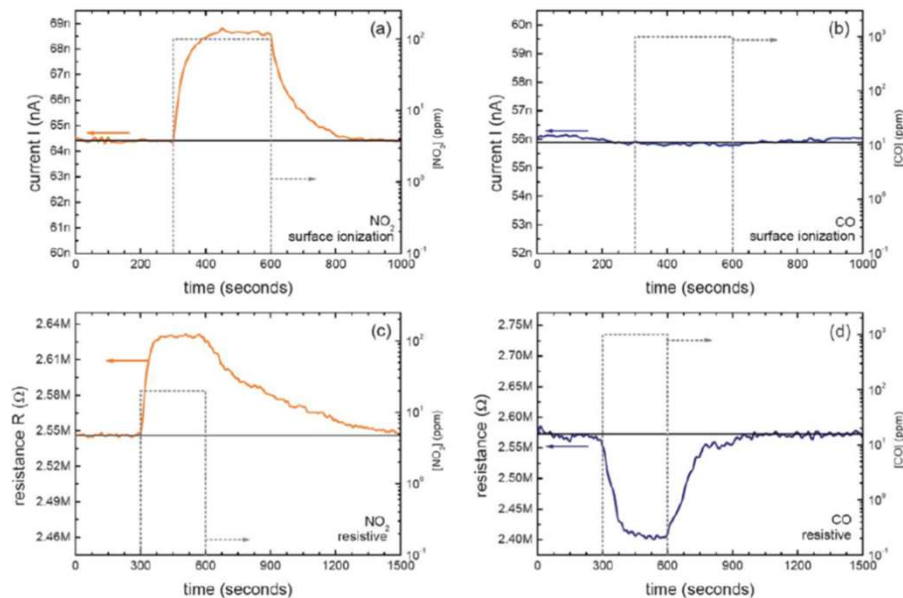
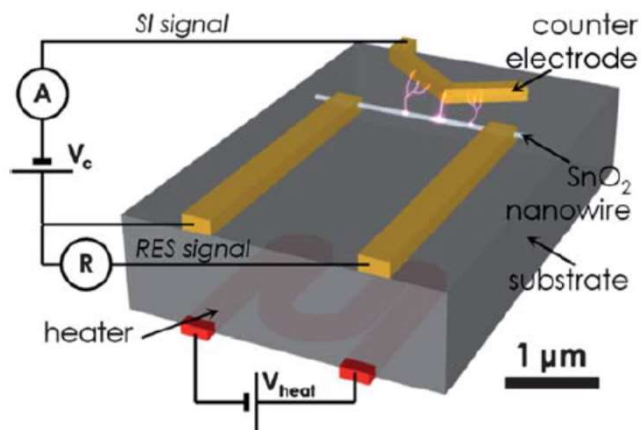
## Ionisation Gas Sensor

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

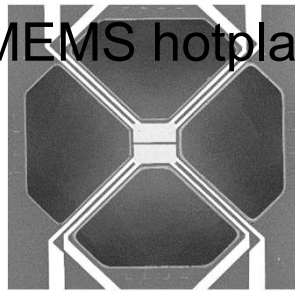
Simultaneous ionisation (current) and conductometric (resistance) measurements at very low operating power



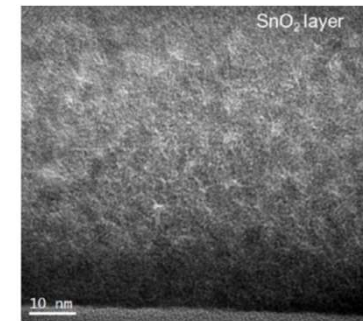
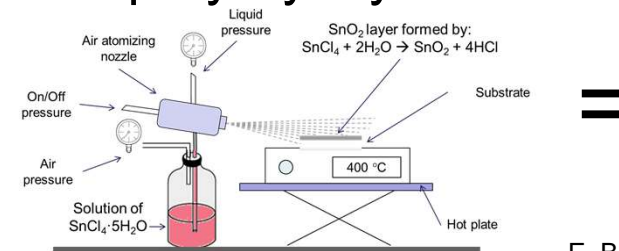
# Fabrication of gas sensing nanostructures

## Nanocrystalline Thin Films

MEMS hotplate

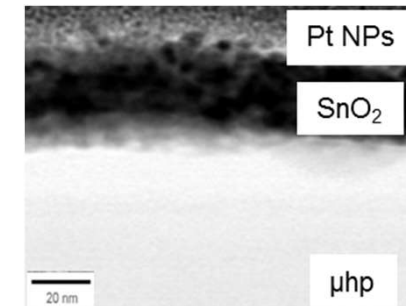


## Spray Pyrolysis



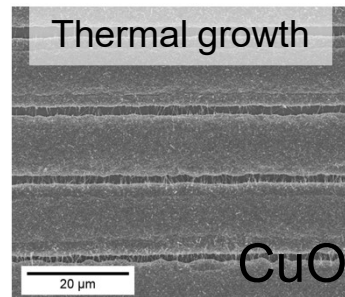
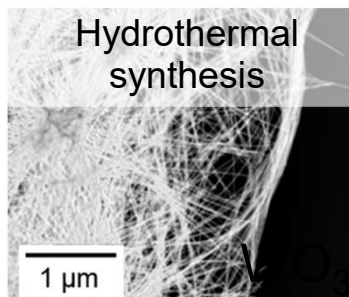
E. Brunet et al., Sens. Act. B 165 (2012) 110-118

## Functionalising Nanoparticles

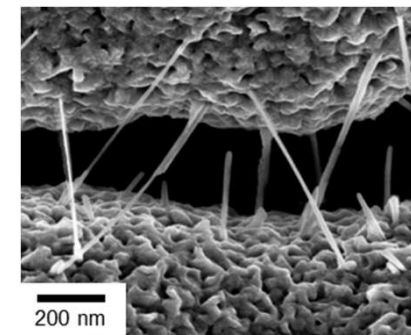


A. Köck, M. Deluca et al., Sensor+Test 2017

## Nanowires



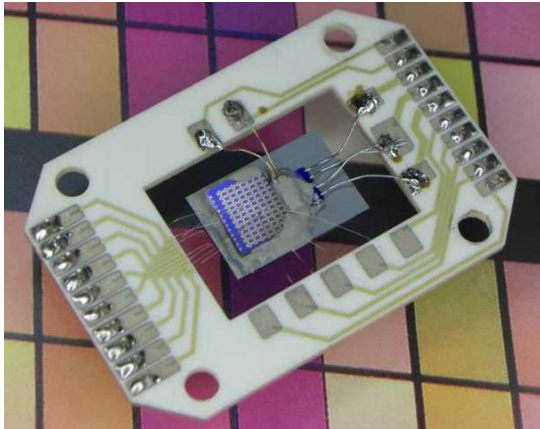
## Transfer printing



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



## Bulk Conductometric



Bulky Pt-heater

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

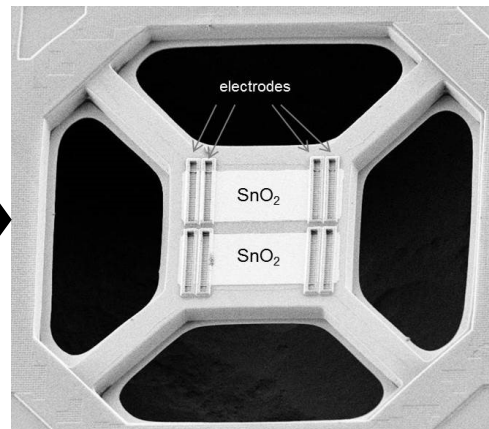
No CMOS-integration

Large power consumption

600 mW operation

**4.3 kJ/day**

## CMOS Conductometric



MEMS polysilicon heater

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

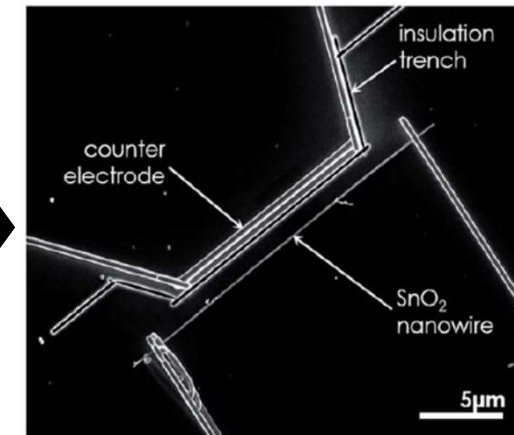
CMOS-integration

Medium power cons.

20 mW operation

**144 J/day**

## Self-heating



Self-heating nanowires

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

CMOS-integration

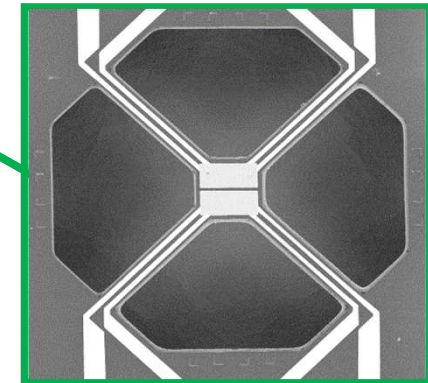
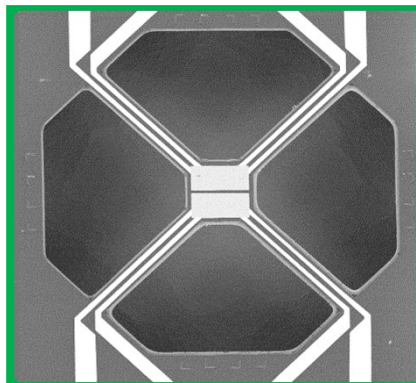
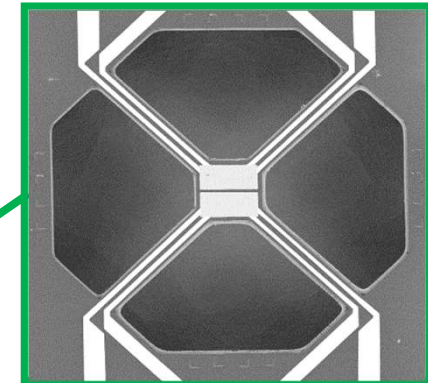
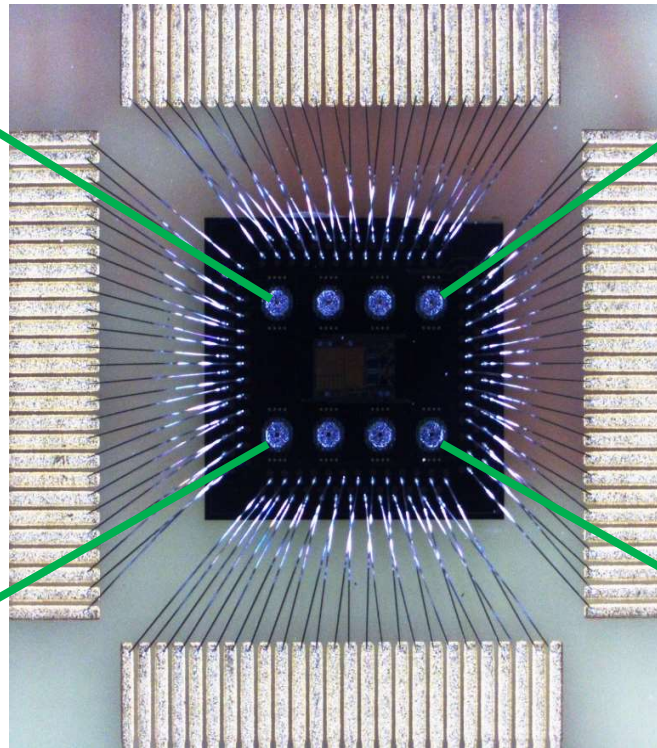
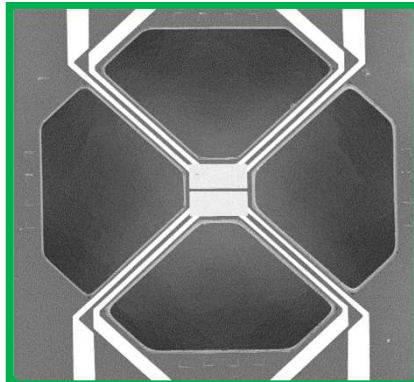
Low power consumption

20  $\mu\text{W}$  operation

**0.144 J/day**

## MEMS resistive arrays

Self-heating nanowires



Power consumption: 20  $\mu$ W

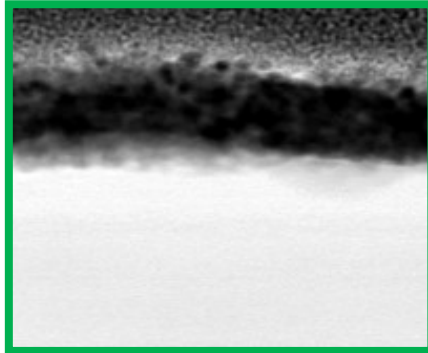
0.144 J/d



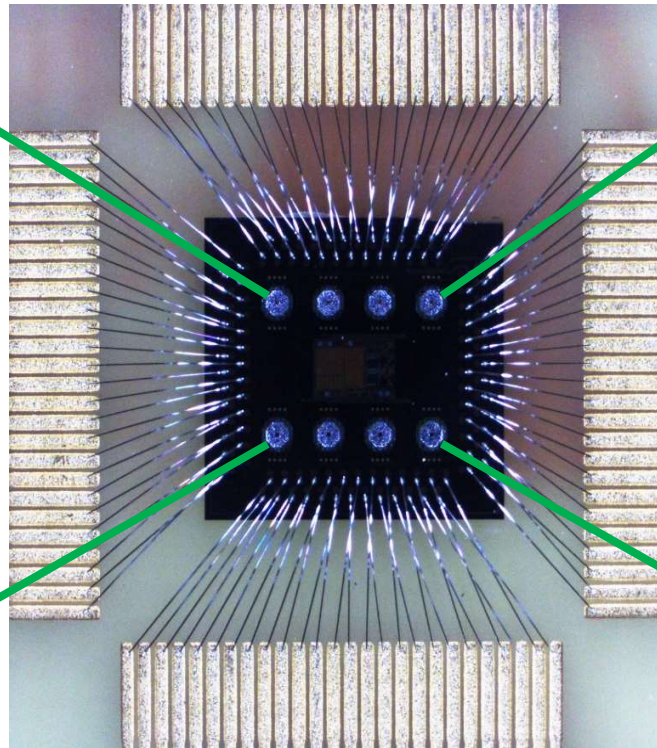
# Highly selective gas sensor arrays



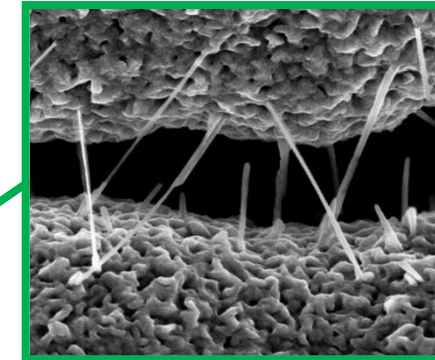
SnO<sub>2</sub> + Pt



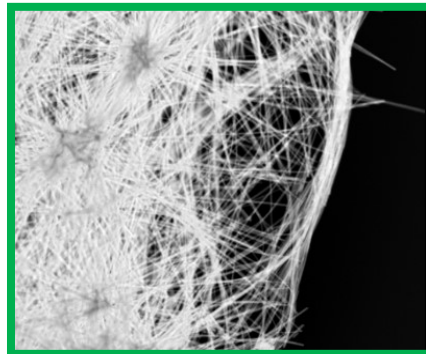
**MEMS resistive arrays**  
Self-heating nanowires



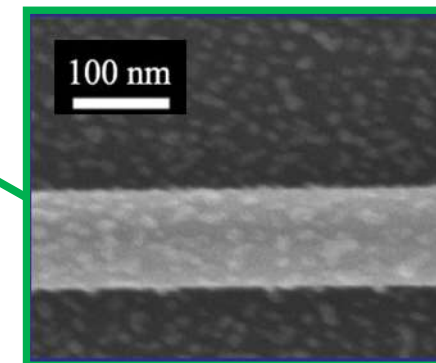
CuO-NWs



WO<sub>3</sub>



CuO-NWs + Au



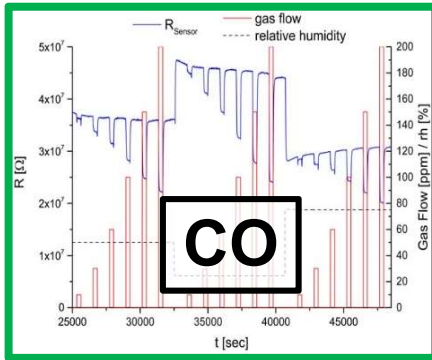
Functionalised with different materials  
Selectivity to different gases



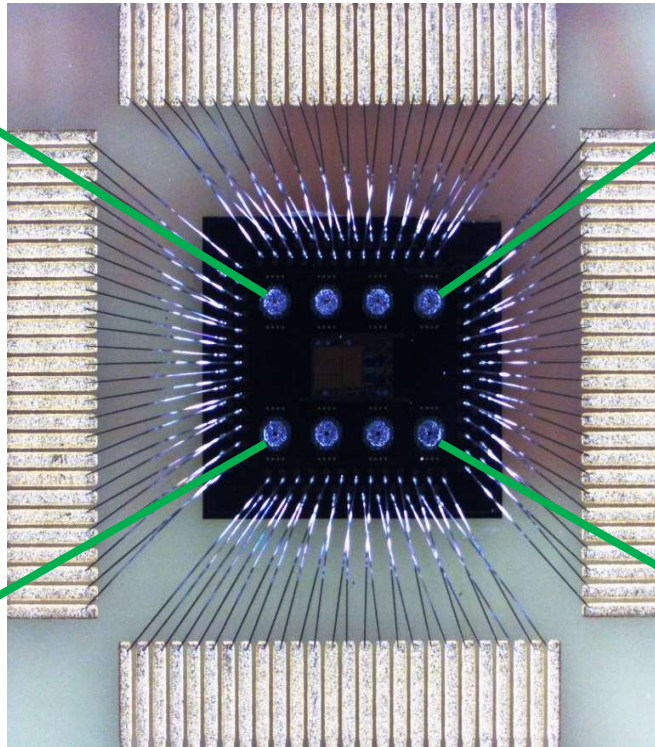
# Highly selective gas sensor arrays



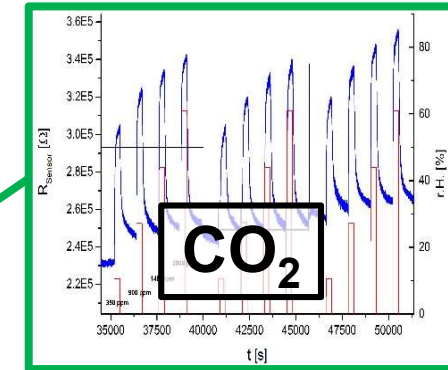
SnO<sub>2</sub> + Pt



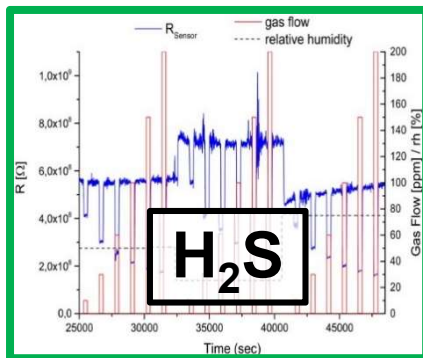
**MEMS resistive arrays**  
Self-heating nanowires



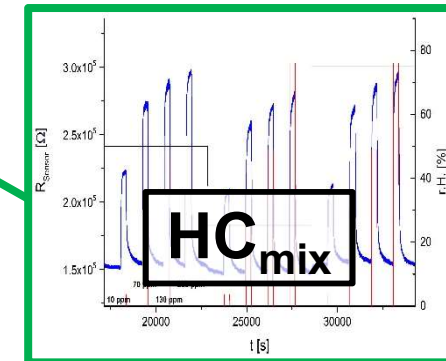
CuO-NWs



WO<sub>3</sub>

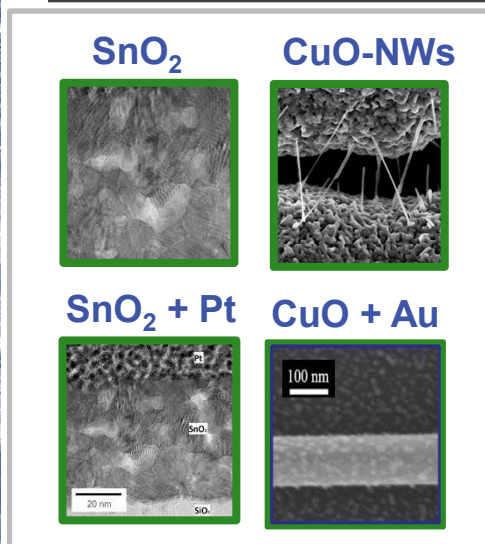


CuO-NWs + Au

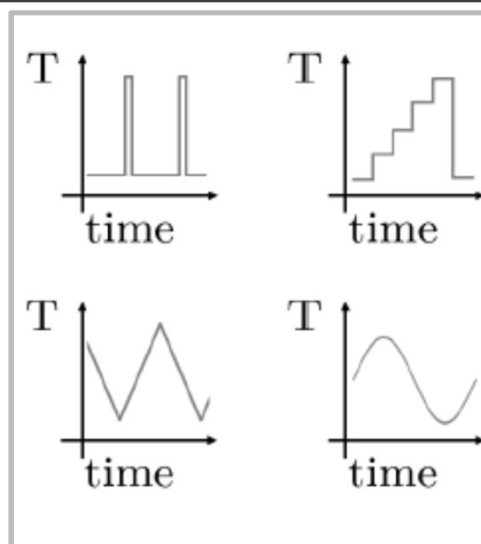


„Cross-Sensitivity“ problem

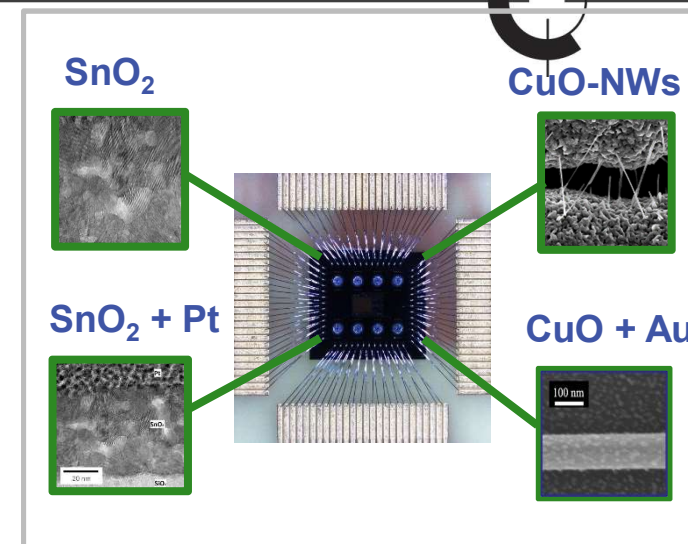
# Multifunctional sensors



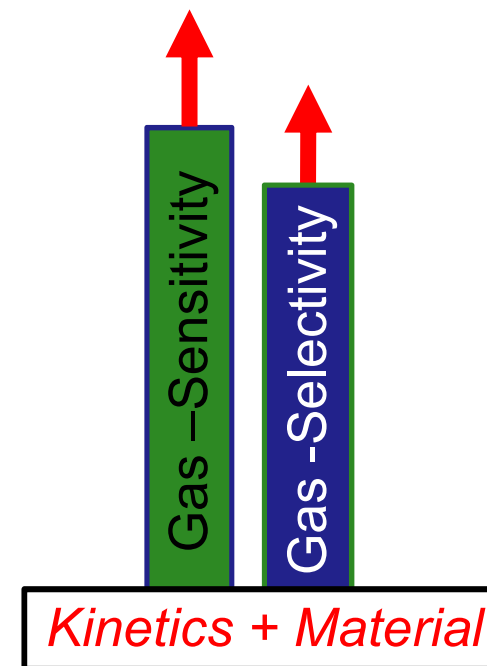
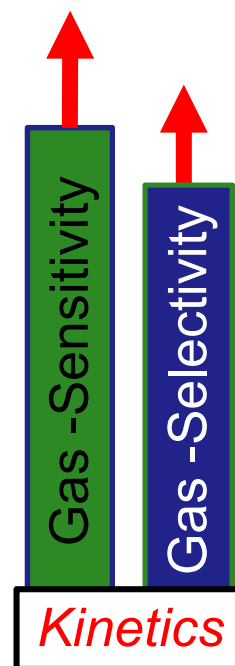
**Single Sensors**



**Temperature Cycles**

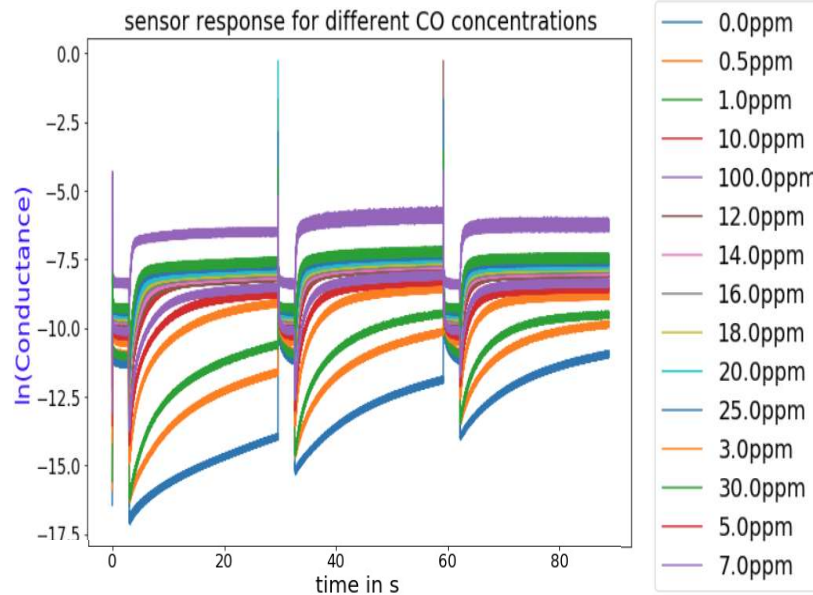
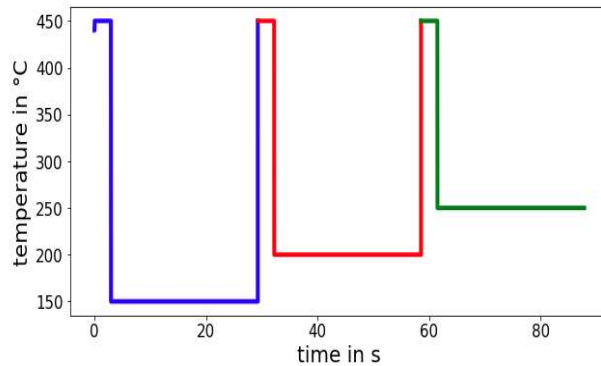


**Sensor Arrays**

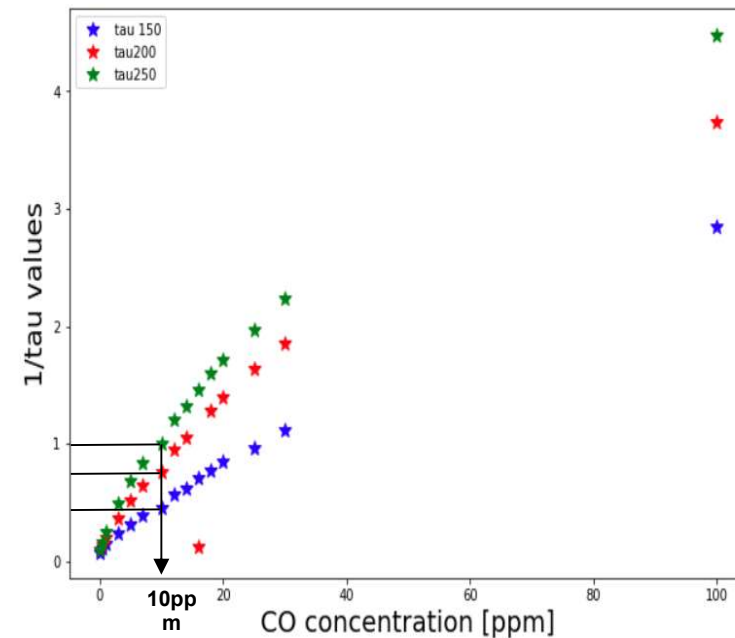




## Temperature cycles for gas quantification



## $\tau$ -Evaluation for gas quantification



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

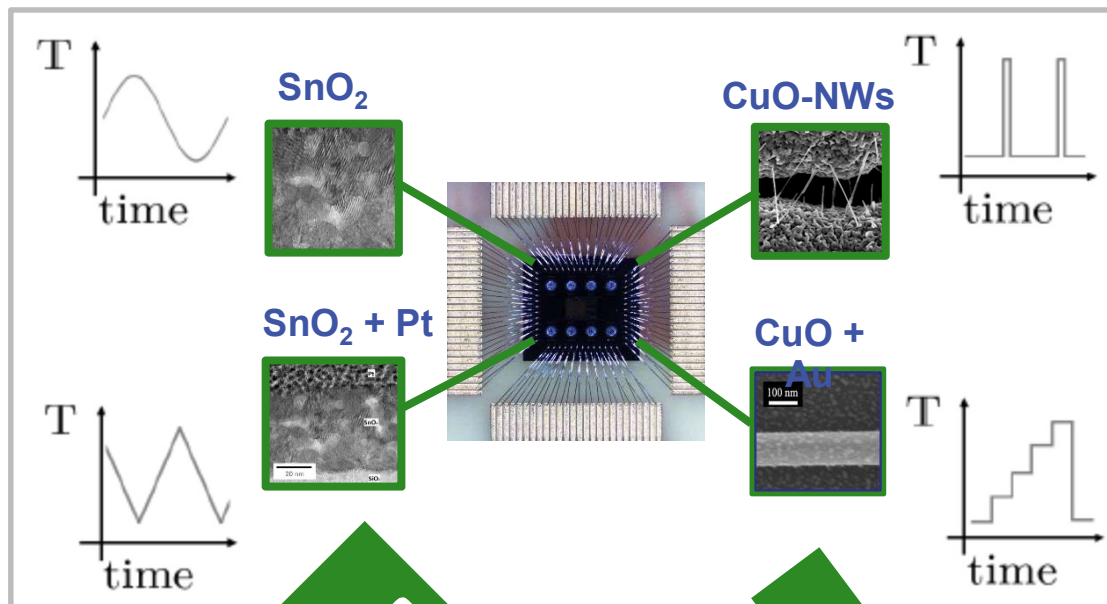
**Faster  
measurement!**

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**

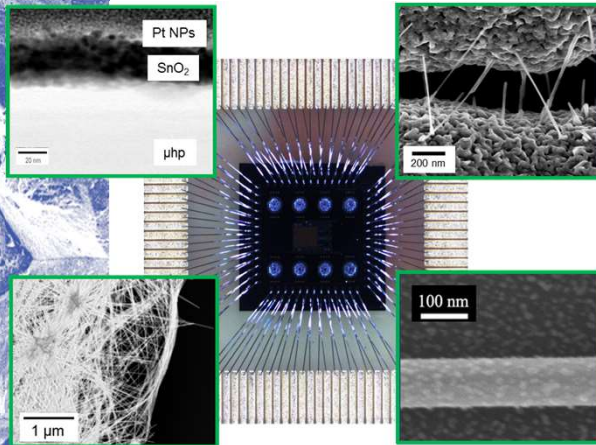




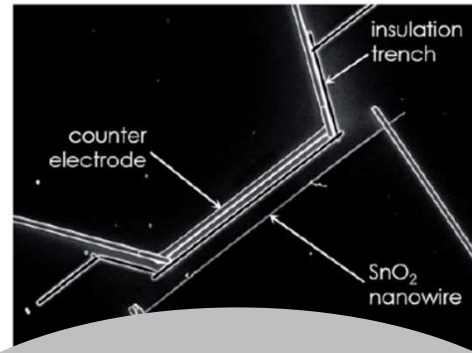
# Highly selective gas sensor arrays



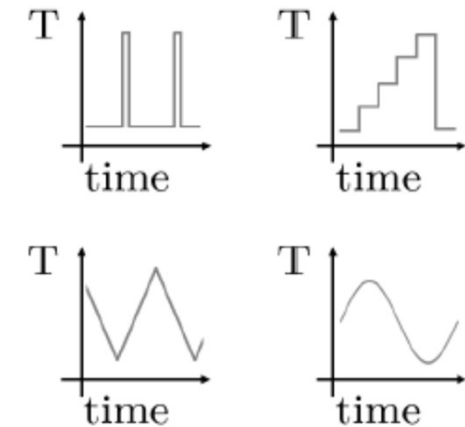
## MEMS arrays



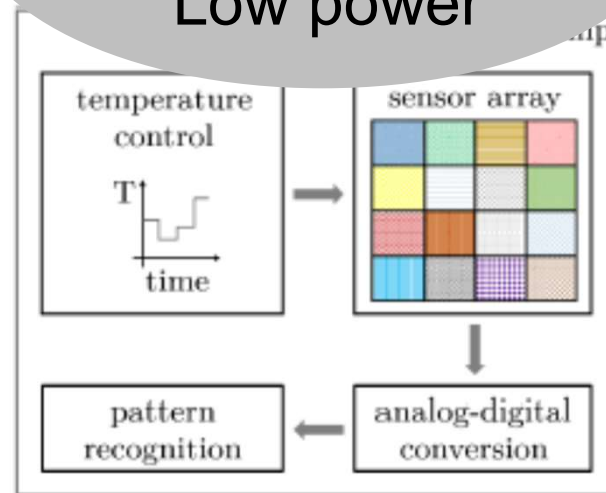
## Ionisation sensor



## Thermal profiles



High sensitivity  
High selectivity  
Low power

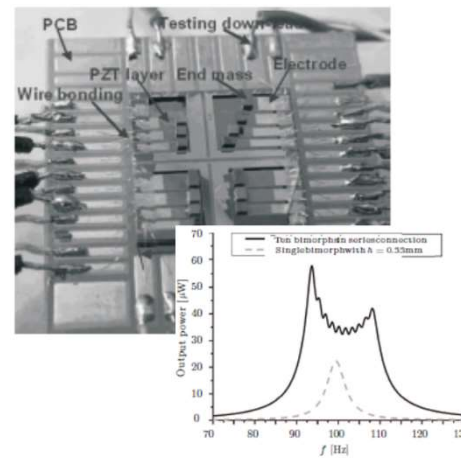


System-on-Chip  
for gas detection

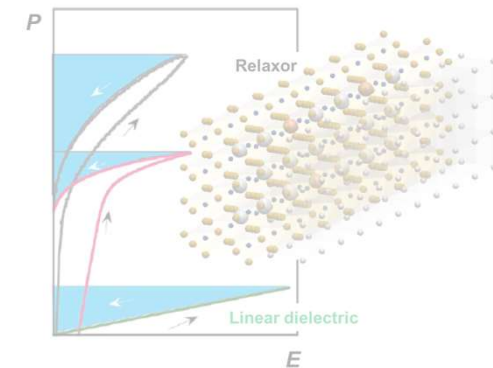
## Low-power gas sensors



## Broadband piezo-harvesters



## High energy-density capacitors

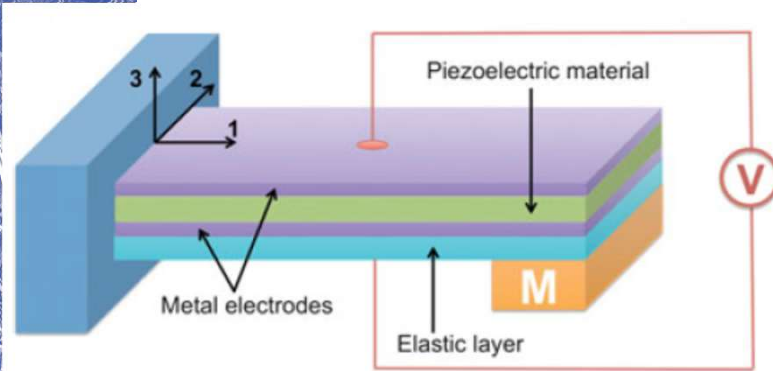




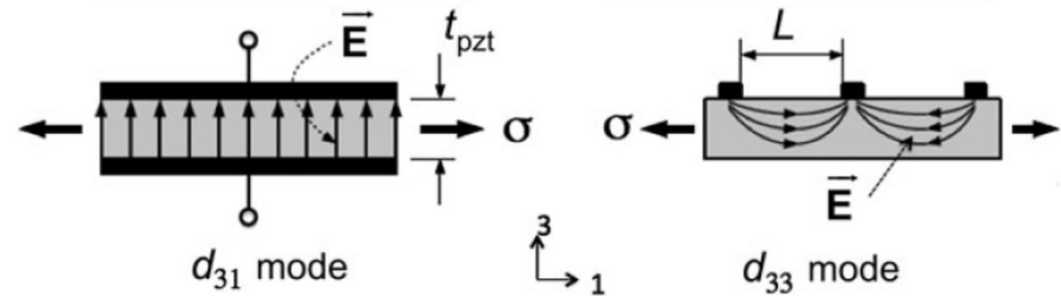
# Piezoelectric energy harvesting



## 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)



$\epsilon_{33}$



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

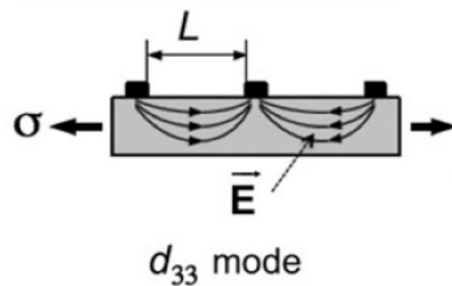
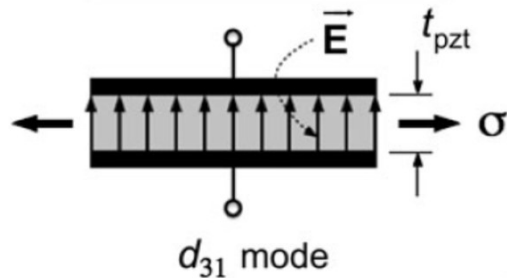
Material	$d_{31}$ (pC/N)	$\epsilon_{33}$	Frequency (Hz)	Power ( $\mu\text{W}/\text{mm}^3$ )
PZT	170	3000	126	20.5
KNN	100	900	1036	6.5
AlN	3	9	214	0.2

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

## Piezoelectric properties

Maximise  $d_{ij}$

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



## Operational range

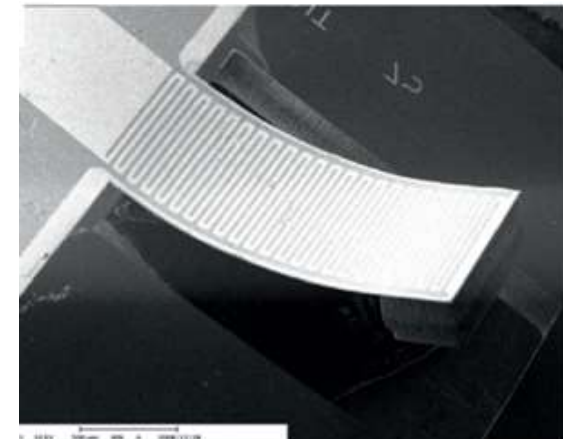
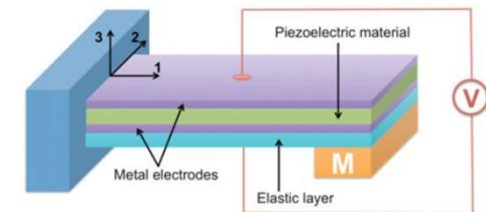
- Frequency matching
- Low-frequency operation
- Broadband operation



Trade-off  $\omega_r$ ,  $Q_m$

## Cost

- Thin film deposition
- MEMS structures



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



# Low-frequency energy harvesting



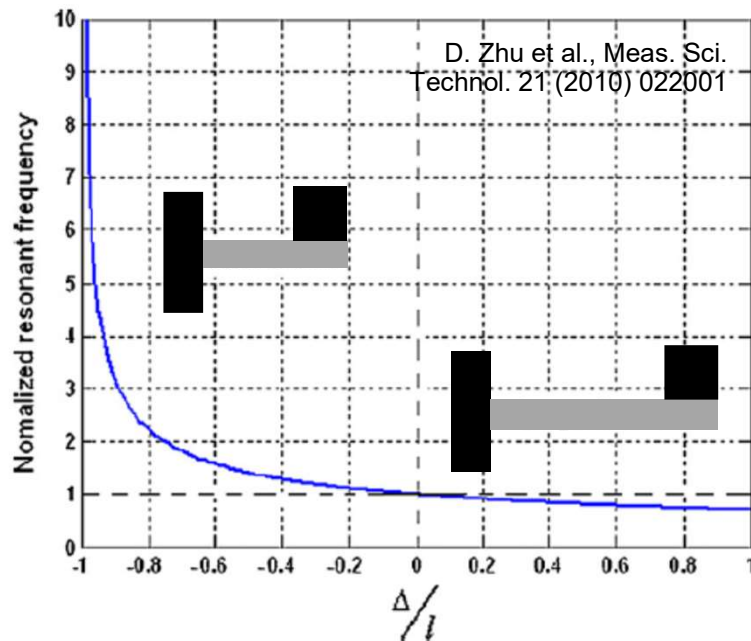
## Resonance frequency of mass-cantilever system

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

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

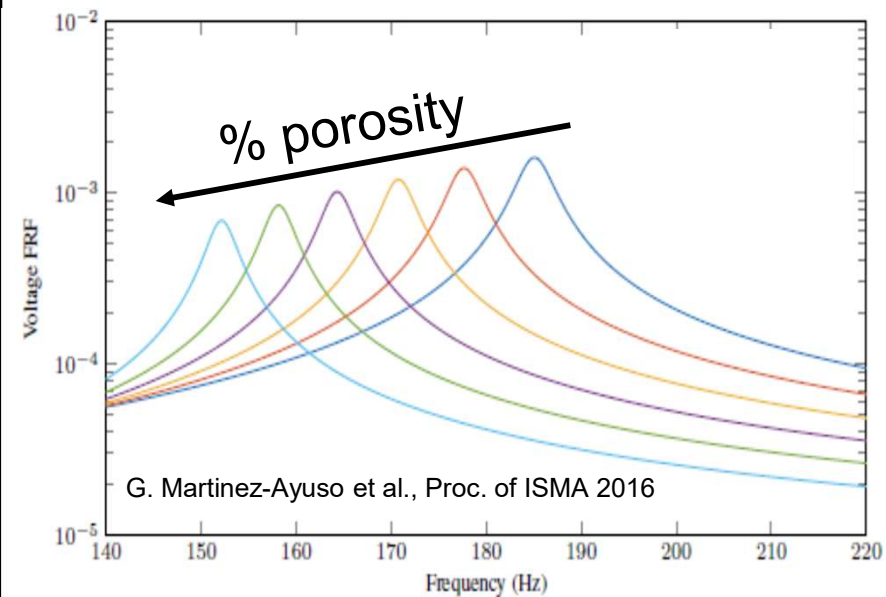
D. Zhu et al., Meas. Sci. Technol. 21 (2010) 022001

### Modify cantilever geometry



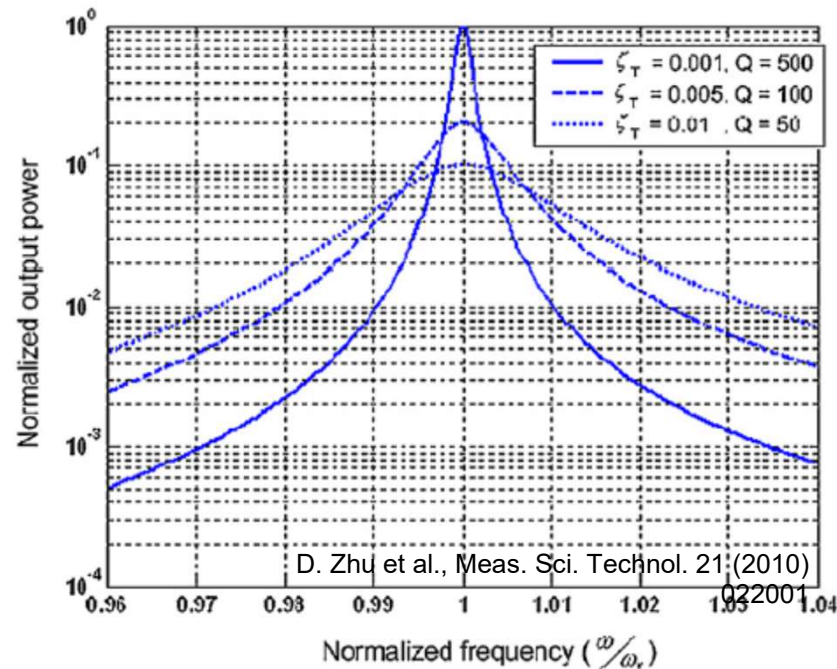
$Q_m$  remains constant

### Modify Young's modulus



$Q_m$  decreases

## Modify $Q_m$

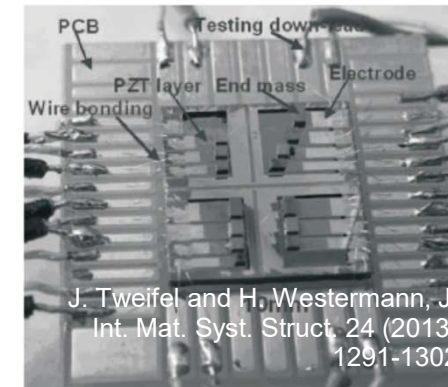


Suitable for low-power applications

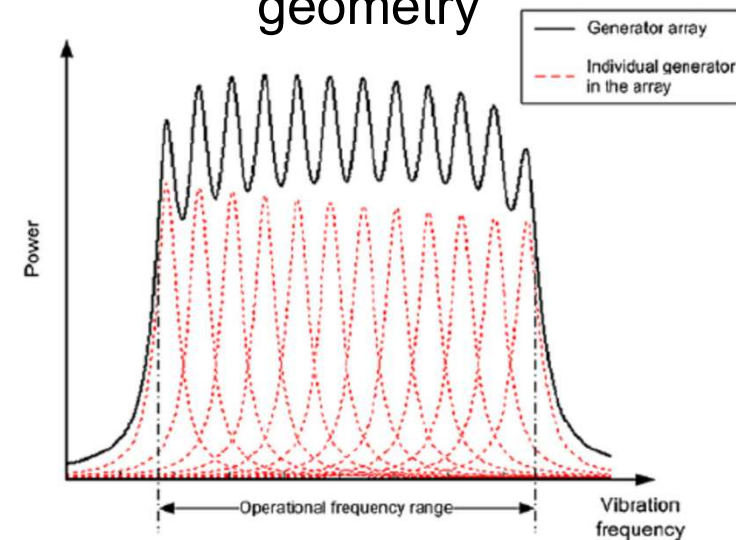
↓  $Q_m =$  ↓ Stiffness

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

## Modify Geometry



## Cantilever array with variable geometry

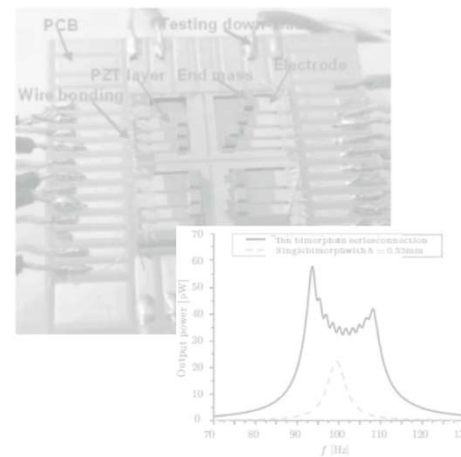


D. Zhu et al., Meas. Sci. Technol. 21 (2010) 022001

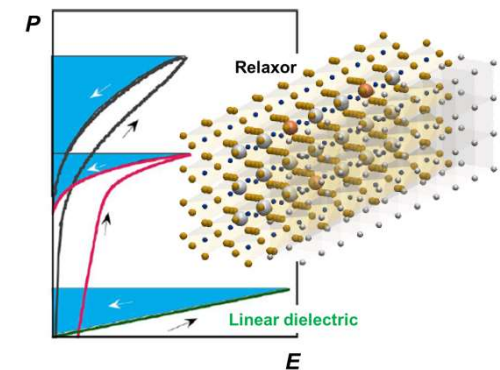
## Low-power gas sensors



## Broadband piezo-harvesters



## High energy-density capacitors





# Energy storage for wireless sensors



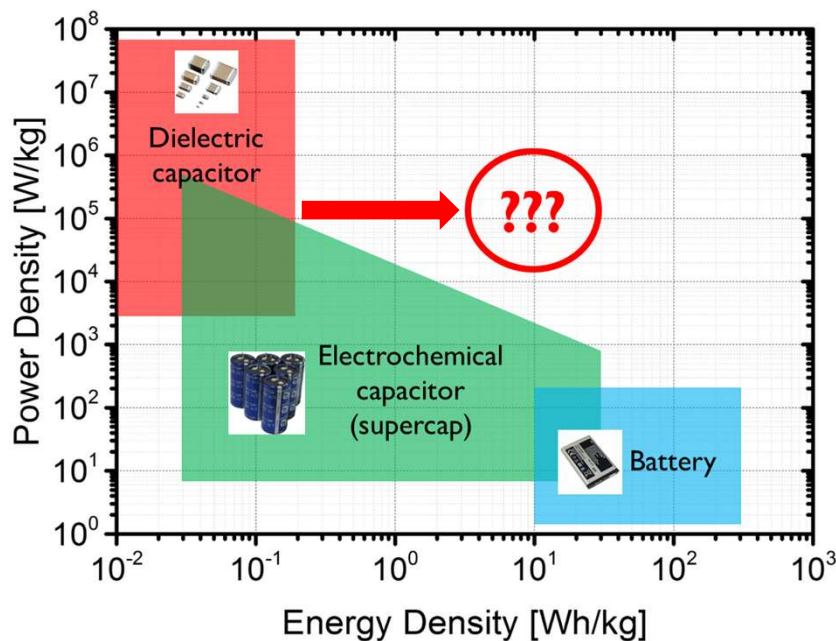
*Energy sources change quickly*  
**Need quick charge/discharge**

**High power density**



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

**High energy density**



## Dielectric capacitors:

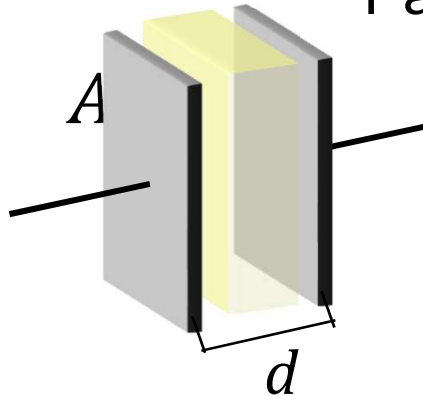
- High power density
- Temperature stability
- Cyclic stability

**Need high energy density**

# Energy density of ceramic capacitors



## Parallel plate capacitor with dielectric



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

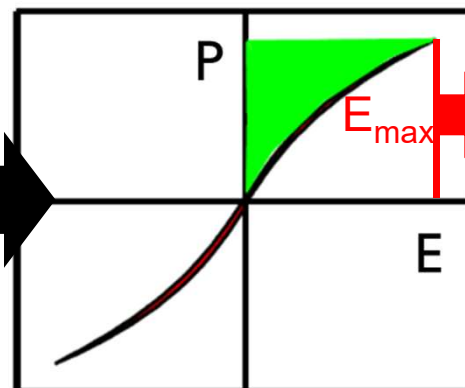
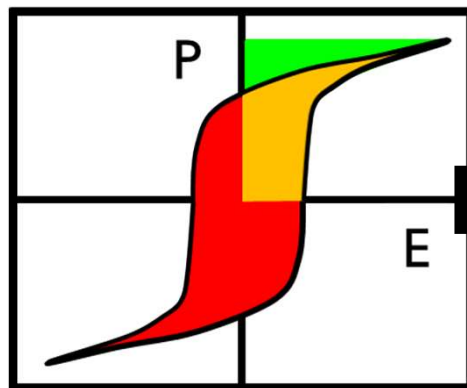
$$J = \frac{U}{Ad} \quad \text{Energy density}$$

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

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

### Ferroelectric

### Relaxor



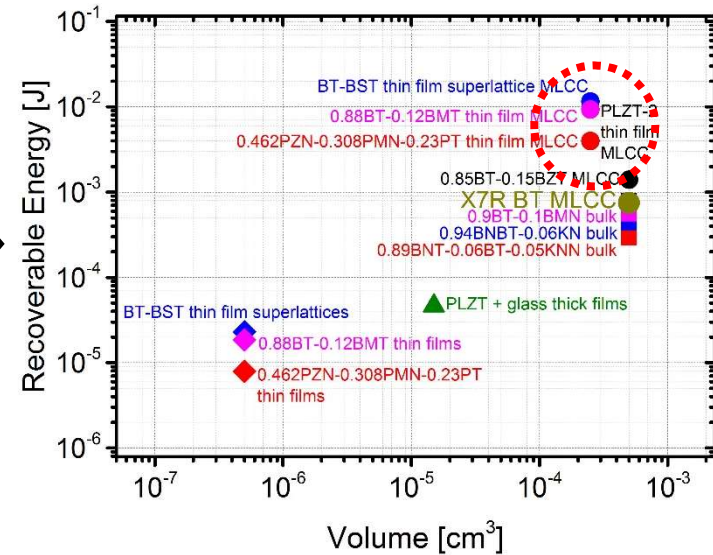
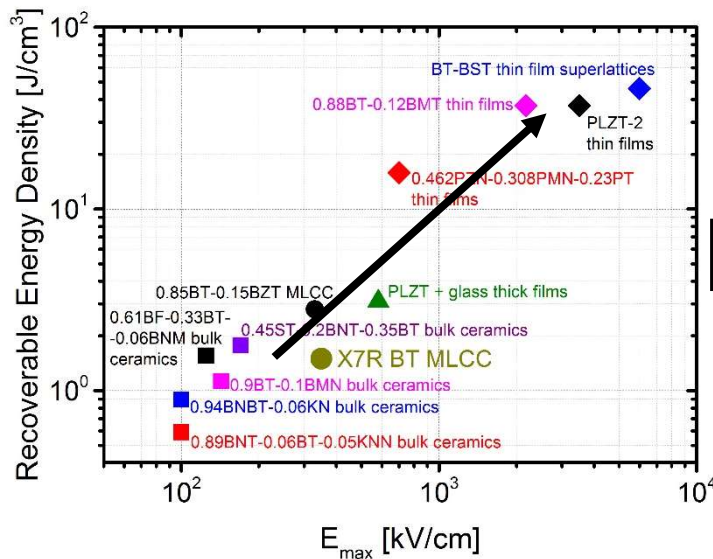
- +  = Stored energy density
- = Recoverable energy density
- = Energy loss (hysteresis)

### Ways to increase energy density:

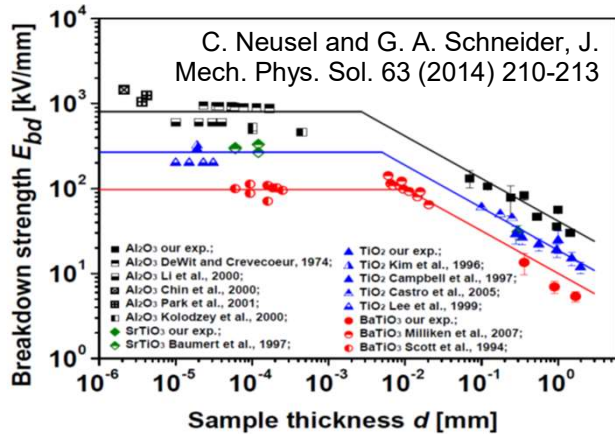
1. Reducing hysteretic losses *while maintaining high permittivity (i.e. P)*
2. Increasing dielectric breakdown strength (DBS) – enhancing  $E_{\max}$



# Increasing the DBS: Thin film processing

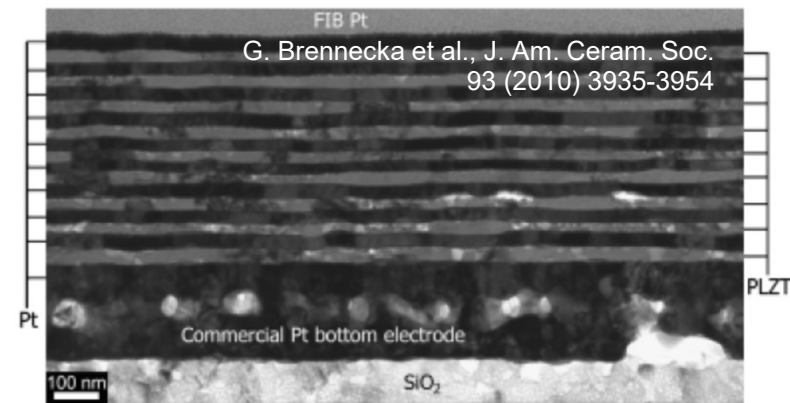


## Reduced layer thickness



Less probability to find a critical defect

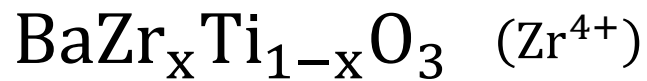
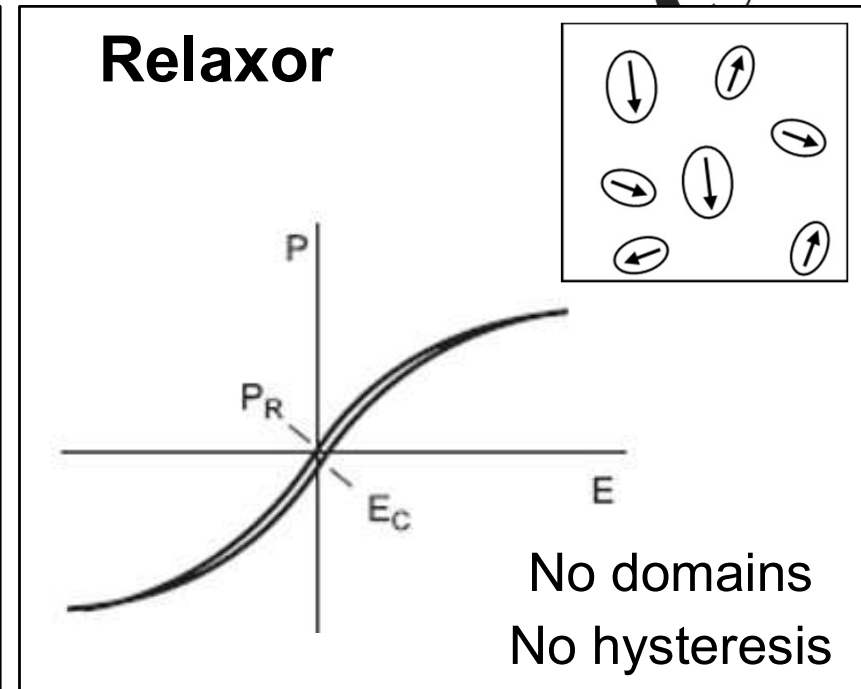
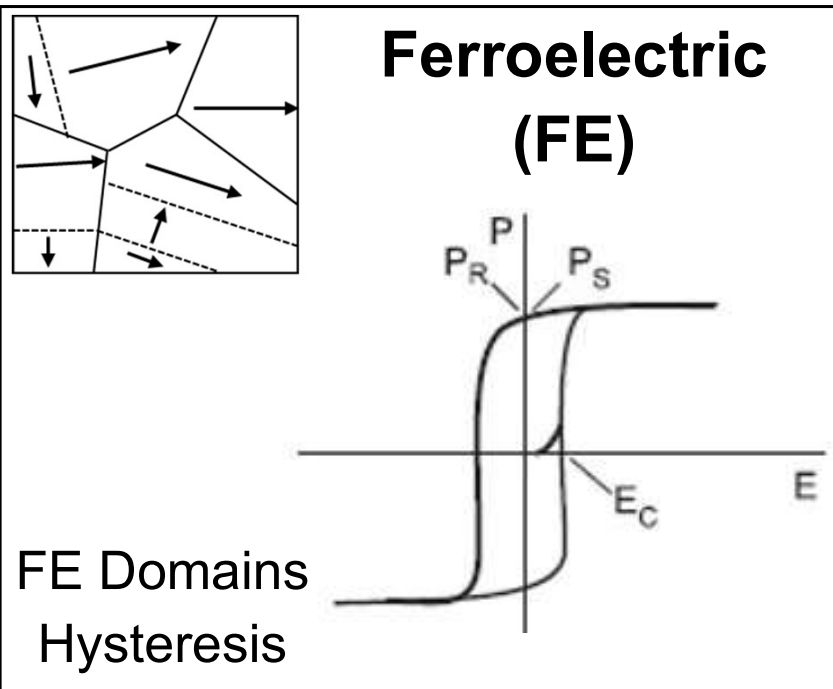
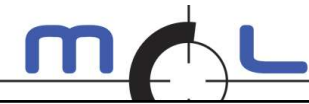
## Chemical solution deposition



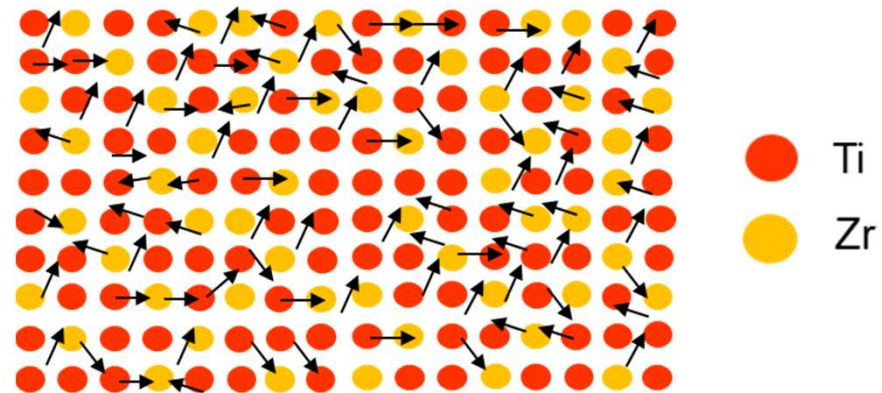
Low porosity and defect density compared to solid-state processing



# Optimising the polarisation: Relaxors



relaxor for  $x = 0.35$

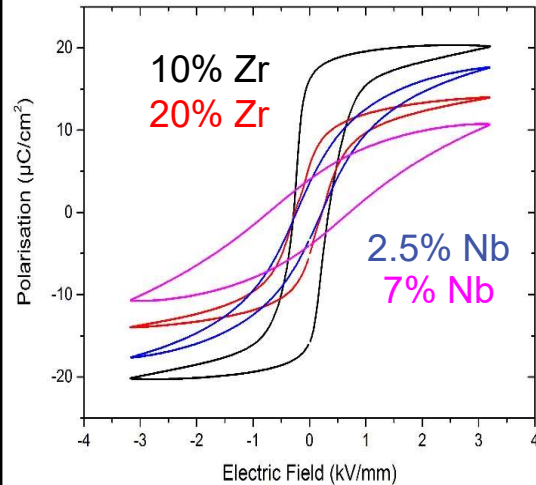


**Relaxors:** Chemical substitution breaks the long-range cooperative displacement of Ti cations and disrupts ferroelectricity

# Optimising the polarisation: Relaxors



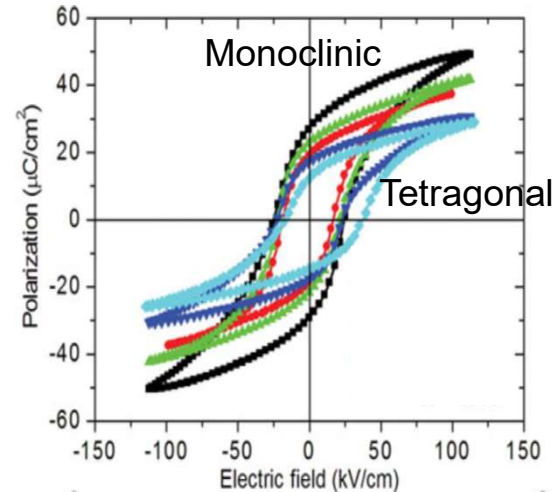
## Composition



*Substitution disrupts ferroelectricity*

M. Deluca et al., unpublished (2019)

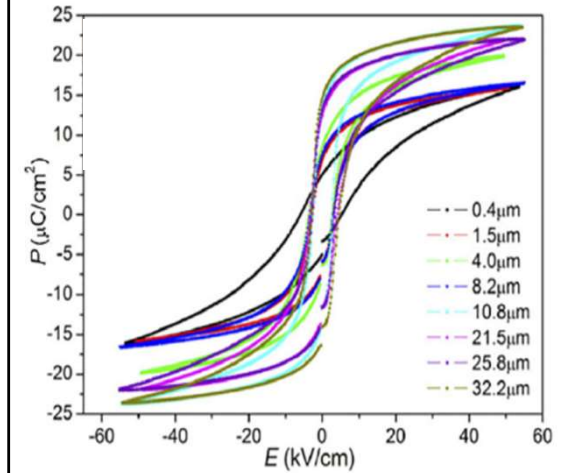
## Symmetry



*Monoclinic phase increases permittivity*

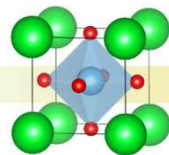
E. C. Lima et al., Ferroel. 465 (2014)

## Grain size

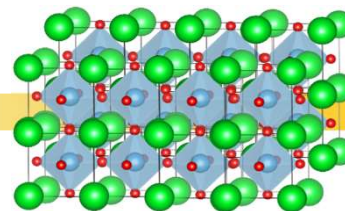


*Small grain size suppresses ferroelectricity*

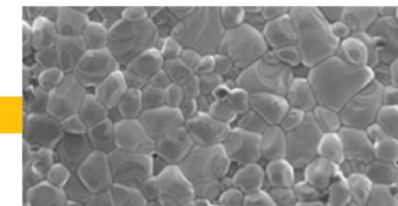
M. Acosta et al., Appl. Phys. Rev. 4 (2017) 041305



**Atomic scale**



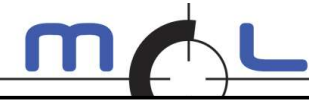
**Nanoscale**



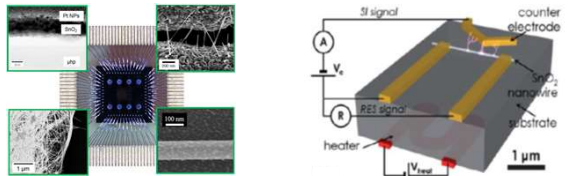
**Mesoscale**

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

# Self-powered wireless sensor nodes

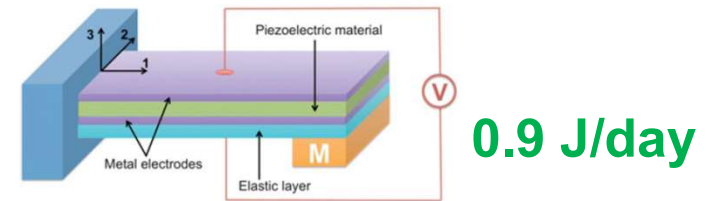


## MEMS resistive + Ionisation gas sensor

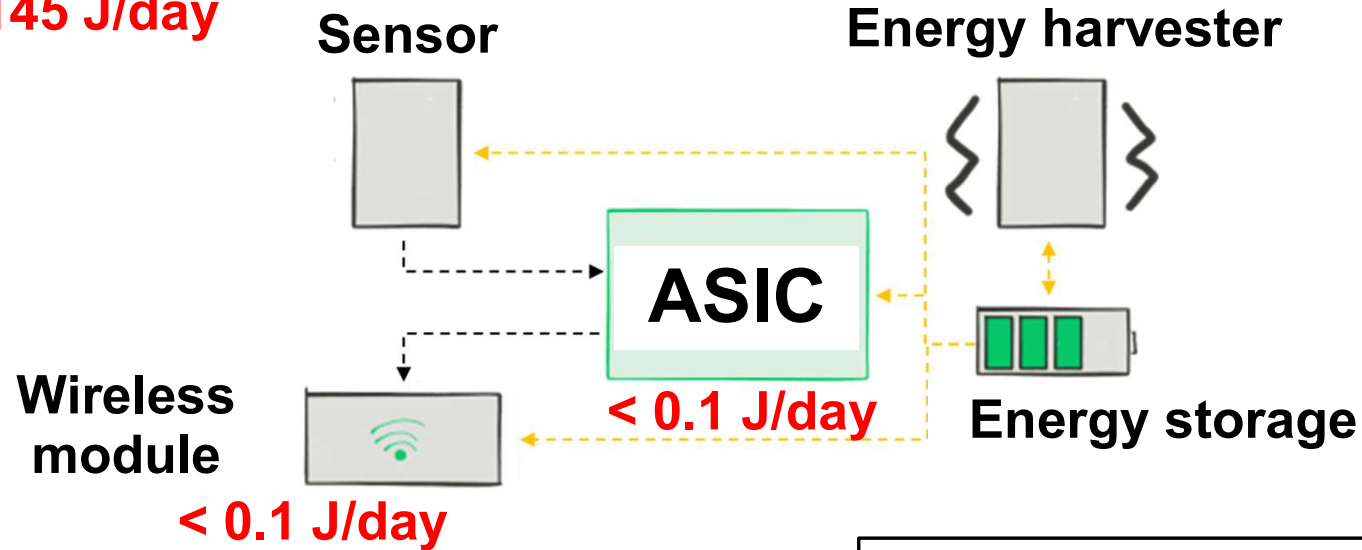


**0.145 J/day**

## Piezoelectric energy harvester

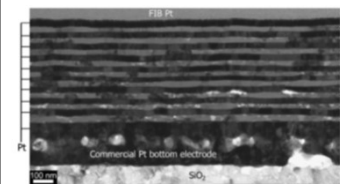


**0.9 J/day**



**Energy autonomous operation possible!**

## Thin film ceramic MLCC



40 J/cm<sup>3</sup>  
8 cycles/hour  
**0.9 J/day**



# Take-home messages:

**Autonomous IoT sensor nodes** must combine the following elements:

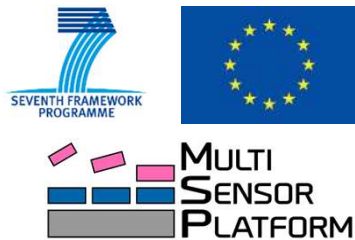
- **Low-power sensors** including ASIC and network element
- **Resilient** energy harvesters such as **broadband** and **low-frequency piezoelectric energy harvesters**.
- **High-power** and **high energy density** energy storage.

**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*



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ERC-COG-2018 – GA. 817190

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



Der Wissenschaftsfonds.

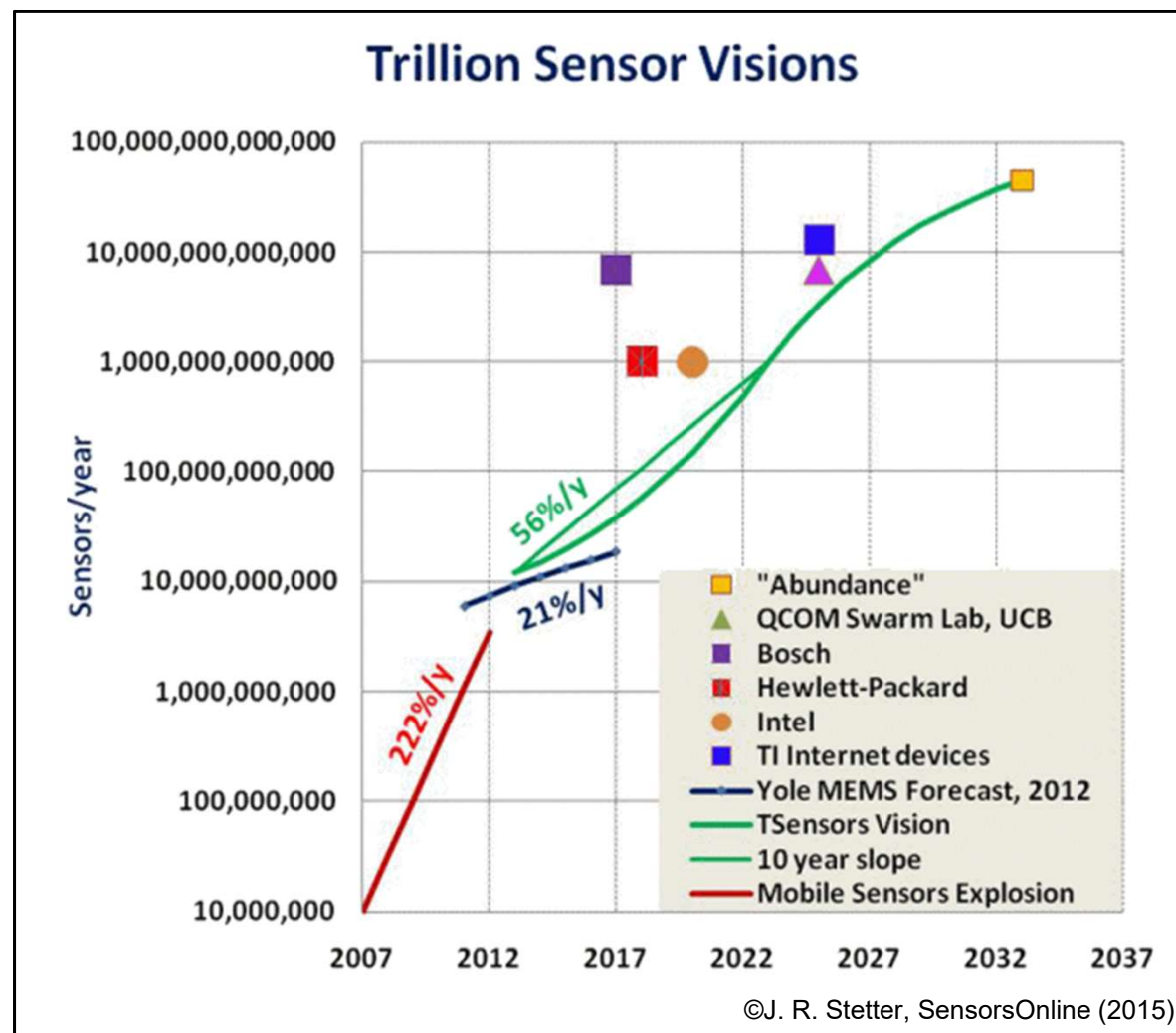
FWF Single Project – Nr. P29563-N36

*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!**

