Surface Ionization on Metal Oxide Gas Sensors

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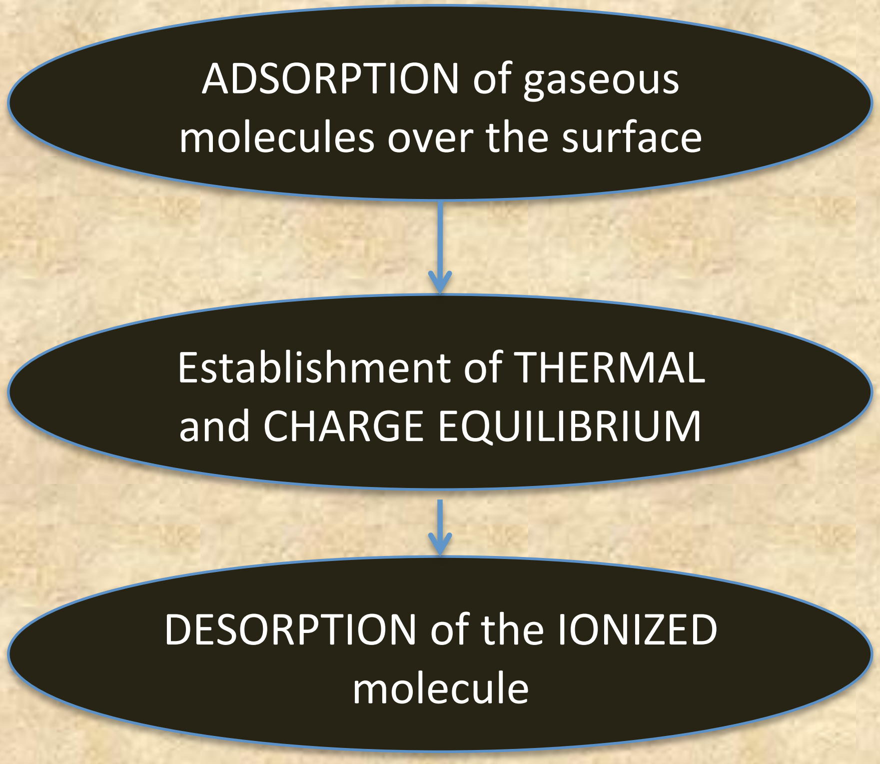
Outline

- Surface ionization (SI)
  - phenomena and devices
- SI devices with planar layout – preparation
  - RuO_x nanorods
  - CuO nanorods
- SI devices with planar layout – characterization
  - Ethanol
  - Acetone
  - NO_2
- Conclusions

Surface Ionization (SI) phenomena

Surface ionization (SI) consists in the formation of positive and negative ions in the course of thermal desorption of molecules. Roughly, it consists of 3 steps:



U.K Rasulev , E.Y. Zandberg; Progr.Surf.Sci.28 (1988) 181

Surface Ionization (SI) phenomena

positive ions

$$\alpha = \frac{n_+}{n_0} = A_+ \exp\frac{q(\varphi - V_+)}{kT}$$

negative ions

$$\alpha = \frac{n_-}{n_0} = A_- \exp\frac{q(V_- - \varphi)}{kT}$$

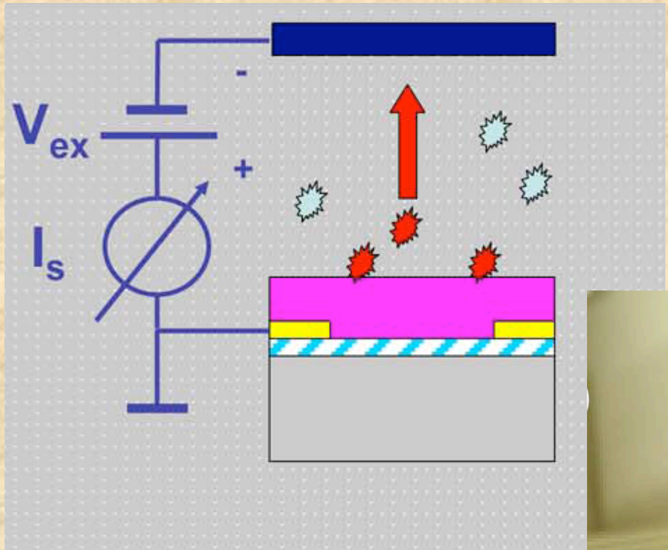
Degree of surface ionization α (ratio between the concentration of ionized and neutral ions) depends on the layer work function φ and on the molecule ionization potential (V_+) or electron affinity (V_-)

Selectivity

Molecule	**qV_+ (eV)**
Acetone	9.703
Ethanol	10.48
O_2	12.07
CO	14.01
NO_2	9.586

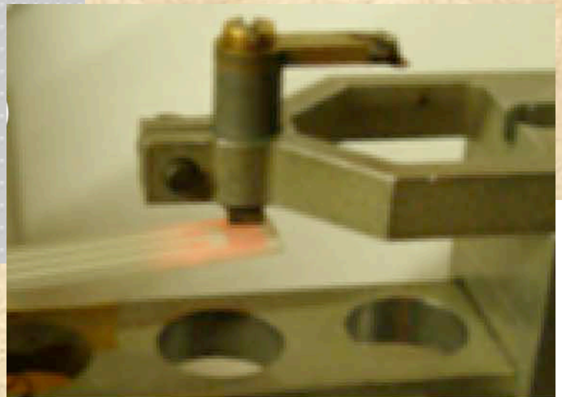
U.K Rasulev , E.Y. Zandberg; Progr.Surf.Sci.28 (1988) 181

Surface ionization (SI) devices - vertical layout



Typical experimental parameters
- Bias V=1000 V
- Electrode-oxide spacing d= 1mm
- Sensor T: 500-700 °C

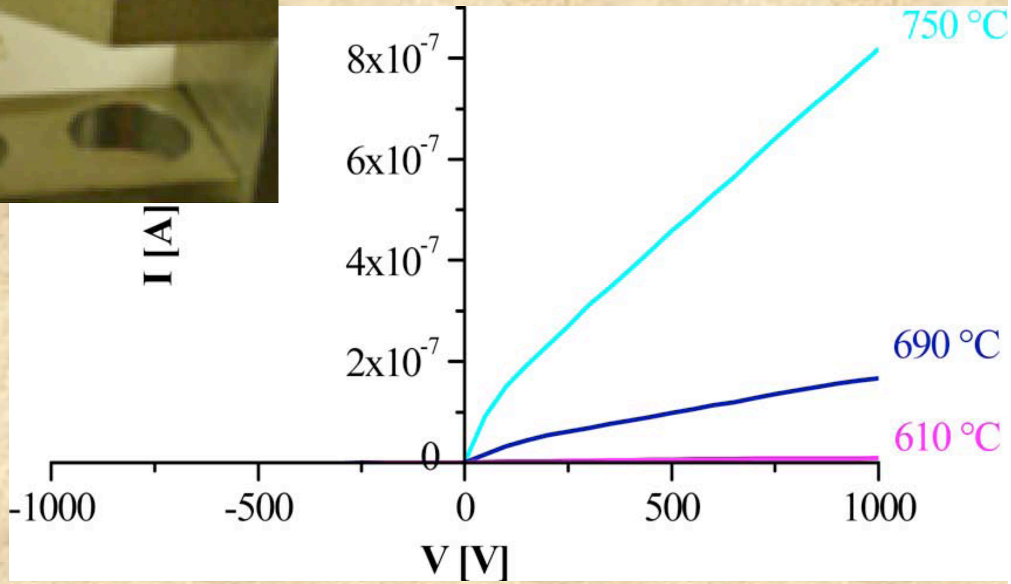
} $E = 10^6$ V/m



1% of ethyne in air
•positive ions generation
•Different electrode temperatures

⬇

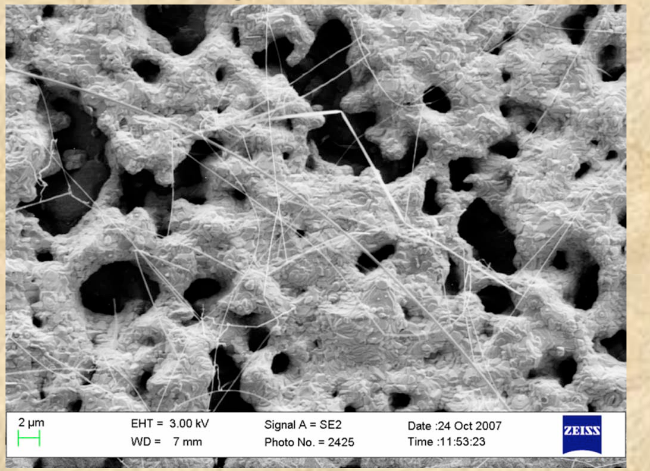
Asymmetric I-V curve

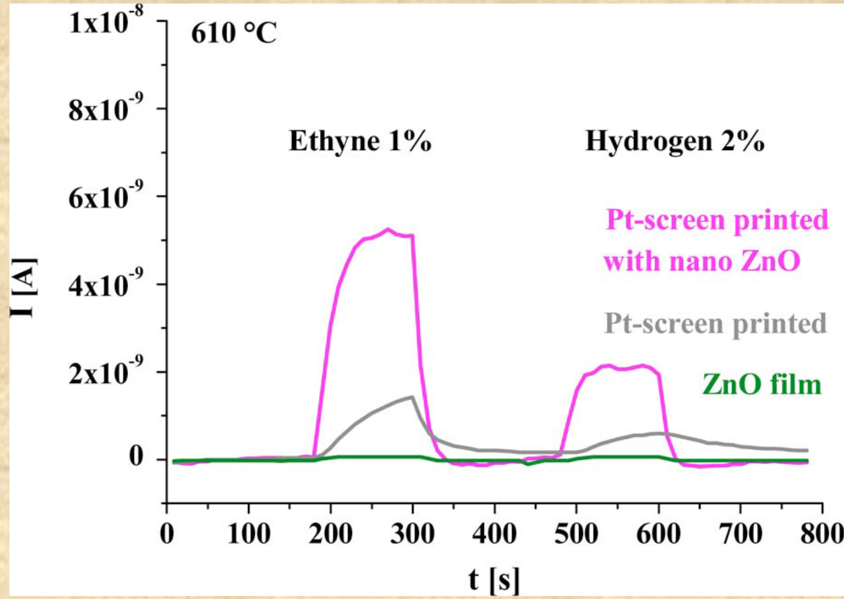


A. Hackner, A. Habauzit, G. Müller, E. Comini, G. Faglia, and G. Sberveglieri; IEEE Sens. J. 9 (2009) 1727

SI devices and nanostructures: aspect ratio

ZnO nanowires grown on a Pt electrode



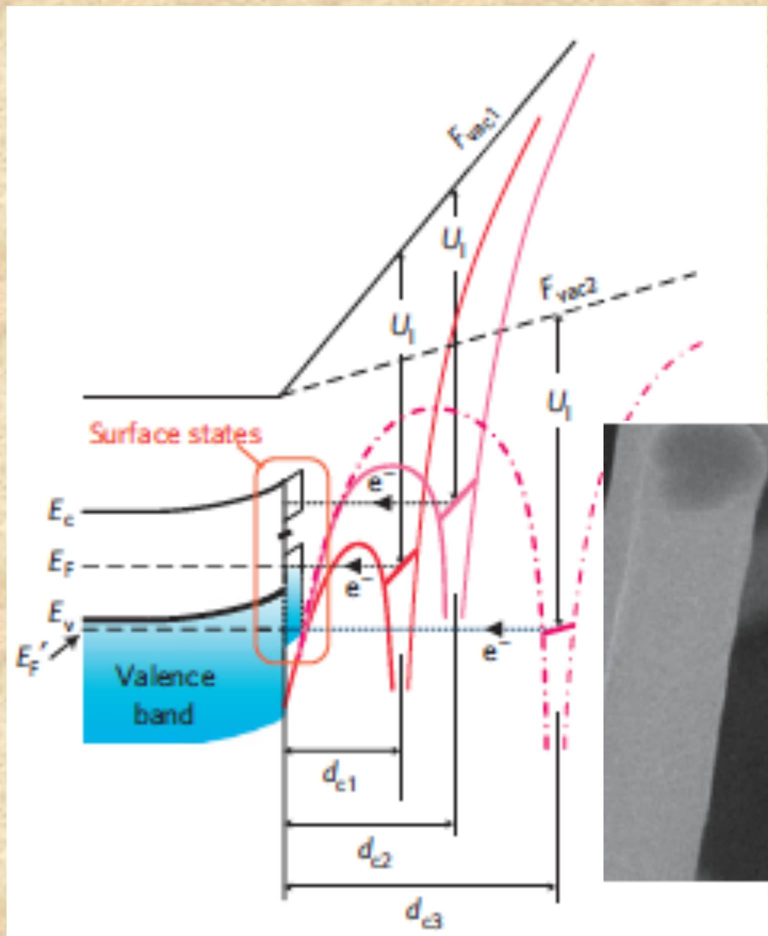


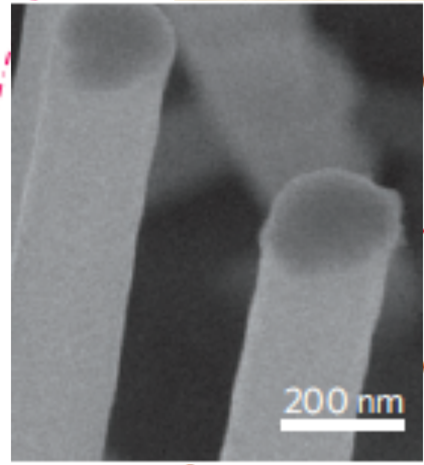
CAPABILITY OF HIGH ASPECT RATIO NANOSTRUCTURES TO CONCENTRATE HIGH ELECTRIC FIELDS AT THEIR APEX

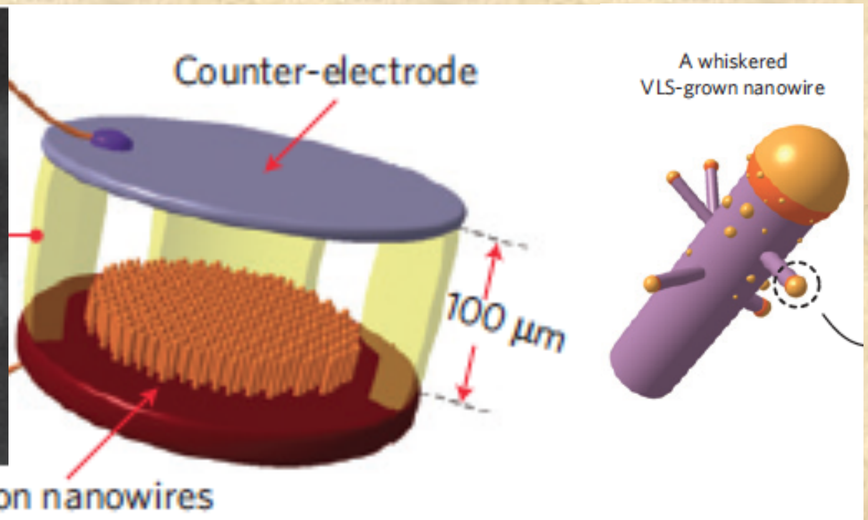
A. Hackner, A. Habauzit, G. Müller, E. Comini, G. Faglia, and G. Sberveglieri; IEEE Sens. J. 9 (2009) 1727
F.H. Read, N.J. Bowring, Nucl. Instrum. Meth. Phys. Res. A 519 (2004) 305–314

SI devices and nanostructures: surf. states

Radius/aspect ratio arguments do not fully explain the ionization current enhancement
➔ Surface states at the semiconductor-metallic tip interface (intrinsic in VLS grown nanowires)







R.B. Sadeghian, M.S. Islam, Nature Materials 10 (2011) 135-140

Single nanowire SI device

+ EXTREME MINIATURIZATION

Ion emitter: a single SnO2 nanowire

➔ Field enhancement

Fabrication: Focused Ion Beam (FIB)

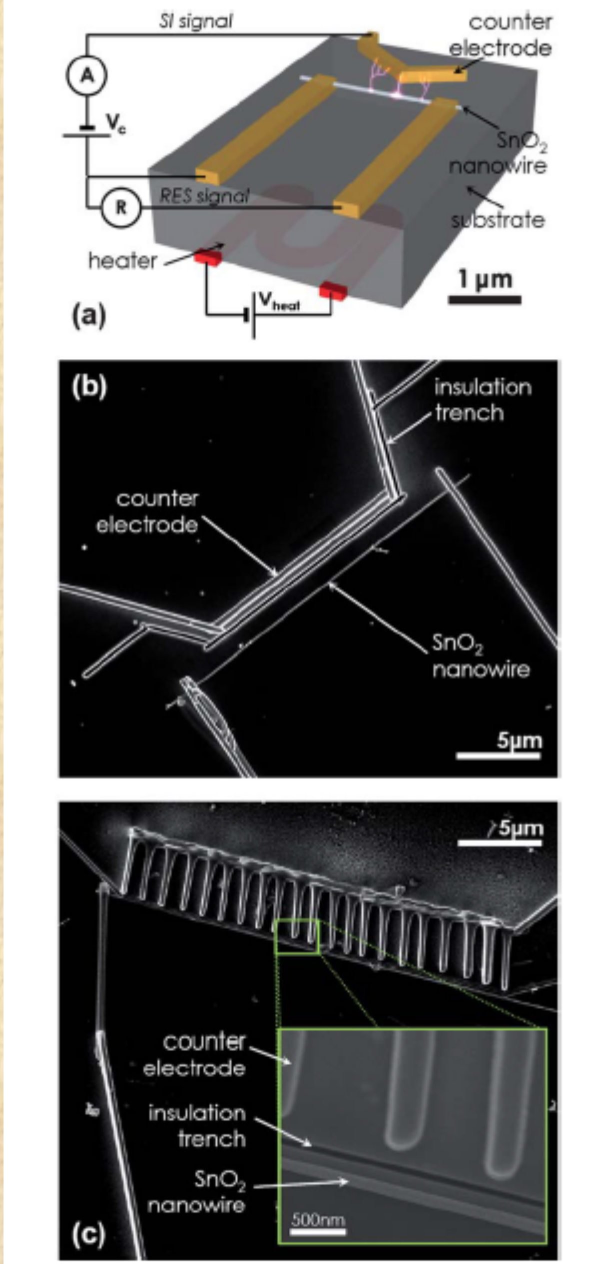
➔ Reduced (≈ 1 μm) and well controlled gap between emitter and electrode (gap comparable with the mean free path of molecules)

+ REDUCED OPERATING BIAS: V≈ few Volts

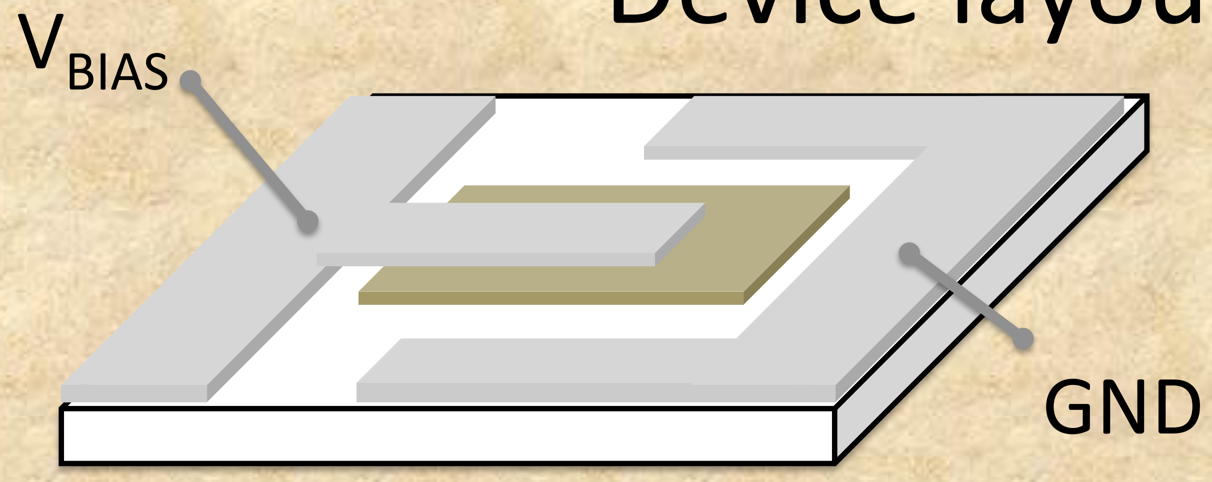
+ REDUCED OPERATING TEMPERATURE: T≈300°C

- TECHNOLOGICAL GAP

F. Hernandez-Ramirez, JD Prades, A Hackner, T Fischer, G Mueller, S Mathur, JR Morante, Nanoscale 3 (2011) 630–634



Device layout



SENSOR STRUCTURE PREPARATION
Sputtering

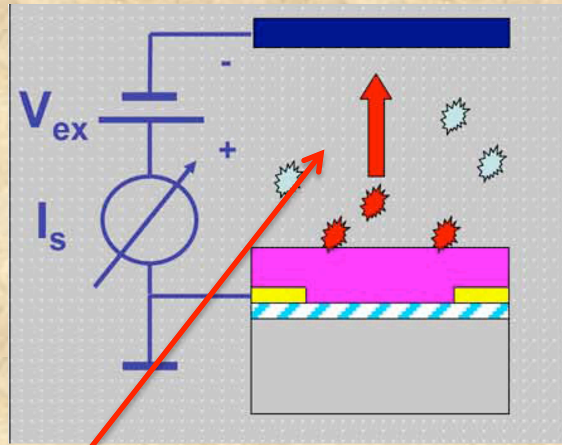
METAL OXIDE LAYER PREPARATION
Sputtering

•**PLANAR TECHNOLOGY**:
➔ Separation between the oxide layer and the counter-electrode is well defined and easily controlled

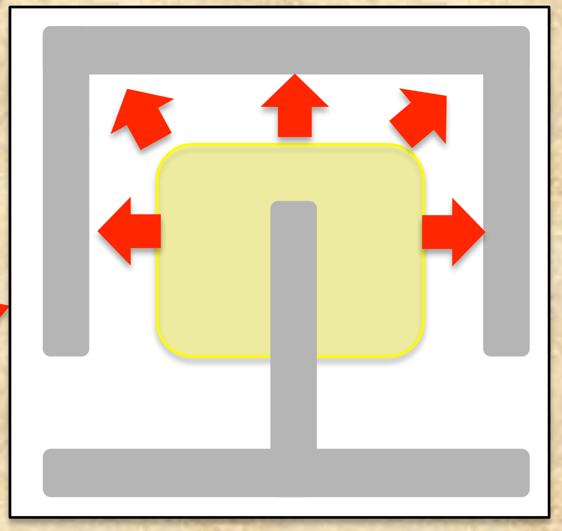
•**NANOROD MORPHOLOGY**:
➔ Local field enhancement

Planar and vertical layout

- With respect to the traditional vertical layout, the planar configuration features:
  - The whole device layout can be prepared through planar fabrication technologies
  - Easier control of electrode separation at the microscale
- On the other hand, a more complicated working mechanism exists:
  - Both electrode are at the same temperature, so they are both active to generate ions;
  - The structure should be carefully designed and prepared to avoid leakage currents



A. Hackner et al, IEEE Sens. J. 9 (2009) 1727



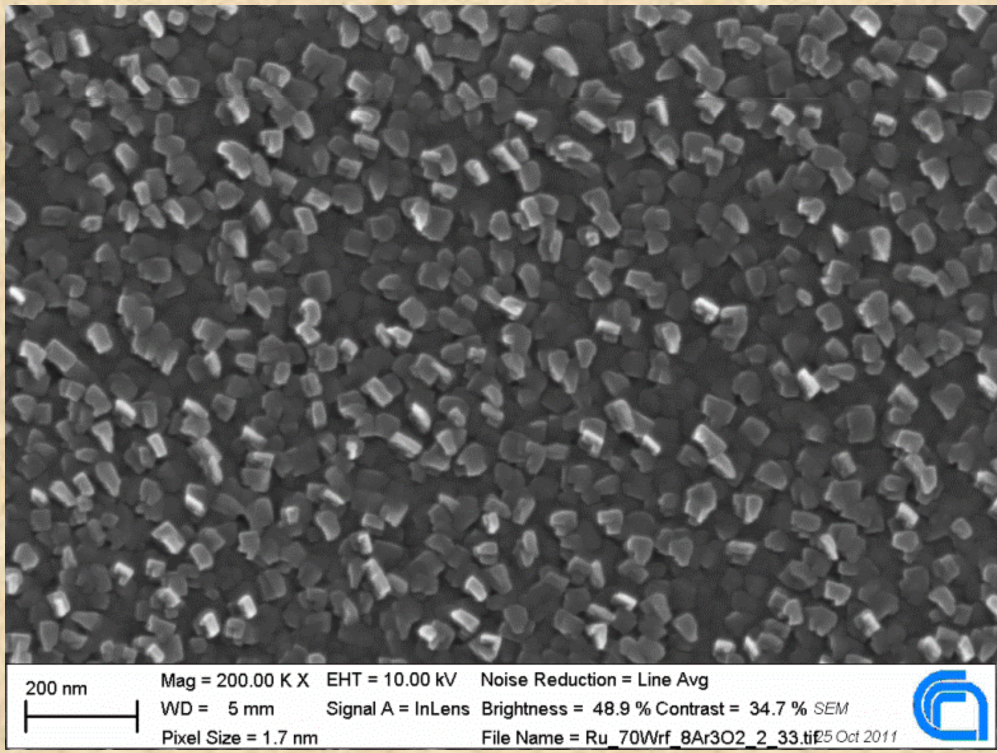
Ionization current

Sensitive layer: RuO_2 nanorods

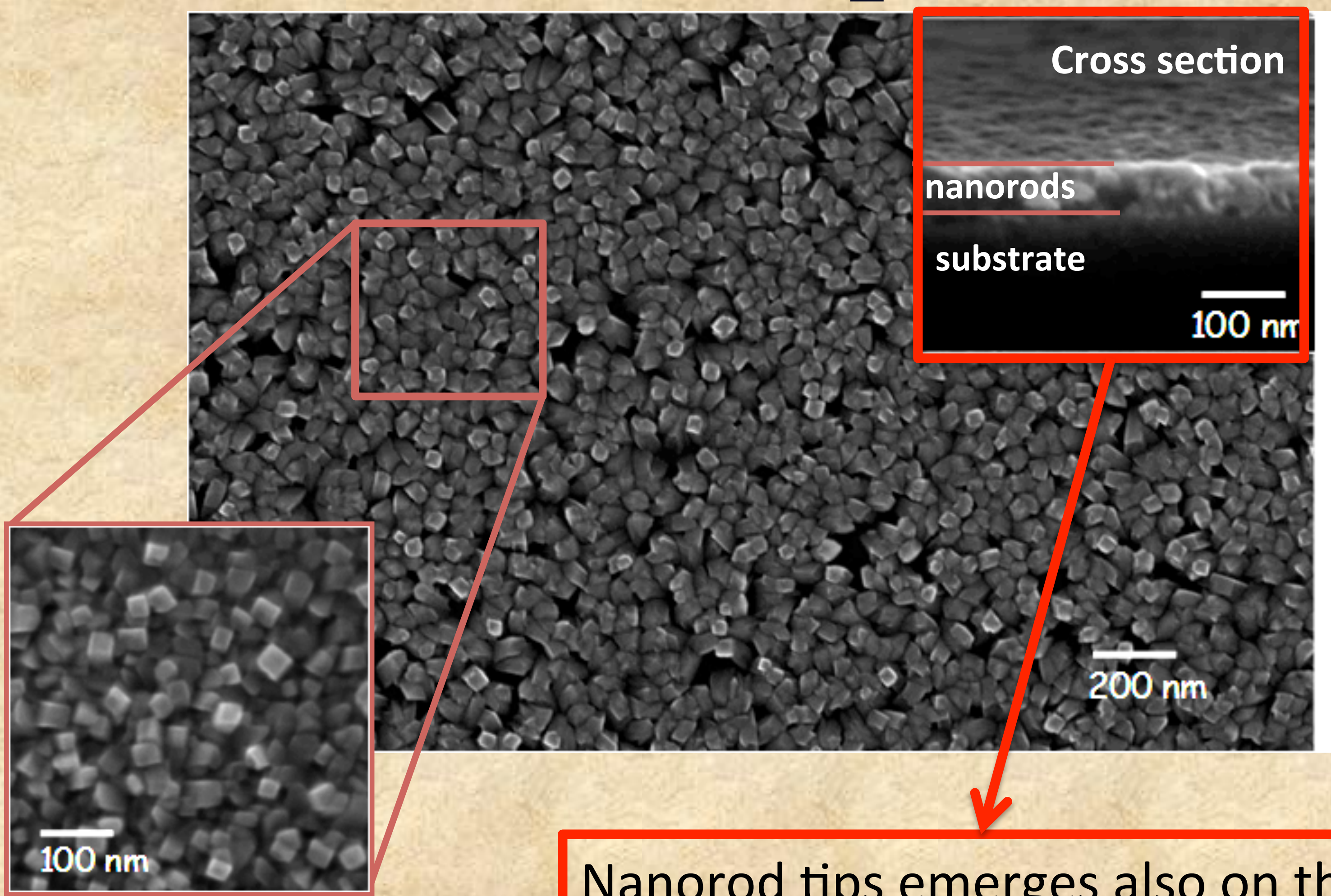
We avoid VLS or VS based method in order to prevent condensation over undesired areas

SYNTHESIS PARAMETERS

•DC sputtering from a metallic Ru target;
•O2/Ar ratio : 3/8
•Substrate T=300 °C
•Time: 15 min



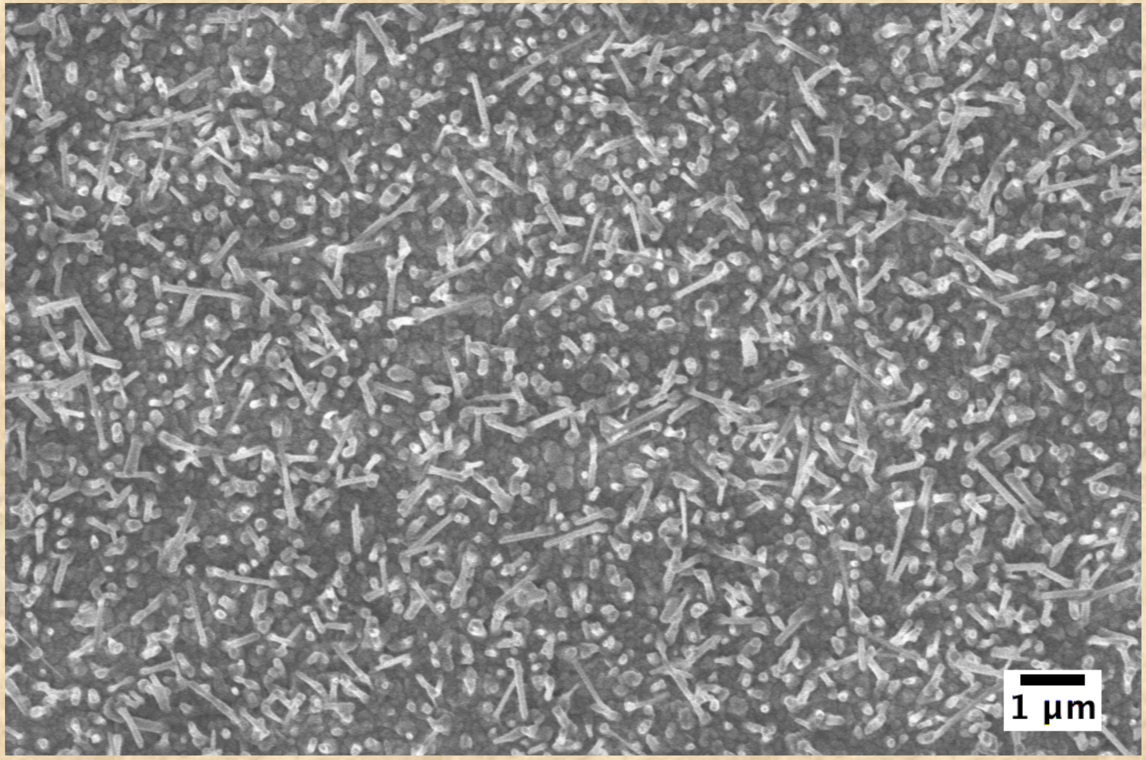
Sensitive layer: RuO_2 nanorods



Nanorod tips emerges also on the lateral side of the oxide layer

Sensitive layer: CuO nanorods

CuO nanowires (NWs) were grown thermally oxidizing a Cu film sputtered on the substrate.



Sputtering parameters
- Target: metallic Cu
- RF Power: 50W
- Flow: 7 SCCM Ar (pressure $5x10^{-3}$ mbar)
- Temperature: RT
- Thickness ≈ 1 µm

Thermal oxidation parameters

Temperature: 400 °C
Flow: 300 SCCM
Oxidation time: 15h
Atmosphere composition: Ar (20%) and O_2 (80%).

CuO nanorods preparation

Sputtering

- Thin layers of metallic Copper were deposited on substrates by sputtering.
- Sputtering parameters:
  - RF Power: 50W
  - Flow: 7 SCCM Ar (pressure 5×10^{-3} mbar)
  - Temperature: RT
  - Thickness ≈ 1 µm

Thermal oxidation

- Temperature: 400 °C
- Flow: 300 SCCM
- Oxidation time: 15h
- Atmosphere composition: Ar (20%) and O2 (80%).

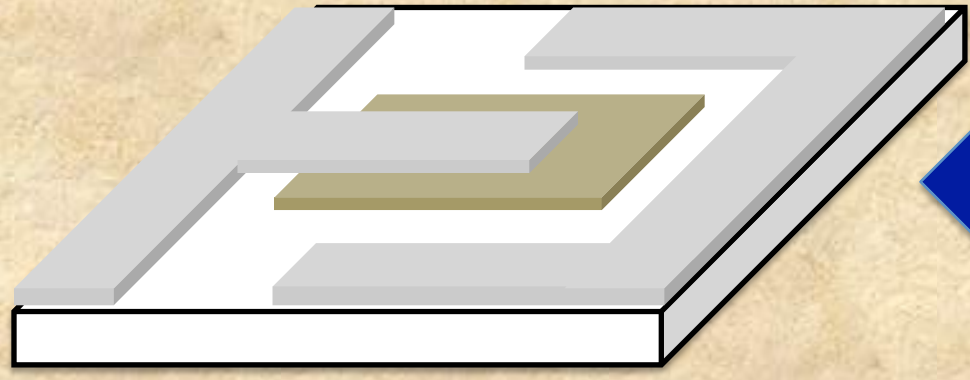
$Cu + O_2 \rightarrow Cu_2O$

$Cu_2O + O_2 \rightarrow CuO$

Measurment with gas

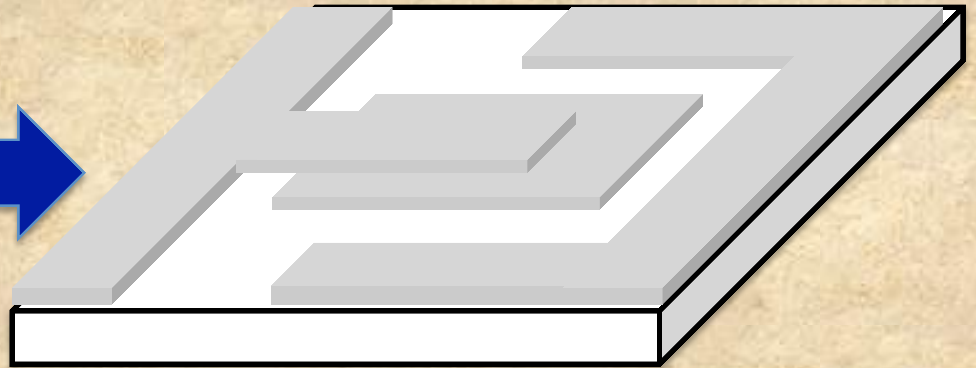
SI devices with planar layout are much less investigated than their counterpart with vertical configuration: we expect similarities but also differences.

To identify the role of the sensing layer we worked with two different configurations:

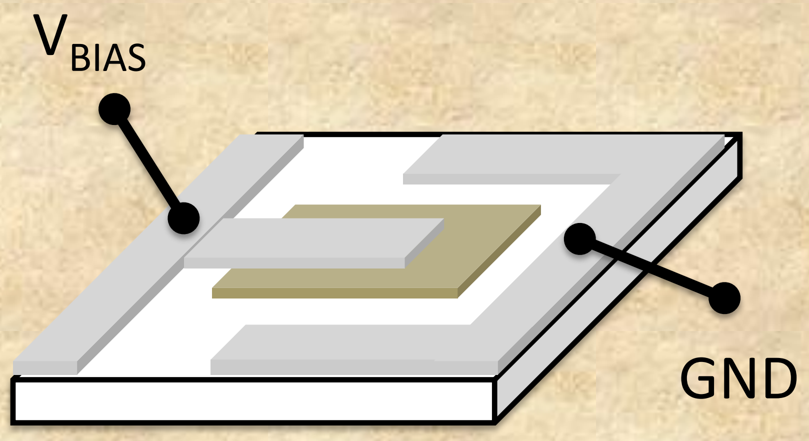


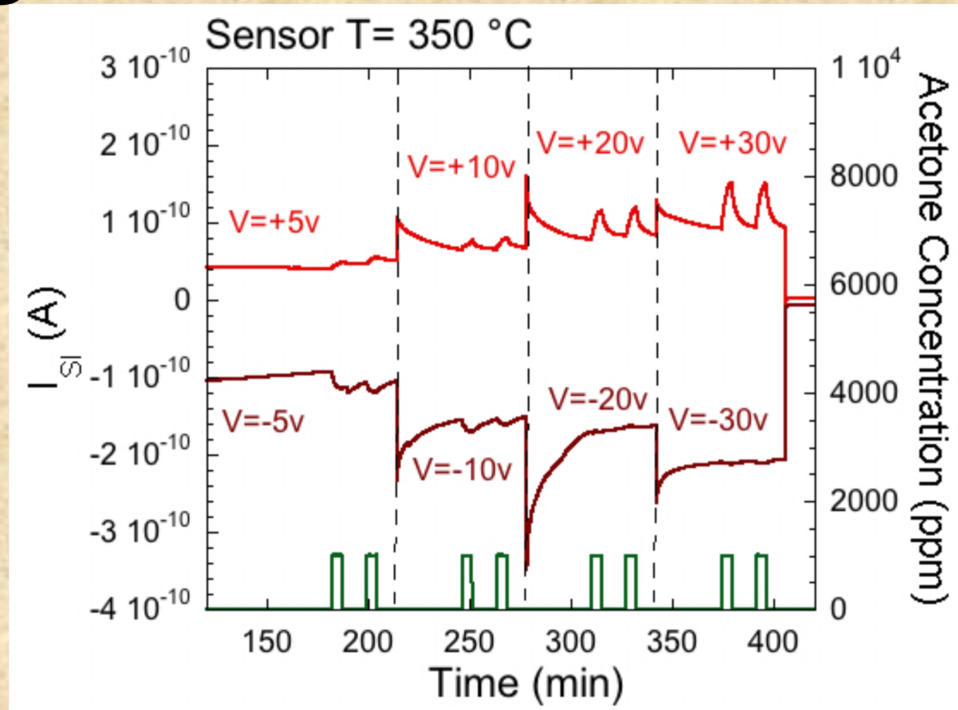
Asymmetric structure:
Oxide – Pt
Nanorods – thin film

Symmetric structure:
Pt – Pt
thin film – thin film



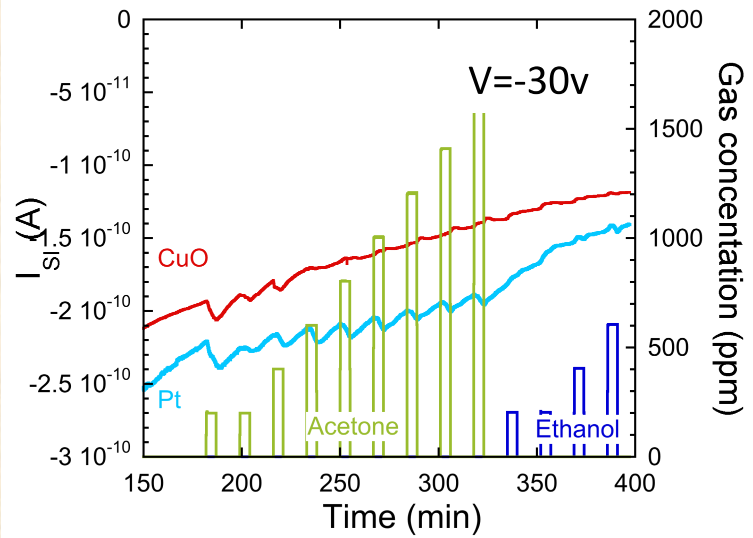
CuO, Voltage bias effects

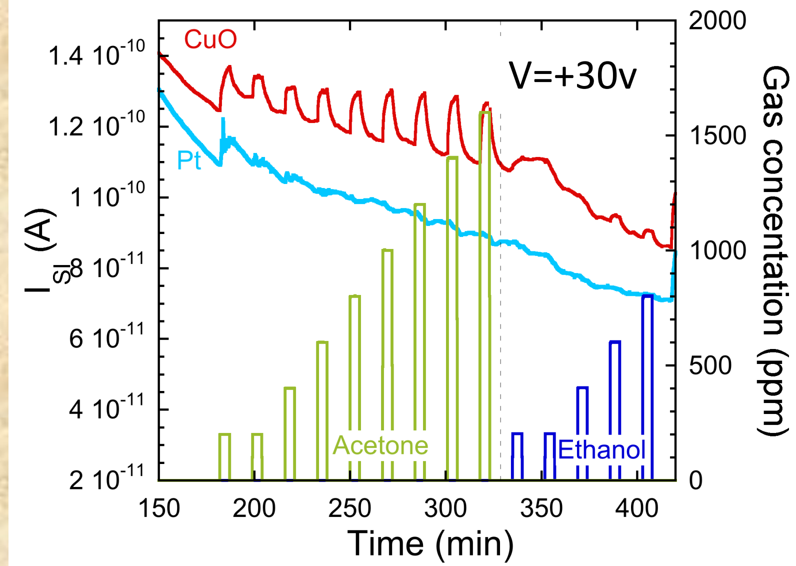




- Asymmetric response with respect to V sign;
- V>0 (CuO positively biased): regular response to acetone @ 20-30 V, the response to two identical acetone concentrations are equal;
- V<0 (CuO negatively biased): almost no response

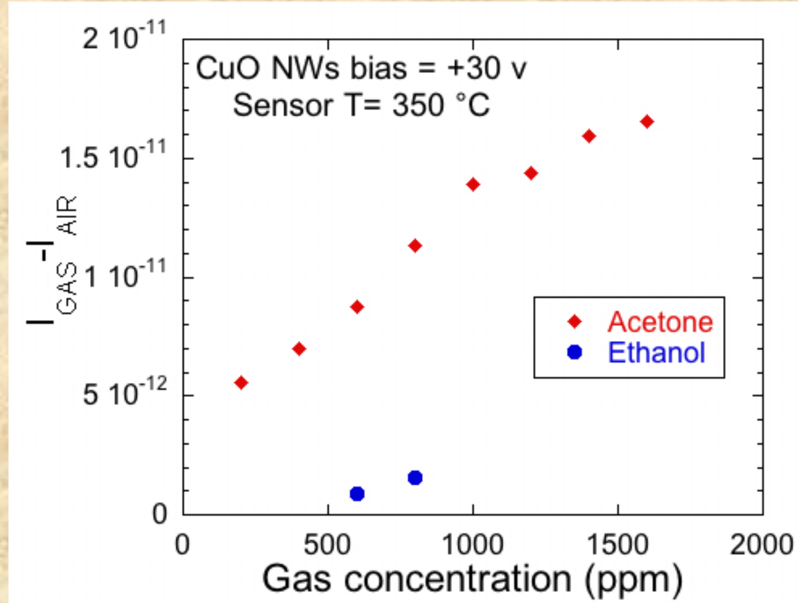
CuO, gas concentration effects



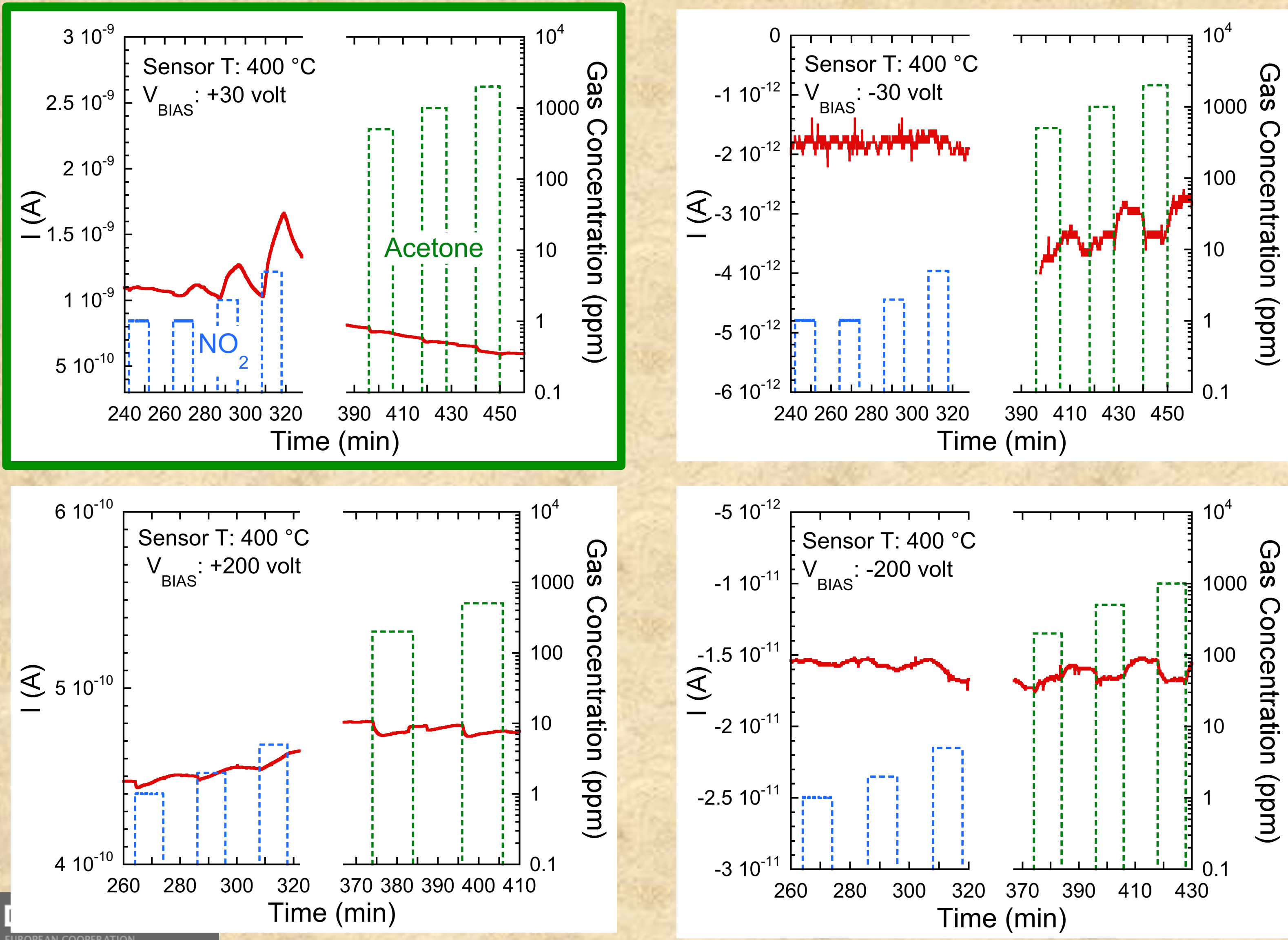


- Only CuO positively biased shows response to gases;

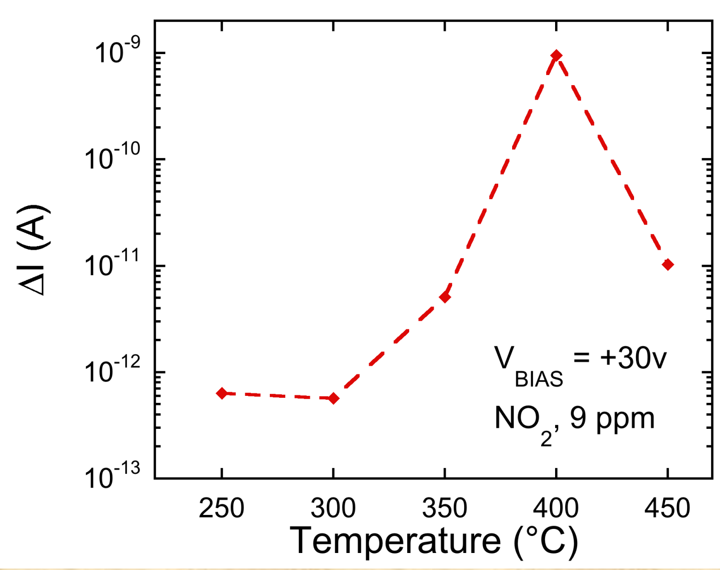
- Response to ethanol is much lower than the response to acetone (in agreement with first ionization energy values)

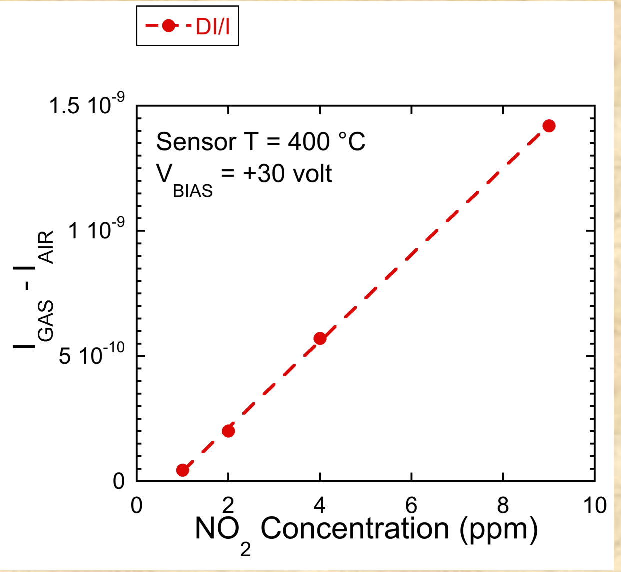


RuO$_x$ – dynamic response



RuO_x – temperature and gas concentration effects





- Peaked dependence on T
- A reliable response can be observed only within a limited range of temperature
- With respect to SI devices with vertical layout: optimal response is observed at much lower temperature

Conclusions

- We've prepared SI devices with horizontal layout by means of well-consolidated planar technology (sputtering)
  - Control of the oxide – counterelectrode separation
  - Exploitation of nanorod morphology for field enhancement
- We looked for a gas-dependent asymmetric behavior:
  - Reliable responses to gases has been observed only with the oxide layer positively biased;
  - Only sensor with asymmetric structure (oxide-Pt) feature a gas-dependent signal
- Responses are observed at T≈300-400 °C and V≈30v (E≈150 kV/m), lower than values needed in SI devices with vertical layout
- Selective response consistent with ionization energy arguments has been observed – despite there is still a large work to do to properly understand the key parameters governing the behavior of these devices

Acknowledgements

S3 – FP7 project N 247768

Surface ionization and novel concepts in nano-MOX gas sensors with increased Selectivity, Sensitivity and Stability for detection of low concentrations of toxic and explosive agents (S3)

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