# European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

## COST Action TD1105

## WGs and MC Meeting at Cambridge, 18-20 December 2013

# On the direct coupling of nanostructured metal oxides and resistive silicon micro hotplate transducers


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COST is supported by the EU Framework Programme

ESF provides the COST Office through a European Commission contract

## Integration of low-dimensional gas sensitive metal oxides onto transducers

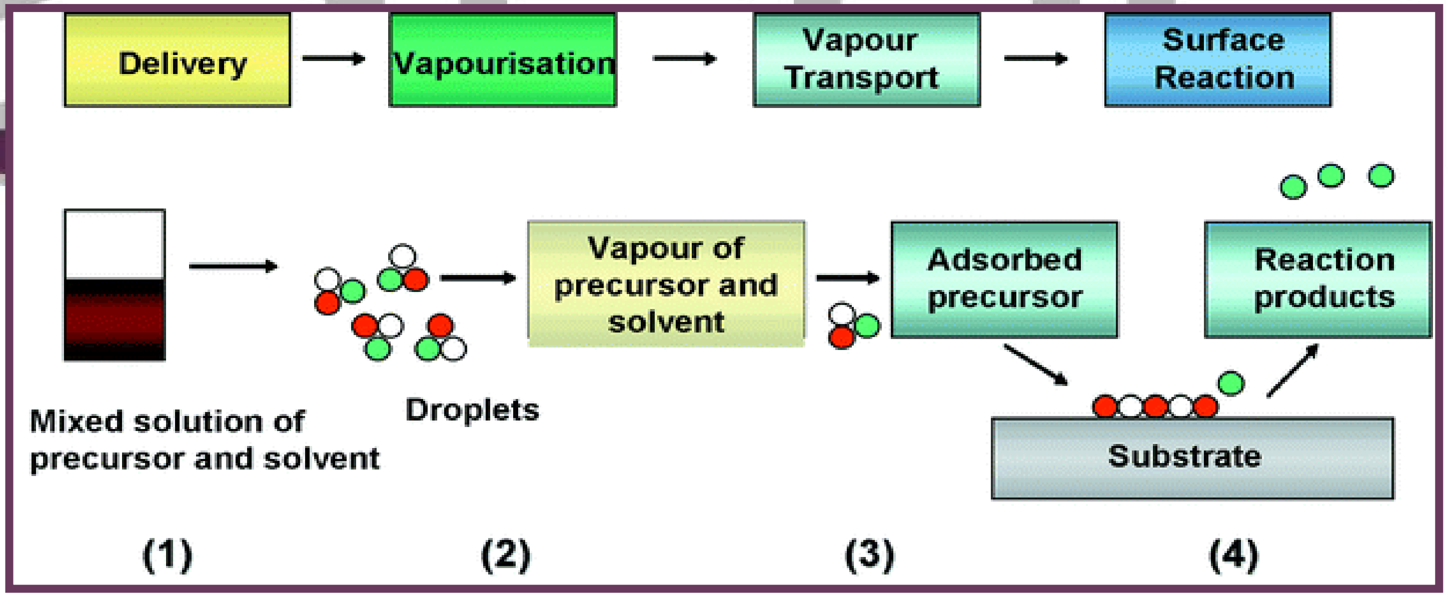
*Promises*

- LDMOX offer very high specific surface area
- Precise surface composition control (case of single crystalline NWs)
- Possibility of NW growth and surface functionalisation
- Integration of MOX nanotubes using smart anodization compatible with Microsystems technology

*Needs*

- Avoid the need of surface pre-treatment for substrates
- Use moderate growth temperatures (for being compatible with different substrates)
- Use scalable methods for mass-production of nanomaterials

# Aerosol-Assisted CVD (VS)




(1) The precursor(s) is (are) dissolved in an organic solvent. (Single source) Enables synthesis of multicomponent materials with controlled stoichiometry.

(2) The mixture is converted into droplets by an ultrasonic modulator. (Simple)

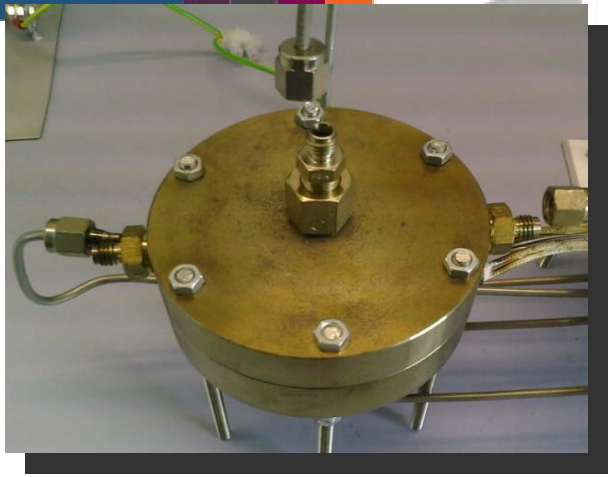
(3) The aerosol of precursor and solvent are transported by a carrier gas into a hot zone where it evaporates.

(4) The vapor of the precursor is then transported to the substrate where it absorbs and reacts to form a film.

(5) Allows rapid formation of the deposited phases at relatively low temperatures due to the small diffusion distances between reactant and intermediates.

(6) Low cost process since the AA-CVD can be performed in an open atmosphere.

# Aerosol-Assisted CVD (VS)

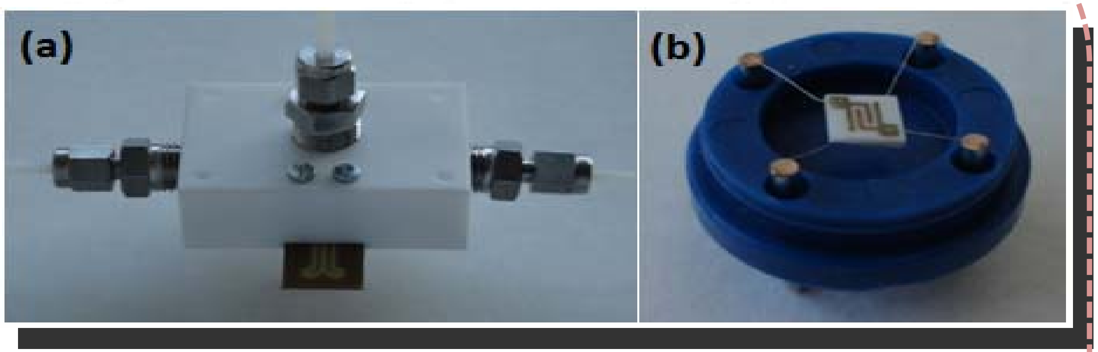


Hot wall AACVD reactor

**Deposition time: 45-60 min**

**Precursor : 150 mg**

**T °C used : up to 500 °C**

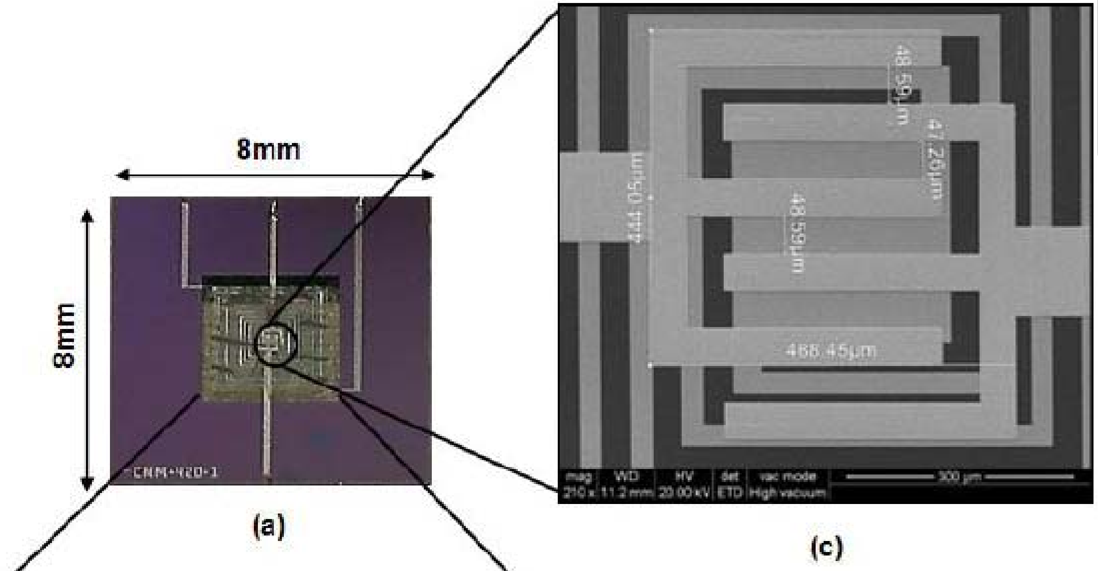


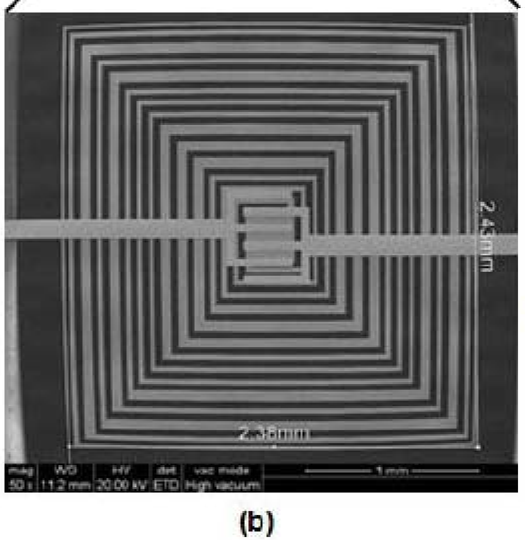

(a) AACVD cold wall reactor, (b) Alumina gas sensor

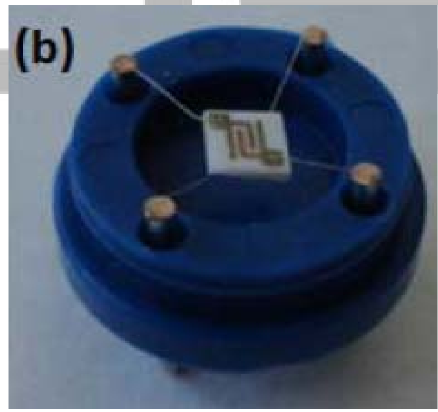
**Deposition time: 15-20 min**

**Precursor : 50 mg**

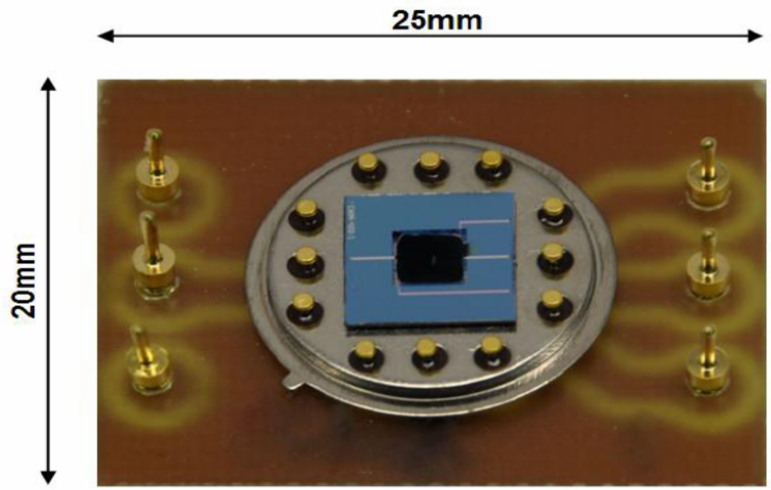
**T °C used : up to 600°C**

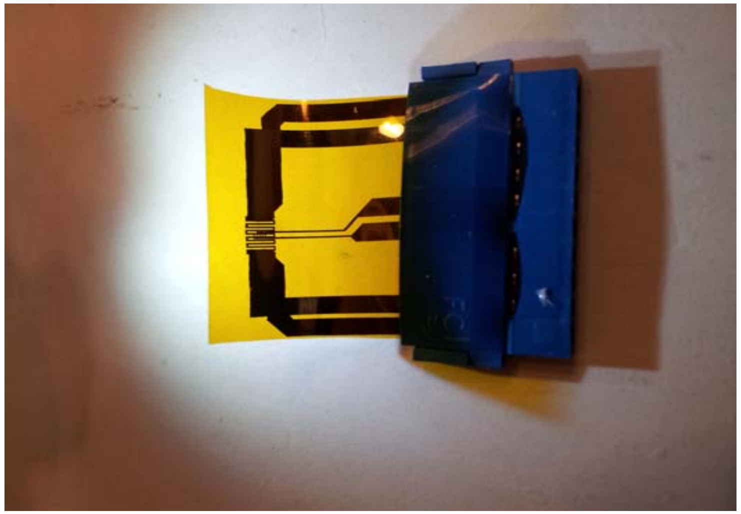



Direct growth of NWs on ceramic, micromachined silicon and flexible substrates



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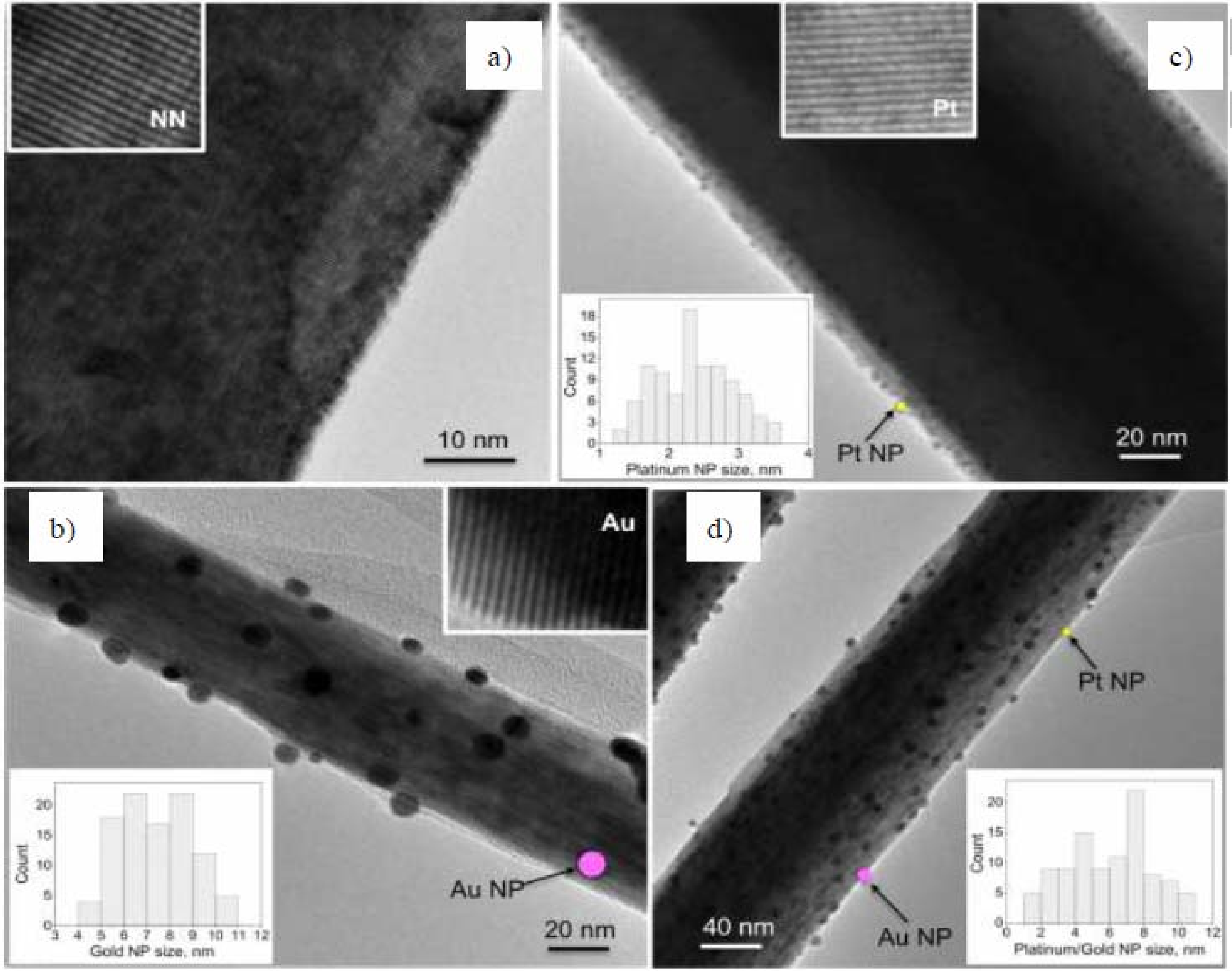
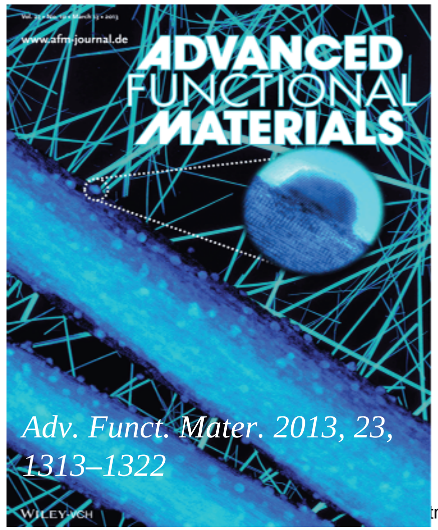
# *Characterization (TEM and HRTEM)*



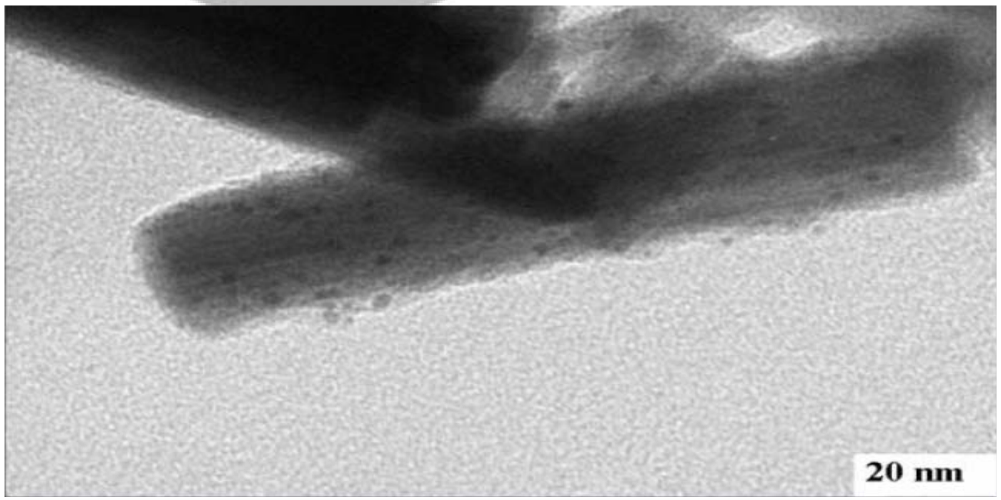

Intrinsic (a) and functionalized samples with gold (b), platinum (c), and gold/platinum (d)

$W(OPh)_6$ (acetone); $HAuCl_4 \cdot 3H_2O$, $H_2PtCl_6 \cdot xH_2O$, (methanol) At 350-450ºC




by the EU Framework Programme

# Characterization (TEM)



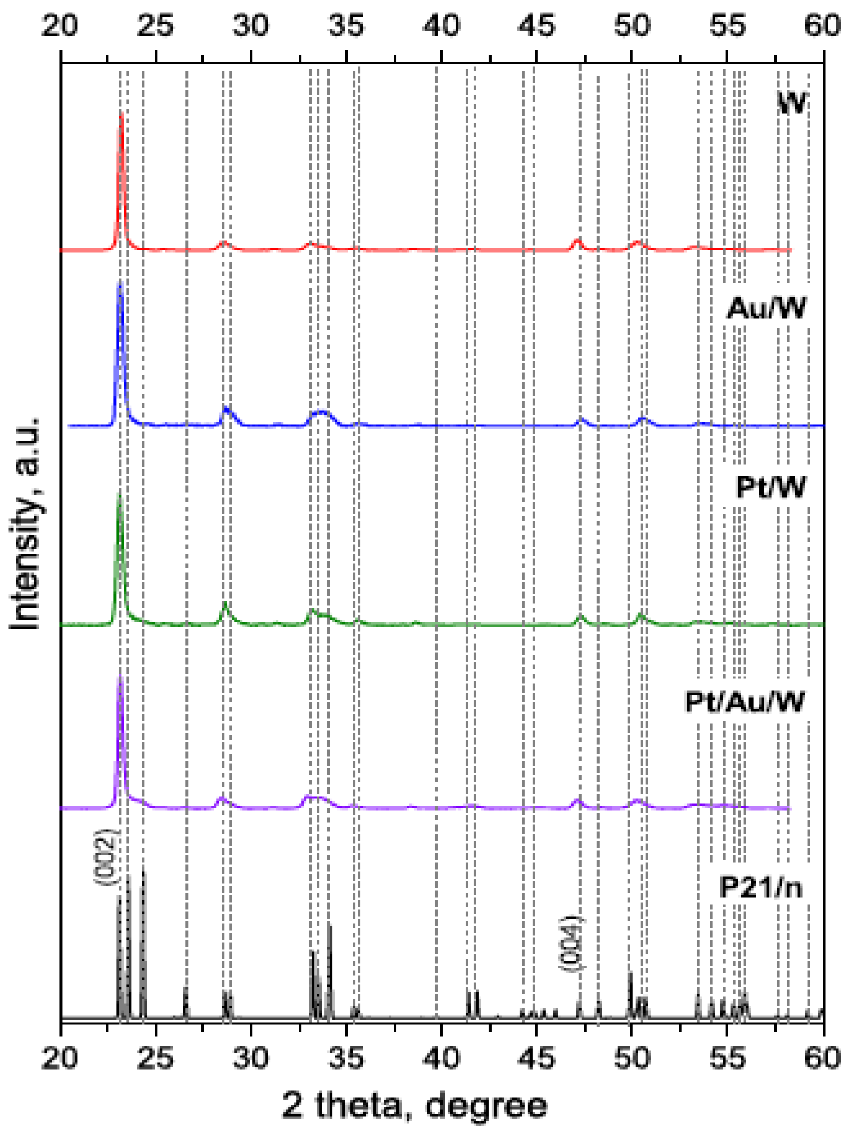

Precursors: W(OPh)$_6$ (acetone); Copper (II) acetylacetonate [Cu($C_5H_7O_2$)$_2$] (methanol)
Growth: At 350ºC
Particle size: 4-8 nm

*Thin Solid Films, 548 (2013) 703-709*

All $WO_3$ NWs with lengths of ≈ 7 μ m and diameters ranging between 60 and 120 nm, corresponding to aspect ratios of ≈ 60–115.

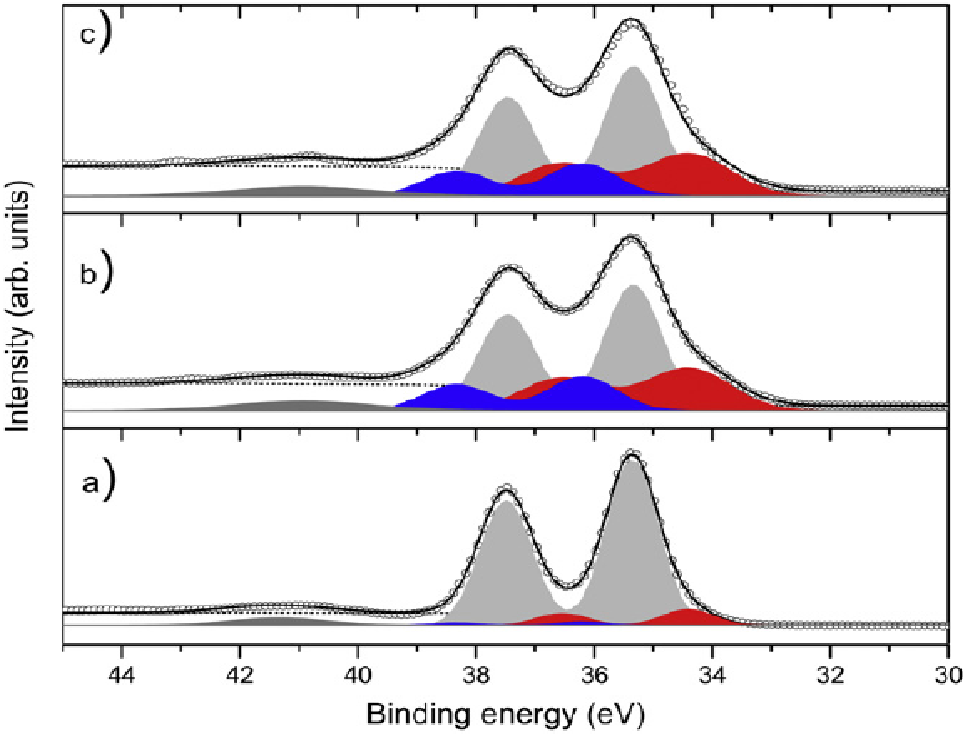
Metal NPs remain stable even when NW mats are annealed at 500ºC in air for 2 hours.

# Characterization (XRD)



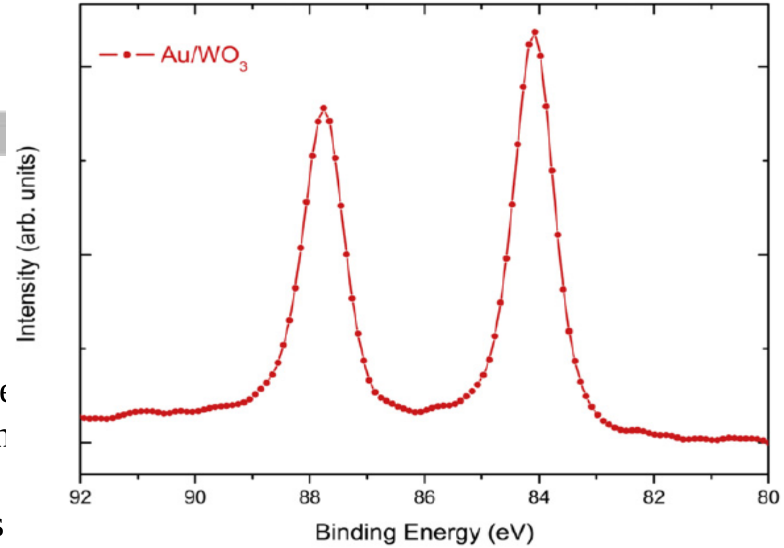

XRD patterns of the (from top to bottom) non-functionalised, functionalised films with gold, Platinum, gold/platinum and typical diffractions of monoclinic phase (ICCD card no. 72-0677).

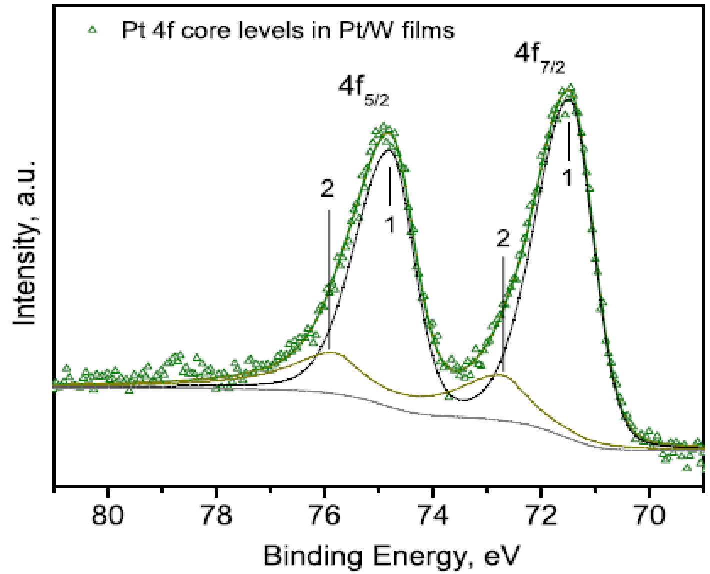
# *Characterization (XPS)*




XPS core levels for pristine $WO_3$ powder (a), $WO_3$ NWs (b) and Au on $WO_3$ NWs (c). Light gray:W4f level for stoichiometric$WO_3$. Red:W4f level for sub-stoichiometric $WO_{3-x}$. Blue: W 4f level of W atoms near surface defects.

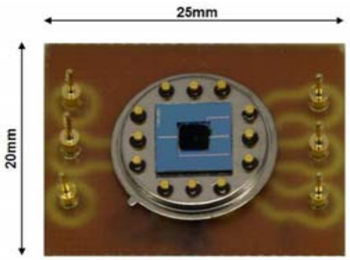
Au and Pt 4f core level recorded on $Au/WO_3$ and Pt/WO3 samples

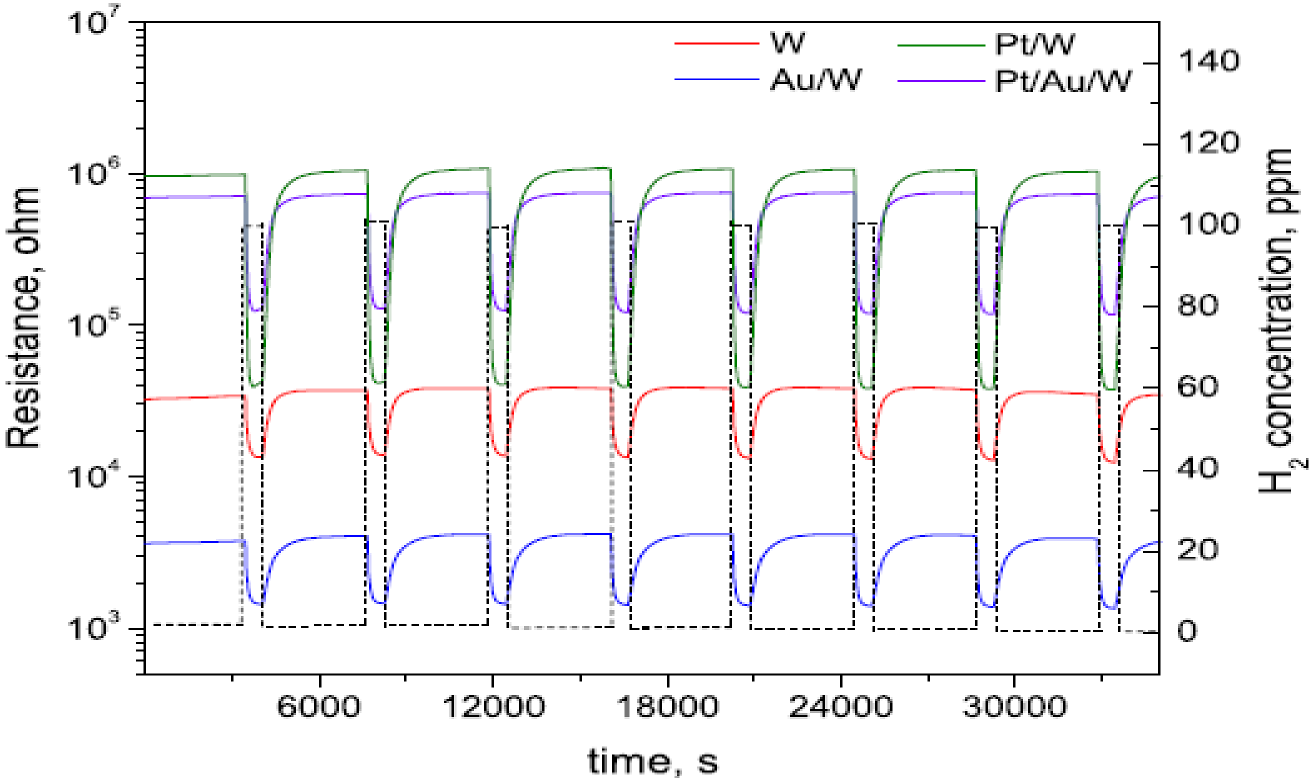



*Mat. Chem. Phys. 134 (2012) 809-813*

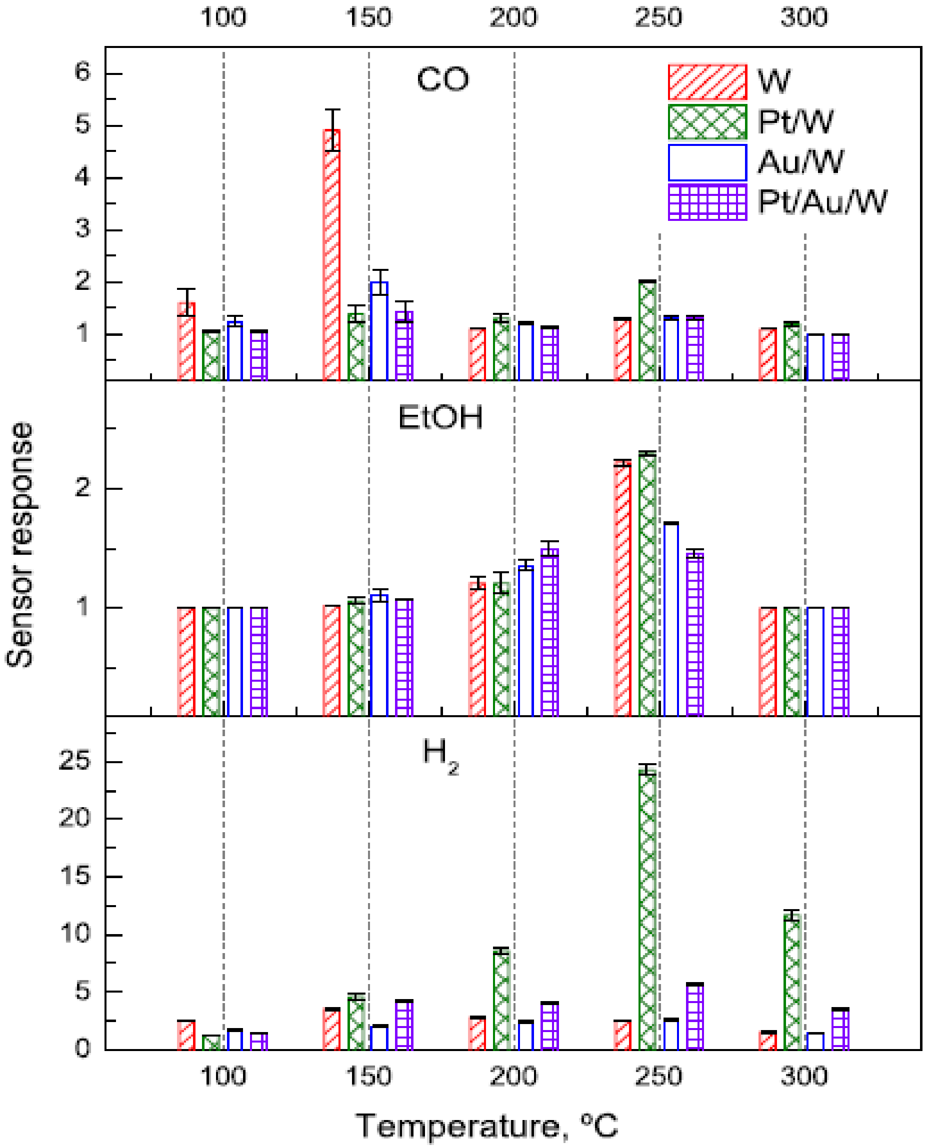
# Gas sensing properties of tungsten oxide NWs *(Silicon micromachined substrates)*




Film resistance changes towards hydrogen 100 ppm at 250 ºC.

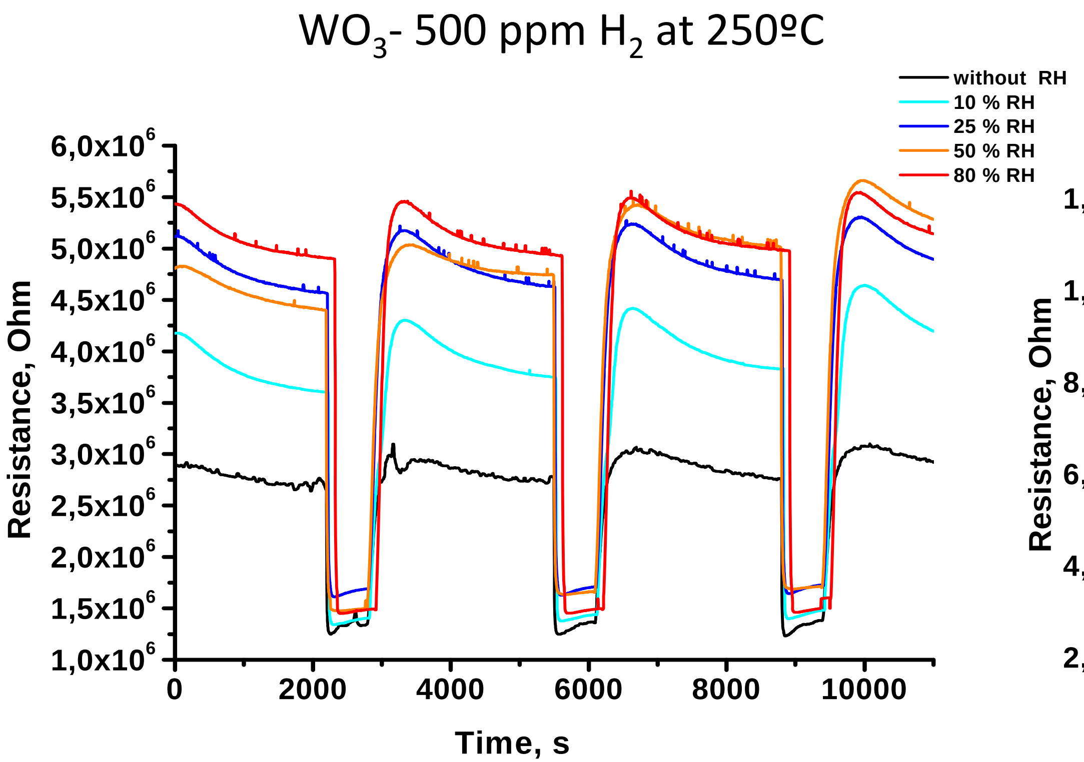
# *Gas sensing properties of tungsten oxide NWs (Silicon micromachined substrates)*

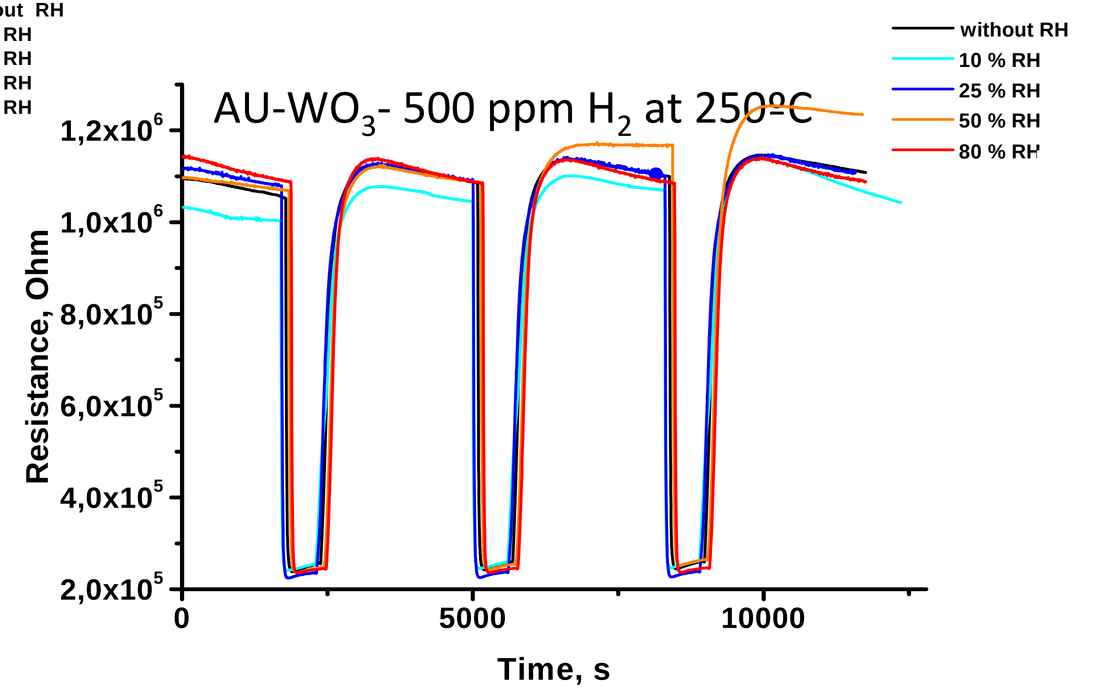



Sensor responses and error bars to 100 ppm of CO, 2 ppm of EtOH, and 100 ppm of $H_2$, as a function of the operating temperature.

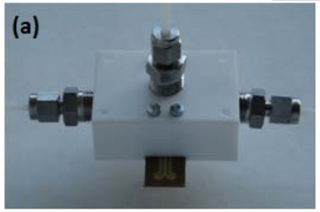
# *Gas sensing properties of tungsten oxide NWs (Silicon micromachined substrates)*

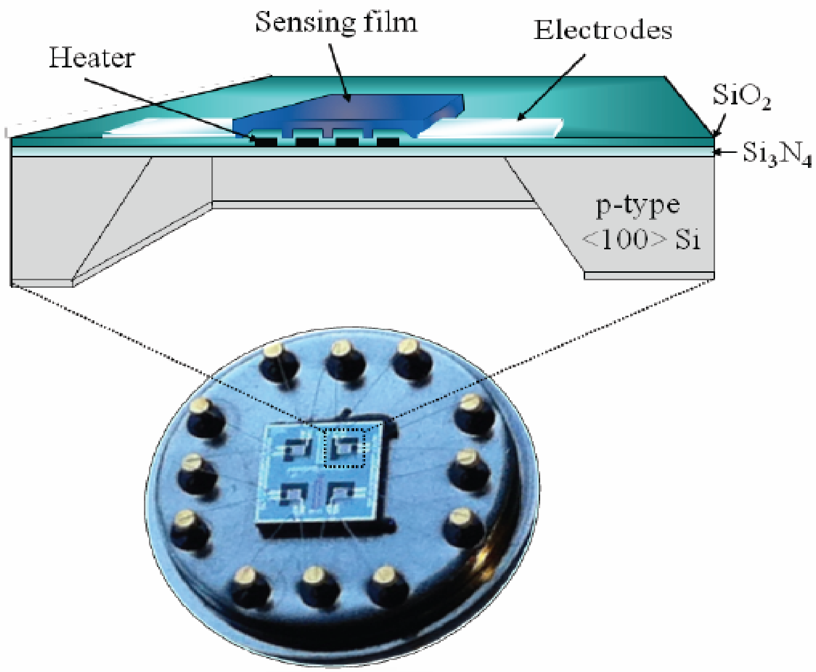
## Humidity effect

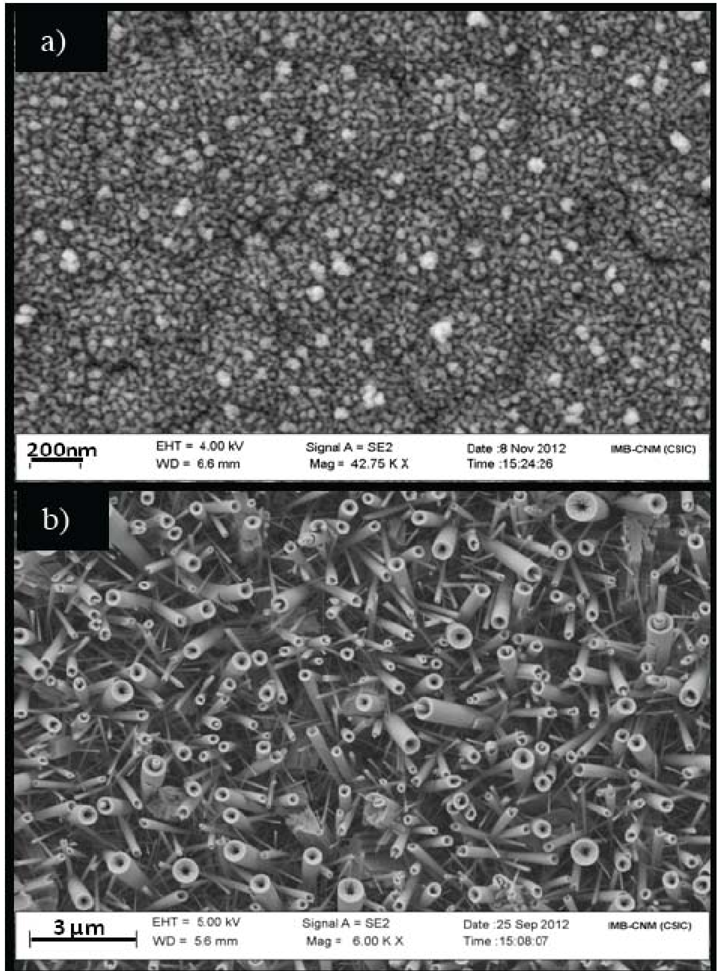


# *Growth of MOx NWs using the heater embedded in micro-hotplates*

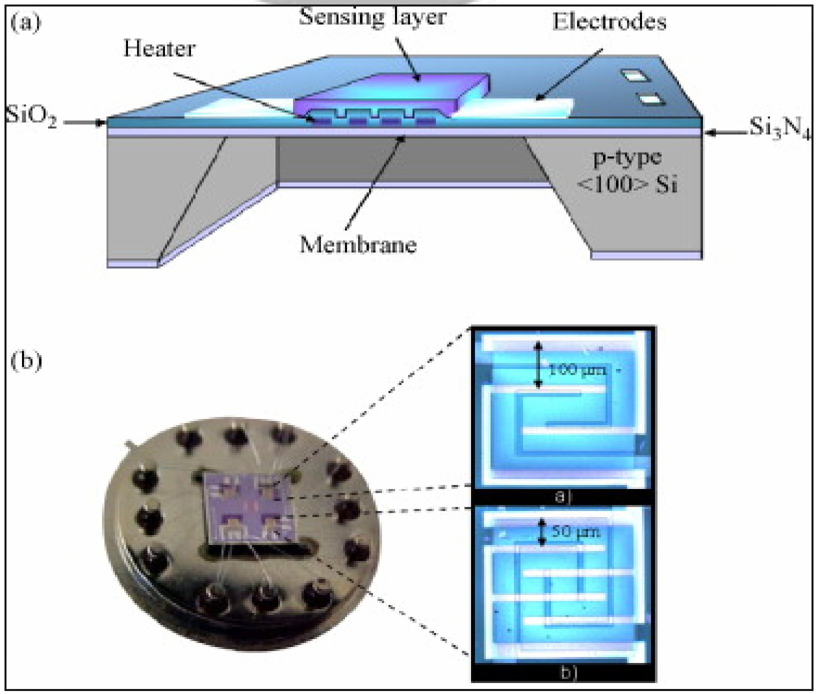


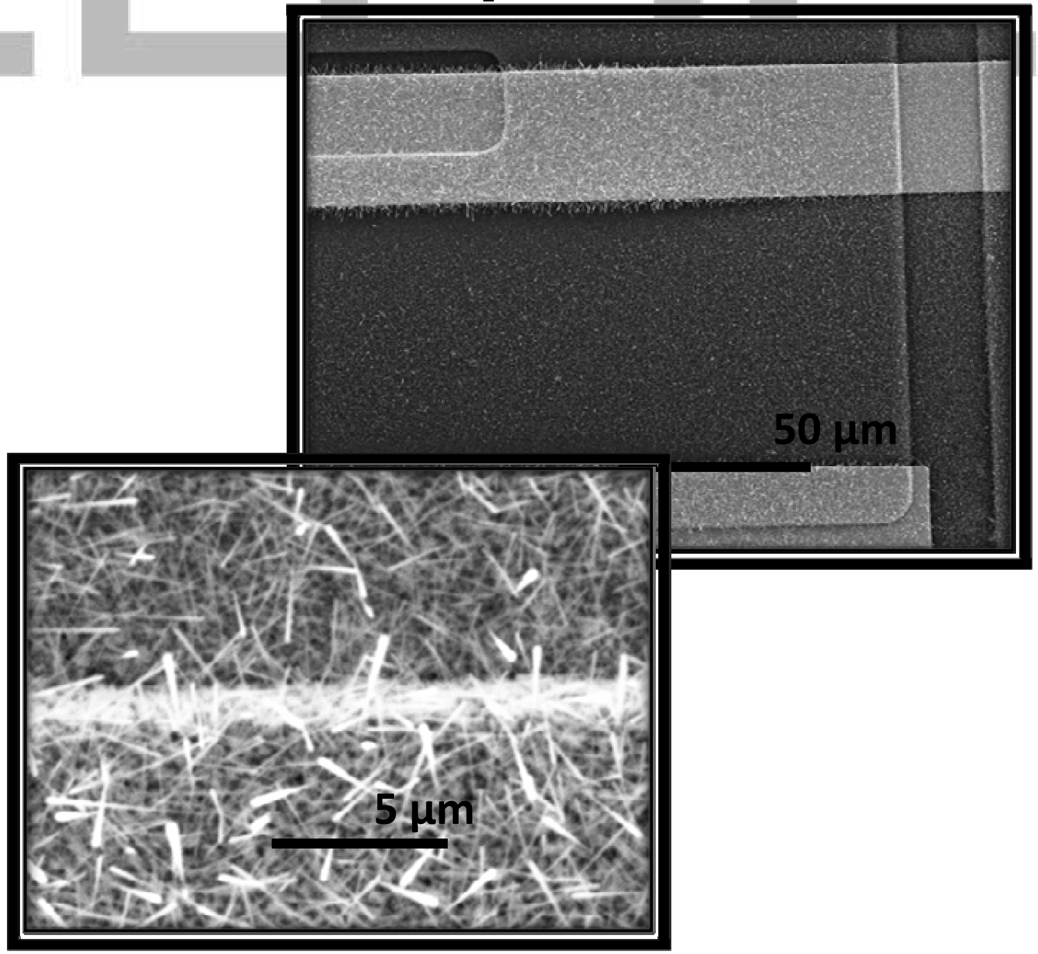




Direct growth of nanomaterials onto micro-hotplate transducers using the integrated heating element to reach and keep reaction temperature during growth.

# *Growth of MOx NWs using the heater embedded in micro-hotplates*

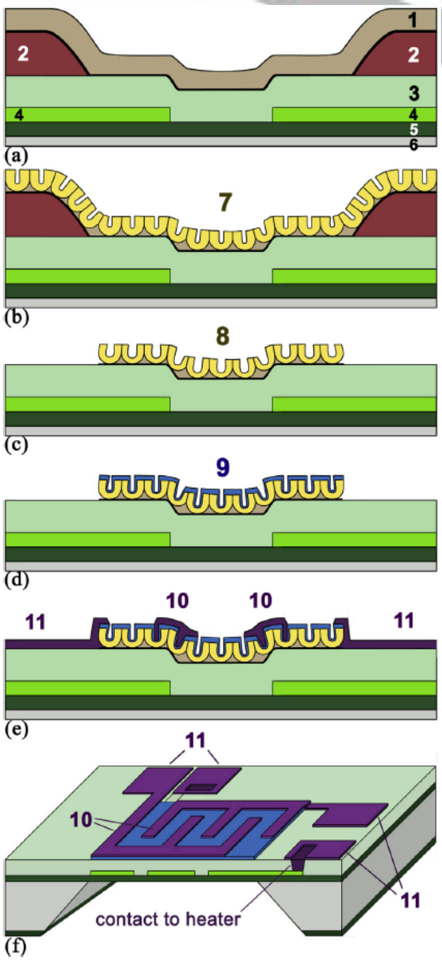


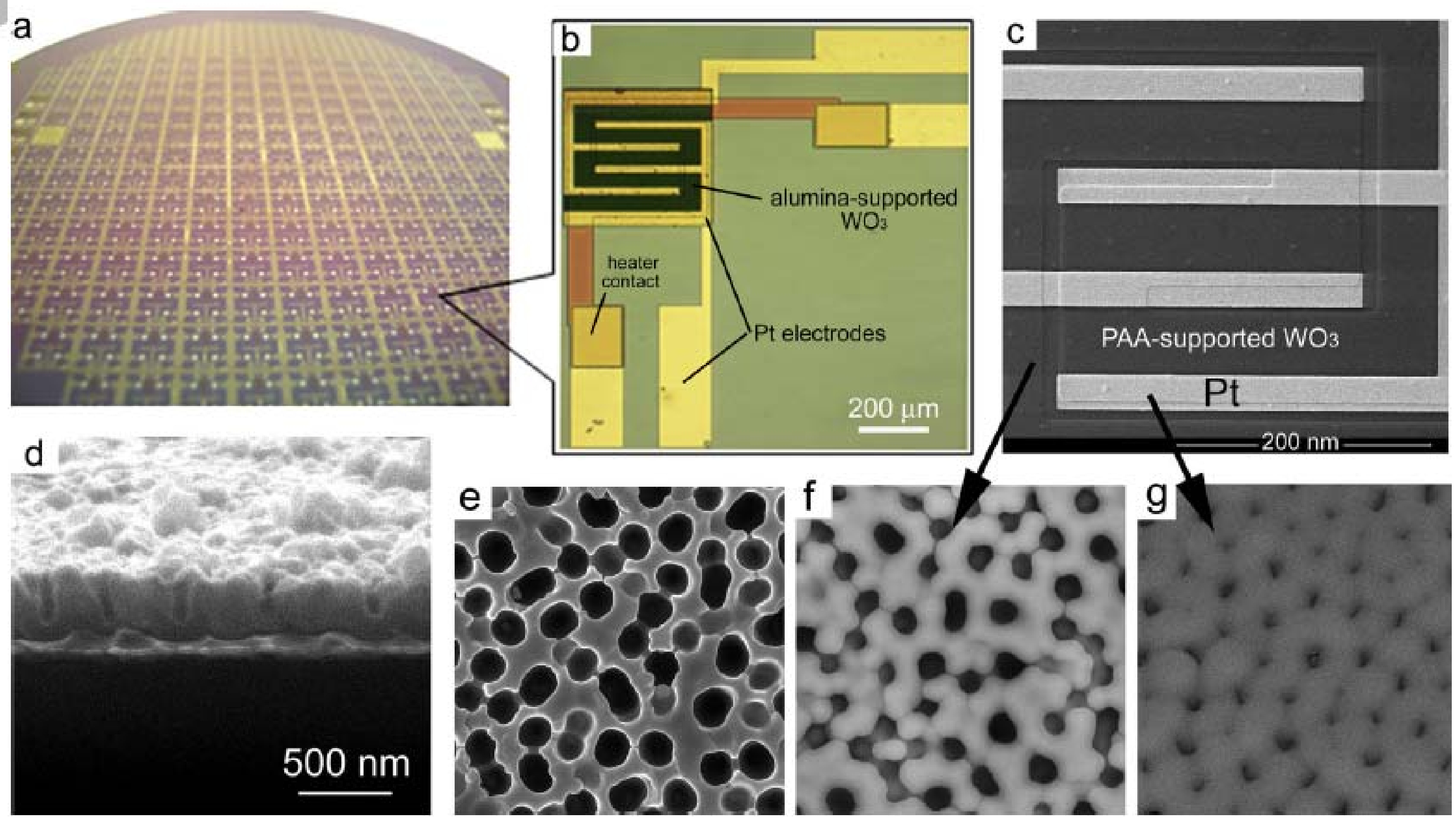

*Schematic view of the micromachined membrane section and view of the 4-microsensors mounted on standard TO-8*




WO3 nanowires deposited on silicon substrate at 600 °C using cold wall reactor

# *MOX nanotubes by smart anodization*



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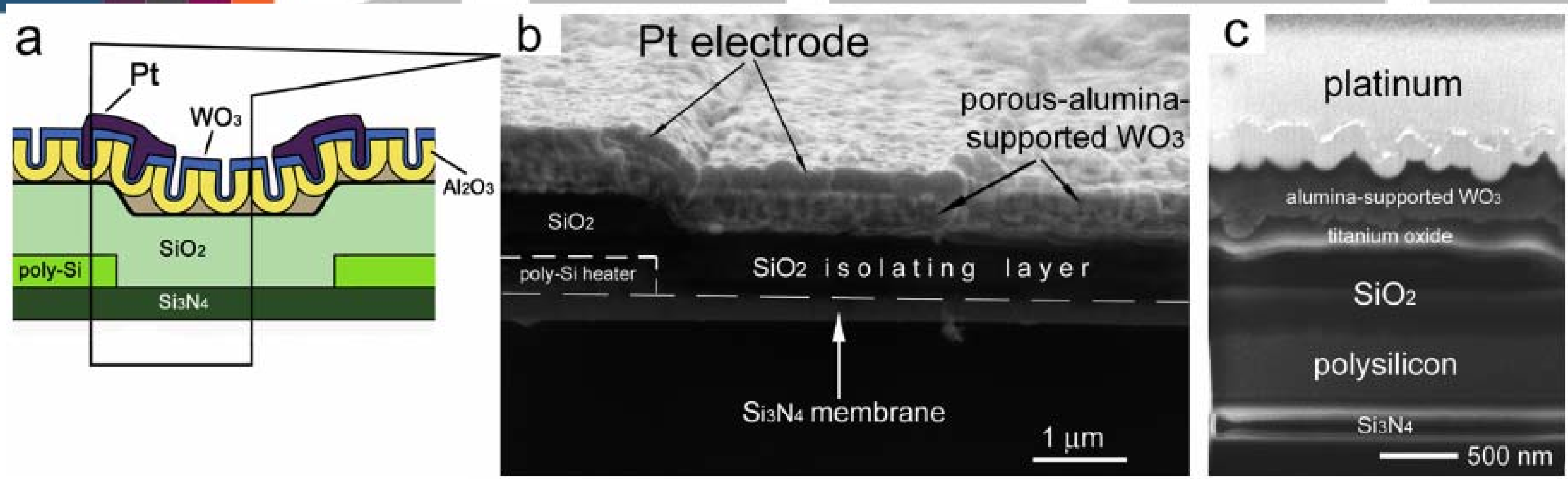


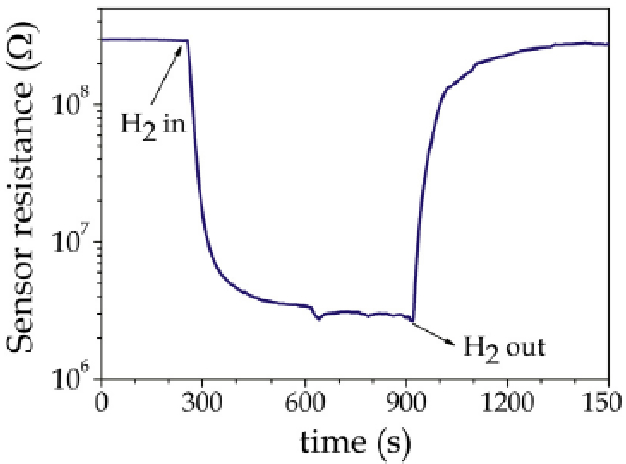


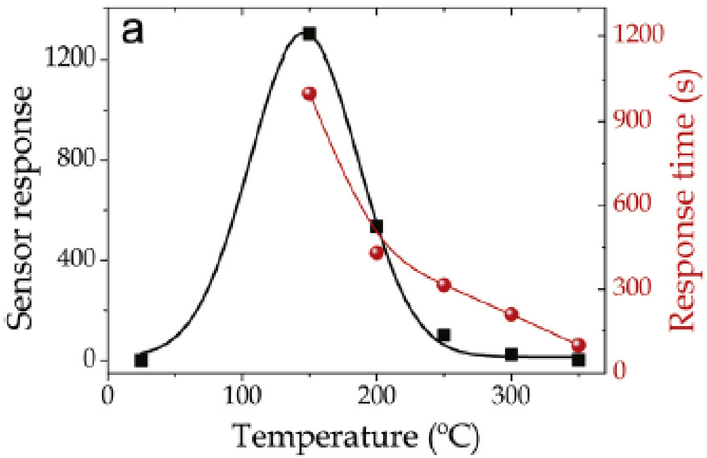


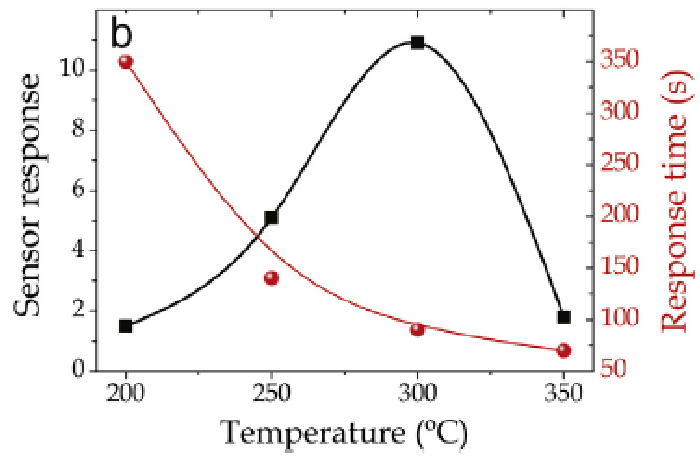

# *Conclusions*

- AA-CVD is a flexible, simple and scalable process for the bottom up integration of NWs in MEMS. One-step growth and decoration of NWs
- Metal decorated tungsten oxide NW sensors show a stable response and baseline (drift below 8% in 12 months)
- Smart anodization is a MEMS compatible strategy for integrating MOX nanostructures onto microhotplates. Sensitivity is highly increased