S^3

Selectivity, Sensitivity, Stability

FP7 EU-RF “S3” project overview

COST Action TD1105

4th December, Rome (Italy)

SEVENTH FRAMEWORK PROGRAMME

Introduction: S3 project overview

- 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
- Project N. 247768
- Public web-site: www.eurussias3.com
- Period: Sept. 1st 2009 – August 31st 2012

S3 partnership

EU partners

* EU coordinator *

Consiglio Nazionale delle Ricerche (CNR) – Prof. G. Sberveglieri

EADS Deutschland GmbH – Innovation Works (EADS) – Dr G. Mueller

Catalonia Institute for Energy Research (IREC) – Prof. J.R. Morante

Eberhard Karls Universitaet Tuebingen (EKUT) – Prof. U. Weimar

University of Cologne, Cologne (UNIKO) – Prof. S. Mathur

RU partners

* RU coordinator *

Kurchatov Institute, Institute of Applied Chemical Physics (RRC) – Prof. N. Zartetski and Prof. A. Vasiliev

Moscow State University, Chemistry Department (MSU) – Prof. A. Gaskov

Research Institute of Electronic Technique (NIIET) – Prof. A. Shaposhnik

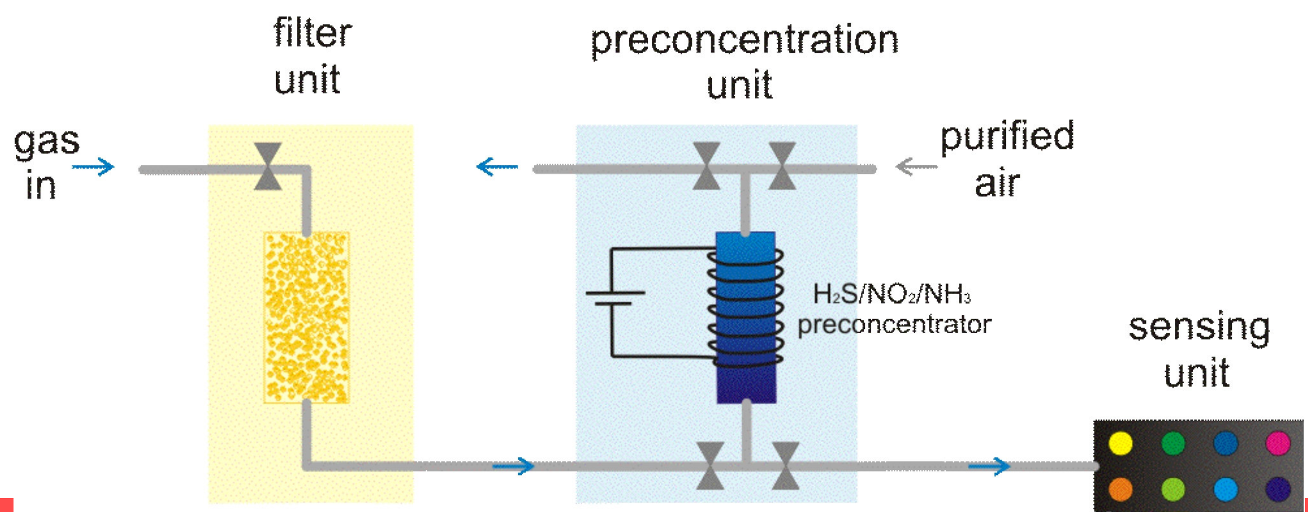
Moscow Engineering Physical Institute, Dept. of Nano and microelectronics (MEPHI) – Prof. V. Pershenkov and Prof. N. Samotaev

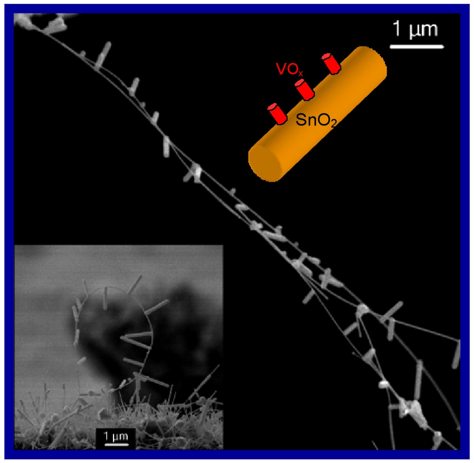
Selectivity, Sensitivity, Stability

S3 goal: Developing breakthrough technologies in gas sensing

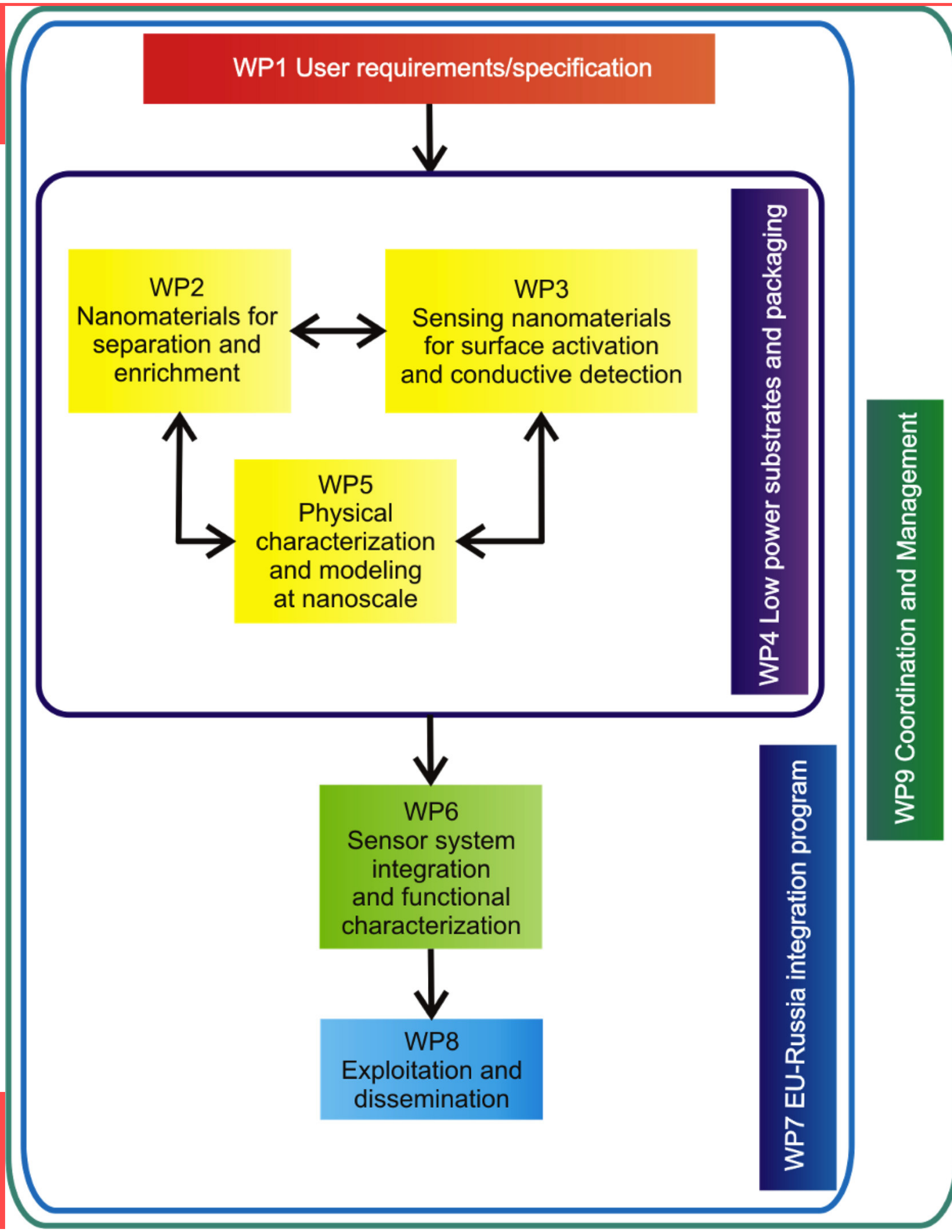
S3 approach:

- Integration of molecularly engineered and functionalized semiconductor nanowires (NWs) and heterostructures into gas sensors
- Exploitation of different transduction mechanisms (resistive, surface ionization, catalytic/thermal)
- Exploitation of different sensor excitations: pulsed-temperature operation and combined self-heated operation mode
- Novel concepts of sampling, filtering and preconcentration of target substances based on nanostructured filter and enrichment materials





Workplan



WP1 User requirements/specification
WP2 Nanomaterials for separation and enrichment
WP3 Sensing nanomaterials for surface activation and conductive detection
WP5 Physical characterization and modeling at nanoscale
WP4 Low power substrates and packaging
WP6 Sensor system integration and functional characterization
WP8 Exploitation and dissemination
WP7 EU-Russia integration program
WP9 Coordination and Management

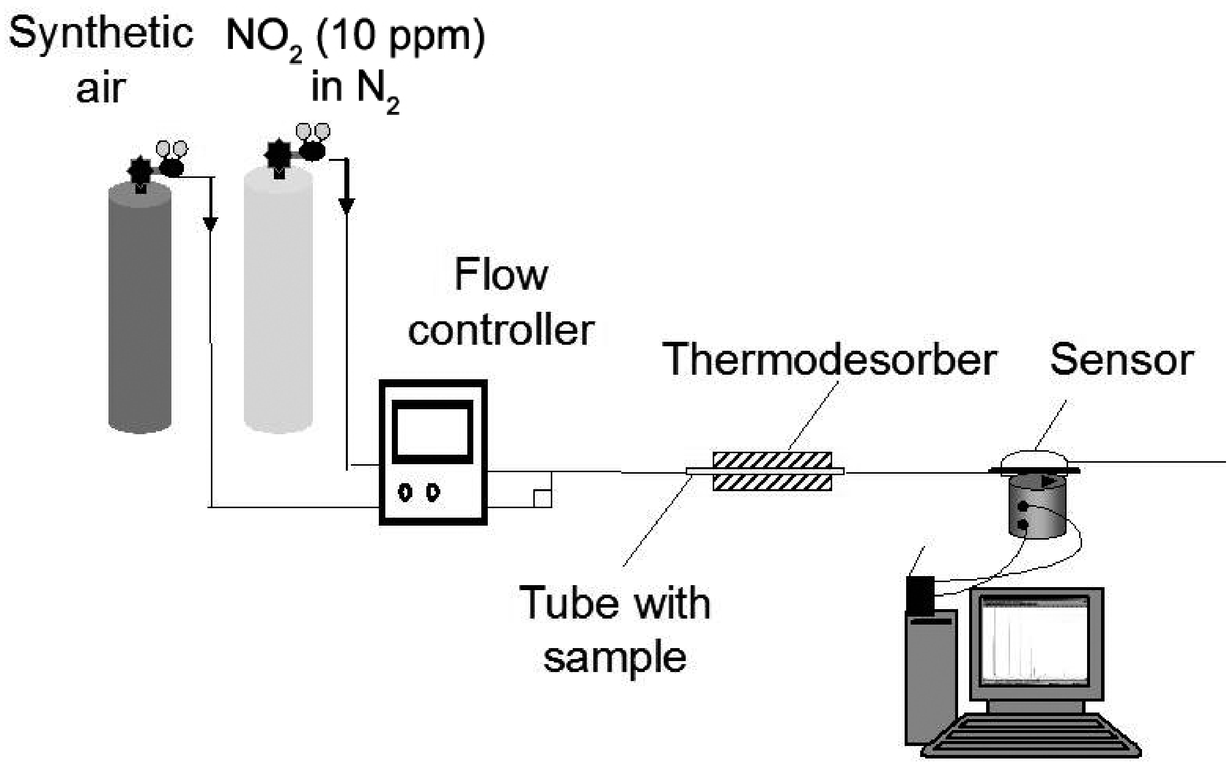
Planning and timetable

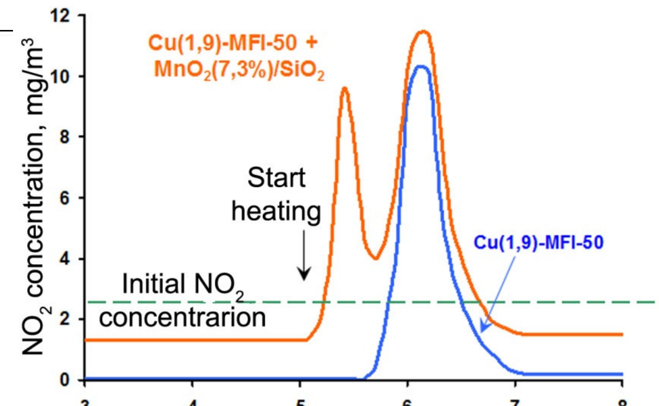
Activity	Title	1-3	4-6	7-9	10-12	13-15	16-18	19-21	22-24	25-27	28-30	31-33	34-36
WP1	**User requirements/ specifications**												
Task 1.1	Detection of explosives (NO2)												
Task 1.2	Industrial environment and safety, (NH3 , H2S)												
WP2	**Nano-materials for separation and enrichment**												
Task 2.1	Preparation of innovative nanomaterials for enrichment												
WP3	**Sensing nano-materials for surface activation and conductive detection**												
Task 3.1	Preparation of Nanowires by PVD												
Task 3.2	Preparation of Nanowires by CVD												
Task 3.3	Chemical modification of NWs												
WP4	**Low power substrates and packaging**												
Task 4.1	Preparation of substrates												
Task 4.2	Packaging												
WP5	**Characterization and modeling at nanoscale**												
Task 5.1	Morphological, Physical and Chemical Characterization												
Task 5.2	Modeling of bulk, surface, adsorption and charge transport												
Task 5.3	Operando investigations												
WP6	**Sensor system integration and Functional Characterisation**												
Task 6.1	Sensor system integration												
Task 6.2	Solid/liquid sampling and vapour conversion												
Task 6.3	Conductometric chemical sensors												
Task 6.4	Novel approaches: surface ionisation-based sensors and catalytic detection												
Task 6.5	Benchmarking												
WP7	**EU-Russia integration program**												
Task 7.1	Exchange of Researchers												
Task 7.2	Tutorials												
Task 7.3	Workshops												
Task 7.4	Joint Doctoral Degrees (JDDs)												
WP8	**Exploitation and Dissemination**												
Task 8.1	Dissemination												
Task 8.2	Exploitation												
WP9	**Coordination and Management**												
Task 9.1	Administrative, financial and legal management												

Selectivity, Sensitivity, Stability

Research summary

Separation and enrichment unit



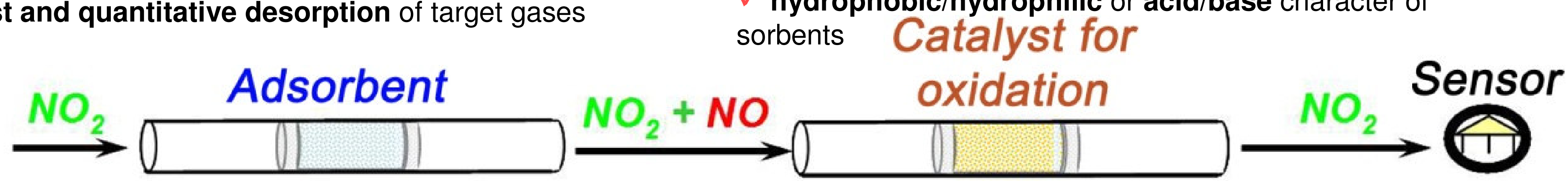


Materials demands

- ✓high active **surface area**
- ✓**thermal stability** at thermo cycling
- ✓**fast and effective sorption** of target gas from gas mixture
- ✓no reactions with target gas with formation of **false products**, minimal accumulation of other substances
- ✓**fast and quantitative desorption** of target gases

Factors influencing on sorbent selectivity

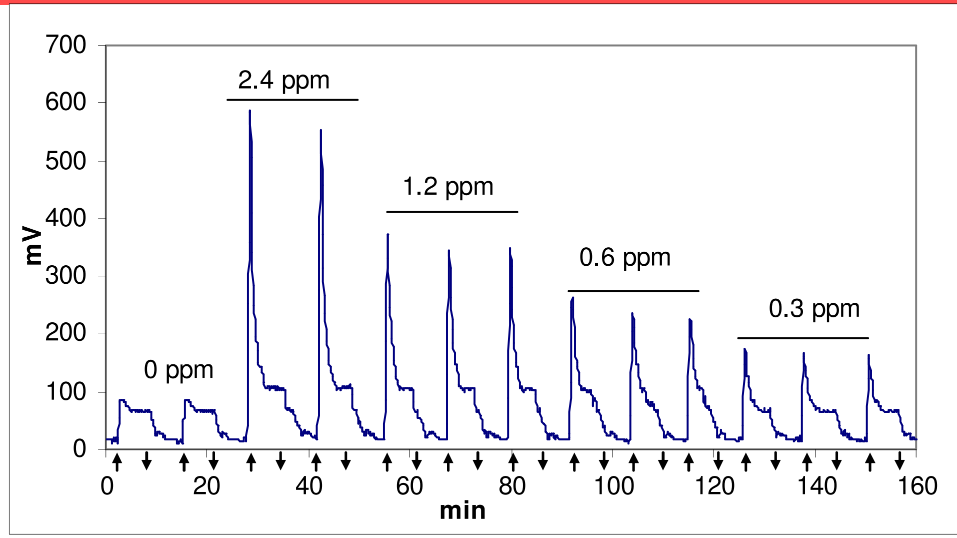
- ✓different **types** and **geometry** of pores network
- ✓specific gas molecule **coordination functions (specific active sites)**
- ✓**active sites** density and localization
- ✓ **hydrophobic**/**hydrophilic** or **acid**/**base** character of sorbents



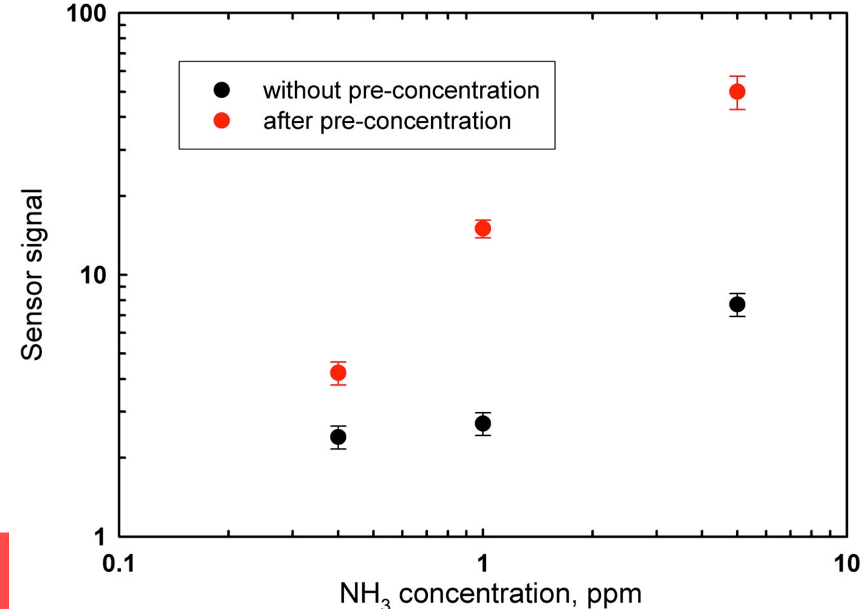
Nanomaterials for separation and enrichment

Preconcentrator-sensor system

H_2S detection
Preconcentrator: Al-MMS-1

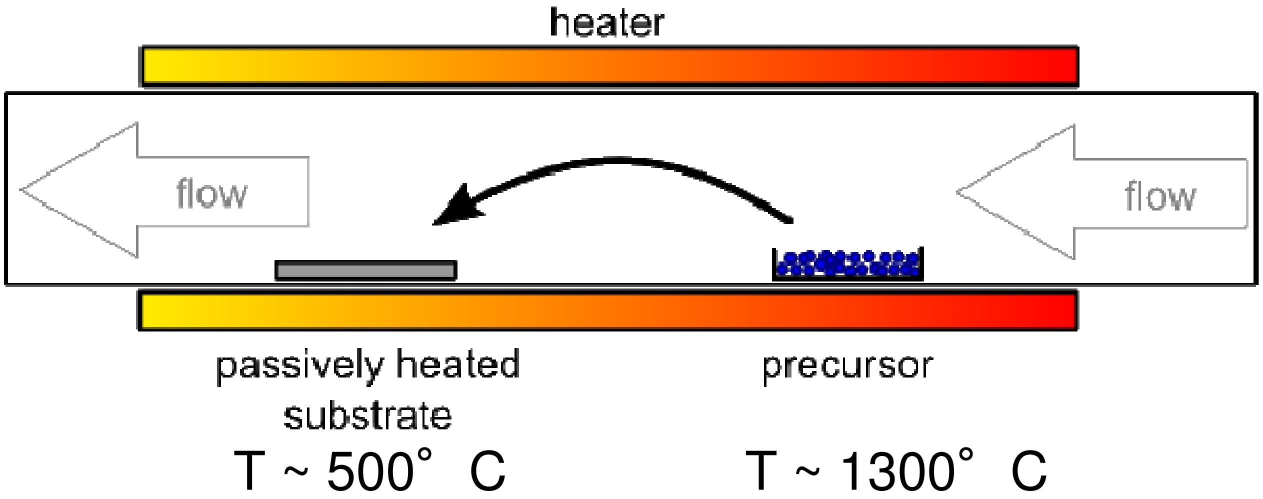


NH_3 detection
Preconcentrator: modified SiO_2



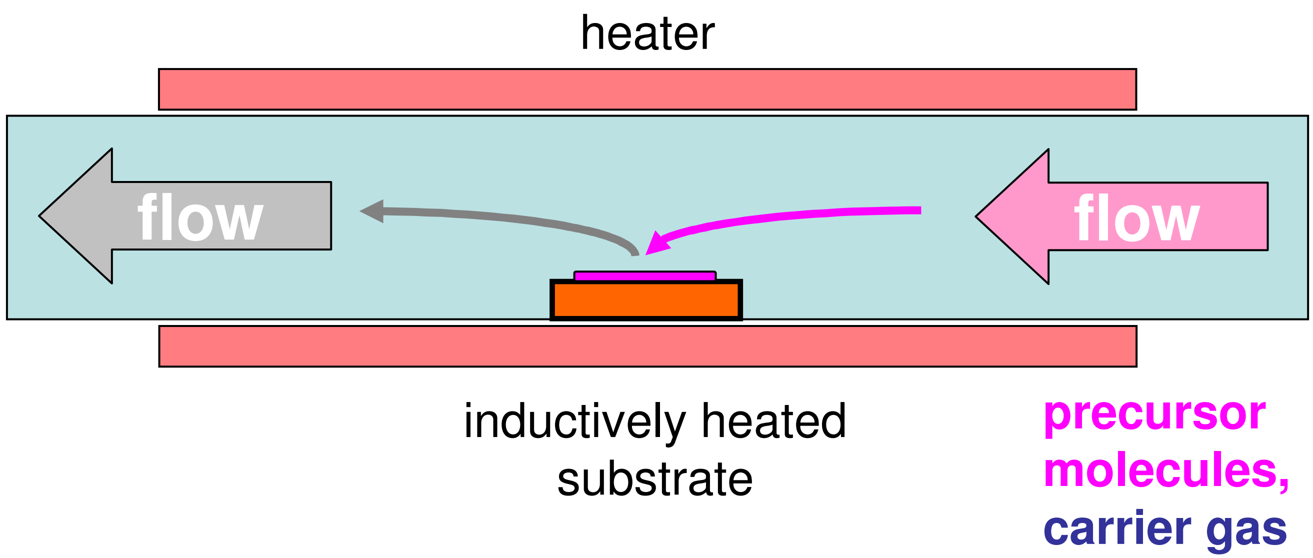
Selectivity, Sensitivity, Stability

Preparation of sensitive materials



- High temperature evaporation of source materials
- vapour phase transport in a thermal gradient
- condensation of vapours on a slightly colder substrate

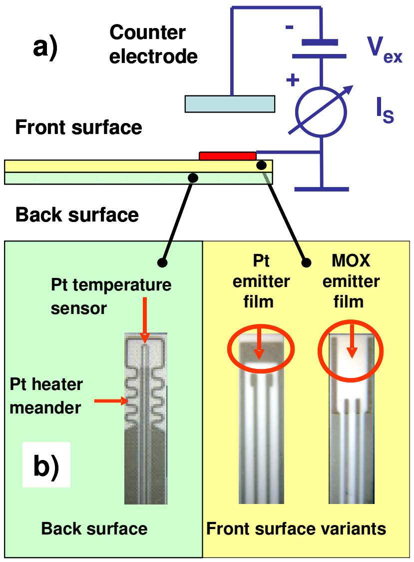
Materials:
- **SnO_2**
- **Fe_2O_3**
- **ZnO**
- **MgO**
- **NiO**
- **CuO**



Sensors packaging

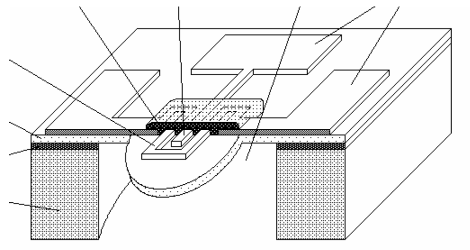
Integration of developed materials and developed substrates

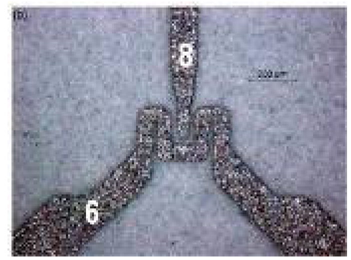
Macroscopic



- Functional characterisation of sensing materials
- Novel sensing mechanisms

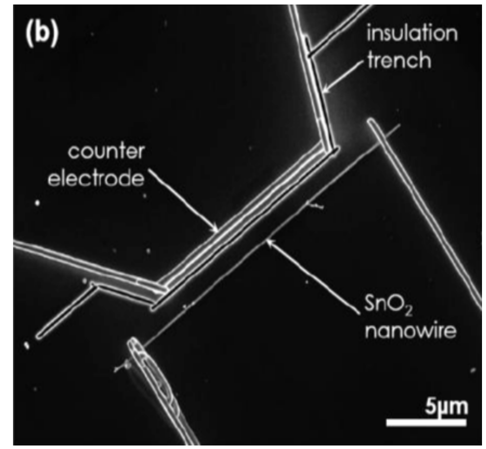
MEMS





- Functional characterisation of sensing materials
- New sensing mechanisms

Single Nanowire



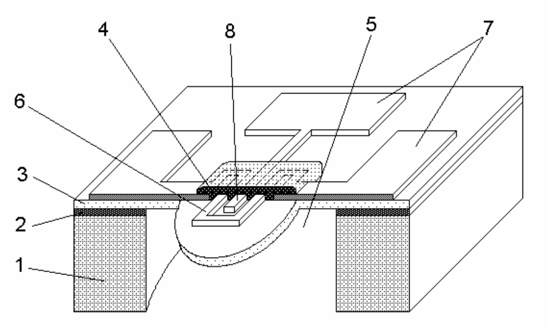
- Physics on nanoscale
- Novel sensing mechanisms

Side Activities: Flexible Substrates

Selectivity, Sensitivity, Stability

Ceramic vs. Silicon hotplates

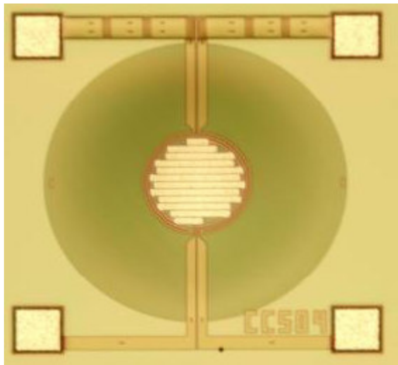
Ceramic microheater



Can sustain high processing temperatures across the entire substrate

Confine deposition / annealing process by shadow masking !

Silicon microheater

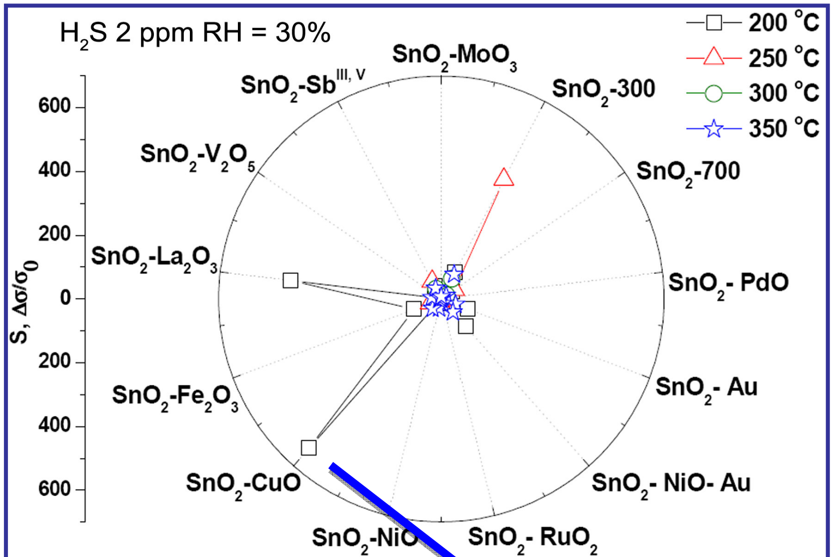


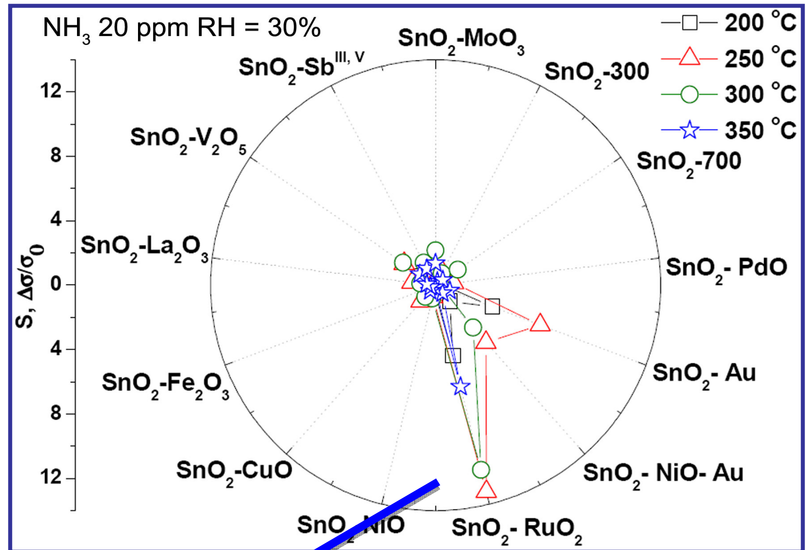
Can sustain high processing temperatures only in membrane centre

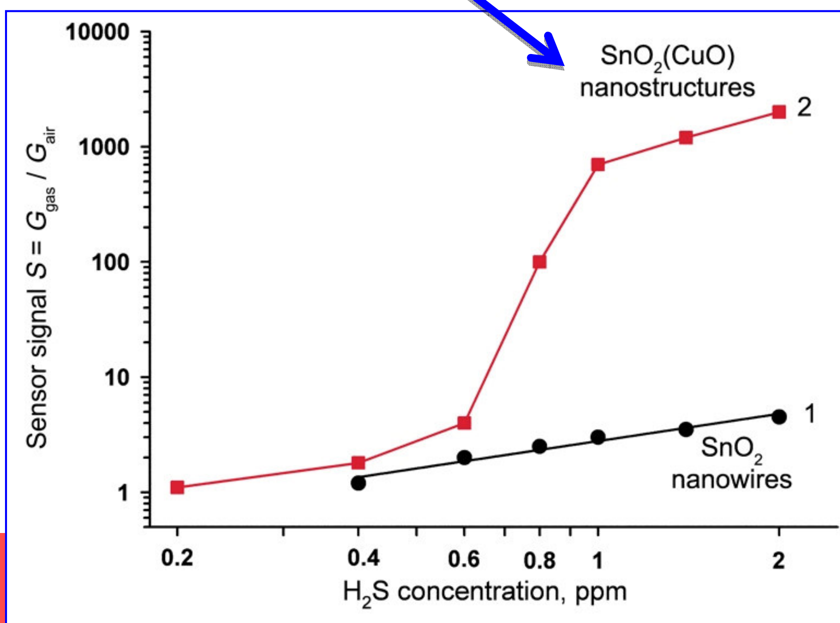
Confine deposition / annealing process to membrane centre !

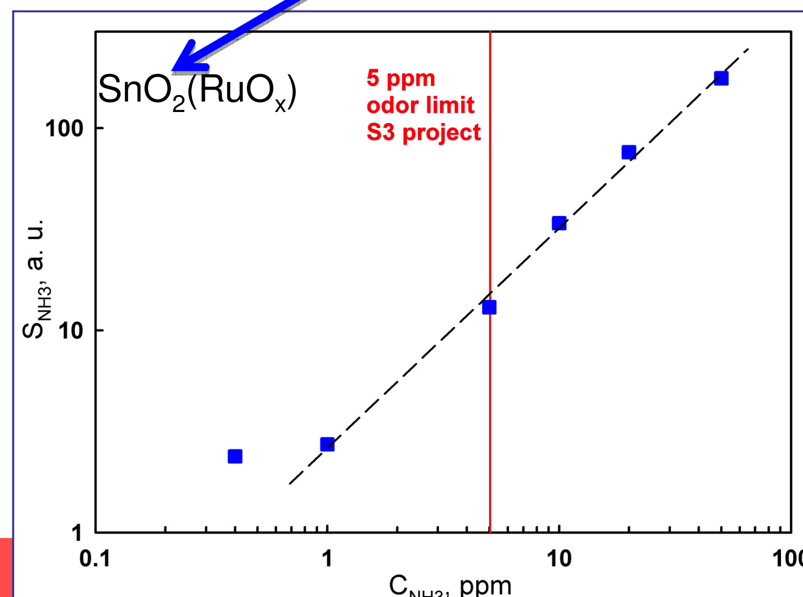
Functionalization process of NWs and NPs

Different materials with different sensing properties



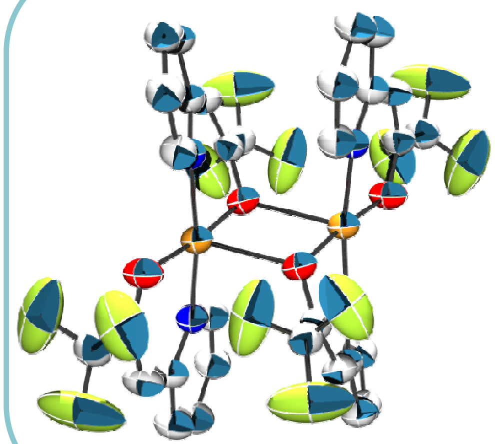




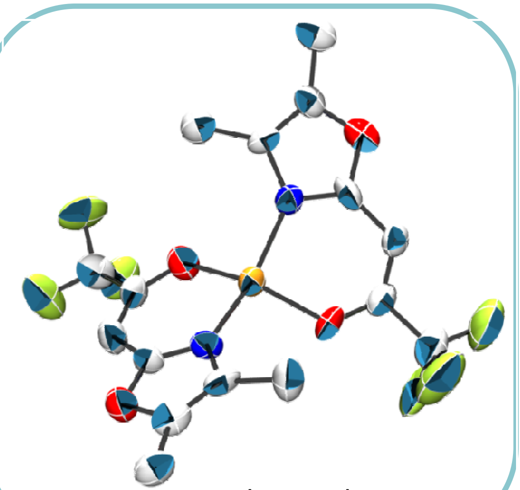


Selectivity, Sensitivity, Stability

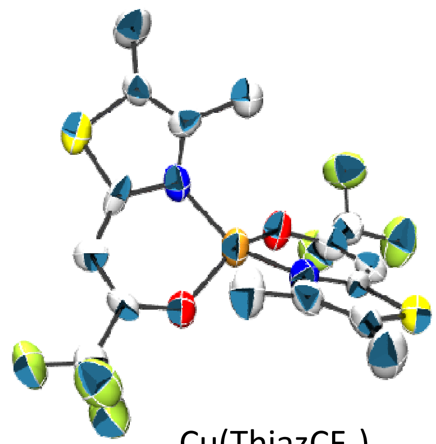
Functionalization Example:
Copper (II) heteroarylalkenolates: New Precursor Family



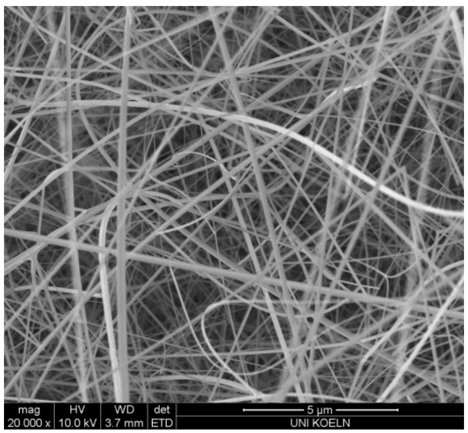
$Cu(PyCF_3)_2$



$Cu(OxCF_3)_2$



$Cu(ThiazCF_3)_2$



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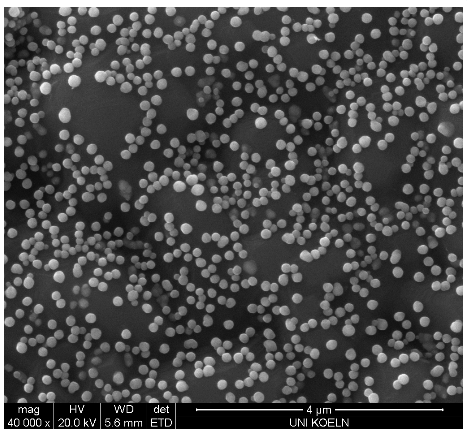

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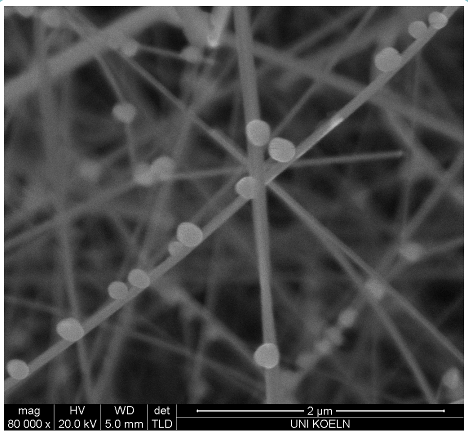


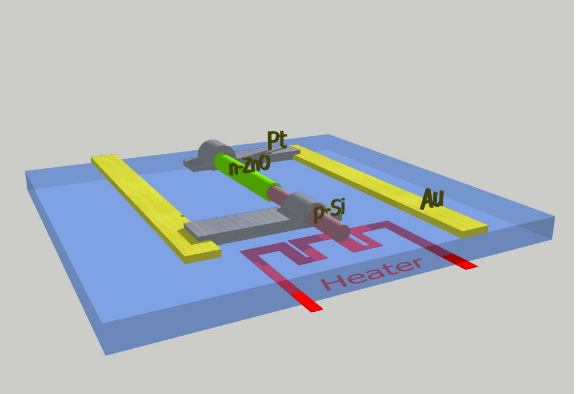
VLS growth of SnO_2 NW's (Au as catalyst, at 725 °C)

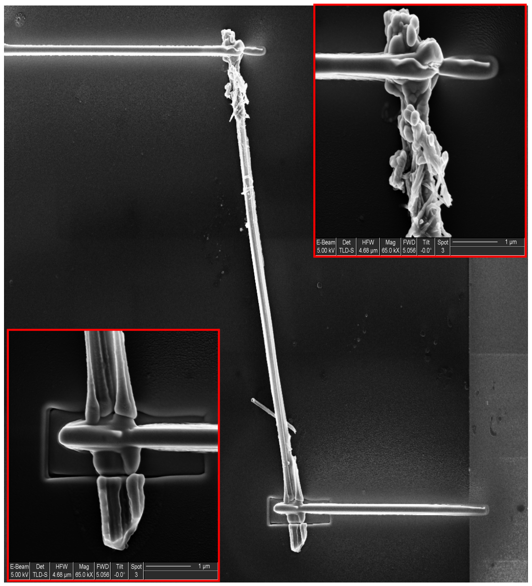
Cu NP's deposited at 750 °C

Selectivity, Sensitivity, Stability

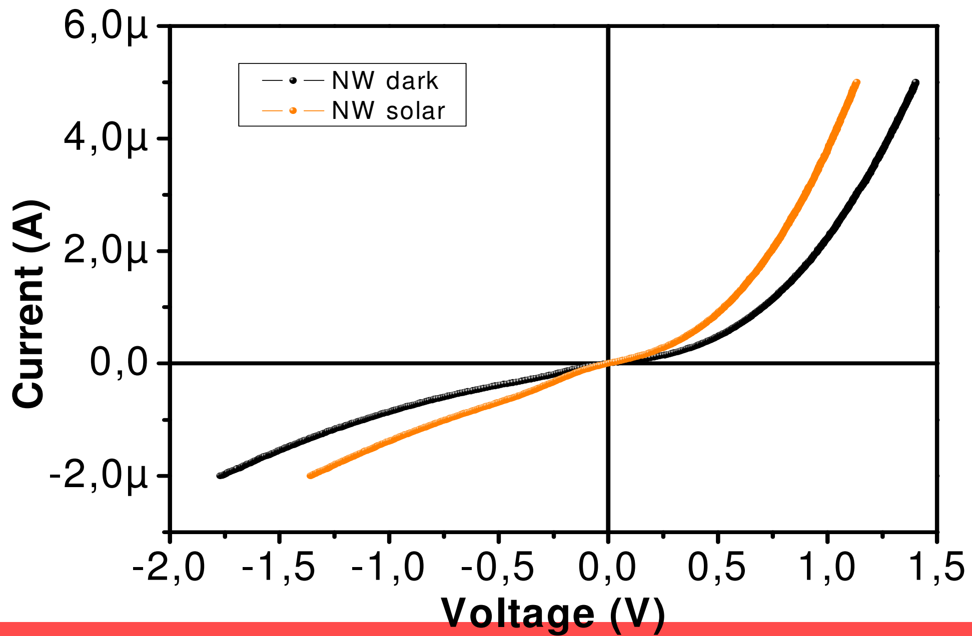
Sensor system integration and Functional Characterisation

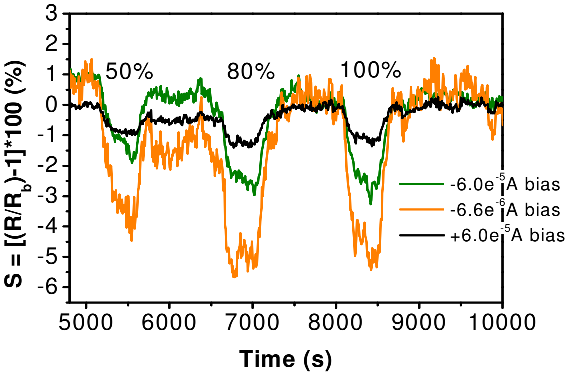
New Concepts & Devices





First devices based on heterostructures (ZnO@Si NWs)

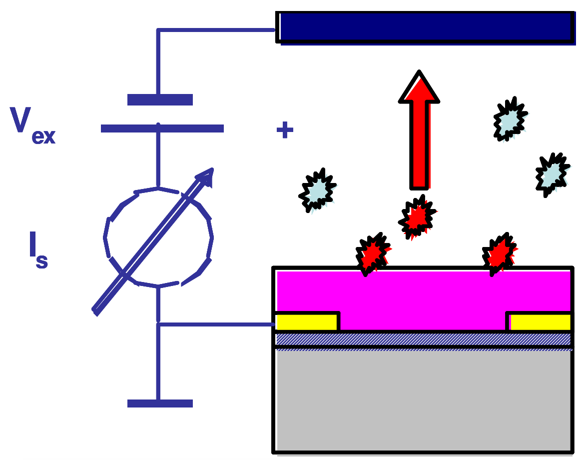


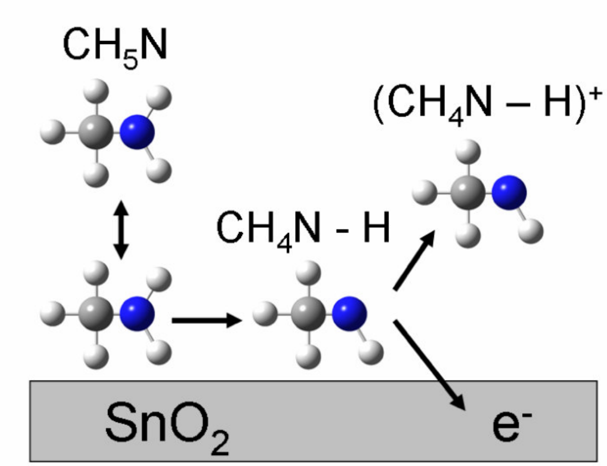


Selectivity, Sensitivity, Stability

Innovative transduction mechanisms

Surface ionisation (SI) response of MOX materials





Surface ionisation (SI) response:

Valence electrons are transferred to empty electron states inside adsorbent solid.

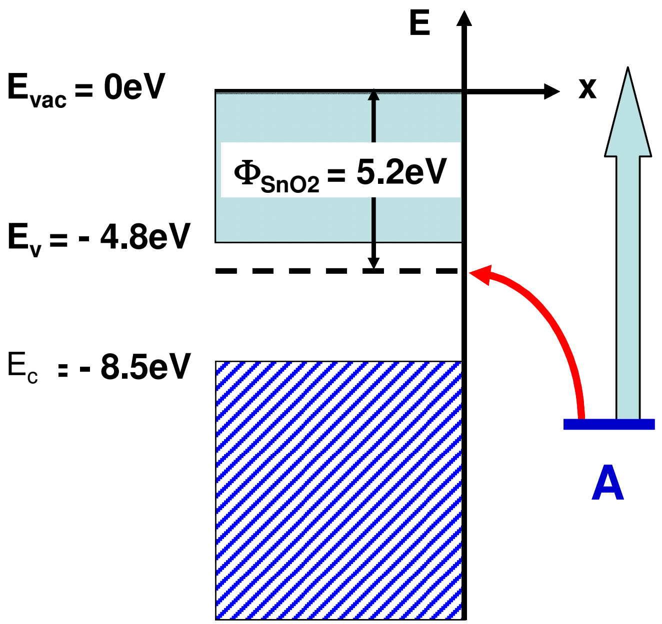
Detection criterion: Ionisation energy

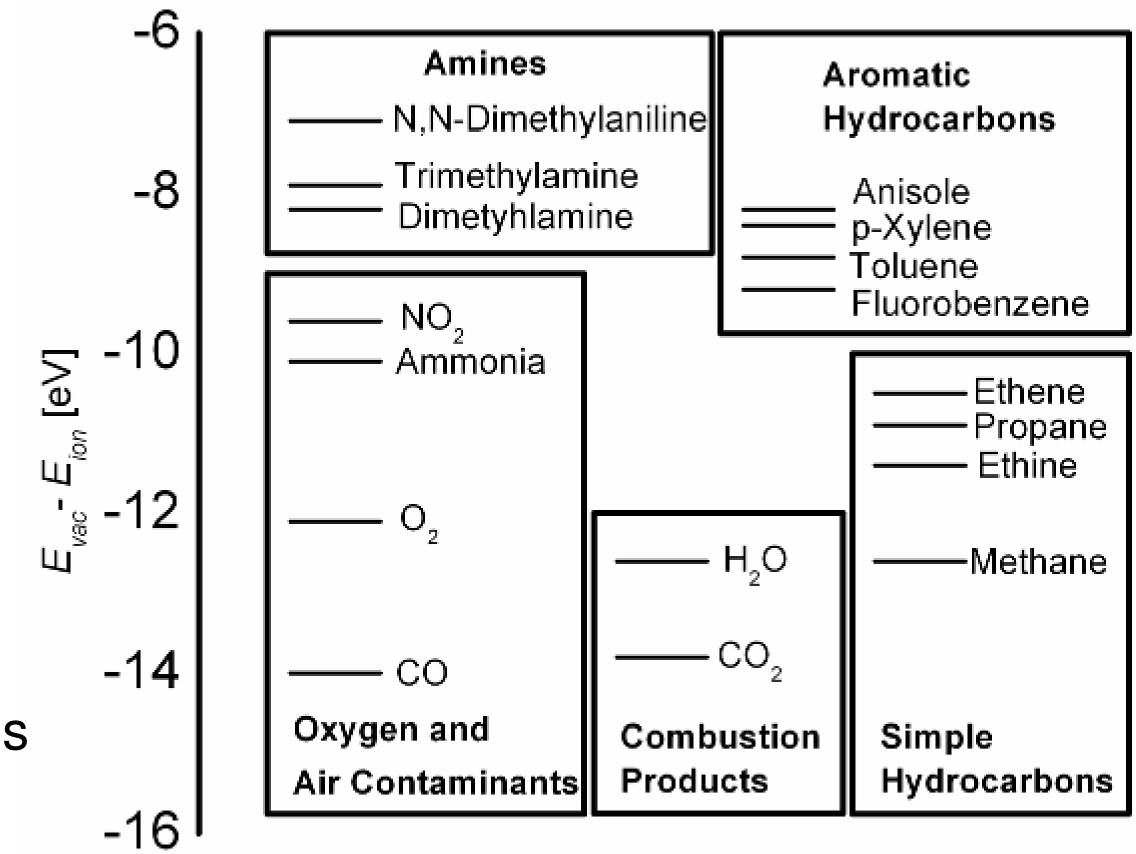
→ Selectivity towards higher interest analytes

T. Fujii and T. Kitai, "Surface ionization mass spectrometry of organic compounds: nitrogen-containing aliphatic organic compounds", Int. J. Mass Spectrom. Ion Processes 71 129-140, 1986.

Innovative transduction mechanisms

Surface ionisation (SI) response of MOX materials





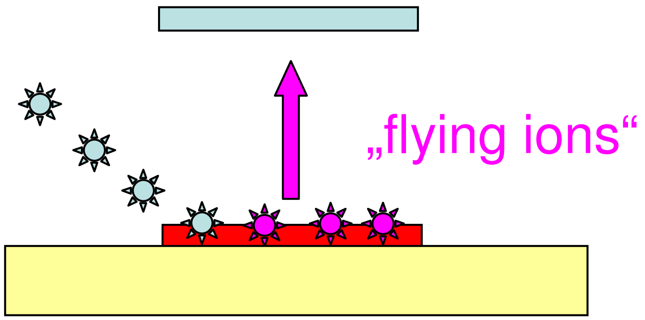
SI detection is blind against high ionisation energy analytes

→ Selectivity against toxic, odorous, reactive analytes !

Group selectivity: amphetamines and amines !!!

SI Response

Vertical SI readout

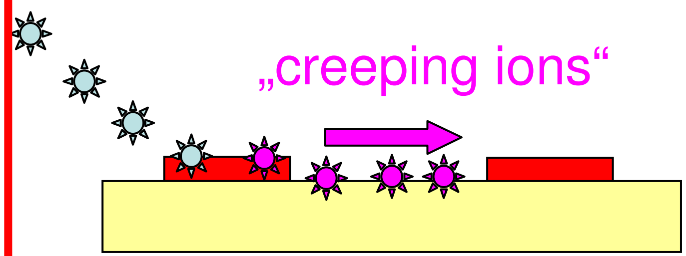


Adsorbate bond needs to be broken
→High temperature operation (600° C)

Large electrode gaps
→ High voltage operation (~1000V)

Excellent selectivity to amines

Planar SI readout



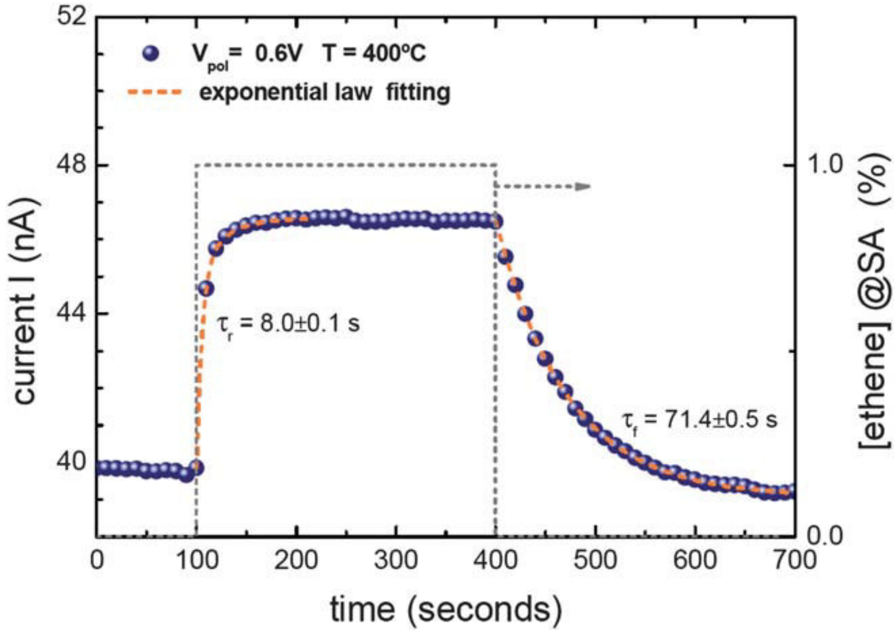
Adsorbate bond needs not to be broken
→ Lower temperature operation (400° C)

Small electrode gaps
→ Lower voltage operation (~10V)

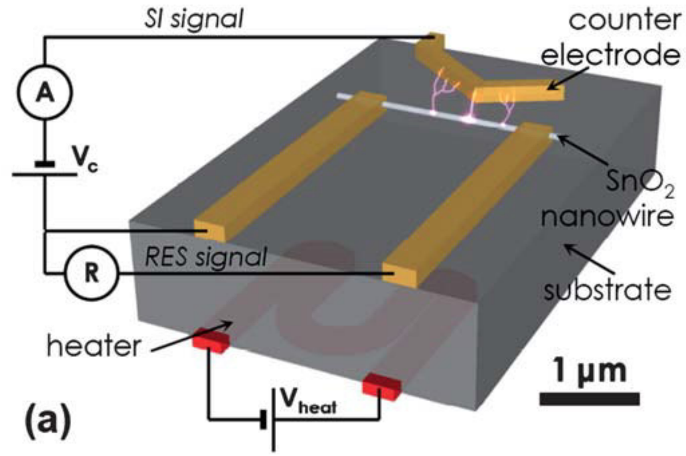
Selectivity to amines ?

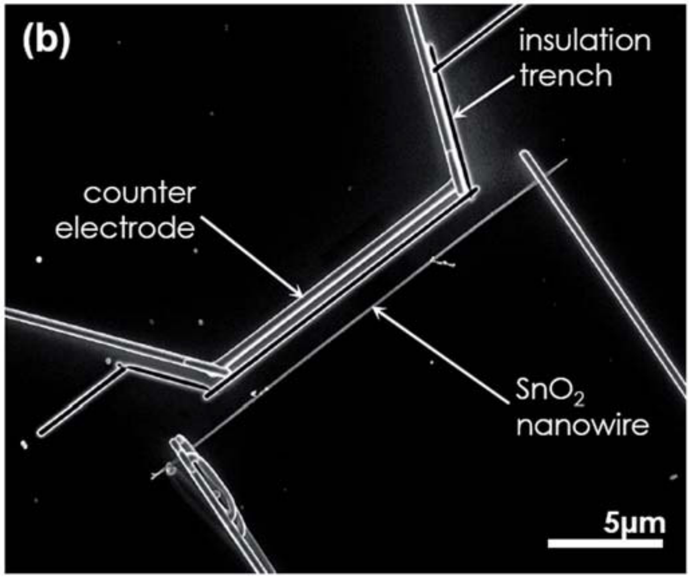
Single nano wire experiment
Surface ionization device

- Linear concentration dependence
- Fast time response
- Ionization current is obtained at low V (a few volts) and low T (300 ° C)

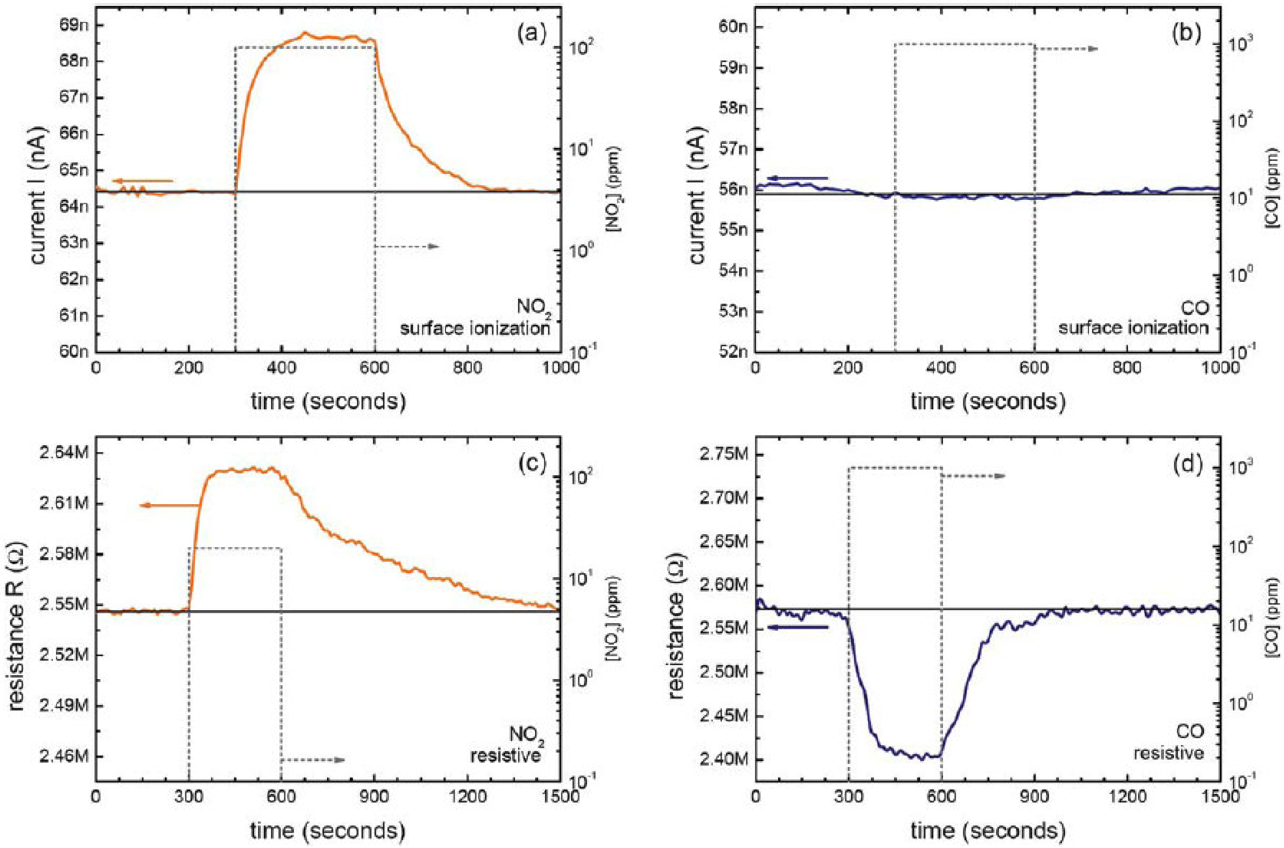


F. Hernandez-Ramirez et al, Nanoscale, 2011, 3, 630–634

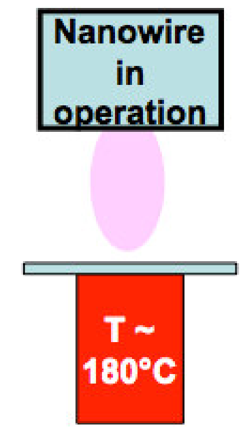




Combination of SI and RES response to address **selectivity**



•Measurements with NO_2 and CO with separated devices (a RES + a SI device);



Open test set-up

Test with dibutylamine (**drug detection**)
•**Fast response time** (1s)

Training and integration material

Exchange of scientists

Younger scientists for periods ranging from one to several months

Senior scientists in the range of several days up to several weeks

Exchanges aim at the planning and execution of joint experiments at specific partner sites, preparation of samples and agreement on measurement protocols.

several exchanges between S3 partners during the last 2 years

Selectivity, Sensitivity, Stability

Training and integration material
Tutorials

Planning and execution of tutorials on topics of general interest (textbook level).

Activities particularly address younger researchers and doctoral students and aim at ensuring comparable levels of technological and scientific skills across the entire S3 consortium.

3 tutorials held within the S3 project

Institut de Recerca en Energia de Catalunya
Catalonia Institute for Energy Research

EADS

S3
Selectivity, Sensitivity, Stability

Tutorials and Workshops

- **Tutorials**
  - tutorials on topics of general interest (textbook level)
  - Activities particularly address younger researchers and doctoral students
  - Technological and scientific skills are standardized across the entire S3 consortium.
  - **1st S3 spring school in Rimini, Italy, 10-14 May 2010**
  - **2nd S3 Summer School at Igora near St. Peterburg, Russia 5 – 8 July 2011**
  - **3rd S3 winter school** February 13-15, 2012, Tuebingen (Germany)
- **Workshops**
  - Frontier Research Workshops (FRW), addressing researchers
    - ✓ **1st S3 Workshop 2010 / Barcelona**
  - Industry Transfer Workshops (ITW), addressing industry
    - ➢ **2nd S3 Workshop Summer 2010 / Athens**

➢ S3 exhibition at SENSORS + TEST (Nuremebrg) 22-24/05/2012

Training and integration material

Joint Doctoral Degrees

The ultimate and most effective integration measure.

Efficiency arises from their long term character and the possibility to collocate young scientists with other scientists in the EU and Russian partner laboratories.

A joint supervision of the Doctoral Degree Work by professors of both universities.

JDD program is running between MSU and UNIBS. Two active JDD students within the S3 project.

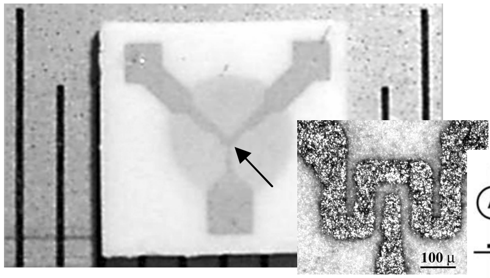
S3

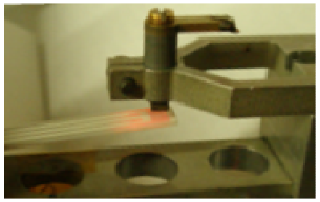
Selectivity, Sensitivity, Stability

S3 results and impact

S3 Results and impact:

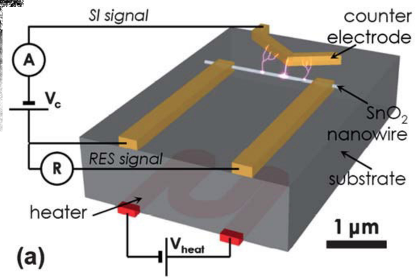
- Increased stability of NW-based sensing materials will positively affect the reliability of the developed sensors
- Increased cooperation between EU Union and Russian groups (exchanges of researchers, common workshops and tutorials, establishment of joint doctoral degrees)

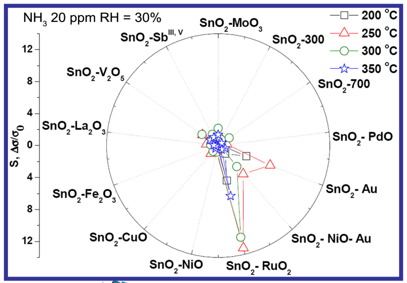


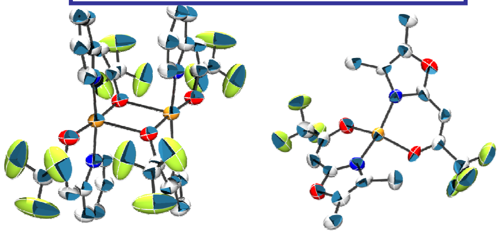


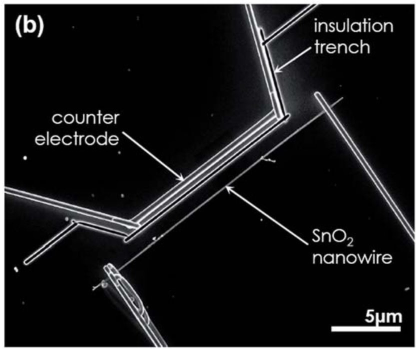
Research Results

- Innovative transduction mechanisms
- Single nanowire devices
- Functionalization processes for NWs and NPs
- Sensor substrates
- Sensor packaging
- Measurement protocols
- Nanomaterials for enrichment and separation



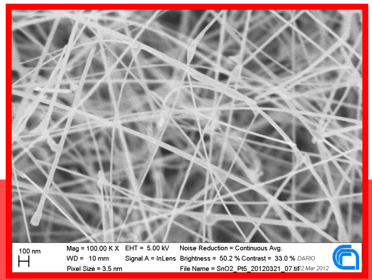






Teaching and integration Results

- Training material
- Integration tools (JDD)



Selectivity, Sensitivity, Stability

Exploitation of S3 results

- **Foundation of spin-off companies**:
  - RU Spin-off “Analit MEPHI”, http:/www.analitmephi.ru/
  - EU-RF spin-off company (in progress)
- **Industrialization and commercialization efforts:**
  - RU partners:
    - negotiations with companies aimed to:
    - co-production of the gas fire detectors for forest areas in the Alps;
    - co-production of flow meters for aerospace applications;
  - EU partners: negotiation with companies aimed to:
    - Integration of CVD synthesis process with MEMS substrates;
    - Development of nanowire based gas sensors;
  - EADS AG actions:
    - Support from commercial partners for commercialization of devices;
    - Licensing technology to supplier SMEs;
  - Incorporate technology supplier SMEs into EADS supply chains;
- **Use of S3 results in follow-on research programs**
  - A total of 6 other projects/project applications benefit from S3 results
  - Surface ionization devices are going to be further developed/exploited in the FP-7 DIRAC (EADS) and SNOOPY (EADS + CNR) projects

Advantages of EU-RF collaboration

- Different and synergetic approaches to research
- Complementary know-how and competences
- EU projects → research oriented
- RF project → industry oriented
- Of course there were challenges to face
  - Different bureaucracy, timings, duration…
  - but…together we were able to overcome these difficulties and gain knowledge and experience
- Now we look for new joint calls for integrated projects in Horizon 2020

Pictures and Awards

Dr. Gerhard Müller (at left), accepts his award as the newest Great Inventor for EADS' Hall of Fame. Joining him on stage are Airbus President and CEO Tom Enders, EADS Chief Technical Officer Jean Botti and EADS CEO Louis Gallois.

Selectivity, Sensitivity, Stability