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

COST Action TD1105

WGs and MC Meeting at ISTANBUL, 3-5 December 2014

Action Start date: 01/07/2012 - Action End date: 30/06/2016

Year 3: 1 July 2014 - 30 June 2015 (*Ongoing Action*)

MASTERING VOC DETECTION FOR BETTER INDOOR AIR QUALITY

Donatella Puglisi / donpu@ifm.liu.se

Participant

Linköping University / Sweden

COST EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

EuNetAir

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

COST is supported by the EU Framework Programme

European Science Foundation — ESF provides the COST Office through a European Commission contract

Scientific context and objectives in the Action

- **Background / Problem statement:** +85 % time spent indoor / costly HVAC systems

Bad air quality causes serious problems on environment, health, society

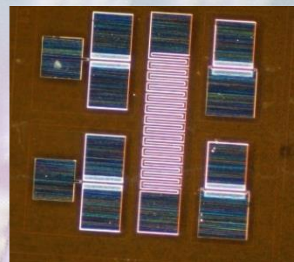
Good air quality is a key-issue!

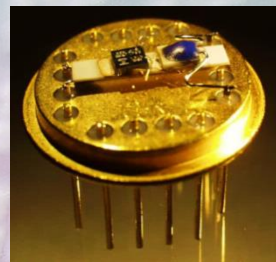
Stringent legislation for NOx and VOCs

Adequate control of emissions for more efficient reduction of hazardous air pollutants

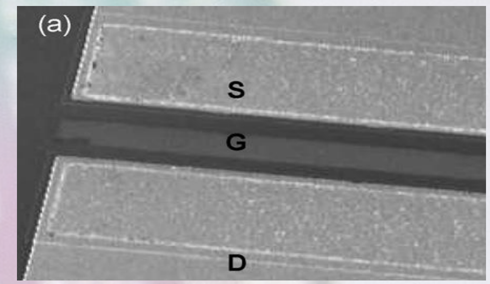
- **Brief reminder of MoU objectives:**
  - WG1: sensor materials and nanotechnology
    - Research on gas-sensitive materials for detection of specific air pollutants
    - Integration in gas sensor devices for indoor AQC
    - Functionalization and surface modification to enhance gas adsorption and sensitivity; stability, reproducibility, and selectivity
    - Material characterization (e.g. AFM, SEM)
  - WG2: Sensors, devices and sensor systems for AQC
    - Design, fabrication, testing, characterization of cost-effective high-performance gas sensors
    - Innovative sensor technologies: SiC-FET and graphene-based sensors

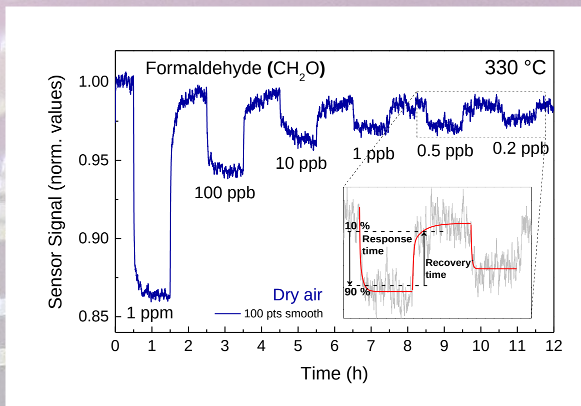
Current research activities (SiC-FET)



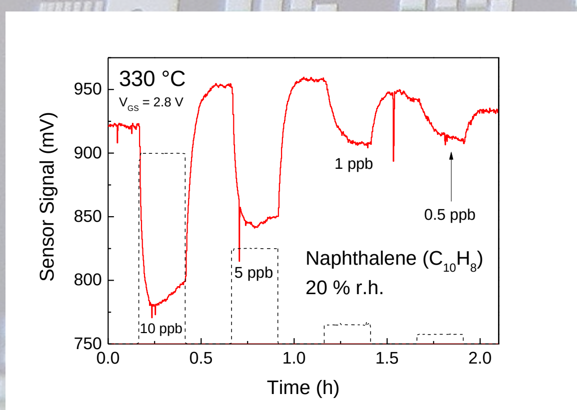


Sensor processing / characterization



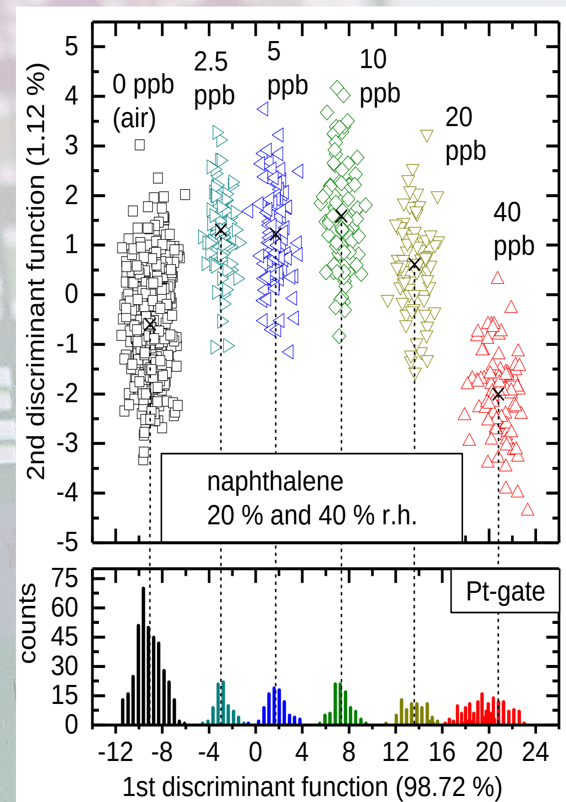


Sensing mechanisms / device operation

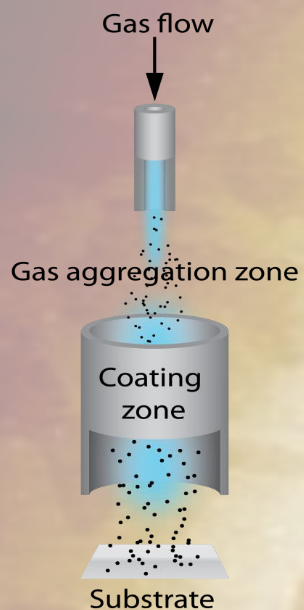


Addressed challenges

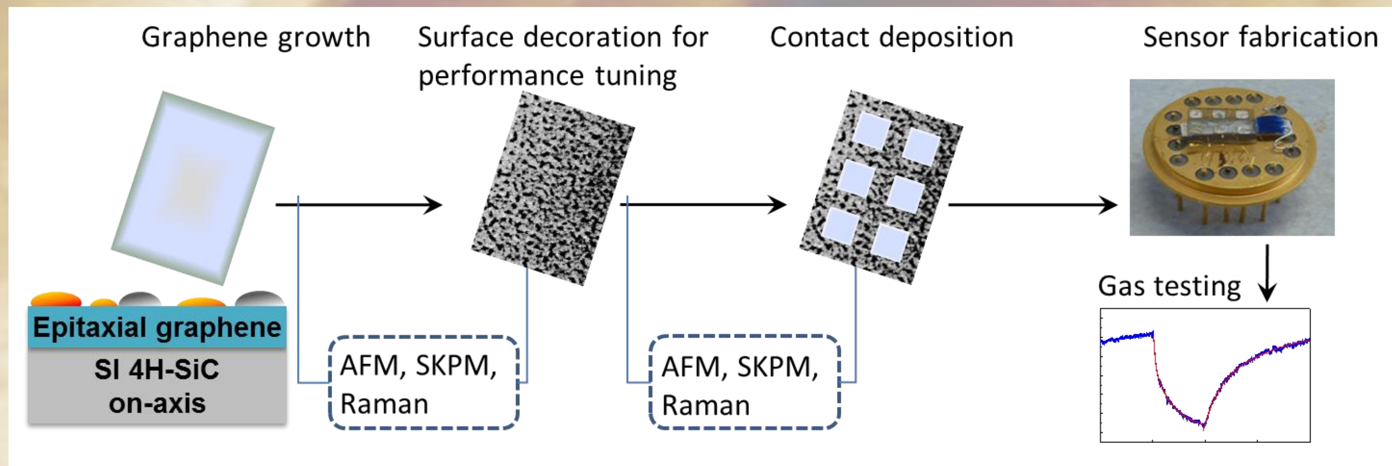
- Sensitivity
- Selectivity



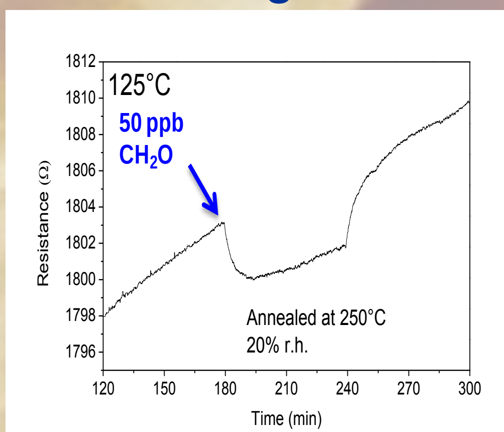
Current research activities (Graphene)

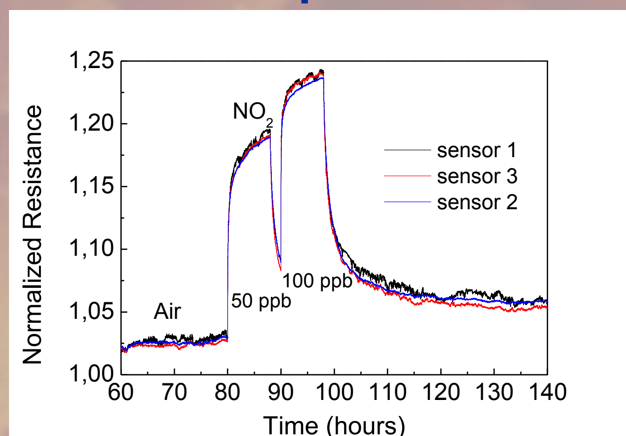


Sensor processing / characterization



Sensing mechanisms / device operation





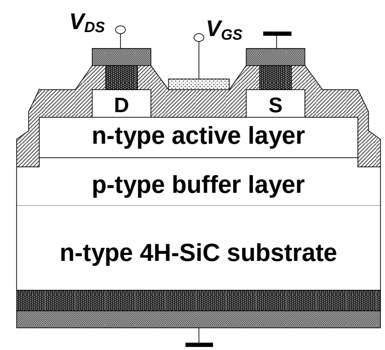
Addressed challenges

- **Sensitivity**
- **Reproducibility**
- **Selectivity**

Ongoing research topics

+15 years experience on high-performance, low-cost FE gas sensors for room and high temperature applications, such as

- car/truck engines and power plants
- emission monitoring
- combustion control and exhaust systems
- **indoor air quality applications**



Why SiC-FET sensors?

- Chemical inertness
- Wide band gap (3.26 eV 4H-SiC)

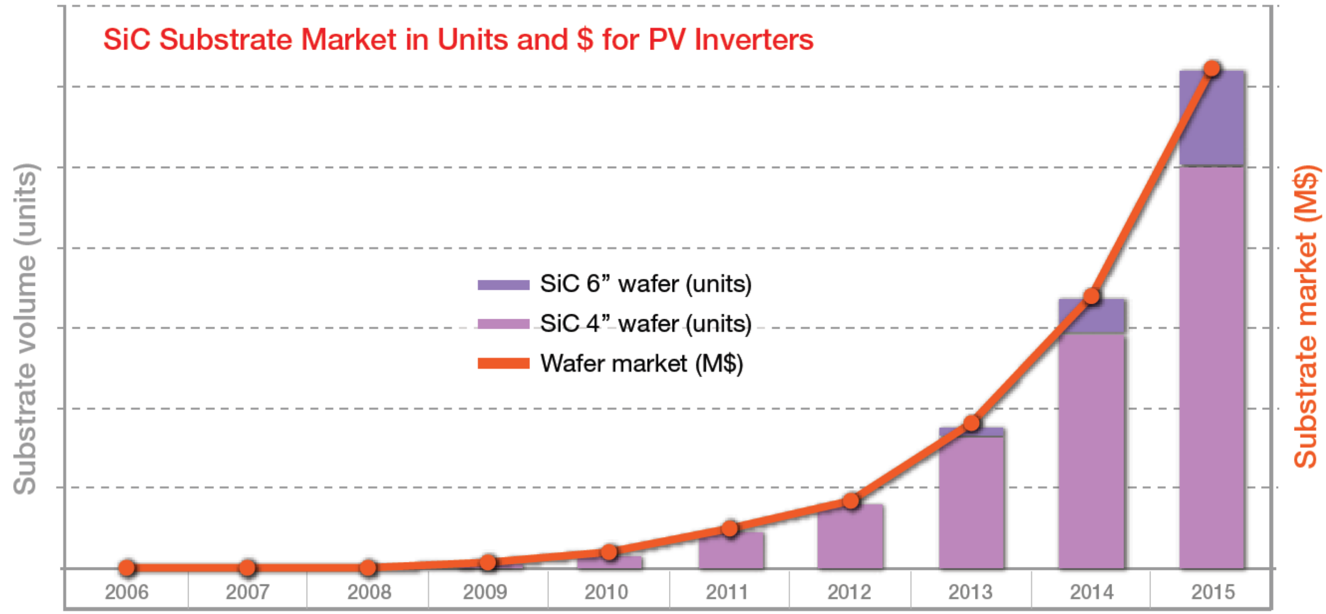
→ **HARSH ENVIRONMENTS**

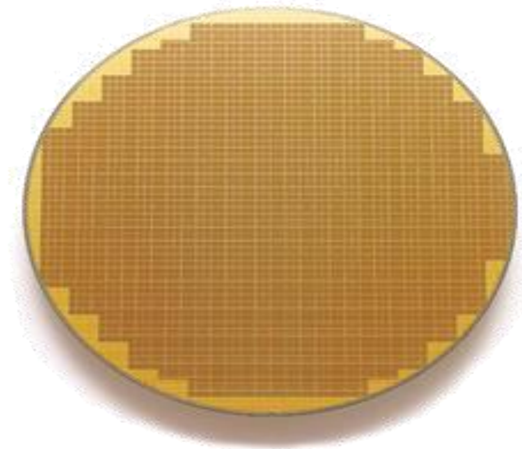
HIGH-TEMPERATURE OPERATION

- High, stable, reproducible performance - Flexibility when using temperature cycling mode
- Possibility to use high temperature for regeneration of the sensor surface

But SiC is so expensive…

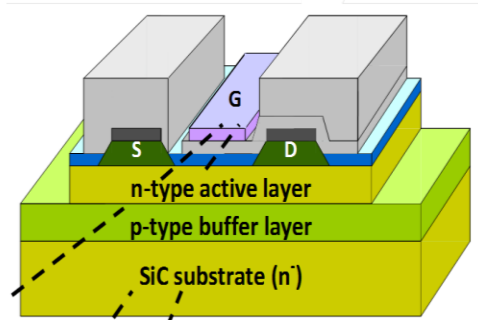
- ❑ **…No!**
- ❑ Yole Développement: transition to 4-inch SiC wafers - a milestone towards reduced cost of SiC technology



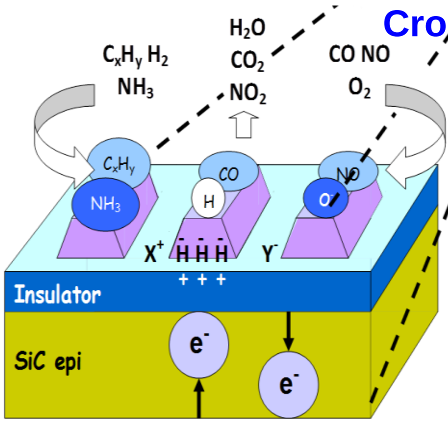


- ❑ The ongoing transition to 6-inch wafers will usher in further cost reduction and SiC market growth
- ❑ 4-inch SiC wafer → ~ 1800 chips (cost < 1 euro/each)
- ❑ The ongoing wafer cost reduction and market expansion in SiC will spill over also to EG/SiC
- ❑ Further steps towards cost-efficient preparation of EG/SiC through up-scaling of sample size in combination with a novel epitaxy technique allowing growth on inexpensive SiC substrates

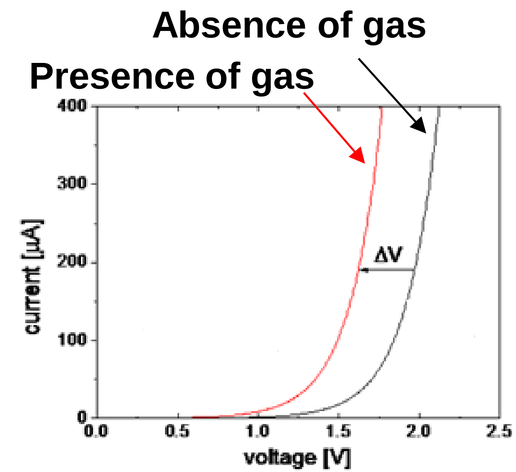
FE sensor platform



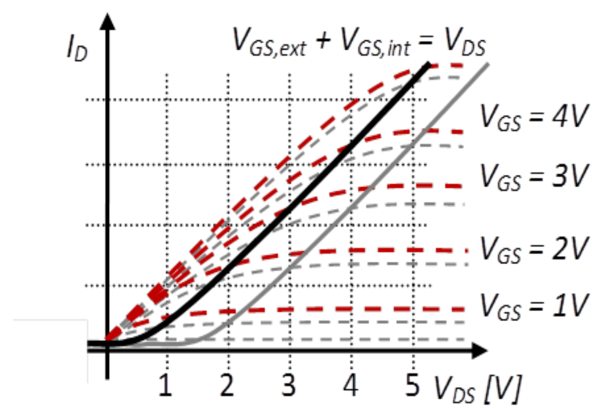
Cross section of a SiC-FET



Gate composed by a porous catalytic metal (Ir, Pt) as sensing layer



- FET current controlled by V_{GS}
- Gas molecules decompose and react on the catalytic metal
- Simple electronics



M. Andersson, R. Pearce, A. Lloyd Spetz, Sens. & Act. B 179 (2013) 95-106.

Sensitivity by

- ➢ Number of **three phase boundaries** gas-metal-oxide
- ➢ Adsorption **sites on the insulator**

Selectivity by

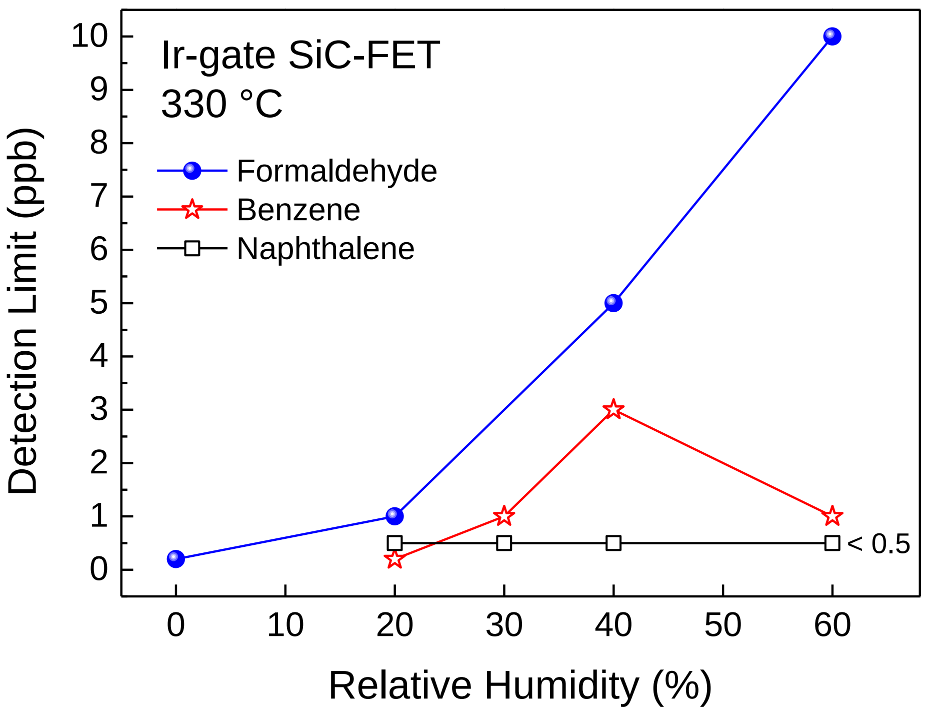
- ➢ Choice of **temperature**
- ➢ Different **catalytic materials**
- ➢ **Structure** of the metal

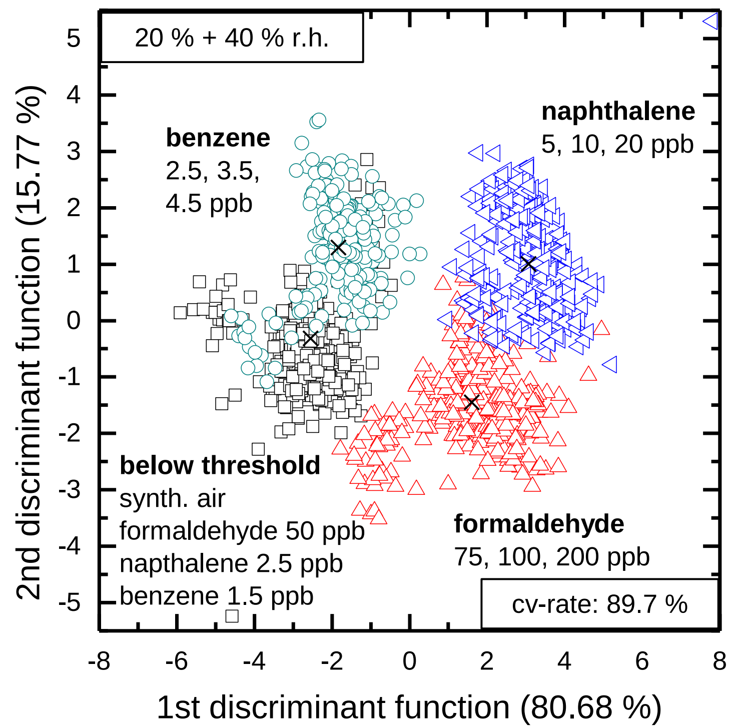
Gas adsorption/reaction at the gate contact → I-V shift

Sensor operation

High sensitivity:
excellent detection limits

High selectivity:
discrimination of VOCs





- Multi-dimensional data evaluated by pattern recognition techniques
- Linear discriminant analysis (LDA) + cross-validation to avoid over-fitting data
- For on demand ventilation, «below threshold» means ventilation not needed
- Robust discrimination against changing humidity level and varying concentration of VOCs

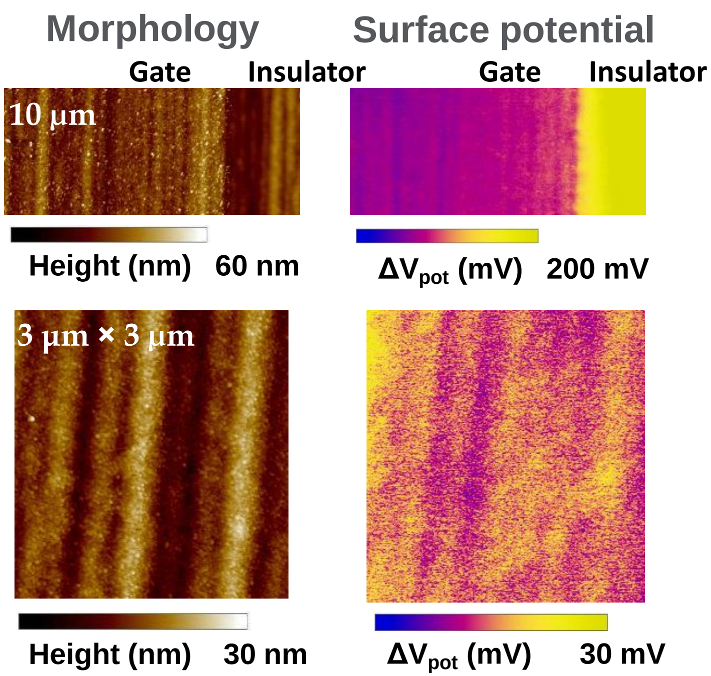
cost
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

In cooperation with Saarland University

Suggested R&I Needs for future research

Innovation – SiC-FET

- Detection limits under threshold of legal requirements
- Discrimination and quantification of specific VOCs
- Stability during long-term operation



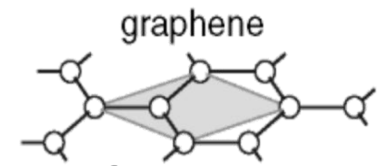
Ir-gate before and after two weeks operation

✓ **Iridium - Sensing layer not degraded is extremely important for our target application (indoor AQC)**

Research directions as R&I NEEDS:

❖ **Development of new materials as sensing layers using PLD** (work in progress in cooperation with Univ. Oulu)

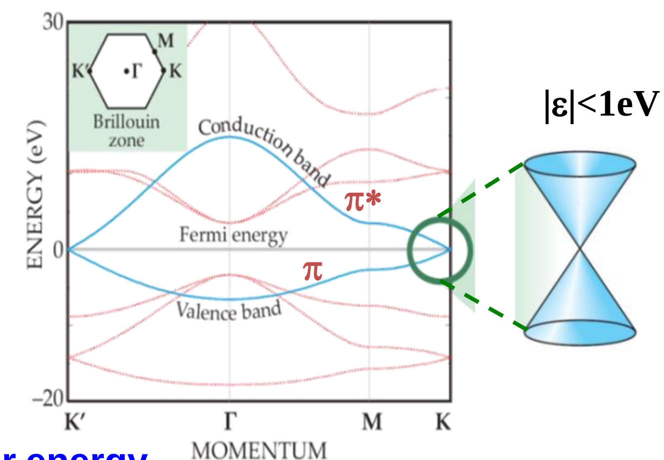
Ongoing research topics



- Increased sensitivity and reproducibility
- Functionalization with metal and metal oxide nanostructures for selectivity tuning
- Controlling layer uniformity and doping
- Effect of surface restructuring during graphene growth on SiC
- Effect of humidity on sensor performance

Why gas sensors in graphene?

- **Unique band structure of graphene leads to a low density of states near the Dirac point (E_D) – small changes in the number of charge carriers result in large changes in the electronic state**
- **Every atom at the surface – ultimate surface to volume ratio**
- **Low noise, chemically stable (in non-oxidizing environment) – enables very low detection limits**



❑ **Graphene is highly sensitive to chemical gating due to its linear energy dispersion and vanishing density of states near the Dirac point and therefore has potential as a low noise, ultra-sensitive transducer.**

Graphensic

manufactures and supplies

Very high quality, wafer scale, epitaxially grown

Graphene on SiC

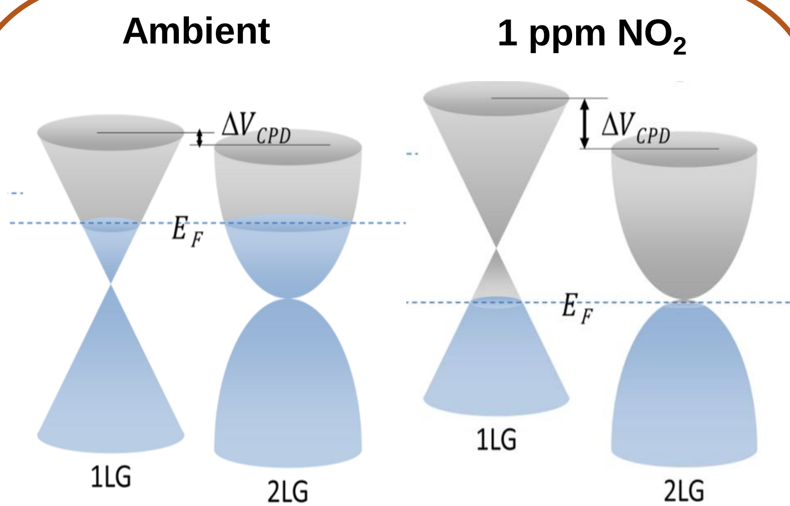
Spin off from Linköping University, Sweden

22.11.2011

- **Produced by sublimation of Si from SiC in Ar at 2000 ºC**
- **Scalable, wafer-size graphene films compatible with standard semiconductor processing**
- **High thickness uniformity (> 90 % 1LG, rest 2LG)**
- **Thickness controlled by temperature**

Graphene sensors issues: sensitivity, reproducibility

ΔS depends on thickness due to differing band structures for 1LG, 2LG,... MLG

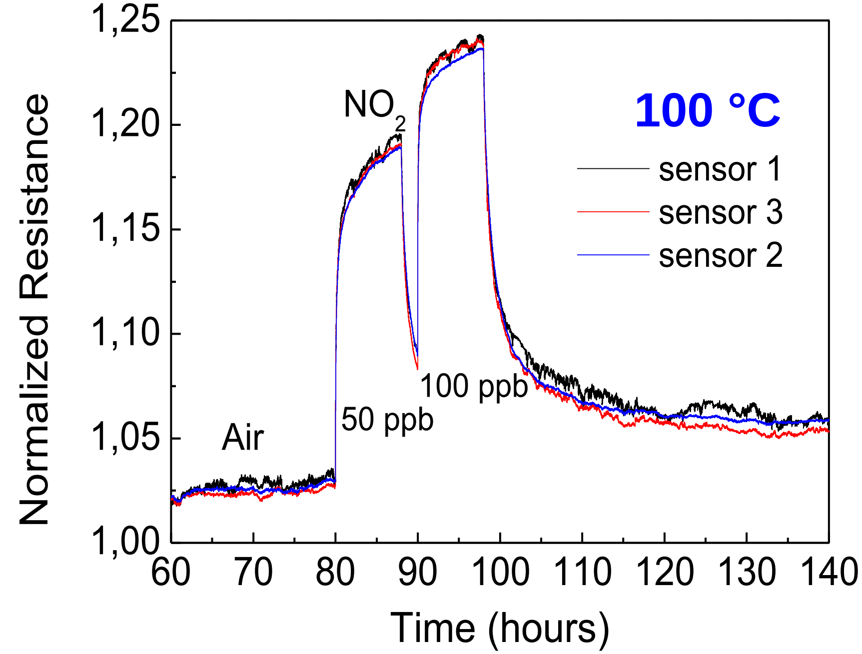


- **NO_2 withdraws electrons**

Same change in charge carriers causes larger shift of the Fermi energy for 1LG

R. Pearce, J. Eriksson, T. Iakimov, L. Hultman, A. Lloyd Spetz, and R. Yakimova, ACS Nano 7 (5), pp 4647–4656 (2013)

Uniform 1LG leads to very reproducible sensor characteristics



NO_2 sensing interesting for:

- Emission control (few ppm)
- **Air quality control (few ppb)**

Epitaxial graphene on SiC enables **highly reproducible** sensor fabrication

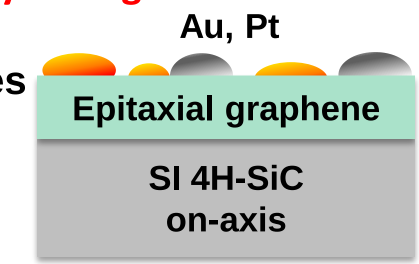
Different sensors fabricated on 100 % 1LG show identical response

1LG is more sensitive to NOx than 2LG or MLG

Uniform 1LG required for maximum sensitivity and reproducibility

Graphene sensors issues: selectivity, response/recovery time

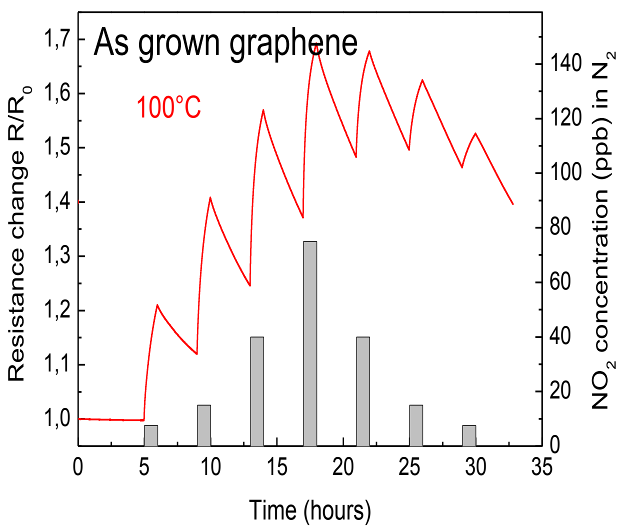
Functionalization with metal and metal oxides nanostructures for selectivity tuning

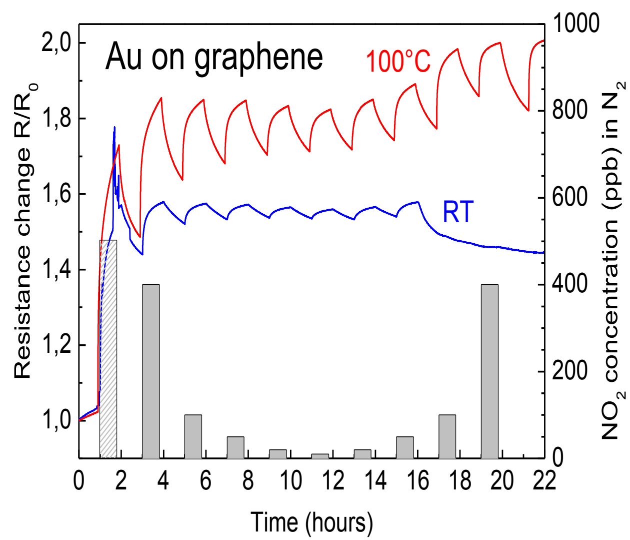


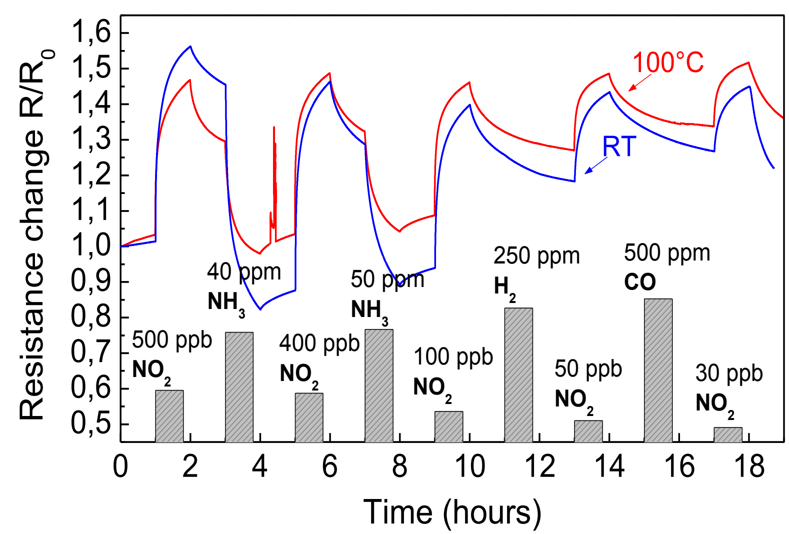
Aim: To develop a reproducible method for functionalization with metal nano structures

- Thin layers of Au and Pt DC sputtered onto EG/SiC at elevated pressure
- Ideally we want islands or nanoparticles to maximize metal-graphene-gas boundaries

Effect of Au decoration on sensor response







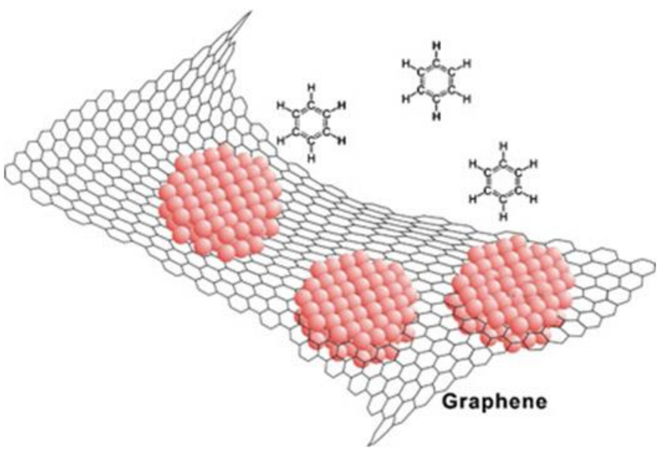
Detection limit < 1 ppb NO_2

Selectivity: blind to H_2 and CO

J. Eriksson, D. Puglisi, Y. H. Kang, R. Yakimova, A. Lloyd Spetz , Physica B 439 (2014) 105–108

Innovation - Graphene

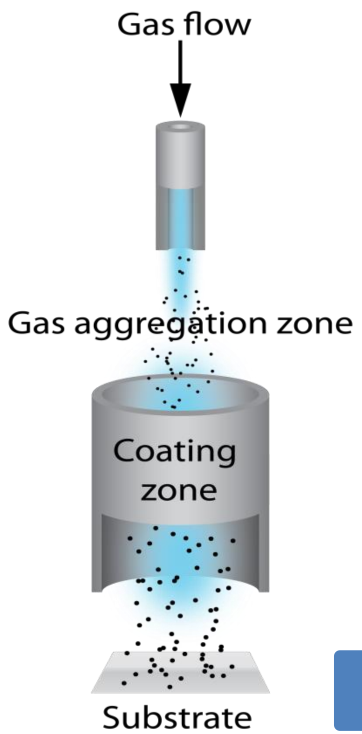
- Reproducible growth
- Wafer-scale films compatible with standard semiconductor processing
- High thickness uniformity (> 90 % 1LG, rest 2LG)
- Decoration changes the surface chemistry but does not alter the graphene band structure



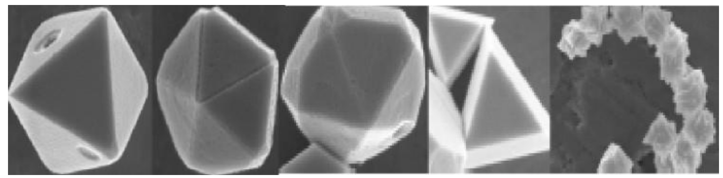
Research directions as R&I NEEDS:

- **Designed nanoparticles by pulsed plasma**: it is expected that decoration with different metals or metal-oxide nanostructures will allow careful targeting of selectivity to specific molecules

Designed Nanoparticles by Pulsed Plasma

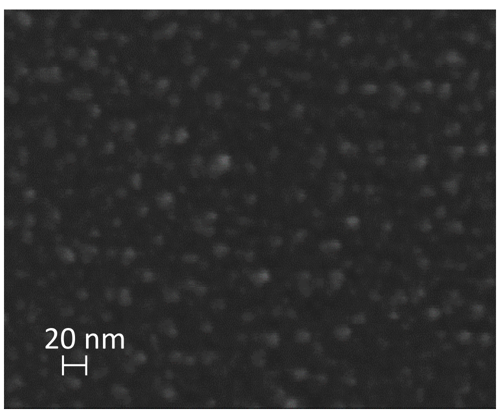


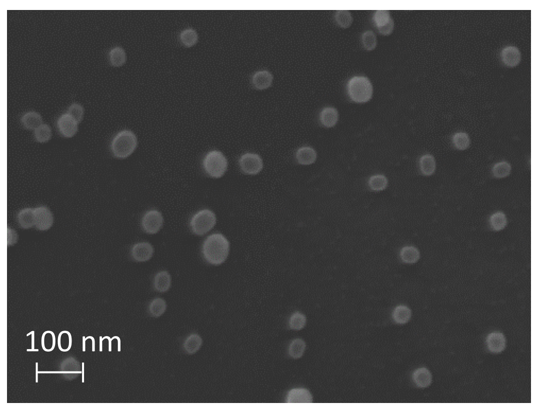
- ❑ Plasma-based nanoparticle (NP) synthesis process
- ❑ Highly versatile (metals, metal-oxides, core-shells) and reproducible thin film deposition technique



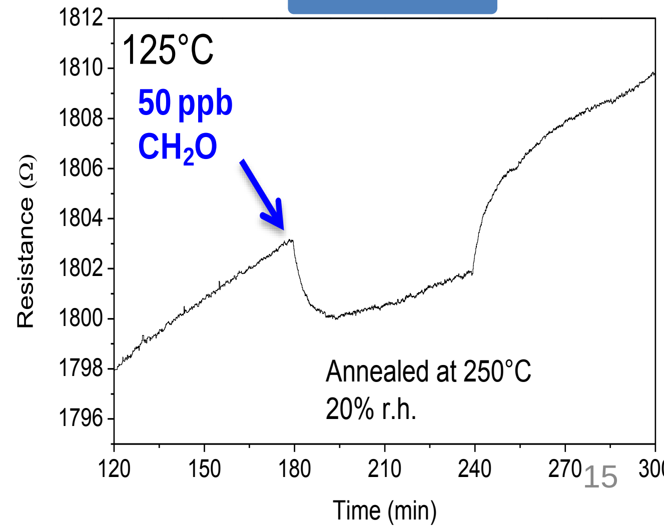
- ❑ Preliminary results show that TiO_2 NPs allow enhanced sensitivity towards formaldehyde and benzene
- ❑ The effect depends on the size of the deposited NPs (< 5 nm, sensitive to benzene; > 50 nm, sensitive to formaldehyde)

TiO_2 NPs (Ø < 5 nm and Ø ≈ 50 nm)

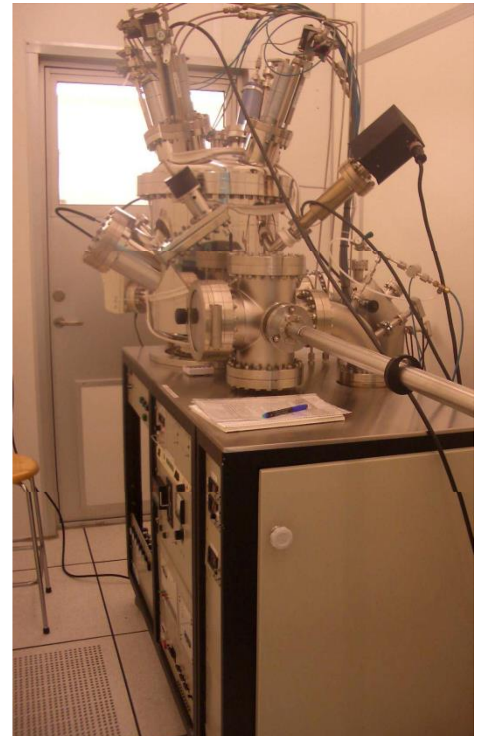




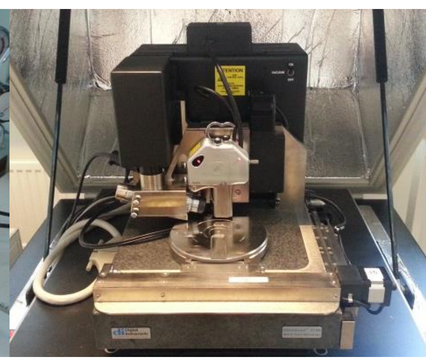
Ø < 5 nm



Research Facilities available for current research

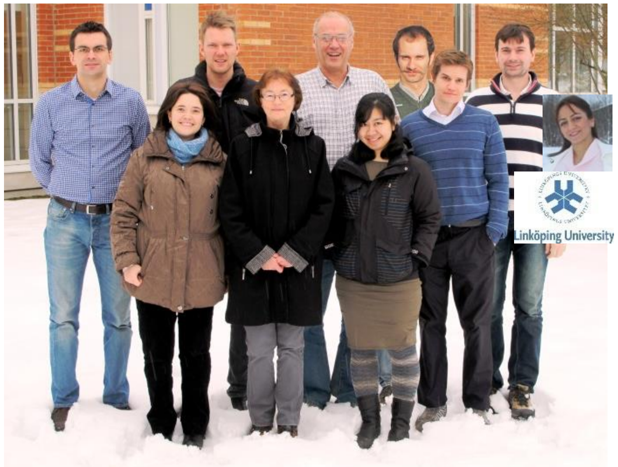


- Clean room, ISO 6 (magnetron sputtering, lithography, CVD, etc.)
- Sensor processing and characterization (gas mixing systems, readout electronics, bonding machine, spot welding, scribers, thermal evaporation, shadow masks, optical microscopes, AFM, SEM, etc.)
- Hardware and software for data acquisition and data analysis
- Gas bottles: CH_2O, C_6H_6, CO, NO, NO_2, NH_3, N_2, O_2, synthetic air
- Other facilities available at: Saarland University, SenSiC, GraphenSiC

Acknowledgements

Applied Sensor Science



Special thanks to (in alphabetic order):

Dr. Mike Andersson, associate professor Linköping University and SenSiC

Manuel Bastuck, PhD student Saarland University

Dr. Robert Bjorklund, senior researcher Linköping University

Christian Bur, joint PhD student Saarland University and Linköping University

Dr. Jens Eriksson, assistant professor Linköping University

Joni Huotari, PhD student University Oulu

Prof. Jyrki Lappalainen, University Oulu

Prof. Anita Lloyd Spetz, Action Vice-Chair, Director of FunMat, Linköping University

Peter Möller, tech. engineer and PhD student Linköping University

Dr. Michele Penza, Action Chair, ENEA

Prof. Andreas Schuetze, SENSIndoor coordinator, Saarland University

Prof. Rositsa Yakimova, Linköping University and GraphenSiC

Thank you for your attention!

(Looking forward to see you in Linköping!)