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

COST Action TD1105

Final Meeting at PRAGUE (CZ), 5-7 October 2016

New Sensing Technologies for Air Quality Monitoring

Action Start date: 01/07/2012 - Action End date: 15/11/2016 - EXTENSION: 15/11/2016

A FLEXIBLE PLATFORM FOR EXTREMELY SENSITIVE GAS SENSING: 2D MATERIALS ON SILICON CARBIDE

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EuNetAir

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

Current research activities

- **Two projects funded by the Swedish Foundation for Strategic research:**

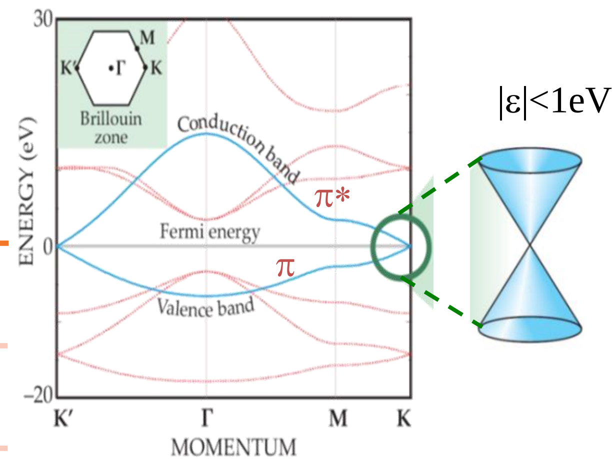
STIFTELSEN för STRATEGISK FORSKNING

  - **“Epitaxial graphene for metrology, sensing, and Electronics”**
  - **“Novel two-dimensional systems: from growth to applications”**

Total budget ≈ 7 M €

Why Graphene chemical sensors?

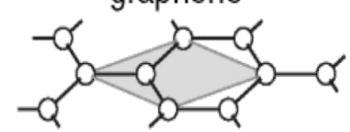
- Low density of states near the Dirac point (E_D) – small changes in the number of charge carriers result in large changes in the electronic state
- Every atom at the surface – ultimate surface to volume ratio
- Low mass, low noise
- **Has potential as a low noise, ultra-sensitive transducer.**



- **100.000** premature annual deaths in Europe due to household pollution

People spend more than 85% of time indoor → Prolonged exposure
Threshold for health effects lower

graphene



Potential applications where ultra-high sensitivity is required:	**Air quality: Monitoring of highly toxic gases in normal living environments (indoor and outdoor)**
	VOCs (formaldehyde, benzene, naphthalene…)
	NOx, Ozone
	Liquid phase: Early detection of disease biomarkers, biological threats

The research involves four research groups* at Linköping University and the company Graphensic AB

*Applied Sensor Science, Semiconductor Materials, Plasma & Coating Physics, Molecular Surface Physics and Nano Science

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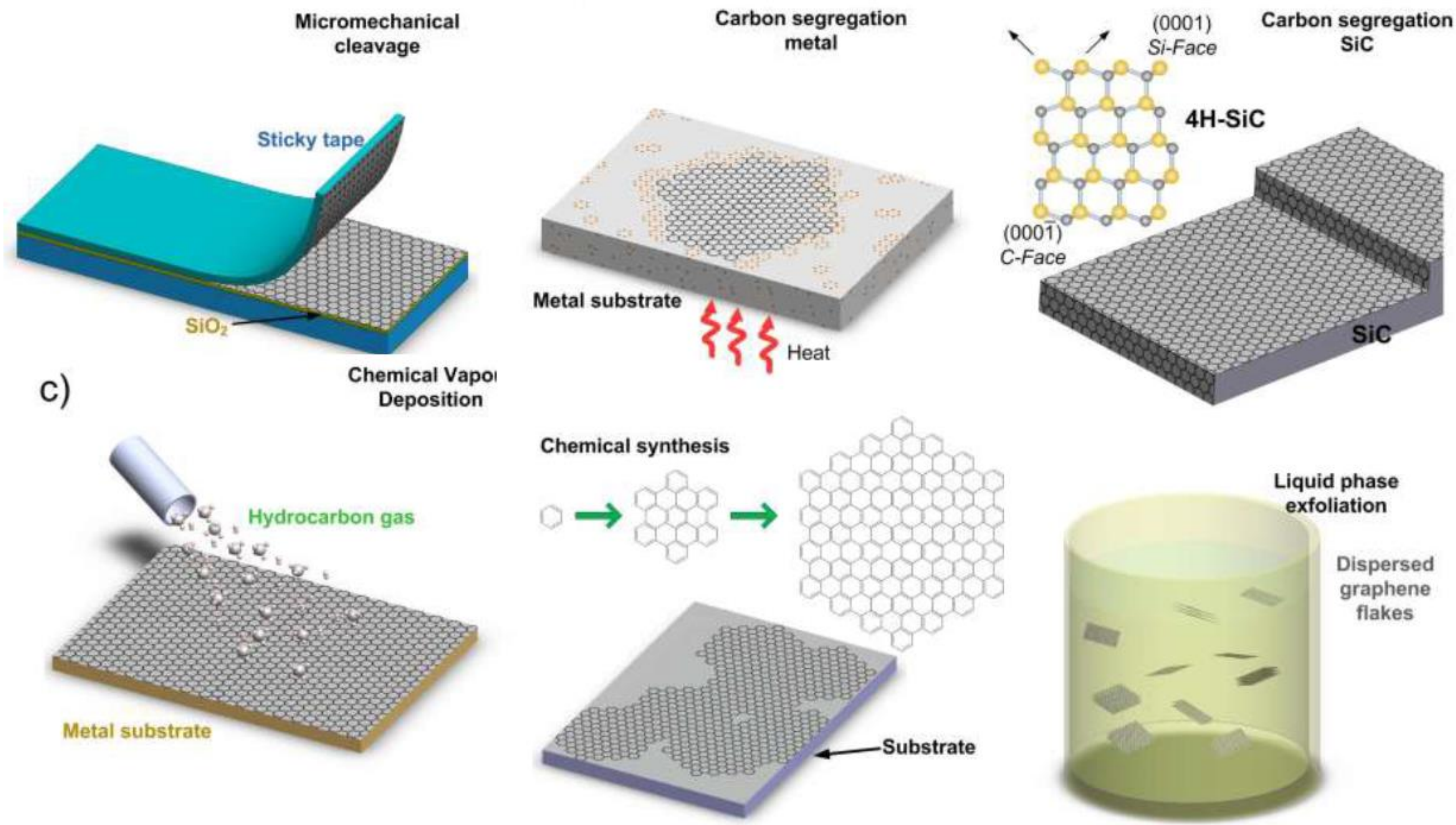
Graphene production

Graphene chemical sensors normally highly sensitive, but suffer from poor reproducibility and selectivity

Reproducibility is an issue that partly arises from the graphene synthesis



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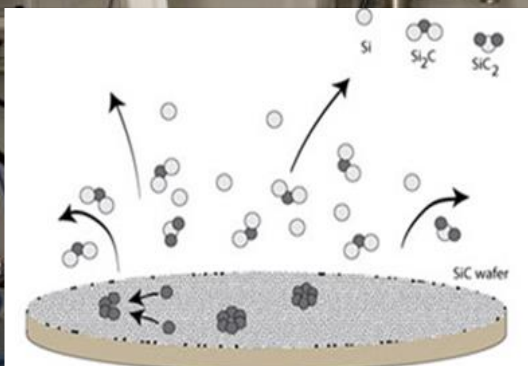
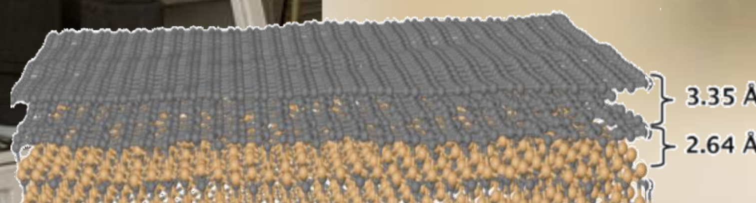
manufactures and supplies

Graphene on SiC





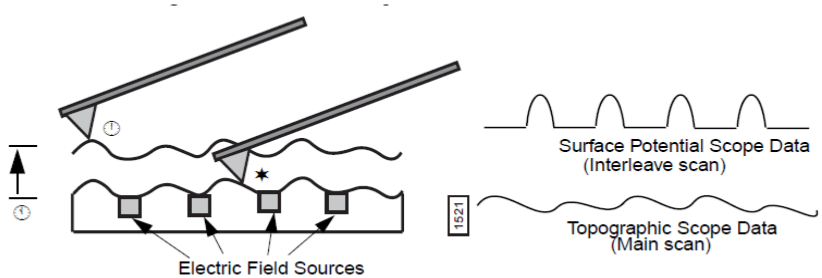
- Sublimation of Si from SiC in Ar at 2000ºC
- Scalable, wafer-scale films compatible with standard semiconductor processing
- High thickness uniformity (98-99% ML, rest 2 ML)
- Thickness controlled by temperature

Spin off from Linköping University, Sweden

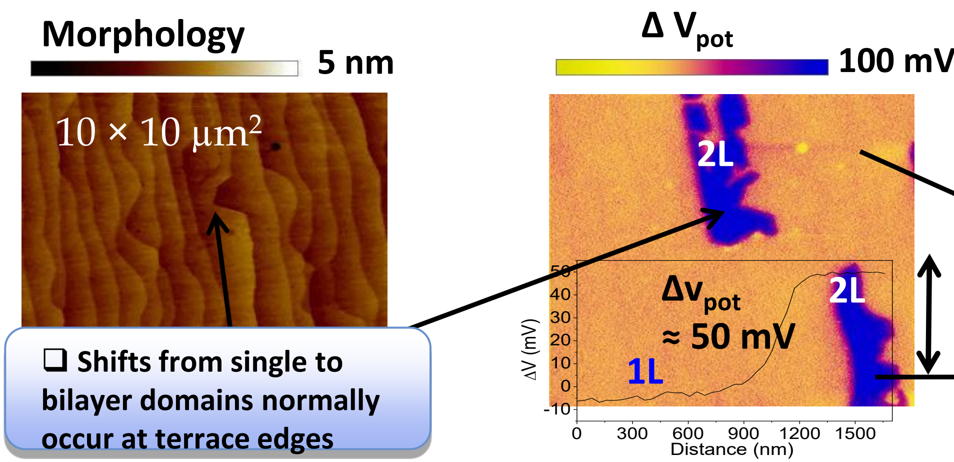
22.11.2011

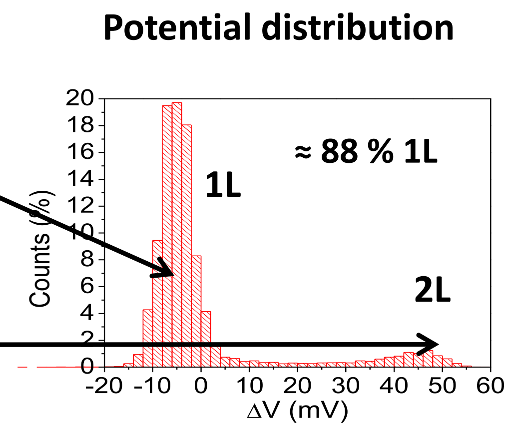
Sensing, single or double layer graphene?

Scanning Kelvin probe microscopy - Nanoscale mapping of graphene thickness uniformity and doping



- Topography is mapped in 1st pass
- Surface Potential is mapped in 2nd pass
- Maps change in work function



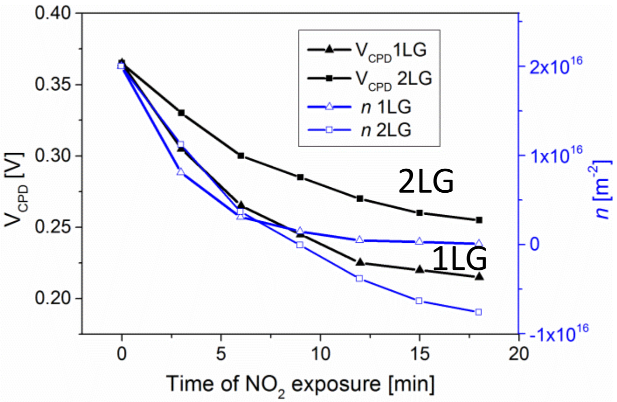


- **$\Delta\Phi$ between 1LG and 2LG allows nanoscale mapping of graphene thickness**
- **Controllable environment allows observing changes in 1LG and 2LG upon gas interaction**

Eriksson et al.,Applied Physics Letters 100 (2012) 24160

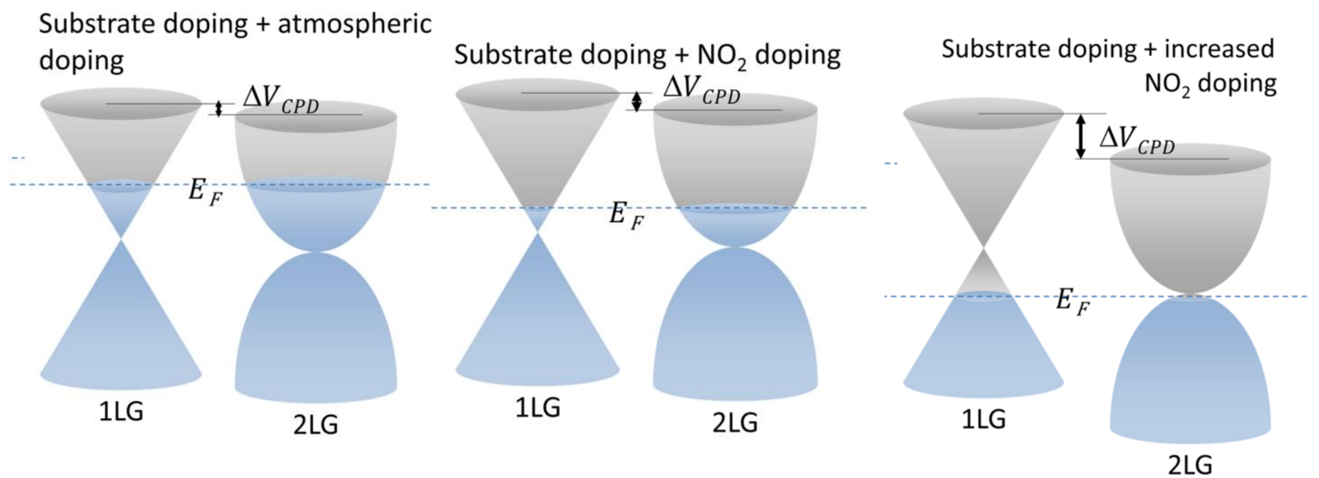
Different sensitivity for 1LG and 2LG

Response to < 1 ppm NO_2 vs. time



Different energy dispersions

- Linear for 1LG
- Parabolic for 2LG



From 1-2L ΔV_{CPD}: Non-invasive estimation of carrier concentration

$$(1) \qquad \Delta n \text{ 1LG} = \frac{2e\,\partial V_{CPD}\sqrt{n}}{\hbar\,\upsilon_F\sqrt{\pi}} - \frac{(e\,\partial V_{CPD})^2}{\hbar^2\,\upsilon_F{}^2\pi}$$

$$(2) \qquad \Delta n \text{ 2LG} = \frac{\delta V_{CPD}\,e\,2m^*}{\hbar^2\pi}$$

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

- Calculated change in carrier concentration not the same for 1 and 2LG
- Different responsivity for 1 and 2LG doesn't account for all difference in sensitivity
- Different sticking coefficients also important

Uniform 1LG leads to reproducible ultra-sensitive sensors

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

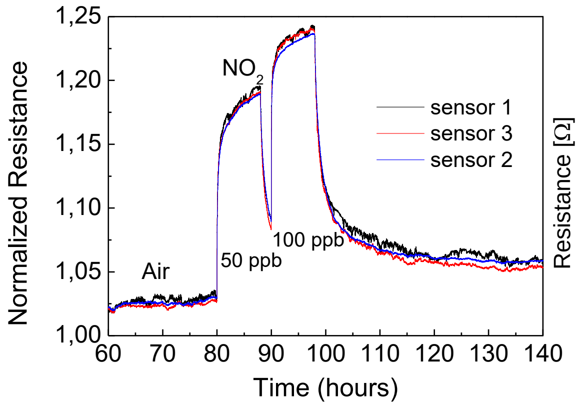
Uniform 1LG required for maximum sensitivity and reproducibility

Different sensors fabricated on 100% 1LG show identical response

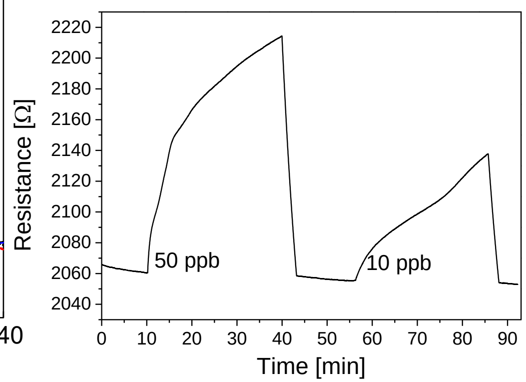
Epitaxial graphene on SiC enables **highly reproducible** sensor fabrication

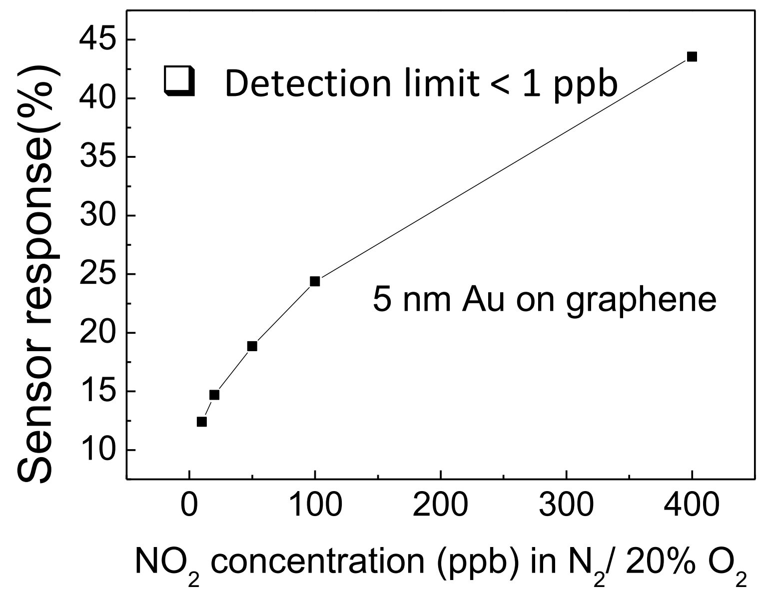
NO_2 response

Reproducibility



Fast recovery by UV-LED





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

NO_2 sensing interesting for:

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

Air Qality: limit levels for NO_2

- Hourly average < 100 ppb
- Yearly average < 20 ppb

cost
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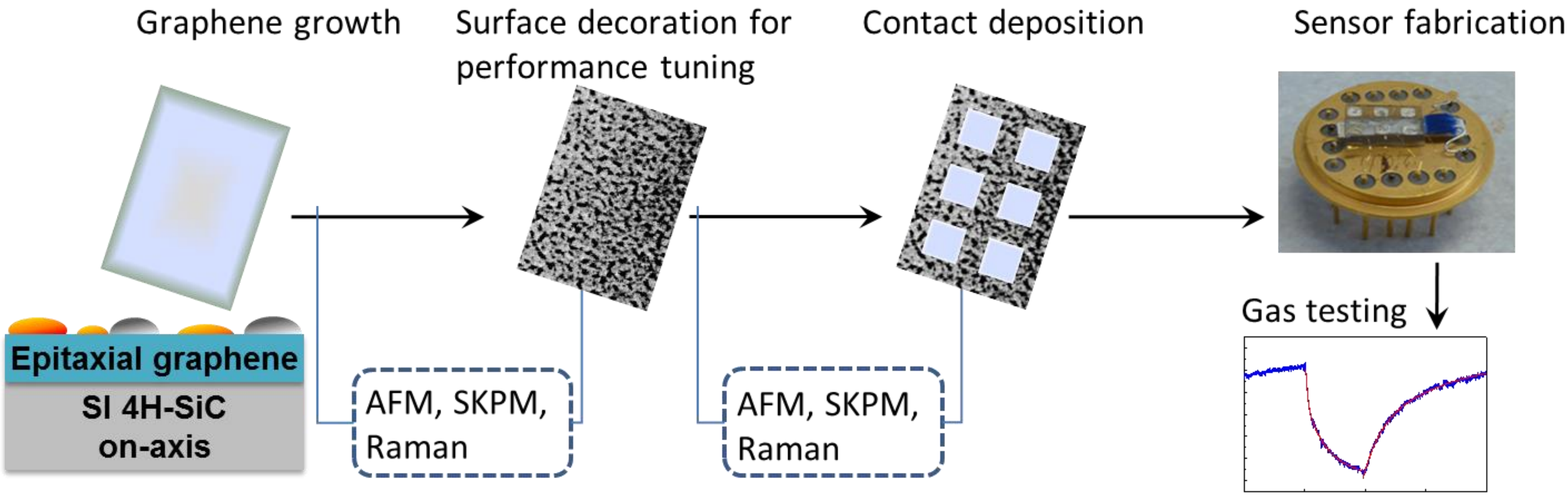
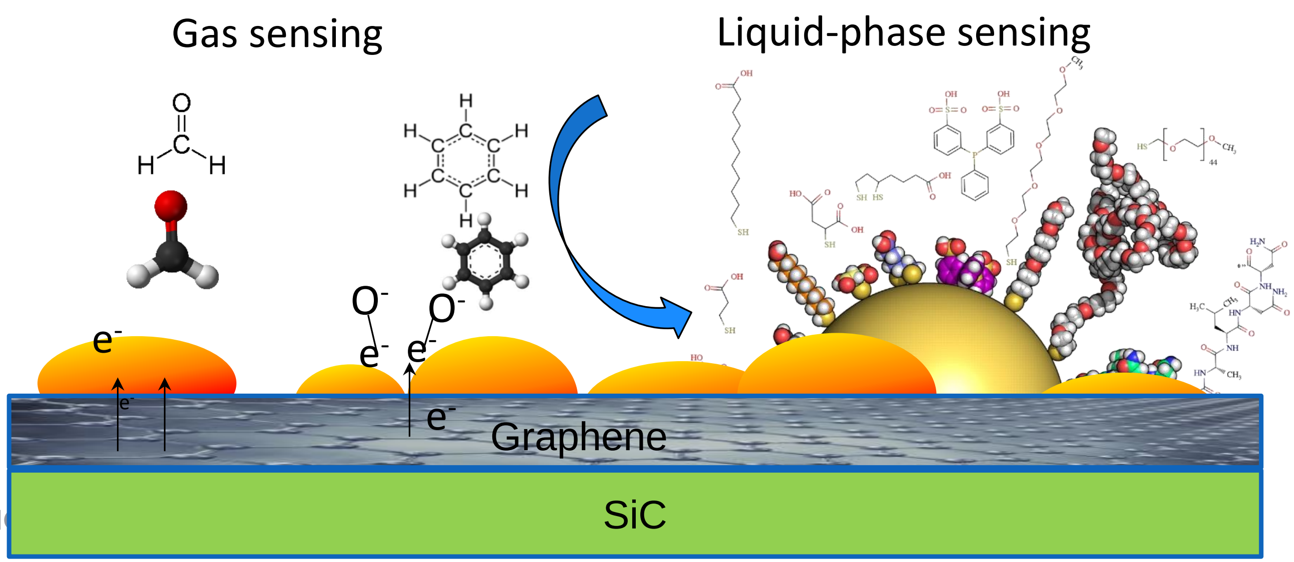
Functionalization with metal and metal oxide nanostructures for selectivity tuning

- **Obstacles: (sensitivity), reproducibility, selectivity, response/recovery time**



Aim:

- ❑ Selectivity/sensitivity tuning
- ❑ Develop a method for functionalization with nano structures that is:
  - Reproducible
  - Scalable
  - Low-cost



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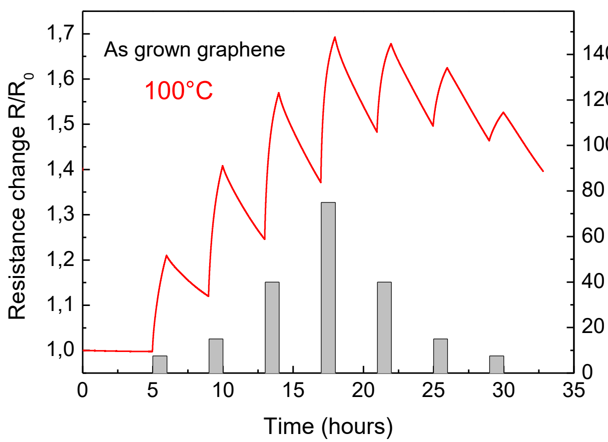
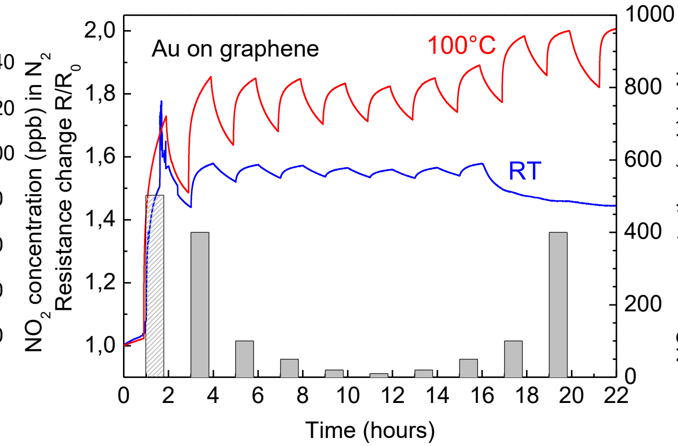
Effect of decoration on sensor response

As-grown graphene

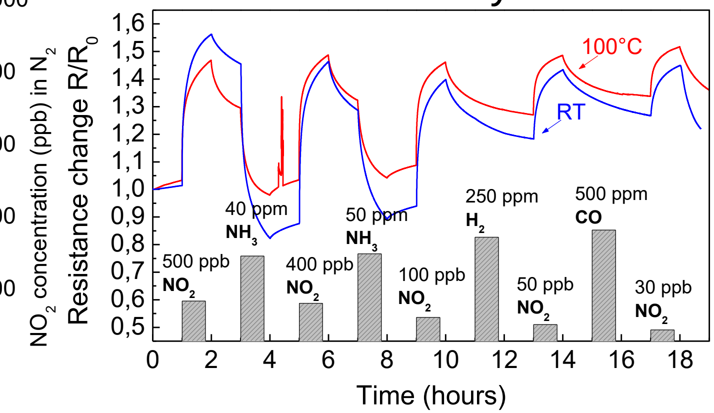
Au decorated graphene

Response to ppb concentrations of NO_2





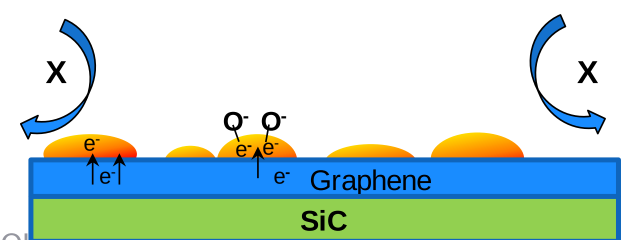
Selectivity



❑ **Effects of metallization:**

- **Improved speed of response**
- **Improved detection limit (< 1 ppb)**
- **More stable base line**
- **Suppressed response to H_2/CO while maintaining NO_2 response (Au < 5 nm)**

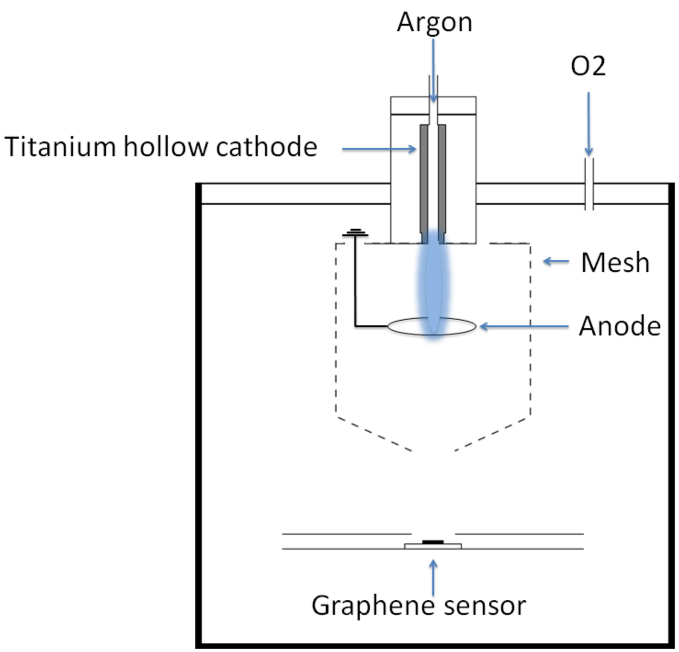
Response %	Response Time (min), 50 ppb NO_2			Recovery Time (min)		
	As-grown	Au, 5 nm	Pt, 2 nm	As-grown	Au, 5 nm	Pt, 2 nm
30%	6	1.5	2	315	15	15
60%	23	9	10	830	45	50
90%	99	74	41	2130	135	175

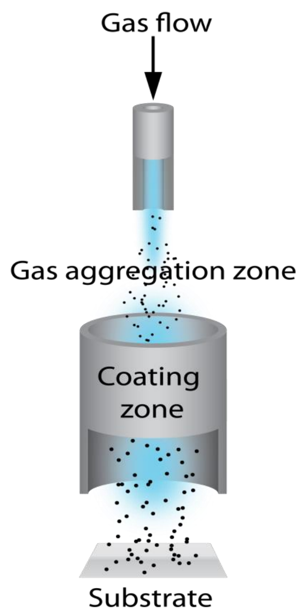


J. Eriksson, D. Puglisi, Y. H. Kang, R. Yakimova, A. Lloyd Spetz , Physica B 439, 105–108 (2014)

Designed Nanoparticles by Pulsed Plasma Hollow Cathode Sputtering

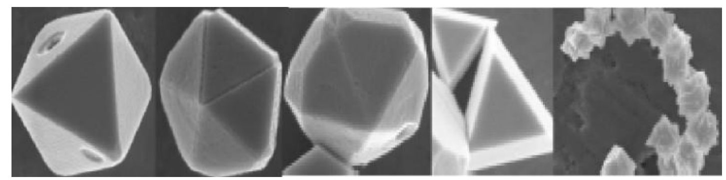
It is expected that decoration with different metals or metal-oxide nanostructures will allow careful targeting of selectivity to specific molecules





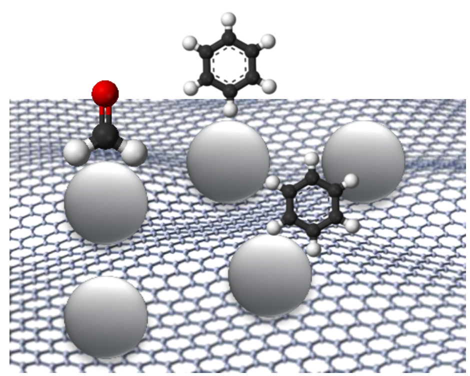
R. Gunnarsson, P&CP, IFM, LiU

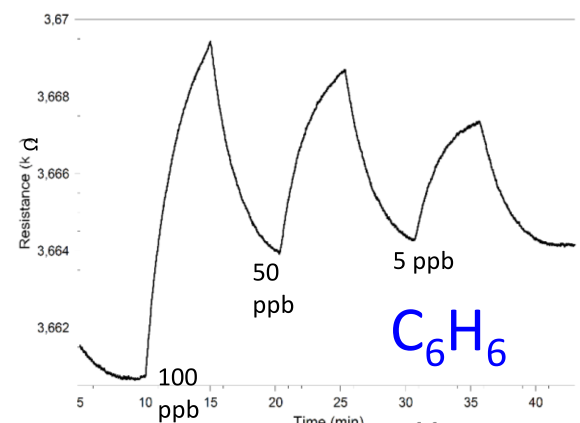
- ❑ Reproducible deposition technique
- ❑ Scalable
- ❑ Expanded range of materials, dimensions, dispersion



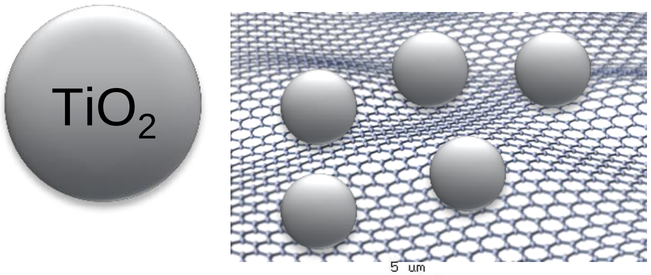
Ø > 50 nm

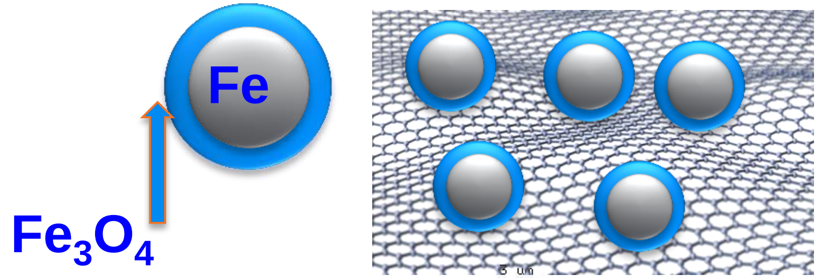
- ❑ Utilize MOx sensitivity and selectivity, with EG as ultra-sensitive transducer
- ❑ TiO_2 and Fe_3O_4 NPs for enhanced sensitivity towards formaldehyde and benzene

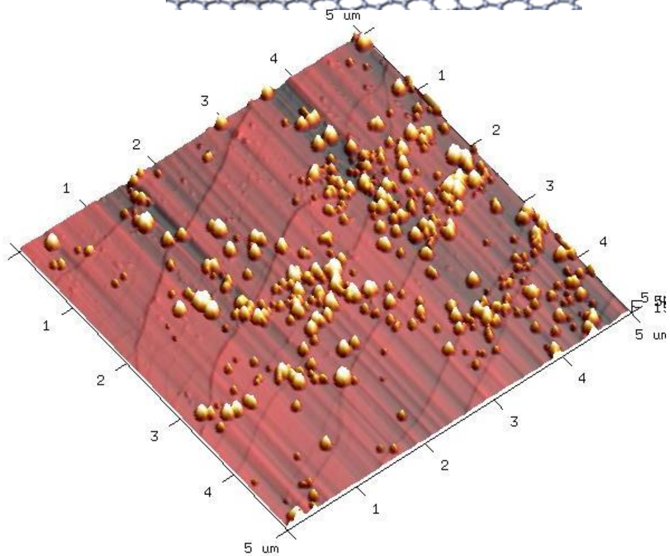


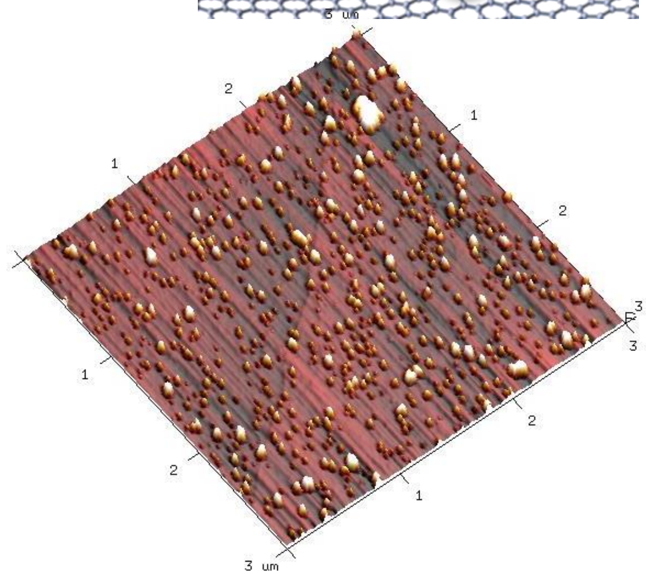


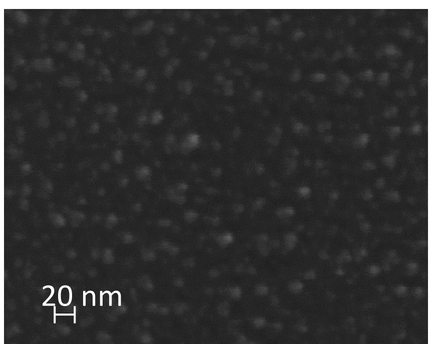
Designed Nanoparticles by Pulsed Plasma Hollow Cathode Sputtering

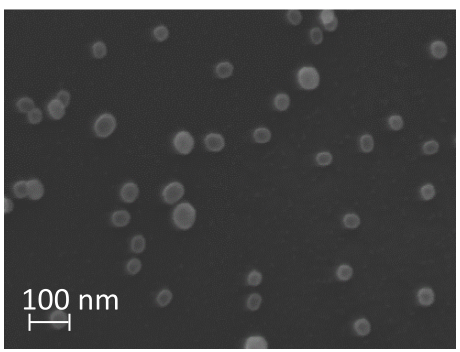






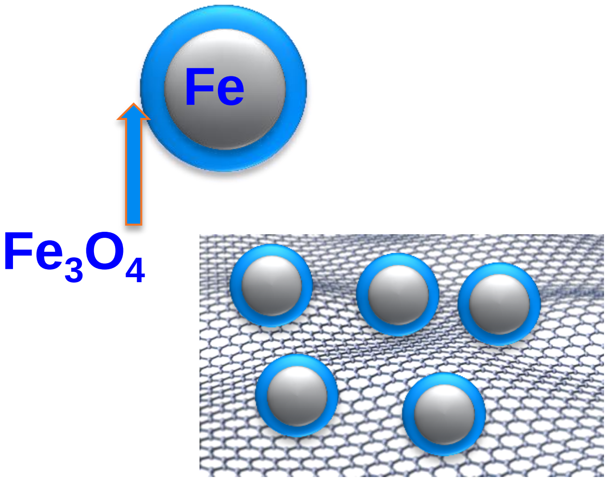






- ❑ Deposition can be inhomogeneous
- ❑ Deposition does not follow steps or other morphological features
- ❑ Size and dispersion can be controlled during growth

XPS: Fe_3O_4 core-shell decorated graphene

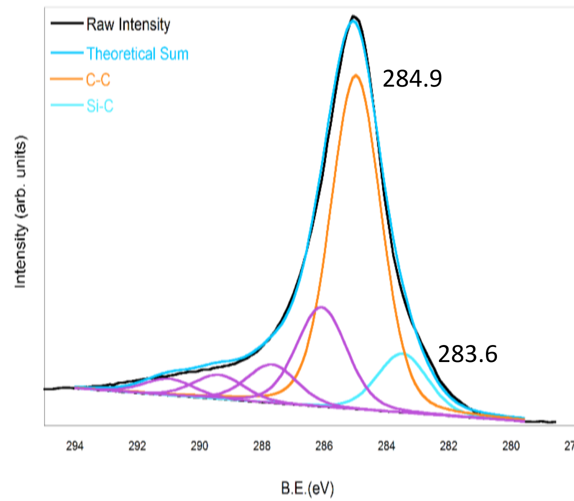


Graphene is intact

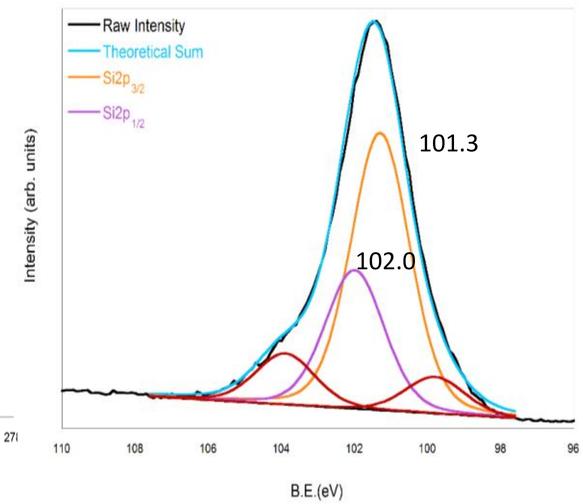
Fe, O present on the surface

As-grown Graphene

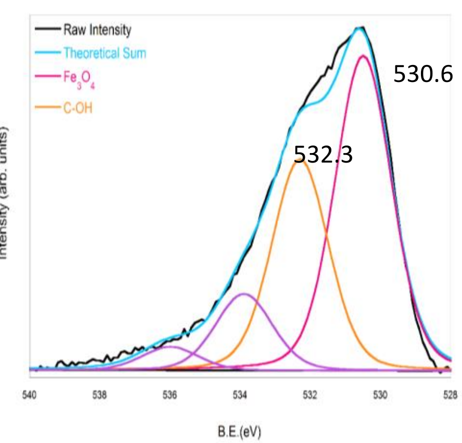
C1s



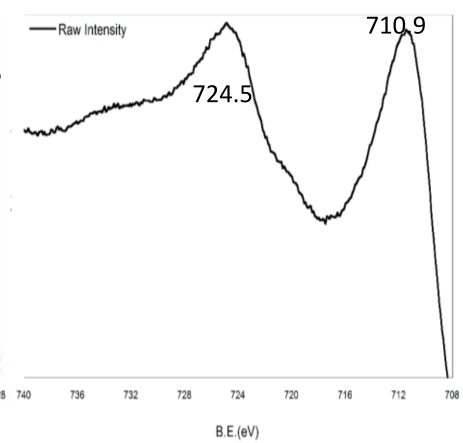
Si2p



O1s

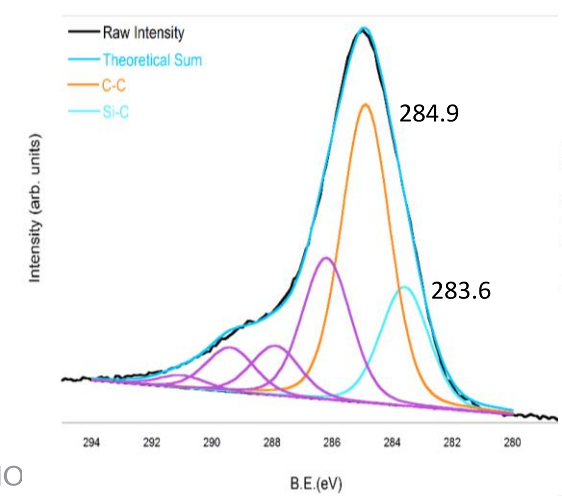


Fe2p

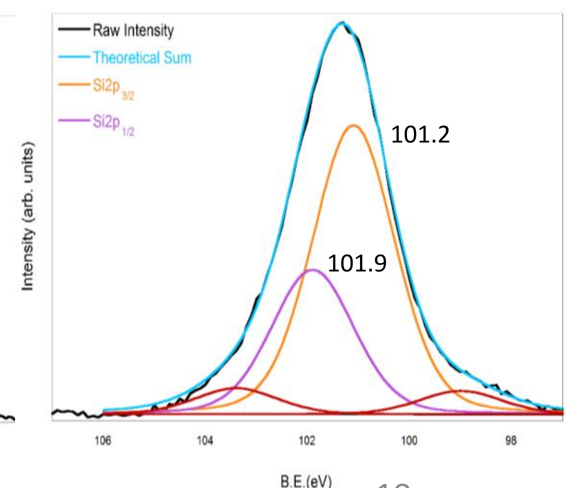


Graphene + Fe_3O_4

C1s

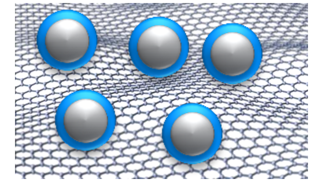


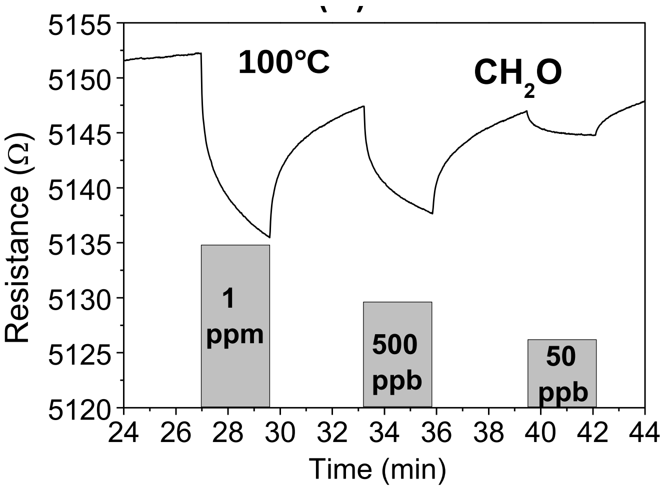
Si2p

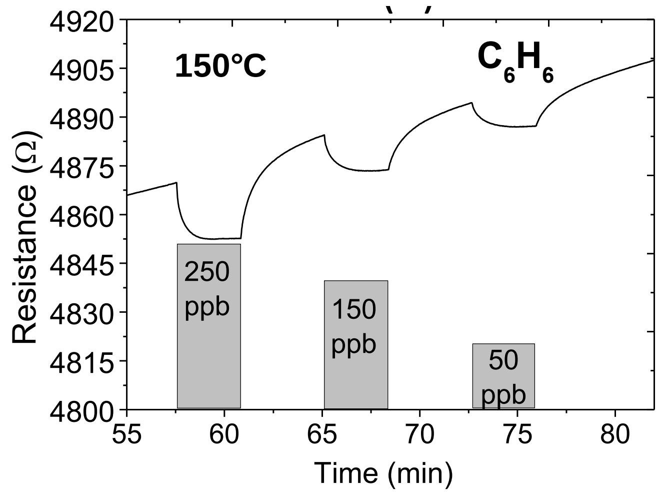


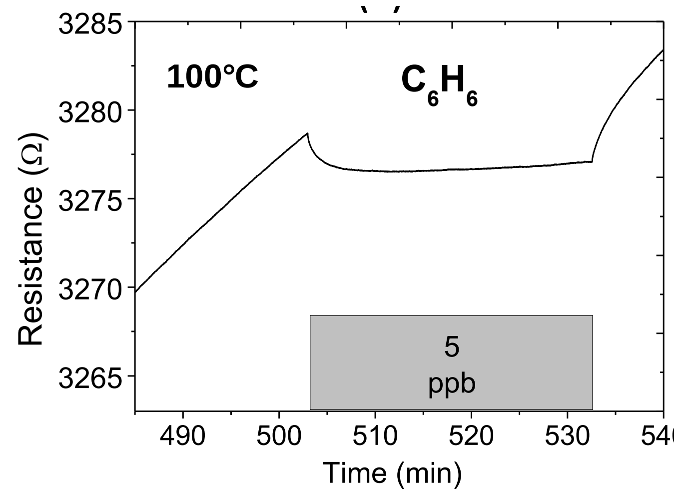
Sensor response to formaldehyde and benzene

Fe_3O_4 core-shell, low surface coverage

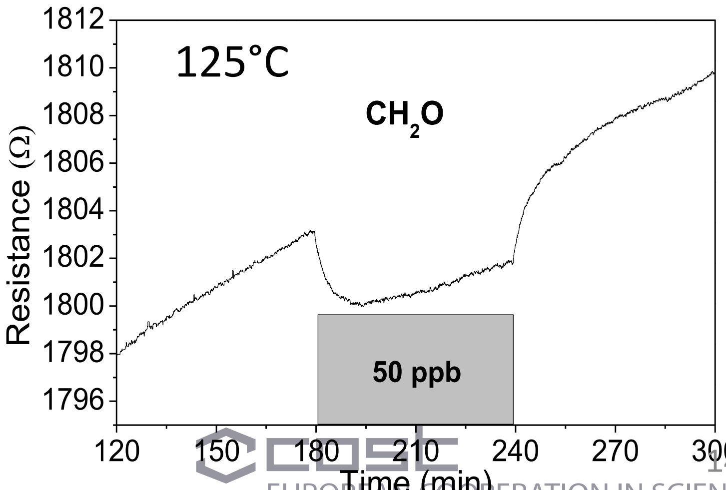


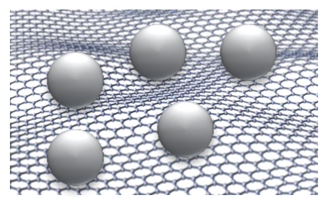




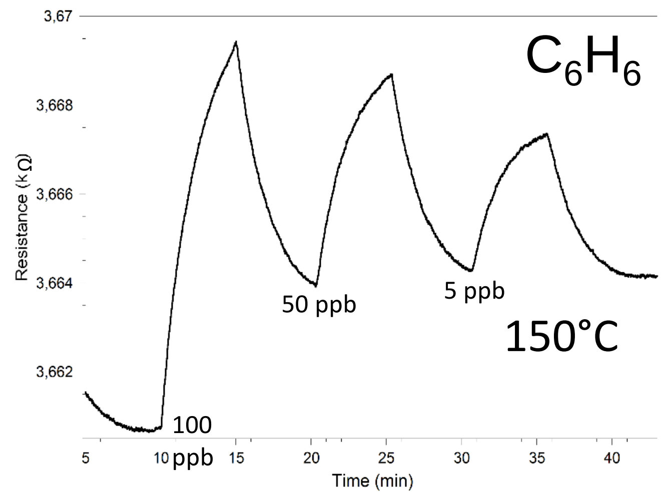


TiO_2, Φ < 10 nm, low coverage





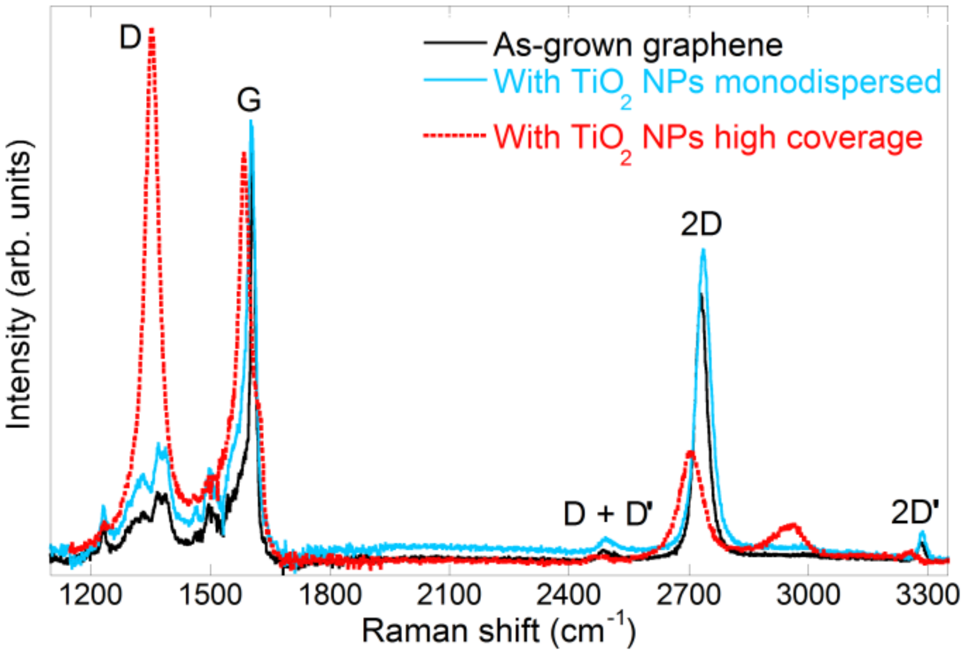
TiO_2, Φ > 50 nm, high(er) surface coverage

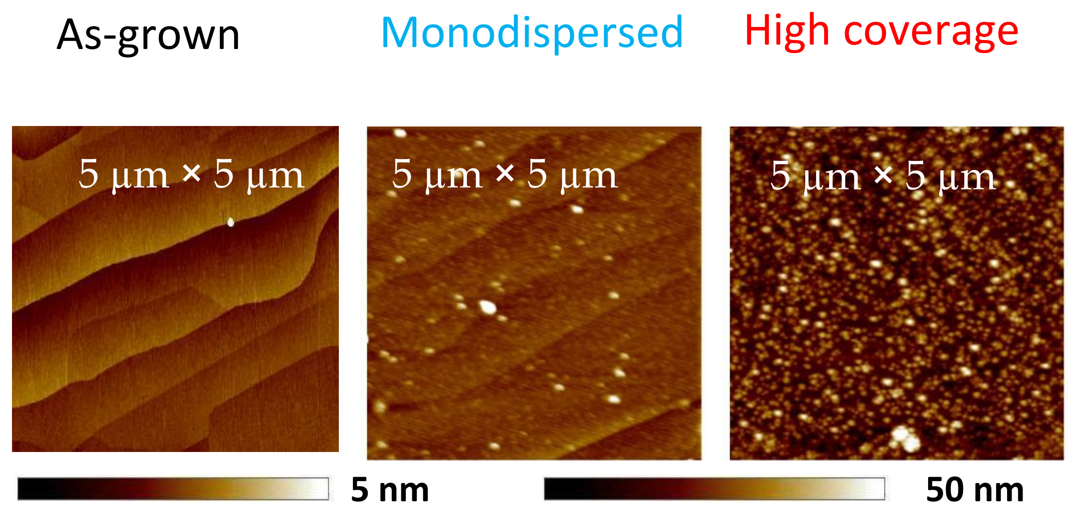


J. Eriksson, D. Puglisi, et al., Materials Science Forum, 858, 1145-1148 (2016)

Micro-Raman and AFM analysis

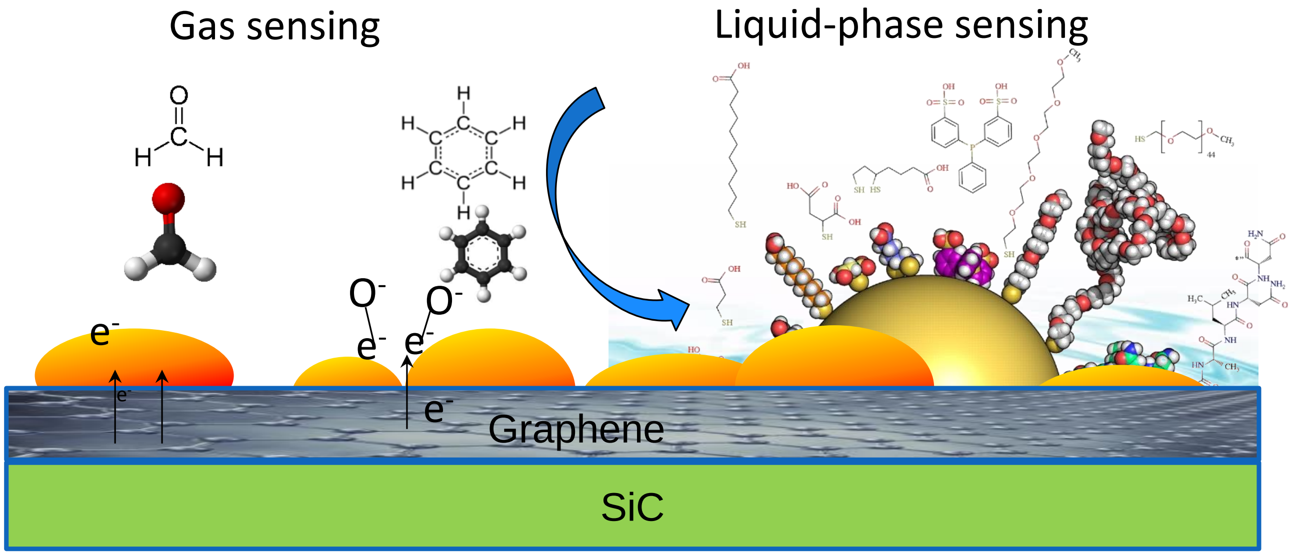
TiO_2



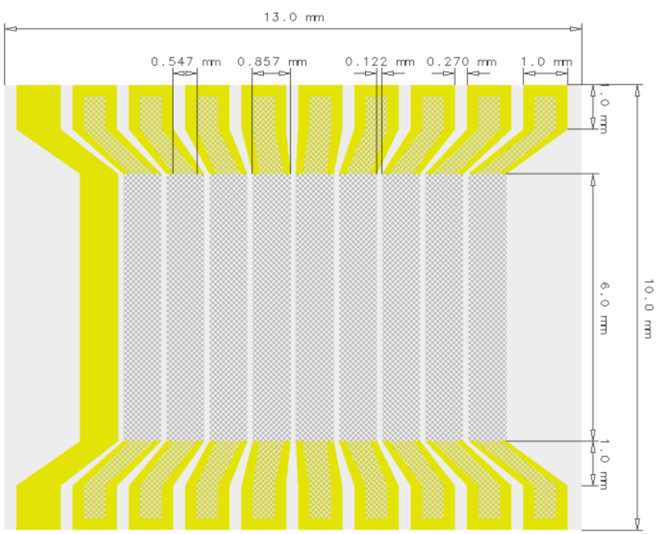


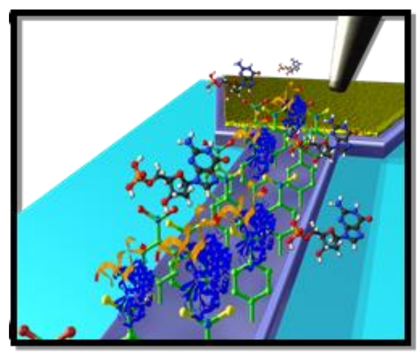
Effects of decoration	Monodispersed: Shape of characteristic peaks unaffected. G peak blue-shifted -> p-type doping
	High surface coverage: Structural damage

Epitaxial Graphene sensor platform



Graphensic Vision: Biosensor platform with "performance" like a physician





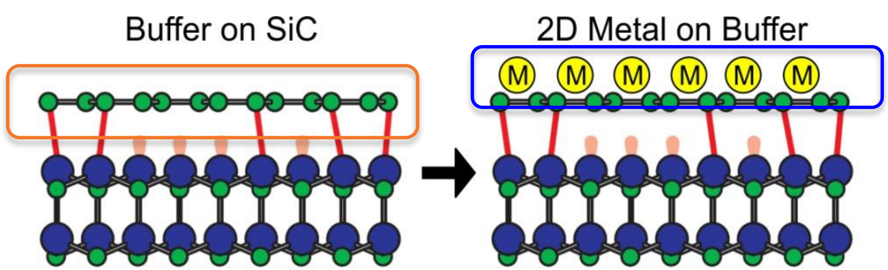
graphensic

2D Materials Beyond Graphene: 2D Pt

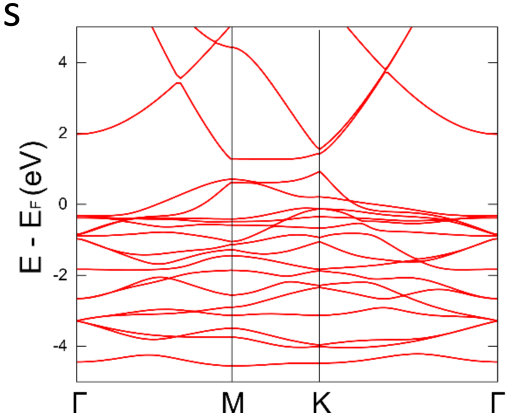
❑ The technology of epitaxial growth of graphene on SiC that was **pioneered at LiU** offers a possibility to develop novel 2D systems beyond graphene

❑ Specially reconstructed SiC surfaces offer unique possibility to arrange metallic materials (e.g. Pt, Pd) on the SiC surface

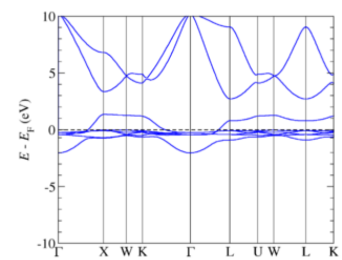
❑ Macroscopic, electrically-continuous 2D metals



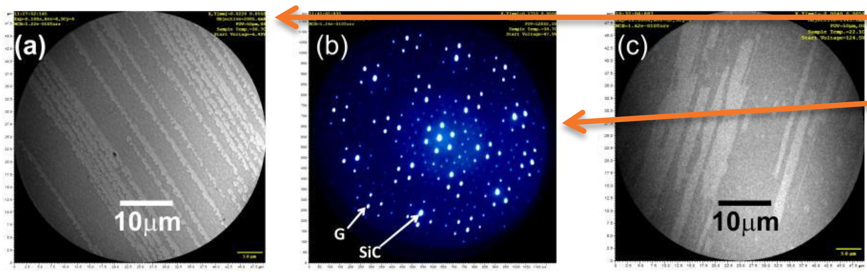
DFT: band structure of monolayer Pt



Bulk Pt



SiC Buffer **SiC Buffer + Pt**



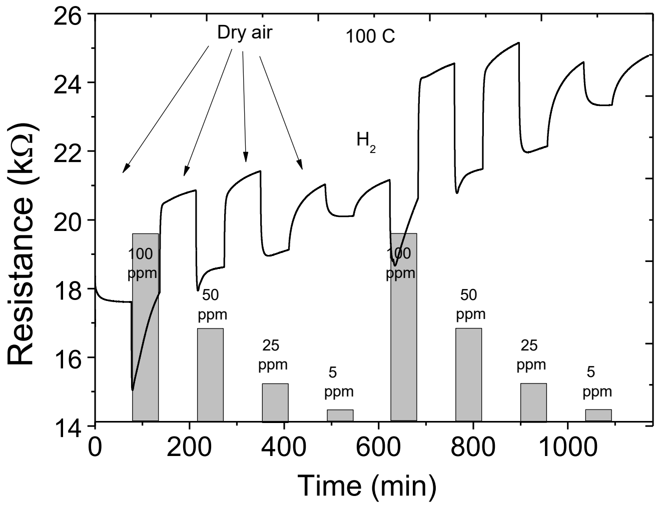
SiC +C (6√3×6√3)R30◦ **2D Pt**

LEEM (Low Energy Electron Microscopy)
μLEED (Low-energy electron diffraction)
XPEEM (X-ray Photo Emission Electron Microscopy)

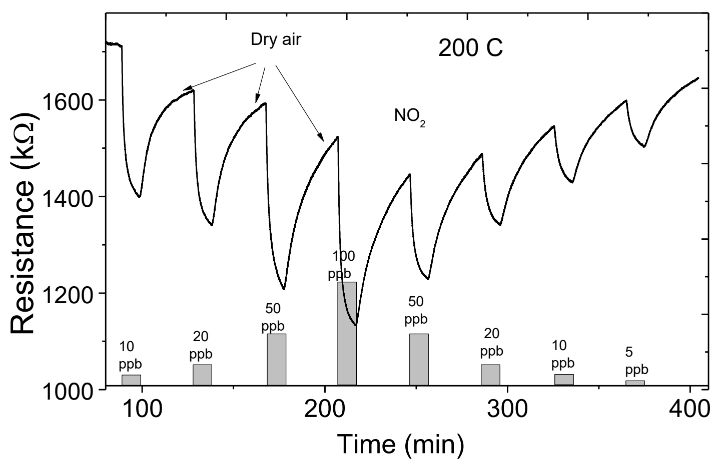
Novel two-dimensional systems to be explored for nano-electronics, catalysis and sensing

2D Materials Beyond Graphene: 2D Pt Sensors

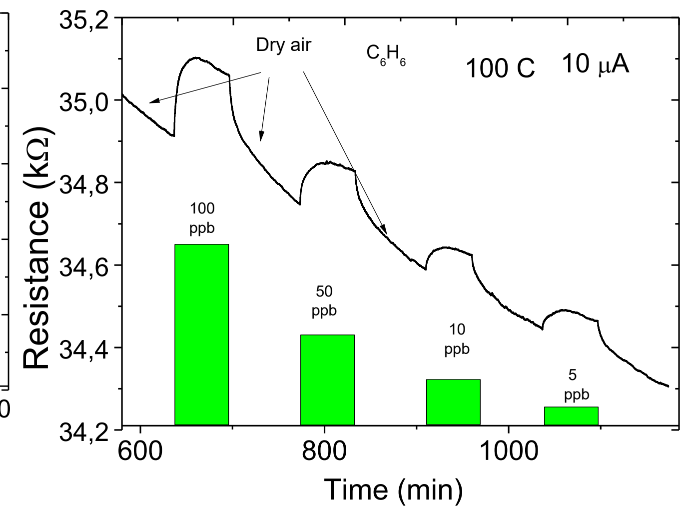
H_2



NO_2



C_6H_6

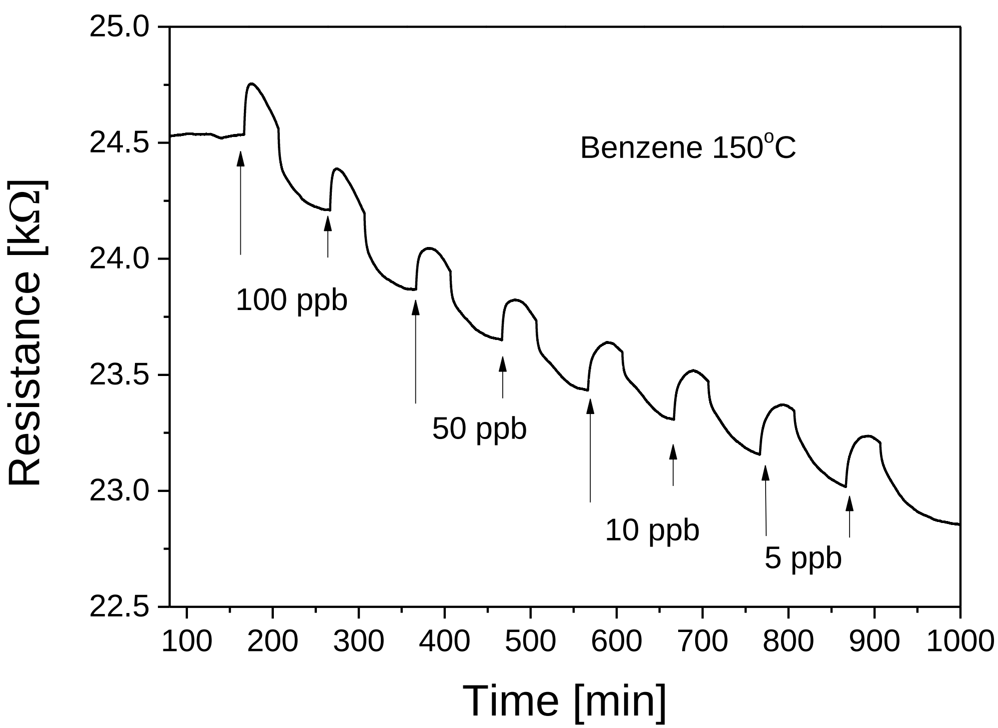


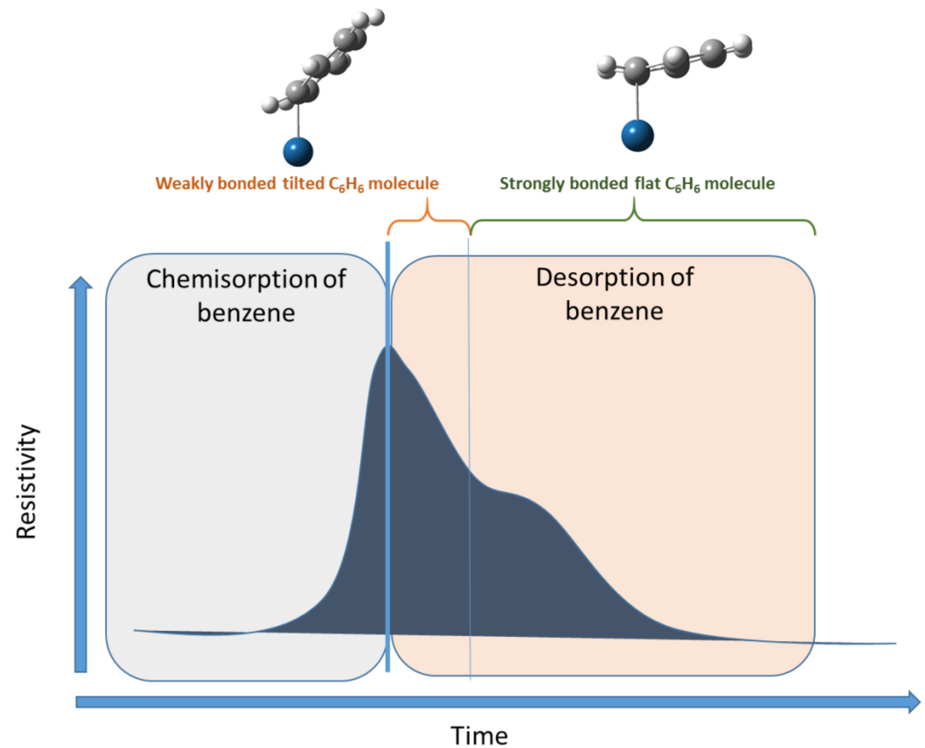
2D Pt on SiC shows promise in terms of higher temperature stability compared to graphene, while maintaining the extreme sensitivity inherent to 2D materials.

- ❑ **Strong and fast response to H_2**
- ❑ **NO_2 – Detection limit good, faster than graphene sensors**
- ❑ **Benzene – low ppb**
- ❑ **Sensitivity, stability, selectivity depend on operating voltage/current**

2D Pt Sensors, ideas from the EuNetAir participants?

Benzene @ 150°C

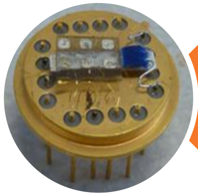




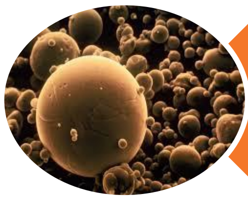
How to explain this two-step response?

DFT calculations show at least two different C_6H_6 configurations

Conclusion/Outlook

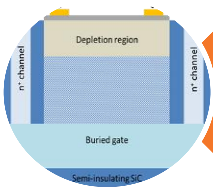


Sensing with epitaxial graphene – promising, ppb level NO_2, CH_2O, and C_6H_6 detection



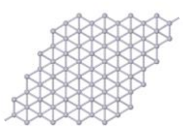
Decoration with Au, Pt, TiO_2, Fe_3O_4 core-shell NPs can result in improved selectivity, sensitivity, stability, and speed

- The effect depends on the material, thickness, and nanostructure of the decoration



GFET sensor development and optimization for most sensitive gas detection

Selectivity: Smart operation



Novel two-dimensional systems to be explored for nano-electronics, catalysis and sensing

FLAG-ERA JTC 2017 call this fall

- Chemical sensors in graphene and related materials

Thanks for your attention!