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COST Action TD1105

2nd International Workshop *EuNetAir* on

New Sensing Technologies for Indoor and Outdoor Air Quality Control

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An account of our efforts towards air quality monitoring in epitaxial graphene on SiC

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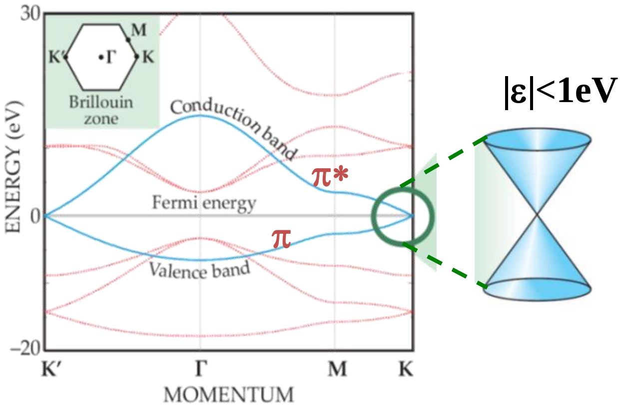
Outline

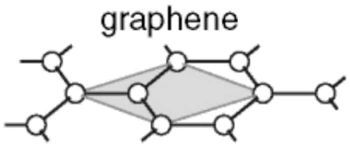
- Why graphene sensors?
- Epitaxial graphene on SiC
- Effect of graphene layer thickness on gas sensitivity and selectivity
- Understanding unintentional doping in epitaxial graphene
- Controlling graphene layer uniformity
- Tuning sensor properties by surface modifications

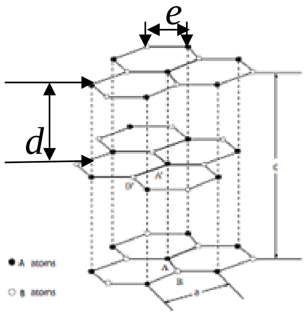
Why Graphene sensors?

- **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 results 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)**



❑ 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.





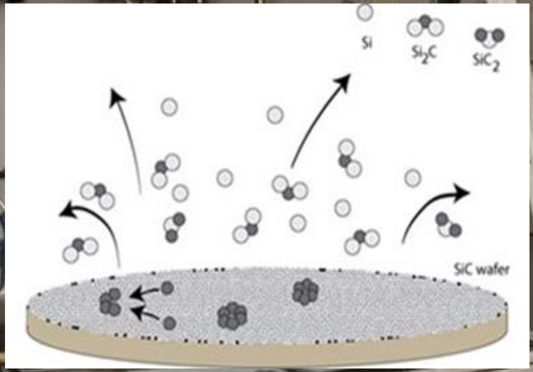
Graphene sensors are normally highly sensitive, but suffer from poor reproducibility, selectivity, and speed of response....

Reproducibility is an issue that partly arises from the graphene synthesis

Graphensic

manufactures and supplies

Graphene on SiC



- Sublimation of Si from SiC in Ar at 2000°C
- Scalable, wafer-scale films compatible with standard semiconductor processing
- High thickness uniformity (> 90% ML, rest 2 ML)
- Thickness controlled by temperature

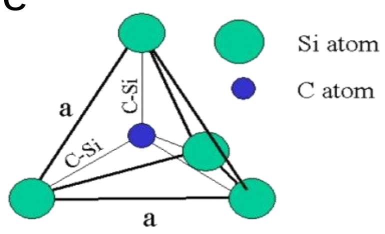
Spin off from Linköping University, Sweden

22.11.2011

Silicon carbide

Ceramic

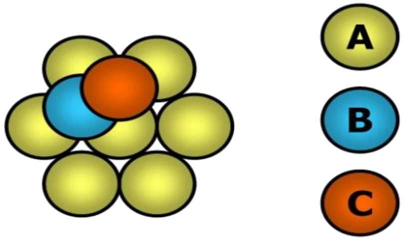
- ☐ High chemical inertness
  - Oxidation resistant
  - Stable at high temperature
- ☐ Hardness
- ☐ Melting point ~ 2700°C
- ☐ Light-weight



Semiconductor

- ☐ Wide band gap
- ☐ High electron drift velocity
- ☐ High breakdown field
- ☐ High thermal conductivity

Polytypism: > 200 chemically identical polytypes

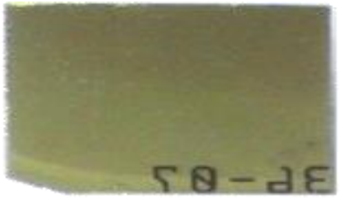


6H-SiC

E_g = 3.0 eV

3C-SiC

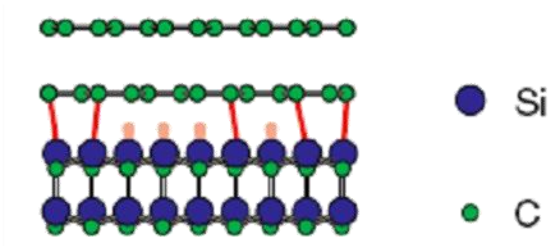
E_g = 2.4 eV



4H-SiC

E_g = 3.2 eV

Graphene production



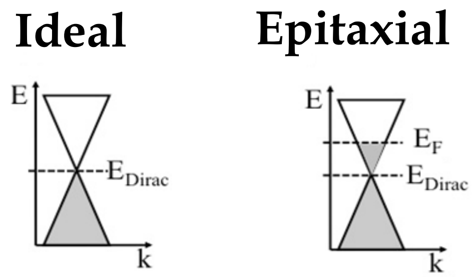
C. Riedl et al. PRL 103 (2009)

- Graphene layers sit on a buffer or interfacial layer
- The buffer layer is covalently bound to the underlying SiC
- Electronic coupling between SiC and graphene

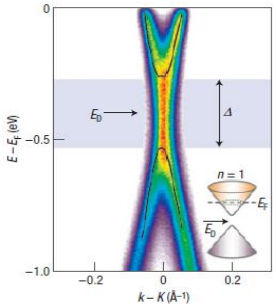
- Graphene on SiC has E_F pinned above the Dirac point
  - Causes electron doping!

Hall measurements show that our graphene has Ns ≈ 10^{12} cm^{-2}

A. Tzalenchuk, et al, Nat Nano, 5, 186-189, (2010)



S. Sonde et al., Physical Review B 80, 241406 (R) (2009)



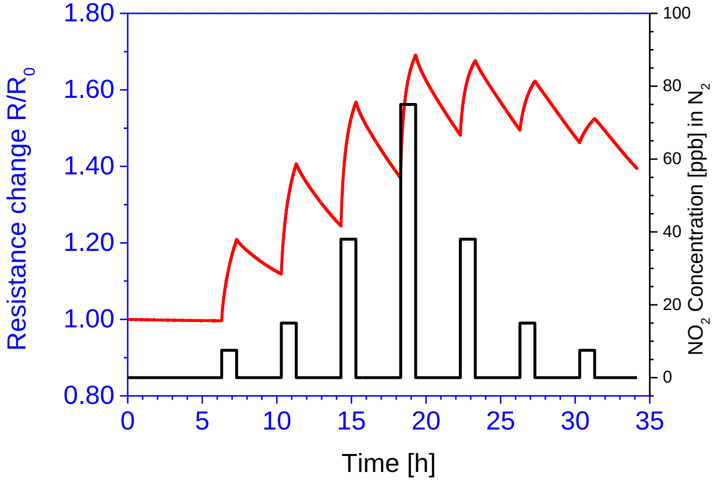
ARPES: E_F 0.4 eV above E_D

S. Y. Zhou, et al., Nat. Mater. ***6****, 770 (2007)*

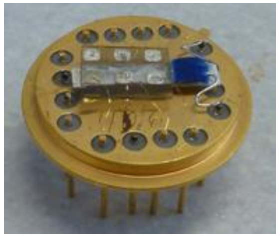
Sensor response to environmental gating

NO_2 strongly electron withdrawing

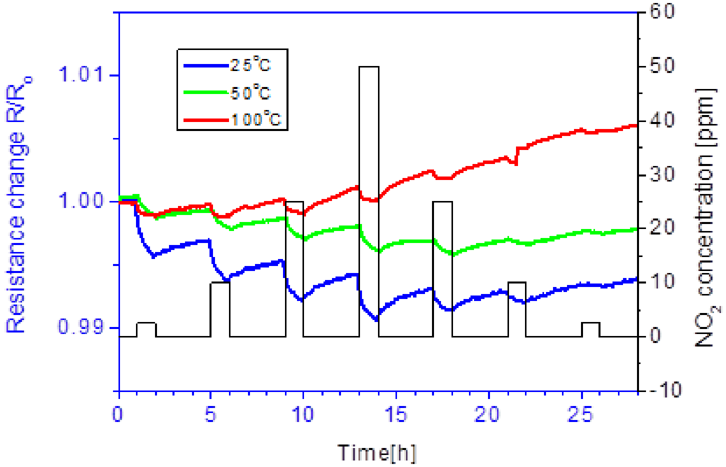
Single layer



Large n-type response to ppb concentration NO_2



Multi layer



Small p-type response to ppm concentration NO_2

Why is single layer more sensitive?

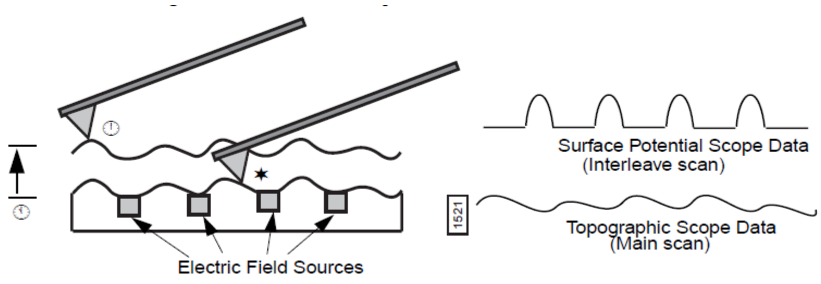
- Current flow through all layers gas adsorption only on top layer
- Different band structure leads to different responsivity; change resistivity with carrier density
- Or difference in sticking coefficients of gases on single and multi layer graphene

*R. Pearce et al. Sens. and actuators B. Chem. , **155**(2): 451-455, 2011*

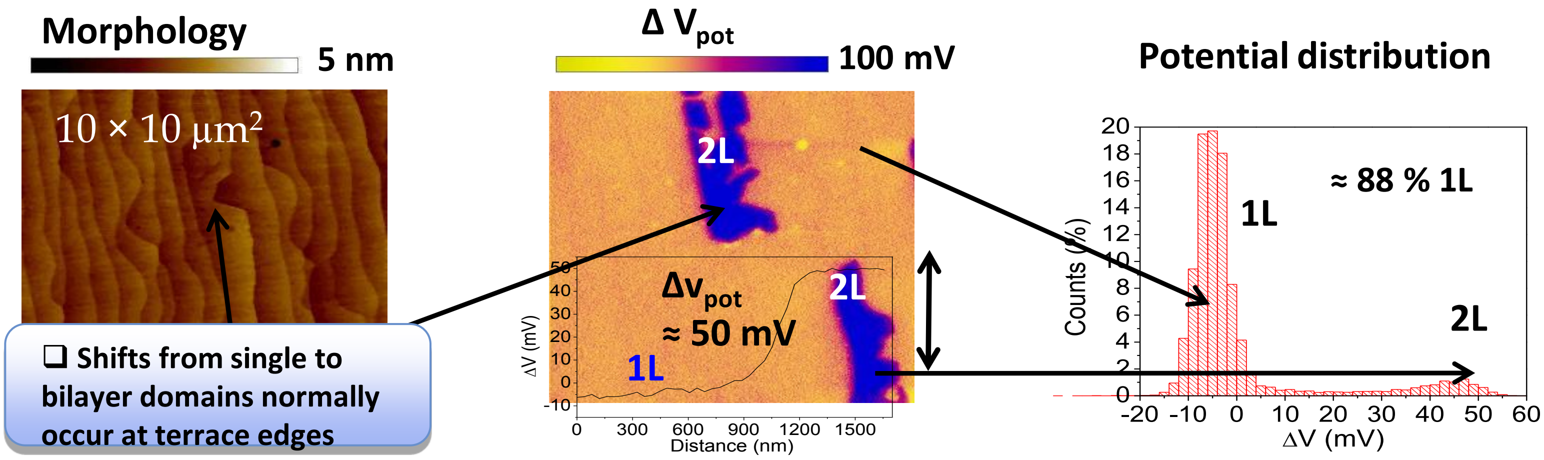
NO_2 sensing, single or double layer graphene?

Scanning Kelvin probe microscopy – work function mapping

Nanoscale mapping of graphene thickness uniformity and doping



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

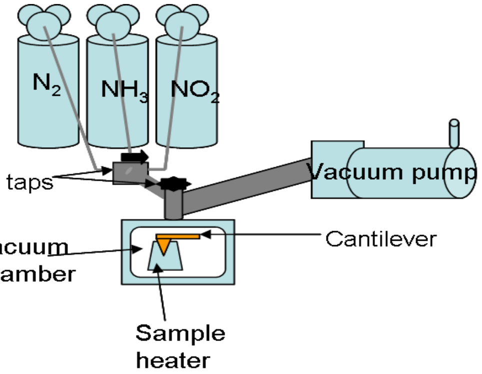


❑ Shifts from single to bilayer domains normally occur at terrace edges

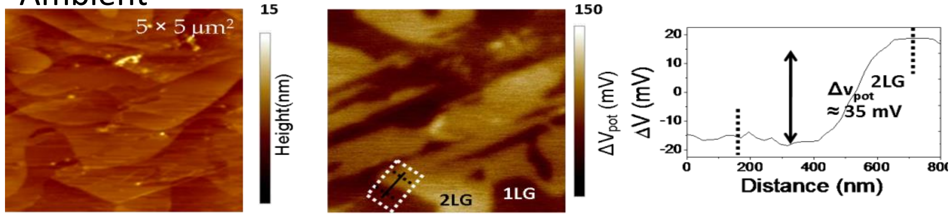
- **ΔΦ between 1LG and 2LG allows nanoscale mapping of graphene thickness**
- **Controllable environment allows observing changes in 1LG and 2LG upon gas interaction**

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

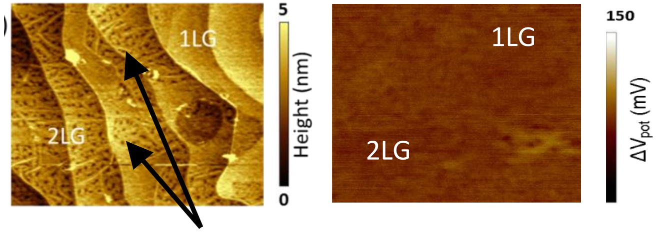
SKPM in controlled environment



Ambient

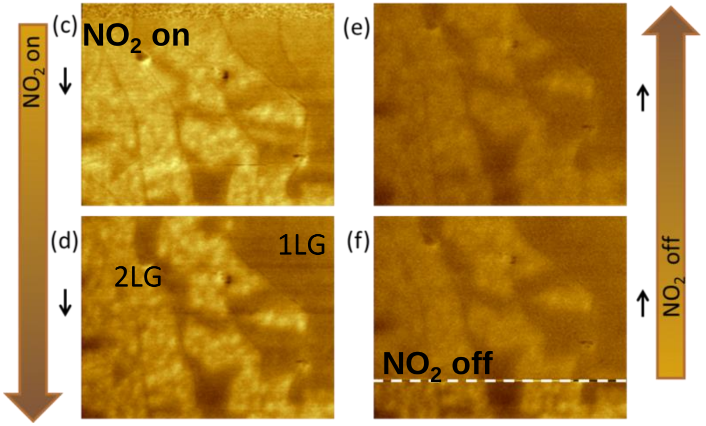


In N$_2$: after vacuum $\Phi_{1LG} = \Phi_{2LG}$

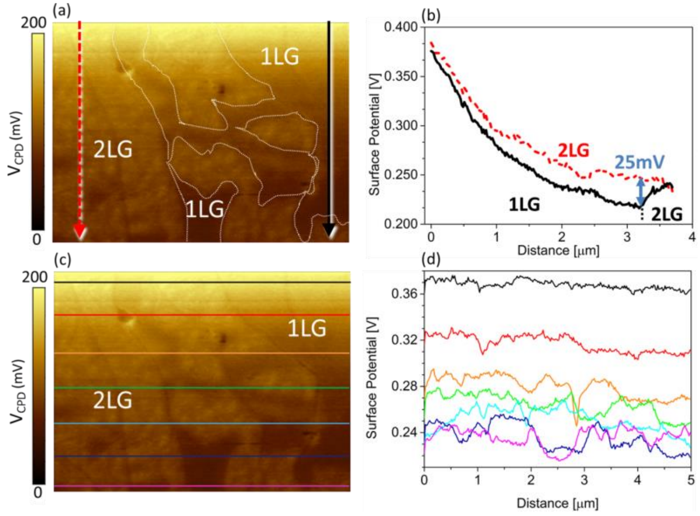


Corrugations in 2LG upon repeated gas exposure and vacuum 'cleaning'

NO$_2$: Electron withdrawing gas increases $\Delta V_{CPD, 2L\text{-}1L}$



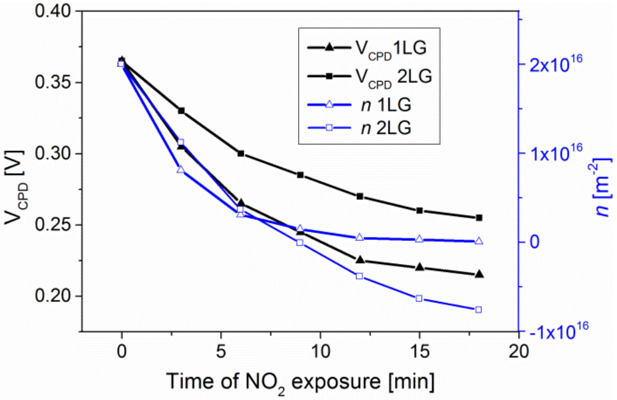
V_{CPD} (1LG) and V_{CPD} (2LG) decrease, but V_{CPD} (1LG) decreases more

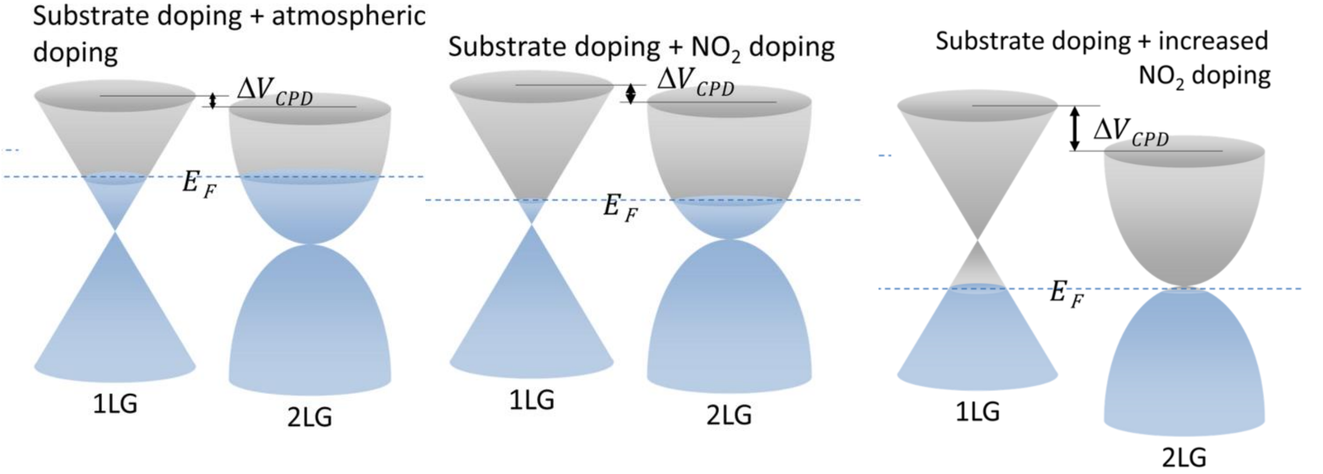


Different shifts for 1LG and 2LG?

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

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

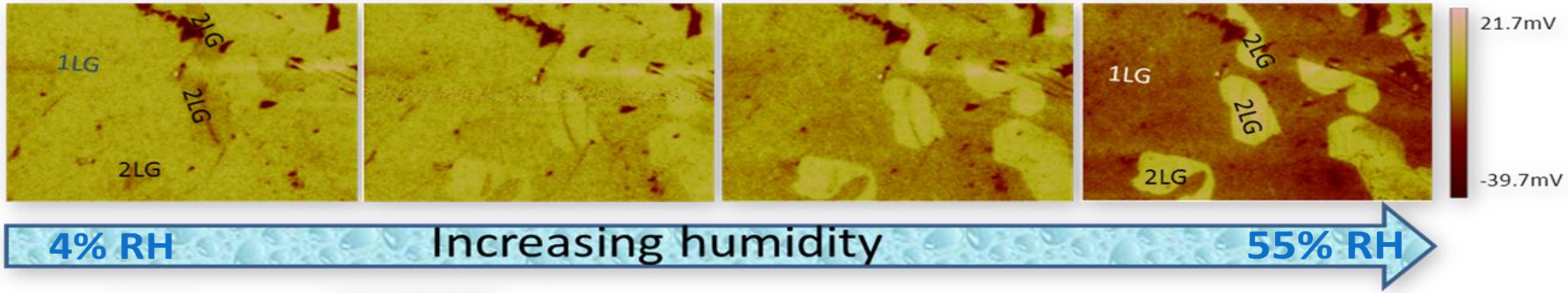
$$(2) \qquad \Delta n\ 2\mathrm{LG} = \frac{\delta V_{CPD}\,e\,2m^*}{\hbar^2\pi}$$

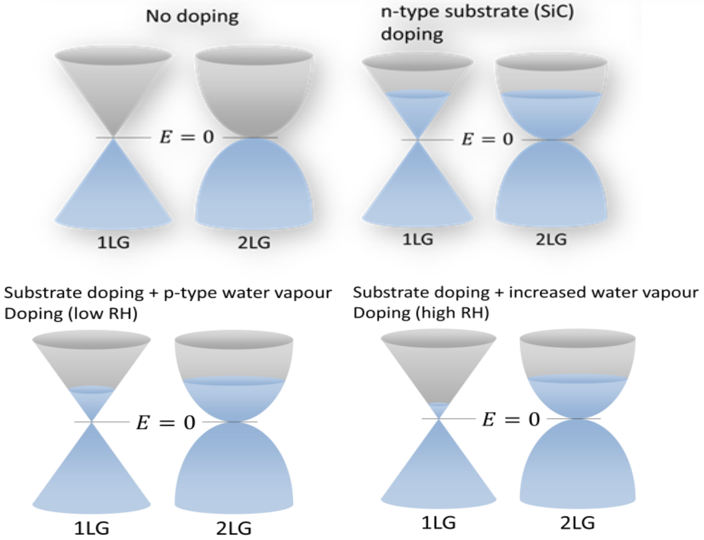
R. Pearce, J. Eriksson, T. Iakimov, L. Hultman, A. Lloyd Spetz and R. Yakimova, ACS Nano 7 (5), pp 4647–4656 (2013)

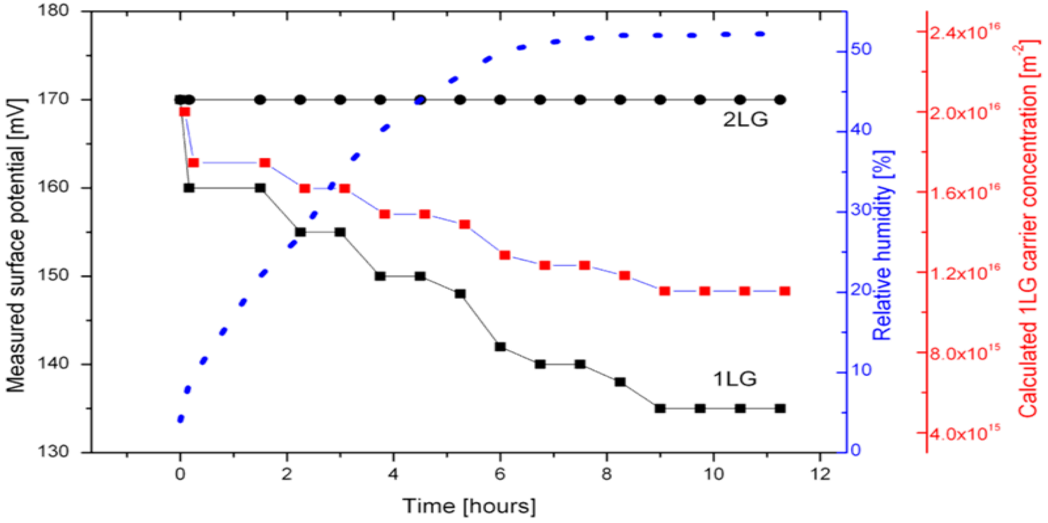
- Calculated change in carrier concentration not the same for 1 and 2LG
- Different responsivity for 1 and 2LG doesn’t account for all difference in sensitivity
- Different sticking coefficients also important

Effect of humidity on surface potential

- Environment affects the surface potential
- V_{CPD} (1LG) decreases
- V_{CPD} (2LG) constant





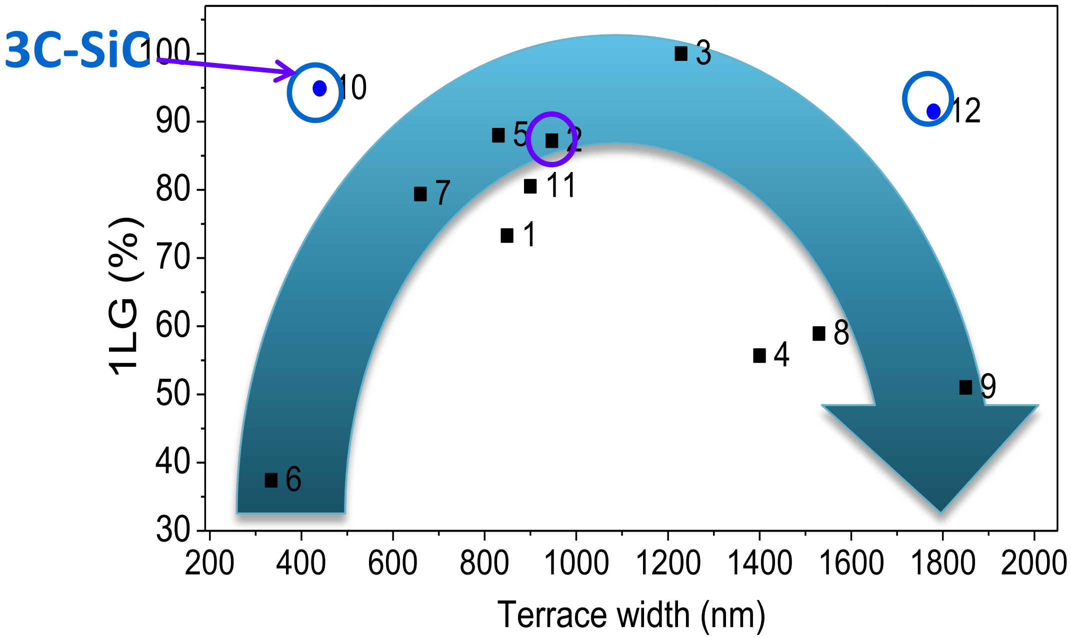


Controlling graphene layer uniformity and unintentional doping

- ☐ Large spread observed in N_S for samples grown under identical conditions
- ☐ There is strong indication that a correlation exists between the substrate surface morphology and the electronic properties of the epitaxial graphene.

Yakes et al., *Nano Lett.* 10, 1559–1562 (2010)

Mono layer coverage depends on terrace width

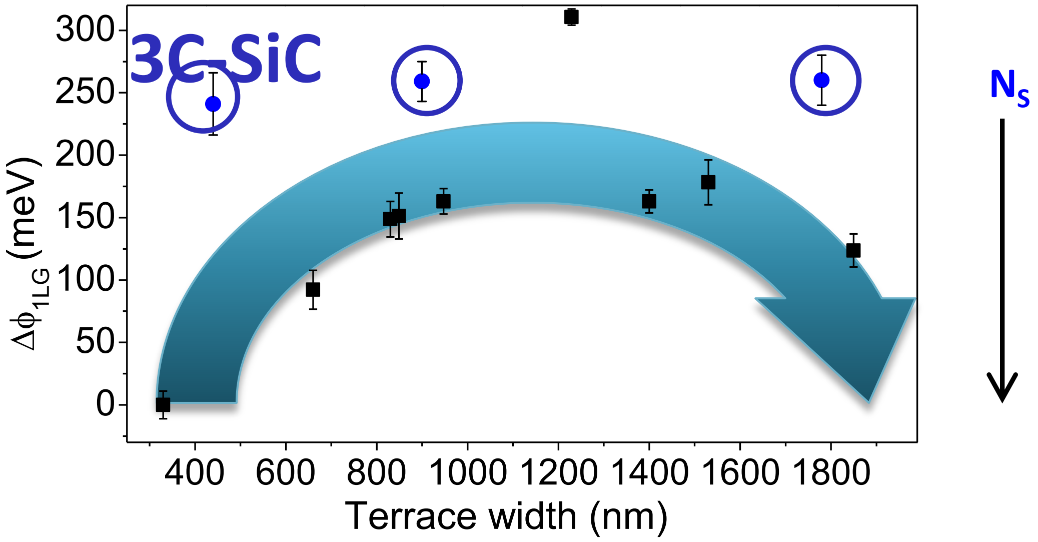


- ❑ Terrace width < 300 nm – no 1LG
- ❑ As the terrace width increases, the area covered by 1LG increases
- ❑ Graphene growth starts at step edges; many step edges → many nucleation sites
- ❑ Terrace width > 1200 nm – gradual decrease of 1LG - Island growth in the absence of steps
- ❑ Substrate polytype and doping for hexagonal SiC (n-type 6H-SiC or SI 4H-SiC) do not significantly influence uniformity
- ❑3C-SiC – higher 1LG % for lower terrace width , 1LG % independent on terrace width

Carrier concentration depends on SiC surface

Φ (so N_S) depends strongly on terrace width

3C-SiC: Lower doping, independent on terrace width



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

Unintentional doping

Variations in ϕ_{1LG} follow variations in E_F:

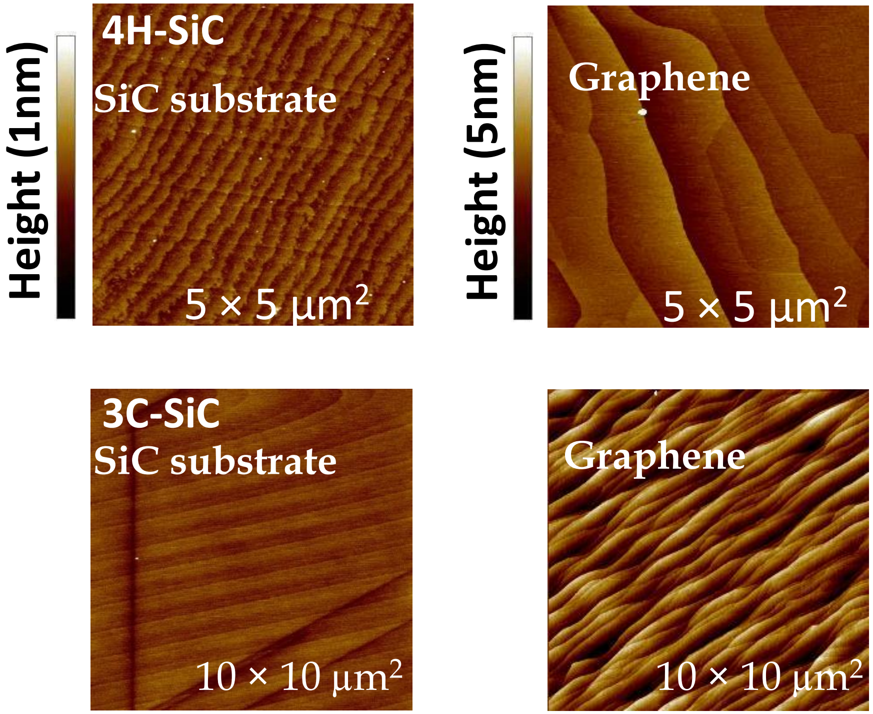
For 1LG: $$\Delta N = \frac{D_0 \Delta E_F^2}{2}$$

$\Delta N_{D,Max} \approx 8 \times 10^{12}$ cm^{-2}

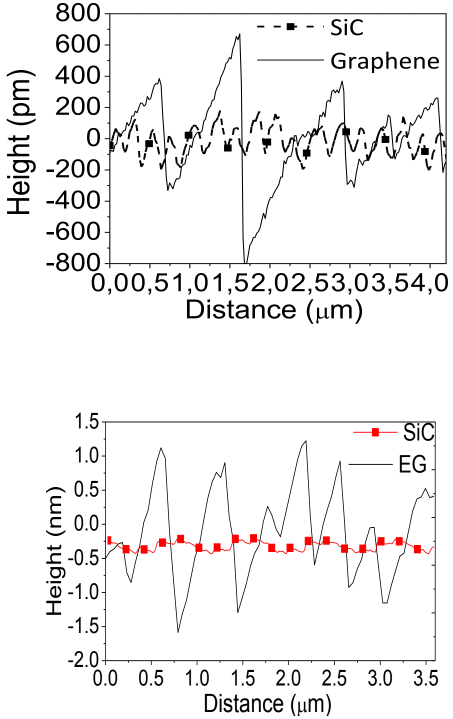
$\sigma_{\Delta ND} \approx 6 \times 10^{11}$ cm^{-2}

Scattering indicates that also other factors affect E_F

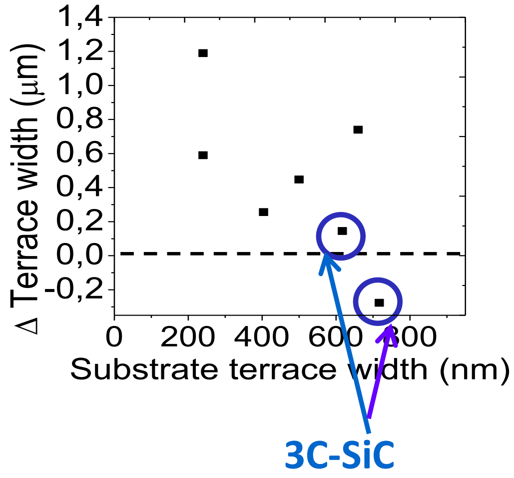
Surface restructuring during Si sublimation



Step profile

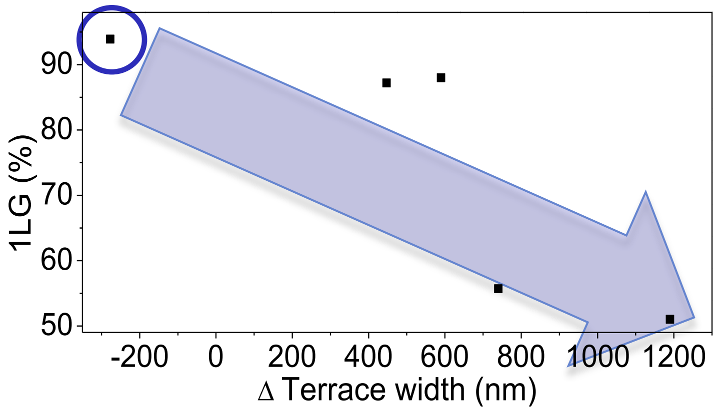


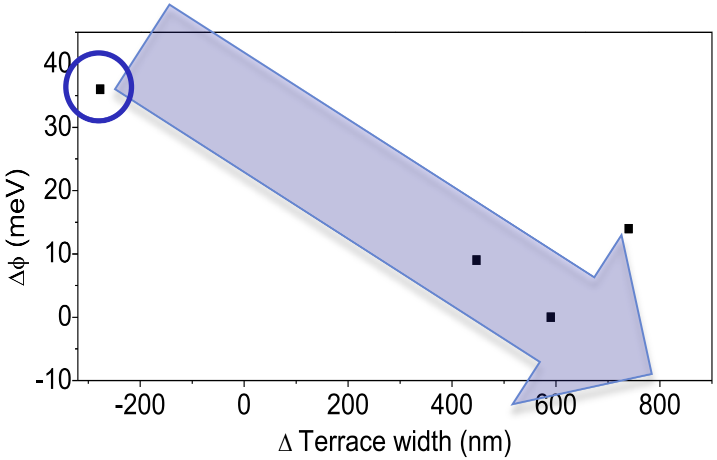
Change in terrace width



- **All substrates undergo significant restructuring during graphene growth**
  - **Differing restructuring of different nominally on-axis SiC substrates**
  - **No correlation seen between SiC step distance before growth and how much the SiC restructures upon graphene growth**
  - **3C-SiC restructures less, and even a reduction of the terrace width is possible**

Effects of surface restructuring





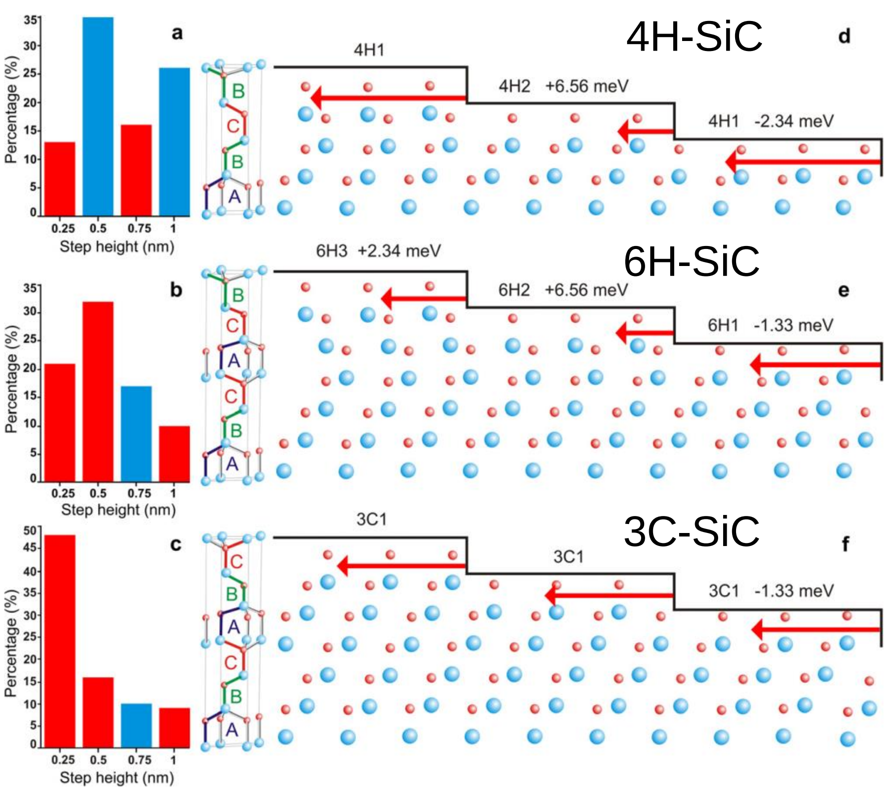
- ☐ **More significant restructuring leads to less uniform graphene**
- ☐ **Work function decreases (n-doping increases) with amount of restructuring**

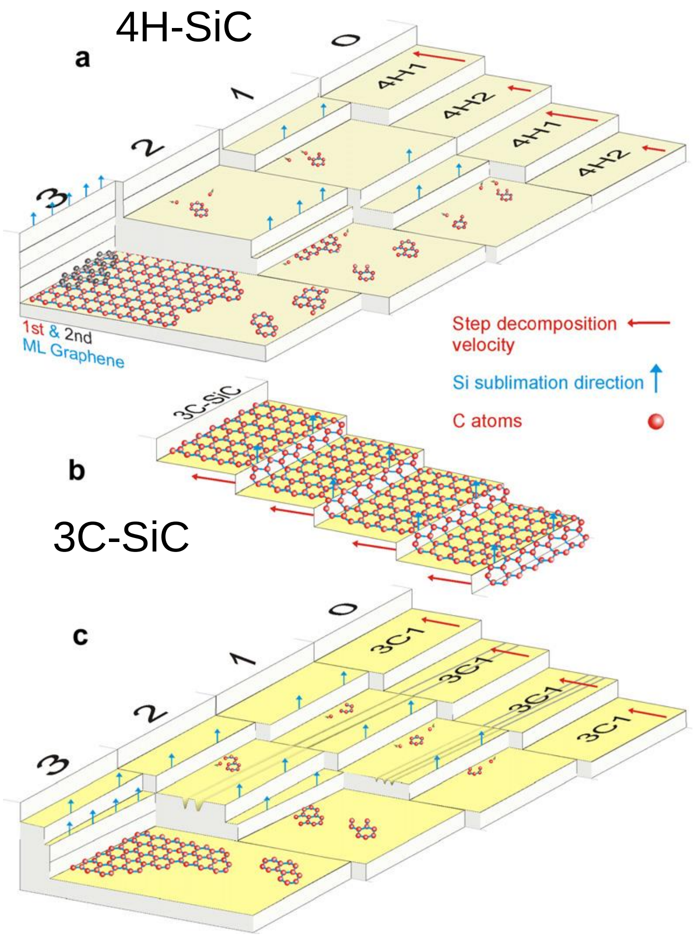
Minimize the restructuring → Use 3C-SiC substrates

Due to less step-bunching, 3C-SiC better lends itself to a well-controlled surface morphology and better control of the electronic properties of the graphene

Eriksson et al., Mater. Sci. Forum 740-742 (2013) 153-156

Step bunching in 4H, 6H, and 3C-SiC

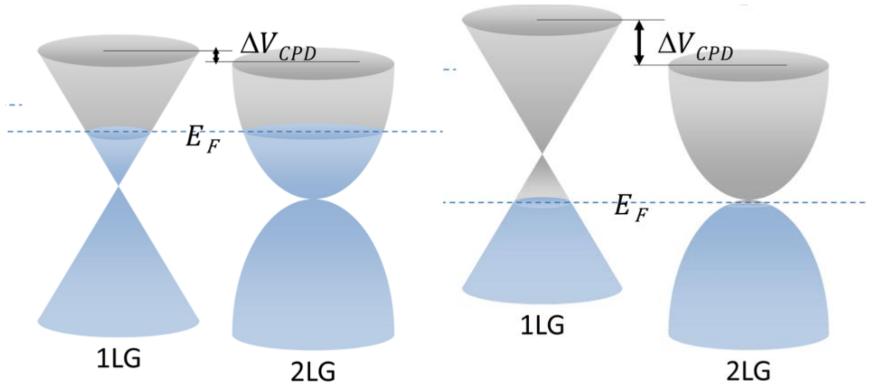




Yazdi et al., Carbon 57 477 –484 (2 0 1 3)

Uniform 1LG leads to very reproducible sensor characteristics

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

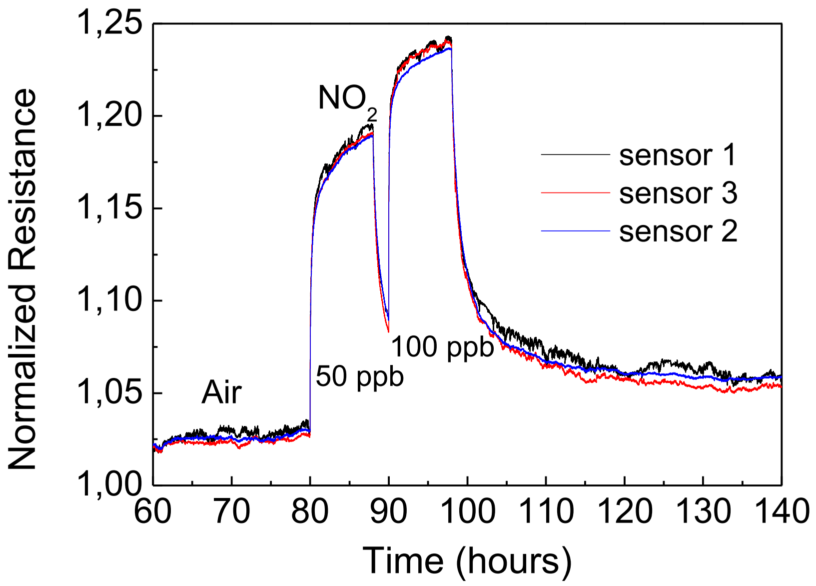


- ➢ NO_2 withdraws electrons

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)

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

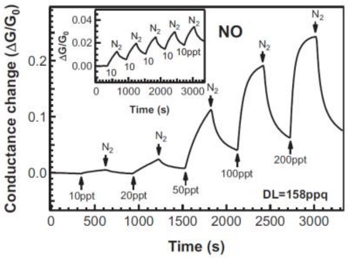
Epitaxial graphene on SiC enables **highly reproducible** sensor fabrication

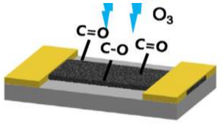
Graphene sensors issues: selectivity, response/recovery time, reproducibility

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

❑ Sensitivity

- UV “cleaning”: ppt and ppq level detection – surpassing specially trained dogs!
  - O-functionalizes graphene





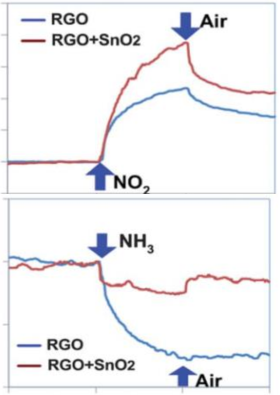
Chen et al., Applied Physics Letters ***101****, 053119 (2012)*

Sensors and Actuators B ***166– 167,*** *172– 176 (2012)*

❑ Selectivity

- Surface functionalizations by e.g. oxygen, nanoparticles, defect engineering, smart operation and smart analysis

J. Mater. Chem. ***22****, 11009 (2012)*

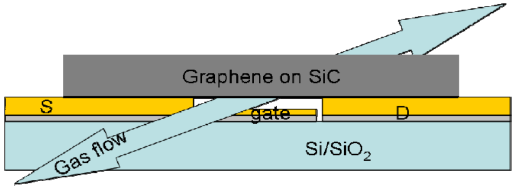


❑ Response/recovery times

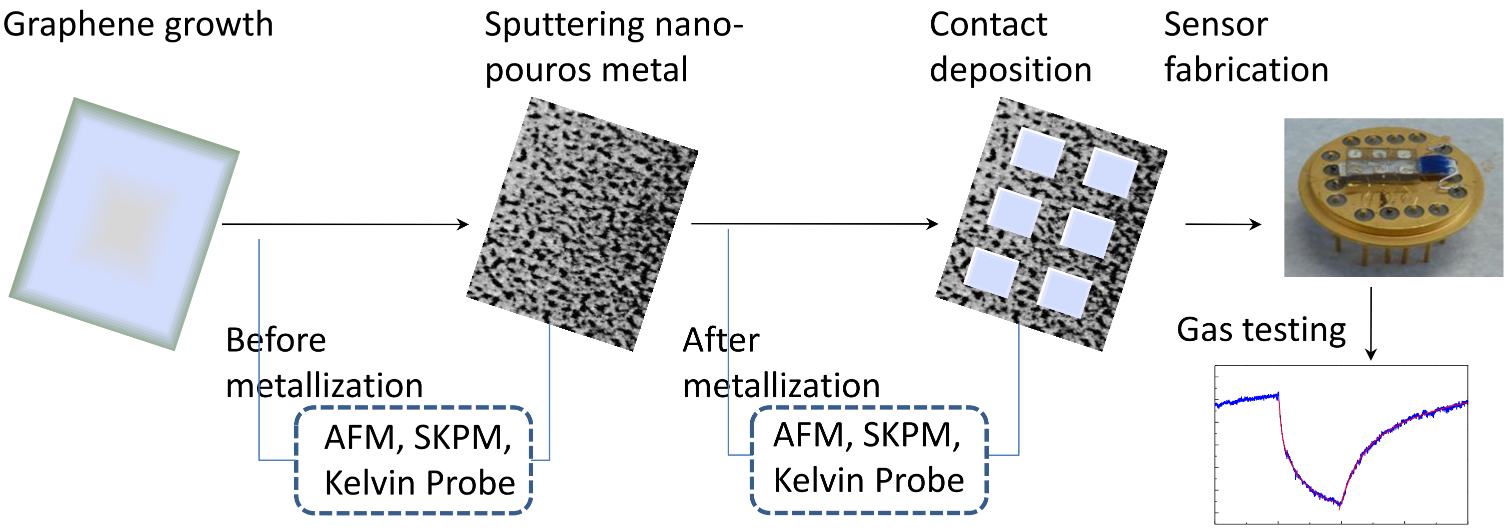
- Functionalization, current-, bias- or temperature cycling. Integration of UV-LED

❑ Reproducibility

- Sensors on epitaxial graphene
- Variations in Ns can be compensated by the use of FET sensor
  - SenSiC AB patent application



Functionalization with metal and metal oxide nanostructures for selectivity tuning



Graphene growth

Sputtering nano-pouros metal

Contact deposition

Sensor fabrication

Gas testing

Before metallization

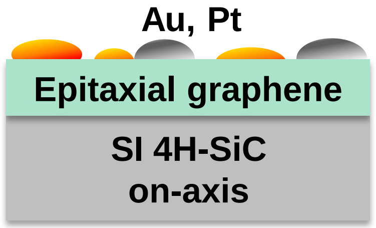
AFM, SKPM, Kelvin Probe

After metallization

AFM, SKPM, Kelvin Probe

Aim: To develop a reproducible method for functionalization with 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



Au, Pt

Epitaxial graphene

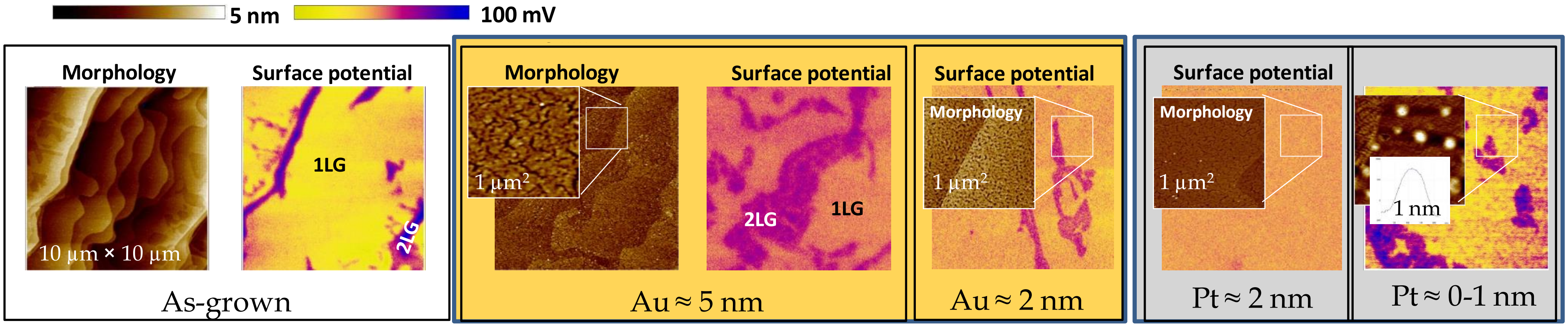
SI 4H-SiC
on-axis

Functionalization with metal and metal oxide nanostructures for selectivity tuning

Scanning Kelvin probe microscopy: Maps surface morphology and surface potential

- **ΔΦ between 1LG and 2LG allows nanoscale mapping of graphene thickness (and doping)**

As-grown **Thin porous metallization**



❑ Morphology shows deposition of continuous porous metal – ideally: islands…

❑ 1LG/2LG potential contrast: surface retains the electronic properties of graphene

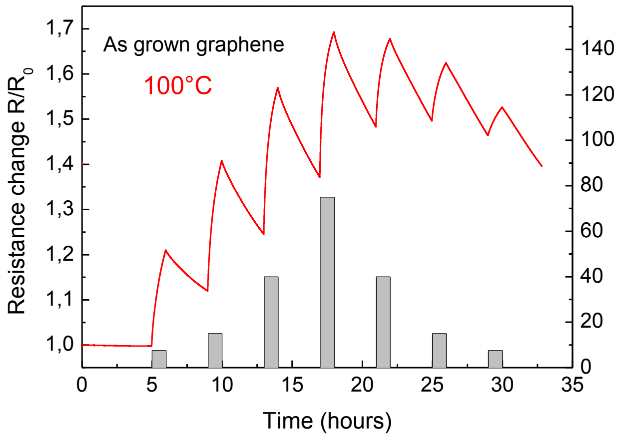
❑ Pt wets the surface better than Au – screens the graphene for ‘thick’ depositions

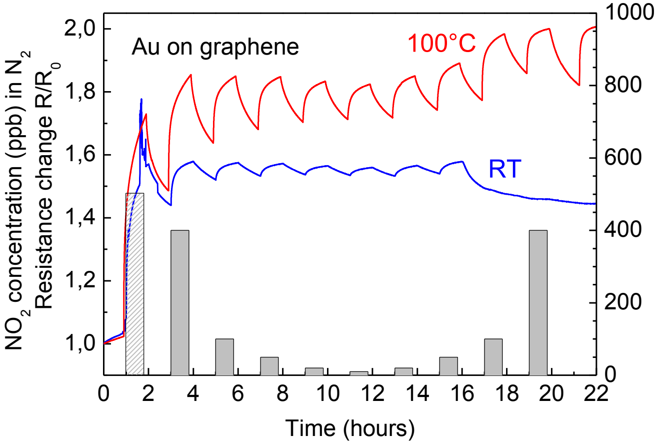
Effect of decoration on sensor response

As-grown graphene

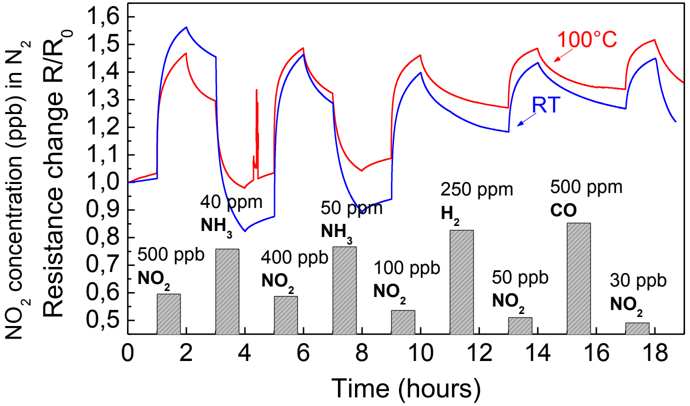
Au decorated graphene

Response to ppb concentrations of NO_2





Selectivity



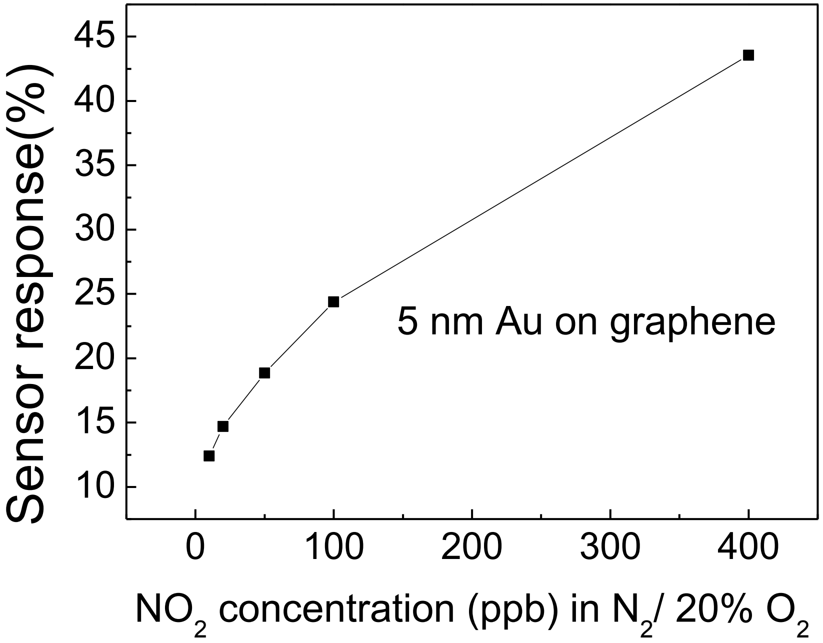
☐ **Effects of metallization:**

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

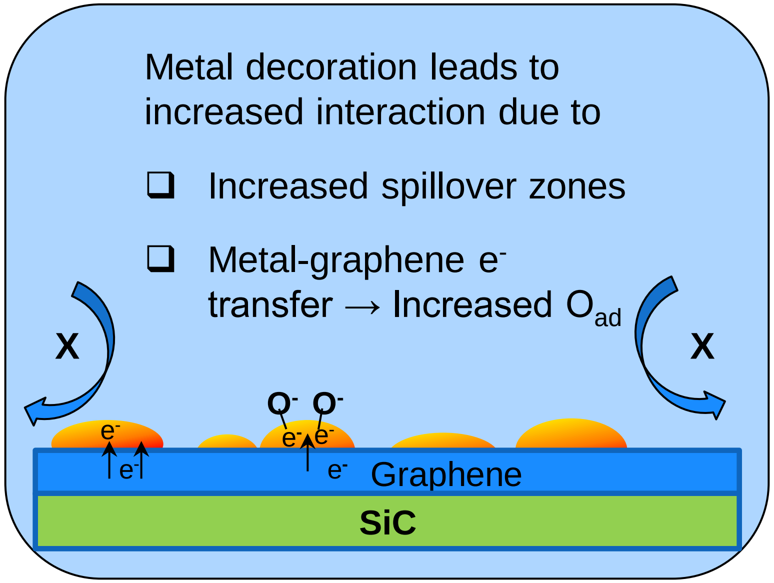
Response %	Response Time (min), 50 ppb NO_2			Recovery Time (min)		
	As-grown	Au, 5 nm	Pt, 5 nm	As-grown	Au, 5 nm	Pt, 2 nm
30%	6	1.5	2.3	316	14	14,8
60%	23	9	10.9	834	47	49
90%	99	74	41.7	2136	135	175,5

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

Increased sensitivity



❑ Detection limit < 1 ppb



Metal decoration leads to increased interaction due to

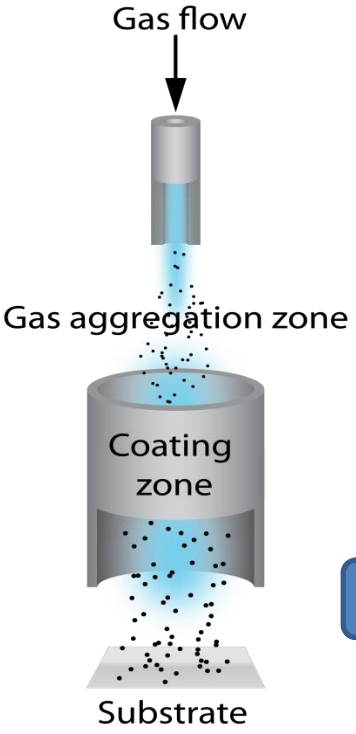
❑ Increased spillover zones

❑ Metal-graphene e^- transfer → Increased O_{ad}

❑ Porous metal grains or nanoparticles increase the probability of interaction between the graphene surface and adsorbates

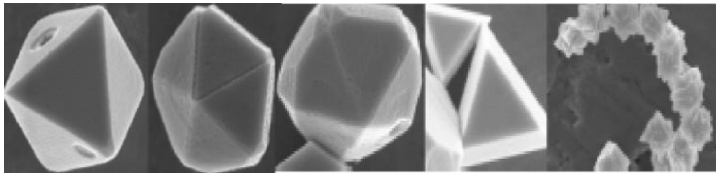
Designed Nanoparticles by Pulsed Plasma

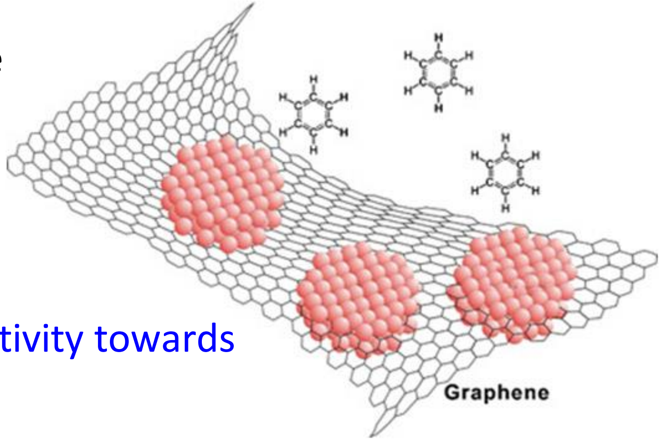
It is expected that decoration with different metals or metal-oxide nanostructures will allow careful targeting of selectivity to specific molecules



❑Plasma-based nanoparticle (NP) synthesis process

❑Highly reproducible thin film deposition technique

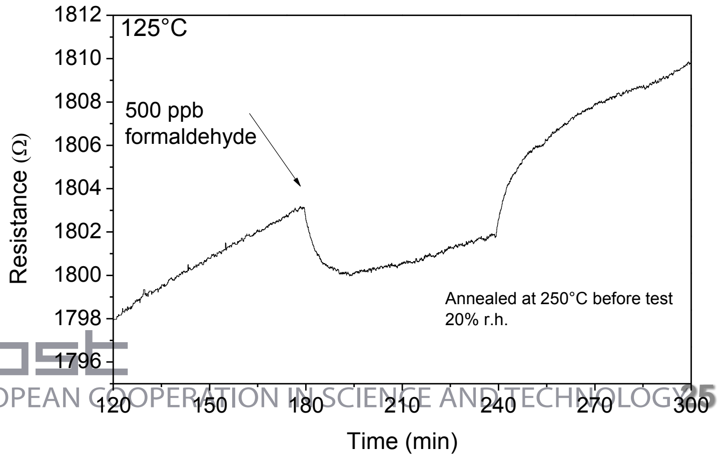




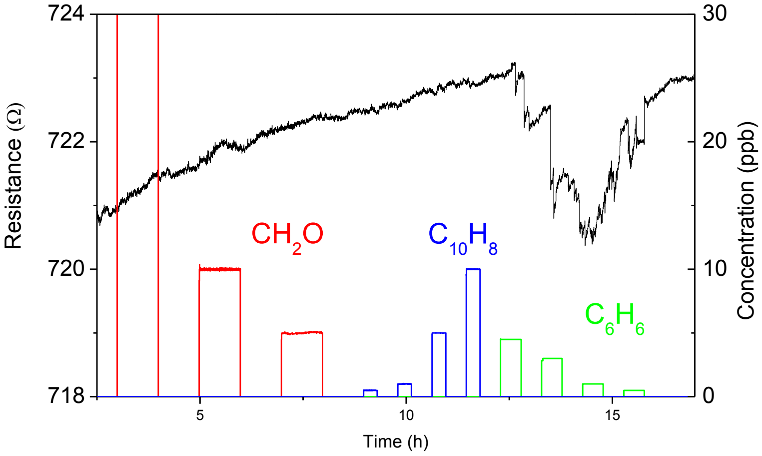
❑Preliminary show that TiO_2 NPs allow enhanced sensitivity towards formaldehyde and benzene

❑ The effect depends on the size of the deposited NPs (< 5 nm, sensitive to benzene, > 50 nm, sensitive to formaldehyde)

EG decorated with TiO_2 (Ø > 50 nm)



EG decorated with TiO_2 (Ø < 5 nm)



CONCLUSIONS

- Sensing with epitaxial graphene – promising, ppb level NO_2 detection
- Obstacles (selectivity and speed) are being overcome
- Thin (0.5 – 5 nm), porous decoration can result in improved selectivity, sensitivity, stability, and response/recovery times
  - The effect depends on the choice, thickness, and nanostructure of the decoration
- Air quality control: ppb level detection limit required,– a likely application
- Emerging interest in detection of VOCs in living environments – ppb level detection crucial. Graphene is an excellent candidate
- It is expected that decoration with different metals or metal-oxide nanostructures will allow careful targeting of selectivity to specific molecules