EuNetAir COST Action TD1105
WGs and MC Meeting in Rome - December 5th, 2012

Gas Sensing with Epitaxial Graphene on SiC

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VINNOVA

SEVENTH FRAMEWORK PROGRAMME

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Gas sensing with epitaxial graphene

- Why graphene?
- Production of epitaxial graphene on SiC
- Gas response of epitaxial graphene gas sensors
- Controlling graphene uniformity and doping
- Effect of graphene layer thickness on sensitivity to chemical gating

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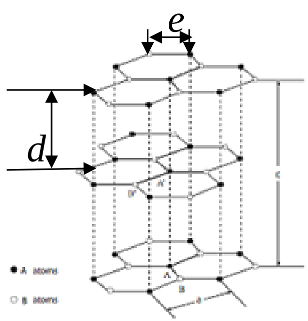
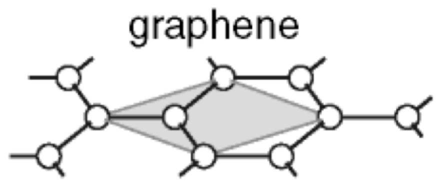
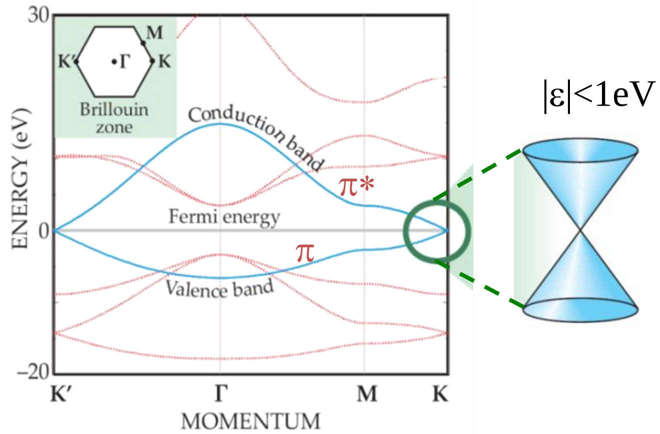
Why Graphene?



a = 2.46Å
c = 6.71Å
d = 3.4Å
e = 1.42Å





sp^2 hybridized carbon atoms in a honeycomb lattice

- Massless, pseudo-relativistic Dirac fermions
- Linear energy-momentum dispersion:
  - p- bands touch at Dirac points
- Ballistic transport at room temperature, and intrinsic mobility $\mu > 10^5$ $cm^2\ V^{-1} s^{-1}$.

Why Graphene sensors?

- Low density of states near the Dirac point (E_D) – small changes in the number of charge carriers results in large resistance changes
- Low noise, chemically stable, conductive even at the limit of no charge carriers

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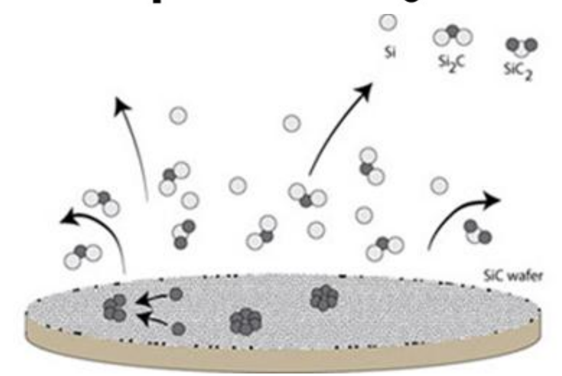
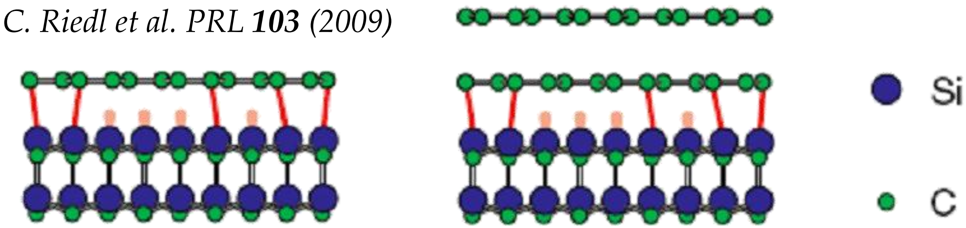
Graphene production

- Graphene is produced by the high temperature sublimation of Si from SiC
- The process is carried out in Ar at 2000°C and atmospheric pressure which gives a more uniform graphene coverage
- Growth on the Si face (0001) SiC gives more control over the number of layers than on the C face (000Ī)
- The potential of producing large-area lithography-compatible films.
- If the carriers remain ballistic, it will lead to a fascinating world of carbon based electronics.

Graphensic

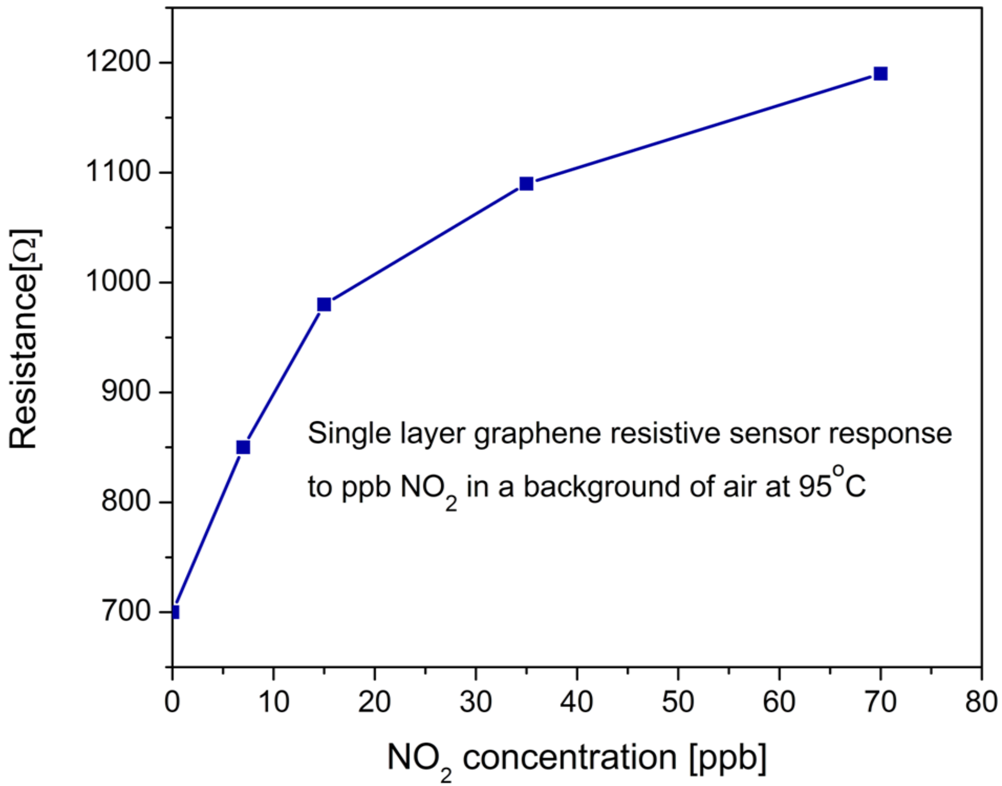


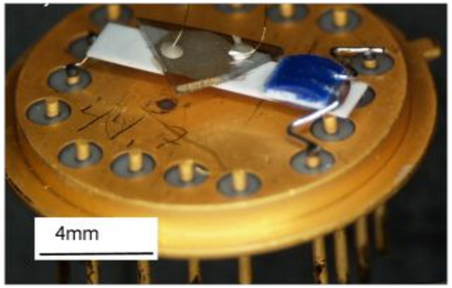
C. Riedl et al. PRL ***103*** *(2009)*



- Graphene layers sit on a buffer or interfacial layer
- The buffer layer is covalently bound to the underlying SiC
- Thickness controlled by temperature

Gas response-single layer graphene





Detection limit of NO_2 < 10 ppb

Detection limits in the low ppt and even ppq range possible for NO_2 and NO

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

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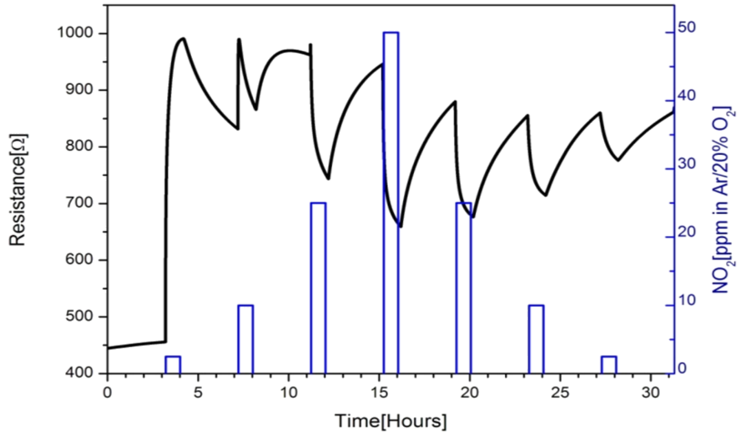
Gas sensing-single layer graphene

ppm concentrations of NO_2 at RT

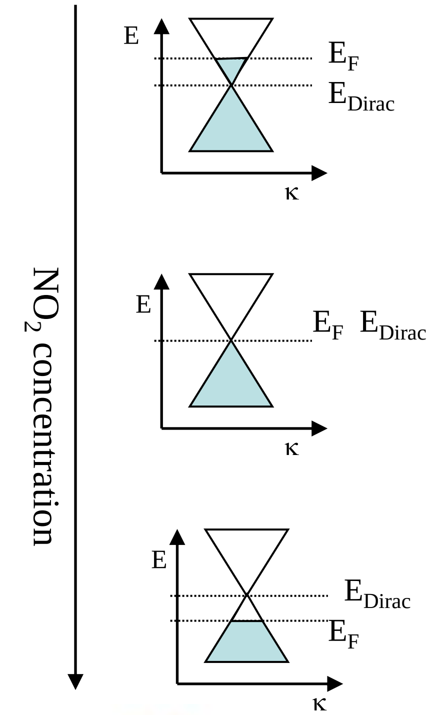
R. Pearce, et al., Sensors and Actuators B: Chemical, 155, (2011), 451-455



Graphene on SiC: n-type conductivity

NO_2 consumes electrons – p-type conductivity

Change in response direction



- Large response to ppb concentrations
- Response and recovery times are long
- Device is initially n-type due to interaction with SiC
- n-p type transition occurs upon prolonged NO_2 exposure
- NO_2 adsorbed on surface withdraws electrons and increases resistance for n-type graphene
- Hole dopes and reduces resistance for p-type graphene

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Controlling the graphene uniformity and the unintentional charge transfer from SiC

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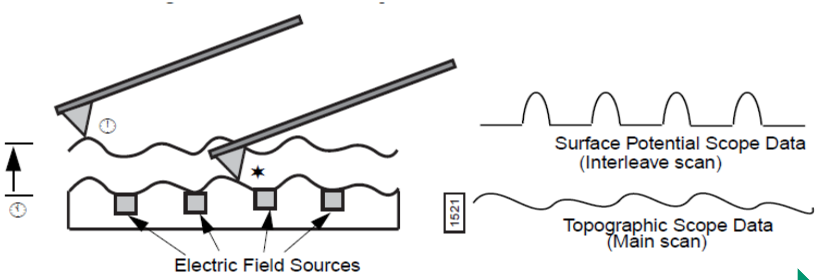
Experimental: Scanning Kelvin probe microscopy – work function mapping

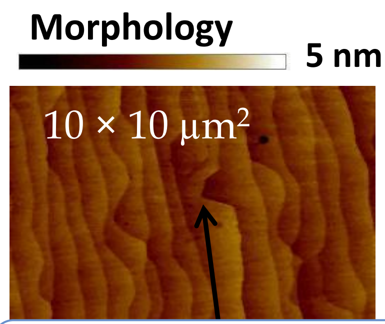
Nanoscale mapping of graphene thickness uniformity and doping

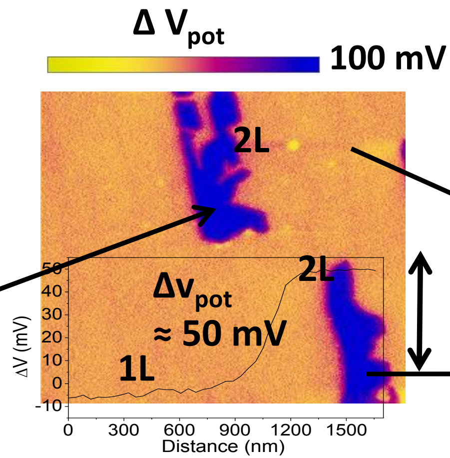


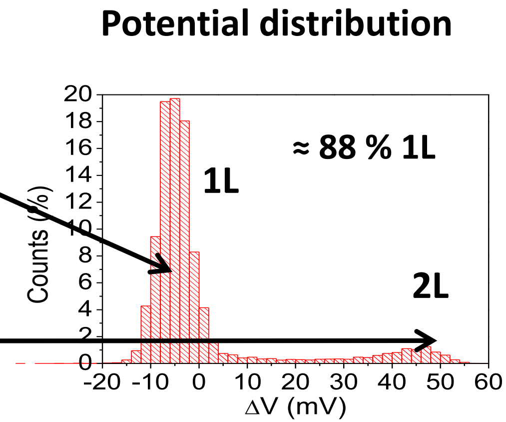
1. Cantilever measures surface topography on first (main) scan.
2. Cantilever ascends to lift scan height.
3. Cantilever follows stored surface topography at the lift height above sample while responding to electric influences on second (interleave) scan.

V_{DC} is adjusted until tip stops resonating

Resulting maps show morphology and local variations in graphene work function







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

➢ **ΔΦ between 1LG and 2LG allows nanoscale mapping of graphene thickness**

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

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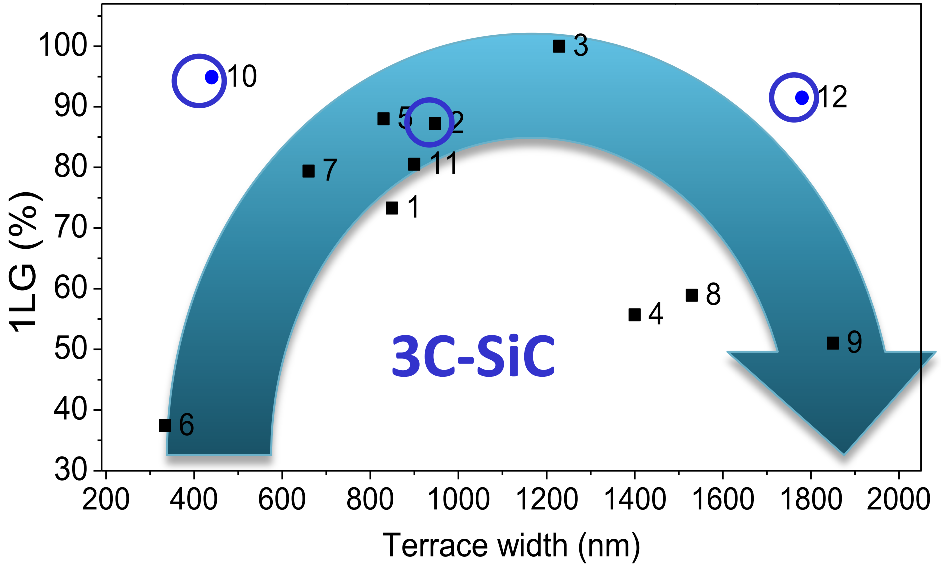
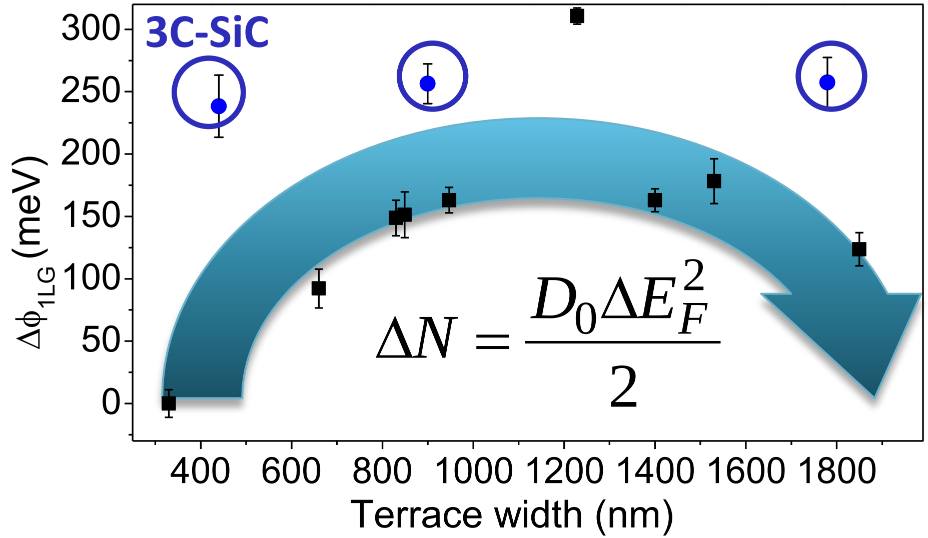
Monolayer coverage vs. terrace width



Mono layer uniformity depends on terrace width

Φ_{1LG} vs. terrace width



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

- Substrate polytype and doping for **hexagonal SiC** (n-type 6H-SiC or SI 4H-SiC) do not significantly influence uniformity or graphene doping
- **3C-SiC – higher 1LG % for lower terrace width, 1LG % independent on terrace width**

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

More suitable for reproducible devices

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

NO_2 sensing, single or double layer graphene?

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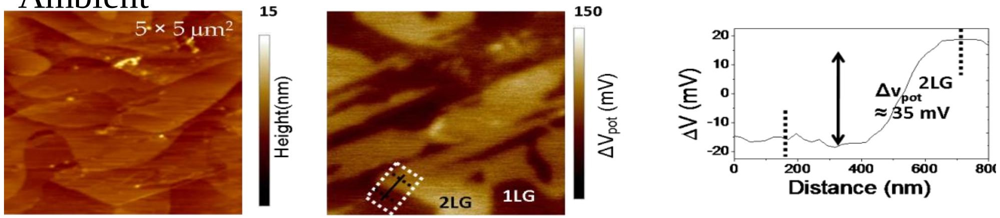
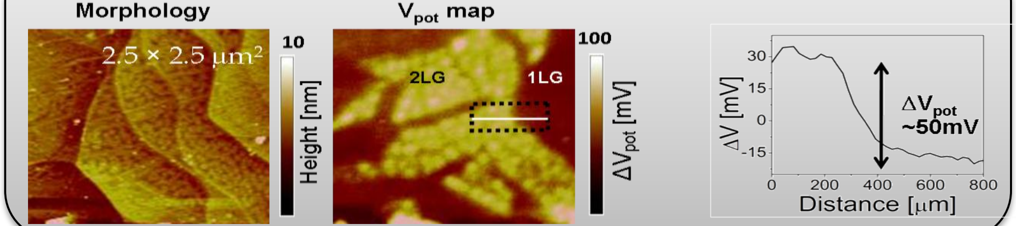
SKPM in controlled environment

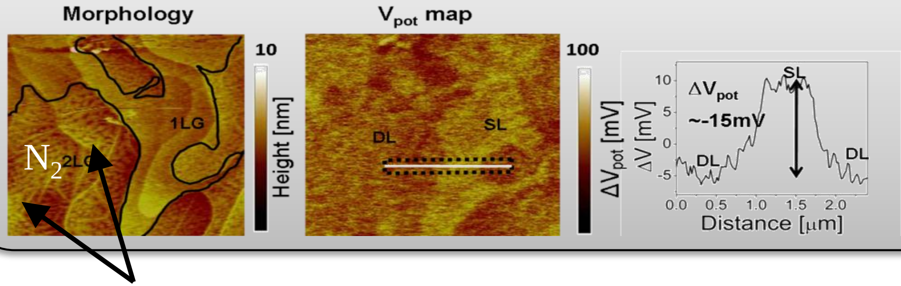
Ambient



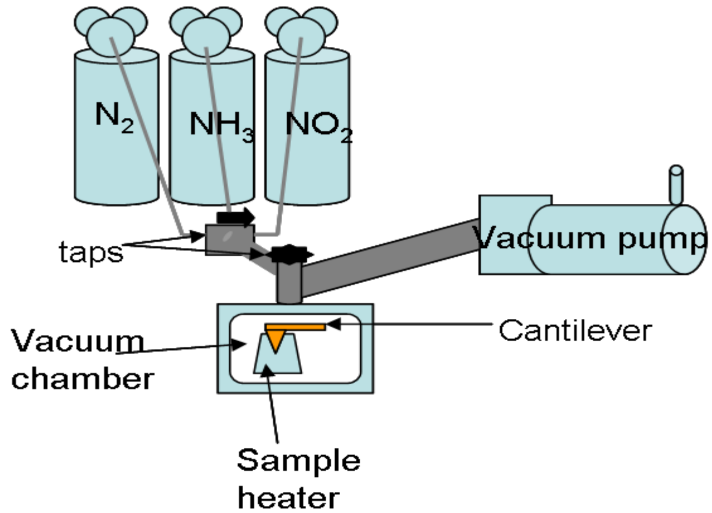
NO_2: Electron withdrawing gas **increases** $DV_{2L\text{-}1L}$



NH_3:Electron donating gas **inverts** $DV_{2L\text{-}1L}$



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



The probe is placed in an environmental chamber:

- **Controlled gas- or vacuum environment**
- **Visualization of how different chemical doping affects the electronic properties of individual 1LG and 2LG domains**

Different shifts for 1LG and 2LG?

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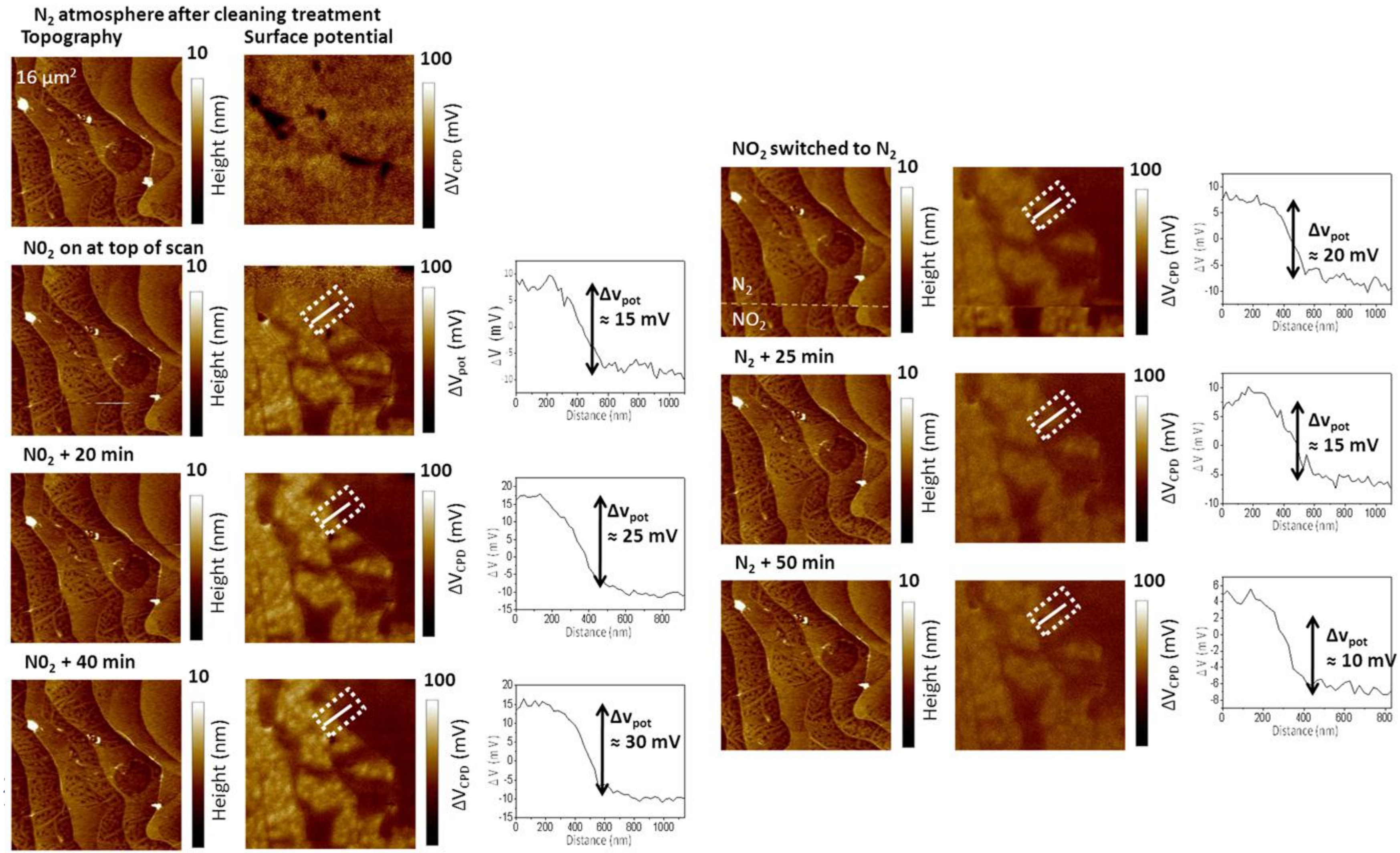
Mapping work function change with environment

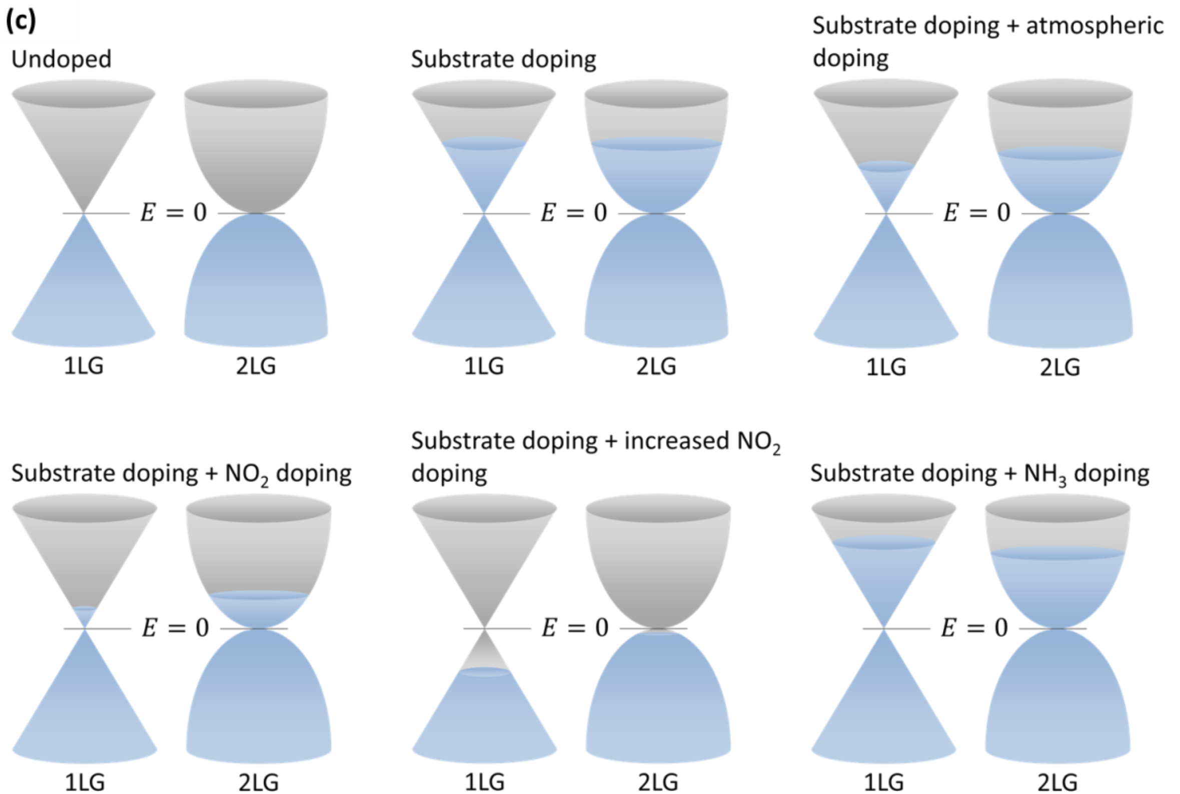


Different shifts for 1LG and 2LG?

Different band structures

- Linear energy dispersion for 1LG
- More parabolic for 2LG

Physical Rev. B **83**, 235434 (2011)



R. Pearce, J. Eriksson, T. Iakimov, L. Hultman, A. Lloyd Spetz and R. Yakimova, ACS nano, accepted

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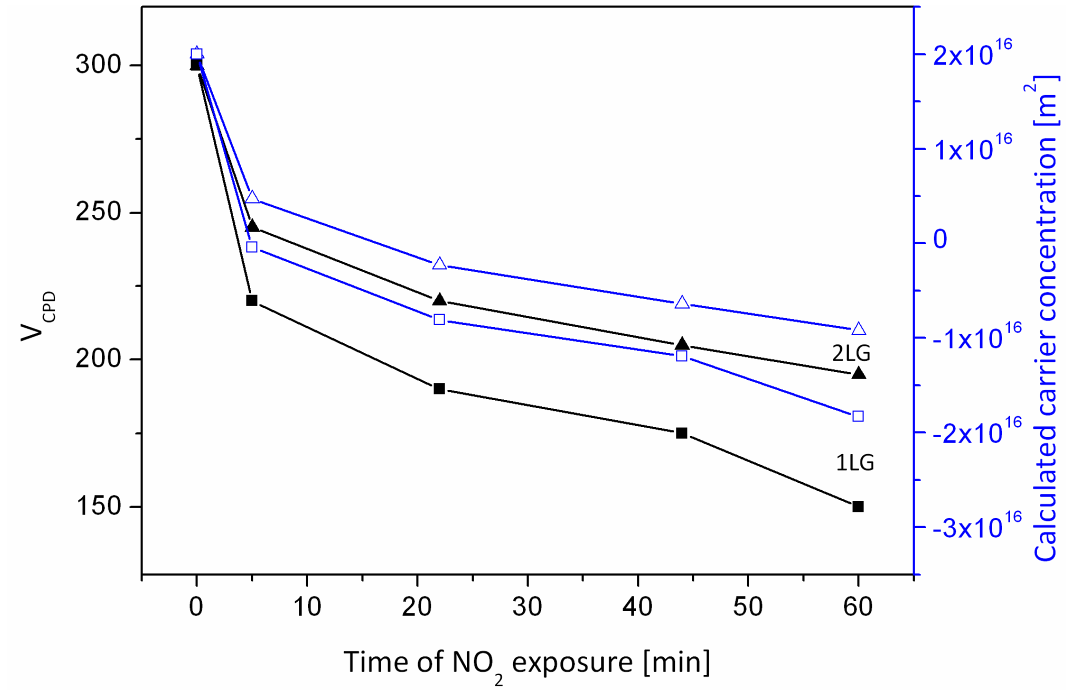
NO_2 adsorption on single and double layer graphene



- 1.5ppm NO_2 in N_2 slowly flowed in to vacuum chamber
- NO_2 withdraws electrons and reduces E_F for both double and single layer graphene
- Due to differences in band structure V_{CPD} reduces more for single layer graphene

- We need uniform 1LG!

From 1-2L ΔV_{CPD}: Non-invasive measurement of substrate induced carriers

(1)
$$\delta n \ 1LG = \frac{e \ \partial V_{CPD} \ 2\sqrt{n}}{\hbar \ \upsilon_F \ \sqrt{\pi}}$$

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

R. Pearce, J. Eriksson, T. Iakimov, L. Hultman, A. Lloyd Spetz and R. Yakimova, ACS nano, accepted

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Conclusion

- Sensing with epitaxial graphene – promising, ppb level NOx detection
- Obstacles: selectivity, response time, reproducibility
- Solutions: decoration with nanostructures, cleaning cycles, T cycles, FET
- Combustion engine NOx sensing: detection limit of 5 ppm, T90 = few seconds – strong improvements in response time required
- NOx sensing in living environments: ppb level detection limit, T90 not crucial – a likely application