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

COST Action TD1105

WGs and MC Meeting at LINKOPING, 3 - 5 June 2015

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

GRAPHENE GAS SENSORS ENHANCED BY UV LIGHT AND PULSED LASER DEPOSITION

Raivo Jaaniso

MC Member

University of Tartu / Estonia

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Motivation

- High potential of graphene – responses to single gas molecules have been demonstrated
- For fully exploiting the potential of graphene new approaches are required for increasing the sensitivity in real atmospheric measurements and for making the devices (partially) selective to different target gases
- **In the present work, we demonstrate the functionalization of single layer graphene by pulsed laser deposition (PLD) and its impact on the sensing properties to NO_2 gas in case of different deposited materials**

University of Tartu

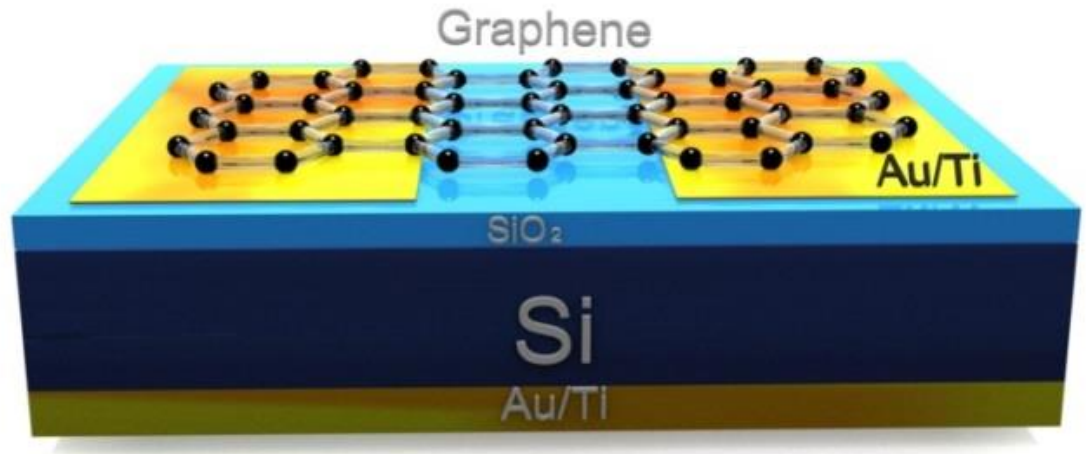
17 500 students
1700 academic staff

Founded 1632
by Swedish King Gustav Adolf II

Institute of Physics

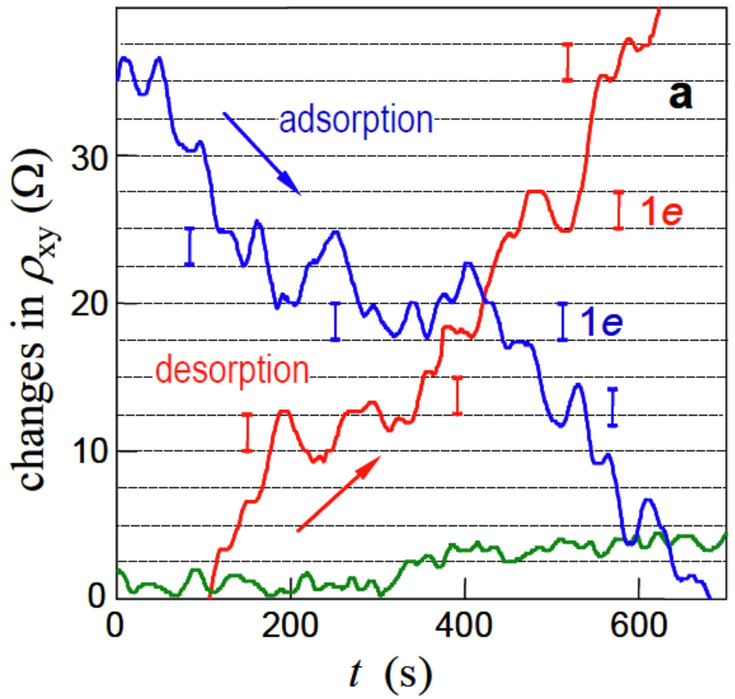
New Physicum - 2014

Graphene



- 2D material,1/2 fully exposed to environment
- High charge carrier mobility (500-10000 $cm^2V^{-1}s^{-1}$ for CVD graphene on substrate), low noise

Detection of single gas molecules

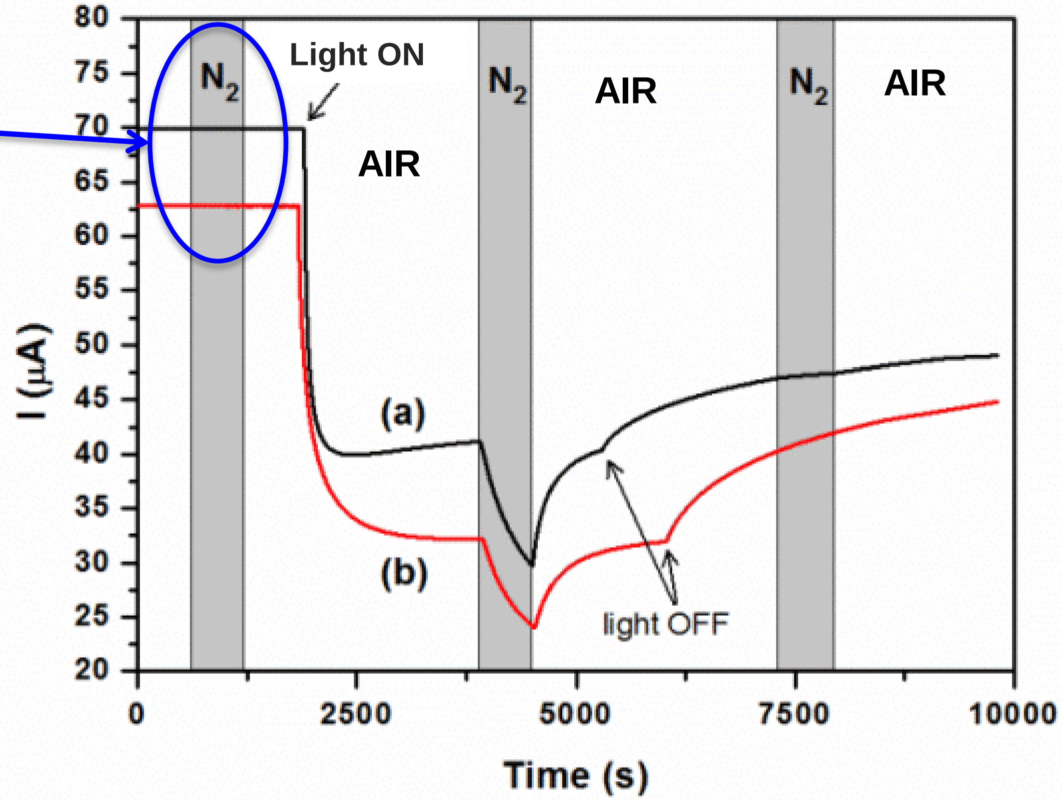


Effect of NO_2 on Hall resistance

Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, K. S. Novoselov, Detection of individual gas molecules adsorbed on graphene, Nat. Mater. 6 (2007) 652-655.

Activation of sensitivity in ambient conditions – O_2

Insensitive in air at room temperature

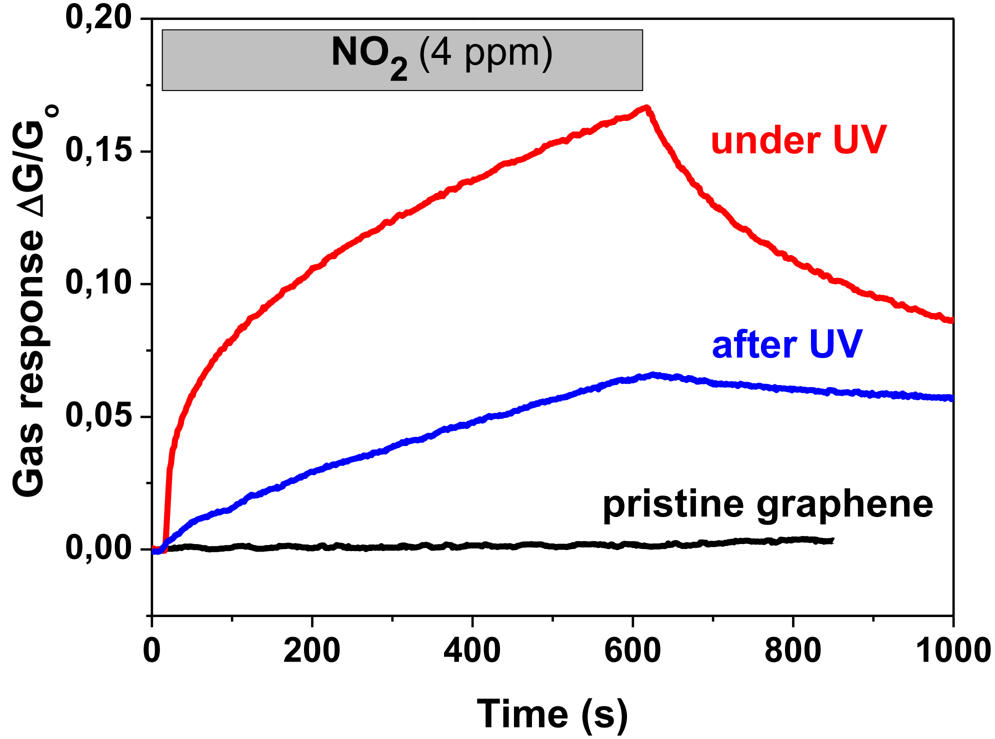


UV light:
365 nm
20 mW/cm^2

(a) RH=0%
(b) RH=50%

A. Berholts, T. Kahro, A. Floren, H. Alles, R. Jaaniso. Photo-activated oxygen sensitivity of graphene at room temperature. Appl. Phys. Lett. 105, 163111 (2014).

Activation of sensitivity in ambient conditions – NO_2



UV light:

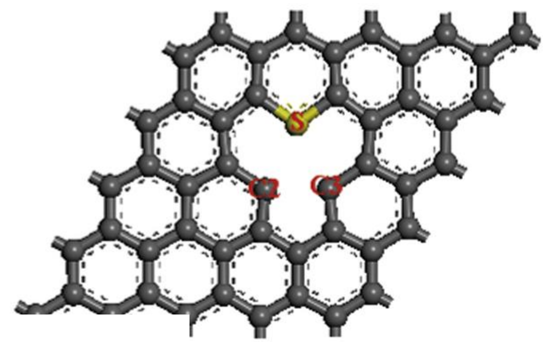
365 nm

20 mW/cm^2

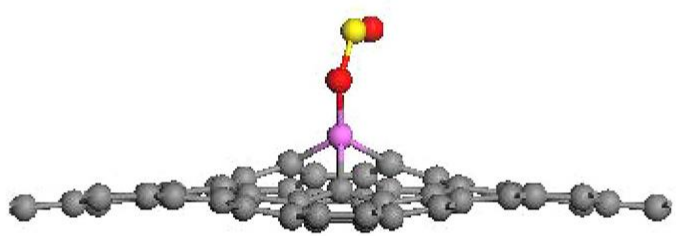
A. Berholts, T. Kahro, A. Floren, H. Alles, R. Jaaniso. Light-activated gas sensitivity of graphene in ambient conditions. Graphene Week 2014, 23-27 June, Göteburg, Sweden.

Modelling

- Plain graphene:
  - very limited adsorption possibilities
  - small adsorption energies (O_2– 0.2 eV, NO_2 – 0.4 eV)



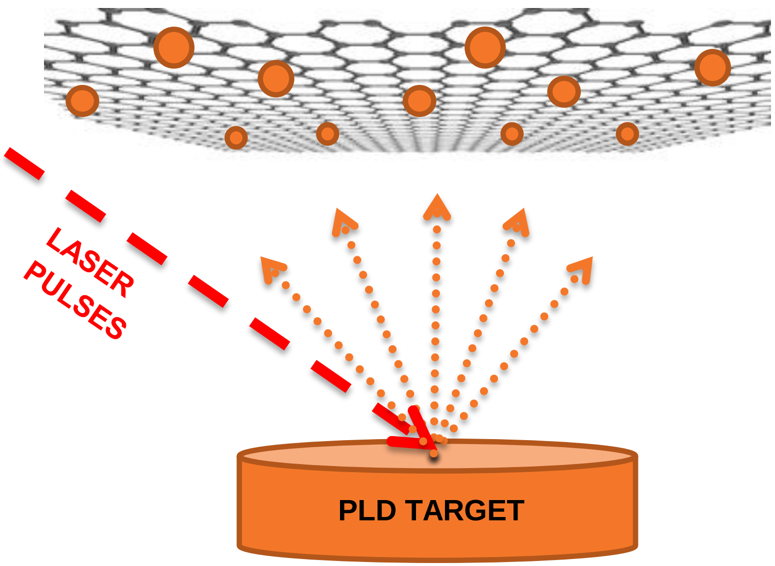
- Defects and edges



- Doping

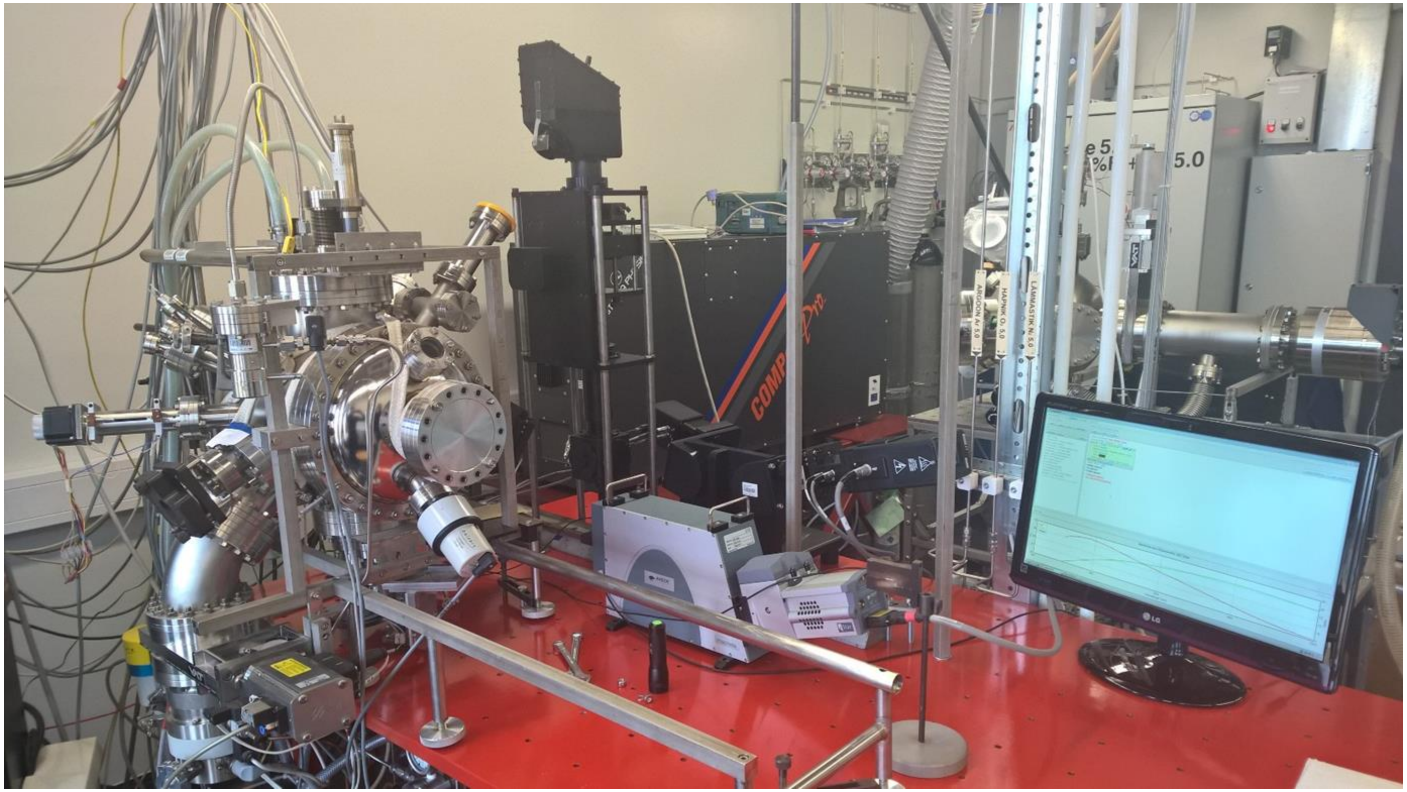
Y. Zou et al. Eur. Phys. J B 81,475, 2011.

Functionalization by pulsed laser deposition (PLD)



- Target can be any solid material
- Particle kinetic energies can be varied between 0.025 and ~1000 eV
- Typical deposition rates - ~1/100th of a monolayer per laser pulse

PLD facilities



KrF laser

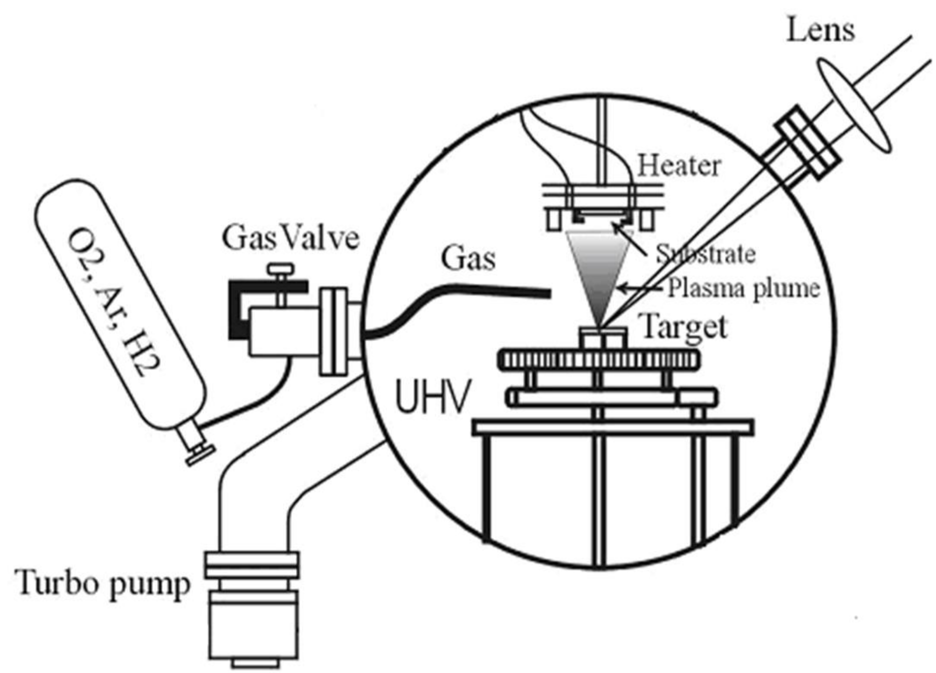
- 248 nm
- 25 ns
- up to 50 Hz

2 UHV chambers

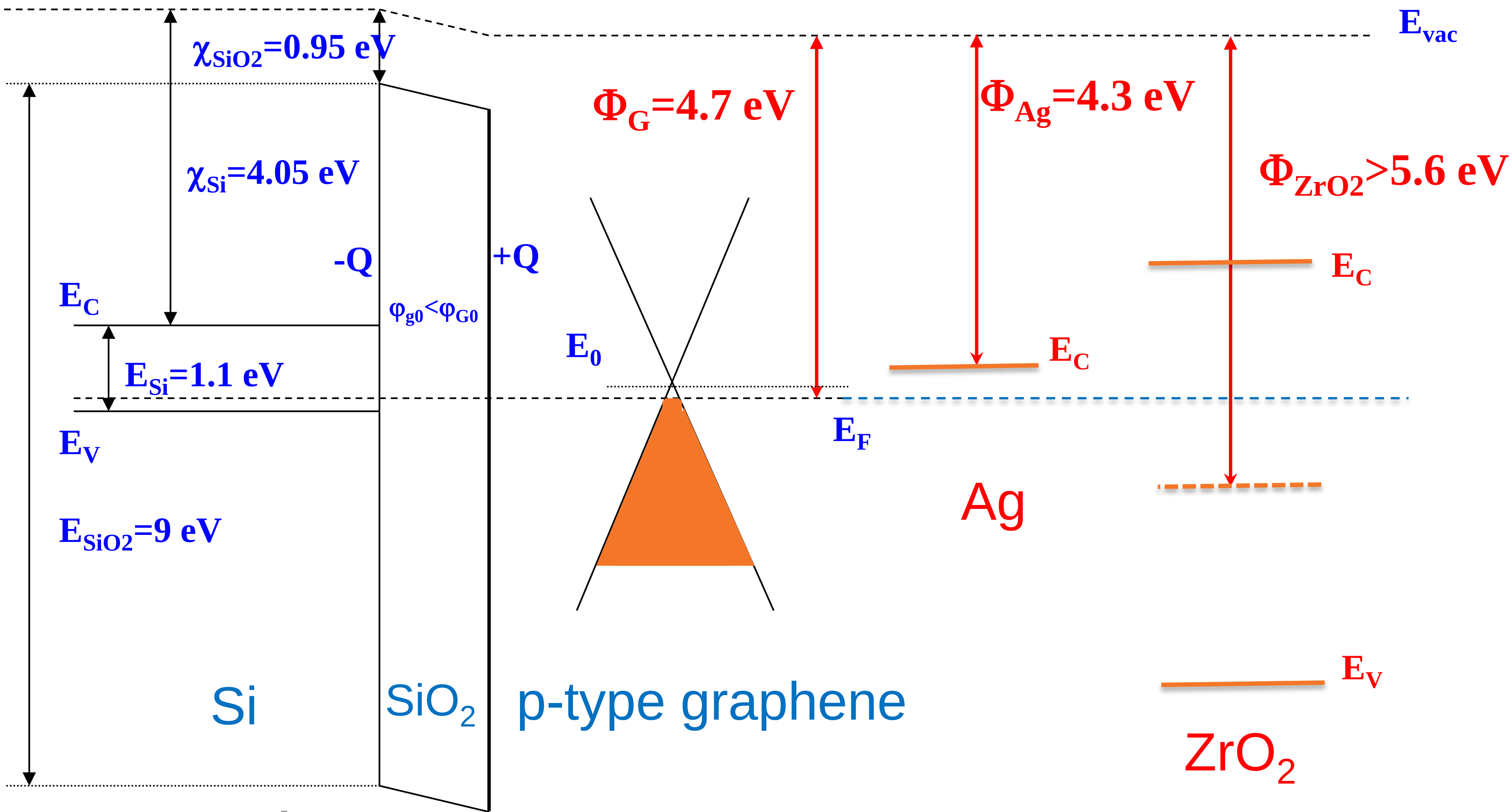
Process control by ellipsometry and plasma spectrometry

PLD processes in this work

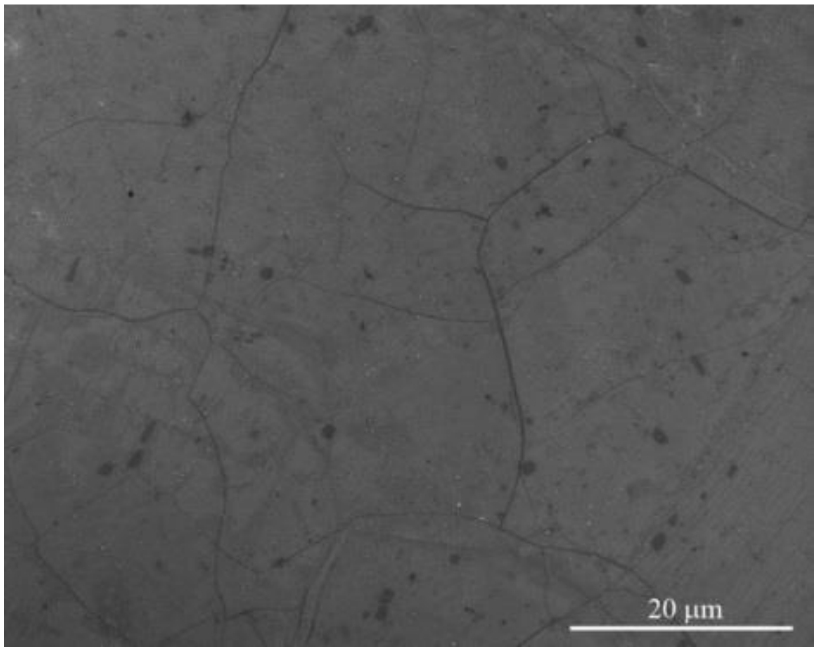
- **Sensor structures**: lab-grown CVD graphene, transferred onto Si/SiO_2 substrates pre-patterned with Ti/Au electrodes
- Functionalization by PLD process using different deposition targets (**ZrO_2** and **Ag**) ablated by KrF excimer laser.
- The process was carried out in oxygen or nitrogen gas at $5x10^{-2}$ mbar.
- A series of depositions was made with the number of laser pulses 20…2850

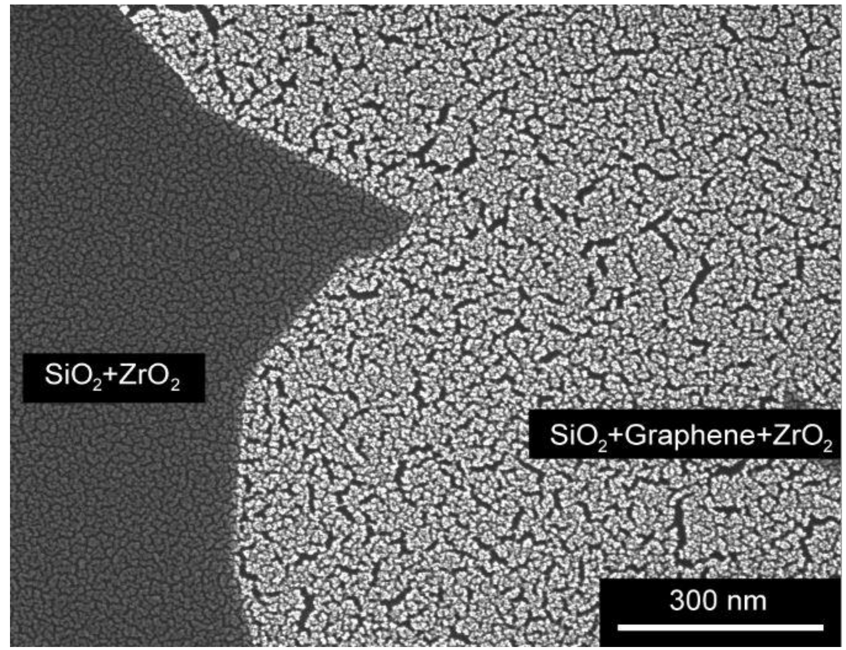


Choice of materials



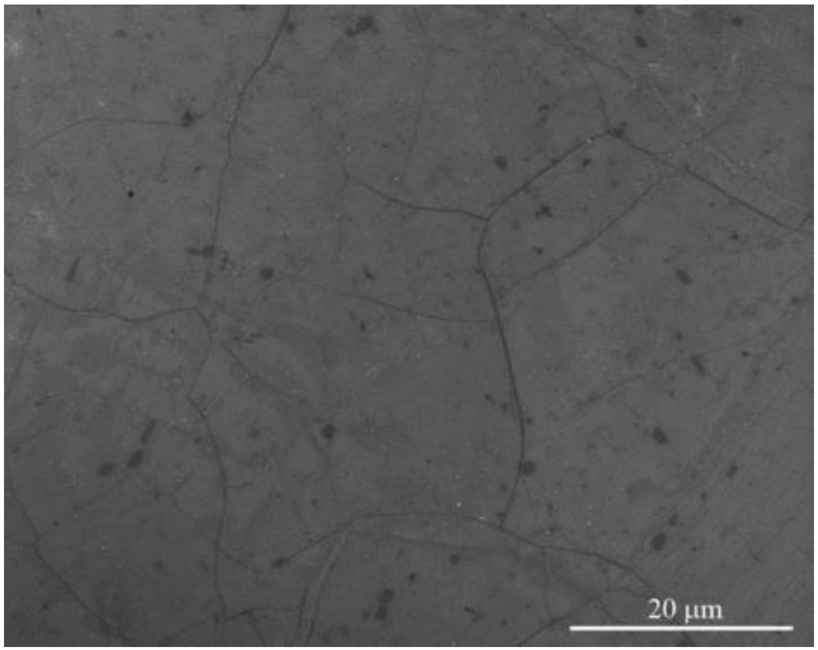
Nanostructured ZrO_2

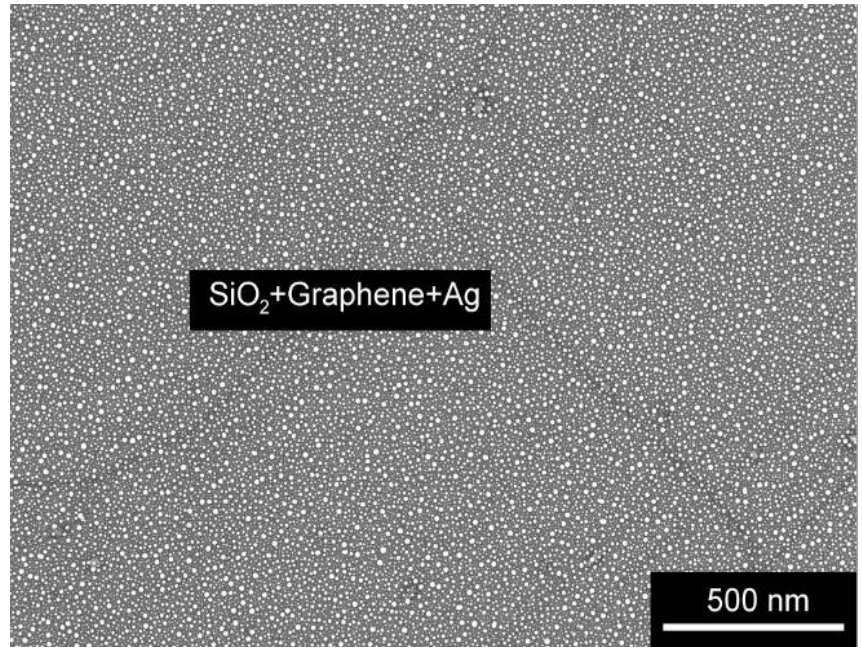




final layer thickness 14 nm; ~50% pores

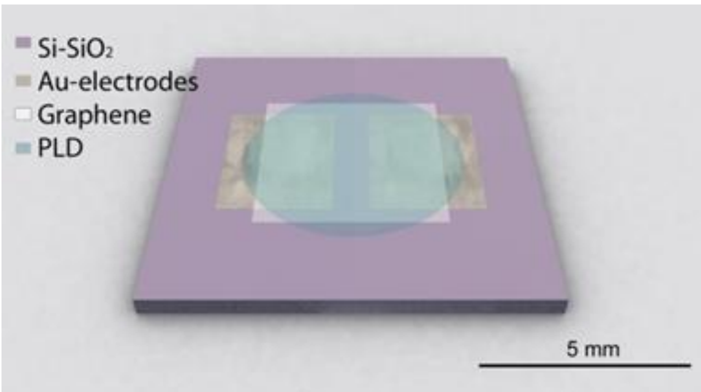
Nanostructured Ag

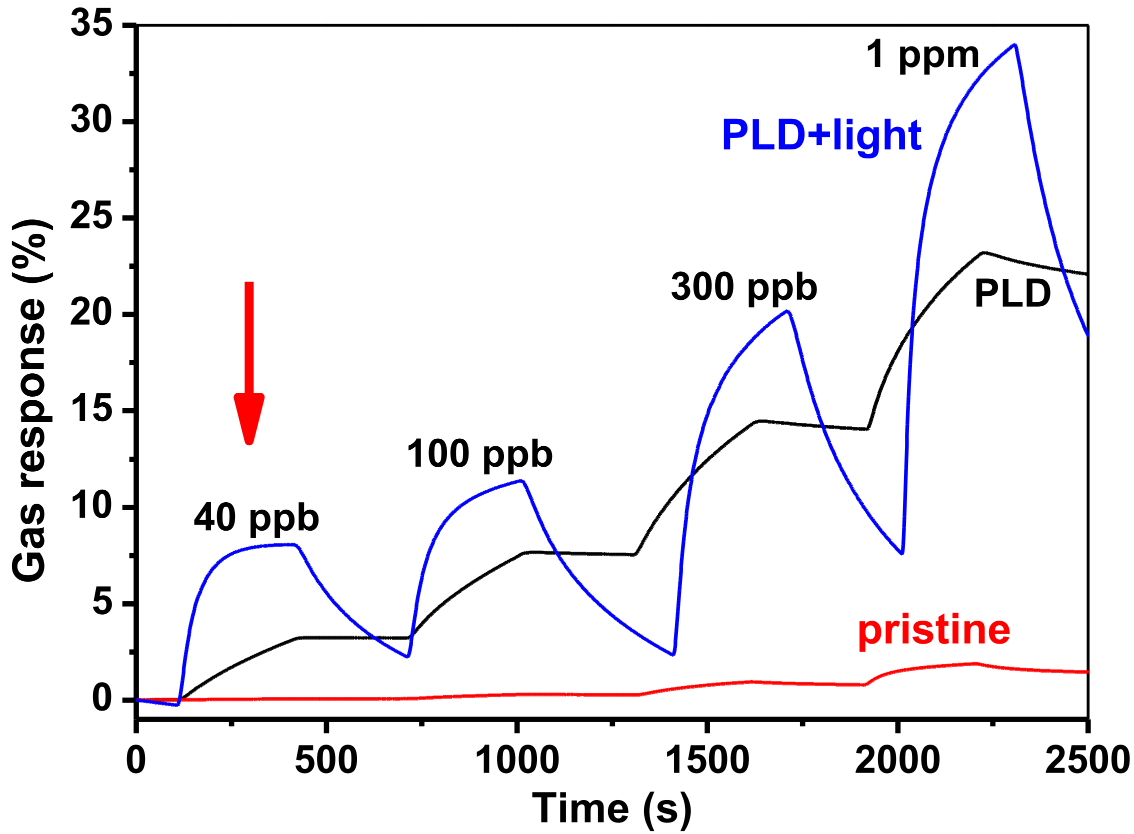




Ag „average“ thickness 1nm; particle diameters ~10 nm

Graphene/ZrO_2 NO_2 in air at RT

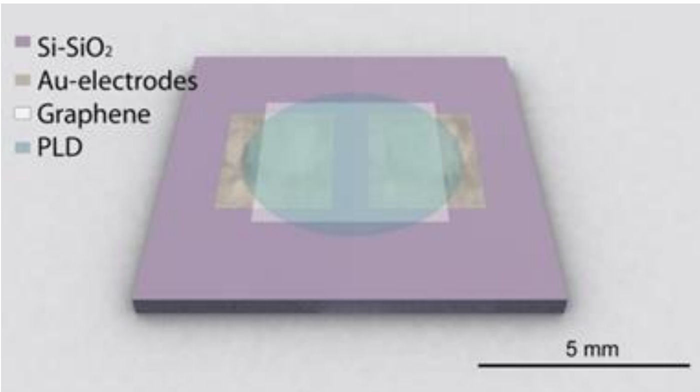




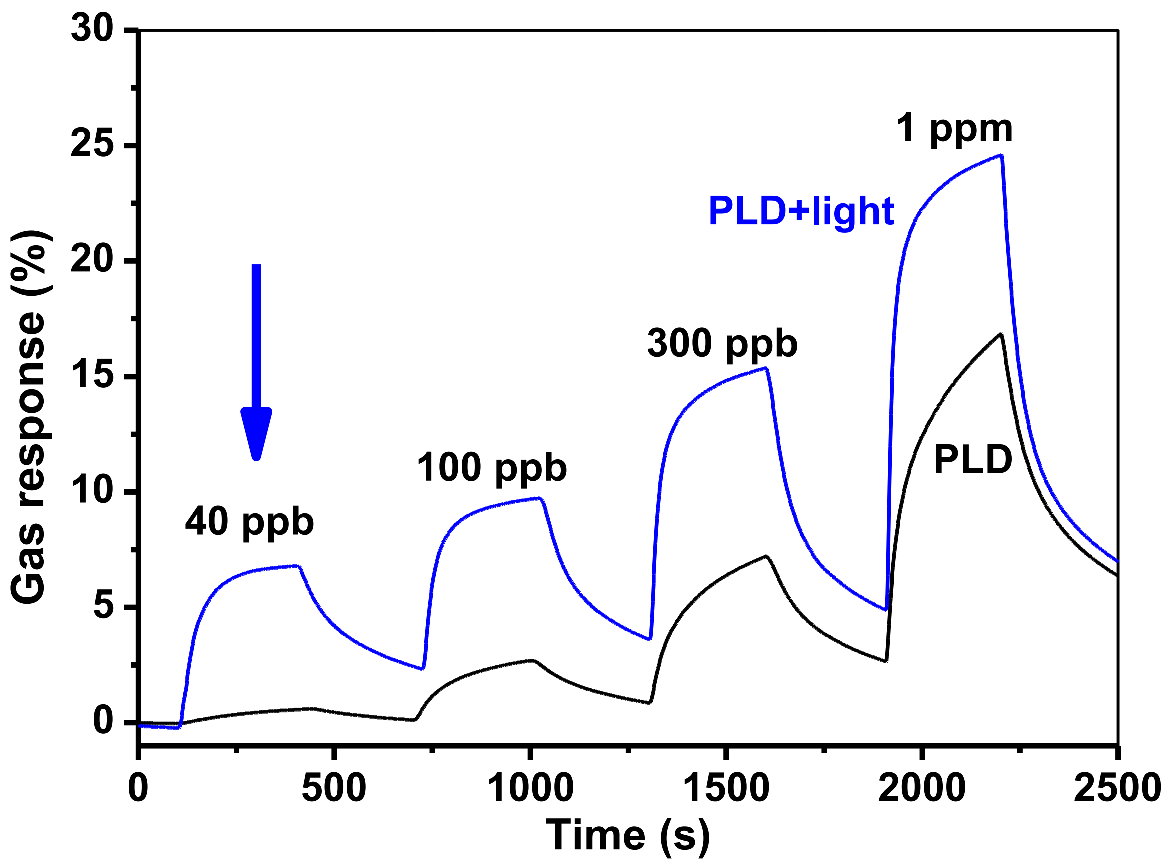
Effect is especially large at low concentrations

Graphene/Ag

NO_2 in air at RT



- Partial recovery w/o light
- Light enhancement is essential at low concentrations

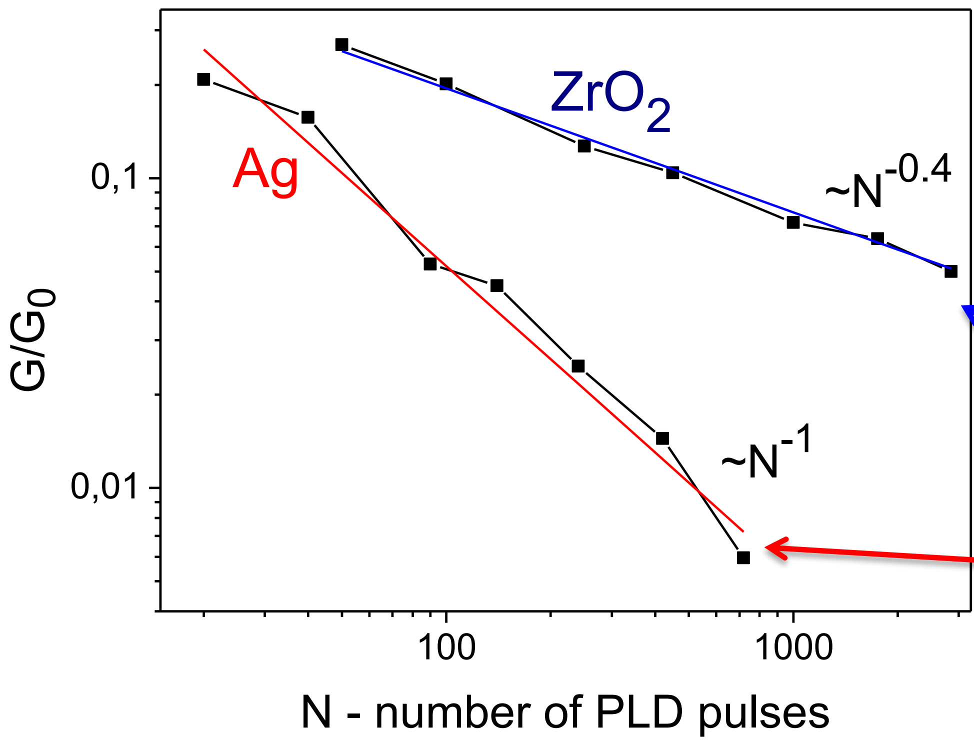


Why increased sensitivity?

Characterisation:

- SEM
- XPS
- XRF
- Spectrometric ellipsometry
- Conductivity
- Raman spectroscopy

Conductivity

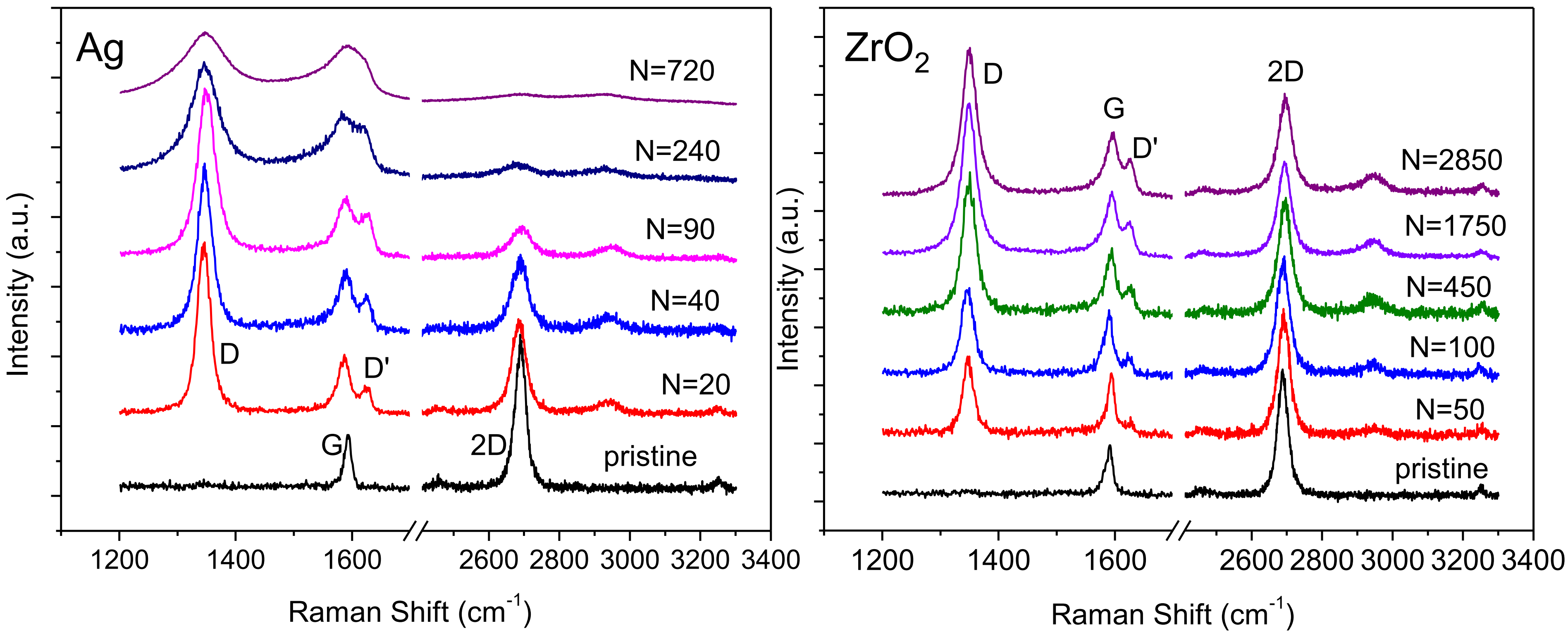


G_0 – conductance of pristine graphene

7 nm layer (if uniform)

1 nm layer (if uniform)

Raman spectra

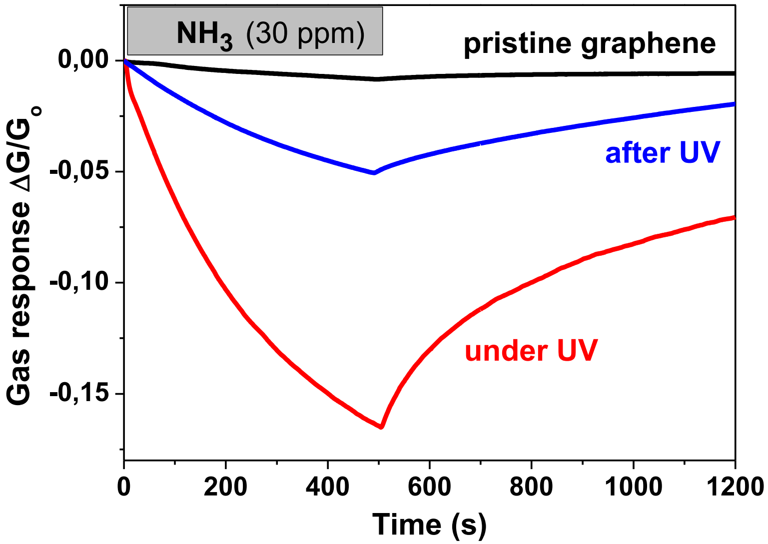


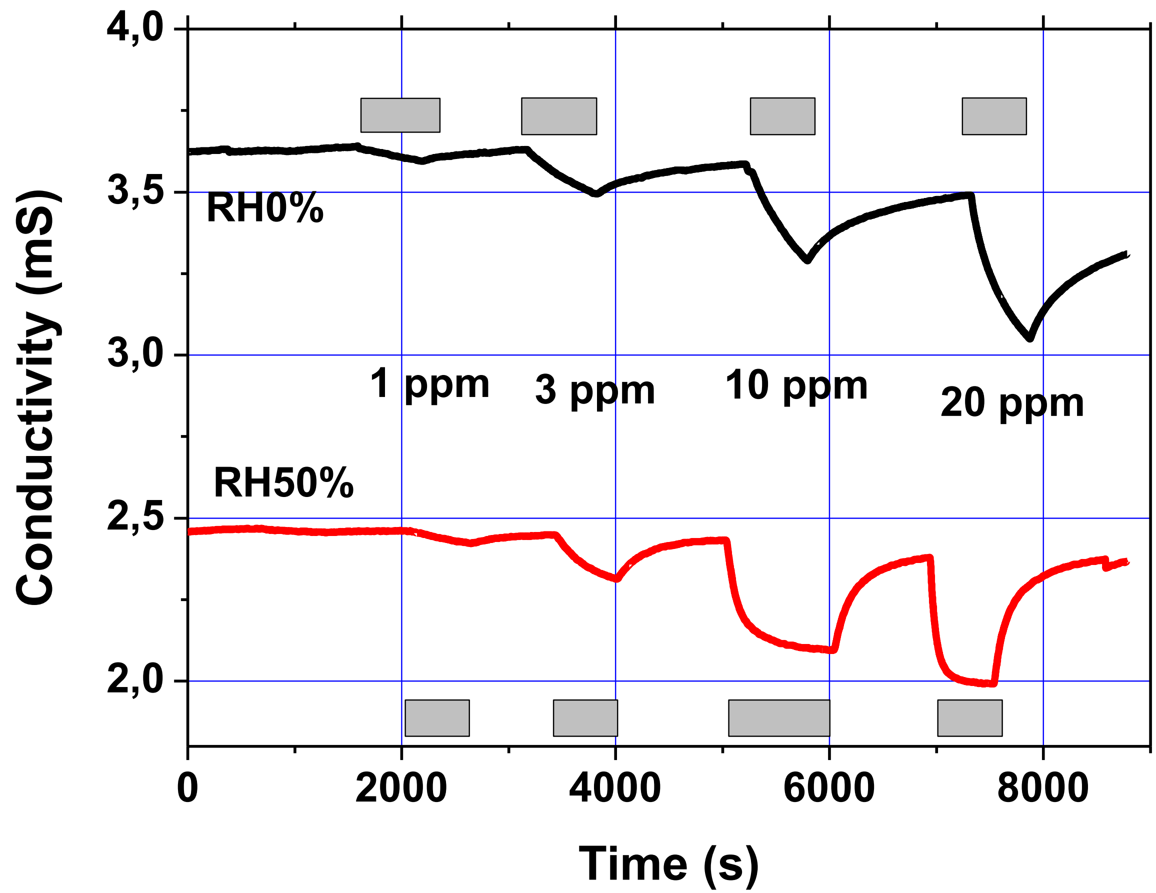
Defect-related lines D and D’ emerge and grow with the number of laser pulses N

Why increased sensitivity?

- Large relative response cannot be explained just by decreased conductivity, new adsorption centres should have been formed.
- Ag has much stronger interaction with graphene than ZrO_2. At the same time, it weakens the interaction with NO_2.
- What about other gases?

UV activation of sensitivity to NH_3





Summary

- PLD can be used to functionalize graphene -> increased AND diversified gas sensitivity
- Mild UV light (365 nm, <1 mW) can activate and enhance gas sensitivity
- Significantly increased sensitivity demonstrated at low NO_2 concentrations, below 100 ppb!

Collaborators and support

Group of Sensor Technologies

- Dr. Tea Avarmaa
- Dr. Margus Kodu
- Artjom Berholts (PhD student)

Lab of Thin Film Technology

- Dr. Harry Alles
- Dr. Ahti Niilisk
- Tauno Kahro (PhD student)

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Thank you very much for your attention!