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DEVELOPING AIR QUALITY SENSORS BY LASER DEPOSITION ON GRAPHENE

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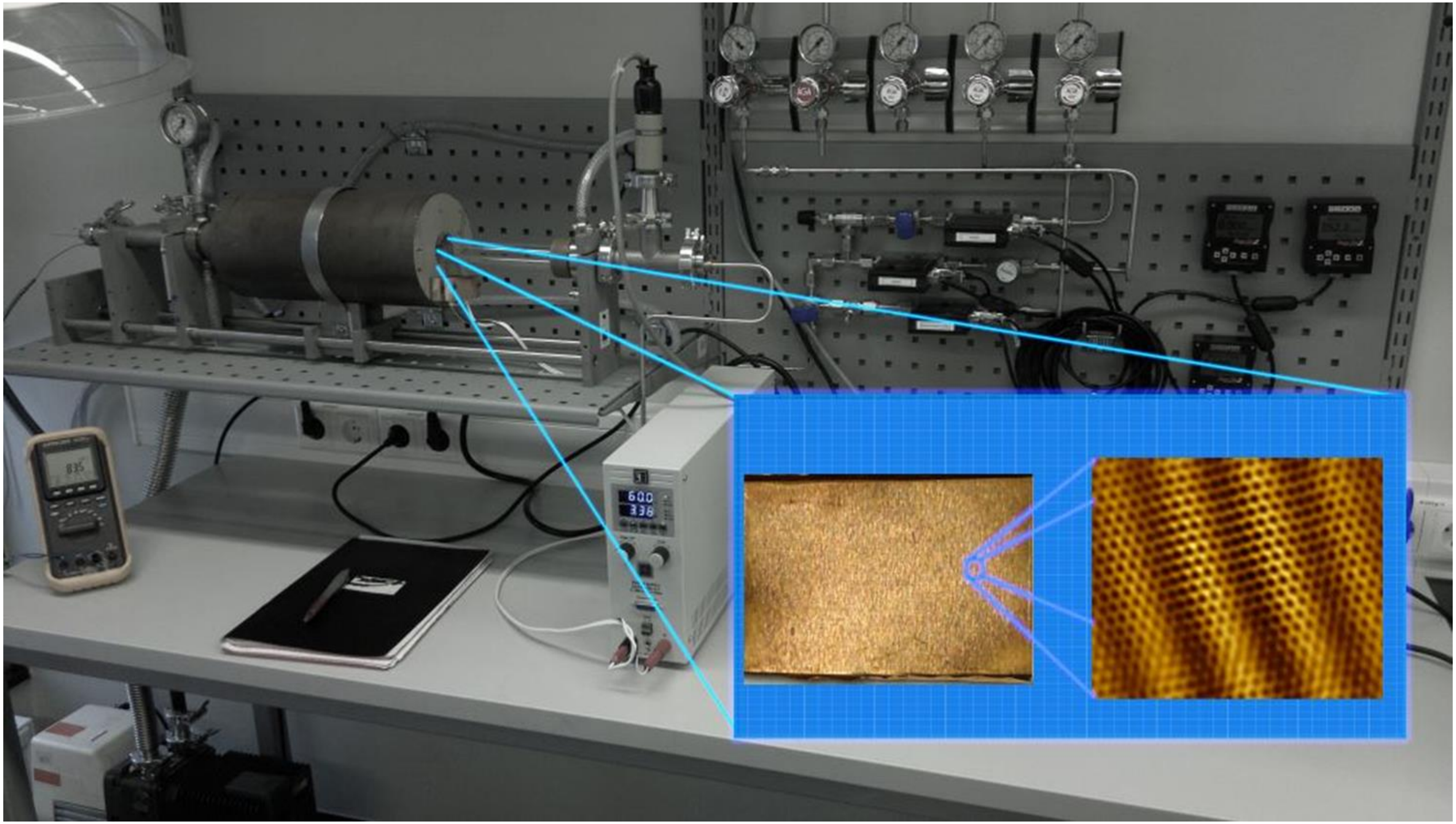
Outline

- Motivation
- Fabrication of graphene sensors
- Sensibilisation by PLD (pulsed laser deposition)
- Benchmarking NO_2 sensors
- Explorations for other gases
- Conclusions

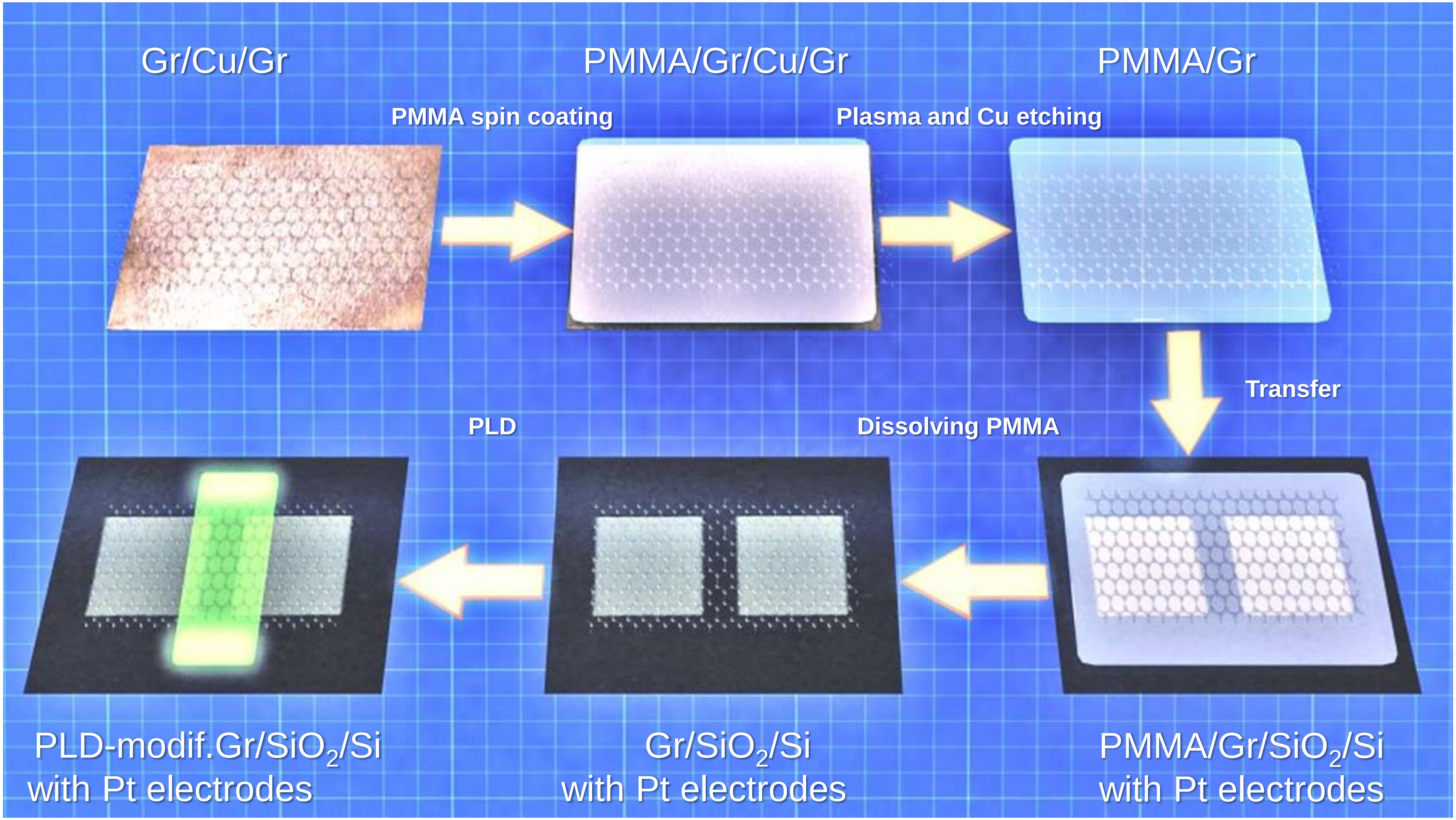
Motivation

- High potential of graphene – fully exposed to environment; responses to single gas molecules have been demonstrated
- For unlocking the potential of graphene new approaches are required for increasing the sensitivity in real atmospheric measurements and for making the devices selective to different target gases
- **A fruitful technique is the sensibilisation of single layer graphene by pulsed laser deposition (PLD). Depending on PLD target material and process parameters, adsorption centres with different properties can be created at the defects, impurities, and phase boundaries.**

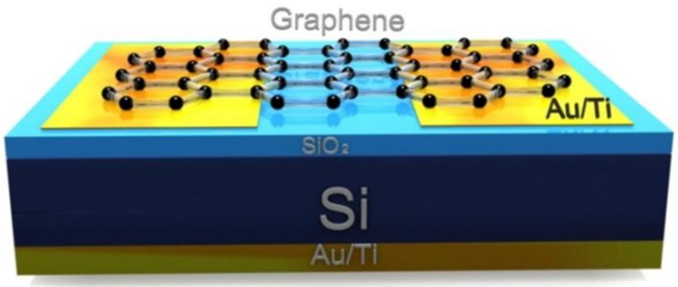
CVD growth of graphene



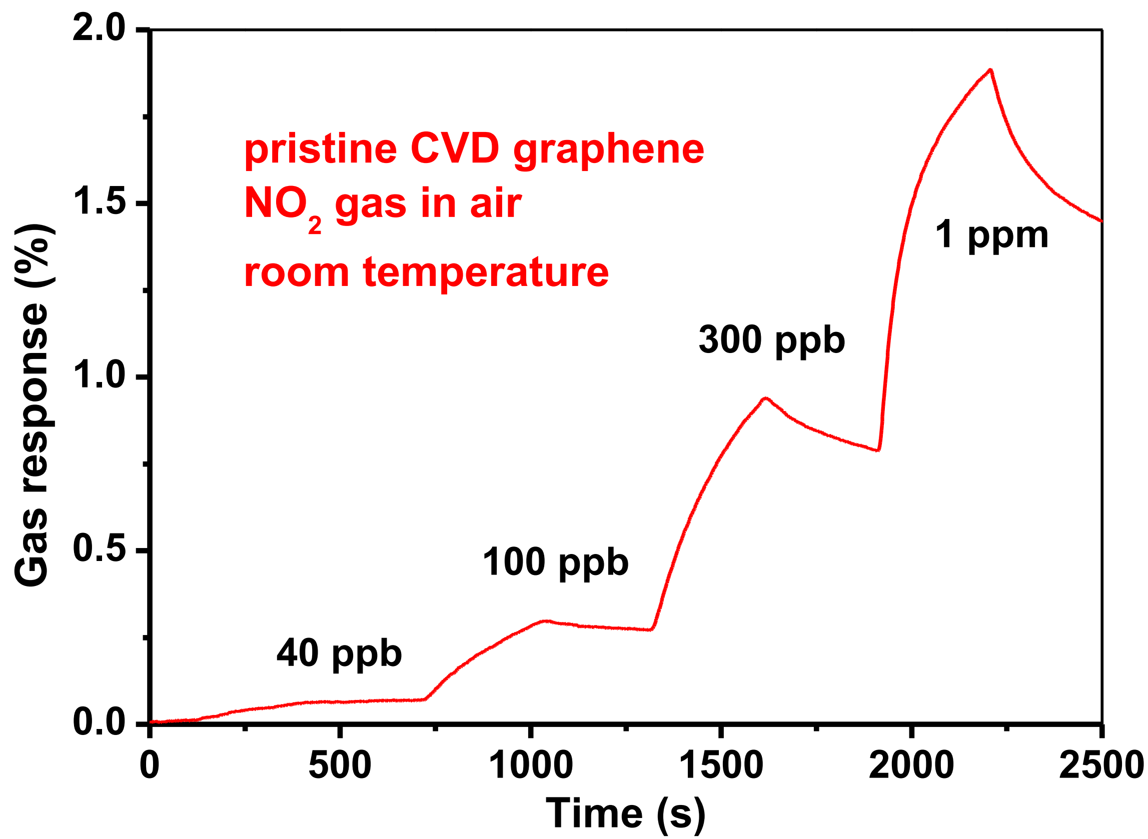
Fabrication of sensors



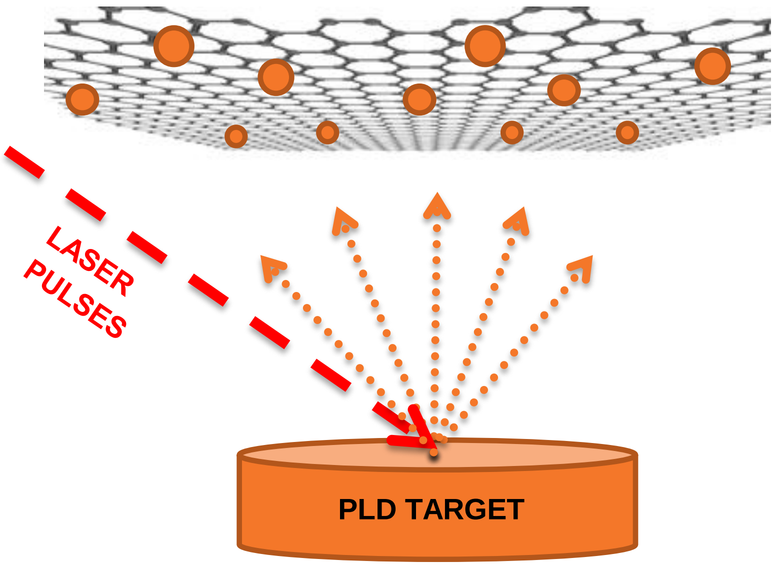
Pristine CVD graphene



In ambient conditions the response is almost absent or <1% level

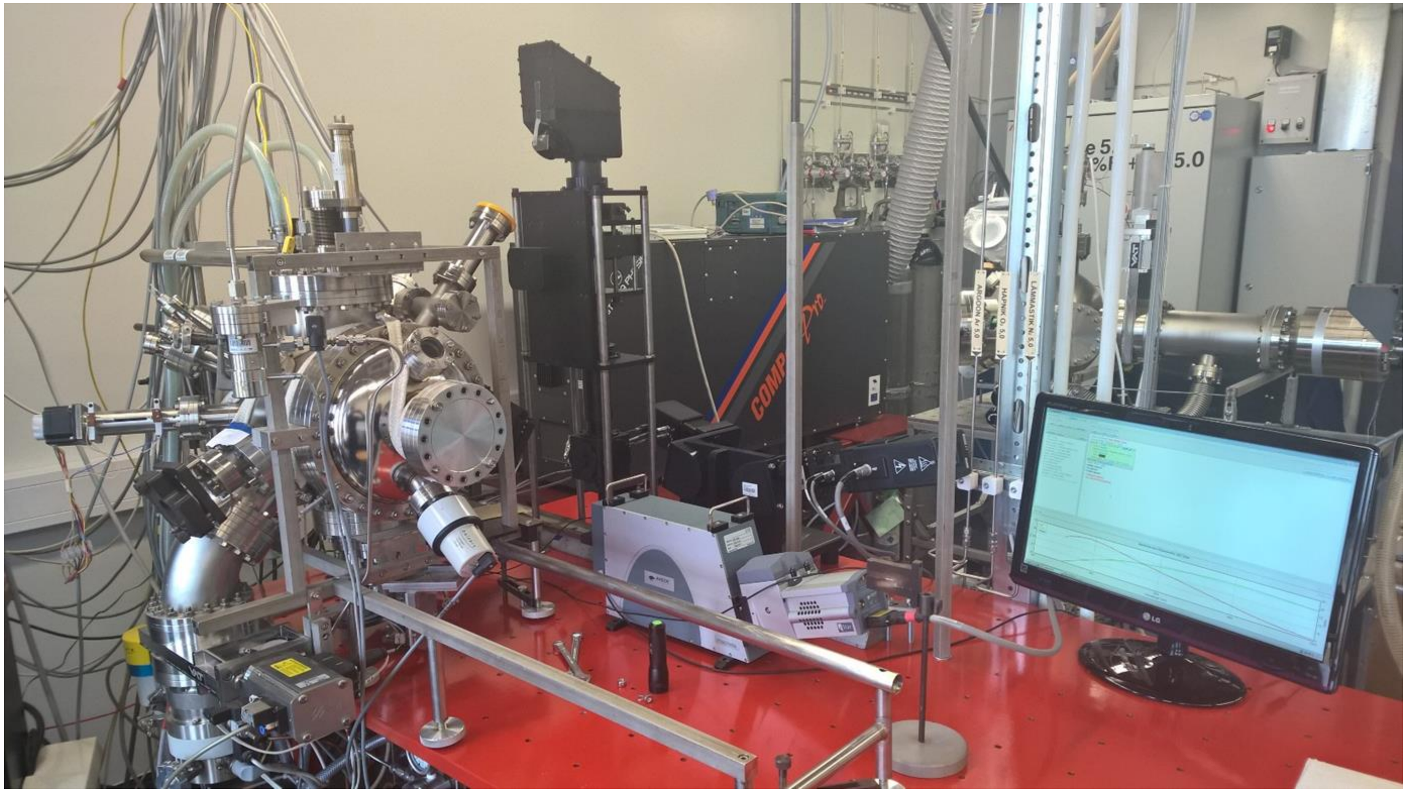


Sensibilisation by pulsed laser deposition (PLD)



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

PLD facility



KrF laser

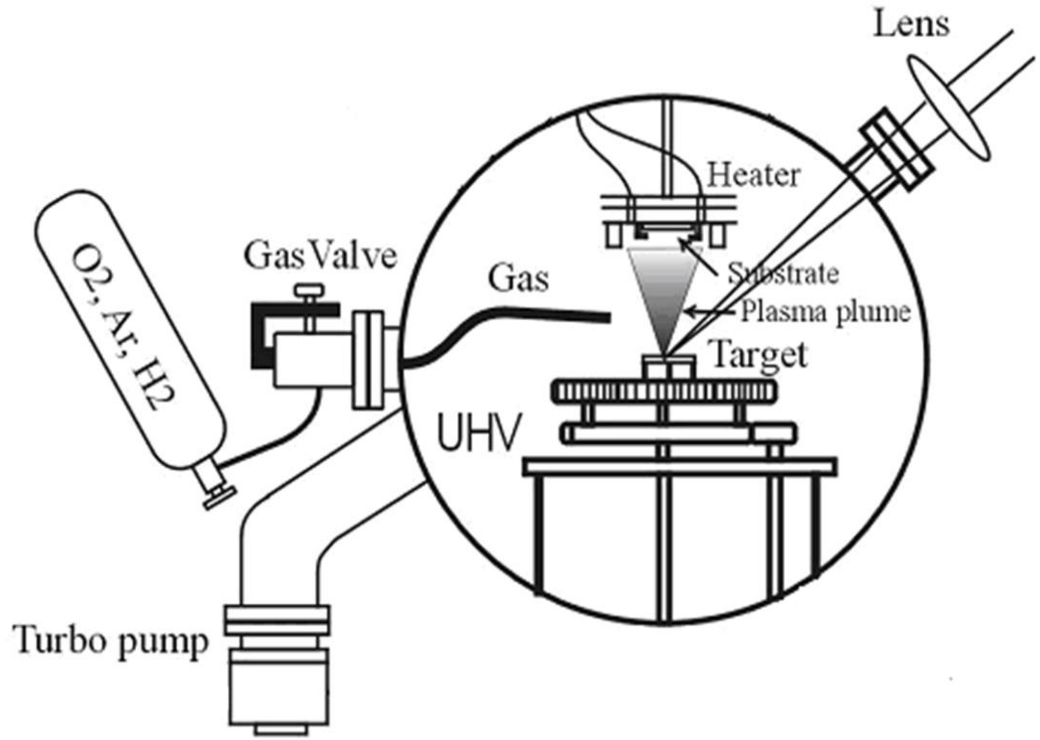
- 248 nm
- 25 ns
- 1 - 50 Hz
- 2-7 mJ/cm^2

Process control by ellipsometry and plasma spectrometry

PLD processes

The process was carried out in

- vacuum ($<10^{-6}$ mbar)
- oxygen or nitrogen gas at $10^{-2} \dots 5x10^{-2}$ mbar



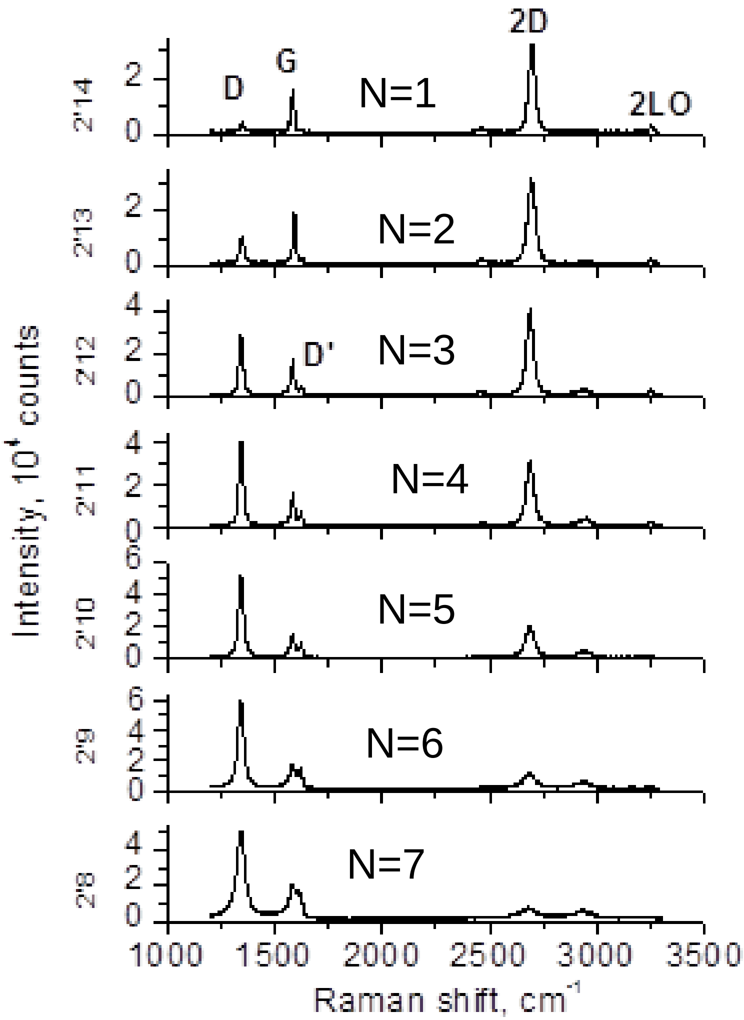
Number of laser pulses 1…3000

Deposition materials (targets):

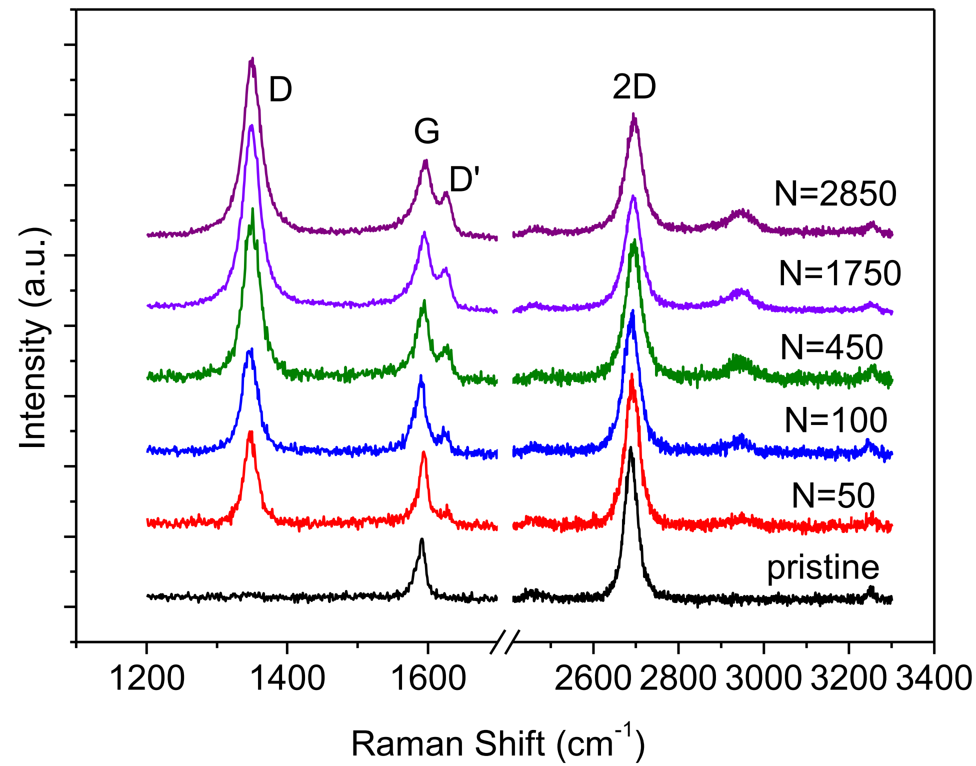
- Oxides (NiO, ZrO_2, SnO_2, TiO_2, V_2O_3)
- Metals (Ag, Au, Pd, Ru)

Raman spectra

P=10^{-6} mbar

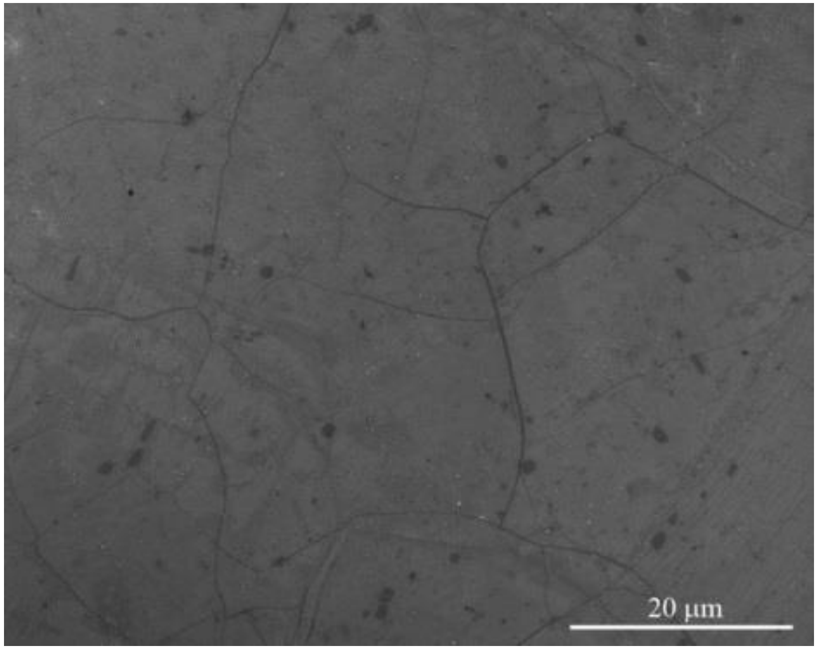


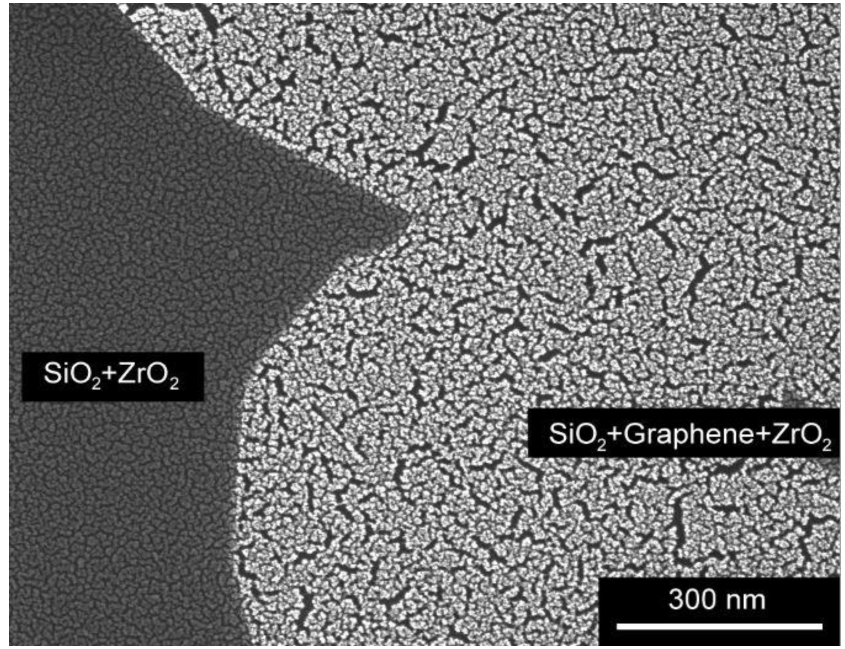
P=10^{-2} mbar



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

SEM images

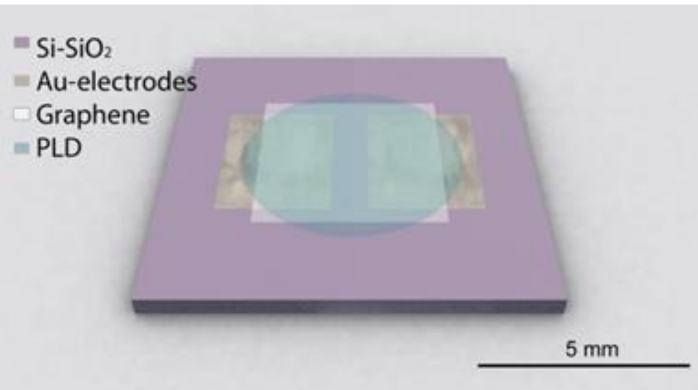


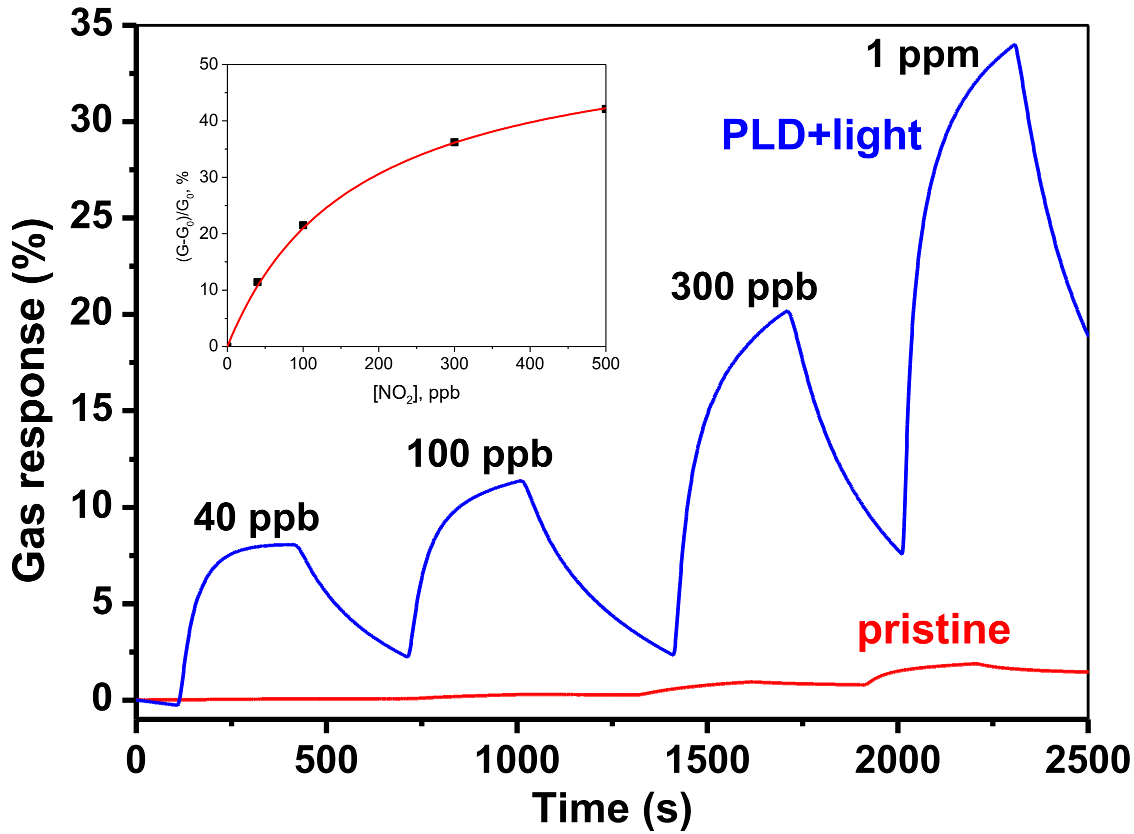


From single defects to porous nanostructures

Graphene/ZrO_2

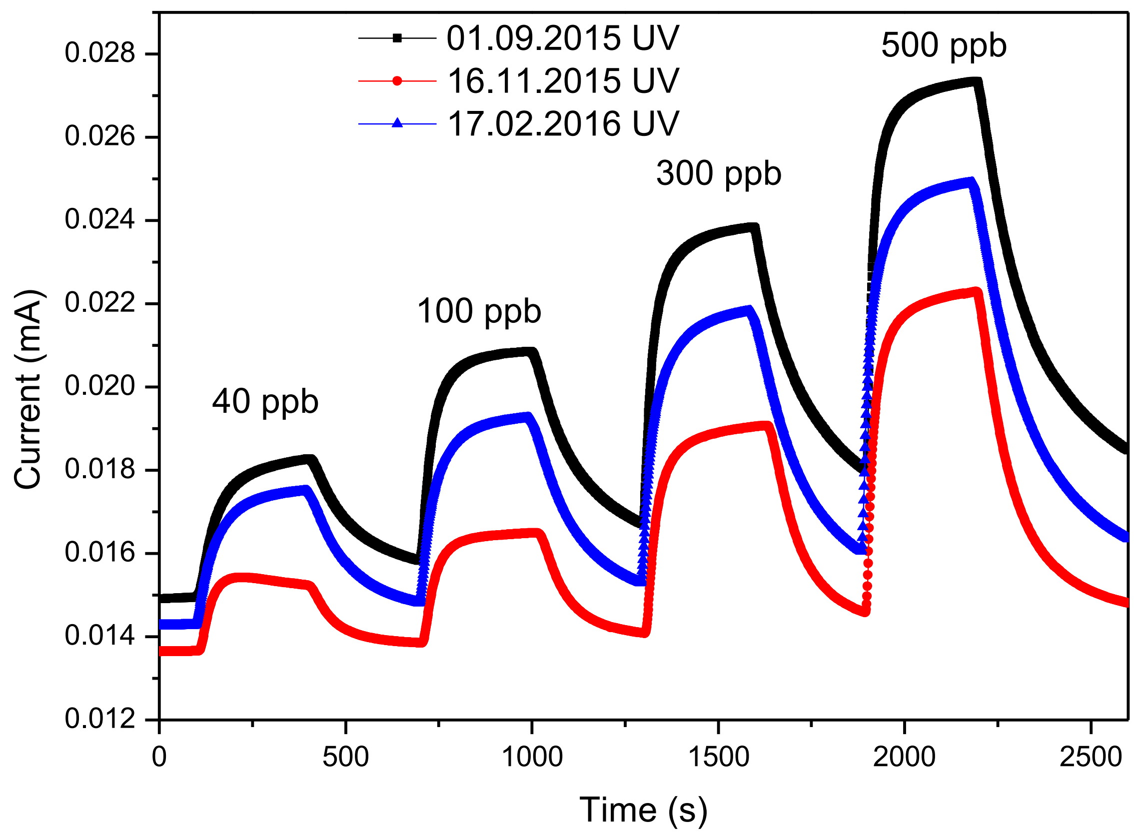
NO_2 in air at RT



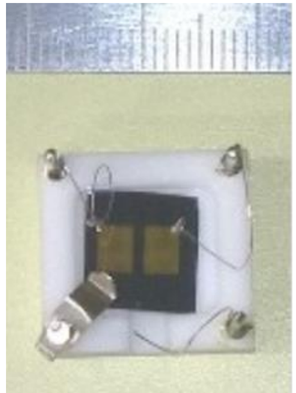


~50 times higher response after PLD

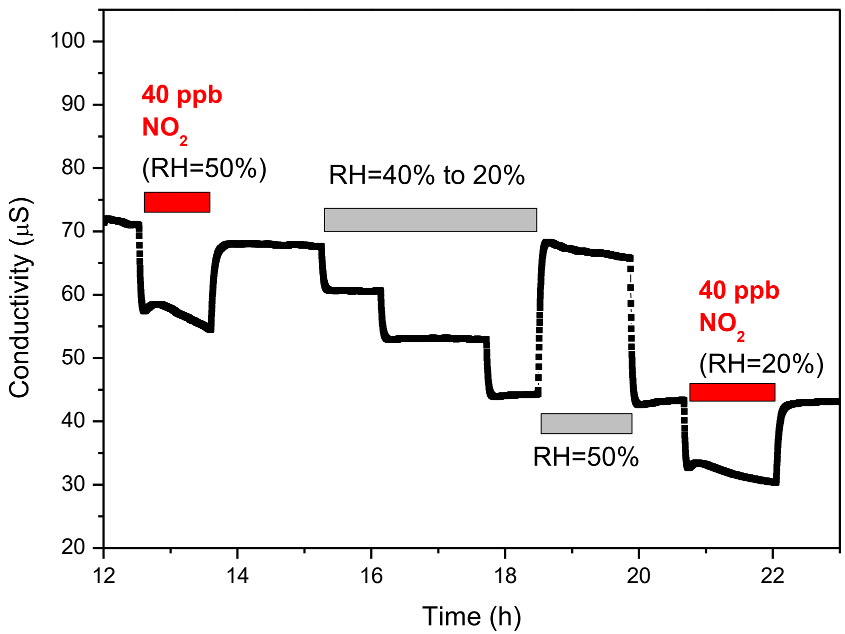
Stability of NO_2 sensor on graphene/PLD(TiO_2)



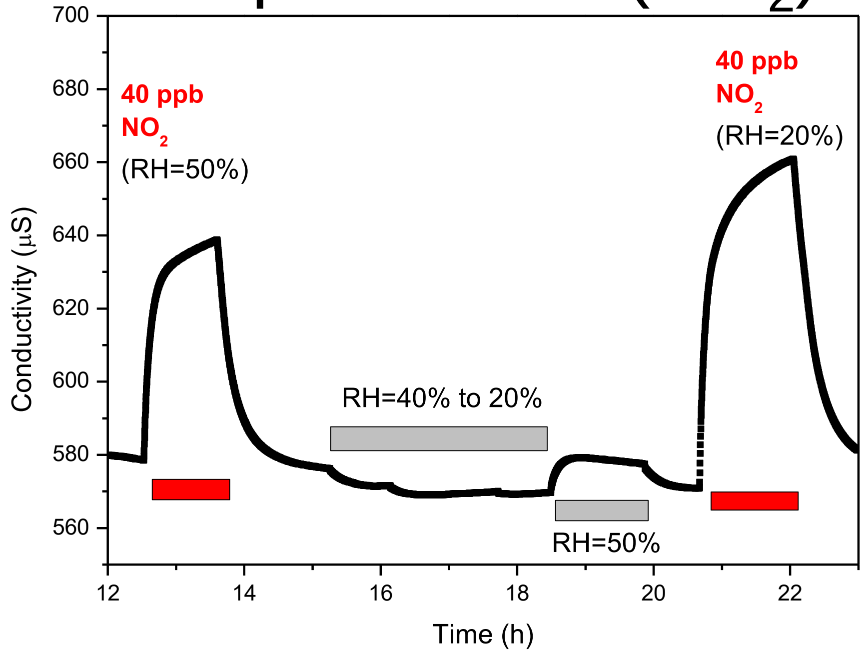
Benchmarking (I)



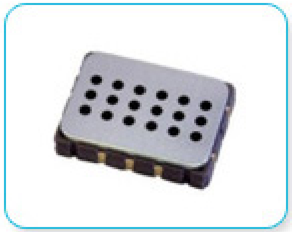
MICS-4514



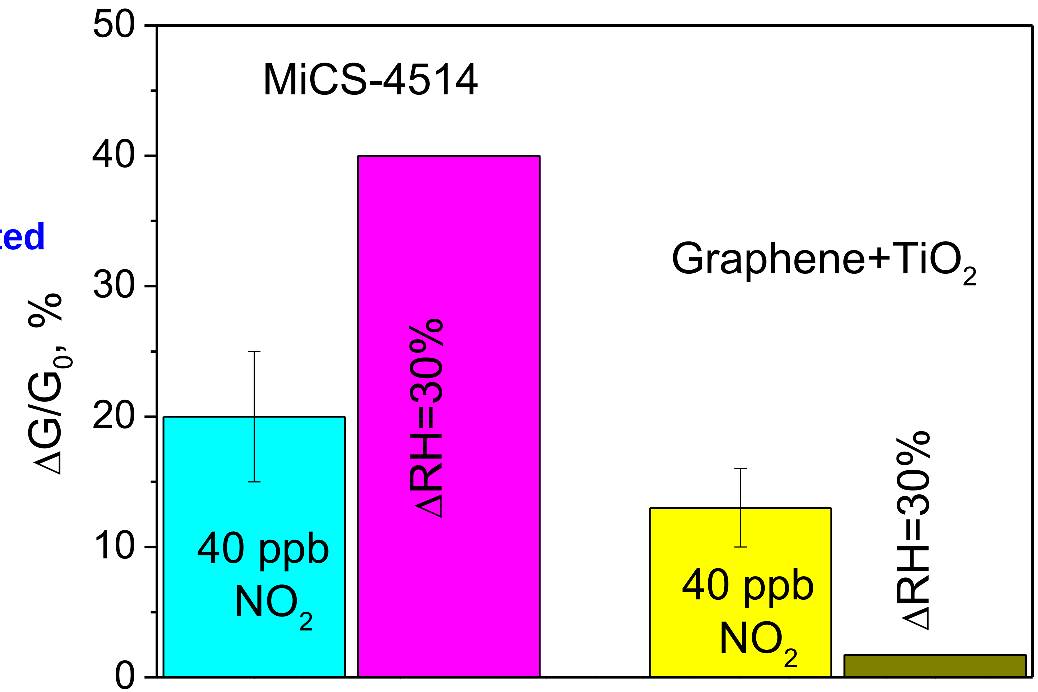
Graphene/PLD(TiO_2)



Benchmarking (II)



SGX Sensortech Limited



Highly selective: responses <1% for CO (100 ppm) and SO_2 (5 ppm)

Beyond NO_2?

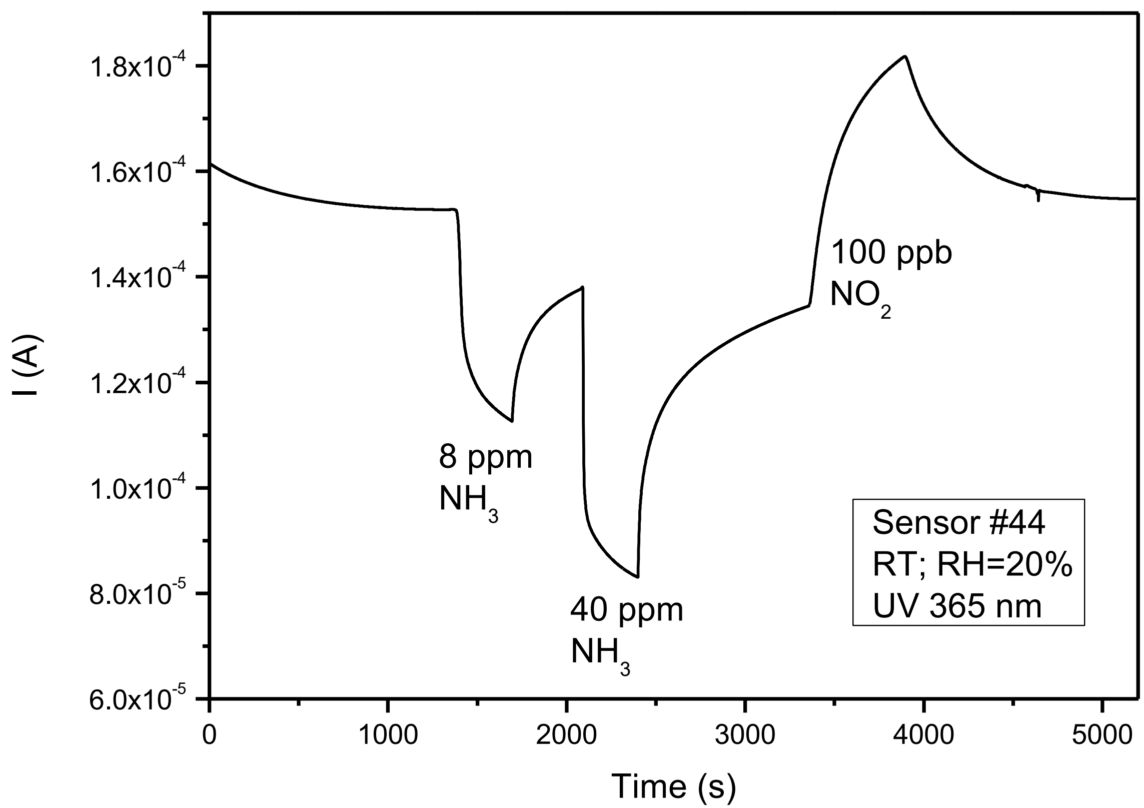
Increased sensitivity towards NO_2 was obtained in case of all PLD targets/processes tested.

Look at electron affinities:

- NO_2 – **2.273** eV
- SO_2 – 1.107 eV
- O_2 – 0.45 eV

Any hope for other gases?

Sensing NH_3 with graphene/PLD(SnO_2)



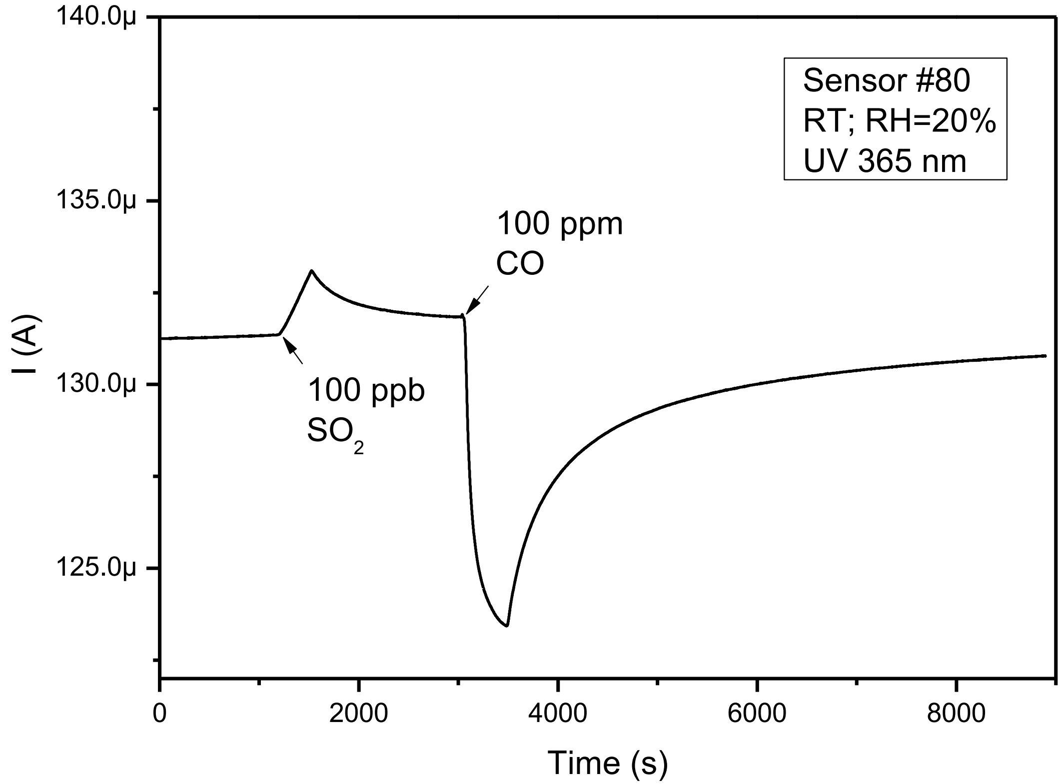
Responses to different gases

Oxide/Gas	NO_2	NH_3	CO	SO_2
TiO_2	X	x	0	0
SnO_2	x	X	0	X*
V_2O_3	x	x	X	x

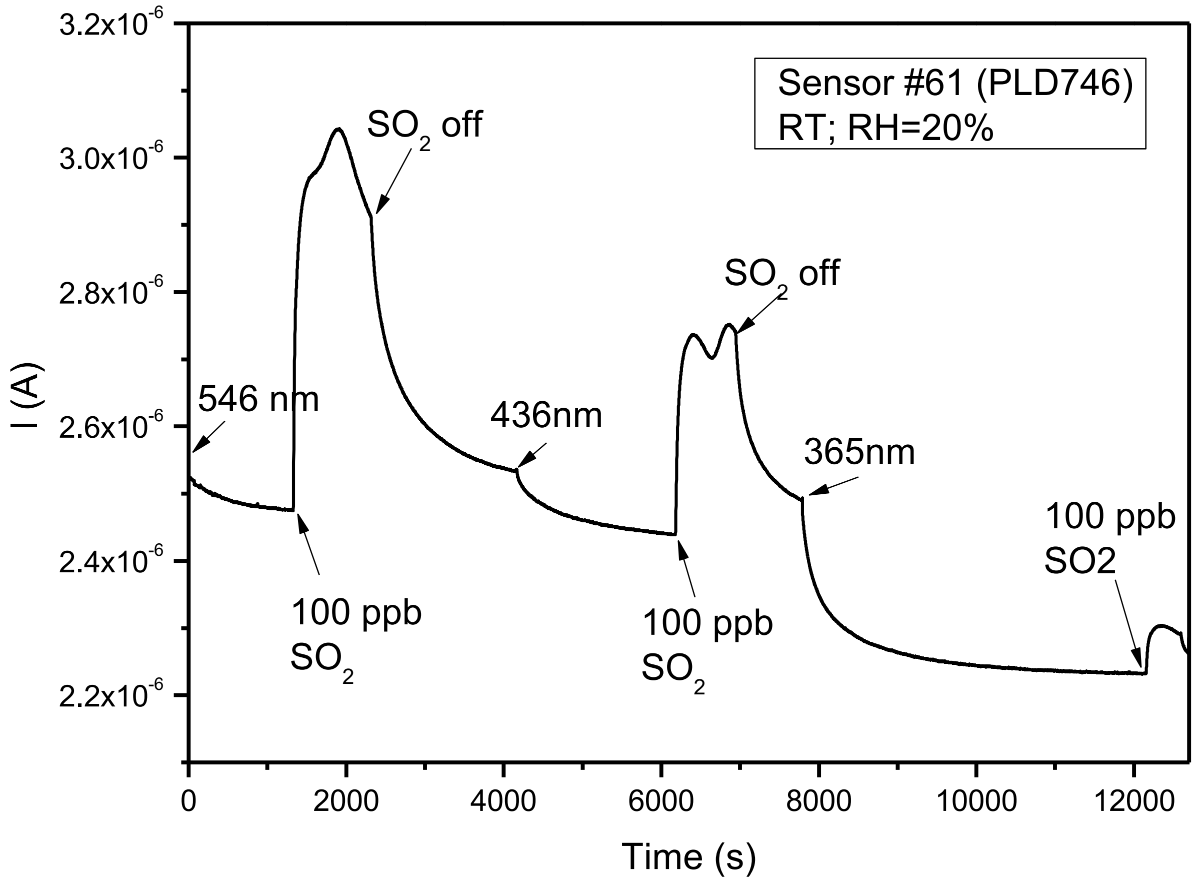
0 – response (almost) absent, x – ‘normal’ response, X - largest response. X* - sensor made by 2-stage deposition.

The gas concentrations were typically at 100 ppb level for NO_2 and SO_2 and at 10 ppm level for CO and NH_3.

Sensing CO with graphene/PLD(V_2O_3)



Sensing SO_2 with graphene/PLD(SnO_2)



2-stage PLD:

1) 6 high energy pulses – defects with average distance ~4 nm

2) 3000 low energy pulses (in back-ground gas) – ~10 nm thick porous coating

CONCLUSIONS

Main achievements:

- Graphene/PLD NO_2 sensors
  - Prototypes fabricated, calibrated, benchmarked
  - Small influence of humidity
  - Stable over 5 months
- Potential for other gases (NH_3, CO, SO_2) demonstrated (for specific PLD targets and process parameters)

open PROBLEMS:

- Understanding the factors behind selectivity!
- New (simpler) fabrication routes?

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!