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Development of a graphene based ammonia and NOx gas sensor

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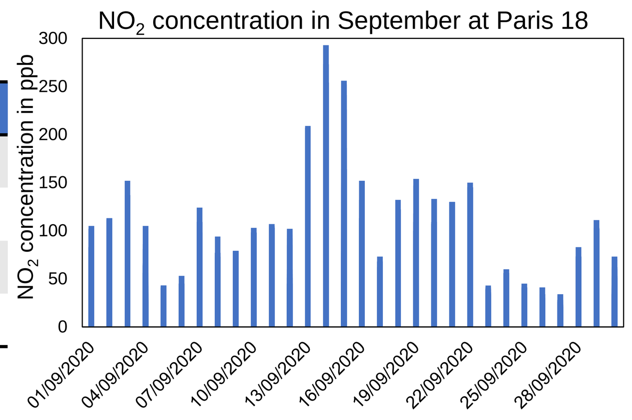
ONERA THE FRENCH AEROSPACE LAB

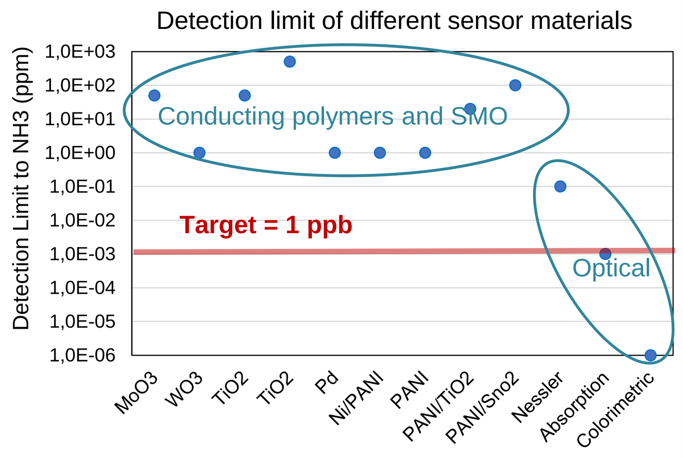
I – Context

- New requirements in NO_2 and NH_3 detection [1]-[2]-[3]: detection limit up to 1 ppb and portable

Application	Detection limit	Response time	Temperature
Environnemental	0,1 ppb	Minutes	RT
Automotive	1 ppm	Up to 1 min	Up to 600°C
Chemical	20 ppm	Minutes	Up to 500°C
Medical	50 ppb	1 min	RT



- But usual sensors do not meet these specifications [4]
  - Conducting polymers and SMO are sensitive to the ppm with high energy consumption
  - Optical techniques suffer from high operating costs and limited portability



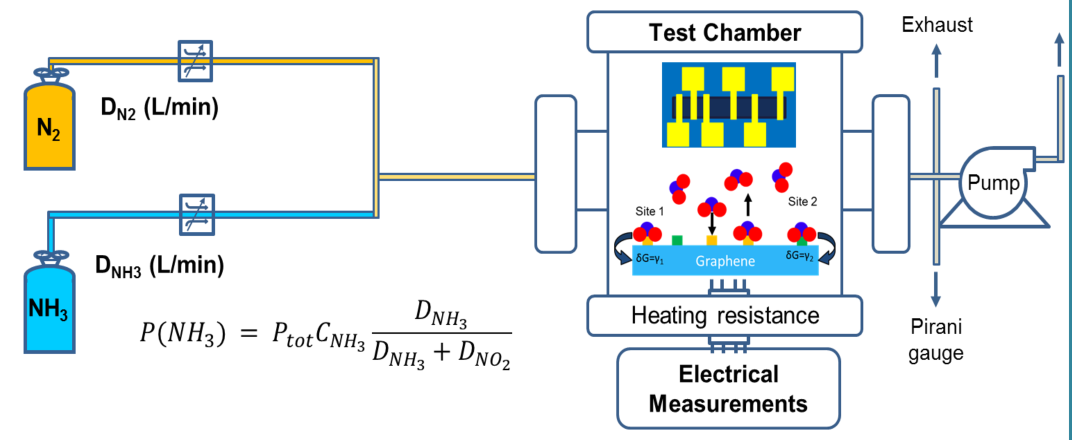
→ Need to develop innovative sensors

→ Graphene based sensor [5]:

- Highly sensitive to NH_3 and NO_2 (up to one molecule) with differentiated response
- Low cost and easy to build

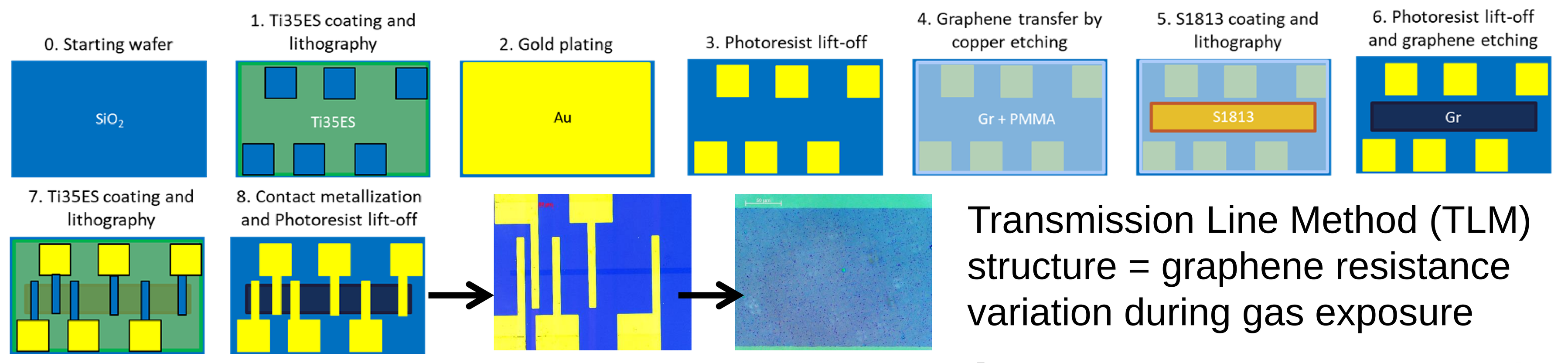
II – Experimental set-up & sensor design

- Gas environment:
  1. NO_2 or NH_3 flow + N_2 purge
  2. Vacuum up to 10^{-7} mbar
  3. Heated and passivated chamber
  4. Electrical Measurements



$$P(NH_3) = P_{tot} C_{NH_3} \frac{D_{NH_3}}{D_{NH_3} + D_{NO_2}}$$

- Production using photolithography methods and graphene transfer:



Transmission Line Method (TLM) structure = graphene resistance variation during gas exposure

→ $R = 2 \times R_c + R_{sheet} \times L/l$

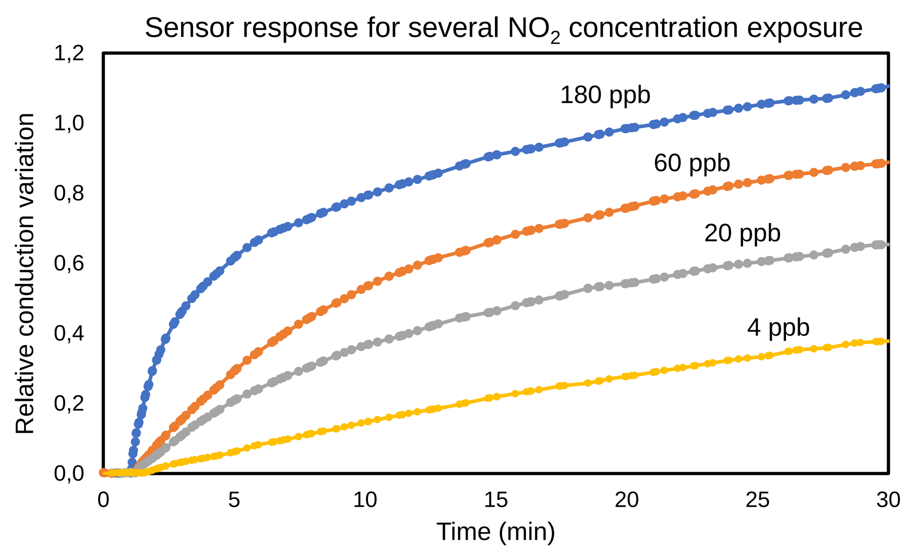
- "Langmuir" adsorption-desorption model with 2 distinct adsorption sites [6].
- Surface diffusion model through crystalline defective sites [7].
- Conductivity evolution: $G(t) = G_\infty - \gamma_1 N_1(\theta_{1,\infty} - \theta_{1,0}) e^{-\frac{t}{\tau_1}} - \gamma_2 N_2(\theta_{2,\infty} - \theta_{2,0}) e^{-\frac{t}{\tau_2}}$

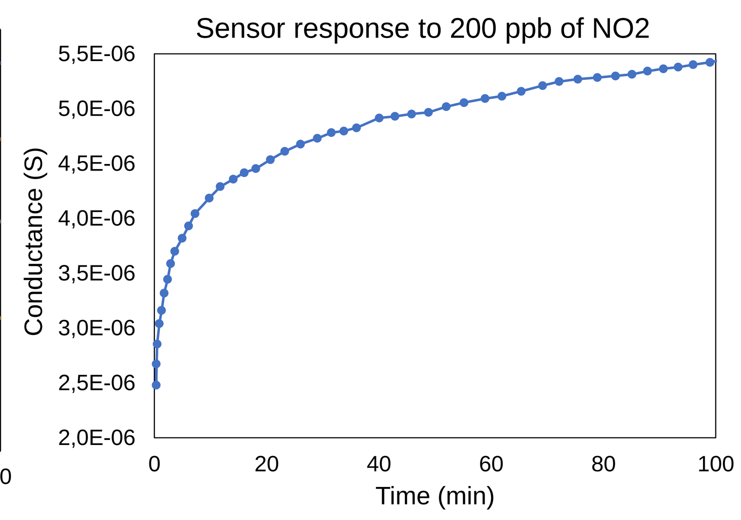
III – Sensor performance

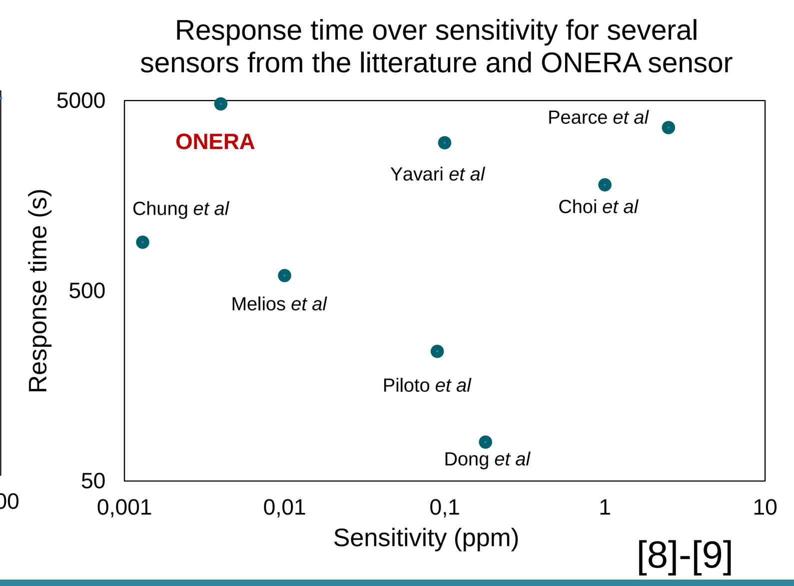
- Wide sensitivity range: From 1 ppb to hundreds of ppb

- Response time to 90% of the sensor response ≈ 5000 s

- Compared to literature:
  - Improved sensitivity
  - Longer response time







[8]-[9]

Pros:

- Sensitive to 1 ppb
- Repeatable measurement thanks to the experimental set-up
- Sensor easy to process and to use

Cons:

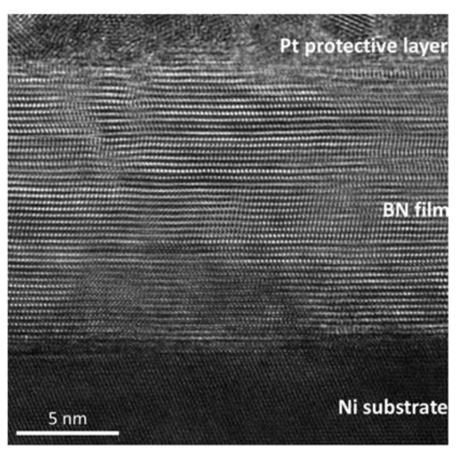
- Low response time, slow and complex kinetic
- Poor selectivity, the exposition to diluting gases (air, H2O, etc.) modify the sensor response
- Sensor reset and instabilities due the substrate

IV – BN substrate

- To enhance graphene mobility and reduce instabilities:

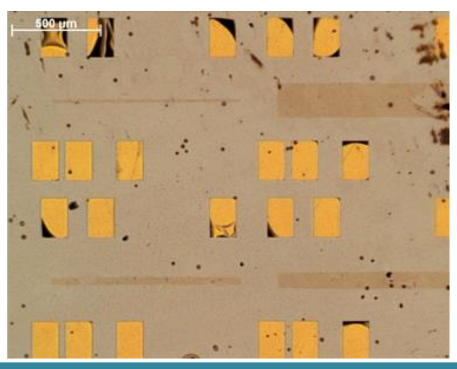
  → BN substrate (graphene structural equivalent, highly insulating)

- A 300K [10]:
  - self-standing Gr : 200 000 cm2/V/s
  - Gr/SiO2 : 20 000 cm2/V/s
  - Gr/BN : 140 000 cm2/V/s
- Expected [11]:
  - Sensitivity enhanced
  - Shorter response time
  - Substrate instabilities reduced
- Issues: few BN sources, no all-CVD devices



Device fabrication using CVD sp2-hybridized BN produced at the ONERA

- 800 nm Ni(111)/120 nm YSZ/Si(111) substrate
- Continuous multilayers BN films
- Regular atomic planes over the entire surface and thickness
- Sensor production directly on the BN growth substrate



After processing:

- Gold electrodes stability
- BN not deteriorated
- Graphene integrity preserved after the process

To do:

- Check BN insulating characteristics
- Experiment the device inside the gas chamber

V – Graphene fluorination

- Graphene functionalization to improve sensor properties:

  → Fluorination (collaboration with Uppsala University)

- Expected [12]:
  - High electron affinity with the ammonia molecule
  - Enhanced sensitivity and selectivity
- Ionic-fluorination [13]:
  - Functionalization as a final step of the process/before gas experimentation
  - Stable up to 200°C
- Electronic-fluorination has to be investigated [14]:
  - XPS: Temperature stability and adsorption/desorption mechanism
  - Raman spectroscopy: time stability under vacuum and inert atmosphere

Perspectives

- Fluorographene gas sensor with Boron Nitride substrate and pbb sensitivity

- Device and process adaptable for the production of various sensors with multilayer BN films on the growth substrate: Hall effect magnetometer, electric field sensor, etc.

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