The graphene sensor

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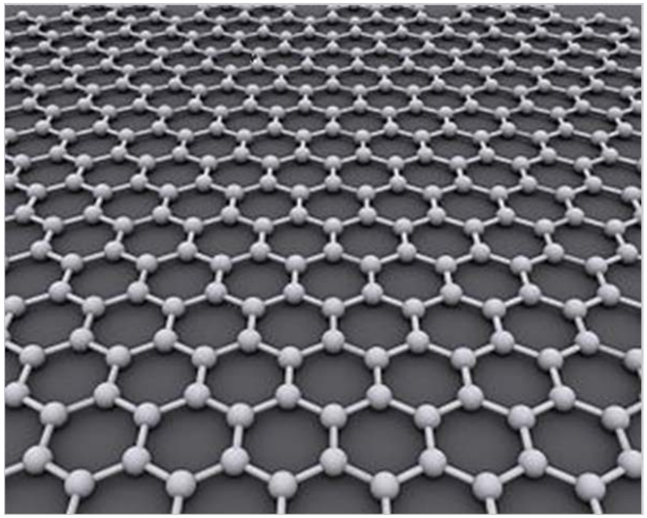
Environmental atmospheric pollutant monitoring – the target of current research

- Nitrogen monoxide (NO) and nitrogen dioxide (NO_2) are typical air pollutants that cause environmental problems.
- There are demands for a small and cheap gas sensor for NO_x detection in ppb concentration range.
- Graphene is the good candidate due to its unique properties.

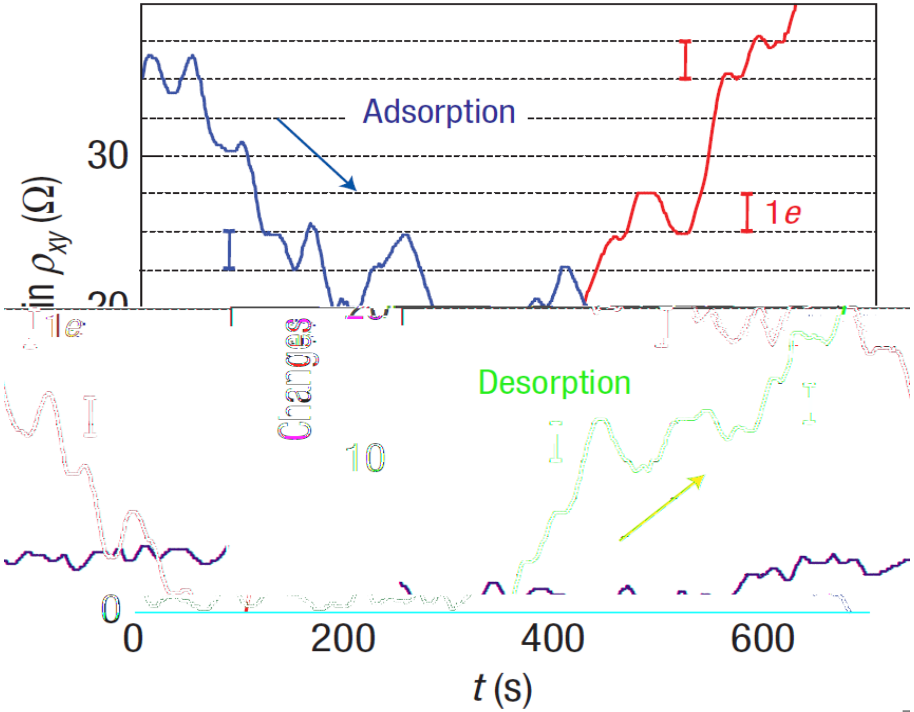
Why we choose graphene?



- Graphene is a two-dimensional crystal comprised of a monolayer of carbon atoms arranged in a hexagonal honeycomb lattice.
- Graphene has unique properties like high surface-to-volume ratio, low electrical noise, and exceptional transport properties associated with its two-dimensional structure.
- Adsorption ability and wide surface area of graphene make it attractive as a gas sensing material.

Detection of individual gas molecules adsorbed on graphene

Nature materials vol 6 (2007)



Changes in Hall resistivity observed during adsorption of strongly diluted NO_2 (blue curve) and its desorption in vacuum at 50°C (red curve). The green curve is a reference - the same device thoroughly annealed and then exposed to pure He.

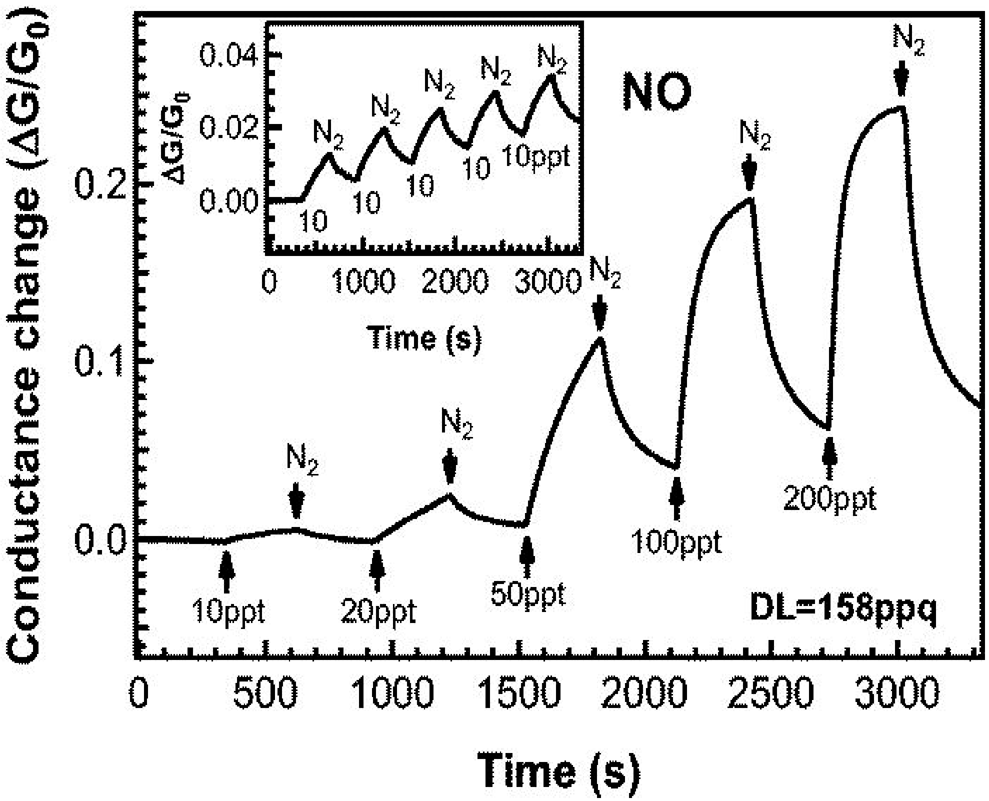
- Measurements were done for NO_2 diluted with ultra-pure He.
- Desorption was performed in vacuum.
- Hall resistivity was measured in magnetic field 10T.
- Experiments showed high potential of graphene-based gas sensor, but measurement setup was very far from condition for real application.

Epitaxially grown graphene based gas sensors for ultra sensitive NO_2 detection

Sensors and actuators. B, Chemical, 155, 2, 451-455 (2011)

- Epitaxially grown single layer and multi layer graphene on SiC.
- Simple resistive devices were fabricated and tested for NO_2 sensitivity.

Gugang Chen, Tereza M. Paronyan, and Avetik R. Harutyunyan
Nanoscale Science and Technology 101 (2012)

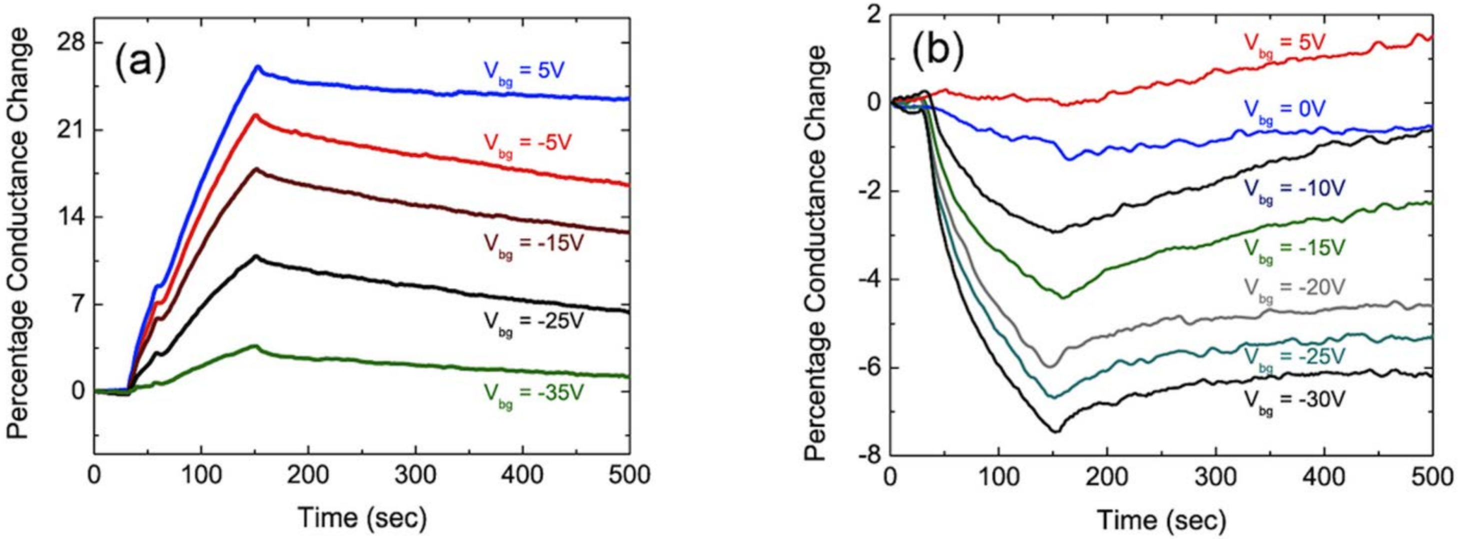


- UV light was applied during response measurement.
- UV irradiation drastically increased sensitivity as well as reduced recovery time.
- All measurements were done with ultrapure carrier gas flow.
- The detection limit was estimated as low as 158ppq.

Response on NO_2 exposure for graphene based sensor under UV irradiation

Electrically tunable molecular doping of graphene

Appl. Phys. Lett. 102, 043101 (2013



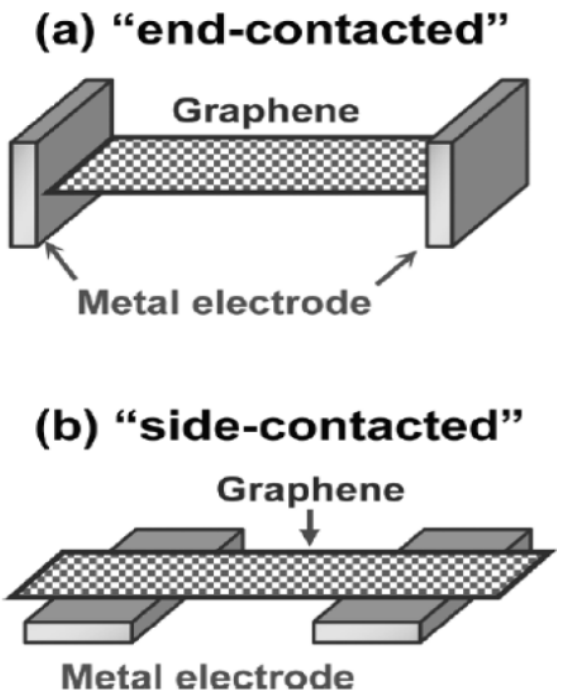
Variation of back gated graphene sensor response on (a) 20 ppm NO_2 exposure and (b) 550 ppm NH_3 exposure.

- Graphene based sensors face the problem of selectivity like other non-functionalized sensors.
- Back gating technique enhances sensitivity and selectivity of molecular detection, with oxidized Si substrate used as a back gate.
- Response on NO_2 gas exposure decreases from 26.1% to 0% under application of negative gate bias, while for NH_3, the response increases from 0% to 7.6%.

Problems with graphene based devices

- Gas sensing application requires operation at elevated temperature, that in turn generates high stress on the interface between metal and graphene on SiC: $\alpha_{SiC}=4x10^{-6}/^{o}C$, $\alpha_{Au}=14x10^{-6}/^{o}C$.
- The low adhesion of the graphene to the SiC or to the oxidized silicon surface leads to its detachment.
- A critical property for graphene based devices is the contact resistance at the metal-graphene interface.
- Instability of the metal-graphene interface contact resistance limits the precision of the gas concentration measurement.

J. Phys. Chem. C, 114, (2010)



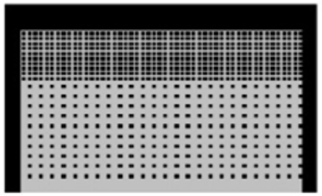
(a) Metal-graphene "end-contacted" interface.
(b) "Side-contacted" interface

- The current-voltage (I-V) characteristics and contact resistance of "end-contacted" metal electrode-graphene interfaces for Ti and Au were calculated.
- For "end-contacted" interfaces there was found a decrease in contact resistance by factors ranging from 6751 for Au to 8.8 for Ti as compared to the "side-contacted" interface.
- This suggests a strong advantage for developing technology to achieve "end-contacted" interface.

Contact shape optimization

a)

b)

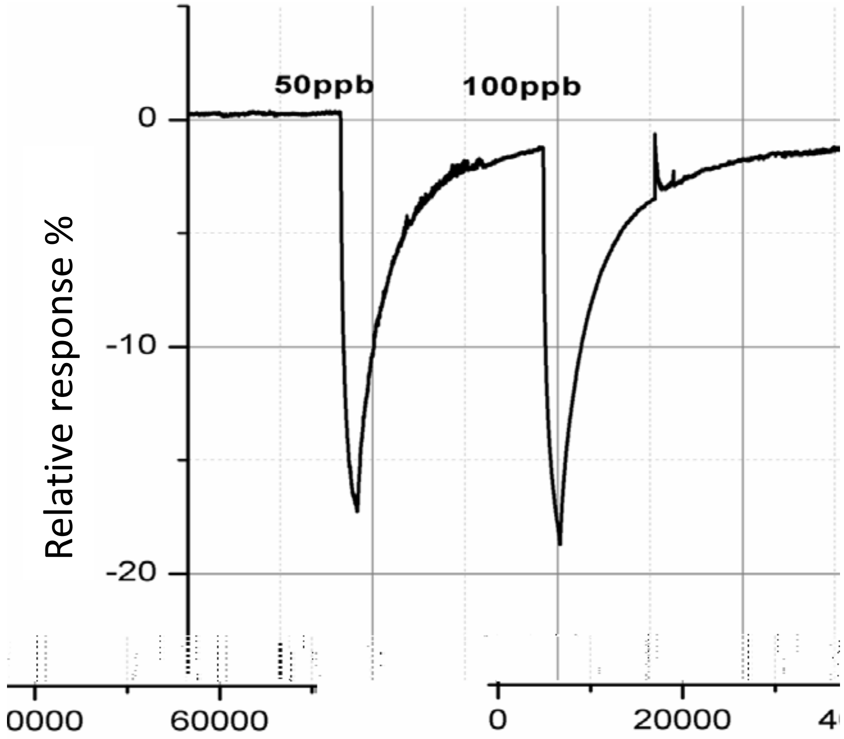


c)

Finger (a), dot (b) and flat (c) contact configurations

- Three different contact types of the first metallization (black color) which is directly bonded to the substrate were used.
- Second metallization always covered the area shown in picture as grey color overlapping the first metallization.
- We expected larger fraction of “end type” contact and therefore lower contact resistance for configurations with fingers (a) and dots (b).
- We expected better adhesion of the top metallization for (a) and (b) contact configurations.
- Configuration (a) shows about 2 times and configuration (b) about 1.5 times less contact resistance as compared to configuration (c).

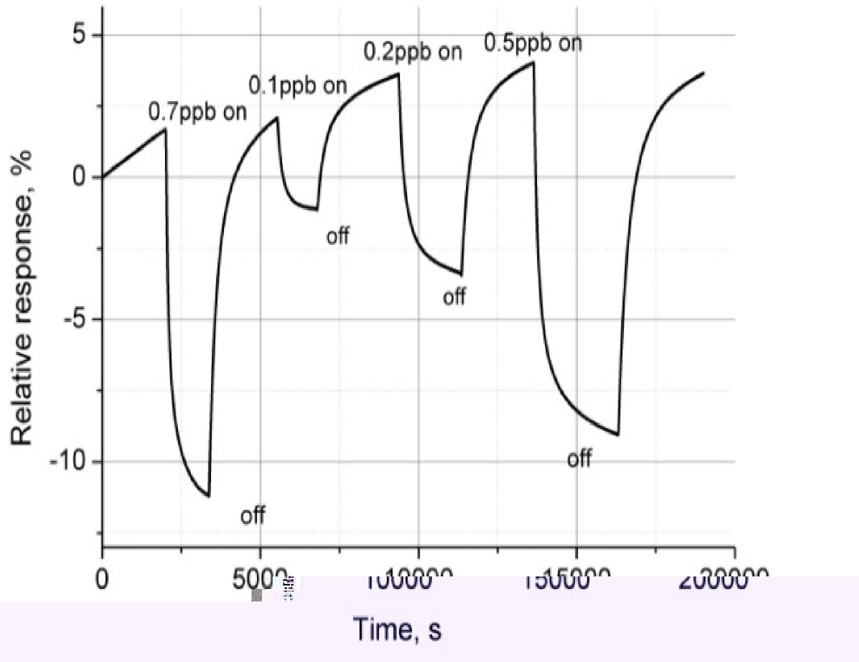
Response on NO_2 exposure for device with "flat contact" configuration



Response on exposure of gas mixture containing NO_2 gas at 100°C for graphene based device.

- Response is high, however noise, ripples and step-like resistivity changes indicate non-perfect contact between graphene and metal electrodes.
- Response, *r*, was expressed as a percentage, %, and defined as the relative change of the sample's resistance under exposure to the gas, $r = (R - R_o) / R$.

Optimized sensor response on NO_2 exposure



- Decrease in resistivity during NO_2 adsorption indicates p-type conductivity.
- Response is high, even for NO_2 concentration as low as 0.1 ppb
- No noise and ripples is recognizing.
- Contacts stability seems much better than for "simple" contact configuration.

Response on exposure of gas mixture containing NO_2 gas at 100^{o}C for graphene based device.

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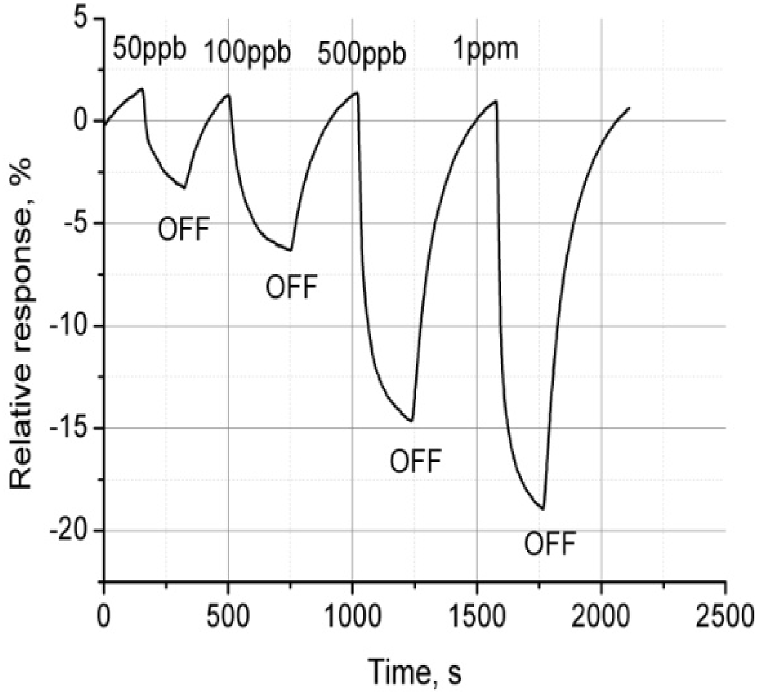
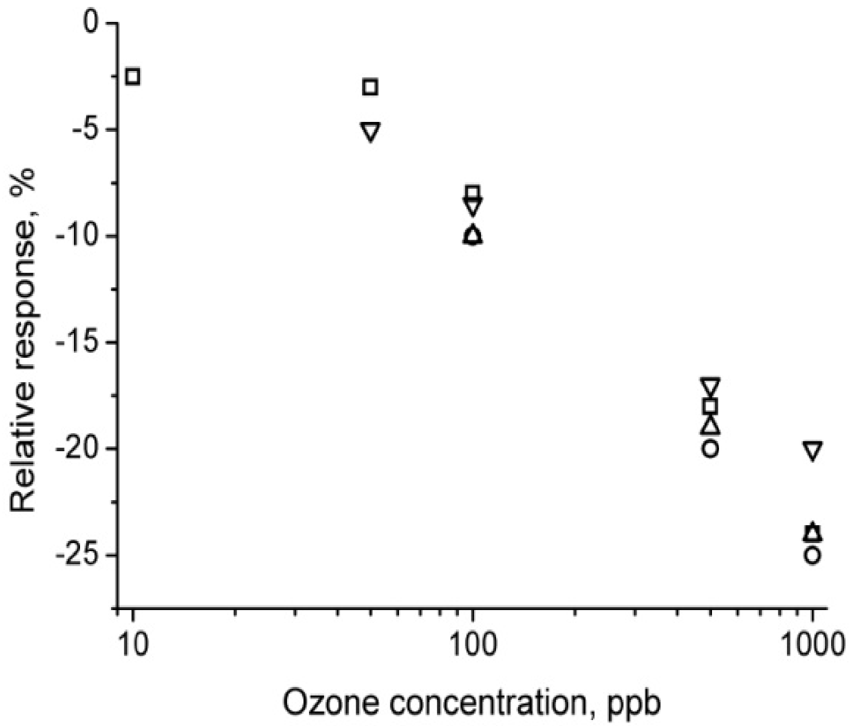
Graphene based device as ozone sensor



Response on exposure of gas mixture containing ozone at 120ºC for graphene based device.

- Calibrated source of ozone, ozone meters and gas analyser were used for the gas generating and the measurement of the output concentration.
- Due to high chemical activity of ozone, it was difficult in the current setup to control reproducibly the gas concentration in sub-ppb range.
- Minimal concentration was set to 50ppb, which is less than curent target value for ozone concentrations 60ppb in directive 2008/50/EC.

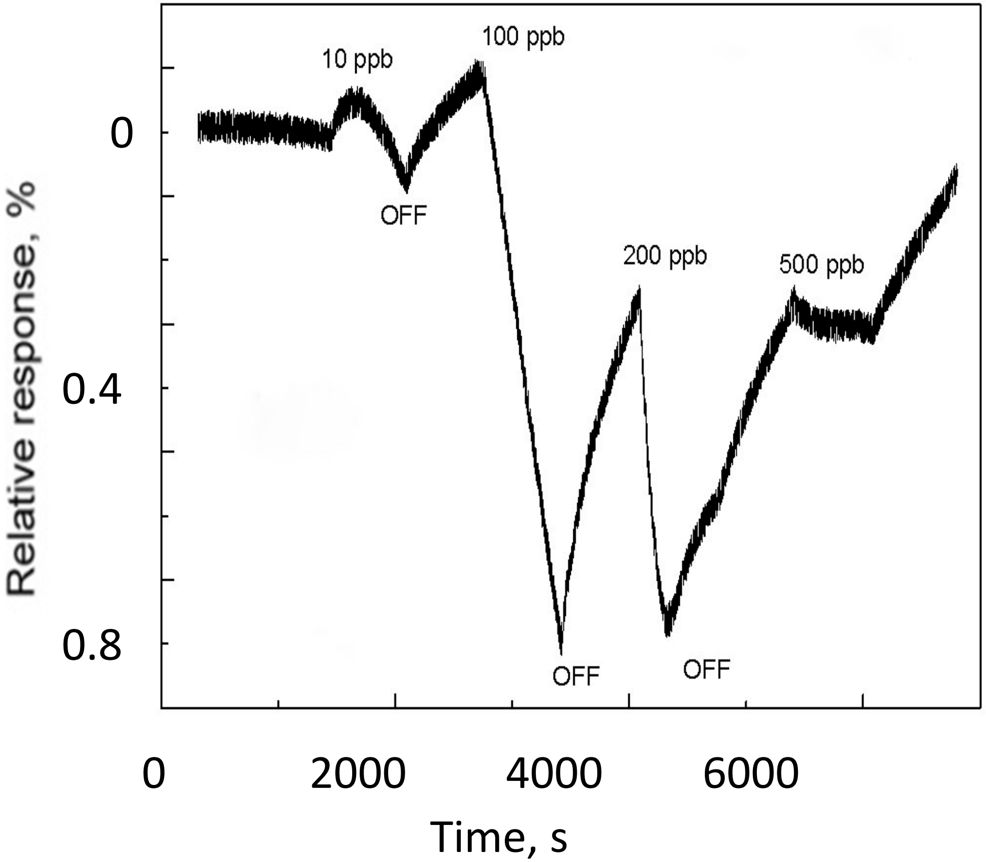
Reliability of the graphene based sensor



Response on exposure of gas mixture containing ozone at 120ºC in 4 measurement circles (marked with different symbols)

- The reliability of the sensor was measured by monitoring its response over a period of several days.
- Response was very stable and reproducibly repeated in several measurement cycles.

Sensor with CVD-grown graphene



- Response is small as compared to sensor based on epitaxial graphene.
- Noise level is significantly higher compare to epitaxial graphene.
- Defects, generated during fabrication, grain boundaries and possible surface contamination can be origin of the reduced sensitivity.

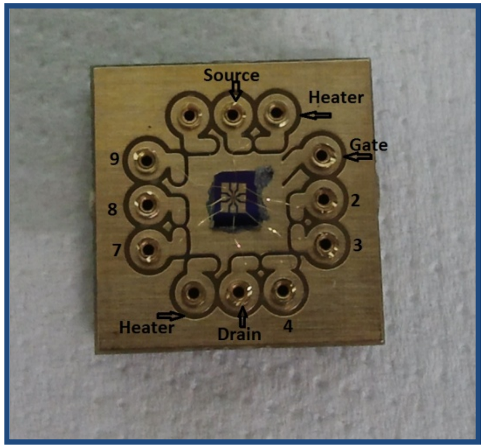
Response on exposure of gas mixture containing NO_2 gas for CVD graphene based device

[redacted]

Mechanical exfoliation of graphene from natural graphite flakes and deposition on Si/SiO_2 substrates (SiO_2 thickness ~ 280 nm)

A sensor is prepared by means of **Electron Beam Lithography** (EBL) to make gold contacts on it.

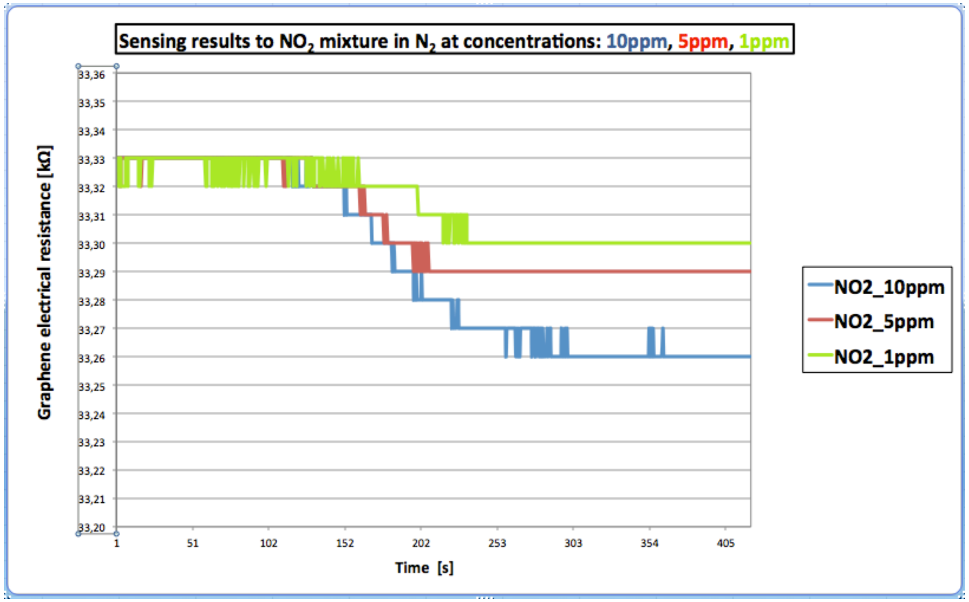
Then it is fixed on a proper **chip-carrier** (purchased from PTB).

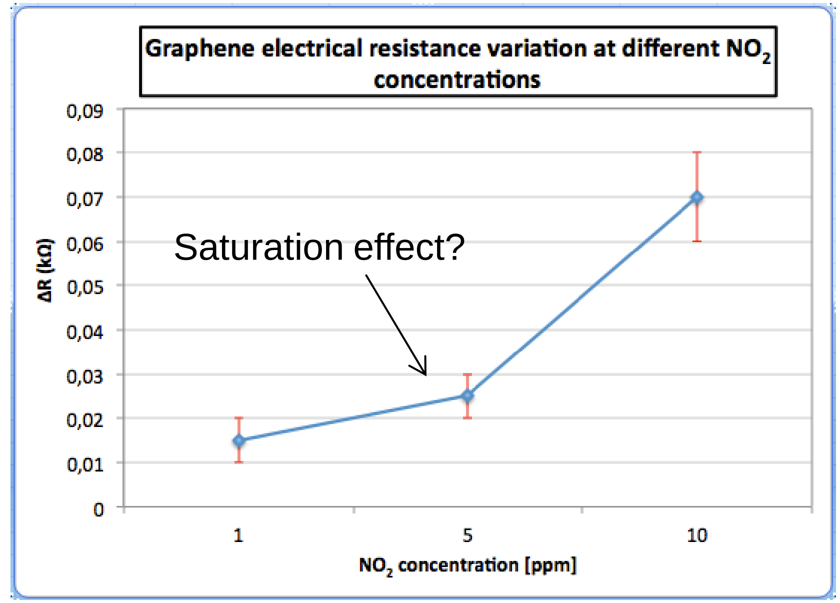


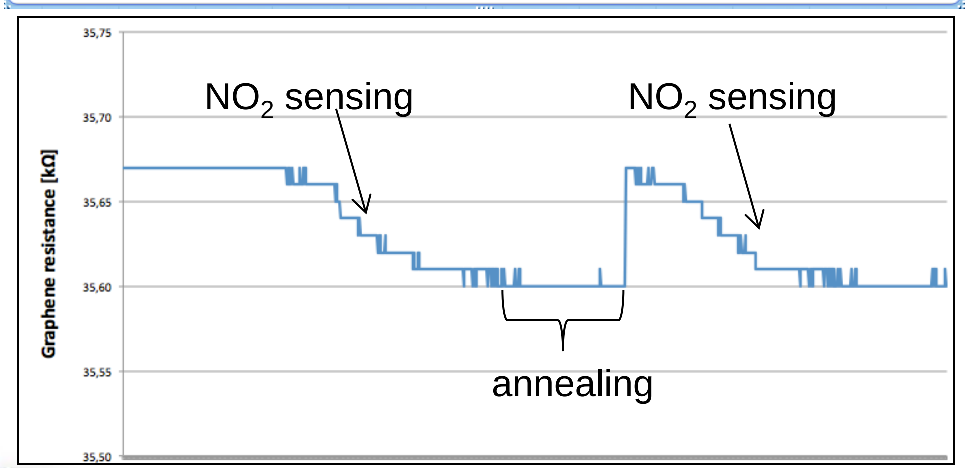
Graphene-based sensor in its final form with the indication of the various contacts.

[redacted]

Sensing results for NO_2 at different concentrations

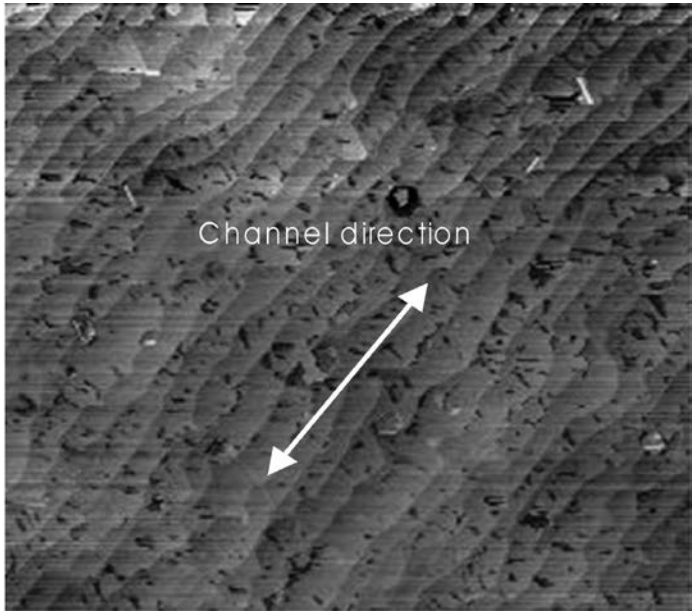


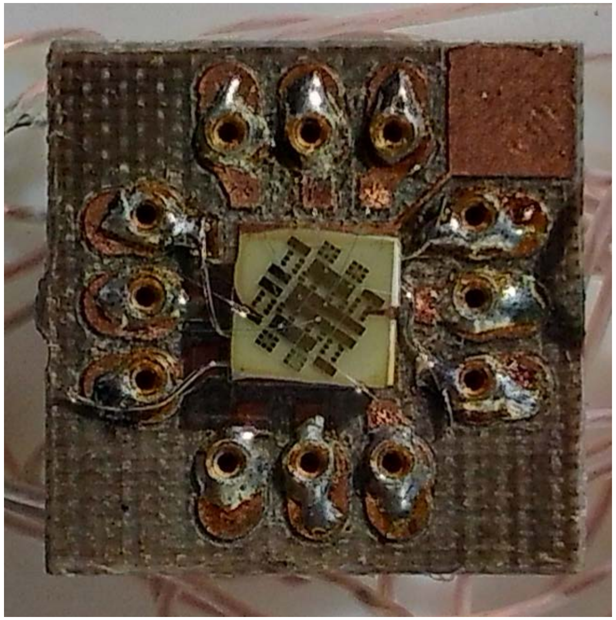




Example of reversibility of the after the annealing process for two consecutive sensings of NO_2 at 10 µmol/mol

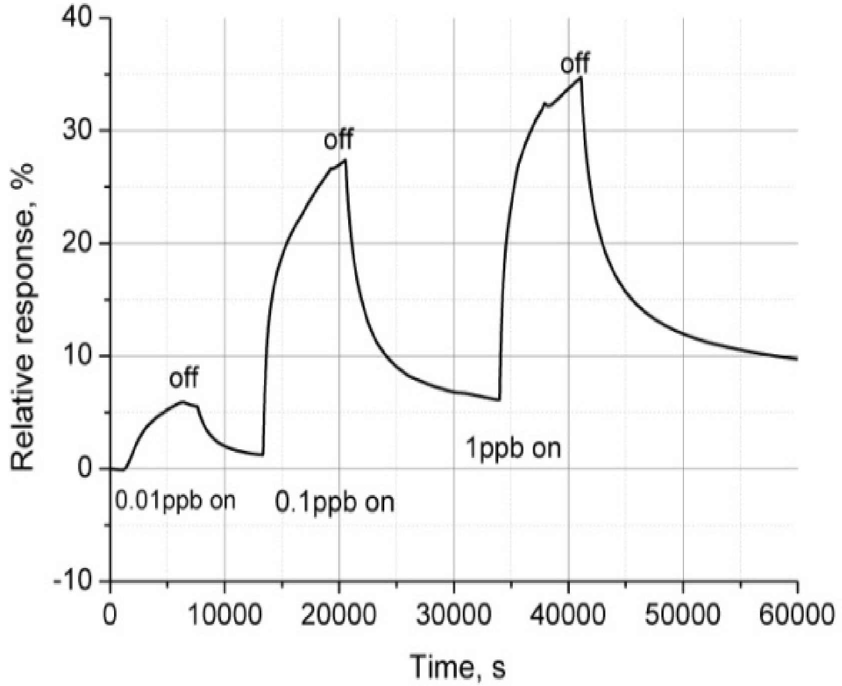
Aligning the sensor's devices along atomic terraces





AFM image of the surface of SiC wafer after annealing (left) and prepared sensor chip on the holder. AFM image area is 12x12 μm and chip area is 5x5 mm

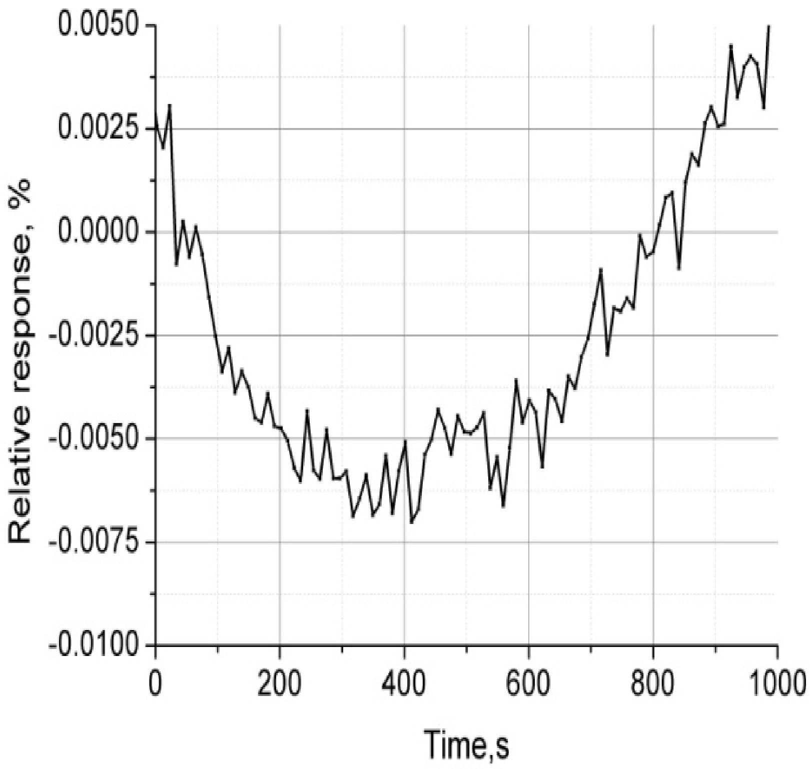
Gas sensor based on terrace-aligned device



Response on exposure of gas mixture containing NO_2 gas at 100°C for aligned graphene based device.

- Increasing of resistivity indicates n-type of conductivity.
- The response 5% at NO_2 concentration is as low as 0.01 ppb.

The detection limit of the graphene based sensor



Noise and drift of a graphene based device

- The peak-to-peak fluctuations were found in the range ± 0.0025% which gives RMS value of noise 0.0004%.
- The drift was found in the range of 0.01% during 15 minute.
- Since 0.01 ppb NO_2 gives a response of 5% the noise limited resolution of the sensor for signal-to-noise ratio 3 can calculated as ~ 3 ppq (parts per quadrillion) and drift limited ~ 20 ppq.

Dependence of response on humidity change

Response of graphene based device on exposure of gas mixture containing NO_2 gas for dry (black curve) and humid (red curve) carrier gas. Sample temperature was 120^{o}C.

- Humidity change from 0.01 to 50% RH (from 1.4 to 7000ppm) gave response of 1%.
- Response on exposure 0.2ppb of NO_2 gas gave the same value of 1%.
- The selectivity toward the water vapor is 35000000.

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- Simple resistive devices, based on epitaxially grown graphene were fabricated and tested for their sensitivity to NO_2 and O_3 gases.
- Graphene layers and the contact configuration were optimized in order to obtain the best performance.
- Devices are extremely sensitive to low concentrations of NO_2 down to ppq range.
- Response was very stable and reproducibly repeated in several measurement cycles supporting potential application of graphene based device as a gas sensor.