A calorimetric study of hydrogen storage on graphene functionalized with Titanium

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Idea of the Experiment

A simple gravimetric measurement or a standard calorimeter would allow to evaluate hydrogen storage in case of amounts of the order of grams or milligrams.

The adsorption of $1\,\mathrm{mg}$ of H_2 on monolayer graphene would need $\sim 450\,\mathrm{m}^2$ of graphene!

We want to measure $10^{-10}\,\mathrm{mol}$ ($\sim 10^{-10}\,\mathrm{g}$) of stored hydrogen, using very small samples.

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Our sample is 5x5 mm^2, corresponding to measure $10^{-10}\,\mathrm{mol}$ ($\sim 10^{-10}\,\mathrm{g}$) of stored hydrogen.

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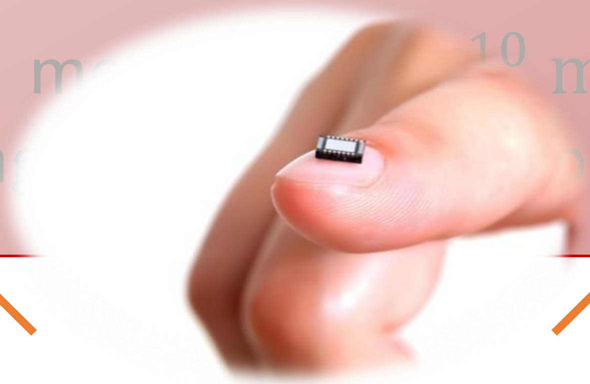

Outline

Introduction

- Hydrogen as an energy carrier
- Graphene for hydrogen storage

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- Calorimetric method
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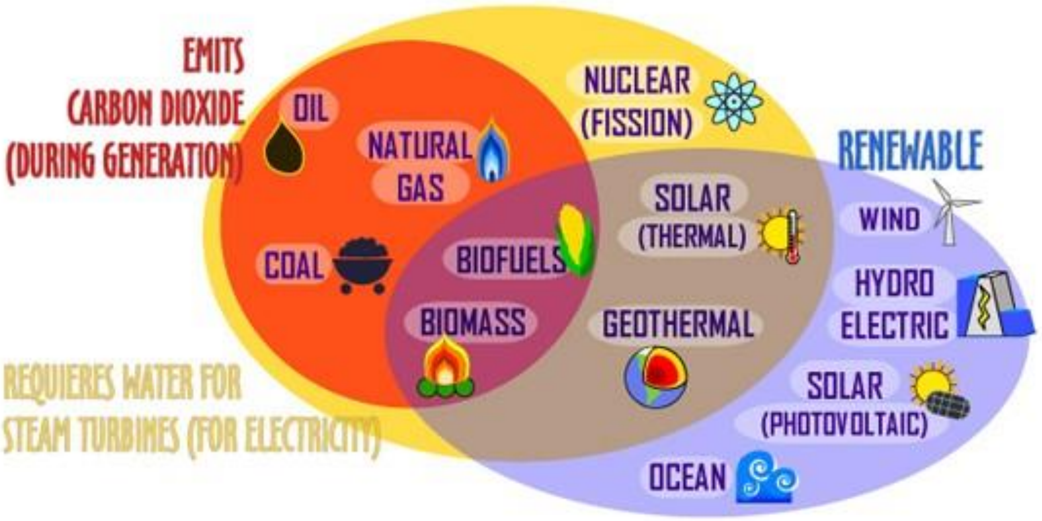
Conclusions & Outlook

Energy sources

Energy can be produced from:

- non-renewable sources (fossil fuels, nuclear, etc.)
- renewable sources (sun, water, wind, etc.)



Energy carriers

Non renewable energy sources usually allow a programmable production/distribution.

Renewable sources need to store it via energy carriers:

- electrochemical carriers (batteries)
- hydrogen

Hydrogen as a fuel

The advantages of H as a fuel are:

- high energy-to-mass ratio
- non-toxic and «clean» (H_2O as only product)
- unlimited resource
- reduction in CO_2 emission
- reduction of oil dependency

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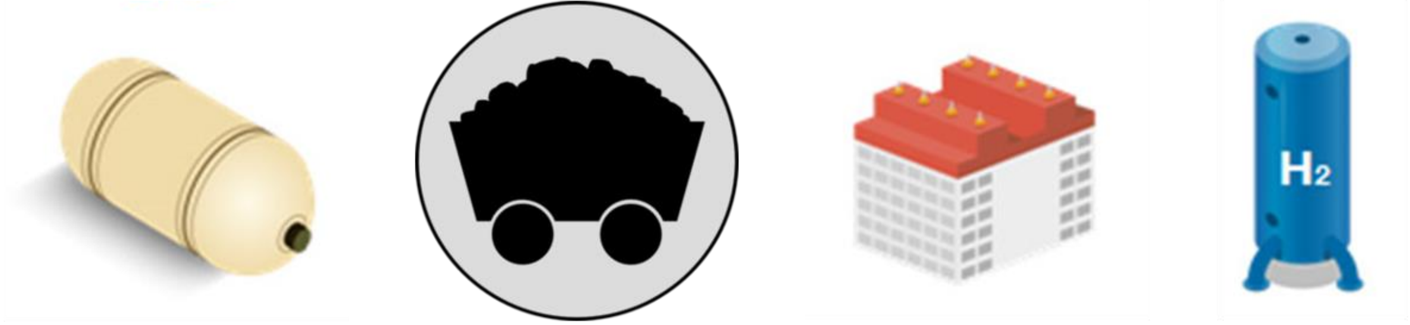

Diesel/Gasoline/ LPG	Gas/Coal	Batteries	Hydrogen
12-14 kWh/kg	6-15 kWh/kg	0.05-0.25 kWh/kg	40 kWh/kg

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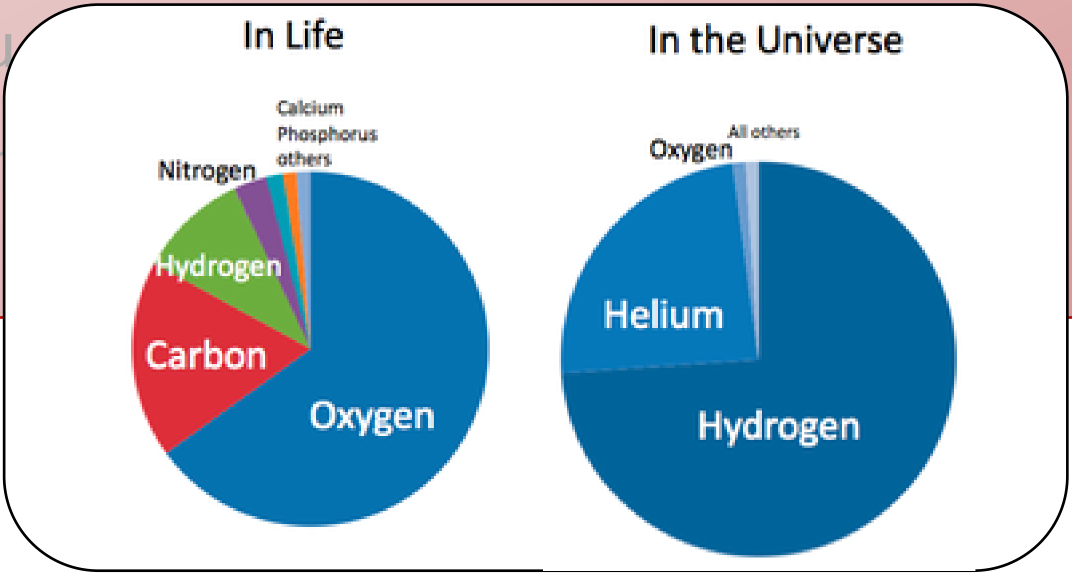

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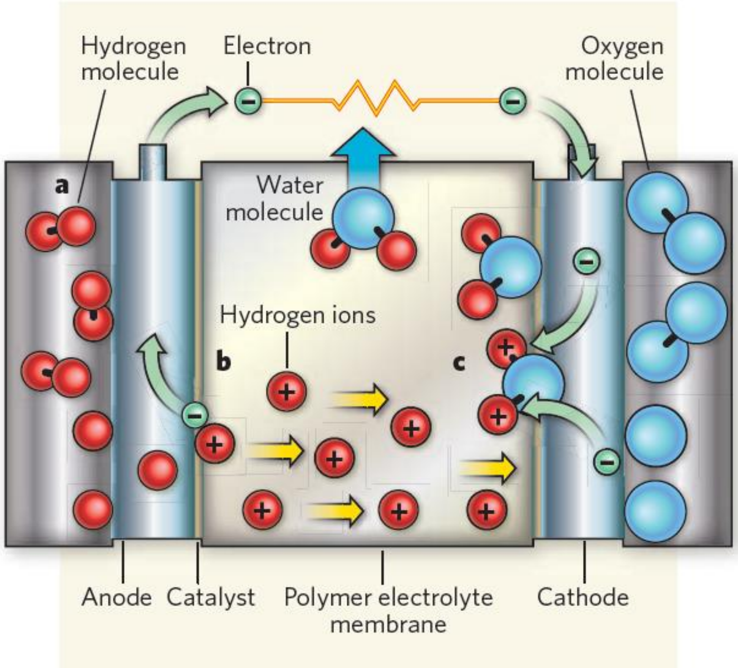
Hydrogen

Hydrogen must be produced (e.g. from the electrolysis of water) and the same amount of energy used for its production is subsequently obtained via hydrogen fuel cells.



$$2H_2 + O_2 \rightarrow 2H_2O$$

$$\Delta H = -2.96\, eV\ (\times 2)$$

Hydrogen storage

- high-pressure tanks:
  - *Volumetric Density*, $VD \sim 36\,\mathrm{kg/m^3}$
  - *Gravimetric Density*, $GD \sim 6$ wt. %
  - Disadvantages: safety of pressurized cylinders, dangerous leaks.

$P \approx 300 - 700$ bar

Hydrogen storage

- cryogenic tanks:
  - $VD \sim 70\ \text{kg/m}^3$
  - $GD \sim 3 - 10\ \text{wt.}\,\%$ (depending on the size of the container)
  - Disadvantages: boil-off losses (0.2% per day), large energy for liquefaction.

$T \approx 21\ \text{K}$

Hydrogen storage

- Solid state materials:
  - *Absorption*: incorporation into the material's structure.
  - *Adsorption*: binding of atomic or molecular H on the material's surface.

Graphene has favorable physical-chemical properties for hydrogen adsorption.

Graphene for H storage

Graphene favorable properties are:

- lightweight, robust and chemically stable
- large specific surface area ($\sim 2600\,\mathrm{m}^2/\mathrm{g}$)
- several production techniques: "top-down" or "bottom-up"
- adsorption by *physisorption* (van der Waals) or by *chemisorption* (chemical bonds).

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- several production techniques: "top-down"

- *physisorption*: low T or high P
$$E_b \approx (0.01 - 0.3)\ \mathrm{eV}$$
$$GD < 3.3\ \mathrm{wt\%}$$

- *chemisorption*: room/low T and atmospheric P
$$E_b \approx (1 - 1.5)\ \mathrm{eV}$$
$$GD < 8.3\ \mathrm{wt\%}$$

Functionalization of graphene

To enhance H_2 adsorption and achieve more stable and large storage capacity, graphene can be chemically decorated with metal atoms, as Li or Ti.

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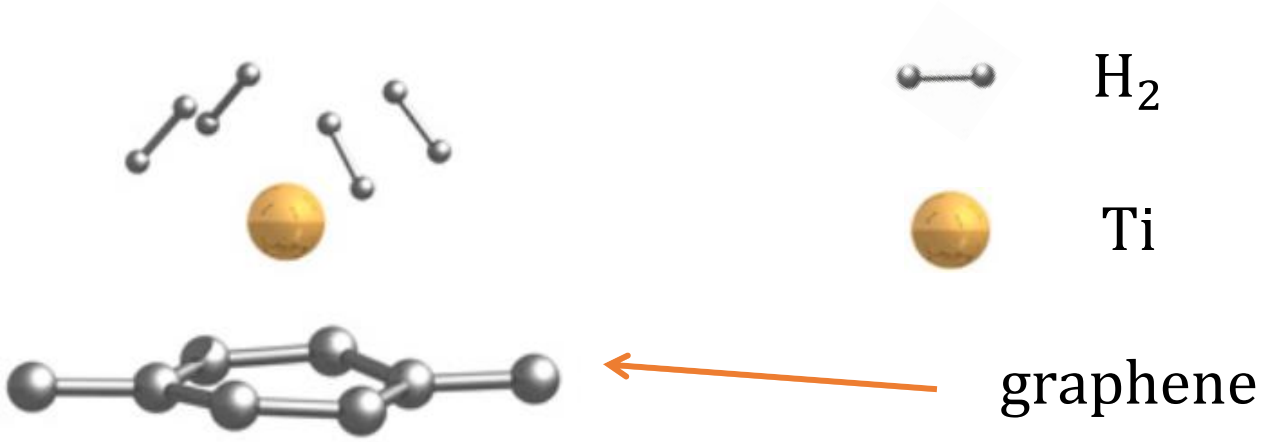
In this study we functionalize the graphene surface using *titanium*, which was already theoretically and experimentally investigated.

Ti-functionalized graphene

Ti is firmly bound onto graphene surface, then up to 4 H_2 molecules are chemisorbed (at room T), with a $E_b \approx (1.1 - 1.5)$ eV.



Yali Liu, et al. "*Titanium-decorated graphene for high-capacity hydrogen storage studied by density functional simulations*" Journal of Physics: Condensed Matter, **22**(44), 445301 (2010)

EXPERIMENT

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The adsorption of H_2 on Ti-decorated graphene at RT is an exothermic process.

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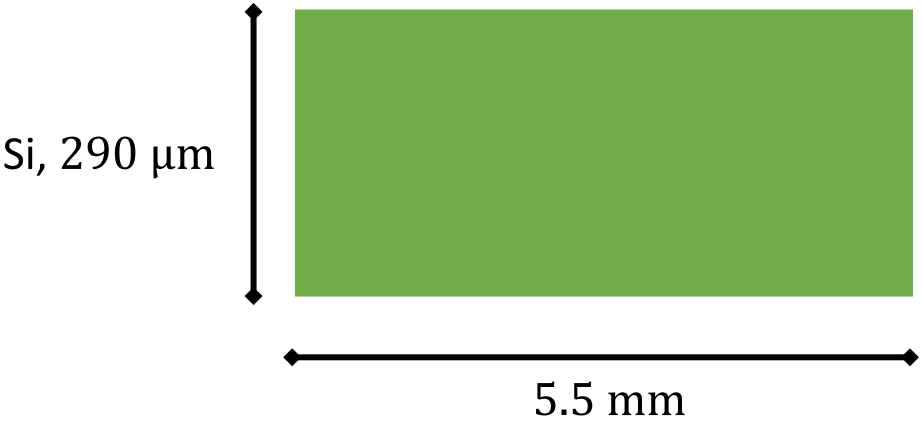
An original calorimetric setup has been designed, suitable for microscopic sample.

Sample's structure

- Si, physical support
- SiO_2, thermal and electrical insulator
- Ti, for the proper sticking of Au
- Au, thermometer



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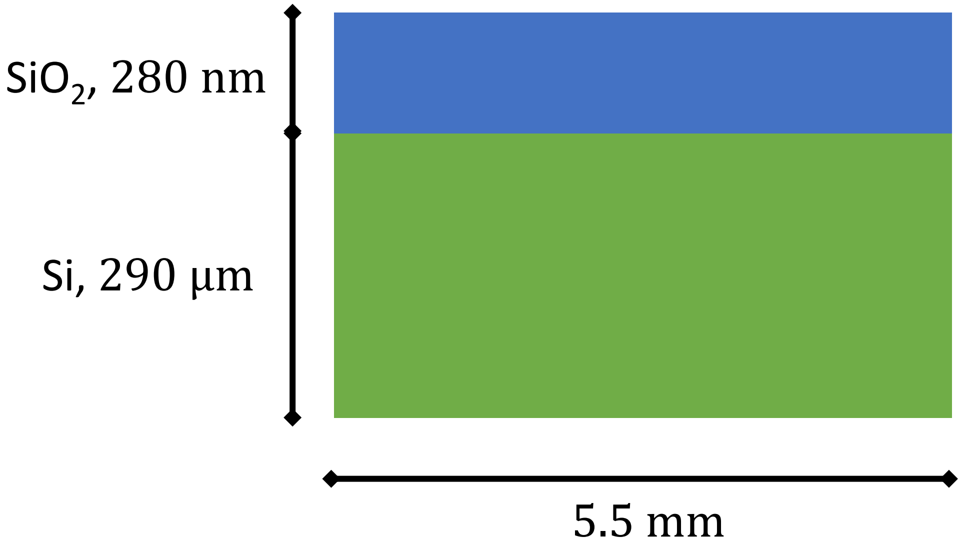

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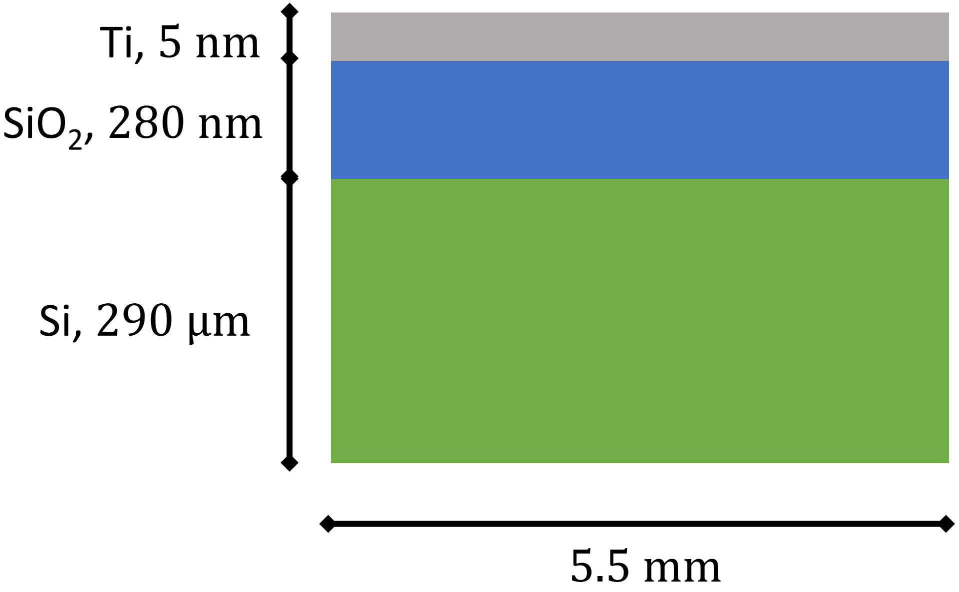

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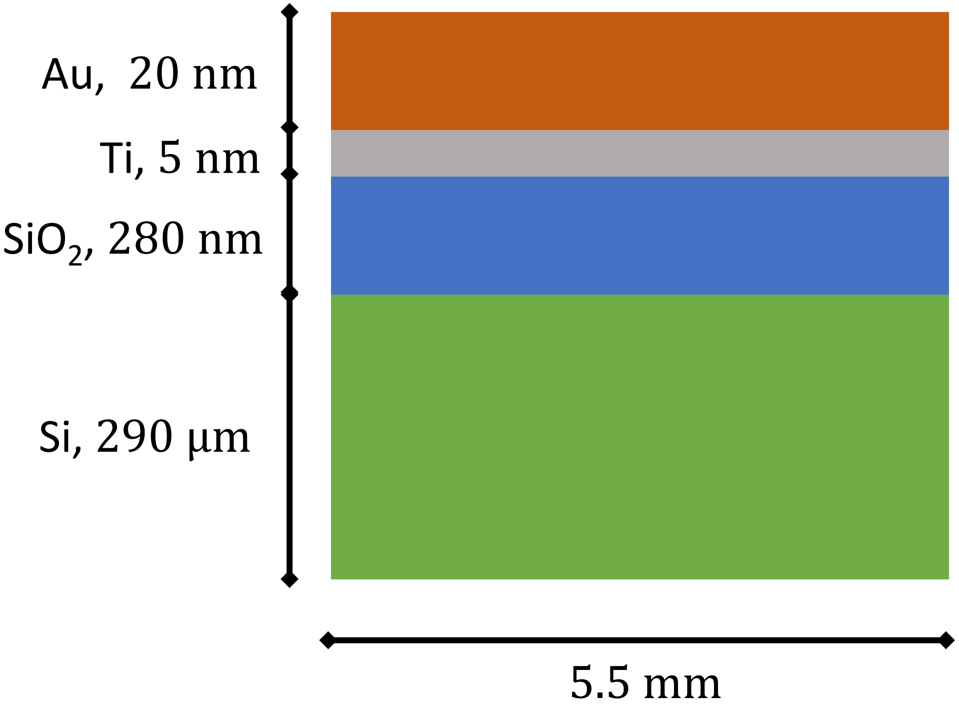

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The idea is to utilize a thin film of gold as a thermometer, exploiting the linear relation:

$$R(T) = R_0[1 + \alpha(T - T_0)]$$

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Gold has:

- suitable resistance temperature coefficient
- good thermal and electrical conductivities
- low chemical reactivity

Thermal model

Heating power $P(t) \longrightarrow \Delta T(t)$
Thermal losses λ through the substrate

$$C\,\frac{d\Delta T(t)}{dt} = P(t) - \lambda\,\Delta T(t)$$

$$\Delta T(t) = T(t) - T_0$$

Thermal model, λ

$$P(t) = P \text{ (fixed)} \longrightarrow \lambda$$

$$\Delta T(t) = T(t) - T_0 = \frac{P}{\lambda}\left[1 - \exp\left(-\frac{t}{\tau}\right)\right]$$

$$\tau = \frac{C}{\lambda}$$

Thermal model, H_2 adsorption

$$P(t) = \frac{\delta H_r(t)}{\delta t}$$

$$\frac{\delta H_r(t)}{\delta t} = C\,\frac{\delta \Delta T(t)}{\delta t} + \lambda\,\Delta T(t)$$

H_r = total enthalpy release

ΔT extimation

Fast thermalization of graphene + Au sensor, no losses through the substrate:

$$\Delta T \sim 5.1\ \mathrm{K}$$

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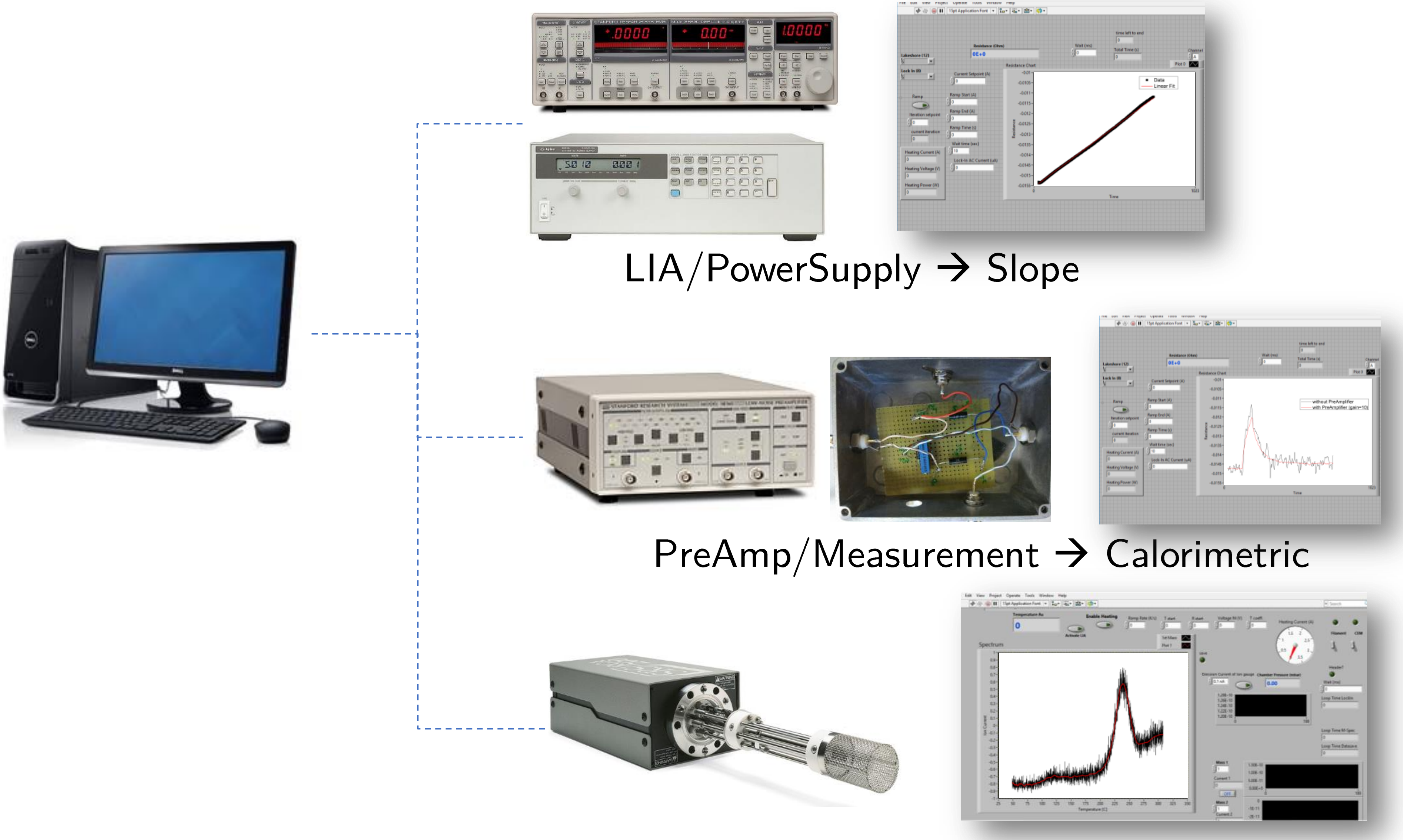
Complete thermalization of the sensor with the entire substrate:

$$\Delta T \sim 6.6 \cdot 10^{-4}\ \mathrm{K}$$

Scheme of the setup

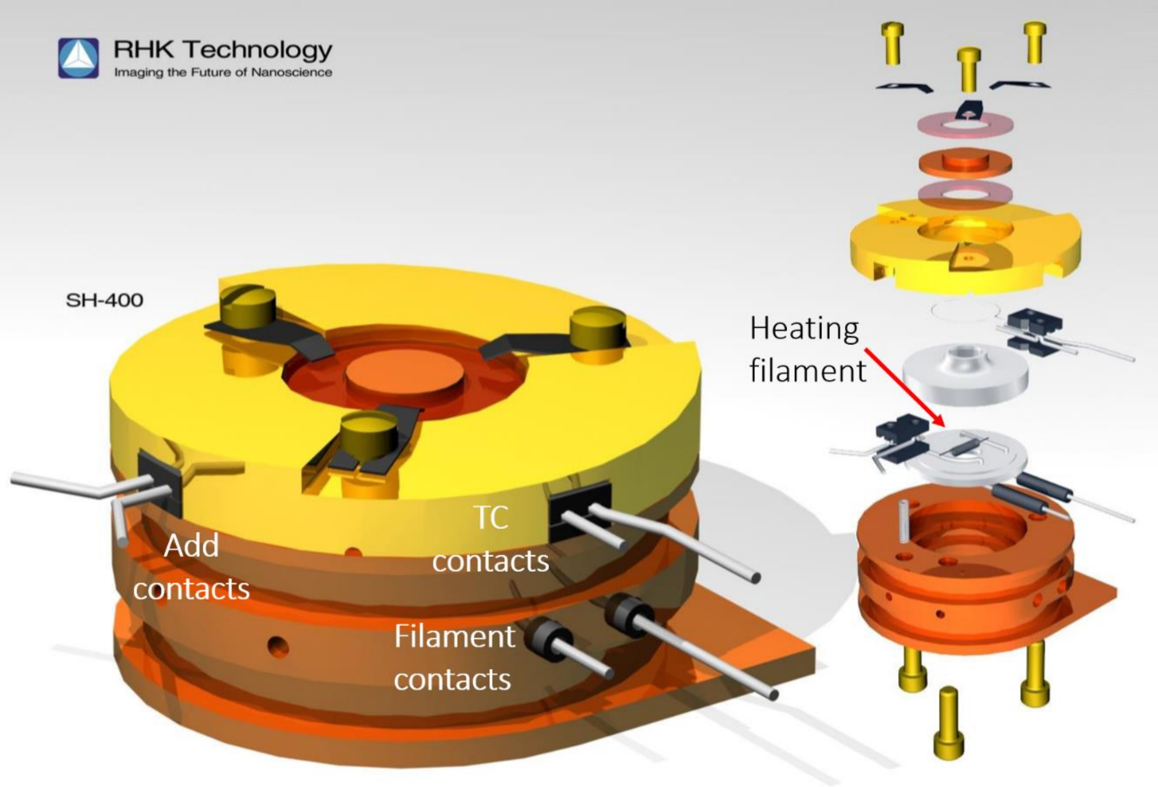


LIA/PowerSupply → Slope

PreAmp/Measurement → Calorimetric

RGA → TDS

Sample holder for UHV

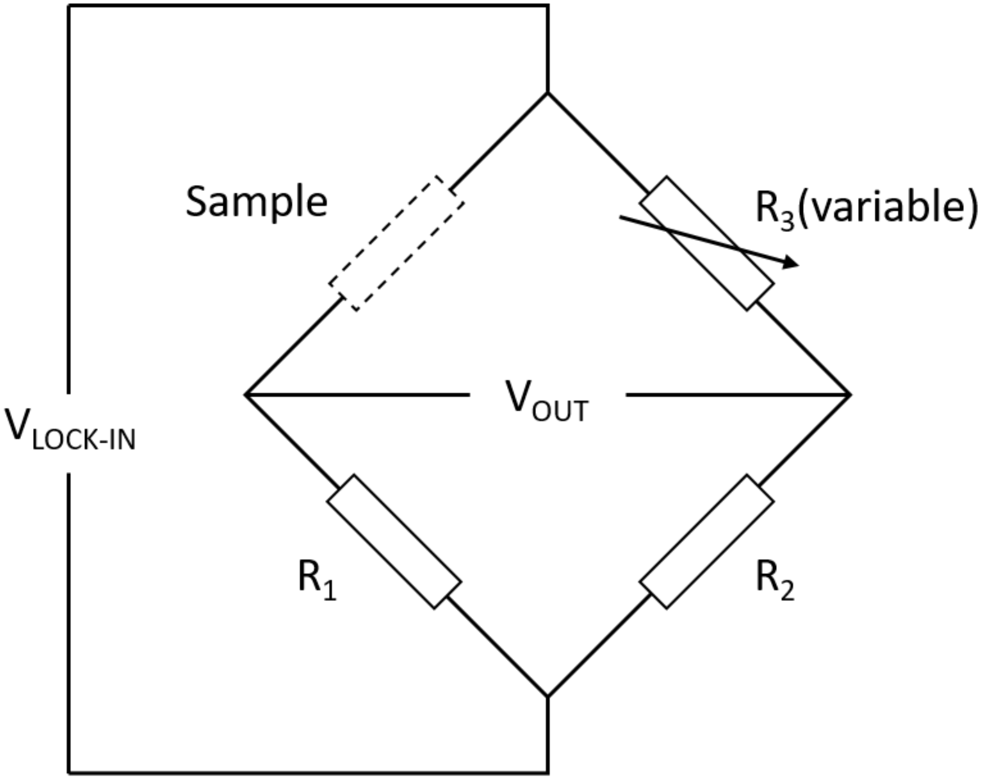


Six contacts:

- 2 → heating
- 4 → measurement

Wheatstone bridge

Finally, for increasing the sensitivity, we use a Wheatstone bridge.



$$R_1 \approx R_2 \approx 1\mathrm{K}\Omega$$

$$R_3 \approx R_S\ (T_0)$$

Procedure for characterization

- calibration of the thermometer (α and ρ), STM images of Au surface

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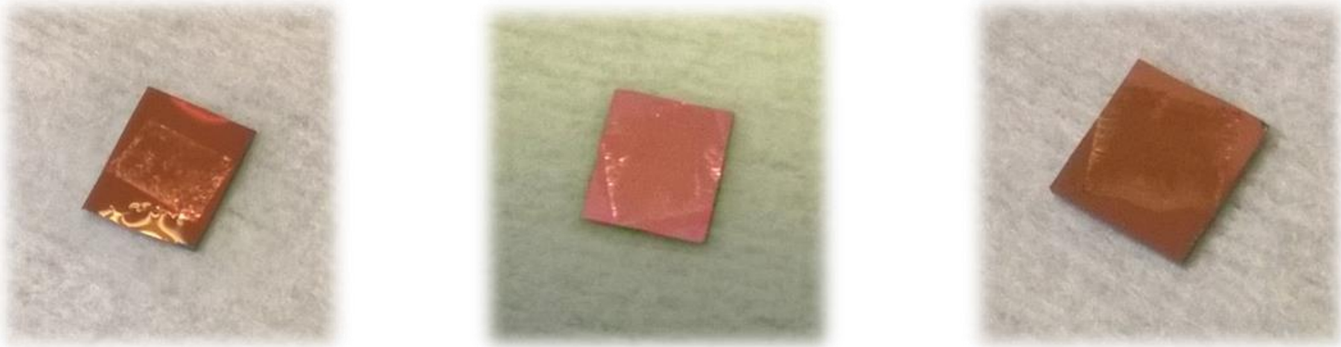
- transfer of monolayer graphene, calibration, Raman spectroscopy, STM on graphene



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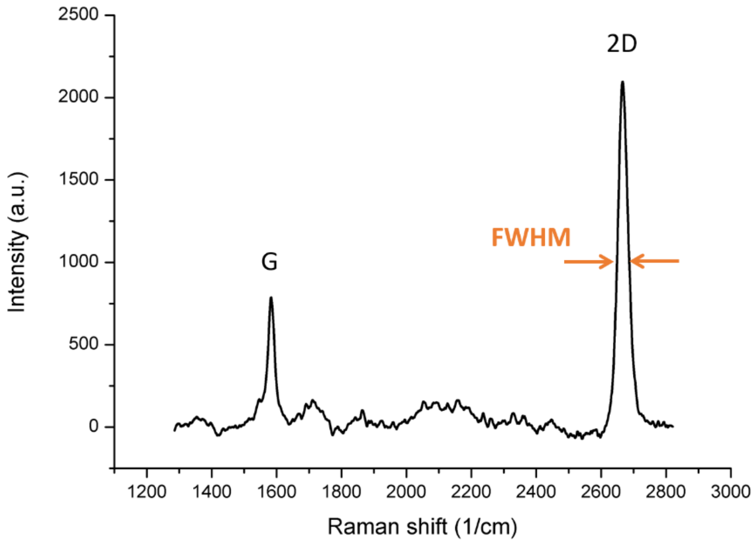
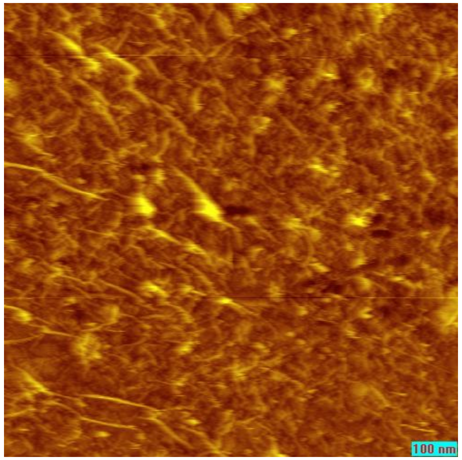
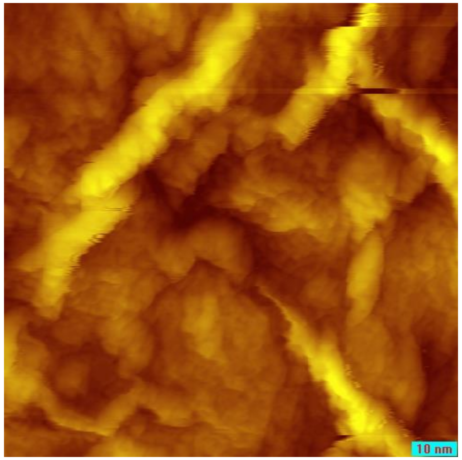




1 µm × 1 µm



100 nm × 100 nm

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- calculation of the heat transfer coefficient
- calibration of the RGA (for the TDS)

Measurement Procedure

- blank measurements on Au samples (D_2 exposure, TDS)

- blank measurements on graphene samples (D_2 exposure, TDS)

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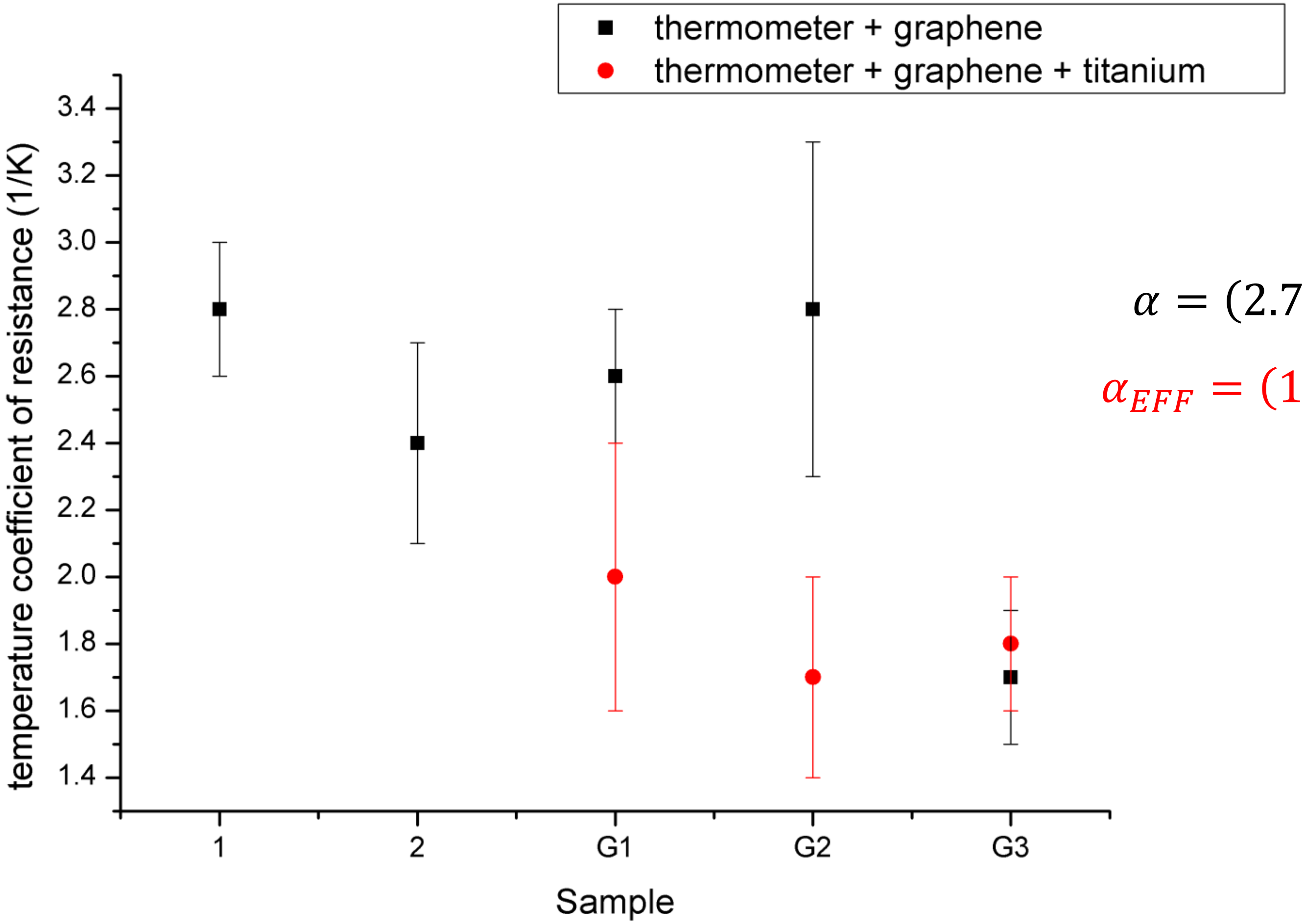
- blank measurements on Au samples (D_2 exposure, TDS)
- blank measurements on graphene samples (D_2 exposure, TDS)
- evaporation of Ti on graphene → D_2 exposure → temperature increase, heat release
- TDS measurement → desorption peak, E_b , D_2 amount, heat release

RESULTS

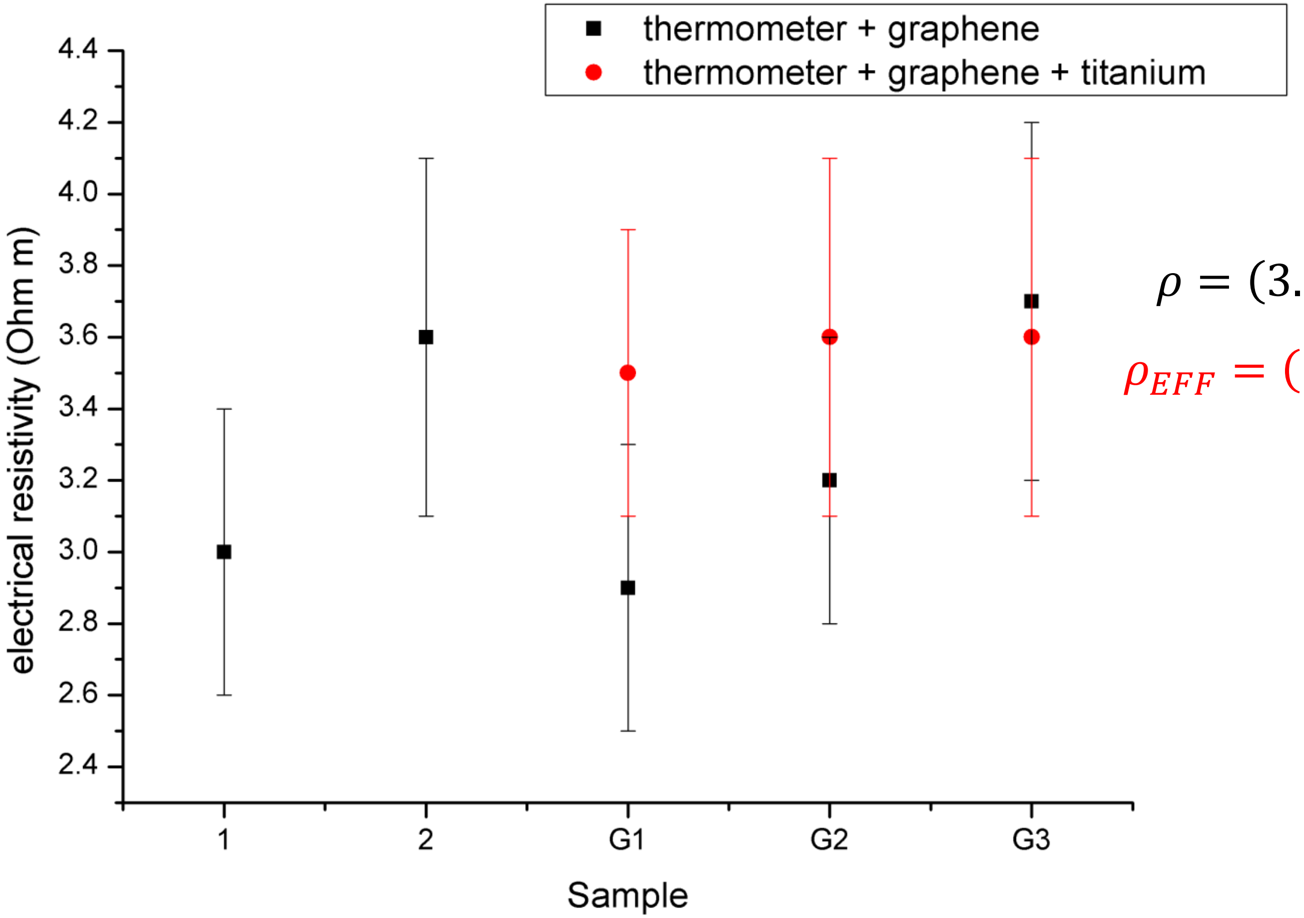
Calibration of the thermometer, α



$$\alpha = (2.7 \pm 0.1) \cdot 10^{-3}\ \mathrm{K}^{-1}$$

$$\alpha_{EFF} = (1.8 \pm 0.3) \cdot 10^{-3}\ \mathrm{K}^{-1}$$

Calibration of the thermometer, ρ

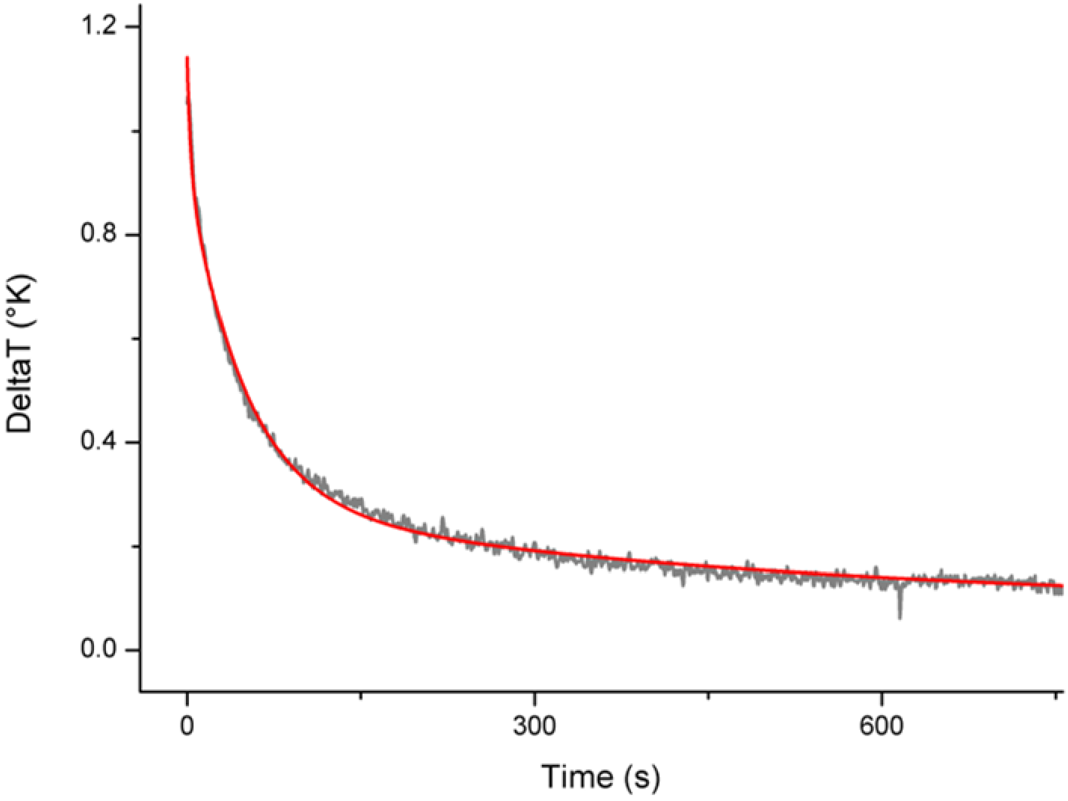


$$\rho = (3.2 \pm 0.4) \cdot 10^{-8}\ \Omega\mathrm{m}$$

$$\rho_{EFF} = (3.6 \pm 0.4) \cdot 10^{-8}\ \Omega\mathrm{m}$$

Heat transfer coefficient

$$\Delta T(t) = \Delta T(0) + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3}$$



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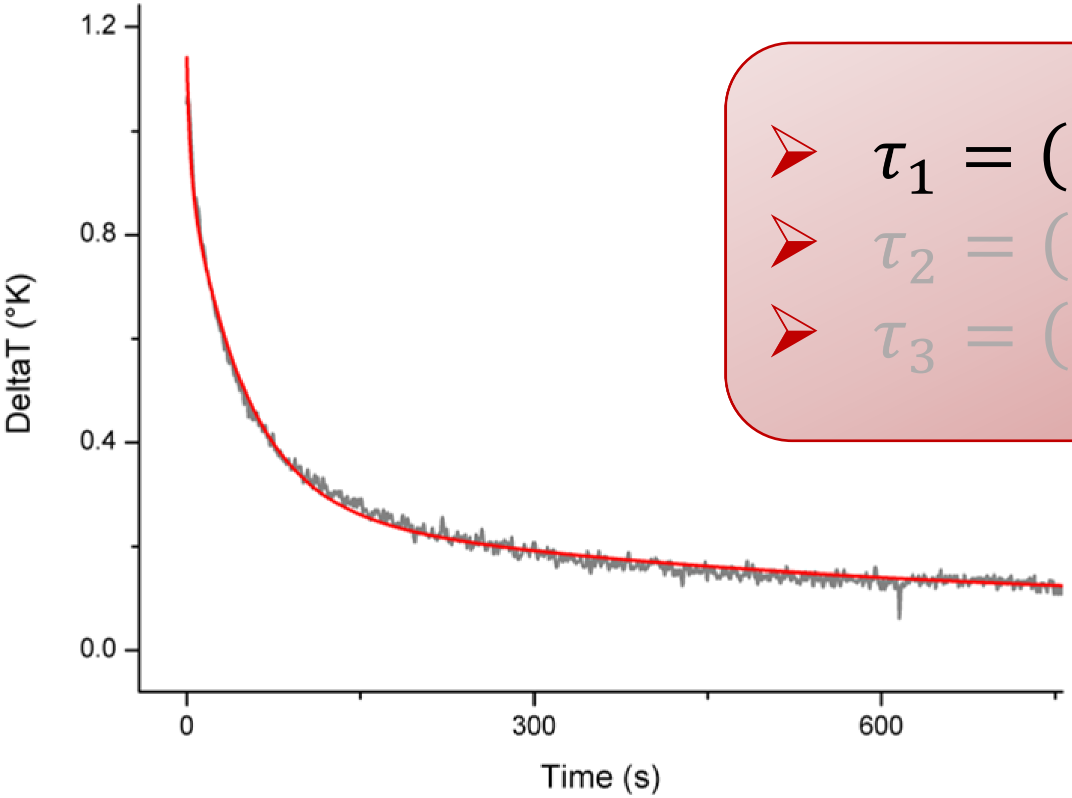

- $\tau_1 = (3.0 \pm 0.2)\ \mathrm{s}$
- $\tau_2 = (47 \pm 2)\ \mathrm{s}$
- $\tau_3 = (475 \pm 5)\ \mathrm{s}$

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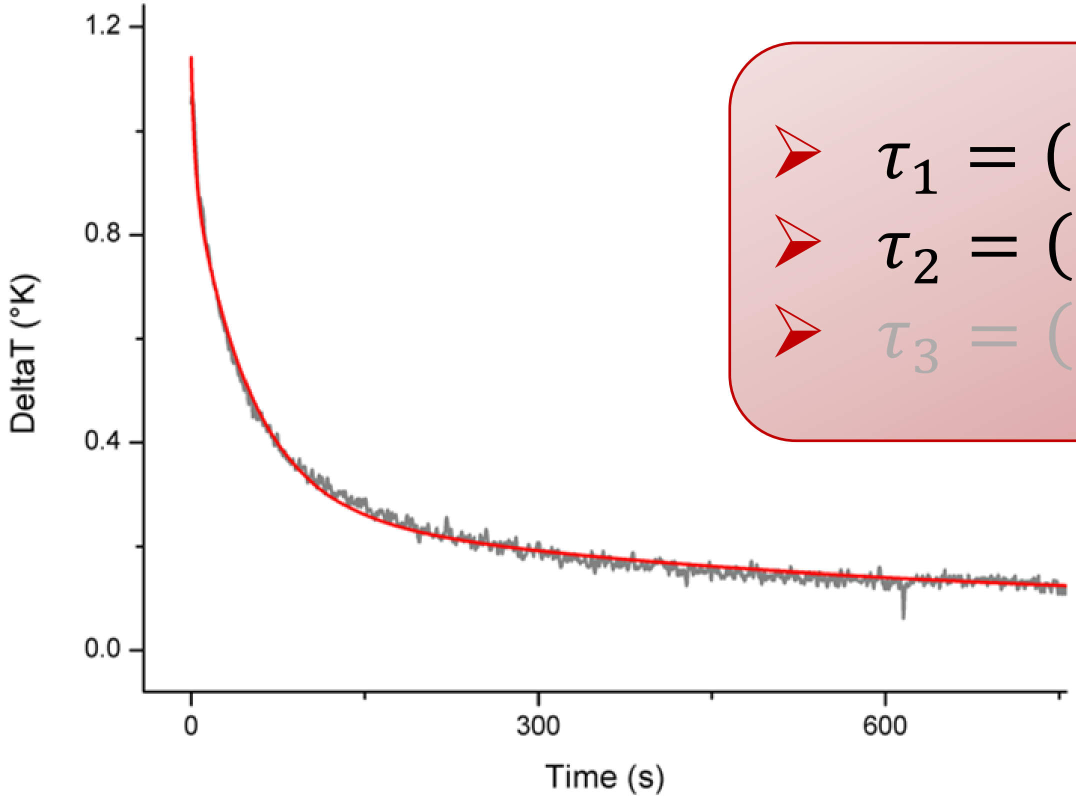

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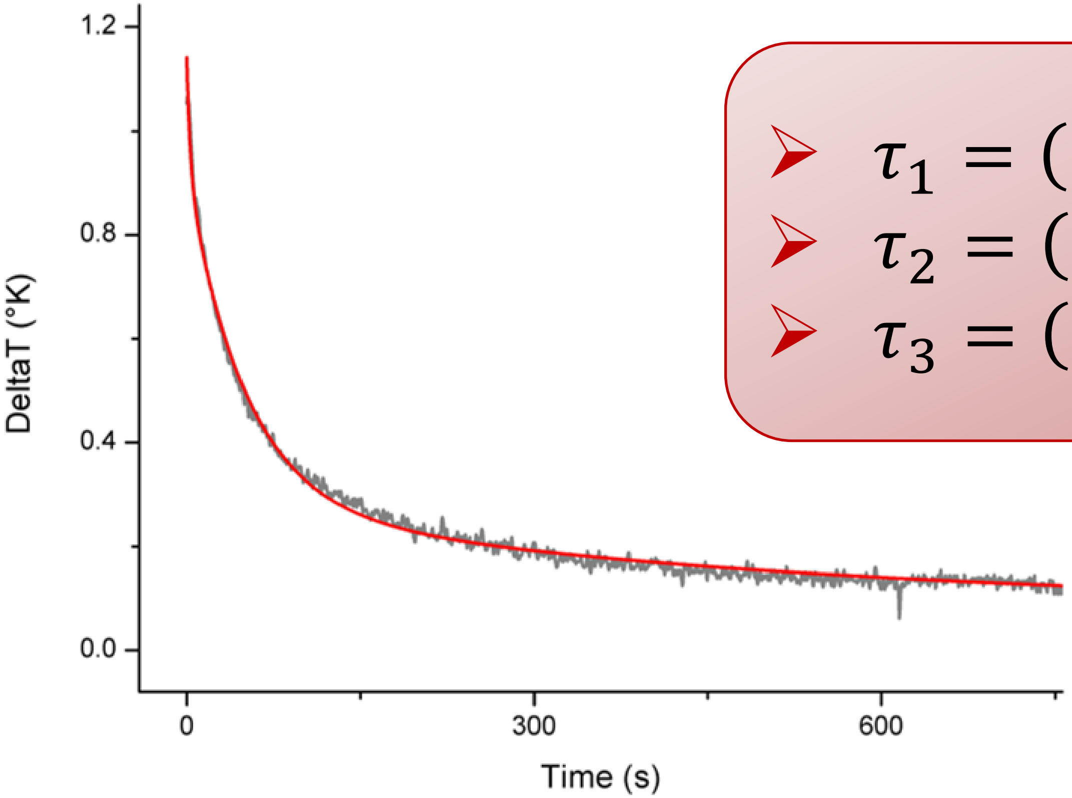

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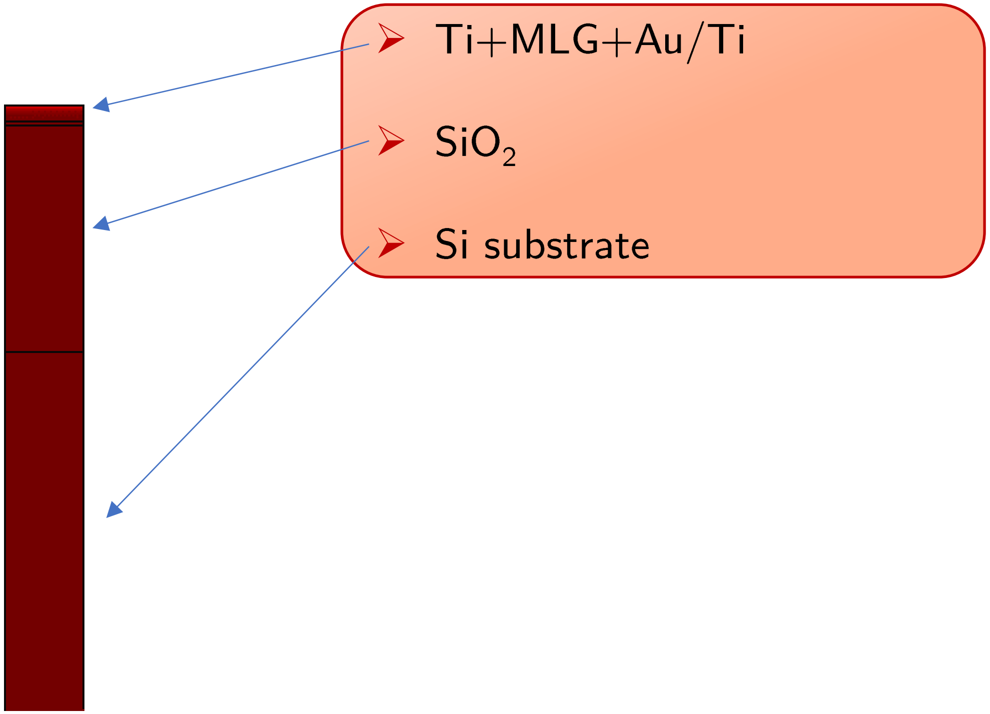
Heat transfer Simulation

Movie of the simulated temperature profile during the firsts 100 ns after appling a source on the top face

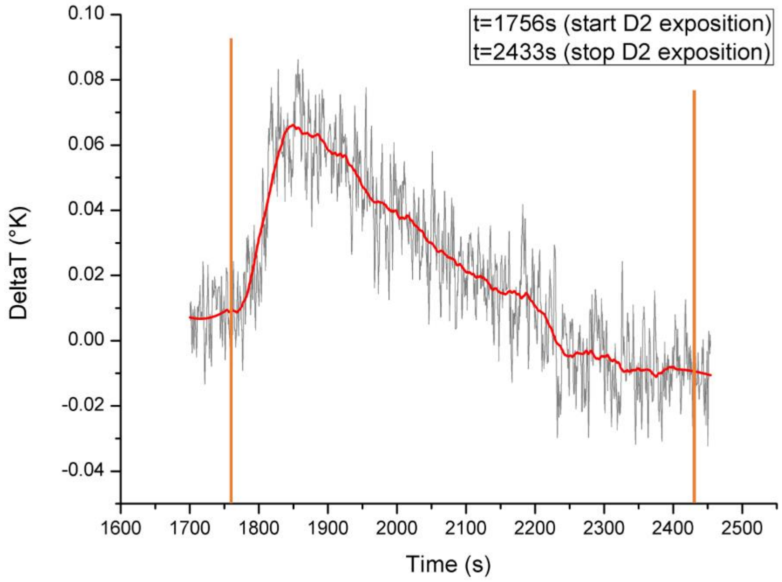


- Ti+MLG+Au/Ti
- SiO_2
- Si substrate

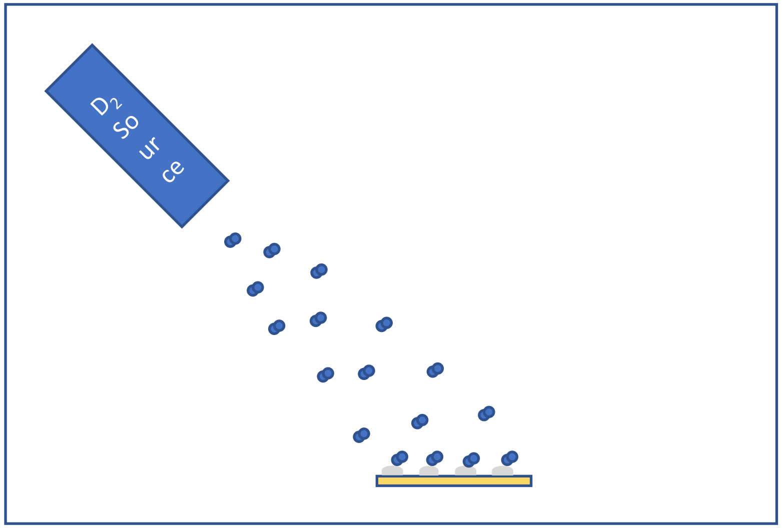
D_2 exposure, calorimetric analysis

SAMPLE G3

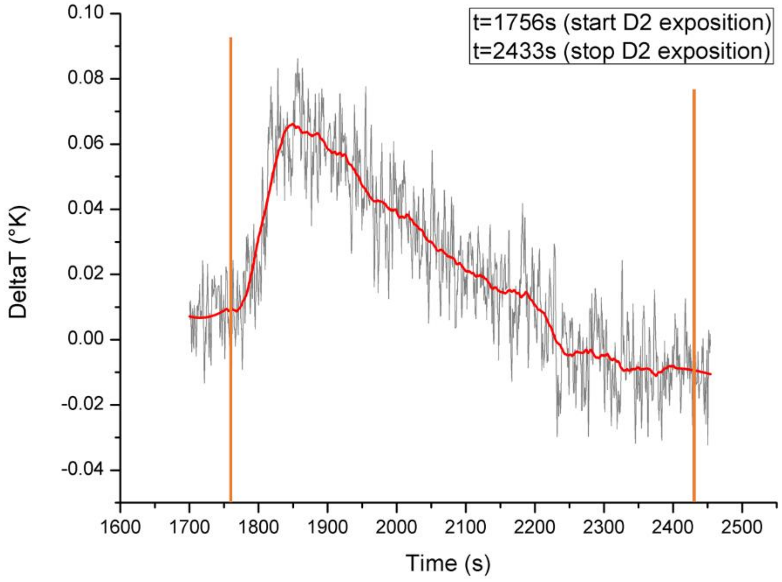
1st Ti deposition → 12.4 ML



$$\Delta T = 0.065 \text{ K}$$



Calorimetric analysis

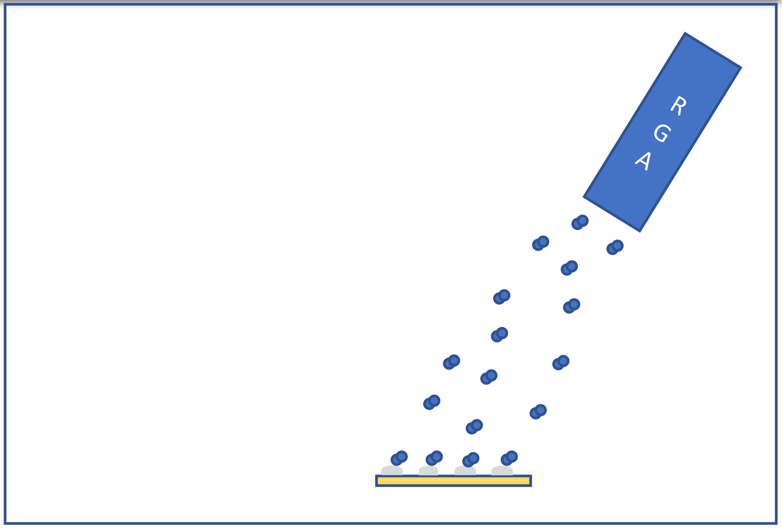


$$\Delta T = 0.065\ \mathrm{K}$$

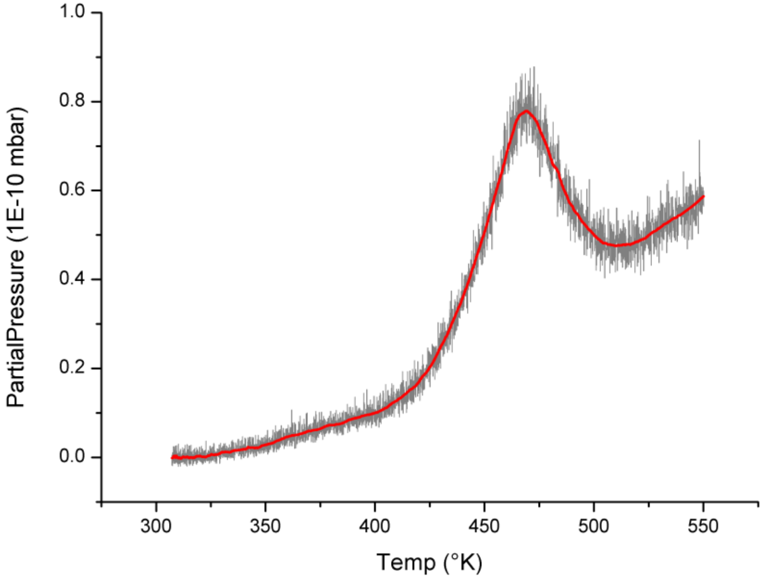
$$\tau_1 = (2.94 \pm 0.63)\ \mathrm{s}\ \rightarrow\ \lambda_{G3} = (5.1 \pm 1.1) \cdot 10^{-6}\ \mathrm{W/K}$$

$$H_r = (23.4 \pm 4.7)\ \mathrm{\mu J}$$

TDS analysis



TDS spectrum vs Temp

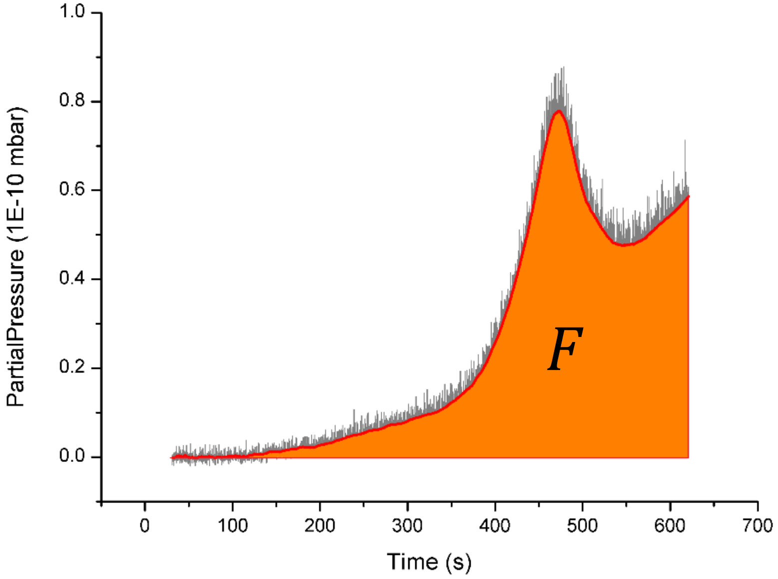


$$\frac{E_b}{k_B T_p} = A\,\tau_m \exp\left(-\frac{E_b}{k_B T_p}\right)$$

$$T_p = (495 \pm 3)\ \mathrm{K} \longrightarrow E_b = (1.32 \pm 0.07)\ \mathrm{eV/molecule}$$

TDS analysis

TDS spectrum vs time



$$pV = F\,S = n\,R\,T$$

$$S \approx 300\,\mathrm{L/s}$$

$$\downarrow$$

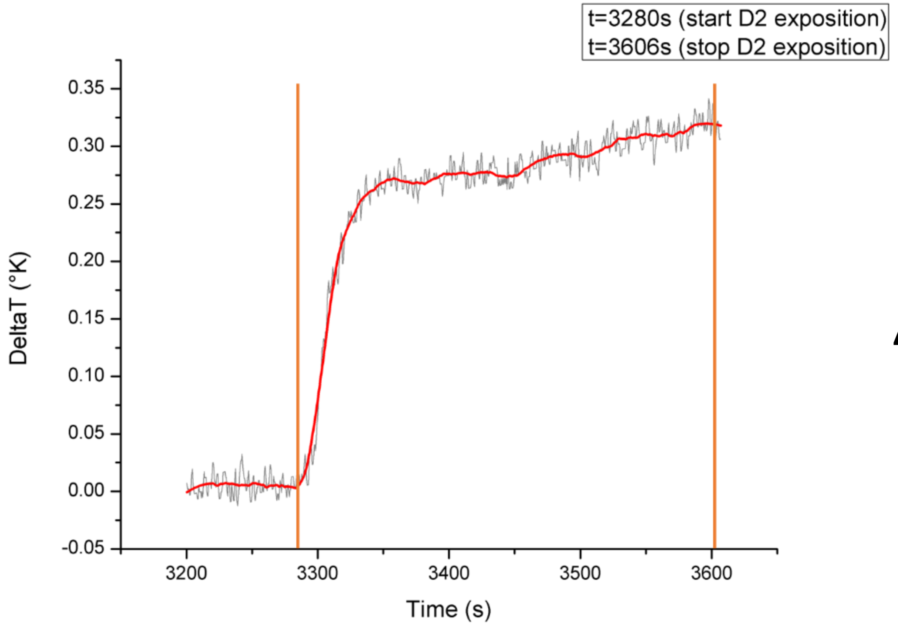
$$n(D_2) \rightarrow 1.71 \cdot 10^{-10}\ \mathrm{mol}$$

$$H_r = n\,N_A\,E_b = (21.8 \pm 1.3)\ \mu\mathrm{J}$$

D_2 exposure, calorimetric analysis

SAMPLE G3

2^{nd} Ti deposition → 16.6 ML

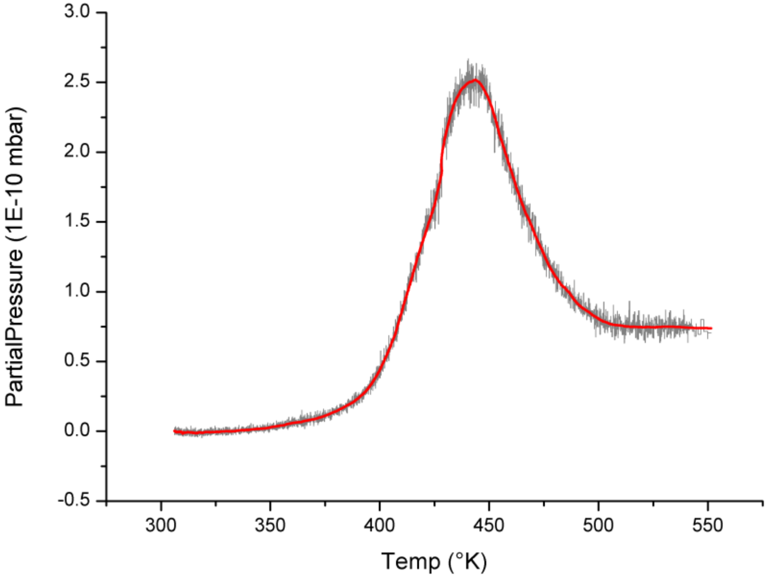


$$\Delta T = 0.25 \text{ K}$$

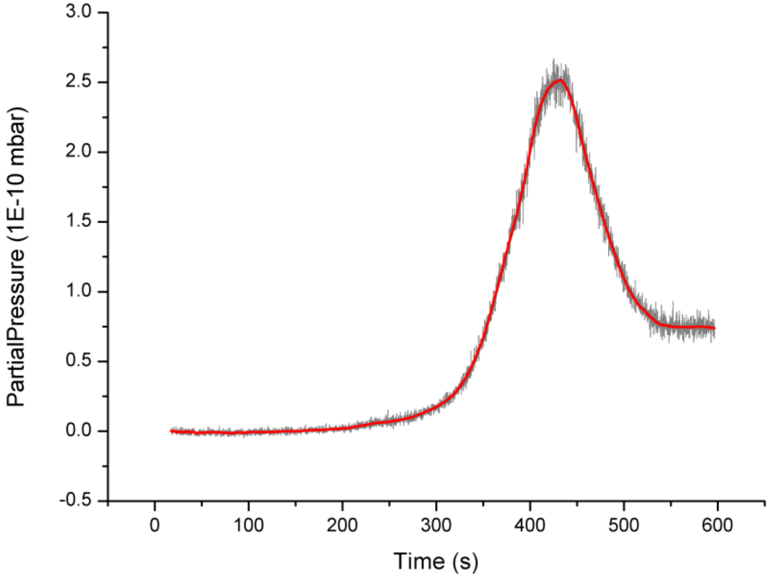
$$H_r = (58 \pm 12)\ \mu\text{J}$$

TDS analysis

TDS spectrum vs Temp



TDS spectrum vs time



$$T_p = (442 \pm 3)\ \mathrm{K}$$

$$E_b = (1.24 \pm 0.09)\ \mathrm{eV/molecule}$$

$$n(D_2) \rightarrow 4.50 \cdot 10^{-10}\ \mathrm{mol}$$

$$H_r = (53.8 \pm 4.3)\ \mu\mathrm{J}$$

Comparison of E_d and H_r

	Ti (ML)	E_b/molecule (eV)	H_r (μJ)	
		TDS	calorimetry	TDS
$G3_{(1)}$	12.4	1.32 ± 0.07	23.4 ± 4.7	21.8 ± 1.3
$G3_{(2)}$	16.6	1.24 ± 0.09	58 ± 12	53.8 ± 4.3

CONCLUSIONS

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- agreement between calorimetry (non destructive, direct, and scalable) and TDS

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- Investigate graphene functionalized with organic molecules

Thank you
for your attention!