

Motivation

- Hydrogen is considered one of the most promising energy carriers. In fact, it can store a large amount of energy (120 MJ/kg versus 44 MJ/kg for gasoline), and the only byproduct of its combustion is water.
- A Hydrogen economy could strongly help to cut down pollution in cities and, in a broader vision, in the global environment.
- Graphene, the first demonstrated two-dimensional atomic crystal [1], has attracted an increasing interest to develop hydrogen storage devices [2-6]. In particular, metal-functionalized graphene has been the object of huge research efforts in both theoretical and experimental fields.
- Here, a new calorimetric technique to evaluate the hydrogen uptake in Ti-functionalized graphene has been successfully developed and tested.

Measuring principle

The idea is to utilize a thin film of gold as a thermometer, exploiting the linear relation between resistance and temperature valid for gold:

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

A heating power $P(t)$ produces a temperature increase $\Delta T(t)$ affected by thermal losses λ through the substrate, according to the relation

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

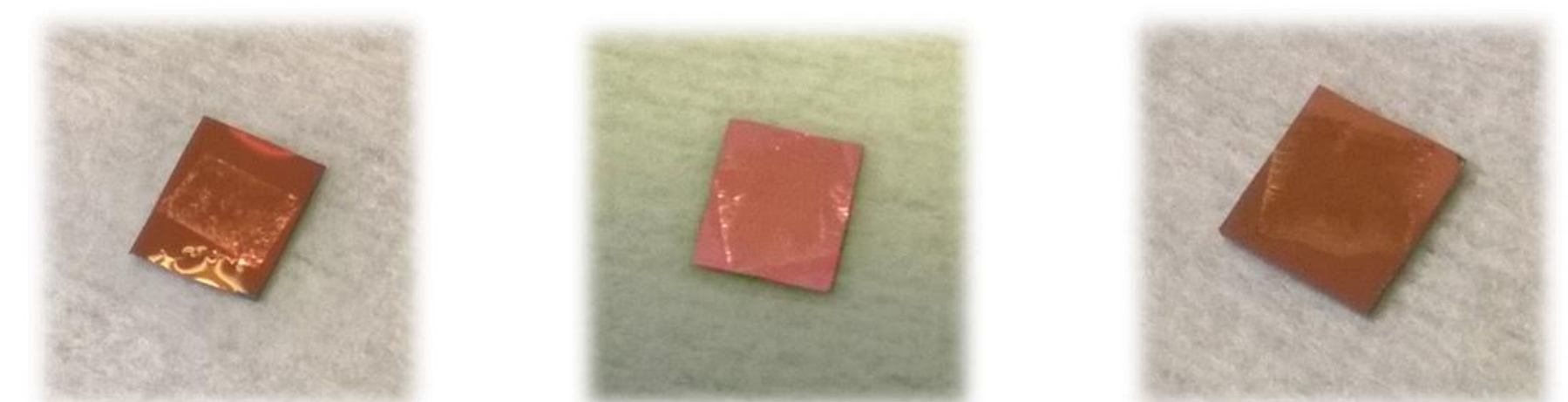
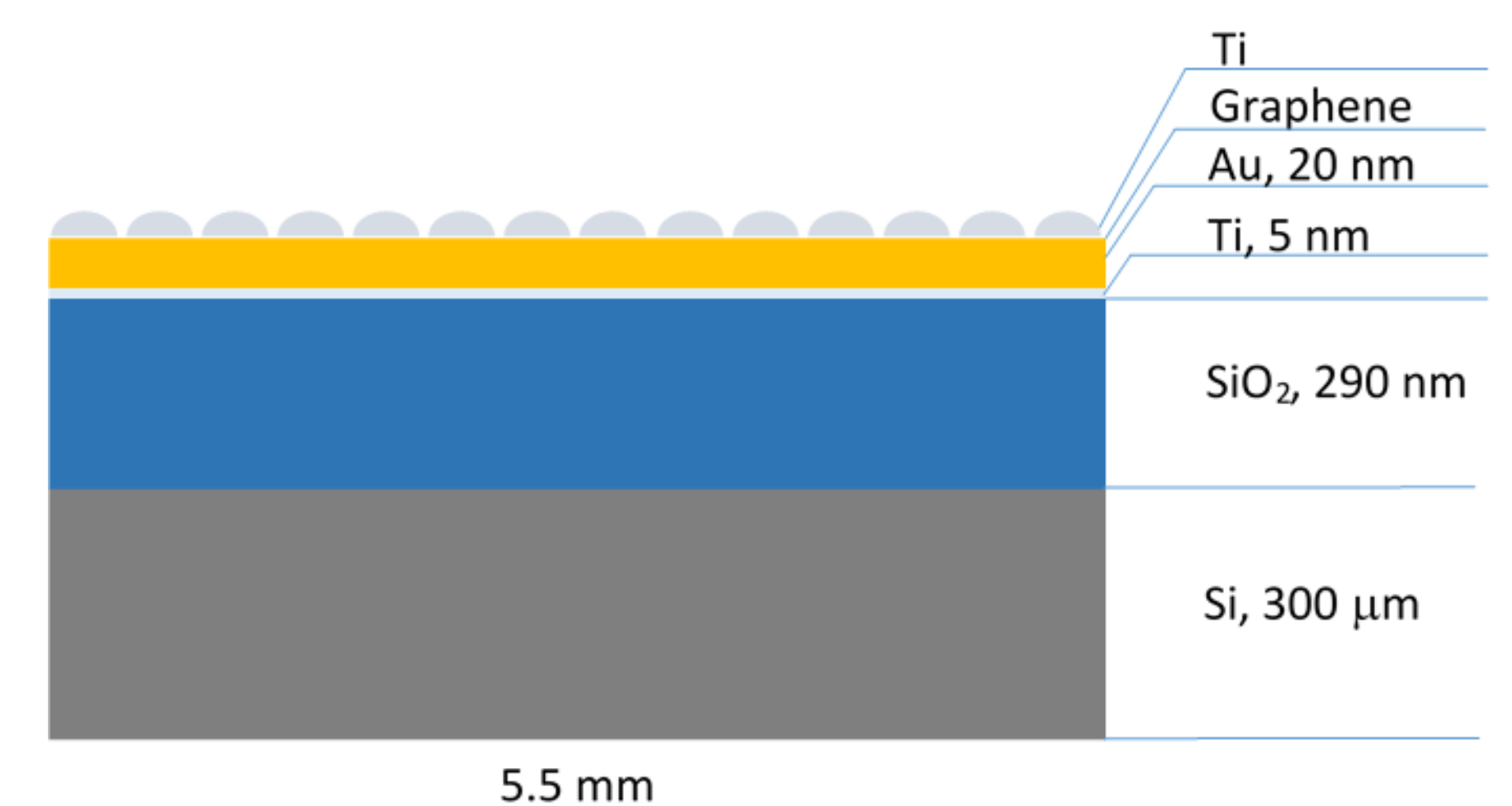
where

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

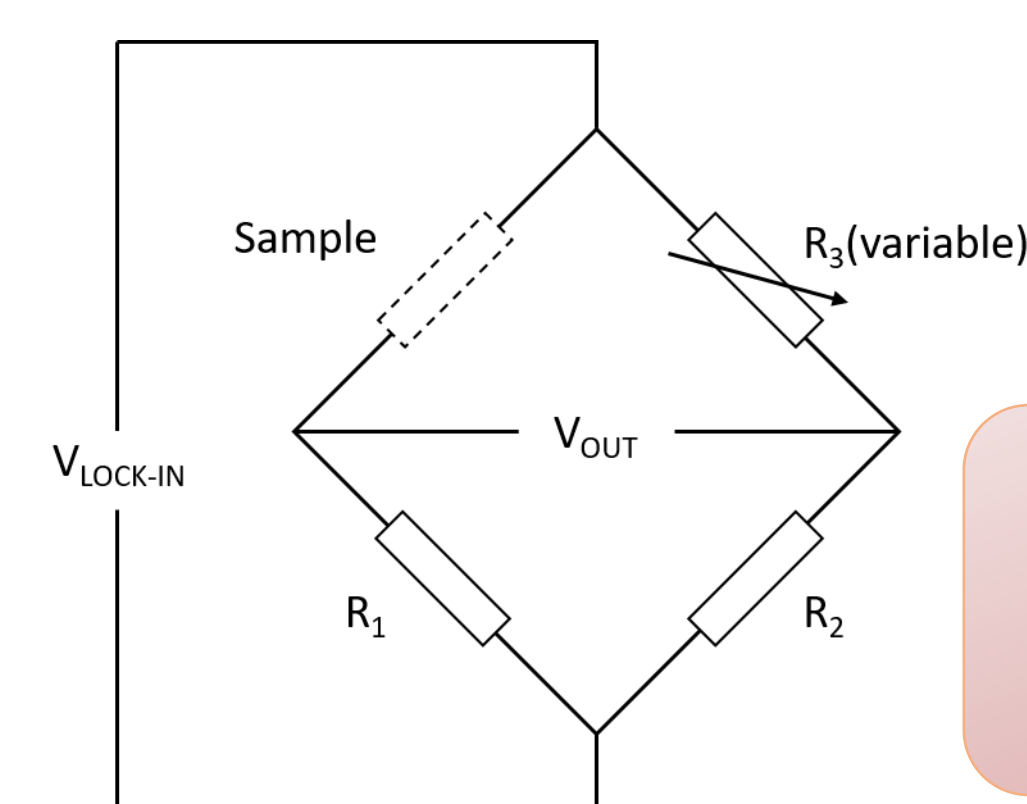
is the change in Temperature with time. The heating power is related to the enthalpy release during the hydrogen adsorption by

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

Sample structure



(Up) Sample structure: gold film thermometer and a CVD graphene foil on top. (Bottom) three samples ready for experiment.



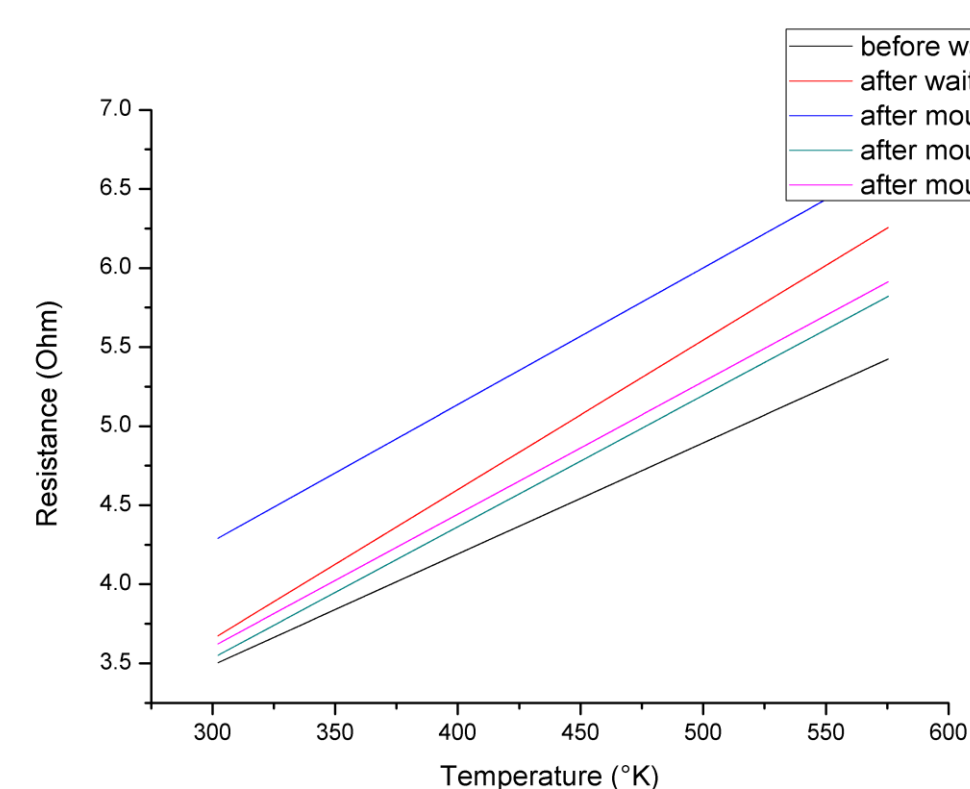
$$R_1 \approx R_2 \approx 1K\Omega$$

$$R_3 \approx R_4(T_0)$$

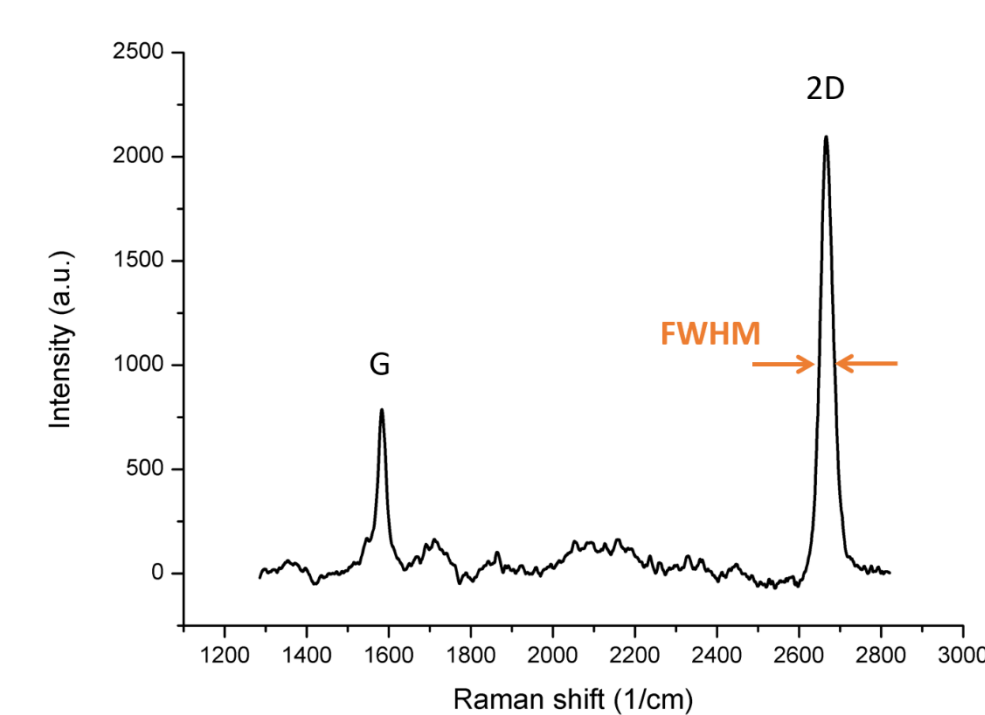
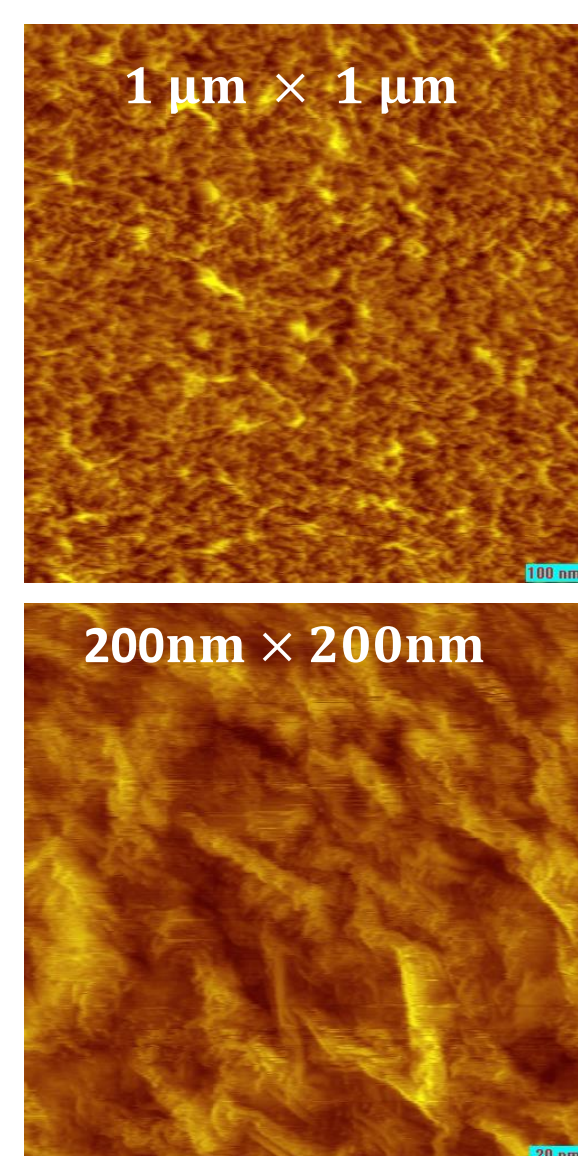
Wheatstone Bridge set-up utilized to measure $\Delta R(T) \rightarrow \Delta T$ during hydrogenation

Sample characterization procedure

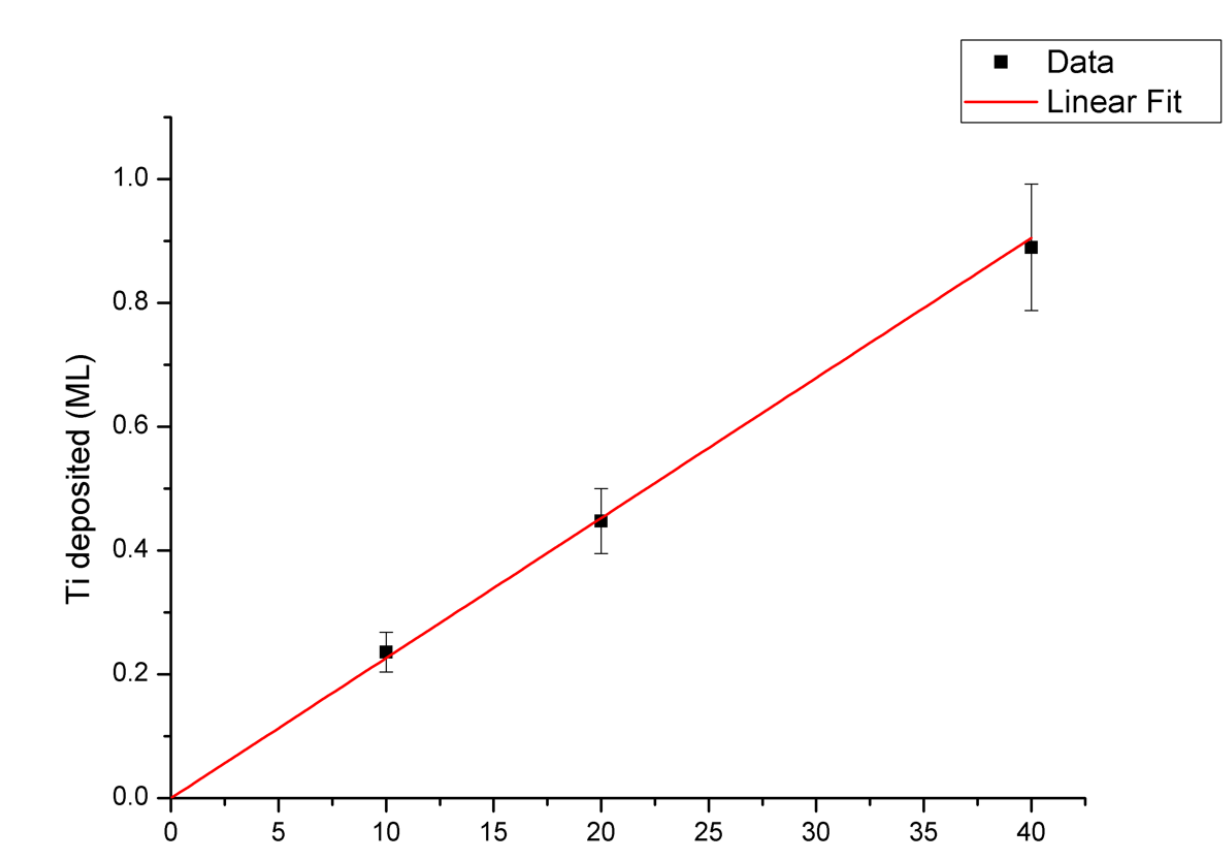
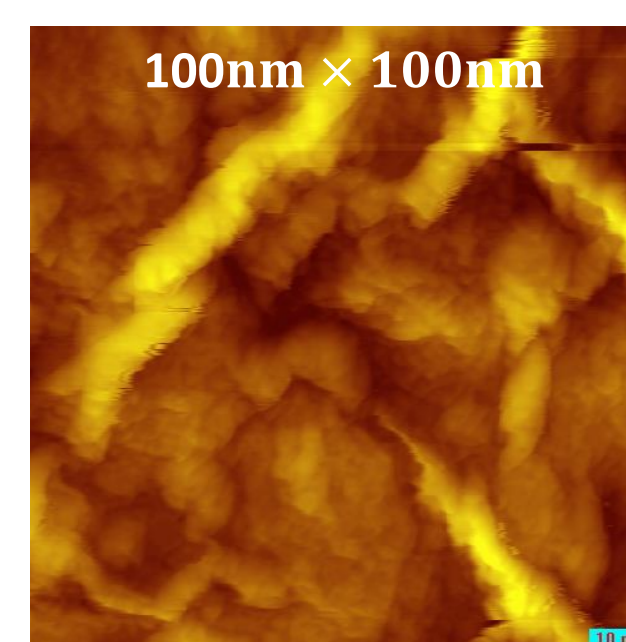
- calibration of the thermometer (slope α and resistivity ρ), STM images of Au surface
- transfer of monolayer graphene, calibration, Raman spectroscopy, STM on graphene
- calibration of the Ti evaporator, evaporation of Ti on graphene, STM on deposited Ti
- calculation of the heat transfer coefficient



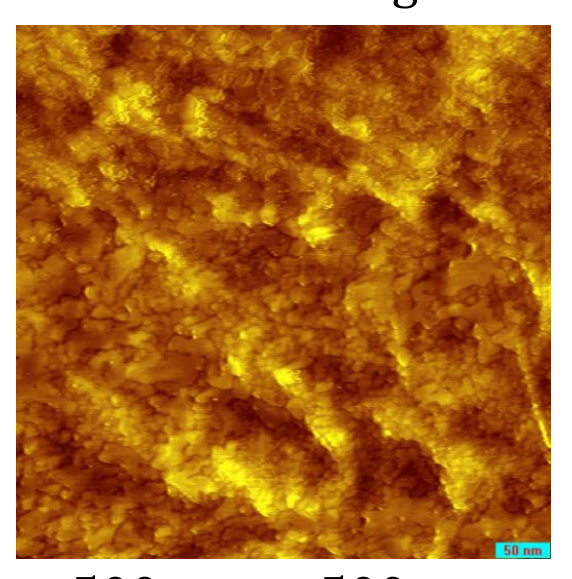
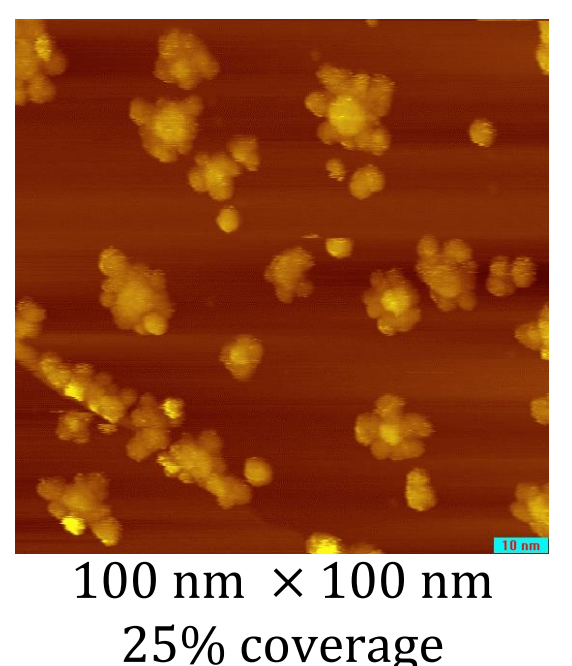
A.) Top: Calibration of the thermometer (slopes), Right: STM images of Au surface



B.) Transfer of monolayer graphene, Raman spectroscopy, STM on graphene

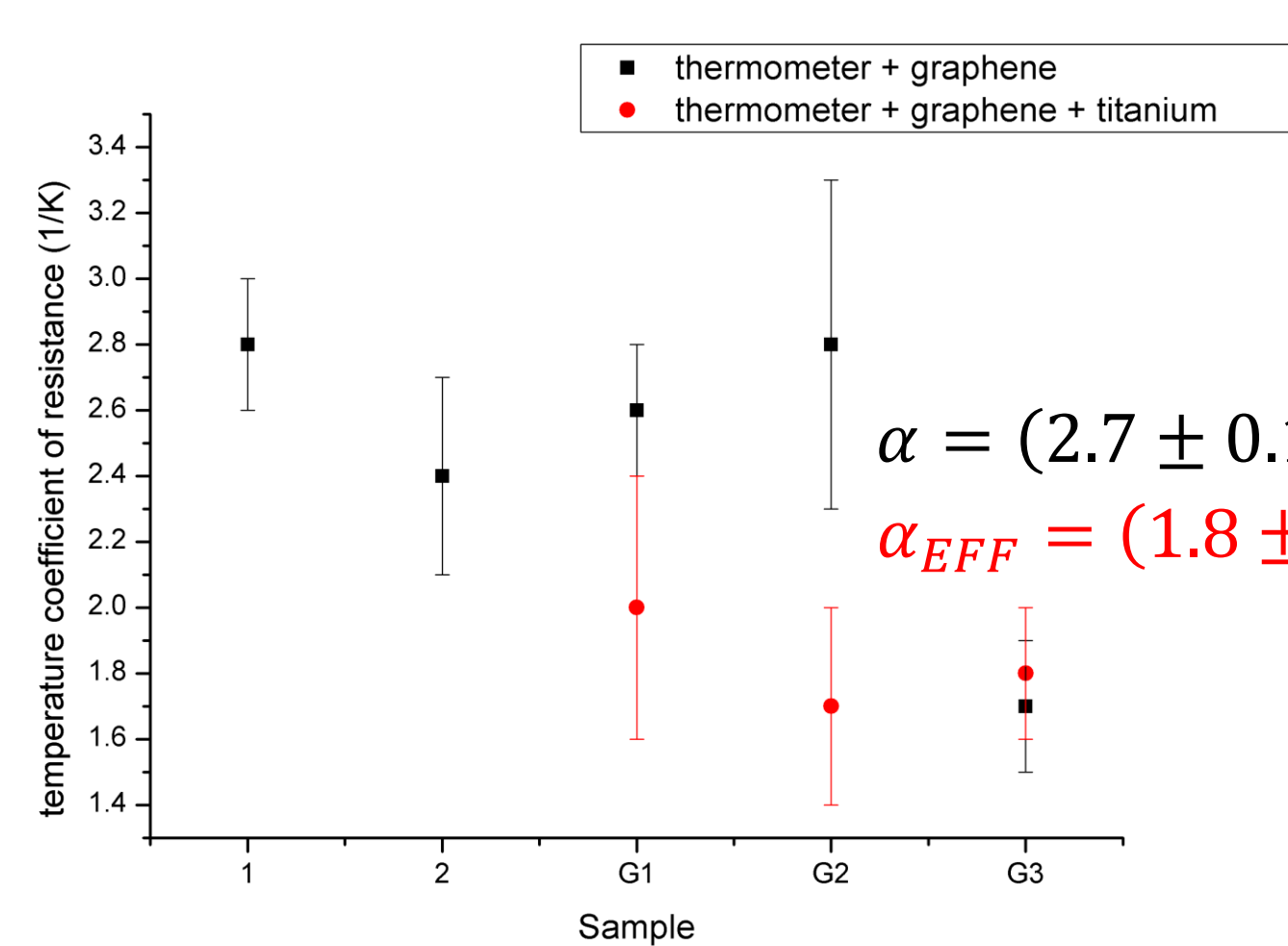


C.) Calibration of Ti evaporator, evaporation of Ti, STM on deposited Ti

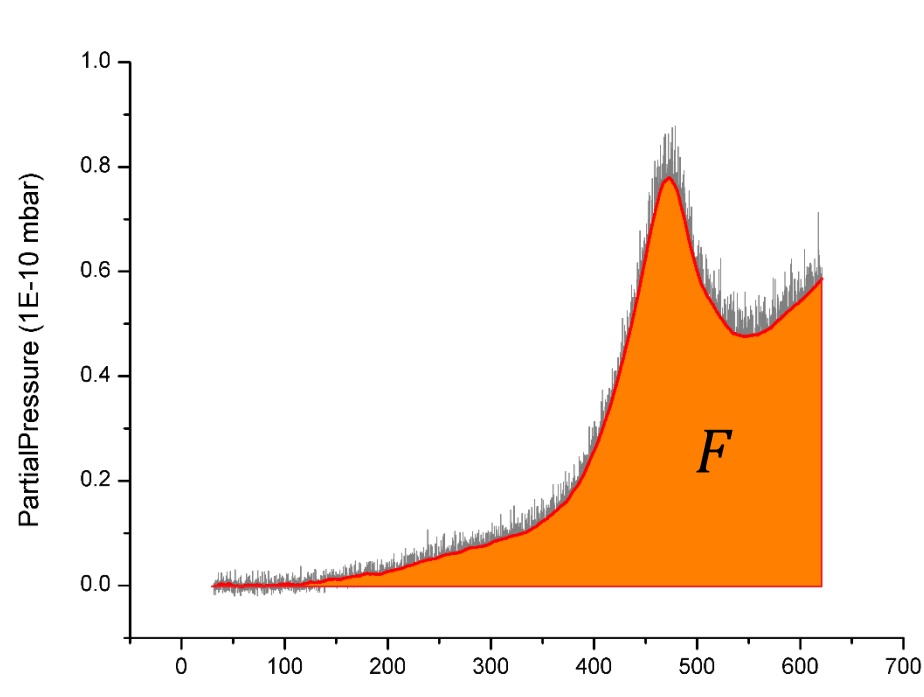


D.) Results: Calculation of the heat transfer

Thermometer calibration



Calibration of the thermometer. We measure α (shown in the figure) and resistivity ρ . α_{EFF} measured after deposition of Ti.

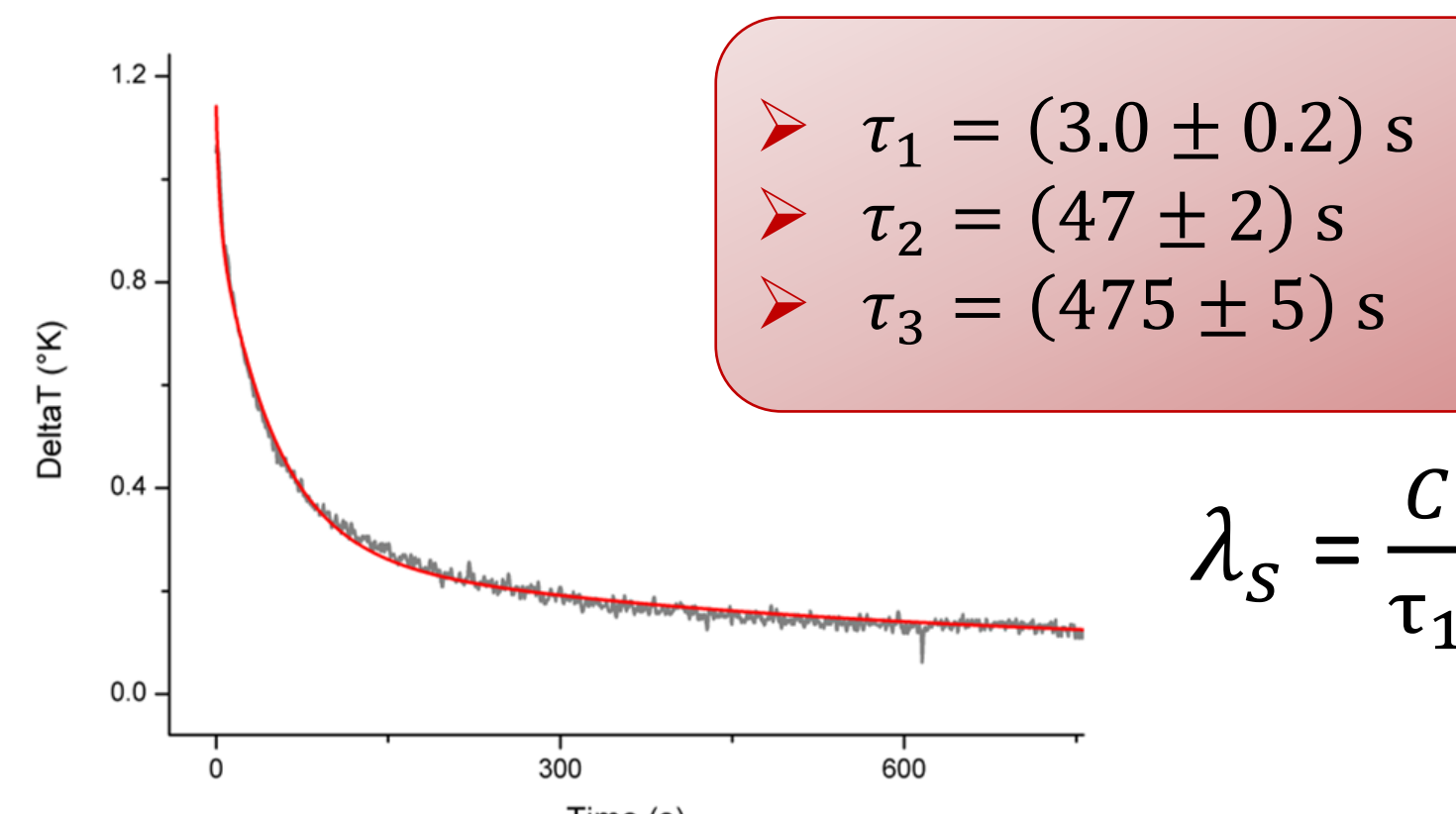


$$H_r = n N_A E_b = (21.8 \pm 1.3) \mu J$$

TDS spectrum vs time. Data allow estimation of hydrogen uptake, in terms of moles, $n(D_2)$.

Heat transfer coefficient

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



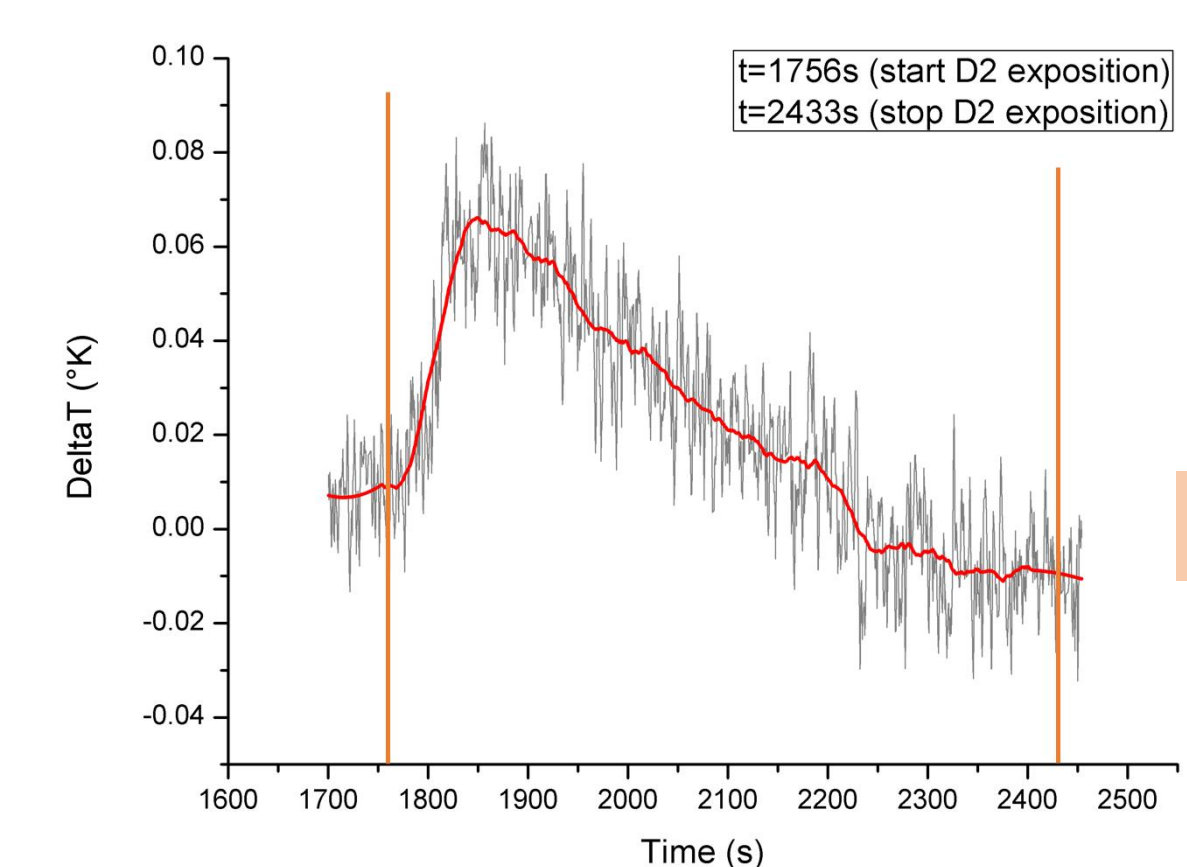
- $\tau_1 = (3.0 \pm 0.2) s$
- $\tau_2 = (47 \pm 2) s$
- $\tau_3 = (475 \pm 5) s$

$$\lambda_s = \frac{C}{\tau_1}$$

Decay signal after a heating step. Heat transfer coefficient λ_s is related to the faster decay time.

Calorimetric analysis

$$\tau = (2.94 \pm 0.63) s \rightarrow \lambda_s = (5.1 \pm 1.1) \cdot 10^{-6} W/K$$



$$\Delta T = 0.065 K$$

$$H_r = (23.4 \pm 4.7) \mu J$$

Thermal signal during hydrogenation of Sample G3 after 1st Ti deposition \rightarrow 12.4 ML

Thermometric results summary

	Ti (ML)	E_d /molecule (eV)	H_r (μJ)	
			calorimetry	TDS
G2 ₍₁₎	8.4	1.29 ± 0.02	22 ± 11	6.75 ± 0.16
G2 ₍₂₎	16.5	1.30 ± 0.06	34 ± 17	26.4 ± 1.4
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

References

- [1] K. S. Novoselov, A. K. Geim, *et al.*, Science, **306**, 666-669, (2004)
- [2] K. M. Fair, *et al.*, Phys. Rev. B, **87**, 014102, (2013)
- [3] E. Durgun, *et al.*, Phys. Rev. B, **78**, 085405, (2008)
- [4] Y. Liu, *et al.*, J. Phys.: Condens. Matter, **22**, 445301 (2010)
- [5] T. Mashoff, *et al.*, Appl. Phys. Lett., **103**, 013903, (2013)
- [6] K. Takahashi, *et al.*, J. Phys. Chem. C, **120**, 12974-12979, (2016)

Conclusions

- We show design of an experimental setup able to directly detect the small H_r during the adsorption of D_2 . Resolution: $\Delta T \sim 0.01 K$ ($\Delta R \sim 0.03 m\Omega$)
- Stable and comparable sample's properties \rightarrow reliability and repeatability
- Agreement between calorimetry (non destructive, direct, and scalable) and TDS.