

# A Sensitive Calorimetric Technique to Study Energy (Heat) exchange at the Nano-Scale

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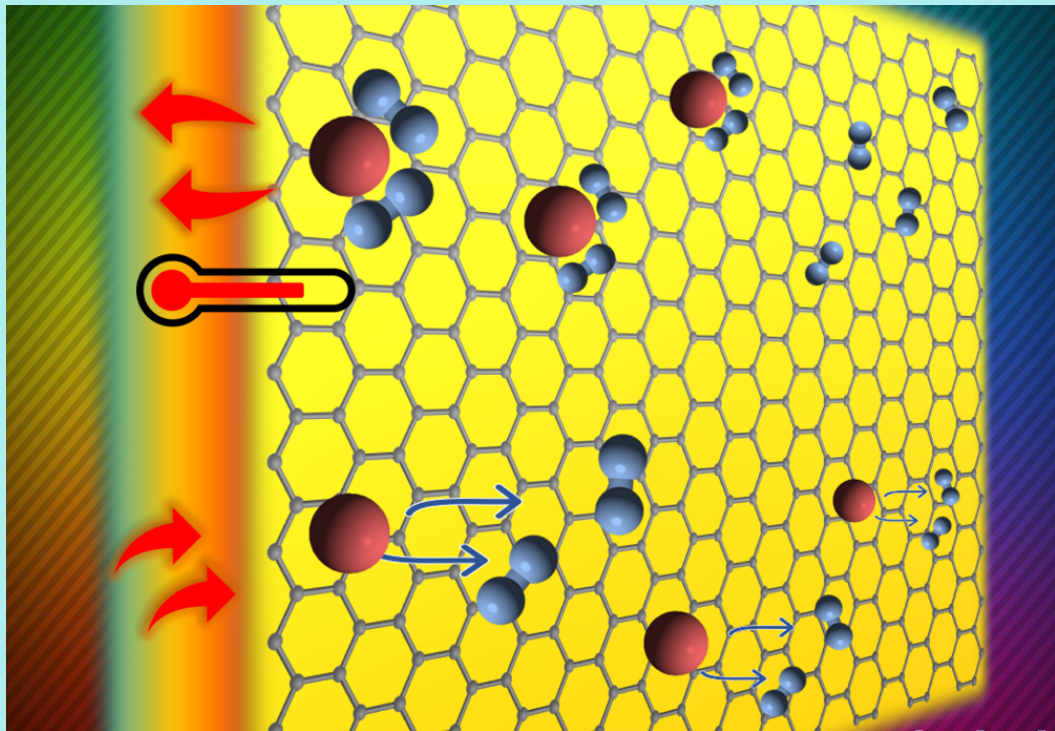
# Outline

- 1 Motivations
- 2 Brief introduction to calorimetry
  - Heat exchange
  - Calorimeters
  - Experimentals
- 3 Experimental setup
  - Thermometer calibration
  - Sample characterization
  - Ti source calibration
- 4 Results
  - Hydrogen uptake
  - Enthalpy of process evaluation

## We need a new technique!

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

Our sample is  $\sim 5 \times 5 \text{ mm}^2$ , corresponding to measure  $10^{-10} \text{ mol}$  ( $\sim$  **fraction of ng**) of stored hydrogen.



## Further motivations

In the last decades, research has resulted in an increasing number of devices at the micro- or nano-scale. **Sensors, catalyzers, and energy storage systems** are more and more developed as **nano-devices** which represent the building blocks for commercial "macroscopic" objects. **A general method for the direct evaluation of the energy balance of such systems is not available at present.** Our calorimetric technique is quite general and can be utilized in a number of experiments:

- H-Storage (utilized for testing the technique)
- Sensors and catalyzers development
- High sensitivity bolometry
- Thermal imaging
- Investigations on small size samples

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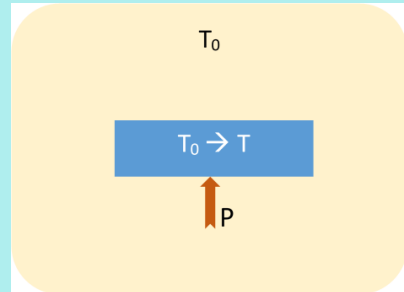
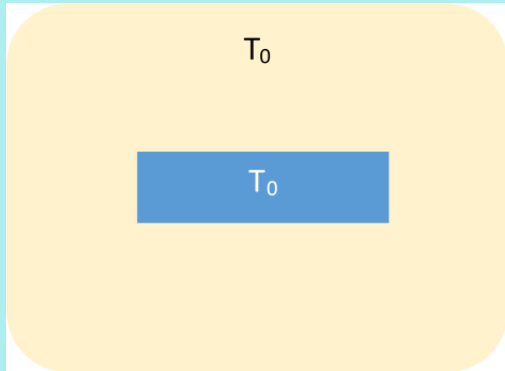
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## Ideal case

In an ideal case thermal losses can be neglected and temperature increases continuously as heating power is supplied.

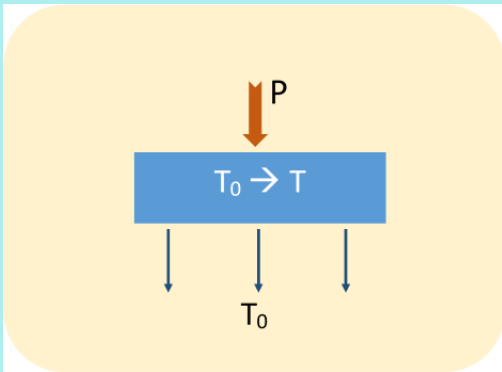


$$\Delta Q = P \cdot t = C \cdot (T - T_0) = C \cdot \Delta T$$

$$C \cdot \frac{dT}{dt} = P$$

## Non-Ideal case

In the real world losses are always present.



$$C \cdot \frac{dT}{dt} = P - \lambda \cdot (T - T_0)$$

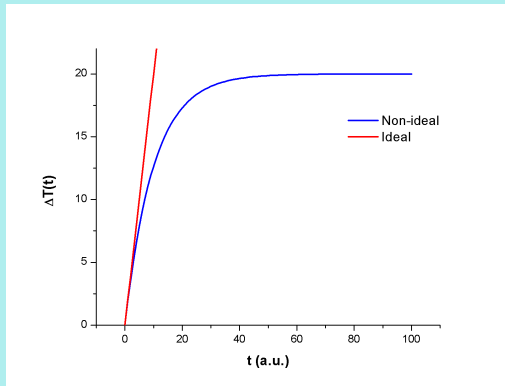
where  $\lambda$  is the heat exchange coefficient.  
The solution is:

$$\Delta T(t) = T(t) - T_0 = \frac{P}{\lambda} \cdot (1 - e^{-\frac{t}{\tau}})$$

where

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

## Non-Ideal case



ideal

$$\Delta Q = C \cdot \Delta T$$

$$C \cdot \frac{dT}{dt} = P$$

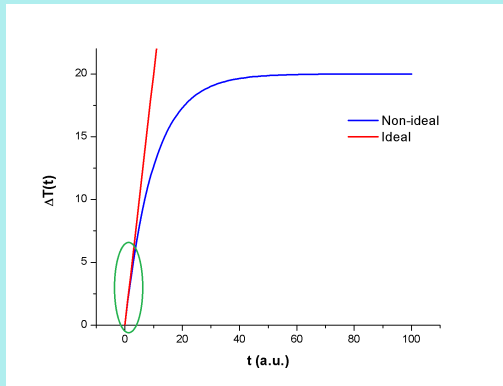
non-ideal

$$\Delta T(t) = T(t) - T_0 = \frac{P}{\lambda} \cdot (1 - e^{-\frac{t}{\tau}})$$

stationary state

$$\frac{dT}{dt} = 0 \Rightarrow (T - T_0) = \frac{P}{\lambda}$$

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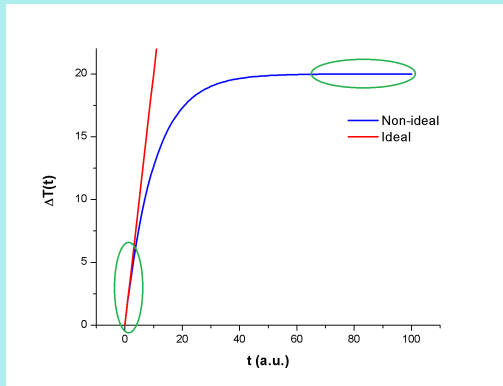
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$$\frac{dT}{dt} = 0 \Rightarrow (T - T_0) = \frac{P}{\lambda}$$

## Heat/Energy balance

The measurement of energy/heat exchange between a system and environment is a very important issue in physical and chemical research. An energy flux accompanies any evolution of a system, giving invaluable information on the processes underlying the evolution.

Calorimetry is the proper tool to investigate heat/energy balance of a system. While the absolute amount of energy in a chemical system is difficult to measure or to calculate, the enthalpy variation is much easier to work with.



# Heat/Energy balance

The enthalpy variation consists in the change in internal energy  $\Delta U$  plus the work  $L$  needed to change the system's volume  $V$ :

$$\Delta H = \Delta U + L = C_p \cdot \Delta T + V \cdot \Delta P = \delta Q + V \cdot \Delta P$$

where  $C_p$  is the heat capacity at constant pressure,  $\Delta T$  and  $\Delta P$  are temperature and pressure variation and  $\delta Q = C_p \cdot \Delta T$ . At constant pressure  $\Delta P = 0$  and  $\Delta H = \delta Q$ .

Brown, M. E. Handbook of Thermal Analysis and Calorimetry; Elsevier, Amsterdam, The Netherlands, 2003; Vol.1

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## commercial devices

It is possible to find a number of commercial calorimeters, specialized to study solid or liquid samples, phase transitions .....

The main question in our case is, essentially, what are the constraints imposed on sample dimensions and by instrument sensitivity.

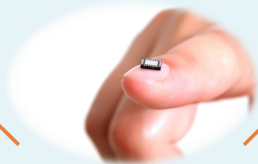
Usual requirements of commercial devices are:

- sample mass in the mg range (10-100 mg);
- sensitivity in energy detection ( $E \geq 1 \text{ mJ}$ )

What does it mean in our system? If we want to detect 10 mg of  $H_2$  on a MLG, considering DOE prescriptions (5.5 wt.%) and the specific surface area of graphene ( $\sim 2600 \text{ m}^2/\text{g}$ ) we will need  $\sim 450 \text{ m}^2$  of MLG

# summarizing

Commercial instruments do not meet a reasonable sample dimension



## Ultra-sensitive thermometry

Very sensitive thermometric techniques have been successfully developed to measure milliKelvin temperature differences in nano-scale devices, mainly in thermoelectric ones.

- quantum dots based thermometers
- Shot noise thermometers (SNT)
- Normal metal-Insulator- Superconductor (NIS) thermometers
- Coulomb Blockade Thermometers (CBT)

Such thermometers, however, can operate only at **Low Temperature** below a few Kelvin. SNT thermometer works at higher temperature too, but sensitivity degrades down to  $\sim 0.5K$  at room temperature.

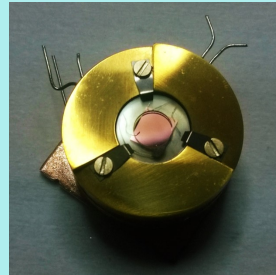
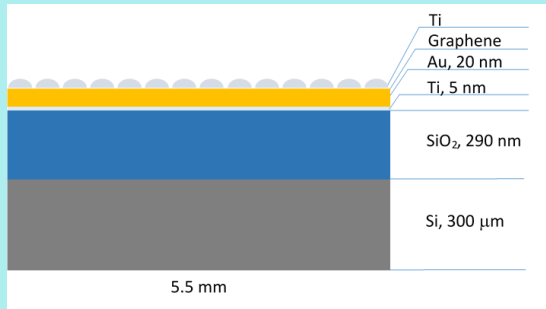
Mavalankar, A.; et al., Applied Physics Letters 2013, **103**, 133116.

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## Sample & holder

Our sample must be loaded on a STM sample holder which limit the maximum physical dimension to about  $6 \times 6 \text{ mm}^2$ . Our gold thermometer has dimensions  $\sim 5.5 \times 5.5 \text{ mm}^2$ .



## limiting scenarios

In our experiment we can consider two limiting situations which give an upper and lower limit to the temperature increase we will measure during hydrogenation of our sample.

- (1) negligible thermal losses (silica acts as a perfect thermal insulator)
- (2) sample fully thermalized (silica acts as a perfect thermal conductor)

In both cases we will neglect the heat capacity of Ti-functionalized MLG and an hydrogen uptake of  $\sim 10^{-10}$  moles will be assumed.



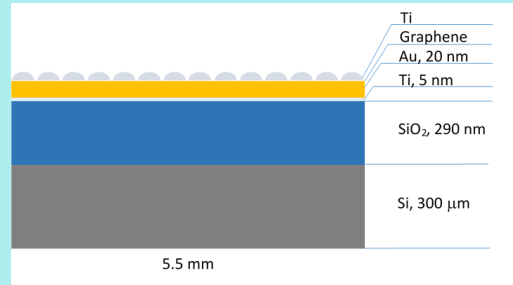
# scenario 1

## scenario 1

In this case the Ti-functionalized MLG, gold film, Ti underneath are completely decoupled from the substrate. So all the energy released during hydrogen adsorption heat up these layers.

$$\Delta T = \frac{E}{C_{Au} + C_{Ti}} \sim 5K$$

where  $C_{Au} = A \cdot d \cdot \rho_{Au} \cdot c_{Au} = 30.3mm^2 \cdot 20 \cdot 10^{-6}mm \cdot 19.3 \cdot 10^{-3}g \cdot 0.129J/(K \cdot g) = (1.51 \pm 0.02) \cdot 10^{-6}J/K$  and, similarly  $C_{Ti} = (0.36 \pm 0.01) \cdot 10^{-6}J/K$ .



we can neglect  $C_{graphene} \sim 10^{-8} J/K$  and the contribution of the Ti deposited on the MLG (a few ML) is negligible ( $C \sim 5 \cdot 10^{-8} J/K$ )

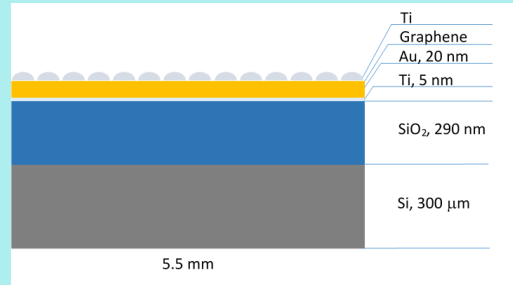
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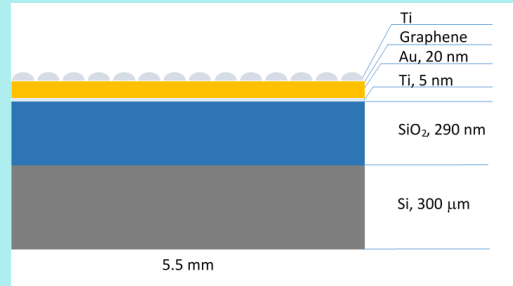
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## scenario 2

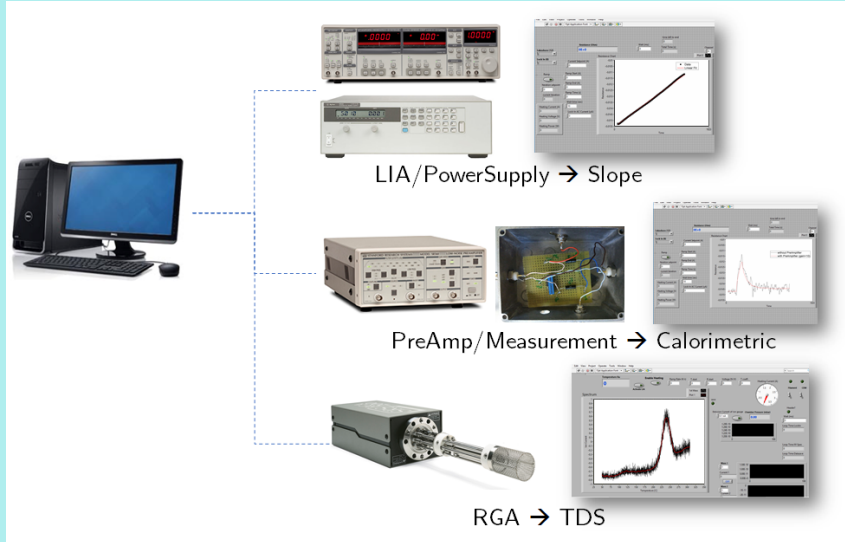
### scenario 2

In this case all the sample thermalize. So all the energy released during hydrogen adsorption heat up the entire sample.

$$\Delta T = \frac{E}{C_{Au} + C_{Ti} + C_{SiO_2} + C_{Si}} \sim 0.7 mK$$



# setup scheme

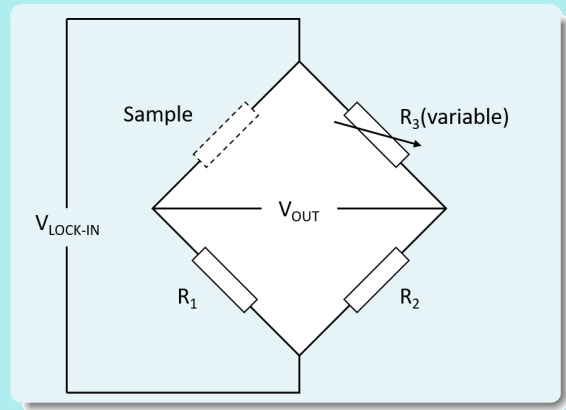


# Thermometer calibration

All experiments are performed in Ultra-High Vacuum (UHV) environment (base pressure  $\sim 10^{-10}$  mbar). Temperature is measured via the gold film resistance, following the linear relation:

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

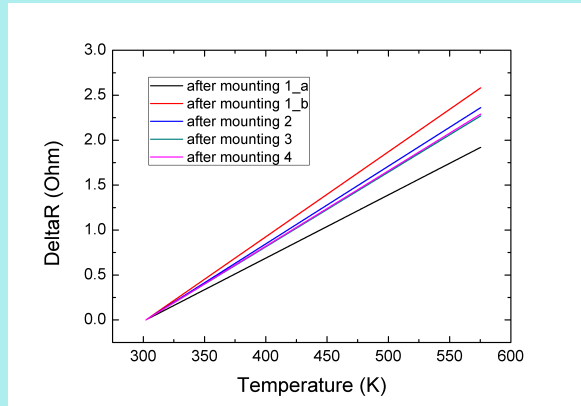
where  $R_0$  is the resistance at the reference temperature  $T_0$  (room temperature in our case) and  $\alpha$  is the resistance temperature coefficient.



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# repeatability



**Figure:** Resistance variation vs. temperature for five different calibration runs on the same sample (Au with MLG). Between mounting 1\_a and 1\_b the sample has been stored for several days in UHV.

# Thermometer characterization

Sample	$R_0$ ( $\Omega$ )	$\alpha_i$ ( $\text{K}^{-1}$ )	$\alpha_f$ ( $\text{K}^{-1}$ )	$\rho_i$ ( $\Omega\text{m}$ )	$\rho_f$ ( $\Omega\text{m}$ )
1	2.96	$(2.8 \pm 0.2) \cdot 10^{-3}$	-	$(3.0 \pm 0.4) \cdot 10^{-8}$	-
2	3.57	$(2.4 \pm 0.3) \cdot 10^{-3}$	-	$(3.6 \pm 0.5) \cdot 10^{-8}$	-
G1	2.95	$(2.6 \pm 0.2) \cdot 10^{-3}$	$(2.0 \pm 0.4) \cdot 10^{-3}$	$(2.9 \pm 0.4) \cdot 10^{-8}$	$(3.5 \pm 0.4) \cdot 10^{-8}$
G2	2.79	$(2.8 \pm 0.5) \cdot 10^{-3}$	$(1.7 \pm 0.3) \cdot 10^{-3}$	$(3.2 \pm 0.4) \cdot 10^{-8}$	$(3.6 \pm 0.5) \cdot 10^{-8}$
G3	3.31	$(1.7 \pm 0.2) \cdot 10^{-3}$	$(1.8 \pm 0.2) \cdot 10^{-3}$	$(3.7 \pm 0.5) \cdot 10^{-8}$	$(3.6 \pm 0.5) \cdot 10^{-8}$
average (with G3)		$(2.4 \pm 0.4) \cdot 10^{-3}$	$(1.8 \pm 0.3) \cdot 10^{-3}$	$(3.2 \pm 0.4) \cdot 10^{-8}$	$(3.6 \pm 0.4) \cdot 10^{-8}$
(without G3)		$(2.7 \pm 0.1) \cdot 10^{-3}$			
literature (bulk) <sup>1</sup>		$3.4 \cdot 10^{-3}$		$2.44 \cdot 10^{-8}$	

**Table:** Comparison of temperature coefficients of resistance  $\alpha$  and electrical resistivity  $\rho$ . Samples 1 and 2 refer to gold thermometer only, while samples G1-3 refer to gold thermometer plus graphene.  $\alpha_i$  and  $\rho_i$  are measured for only Au thermometer with or without MLG, while  $\alpha_f$  and  $\rho_f$  are measured for the Au thermometer with Ti-MLG.

<sup>1</sup> Serway, R.; Jewett, J., 5th ed.; Brooks Cole, Pacific Grove, USA, 2012



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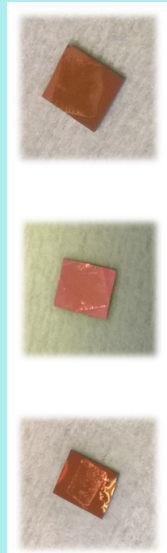
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## Graphene transfer

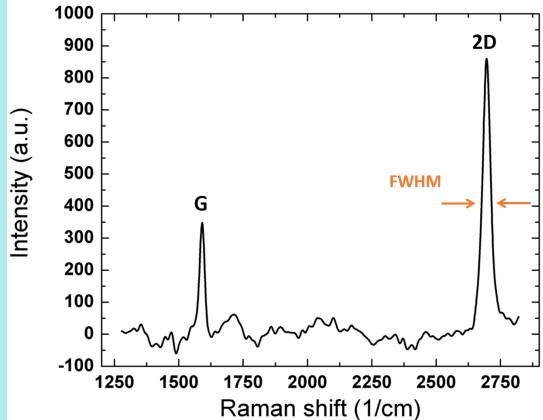
We used a standard PMMA–assisted transfer process for transferring the graphene onto gold–coated SiO<sub>2</sub>/Si substrates.

- graphene/Cu cleaning
- spin coating with PMMA
- removing back layer of graphene
- Cu etching
- PMMA/Gr rinse and transfer on substrates
- PMMA remove, rinse and dry

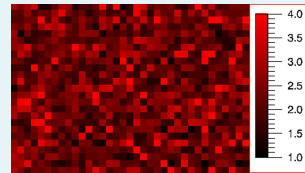
Gabriela Borin Barin, et al., Carbon 2015, **84**, 82–90.



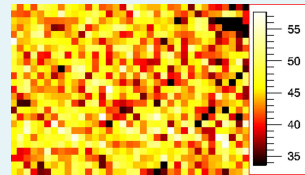
# Raman Spectroscopy



**Figure:** Raman spectrum of the graphene used in our devices, showing the expected *G* and *2D* peaks for monolayer graphene.



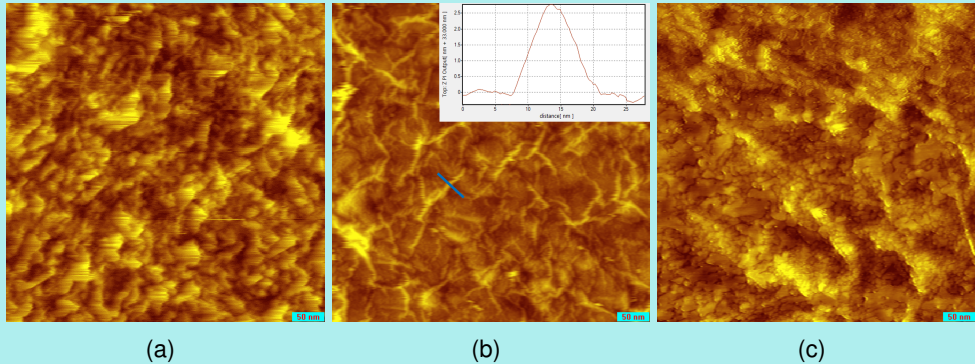
(a)



(b)

**Figure:** (a) Raman intensity ratio map: each pixel gives the ratio between the intensity of the *2D* peak vs the *G* peak. (b) Raman map showing the FWHM (in cm<sup>-1</sup>) of the *2D* peak.

# STM analysis

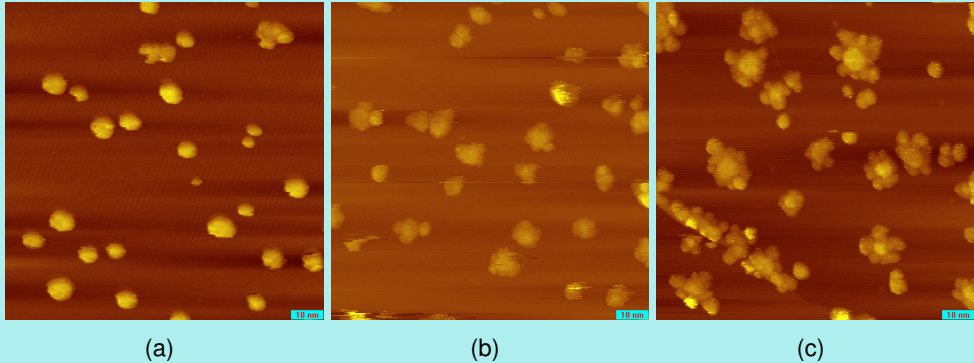


**Figure:** (a) STM image of the Au layer. Image parameters:  $V=1.0$  V,  $I=1.0$  nA, average RMS roughness:  $(0.8 \pm 0.2)$  nm. (b) STM image of the MLG transferred on the Au layer. Image parameters:  $V=0.6$  V,  $I=0.5$  nA, average RMS roughness:  $(1.7 \pm 0.5)$  nm. The inset shows a cross-sectional plot of a wrinkle taken along the blue line in the STM image. (c) STM image of 12.4 ML Ti evaporated on MLG. Image parameters:  $V=0.2$  V,  $I=0.09$  nA, average RMS roughness:  $(2.0 \pm 0.5)$  nm. All images  $500 \times 500$  nm<sup>2</sup>.

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# STM analysis



**Figure:** STM images ( $100 \times 100 \text{ nm}^2$ ) of Ti deposited on SiC. (a) 10 s. (b) 20 s. (c) 40 s. Parameters for all images:  $V = 0.3 \text{ V}$ ,  $I = 0.2 \text{ nA}$ .

# Source Calibration

Deposition time	Area coverage	Ti deposited
10s	$(8.2 \pm 1.6)\%$	$(0.24 \pm 0.03)\text{ML}$
20s	$(14 \pm 3)\%$	$(0.45 \pm 0.05)\text{ML}$
40s	$(25 \pm 2)\%$	$(0.89 \pm 0.10)\text{ML}$

Table: Area coverage and amount of Ti deposited.

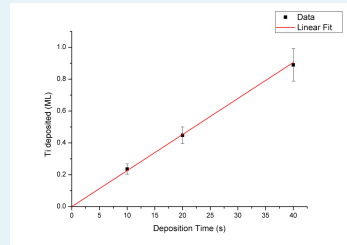
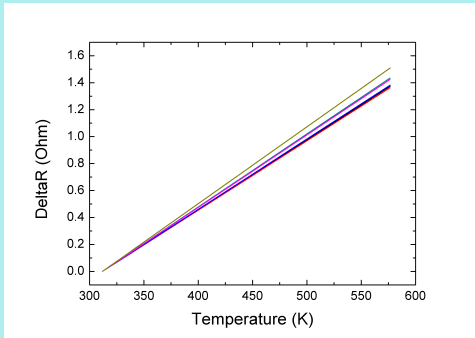


Figure: Fit of the calibration data taken from Table.

following the method described in: T. Mashoff, M. Takamura, S. Tanabe, H. Hibino, F. Beltram and S. Heun, Applied Physics Letters, 2013, **103**, 013903.

# Thermometer + MLG + Ti characterization



**Figure:** Resistance variation ( $\Delta R = R(T) - R_0$ ) vs. temperature for six different heating experiments on the same Au+Ti-MLG sensor.

Ramp	$\alpha_f$ ( $\text{K}^{-1}$ )
1	$(1.57 \pm 0.01) \cdot 10^{-3}$
2	$(1.56 \pm 0.01) \cdot 10^{-3}$
3	$(1.58 \pm 0.02) \cdot 10^{-3}$
4	$(1.64 \pm 0.02) \cdot 10^{-3}$
5	$(1.63 \pm 0.02) \cdot 10^{-3}$
6	$(1.72 \pm 0.02) \cdot 10^{-3}$

**Table:** Temperature coefficient of resistance ( $\alpha_f$ ) for each of the heating ramps presented in Figure. The average value is  $\alpha_f = (1.62 \pm 0.05) \cdot 10^{-3} \text{ K}^{-1}$ .



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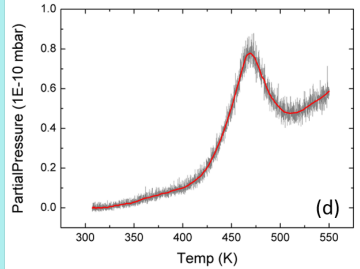
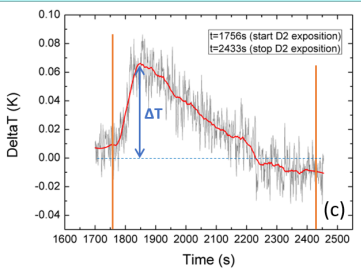
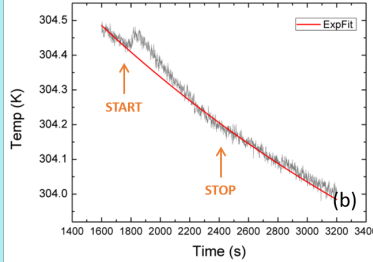
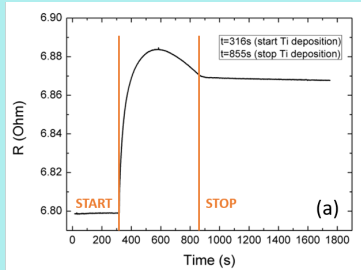
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## hydrogenation sequence

All samples' Hydrogenation experiments follow the same protocol. The main step of the process can be summarized in:

- Sensor resistance variation during Ti deposition ( $\sim 600$ s) on MLG;
- Sensor temperature variation during exposure of the Ti film to  $D_2$ ;
- TDS spectrum of Ti-MLG sample after 5 min of  $D_2$  exposure at  $P_{D_2} = 1.0 \cdot 10^{-7}$  mbar

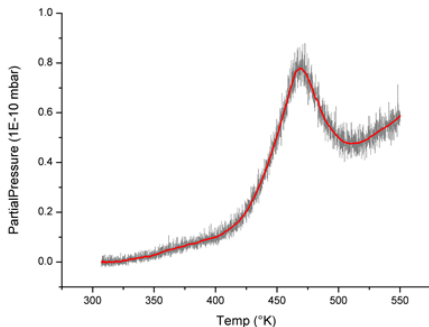
# Calorimetry during hydrogenation



(a) Ti deposition (for 539 s, 12.4 ML of Ti) on MLG.  
(b) Exposure of the Ti film to D<sub>2</sub> (red line: exponential fit of the thermalization background).  
(c) Thermalization background subtracted. A  $\Delta T = 0.065$  K is clearly detected.  
(d) TDS spectrum of Ti-MLG (Red line: smoothing).

# TDS analysis

TDS spectrum vs Temp

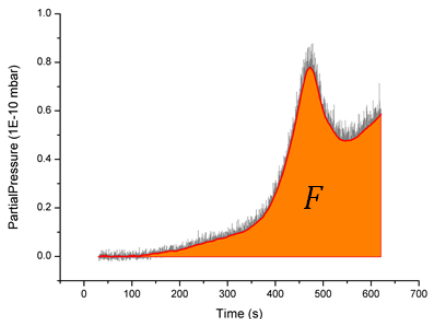


$$\frac{E_d}{k_B T_p} = A \tau_m \exp\left(-\frac{E_d}{k_B T_p}\right)$$

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

## TDS analysis

TDS spectrum vs time



$$p V = F S = n R T$$

$$S \approx 300 \text{ L/s}$$



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

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

# Outline

- 1 Motivations
- 2 Brief introduction to calorimetry
  - Heat exchange
  - Calorimeters
  - Experimentals
- 3 Experimental setup
  - Thermometer calibration
  - Sample characterization
  - Ti source calibration
- 4 Results
  - Hydrogen uptake
  - Enthalpy of process evaluation

# Thermal model

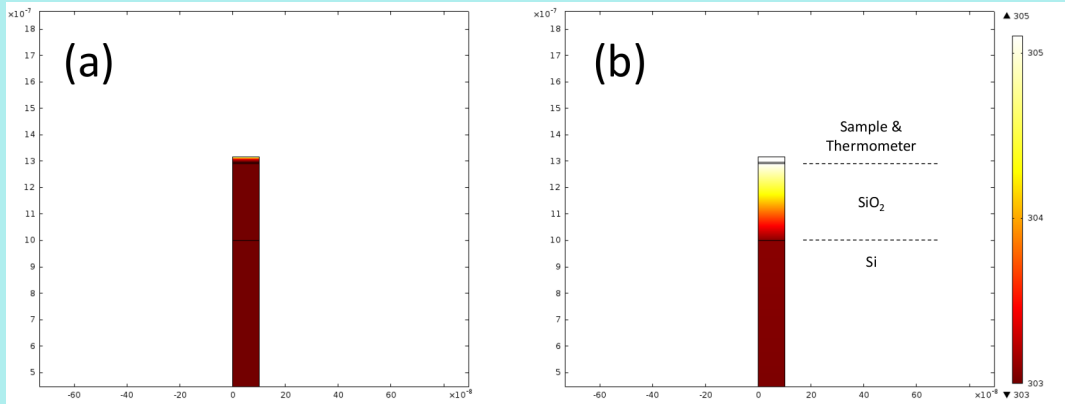
We can describe the system with a simple thermal model in which the thermometer is heated by the absorption of a thermal power  $P(t) = \delta H_r / \delta t$  while at the same time it releases energy by heat losses towards the substrate. These two contributions are related by the following equation:

$$\delta H_r / \delta t = C \cdot \delta \Delta T(t) / \delta t + \lambda \cdot \Delta T(t)$$

The sensor heat capacity  $C$  and the thermal exchange coefficient  $\lambda$  must be evaluated.

M. Cassettari, F. Papucci, G. Salvetti, E. Tombari, S. Veronesi, G. Johari, "Simultaneous measurements of enthalpy and heat capacity of a thermosetting polymer during the curing process" Review of Scientific Instruments 1993, **64**, 1076-1080

# COMSOL simulation of Temperature distribution



**Figure:** (a) Temperature distribution at  $t = 1$  ns when the temperature jump of 2 K has just been applied to the topmost layer of the stack. All other parts of the stack are still at 303 K. (b) Temperature distribution at  $t = 0.1 \mu\text{s}$ .



## Heat capacity evaluation

We can describe the system with a simple thermal model in which the thermometer is heated by the absorption of a thermal power  $P(t) = \delta H_r / \delta t$  while at the same time it releases energy by heat losses towards the substrate. These two contributions are related by the following equation:

$$\delta H_r / \delta t = C \cdot \delta \Delta T(t) / \delta t + \lambda \cdot \Delta T(t)$$

The sensor heat capacity  $C$  include the graphene layer, the Au thermometer, and the SiO<sub>2</sub> layer underneath. We obtain the total heat capacity  $C = (15.0 \pm 0.2) \cdot 10^{-6}$  J/K.

## Heat losses evaluation

We expect that three time scales will be involved:

- a short one, related to the sample and thermometer thermalization
- an intermediate one, related to the substrate thermalization
- a long one, related to the thermalization towards the environment (sample holder).

To experimentally verify, we heated the sample for a short time with a known thermal power, then we switched off the heating and monitored the cooling process.

The cooling curve can be described as the sum of three exponential decays with very distinct time scales, listed in the Table.

Decay time	Exp. value (s)
$\tau_1$	$(2.9 \pm 0.6)$
$\tau_2$	$(47 \pm 2)$
$\tau_3$	$(475 \pm 5)$

Table: Characteristic decay times obtained from the fit of the cooling data.

This allows us to calculate  $\lambda$  as  
 $\lambda = C/\tau_1 = (5.1 \pm 1.1) \cdot 10^{-6}$  W/K.

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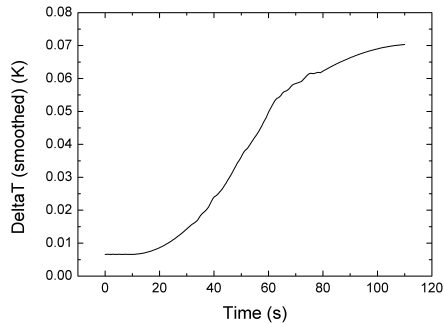
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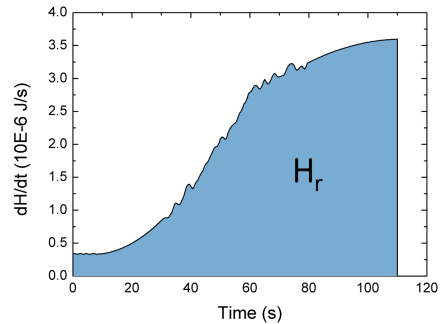
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This allows us to calculate  $\lambda$  as  
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# Enthalpy calculation I



(a)



(b)

**Figure:** (a) Rising part of  $\Delta T(t)$  (smoothed) at the beginning of  $D_2$  exposure of the Ti-MLG (same data as Figure 36(c)). (b)  $\delta H_r / \delta t$  for the same measurement (the area integration is shown in light blue).

## Enthalpy calculation II

### Experimental results

From the equation:

$$\delta H_r / \delta t = C \cdot \delta \Delta T(t) / \delta t + \lambda \cdot \Delta T(t)$$

performing a point-by-point derivative of the measured  $\Delta(T)$  curve and a point-by-point integration of  $\delta H_r / \delta t$ , with the experimental parameters

- $\tau = (2.9 \pm 0.6)s$
- sample heat capacity  $C = (15.0 \pm 0.2) \cdot 10^{-6} J/K$
- Heat exchange coefficient  $\lambda = (5.1 \pm 1.1) \cdot 10^{-6} W/K$

The enthalpy release during the  $D_2$  adsorption results to be  $H_r = (23.4 \pm 4.7)\mu J$

L. Basta, S. Veronesi, Y. Murata, Z. Dubois, N. Mishra, F. Fabbri, C. Coletti, S. Heun, "A sensitive calorimetric technique to study energy (heat) exchange at the nano-scale", submitted to Nanoscale

## Final remarks

The enthalpy release due to hydrogen adsorption on a Ti-functionalized MLG has been measure in two different ways:

- TDS which is a consolidated technique
- during H adsorption via calorimetry, which is a new developed technique

### TDS results

- Binding energy  $(1.32 \pm 0.07)$  eV/molecule
- Desorbed  $D_2$  molecules  
 $n = (1.03 \pm 0.01) \cdot 10^{14}$   
corresponding to  
 $(1.71 \pm 0.01) \cdot 10^{-10}$  moles
- released enthalpy  
 $H_r = n \cdot E_d = (21.8 \pm 1.3) \mu J$

### Calorimetry results

- sample heat capacity  
 $C = (15.0 \pm 0.2) \cdot 10^{-6} J/K$
- Heat exchange coefficient  
 $\lambda = (5.1 \pm 1.1) \cdot 10^{-6} W/K$
- released enthalpy  
 $H_r = (23.4 \pm 4.7) \mu J$

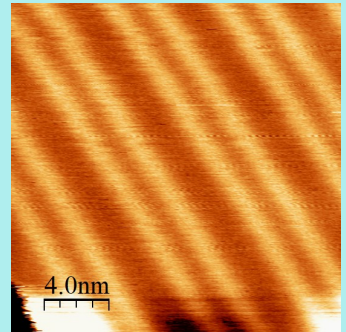
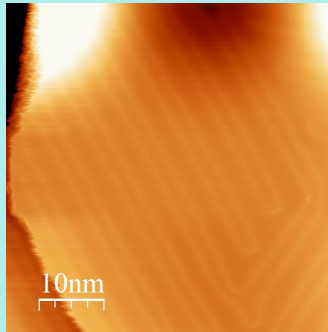
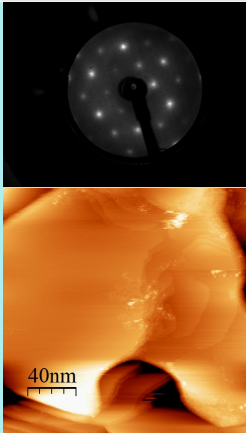
## Conclusions

First direct measurement of enthalpy release during Hydrogen adsorption process

- resistance readout sensitivity  $\sim 0.03m\Omega$
- temperature variation sensitivity 10 mK
- $H_2$  detected during adsorption  $\sim 0.2ng$  or  $(1.71 \pm 0.01) \cdot 10^{-10}$  moles
- corresponding to a released enthalpy  $H_r = (23.4 \pm 4.7)\mu J$
- in good agreement with TDS evaluation  $H_r = n \cdot E_d = (21.8 \pm 1.3)\mu J$
- advantages: calorimetric evaluation is direct and do not need  $H_2$  desorption, while TDS need the desorption of the loaded  $H_2$

# Outlook

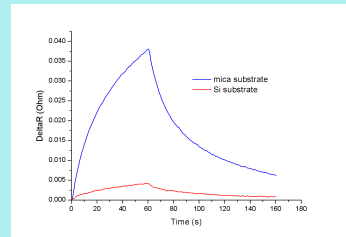
An issue to solve is relative to surface roughness. Atomically speaking Gold thermometer has a rough surface which do not allow atomic resolution with STM. Mica allow surface reconstruction of Gold, solving this problem.





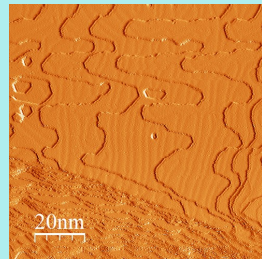
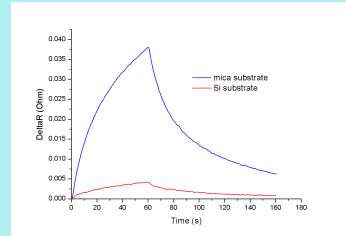
# Outlook

- new sensor substrate (Mica) allowing better performances
- possibility to obtain gold re-crystallization in situ
- atomically flat surface to fully exploit STM potentiality
- application to sensors
- application to flexible detectors



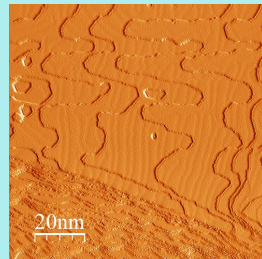
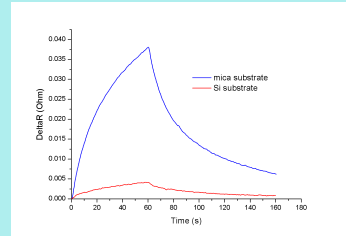
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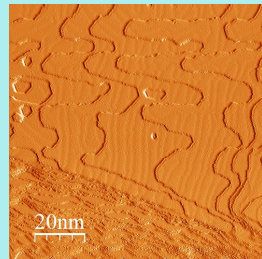
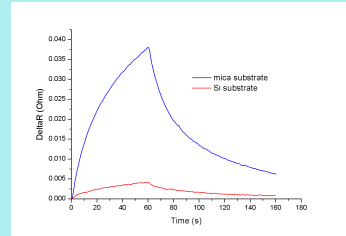
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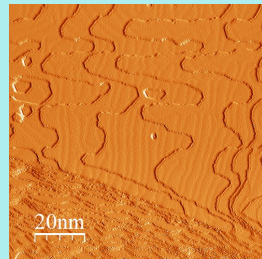
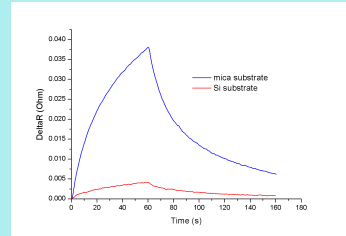
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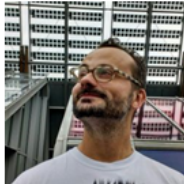


# Outlook

- new sensor substrate (Mica) allowing better performances
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# People



thanks

*Thank you for your attention*