Sensing energy (heat) exchange at the nano-scale during H_2-uptake on Ti-functionalized graphene

S. Veronesi,[1] L. Basta,[1] Y. Murata,[1] Z. Dubois,[1] N. Mishra,[2,3]
F. Fabbri,[2,3] C. Coletti[2,3] and S. Heun[1]

[1]NEST Istituto Nanoscienze-CNR and Scuola Normale Superiore, Piazza S. Silestro 12,
56127 Pisa, Italy
[2]Center for Nanotechnology Innovation @ NEST, Istituto Italiano di Tecnologia, Piazza S. Silvestro 12,
56127 Pisa, Italy
[3]Graphene Labs, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

Bologna, Materials 2018, 22-26 October

Outline

1. Motivation
2. Experimental setup
    - Calorimetry
    - Setups
    - Samples characterization
3. Experimental Results
    - Hydrogen uptake
    - Enthalpy of process evaluation
4. Conclusions and Outlook

Motivation

A detailed knowledge of the energy exchange in the fast growing family of micro and nano-systems could allow to obtain valuable information about the chemistry and physics at the nano-scale. A calorimetric evaluation of tiny samples would represent a precious source of information in developing

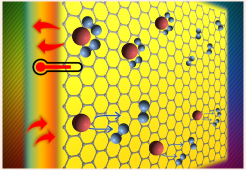
- Sensors
- Catalyzers
- Molecules of pharmaceutical interest
- H-Storage devices

Even if performance is improving with time, commercial calorimeters are still far from the access to nano-scale samples.

Motivation

A detailed knowledge of the energy exchange in the fast growing family of micro and nano-systems could allow to obtain valuable information about the chemistry and physics at the nano-scale. A calorimetric evaluation of tiny samples would represent a precious source of information in developing

- Sensors
- Catalyzers
- Molecules of pharmaceutical interest
- H-Storage devices



Even if performance is improving with time, commercial calorimeters are still far from the access to nano-scale samples.

Outline

1. Motivation
2. Experimental setup
   - Calorimetry
   - Setups
   - Samples characterization
3. Experimental Results
   - Hydrogen uptake
   - Enthalpy of process evaluation
4. Conclusions and Outlook

commercial devices

Usually commercial devices require:

- sample mass in the mg range (usually 10 mg)
- limited energy sensitivity ($\sim$ mJ)

Sensitive thermometric techniques are able to measure milli-Kelvin temperature differences in devices at the nano-scale. But, they can operate only at low temperatures (below a few Kelvin).

What does it mean for Ti-Hydrogen system? If we want to detect 10 mg of H_2 on a MLG, considering US Department of Energy DOE prescriptions (5.5 wt.%) and the specific surface area of graphene ($\sim 2600 m^2/g$) we will need $\sim$ **$450 m^2$** of MLG.

commercial devices

Usually commercial devices require:

- sample mass in the mg range (usually 10 mg)
- limited energy sensitivity ($\sim$ mJ)

Sensitive thermometric techniques are able to measure milli-Kelvin temperature differences in devices at the nano-scale. But, they can operate only at low temperatures (below a few Kelvin).

What does it mean for Ti-Hydrogen system? If we want to detect 10 mg of H_2 on a MLG, considering US Department of Energy DOE prescriptions (5.5 wt.%) and the specific surface area of graphene ($\sim 2600 m^2/g$) we will need $\sim$ **$450 m^2$** of MLG.

commercial devices

Usually commercial devices require:

- sample mass in the mg range (usually 10 mg)
- limited energy sensitivity ($\sim$ mJ)

Sensitive thermometric techniques are able to measure milli-Kelvin temperature differences in devices at the nano-scale. But, they can operate only at low temperatures (below a few Kelvin).

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

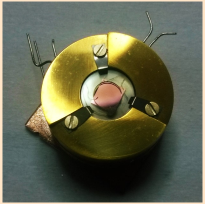
Our original calorimetric technique has been tested on a Ti-functionalized MLG sample, which is a system well investigated. Overall sample mass is **10 ng**, 6 order of magnitude lower than commercial device request.

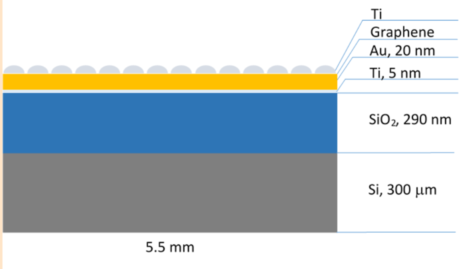
Our original calorimetric technique has been tested on a Ti-functionalized MLG sample, which is a system well investigated. Overall sample mass is **10 ng**, 6 order of magnitude lower than commercial device request.

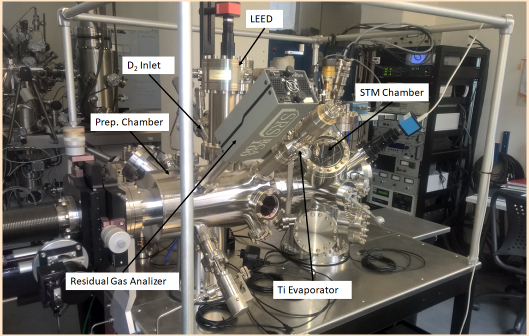
Outline

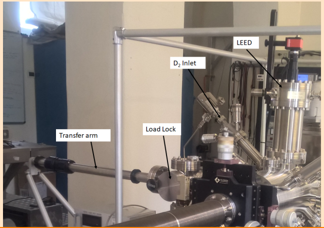
1. Motivation
2. Experimental setup
   - Calorimetry
   - Setups
   - Samples characterization
3. Experimental Results
   - Hydrogen uptake
   - Enthalpy of process evaluation
4. Conclusions and Outlook

Sample & holder









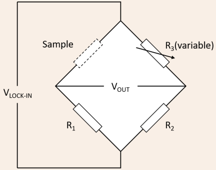
Thermometer working principle

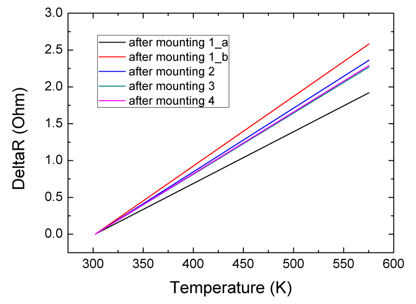
All experiments are performed in Ultra-High Vacuum (UHV) environment (base pressure $\sim 10^{-10} mbar$).

Temperature is measured via the gold film resistance, following the linear relation:

$$\boldsymbol{R(T) = R_0\,[1 + \alpha\,(T - T_0)]}$$

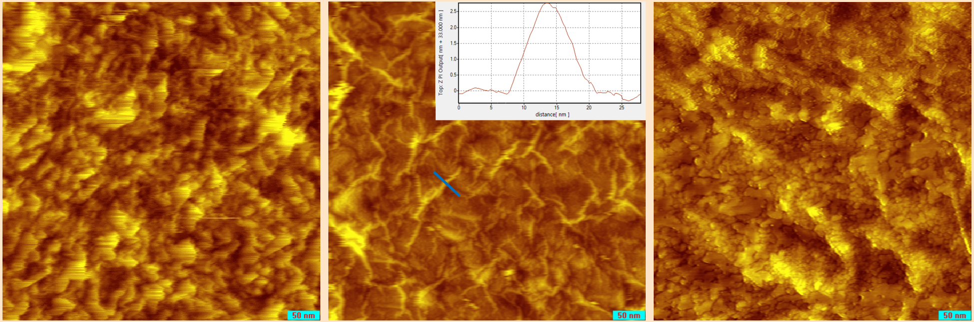
where R_0 is the resistance at the reference temperature T_0 (room temperature in our case) and α is the resistance temperature coefficient.





Outline

STM analysis



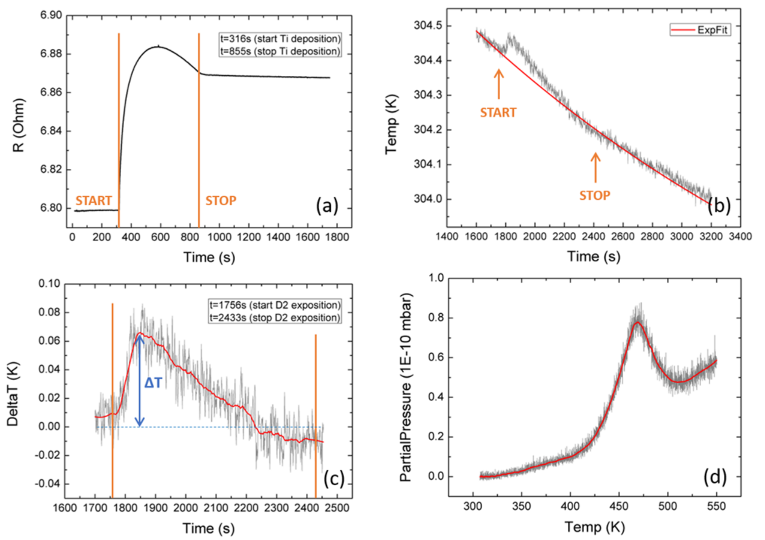
(a) (b) (c)

Figure: (a) STM image of the Au layer. Image parameters: V=1.0 V, I=1.0 nA, average RMS roughness: (0.8 ± 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 ± 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 ± 0.5) nm. All images 500 × 500 nm^2.

Outline

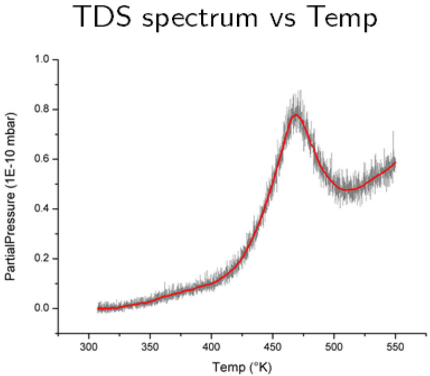
1. Motivation
2. Experimental setup
    - Calorimetry
    - Setups
    - Samples characterization
3. Experimental Results
    - Hydrogen uptake
    - Enthalpy of process evaluation
4. Conclusions and Outlook

Calorimetry during hydrogenation



(a) Ti deposition (for 539 s, 12.4 ML of Ti) on MLG. (b)Exposure of the Ti film to D_2(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

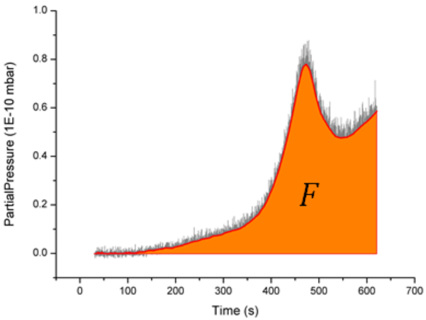

TDS spectrum vs Temp

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

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

TDS analysis

TDS spectrum vs time



$$\boxed{p\,V = F\,S = n\,R\,T}$$

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

$$\downarrow$$

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

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

Outline

Thermal model

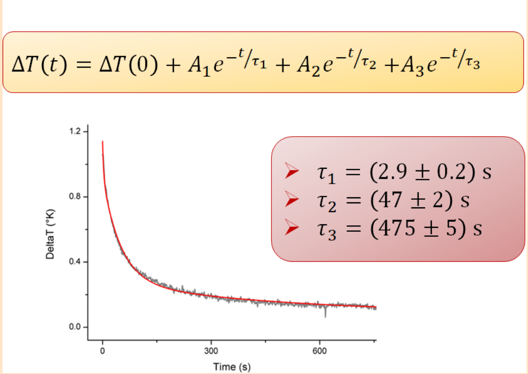
We can describe the system with a simple thermal model in which the thermometer is heated by the absorption of a thermal power $\boldsymbol{P(t) = \delta H_r/\delta t}$ while at the same time it releases energy by heat losses towards the substrate. These two contributions are related by the following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

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

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

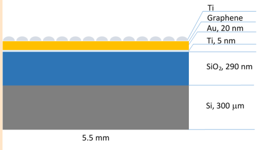
M. Cassettari, F. Papucci, G. Salvetti, E.Tombari, S.Veronesi, G. Johari, "Simultaneous measurements of enthalpy and heat capacity of a thermosetting polymer during the curing process" Review of Scientific Instruments 1993, **64**, 1076-1080

Heat capacity and losses evaluation



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

- $\tau_1 = (2.9 \pm 0.2)$ s
- $\tau_2 = (47 \pm 2)$ s
- $\tau_3 = (475 \pm 5)$ s

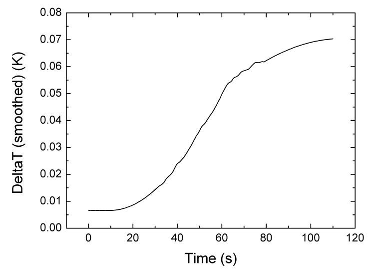


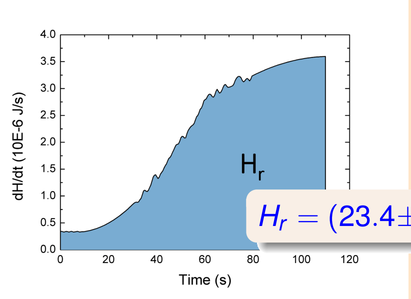
From the decay curve analysis and comsol simulation can be figure out

- the total heat capacity $C = (15.0 \pm 0.2) \cdot 10^{-6}$ J/K with $C = C_{Au} + C_{Ti} + C_{SiO_2}$.
- The heat exchange coefficient λ as $\lambda = C/\tau_1 = (5.1 \pm 1.1) \cdot 10^{-6}$ W/K.

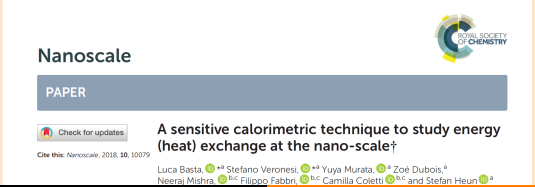
Enthalpy calculation

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





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



ROYAL SOCIETY OF CHEMISTRY

Nanoscale

PAPER

Check for updates

Cite this: *Nanoscale*, 2018, **10**, 10079

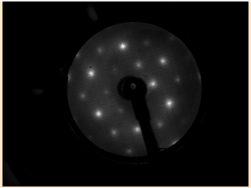
A sensitive calorimetric technique to study energy (heat) exchange at the nano-scale†

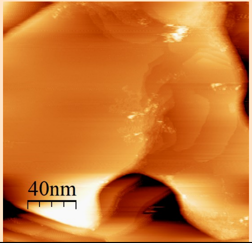
Luca Basta, *[a] Stefano Veronesi, *[a] Yuya Murata, [a] Zoé Dubois,[a] Neeraj Mishra, [b,c] Filippo Fabbri, [b,c] Camilla Coletti [b,c] and Stefan Heun [a]

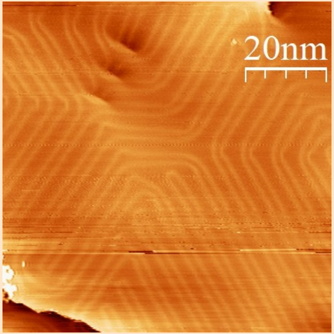
Next generation of thermometer based on Mica substrate

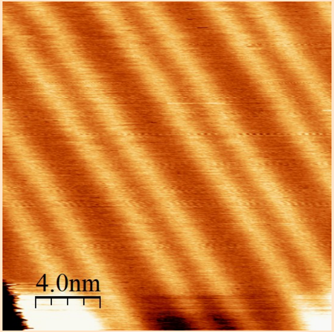
Next generation of thermometer

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 allows surface reconstruction of Gold, solving this problem.



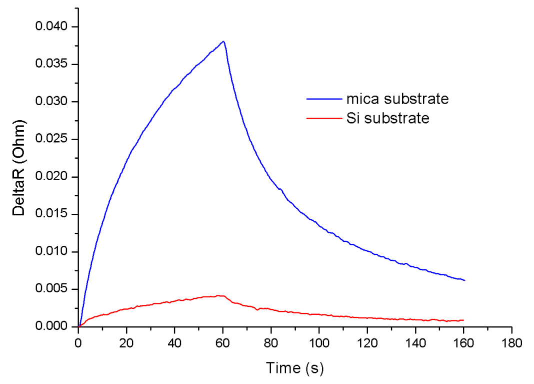






Next generation of thermometer

Moreover, the new sensor substrate (Mica) allows a better performance in terms of sensitivity.



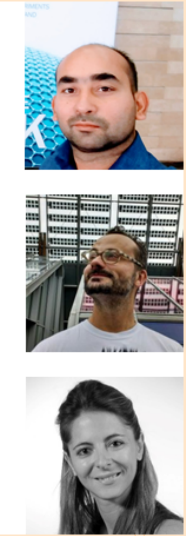
Conclusions and Outlook

First direct measurement of enthalpy release during Hydrogen adsorption process

- resistance readout sensitivity $\sim 0.03 m\Omega$
- temperature variation sensitivity $10 mK$
- H_2 detected during adsorption $\sim 0.2 ng$ or $(1.71 \pm 0.01) \cdot 10^{-10}$ moles
- advantages:
  - calorimetric evaluation is direct and do not need H_2 desorption, while TDS need the desorption of the loaded H_2
  - in presence of a **desorption barrier** the calorimetric evaluation is not affected while TDS would include it
- Simultaneous investigation of energy transfer mechanisms and STM analysis on the same physical support

People

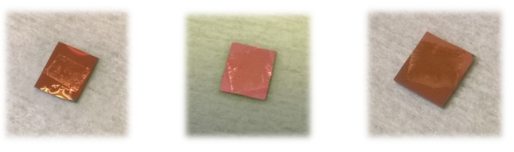

NEST
SCUOLA NORMALE SUPERIORE PISA
National Enterprise for nanoScience and nanoTechnology
iit @NEST
ISTITUTO ITALIANO DI TECNOLOGIA
CENTER FOR NANOTECHNOLOGY INNOVATION
NEST
SCUOLA SUPERIORE SANT'ANNA PISA
CNRNANO
PISA NEST

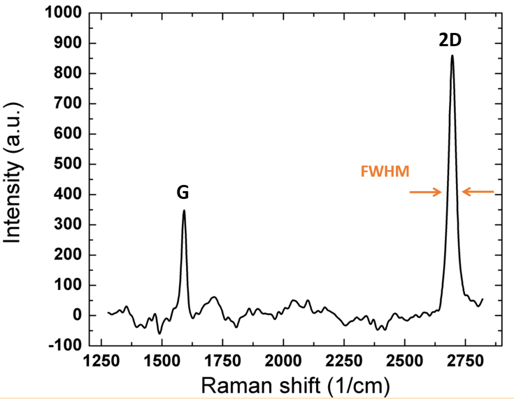


thanks

Thank you for your attention

Raman Spectroscopy





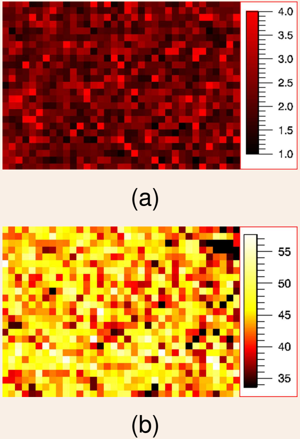


Figure: (a) Raman intensity ratio map: each pixel gives the ratio between the intensity of the $2D$ peak vs the G peak. (b) Raman map showing the FWHM (in cm^{-1}) of the $2D$ peak.

COMSOL simulation

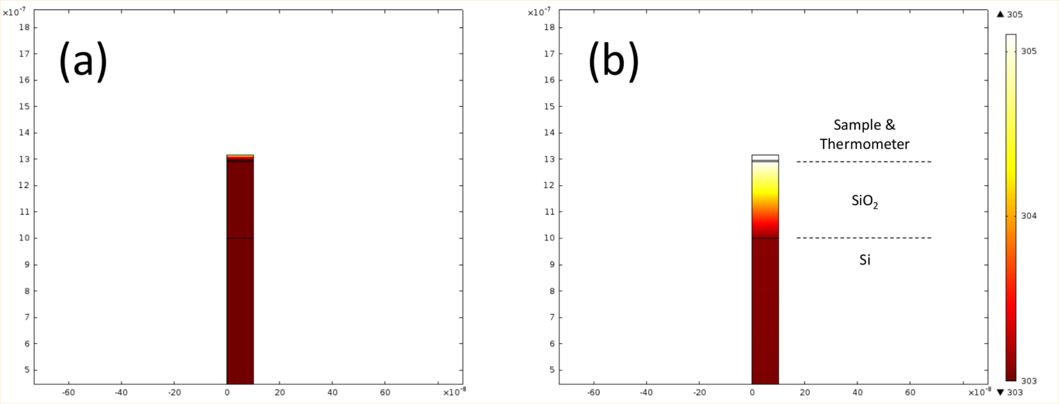
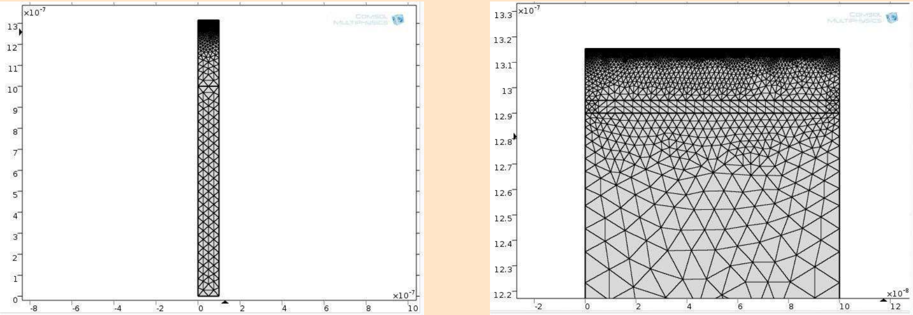


Figure: (a) Temperature distribution at t = 1 ns when the temperature jump of 2 K has just been applied to the topmost layer of the stack. All other parts of the stack are still at 303 K. (b) Temperature distribution at t = 0.1 μs.

Simulation mesh



(a) (b)

Figure: (a) Evaluation mesh (free Triangular with a Normal Size) utilized in the COMSOL simulation. (b) Zoom–in of the top part of the sample.

Thermometer + MLG + Ti characterization

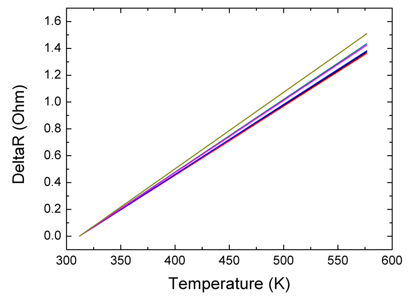


Figure: Resistance variation ($\Delta R = R(T) - R_0$) vs. temperature for six different heating experiments on the same Au+Ti–MLG sensor.

Ramp	α_f **(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 (α_f) for each of the heating ramps presented in Figure. The average value is $\alpha_f = (1.62 \pm 0.05) \cdot 10^{-3}\ \mathrm{K}^{-1}$.

Calorimetry

The enthalpy variation consists in the change in internal energy ΔU plus the work L needed to change the system's volume V. Working at constant pressure allows a simplified relation between Enthalpy variation ΔH and heat exchanged δQ:

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

In case of exothermic or endothermic reactions (with time-independent C_p):

$$\frac{\delta H_r}{\delta t} = C_p \cdot \frac{\delta \Delta T}{\delta t} + \lambda \cdot \Delta t$$

where $\lambda \cdot \Delta t$ represent losses toward the substrate