

Bridging heat exchange and surface physics investigations on samples at the nano-scale

S. Veronesi,¹ L. Basta,¹ T. Papa,¹ Z. Dubois,¹ N. Mishra,^{2,3}
F. Fabbri,¹ C. Coletti,^{2,3} Y. Murata,¹ and S. Heun¹

¹NEST Istituto Nanoscienze-CNR and Scuola Normale Superiore, Piazza S. Silestro 12,
56127 Pisa, Italy

²Center for Nanotechnology Innovation @ NEST, Istituto Italiano di Tecnologia, Piazza S. Silvestro 12,
56127 Pisa, Italy

³Graphene Labs, Istituto Italiano di Tecnologia, Via Morego 30, 16163 Genova, Italy

Udine (online), AICAT2020, January 27-28 - 2021



Outline

- 1 Motivation
 - Nano-scale Calorimetry
- 2 Experimental setup
 - Setups
- 3 Experimental Results
 - Hydrogen uptake
 - Evaluation of process enthalpy
- 4 Thermometer 2.0 Gold on Mica
- 5 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

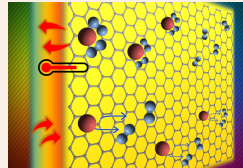
- Sensors
- Catalyzers
- Molecules of pharmaceutical interest
- **H-Storage model systems**

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 model systems**



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

Outline

- 1 **Motivation**
 - Nano-scale Calorimetry
- 2 Experimental setup
 - Setups
- 3 Experimental Results
 - Hydrogen uptake
 - Evaluation of process enthalpy
- 4 Thermometer 2.0 Gold on Mica
- 5 Conclusions and Outlook

samples and signals

In performing calorimetry on nano-systems in an UHV environment, two aspects must be taken into account:

- sample mass
- thermal signal characteristics

Typically a sample based on a 2D material spans at most over a few square mm area, that means a mass in the ng range.

A chemical reaction occurring in an UHV environment between a functionalized surface and a gas atom/molecule runs slowly.

At a gas supply pressure of 10^{-7} - 10^{-8} mbar, the time necessary to have a monolayer on the surface is 10-100 s.

samples and signals

In performing calorimetry on nano-systems in an UHV environment, two aspects must be taken into account:

- sample mass
- thermal signal characteristics

Typically a sample based on a 2D material spans at most over a few square mm area, that means a mass in the ng range.

A chemical reaction occurring in an UHV environment between a functionalized surface and a gas atom/molecule runs slowly.

At a gas supply pressure of 10^{-7} - 10^{-8} mbar, the time necessary to have a monolayer on the surface is 10-100 s.

samples and signals

In performing calorimetry on nano-systems in an UHV environment, two aspects must be taken into account:

- sample mass
- thermal signal characteristics

Typically a sample based on a 2D material spans at most over a few square mm area, that means a mass in the ng range.

A chemical reaction occurring in an UHV environment between a functionalized surface and a gas atom/molecule runs slowly.

At a gas supply pressure of 10^{-7} - 10^{-8} mbar, the time necessary to have a monolayer on the surface is 10-100 s.

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 this mean for the Ti-Hydrogen system? If we want to detect 10 mg of H_2 on a MLG, considering the US Department of Energy 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.

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 this mean for the Ti-Hydrogen system? If we want to detect 10 mg of H_2 on a MLG, considering the US Department of Energy 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.

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).

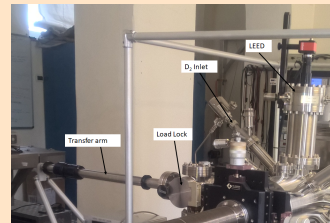
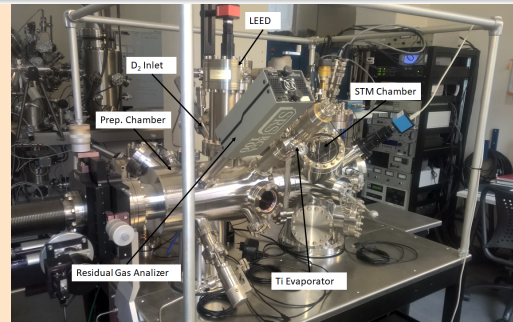
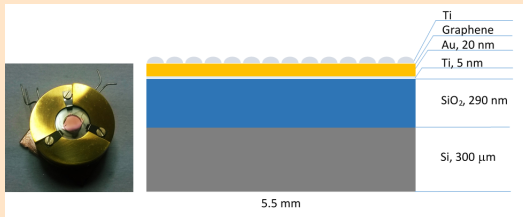
What does this mean for the Ti-Hydrogen system? If we want to detect 10 mg of H_2 on a MLG, considering the US Department of Energy DOE prescriptions (5.5 wt.%) and the specific surface area of graphene ($\sim 2600 \text{ m}^2/\text{g}$) we will need $\sim 450 \text{ m}^2$ of MLG.

Outline

- 1 Motivation
 - Nano-scale Calorimetry
- 2 **Experimental setup**
 - **Setups**
- 3 Experimental Results
 - Hydrogen uptake
 - Evaluation of process enthalpy
- 4 Thermometer 2.0 Gold on Mica
- 5 Conclusions and Outlook

Sample & holder

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



Thermometer and thermal model

All experiments are performed in **Ultra-High Vacuum (UHV)** environment (base pressure $\sim 10^{-10} \text{ mbar}$). 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 α is the **resistance temperature coefficient**.

We can describe the system with a simple **thermal model** in which the thermometer is **heated** by the absorption of a thermal power $P(t) = \delta H_r / \delta t$, where H_r is the released enthalpy, 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** λ 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

Thermometer and thermal model

All experiments are performed in **Ultra-High Vacuum (UHV)** environment (base pressure $\sim 10^{-10} \text{ mbar}$). 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 α is the **resistance temperature coefficient**.

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

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

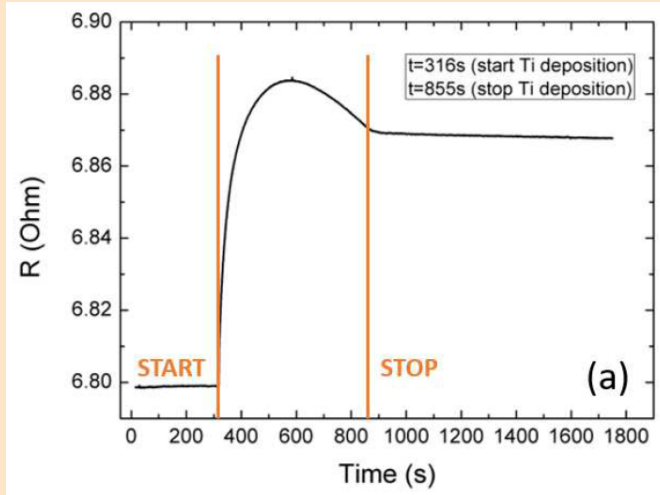
The sensor **heat capacity** C and the **thermal exchange coefficient** λ must be **evaluated**.

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

Outline

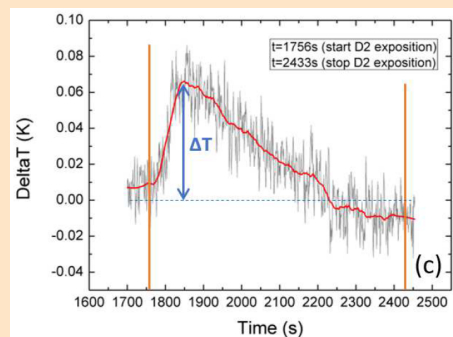
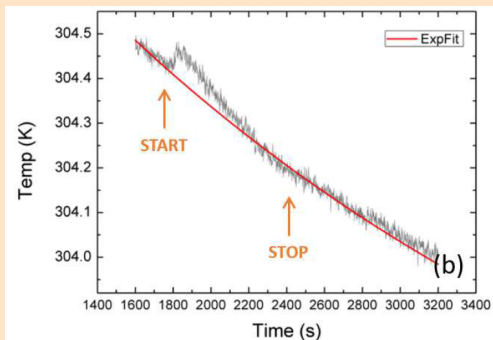
- 1 Motivation
 - Nano-scale Calorimetry
- 2 Experimental setup
 - Setups
- 3 **Experimental Results**
 - **Hydrogen uptake**
 - Evaluation of process enthalpy
- 4 Thermometer 2.0 Gold on Mica
- 5 Conclusions and Outlook

Calorimetry during hydrogenation: Ti-functionalization



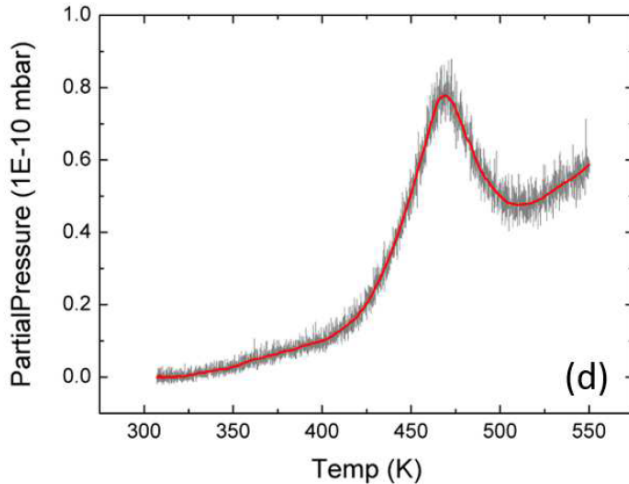
(a) **Ti deposition:**
thermometer heating
during the Ti deposition
(for 539 s, 12.4 ML of Ti)
on MLG.

Calorimetry during hydrogenation: heat release



- (b) Exposure of the Ti film to D₂ (red line: exponential fit of the thermalization background).
(c) Thermalization background subtracted. A $\Delta T = 0.065$ K is clearly detected.

Calorimetry during hydrogenation: TDS analysis



(d) TDS spectrum of Ti-MLG (Red line: smoothing).

Outline

- 1 Motivation
 - Nano-scale Calorimetry
- 2 Experimental setup
 - Setups
- 3 **Experimental Results**
 - Hydrogen uptake
 - **Evaluation of process enthalpy**
- 4 Thermometer 2.0 Gold on Mica
- 5 Conclusions and Outlook

Enthalpy calculation

Calorimetry

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

- Total heat capacity

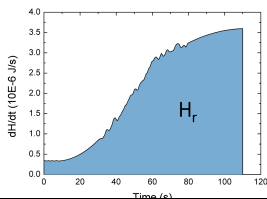
$$C = (15.0 \pm 0.2) \cdot 10^{-6} \text{ J/K}$$

$$\text{with } C = C_{Au} + C_{Ti} + C_{SiO_2}$$

- Heat exchange coefficient λ

$$\lambda = C / \tau_1 = (5.1 \pm 1.1) \cdot 10^{-6} \text{ W/K}$$

- Enthalpy release $H_r = (23.4 \pm 4.7) \mu\text{J}$



TDS analysis

- Binding energy

$$E_d = (1.32 \pm 0.07) \text{ eV/Molecule}$$

- Amount of adsorbed D_2

$$n(D_2) = 1.7 \times 10^{-10} \text{ moles}$$

- Enthalpy release

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

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,¹ Stefano Veronesi,¹ Yuya Murata,² Zoé Dubois,³ Neeraj Mishra,¹ Filippo Fabbri,¹ Camilla Coletti,¹ and Stefan Heun^{1*}

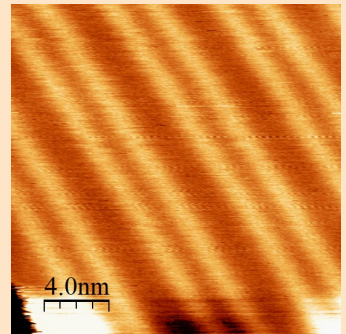
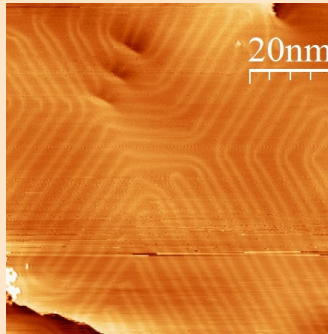
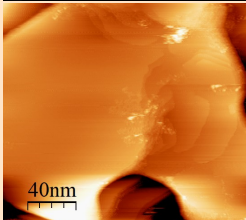
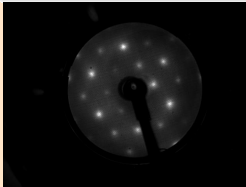


Next generation of thermometer

An issue to solve is relative to surface roughness. Atomically speaking Gold on SiO_2 thermometer has a rough surface which does not allow atomic resolution with STM. Mica allows Gold epitaxial recrystallization and surface reconstruction, solving this problem.

Next generation of thermometer

An issue to solve is relative to surface roughness. Atomically speaking Gold on SiO_2 thermometer has a rough surface which does not allow atomic resolution with STM. Mica allows Gold epitaxial recrystallization and surface reconstruction, solving this problem.

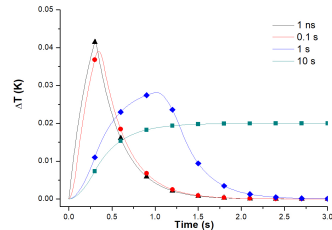
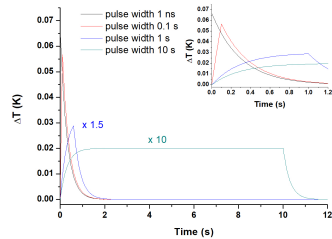


thermometer simulation

main contribution to thermalization time:

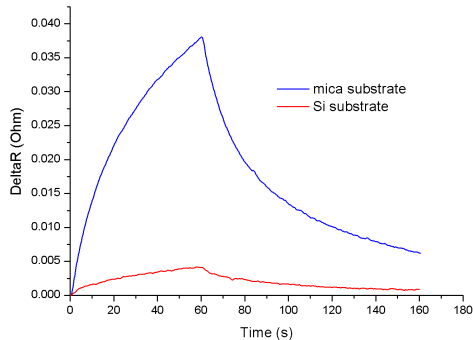
- Gold film $t_{Au} = d^2/\alpha \sim 4 \times 10^{-12} \text{ s}$
- Interface gold-mica
- Mica substrate $t_{Mica} = d^2/\alpha \sim 0.3 \text{ s}$
- Interface mica-holder

Simulation	Heating duration	Integration time	$\Delta E/E$
	s	ms	
1	10^{-9}	300	0.04
2	10^{-1}	300	0.053
3	1	300	0.007
4	10	300	0.005



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 $\sim 0.03m\Omega$
- temperature variation sensitivity $10mK$ (Si substrate), $4mK$ (Mica substrate)
- H_2 detected during adsorption $\sim 0.2ng$ or $(1.71 \pm 0.01) \cdot 10^{-10}$ moles
- advantages:
 - calorimetric evaluation is direct and does 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

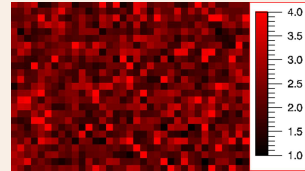
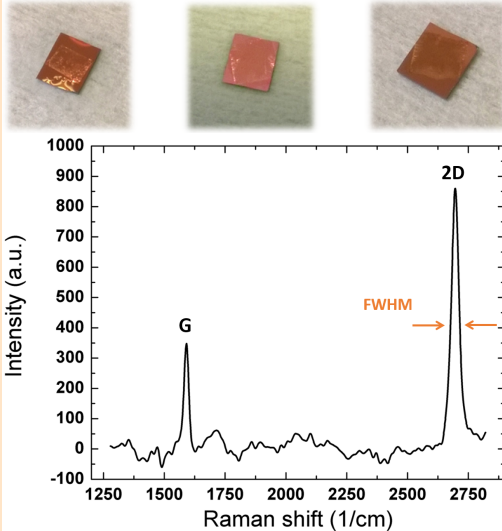
People



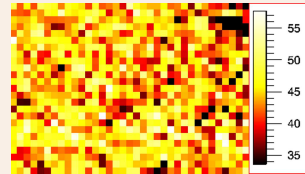
thanks

Thank you for your attention

Raman Spectroscopy



(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^{-1}) of the 2D peak.

COMSOL simulation

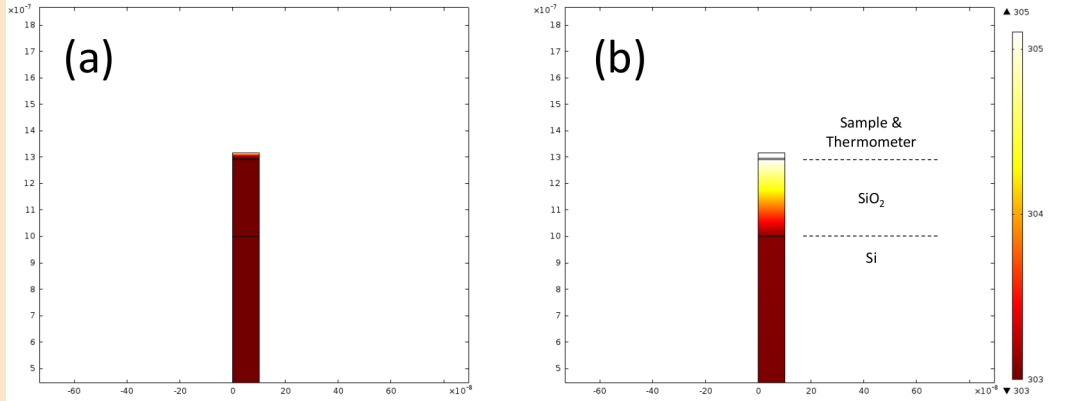
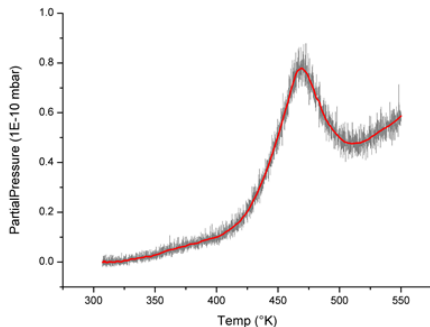


Figure: (a) Temperature distribution at $t = 1 \text{ ns}$ when the temperature jump of 2 K has just been applied to the topmost layer of the stack. All other parts of the stack are still at 303 K. (b) Temperature distribution at $t = 0.1 \mu\text{s}$.

TDS analysis

TDS spectrum vs Temp

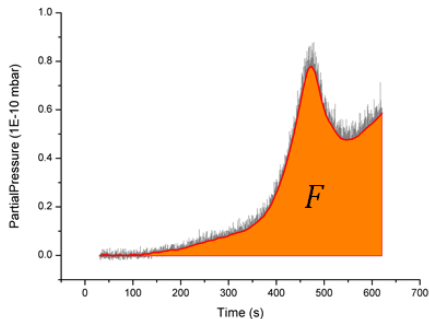


$$\frac{E_d}{k_B T_p} = A \tau_m \exp\left(-\frac{E_d}{k_B T_p}\right)$$

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

TDS analysis

TDS spectrum vs time



$$pV = FS = nRT$$

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

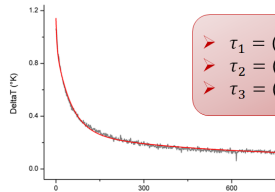


$$n(D_2) \rightarrow 1.71 \cdot 10^{-10} \text{ mol}$$

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

Heat capacity and losses evaluation

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



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

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

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

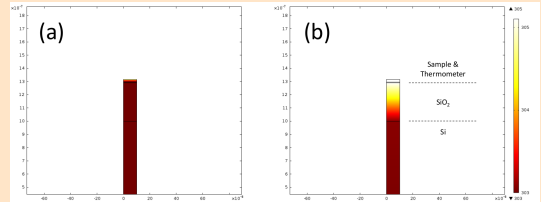
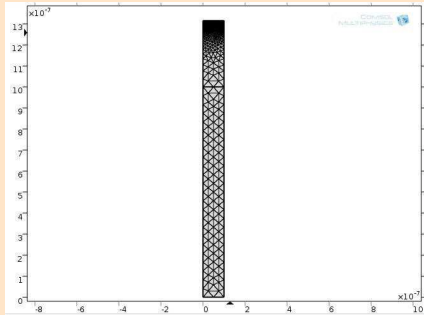
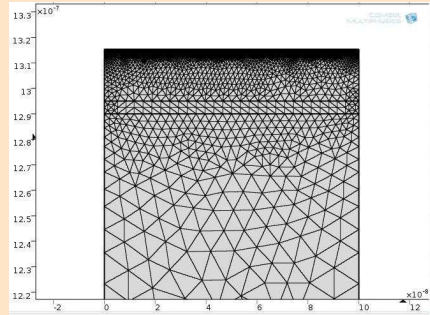


Figure: (a) Temperature distribution at $t = 1 \text{ ns}$ when the temperature jump of 2 K has just been applied to the topmost layer of the stack. All other parts of the stack are still at 303 K. (b) Temperature distribution at $t = 0.1 \mu\text{s}$.

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

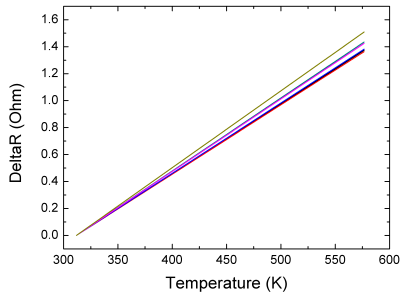
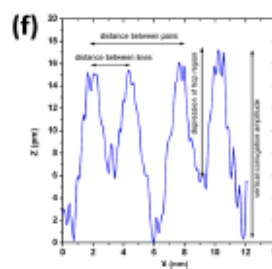
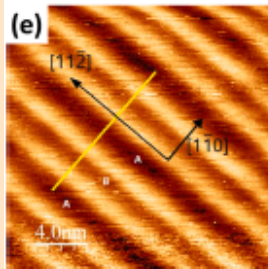
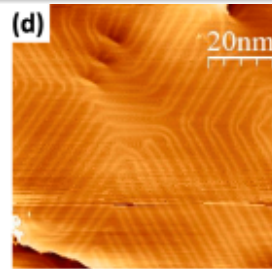
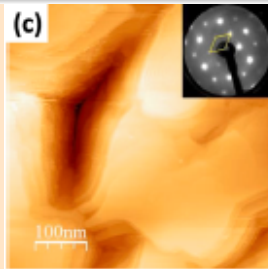


Figure: Resistance variation ($\Delta R = R(T) - R_0$) vs. temperature for six different heating experiments on the same Au+Ti-MLG sensor.

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 $\alpha_f = (1.62 \pm 0.05) \cdot 10^{-3} \text{ K}^{-1}$.

Profile



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