Investigating simultaneously energy (heat) exchange and surface physics on samples at the nanoscale

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Outline

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.

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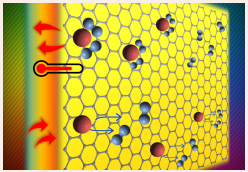

Even if performance is improving with time, commercial calorimeters are still far from the access to nano-scale samples.

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samples and signals

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

- sample mass
- thermal signal characteristics

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

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

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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.

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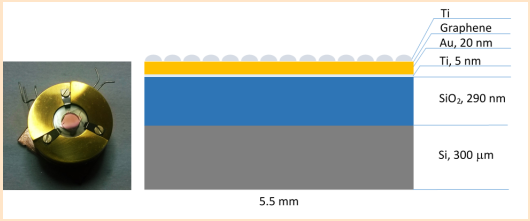
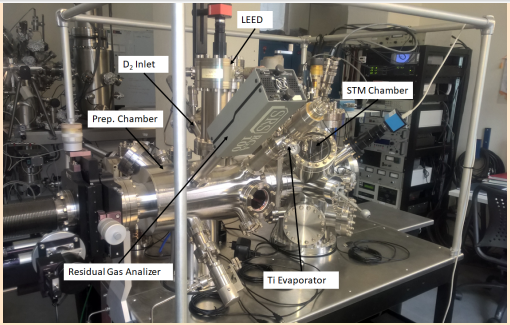
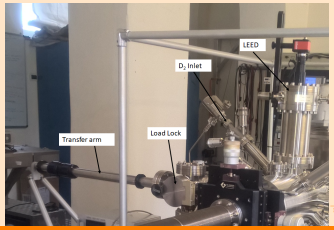
Sample & holder

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 orders of magnitude lower than commercial device request.







Thermometer and thermal model

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.

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:

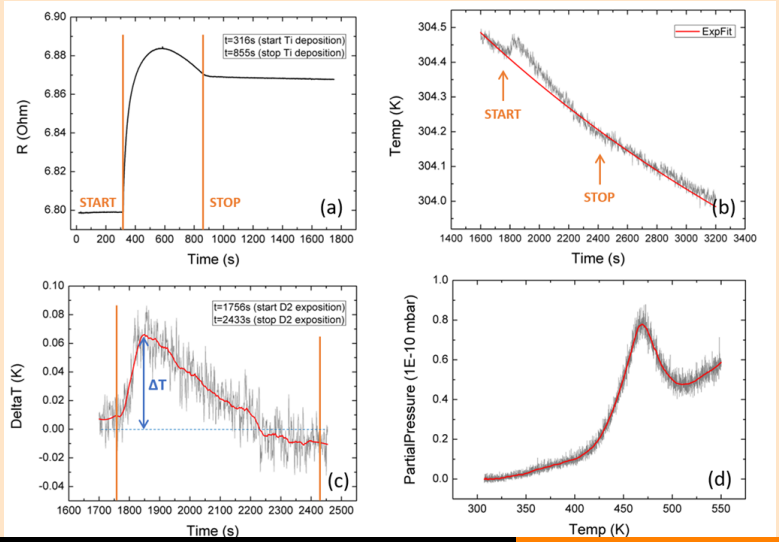
$$\delta H_r / \delta t = C \cdot \delta \Delta T(t) / \delta t + \lambda \cdot \Delta T(t)$$

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

Outline

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)

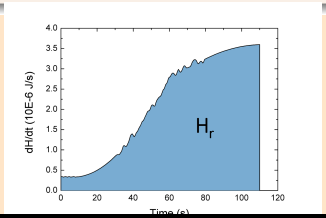
Outline

Enthalpy calculation

Calorimetry

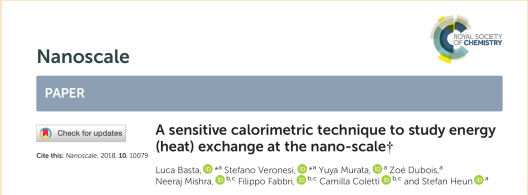
$$\delta H_r/\delta t = C \cdot \delta \Delta T(t)/\delta t + \lambda \cdot \Delta T(t)$$

- Total heat capacity
  $C = (15.0 \pm 0.2) \cdot 10^{-6}$ J/K
  with $C = C_{Au} + C_{Ti} + C_{SiO_2}$.
- Heat exchange coefficient λ
  $\lambda = C/\tau_1 = (5.1 \pm 1.1) \cdot 10^{-6}$ W/K.
- Enthalpy release $H_r = (23.4 \pm 4.7)\mu J$



TDS analysis

- Binding energy
  $E_d = (1.32 \pm 0.07) Ev/Molecule$
- Amount of adsorbed D_2
  $n(D_2) = 1.7x10^{-10} moles$
- Enthalpy release
  $H_r = (21.8 \pm 1.3)\mu J$


Nanoscale

PAPER

Check for updates

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

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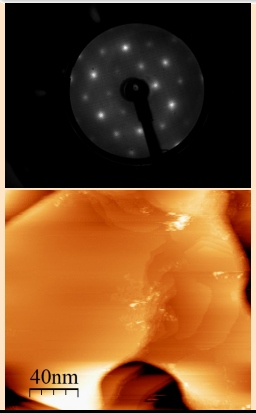
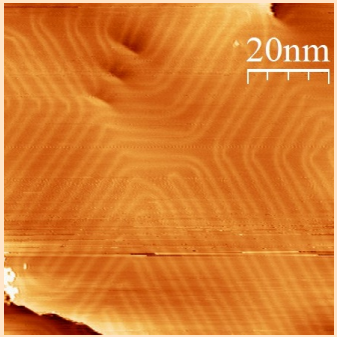
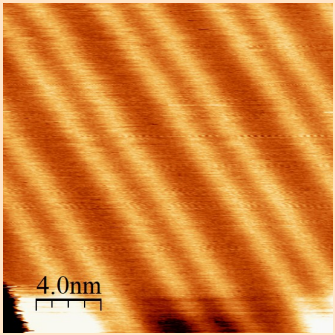
Luca Basta, Stefano Veronesi, Yuya Murata, Zoé Dubois, Neeraj Mishra, Filippo Fabbri, Camilla Coletti and Stefan Heun

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.





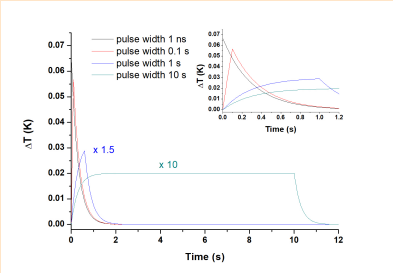


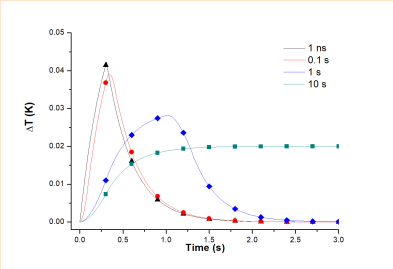
thermometer simulation

main contribution to thermalization time:

- Gold film $t_{Au} = d^2/\alpha \sim 4x10^{-12}s$
- Interface gold-mica
- Mica substrate $t_{Mica} = d^2/\alpha \sim 0.3s$
- Interface mica-holder

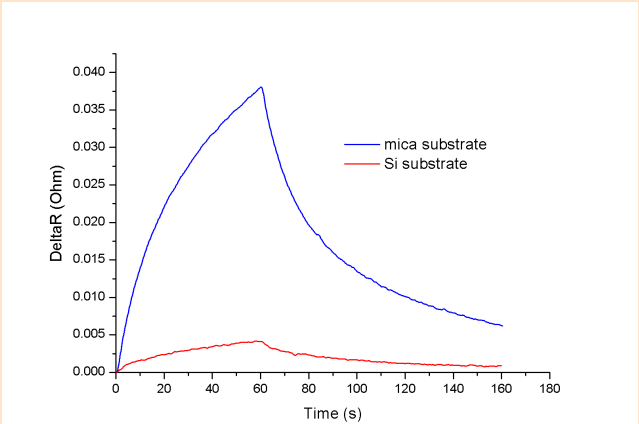
Simulation	Heating duration	Sampling rate	ΔE/E
	s	ms	
1	10^{-9}	300	0.53
2	10^{-1}	300	0.49
3	1	300	0.24
4	10	300	0.024





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 $10mK$ (Si substrate), $4mK$ (Mica sustrate)
- H_2 detected during adsorption $\sim 0.2ng$ 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

thanks

Thank you for your attention