An atomically flat, monocrystalline gold film thermometer on mica to study energy (heat) exchange at the nano-scale

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Motivation

There is a great interest in the scientific community to apply calorimetry to samples with mass in the nanogram range. 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 [1] would represent a precious source of information in developing

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

The possibility to have an atomically flat thermal probe represents an added value, because it would provide the unique opportunity to perform Scanning Probe Microscopy (SPM) together with calorimetry.

Measuring principle

The idea is to utilize a thin gold film 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 [2, 3]

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

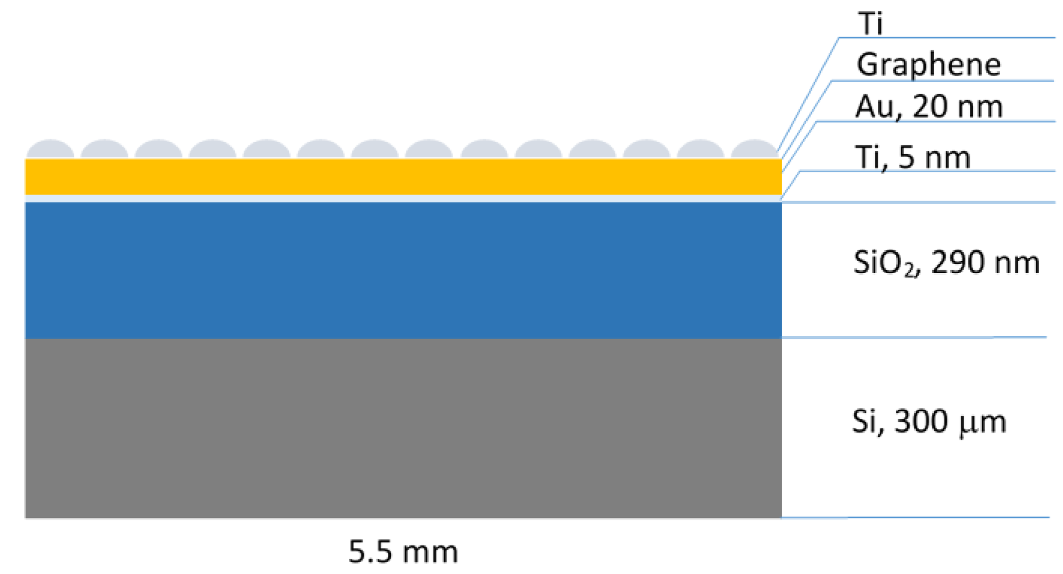
where

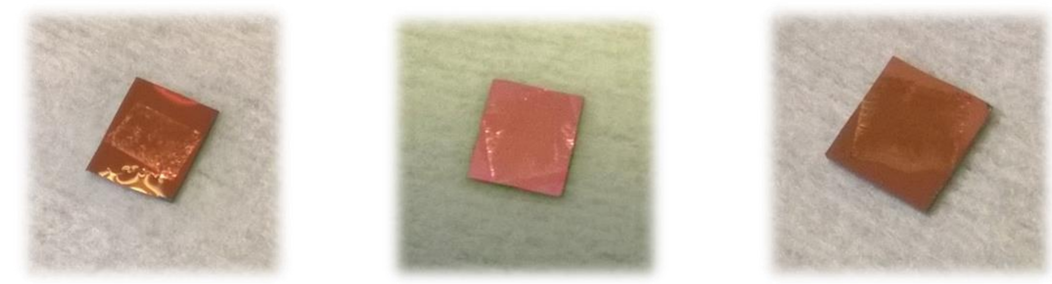
$$\Delta T(t) = T(t) - T_0$$

is the change in Temperature with time. The heating power is related to the enthalpy release during a chemical reaction

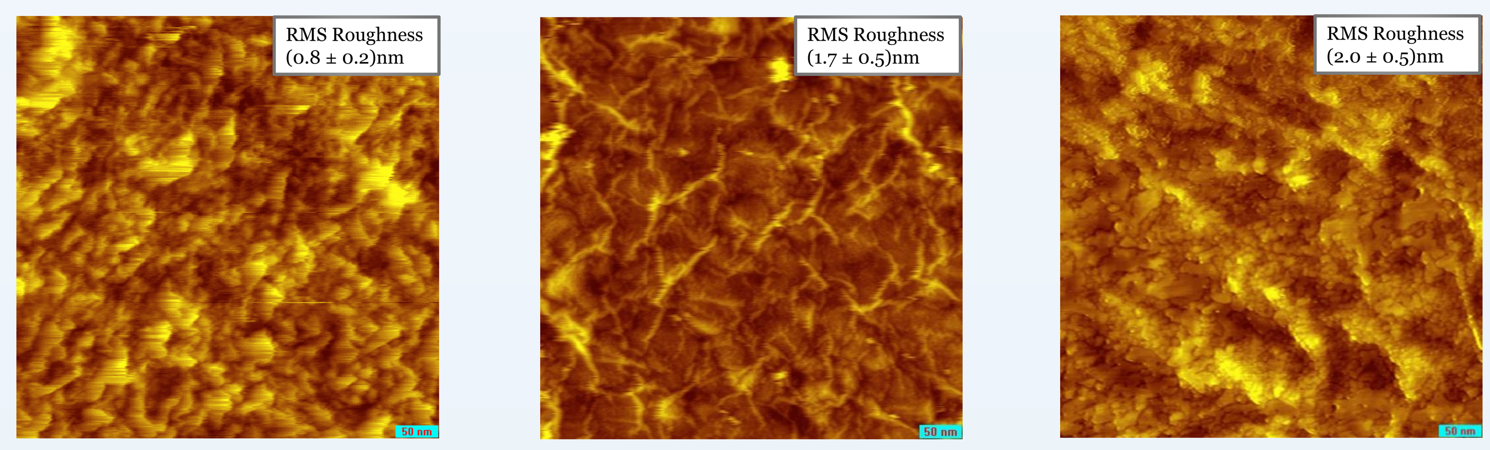
$$P(t) = \frac{\delta H_r(t)}{\delta t}$$

Thermometer: first generation





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



STM image of the Au surface (500x500 nm)

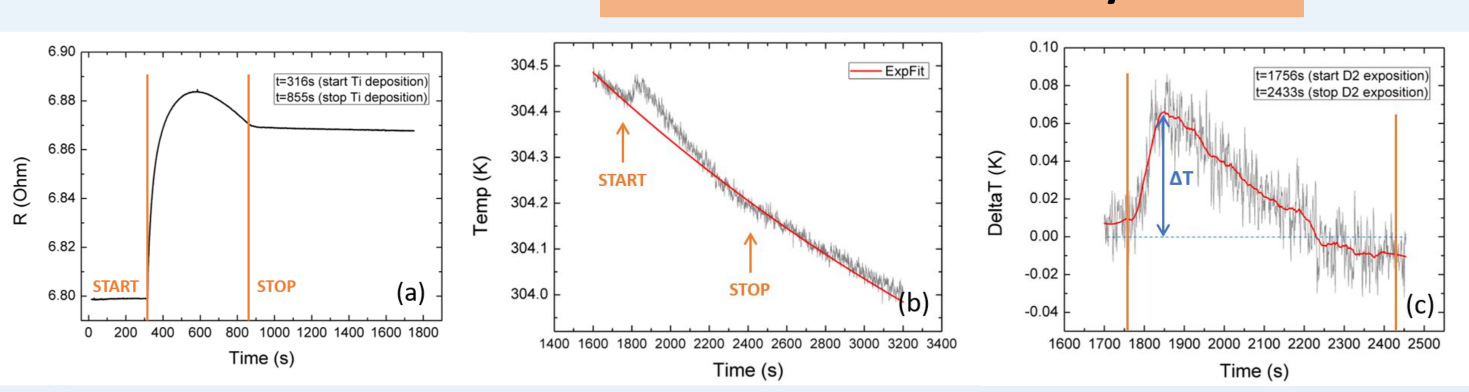
STM image of MLG on thermometer

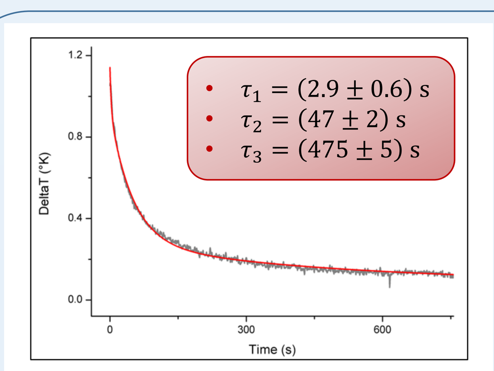
STM image of Ti + MLG on thermometer

STM analysis of the sample surface which results rough at atomic level.

H-storage: Evaluation of the enthalpy release in Ti-MLG

Thermal analysis





Sensor cooling curve after an heat pulse. Thermal exchange coefficient λ is evaluated from τ_1

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

$C_{sensor} = (15.0 \pm 0.2)\cdot 10^{-6}$ J/K $\quad \lambda_S = \frac{C}{\tau_1}$

$\tau_1 = (2.94 \pm 0.63)$ s $\rightarrow \lambda_S = (5.1 \pm 1.1)\cdot 10^{-6}$ W/K

Thermal signal during hydrogenation of Sample G2 after 1st Ti deposition → 12.4 ML

THE THERMAL MODEL

Thermal power $P(t) = \delta H_r/\delta t$

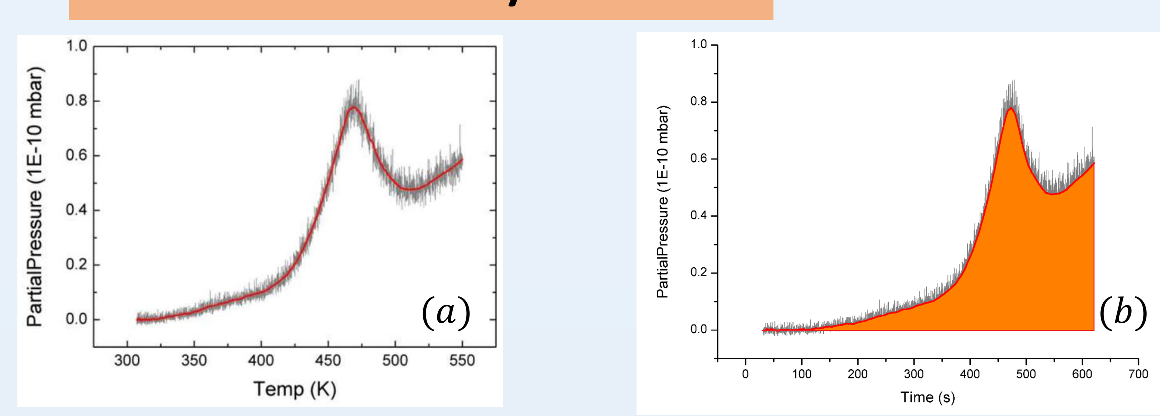
$$\frac{\delta H_r}{\delta t} = C_{sensor}\cdot\frac{\delta \Delta T(t)}{\delta t} + \lambda\cdot\Delta T(t)$$

with $C_{sensor} = C_{MLG} + C_{Au} + C_{Ti} + C_{SiO2}$ [1]

- point-by-point derivative of the measured $\Delta T(t)$ curve
- point-by-point integration of $\frac{\delta H_r}{\delta t}$

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

TDS analysis

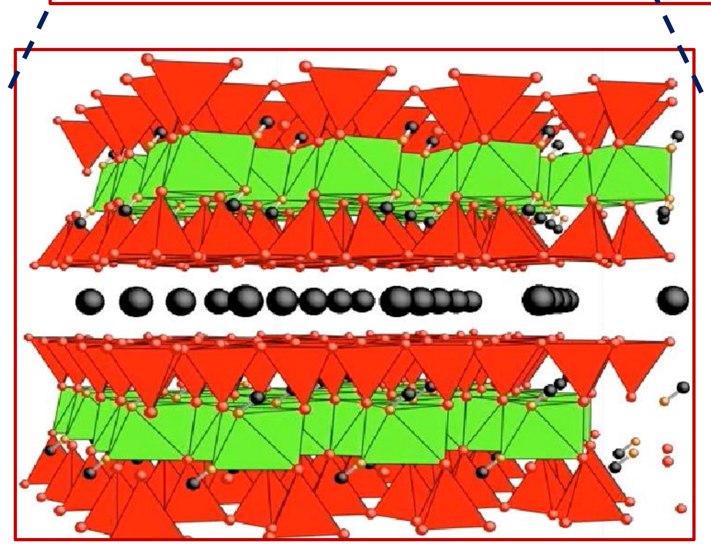


$T_p = (469 \pm 3)$K ⟶ $E_d = (1.32 \pm 0.07)$ eV/molecule $\quad n(D_2) \rightarrow 1.71\cdot 10^{-10}$ mol

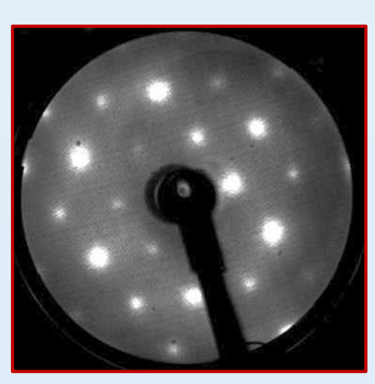
$$H_r = n\,N_A\,E_b = (21.8 \pm 1.3)\ \mu J$$

TDS spectrum vs temperature (a) and vs time (b). Data allow estimation of hydrogen uptake, in terms of binding energy (E_d) and moles, $n(D_2)$.

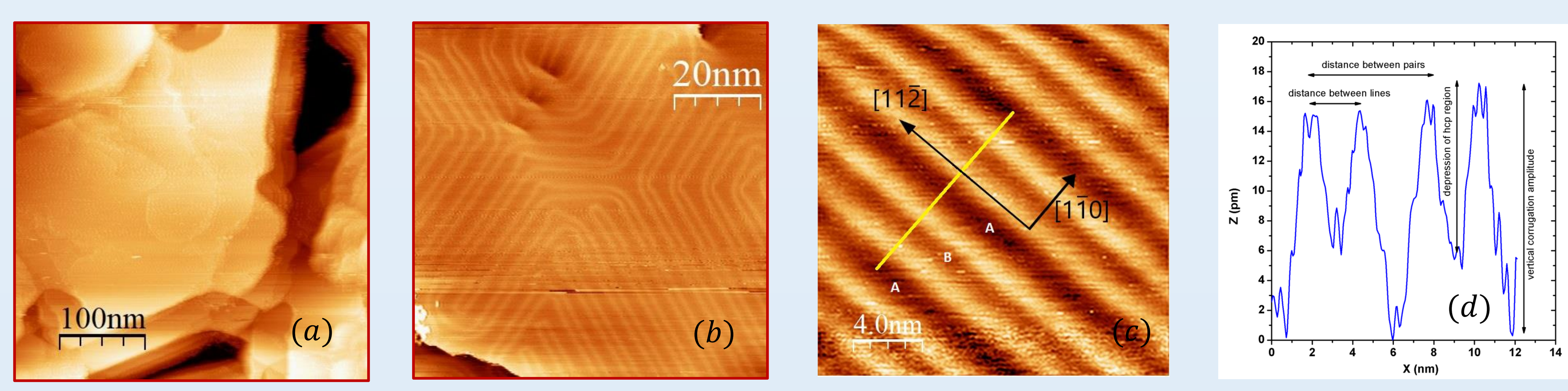
Thermometer: second generation



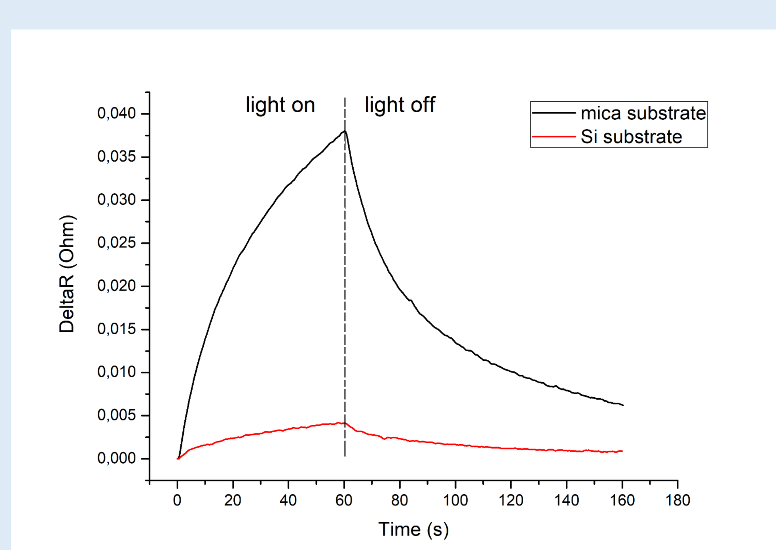
Mica structure



Low Energy Electron Diffraction (LEED) pattern



STM images of a gold film thermometer on Mica after re-crystallization [3]. (a) 500x500 nm²; (b) 80x80 nm²; (c) corrugation lines typical of surface reconstruction. Letters label the fcc (A) and hcp (B) regions. Crystallographic directions are indicated; (d) section view of the corrugation lines.



- $\Delta R_{mica} = 0.038\ \Omega$
- $\Delta R_{Si} = 0.004\ \Omega$

The new sensor is **10 times** more sensitive!

Response of the two sensors (gold-on-mica and gold-on Si) to the same heat pulse [3]. Thermometers are heated by illumination with a lamp for 60 seconds.

Conclusions

- Improvement of gold film thermometers in terms of sensitivity: $\lambda_{mica} \sim 2\times 10^{-7}$ W/K vs $\lambda_{Si} \sim 5\times 10^{-6}$ W/K
- Detailed study of the gold surface re-crystallization allowed by the mica substrate
- Simultaneous investigation of energy transfer mechanisms and surface physics on the same physical support.
- Demonstrated the gold film thermometers stablility up to 200 °C. Stability range could be improved with a Ti layer.

References

[1] L. Basta, et al. , *Nanoscale*, 10:10079-10086, 2018.
[2] M. Cassettari, S. Veronesi et al., *Review of Scientific Instruments*, 1993, **64**,1076–1080.
[3] S. Veronesi et al., *submitted to Nanoscale Advance*.