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

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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.

Calorimetry

Working at constant pressure allows a simplified relation between Enthalpy variation ΔH and heat exchanged δQ:

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

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

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

IDEAL CASE

Calorimetry

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):

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

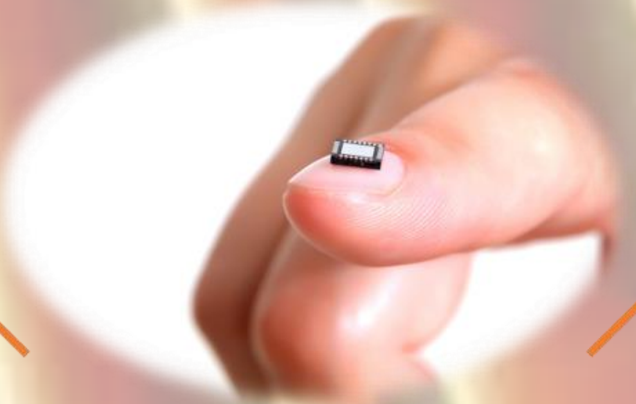
REAL CASE

Commercial calorimeters

Usual requirements of commercial devices:
- sample mass in the mg range (usually 10 mg)
- limited energy sensitivity (~mJ)

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

What does it mean in our 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 (~2600 m^2/g) we will need ~**450** m^2 of **MLG**



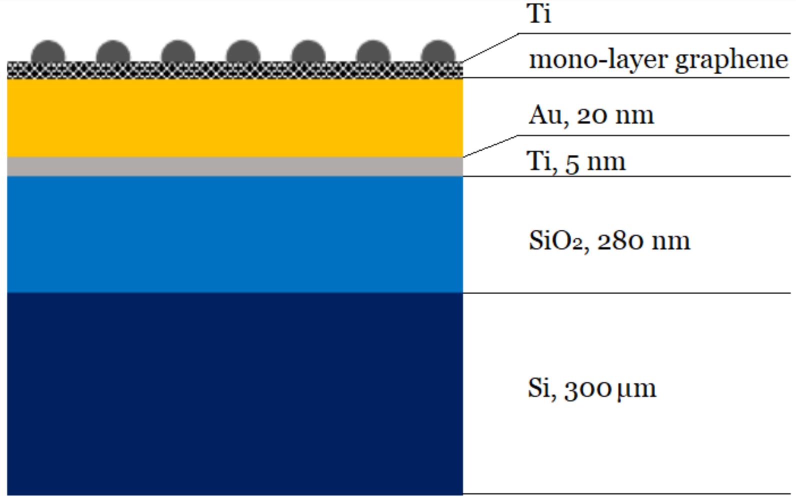
Our original calorimetric technique has been tested on a Ti-functionalized MLG sample, which is a system well investigated. Overall sample mass is **10 ng**, 6 order of magnitude lower than commercial device request.

First prototype of the gold film thermometer

The electrical resistance of the Au film increases with temperature, following a linear relation:

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

The temperature increase of the sensor causes a resistance increase of the gold layer, that can be measured with a Wheatstone Bridge cascaded to a high quality PreAmplifier.



[1] L. Basta et al. *Nanoscale*, 10:10079-10086, 2018.

EXPERIMENTAL STEPS:

- Calibration (heating cycles ⇒ α)
- Graphene transfer
- Ti functionalization in situ (6.5 ML)
- D_2 exposure (5 minutes, 1.0×10^{-7}mbar)
- Final calibration

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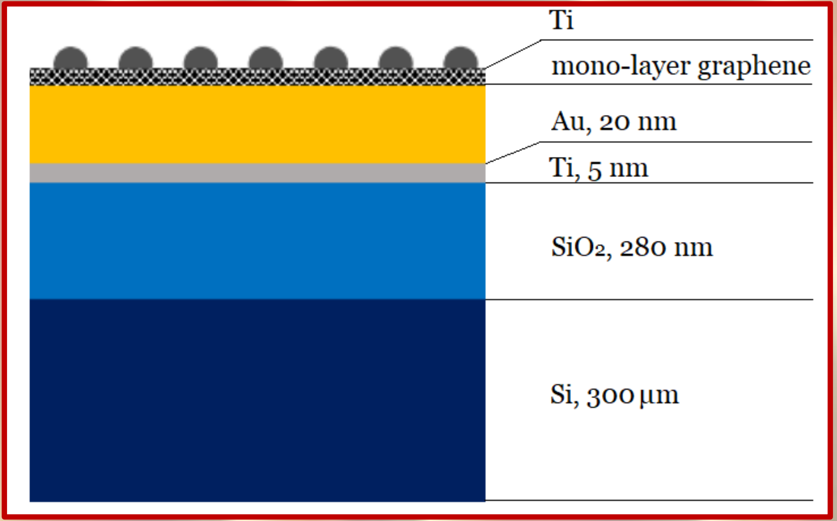
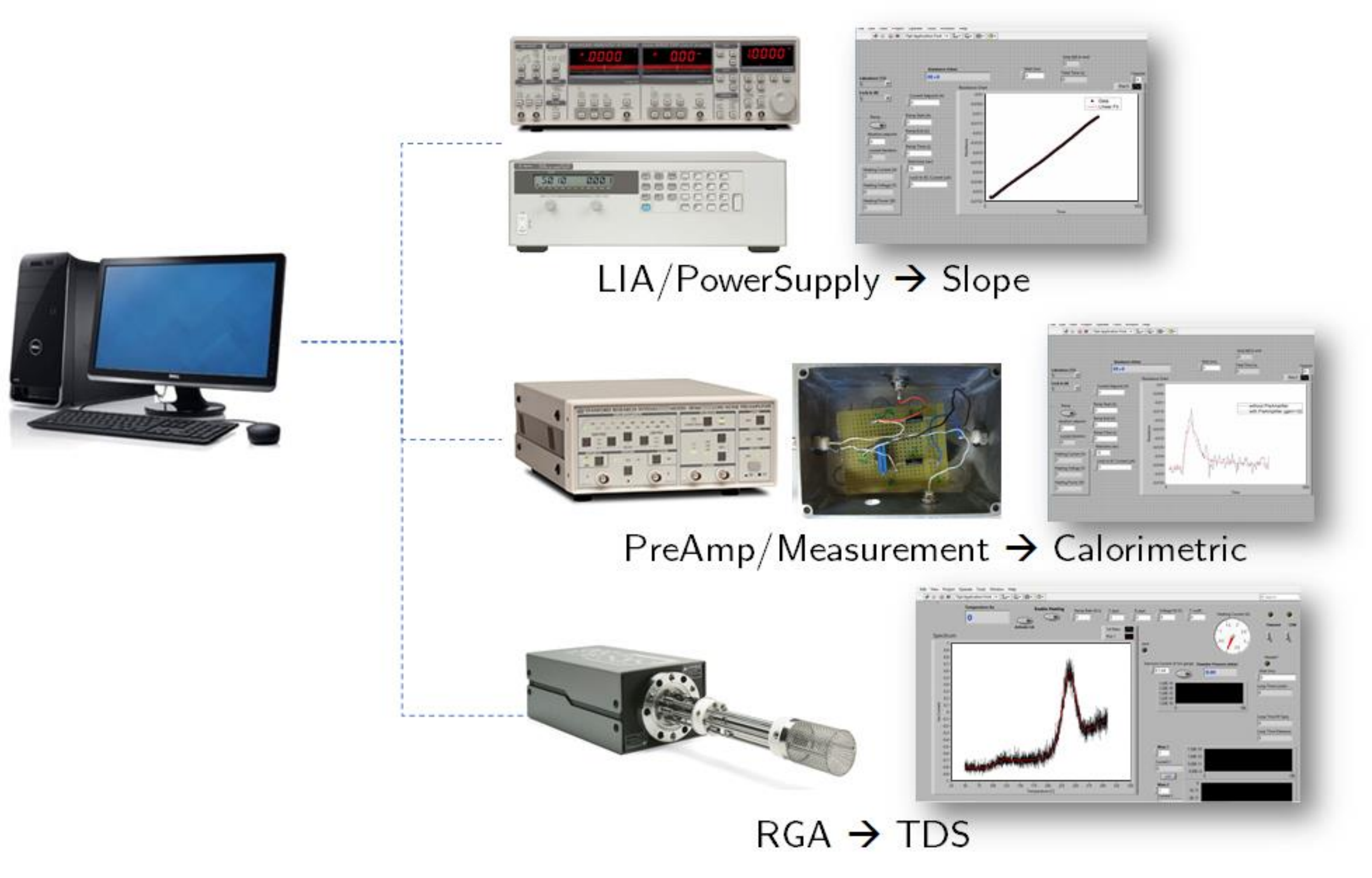


[1] L. Basta et al. *Nanoscale*, 10:10079-10086, 2018.

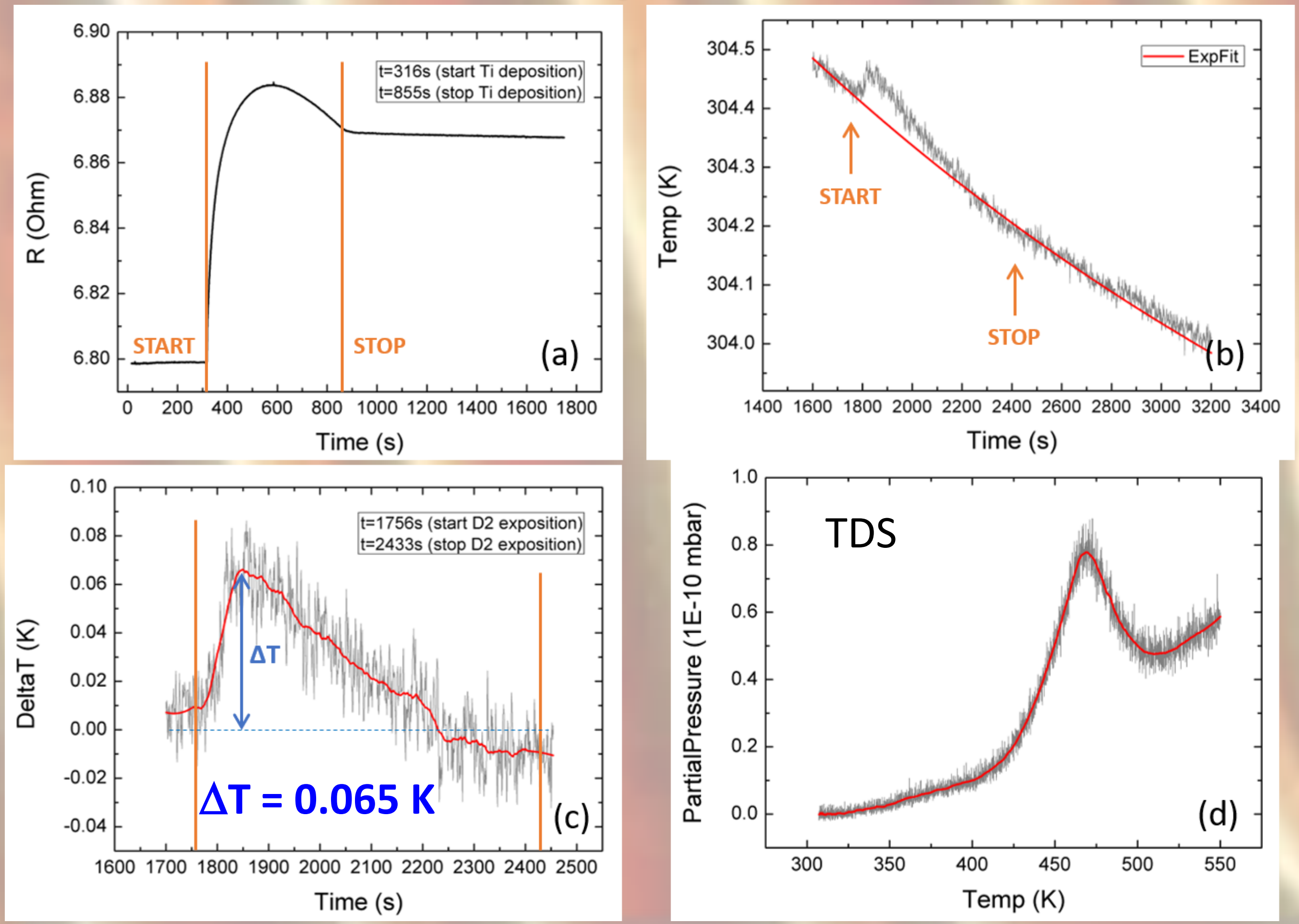
The enthalpy release due to hydrogen adsorption on a Ti-functionalized MLG has been measured in two different ways:

- during the hydrogen adsorption, via calorimetry
- after the hydrogen adsorption, via Thermal Desorption Spectroscopy (TDS)

Experimental setup



Calorimetric analysis



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

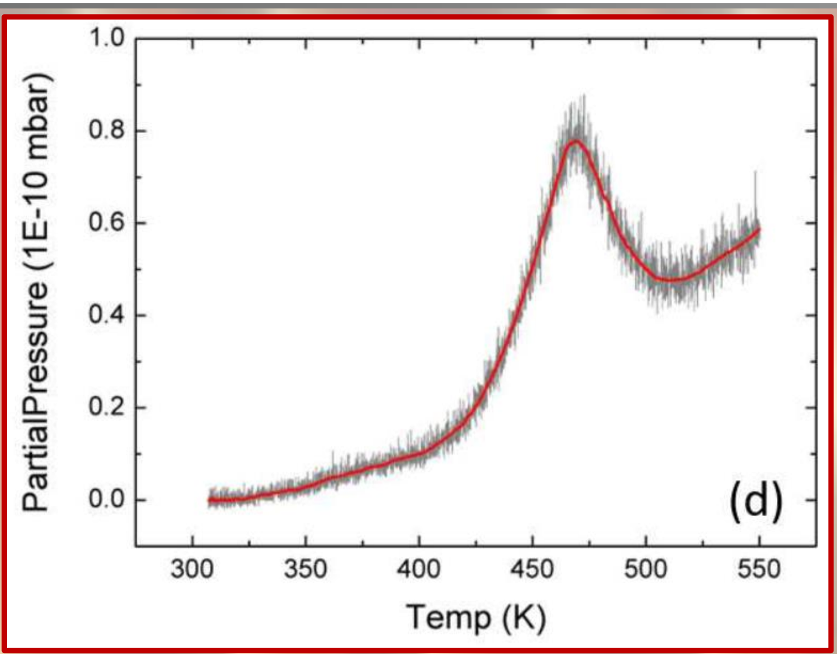
$$H_r \simeq (23 \pm 5)\ \mu J$$

[1] L. Basta et al. A sensitive calorimetric technique to study energy (heat) exchange at the nanoscale. *Nanoscale*, 10:10079-10086, 2018.

Thermal Desorption Spectroscopy (TDS) analysis

By heating the sample at constant rate, the adsorbed species are removed.

- TDS Spectrum vs Temperature ⇨ binding energy $E_b = E_d$
- TDS Spectrum vs Time ⇨ desorbed moles n .



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

$T_p = (469 \pm 3)\text{K} \longrightarrow E_d = (1.32 \pm 0.07)$ eV/molecule

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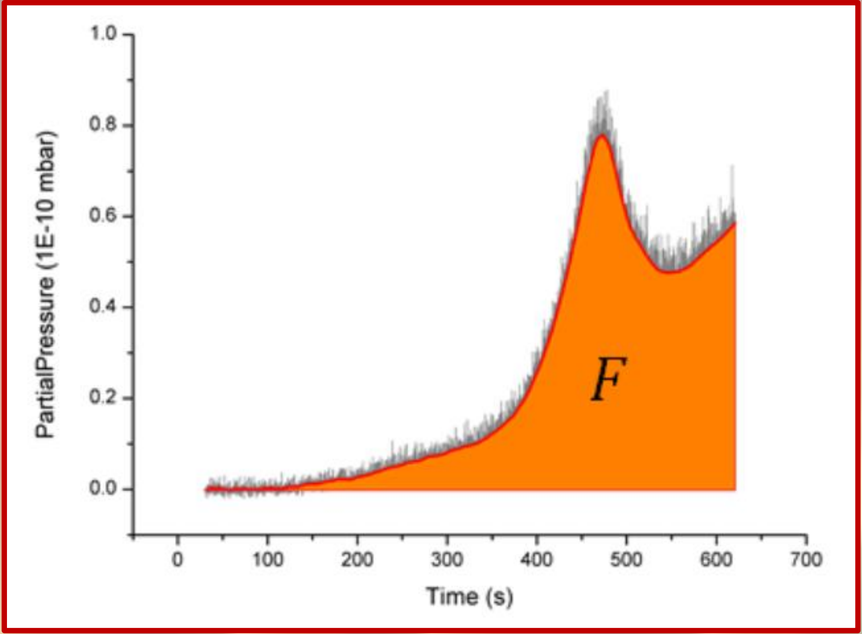

$$P \cdot V = F \cdot S = n \cdot R \cdot T \Rightarrow n \,(\text{from } F,\, S \approx 300\,\text{L/s})$$

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

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- TDS Spectrum vs Temperature ⇨ binding energy $E_b = E_d$
- TDS Spectrum vs Time ⇨ desorbed moles n .

The enthalpy release can be calculated from the binding energy and the amount of desorbed moles:

$$H_r = nN_AE_b \simeq (22 \pm 1)\ \mu J$$

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Performances

First direct measurement of the enthalpy released during a hydrogen adsorption process

- resistance variation sensitivity of ~ $\mathbf{0.03\ m\Omega}$
- temperature variation sensitivity ~ $\mathbf{10\ mK}$
- D_2 detected during adsorption ~ $\mathbf{0.2\ ng}$ or 10^{-10}mol
- corresponding to a released enthalpy $H_r \simeq (23 \pm 5)\ \mu J$
- in good agreement with TDS evaluation $H_r \simeq (22 \pm 1)\ \mu J$
- main advantage: the calorimetric evaluation is direct and does not need the hydrogen desorption, while TDS needs the desorption of the loaded hydrogen

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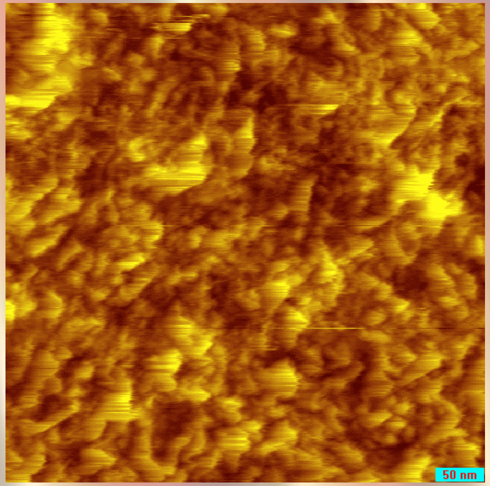
Improvements

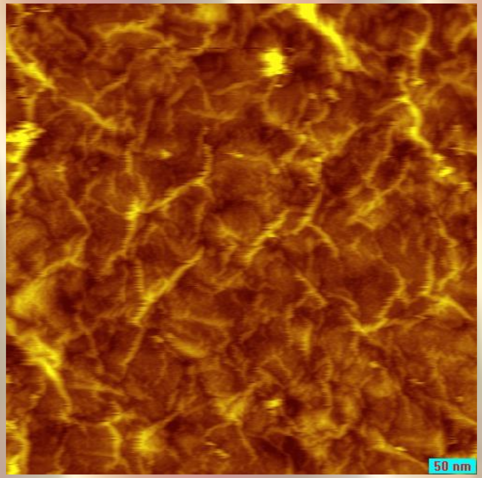
- Thermometer surface is rough (atomically speaking)
- Si thermal conductivity is relatively high

These are the two main directions to improve thermometer performances.



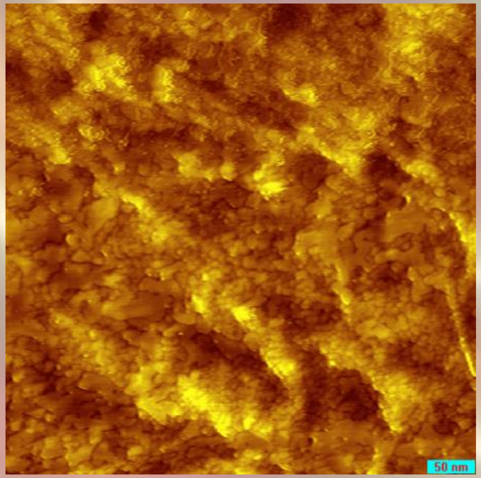
RMS Roughness (0.8 ± 0.2)nm

STM image of bare Au surface (500x500 nm)



RMS Roughness (1.7 ± 0.5)nm

STM image of MLG on thermometer

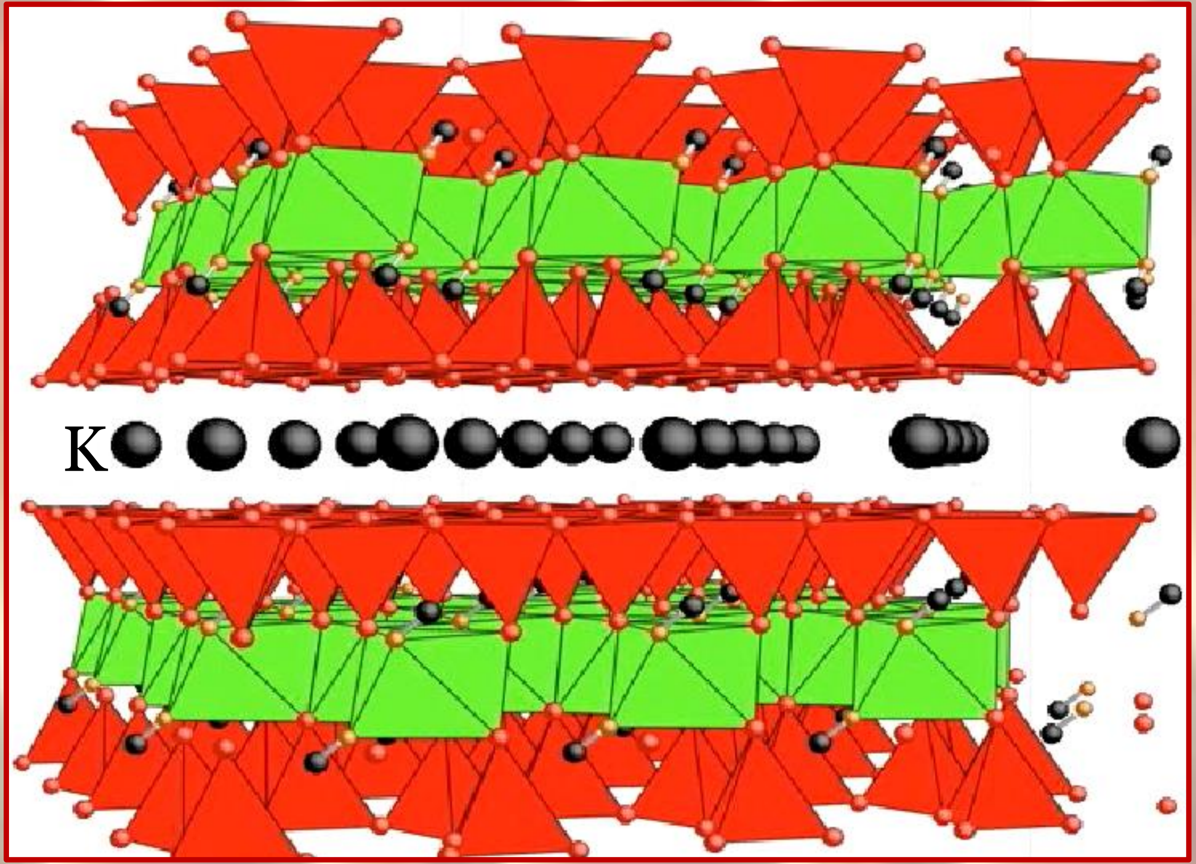


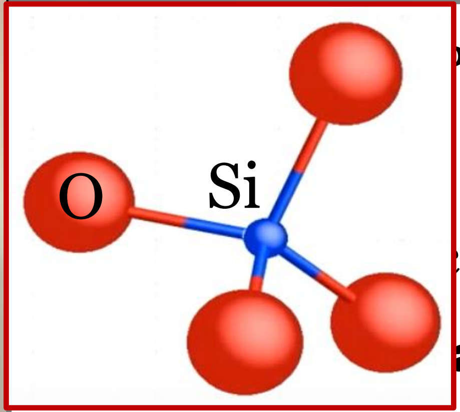
RMS Roughness (2.0 ± 0.5)nm

STM image of Ti + MLG on thermometer

[1] L. Basta et al. A sensitive calorimetric technique to study energy (heat) exchange at the nanoscale. *Nanoscale*, 10:10079-10086, 2018.

New substrate: Muscovite Mica - $KAl_2(AlSi_3)O_{10}(OH)_2$





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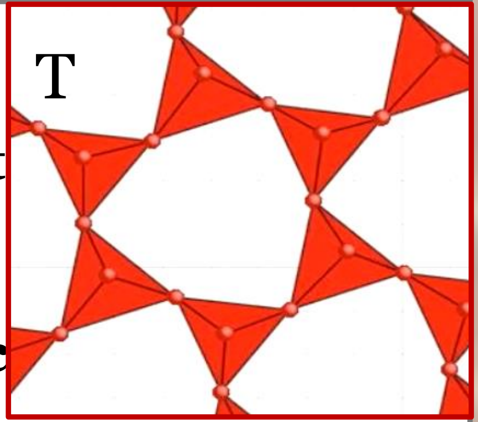
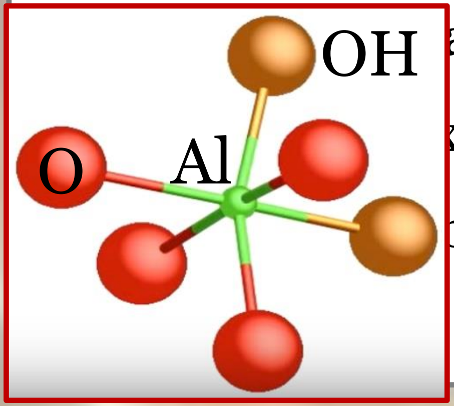


- Capability to allow gold surface



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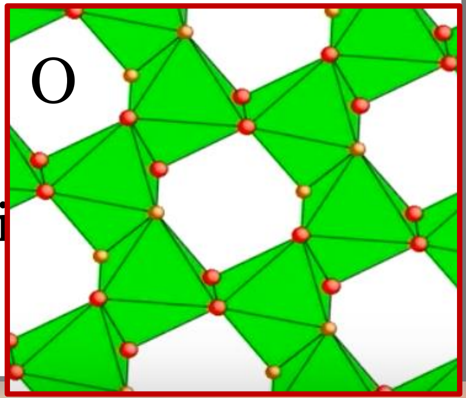
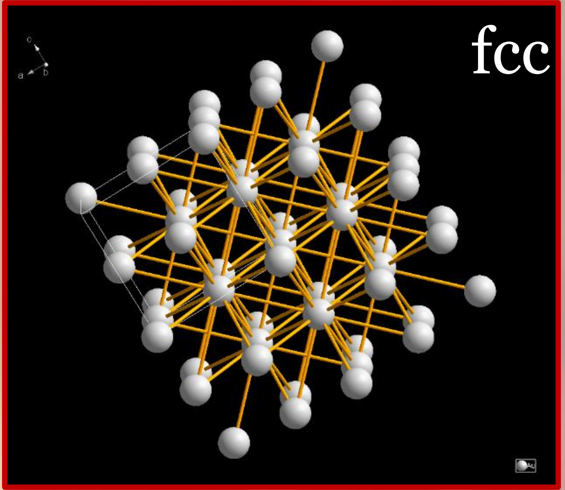
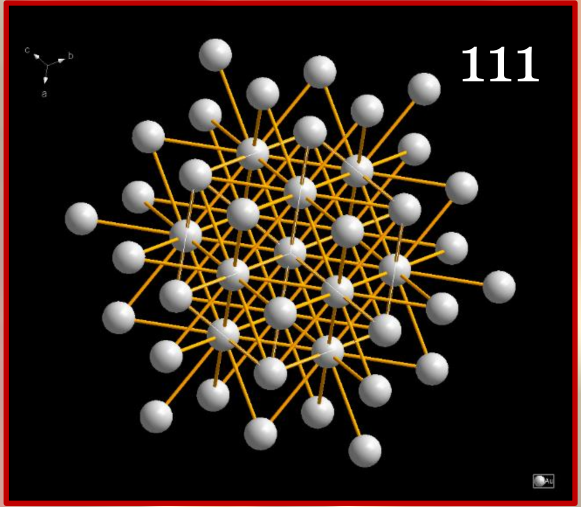
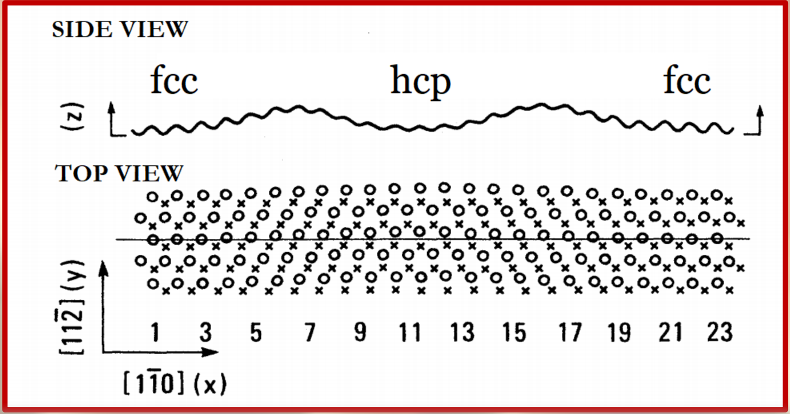


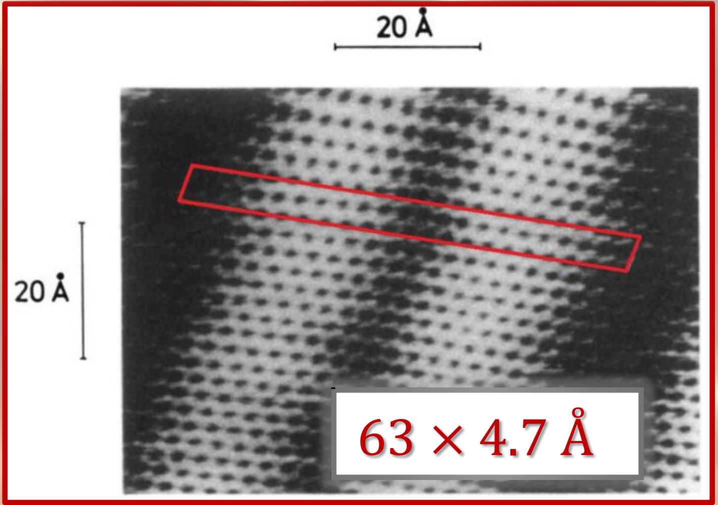
Au(111) herringbone reconstruction

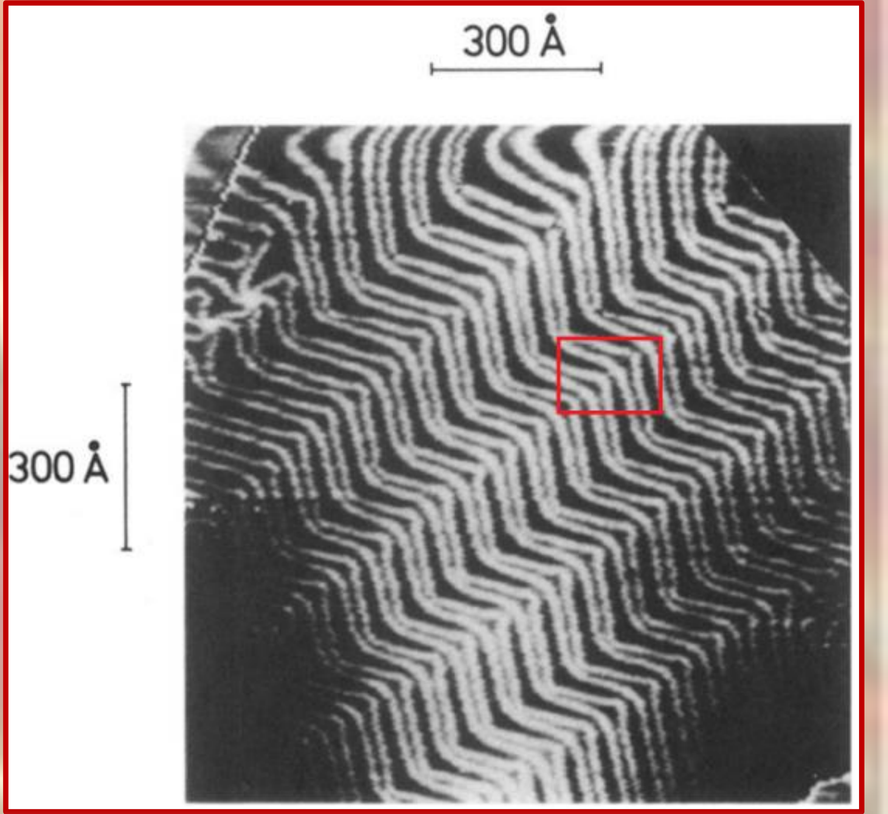






Ch. Wöll et al. *Phys. Rev. B*, 39:7988-91, 1989.





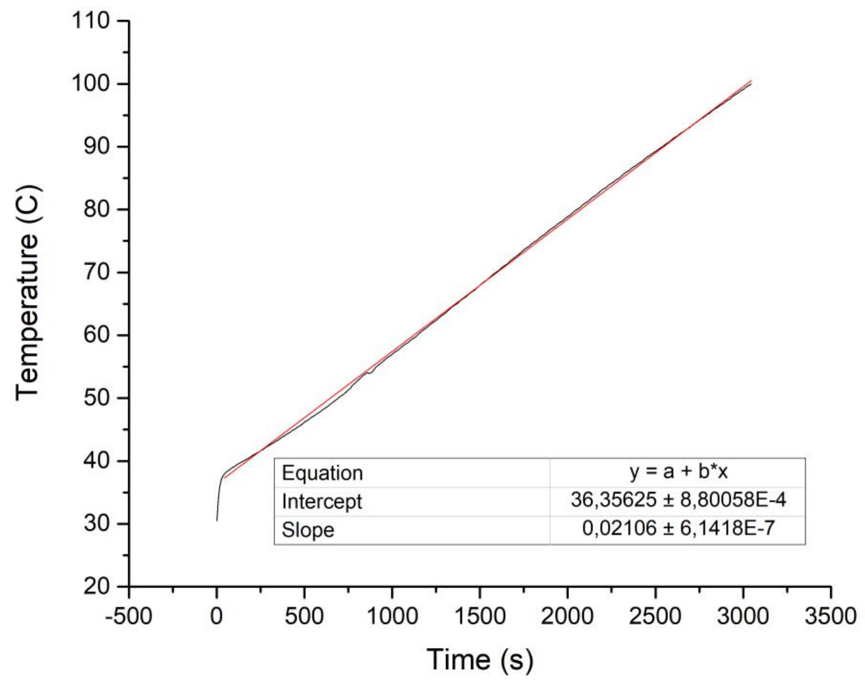
J. V. Barth et al. *Phys. Rev. B*, 42:9307-9318, 1990.

Thermometer Fabrication - overview

- Scotch-tape freshly cleaved substrate
- Loading in metal evaporator
- Substrate drying overnight at 200°C
- Gold deposition at room temperature, deposition rate of 1 Å/s
- Cutting in ~ 5x5 mm^2 samples

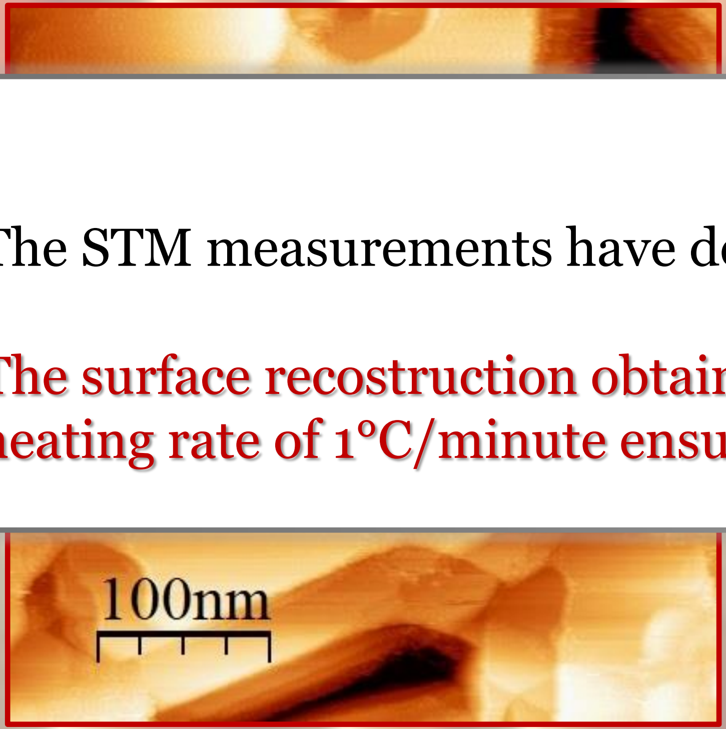
M5/M6-series: Au/mica

Several heating ramps have been performed in the UHV chamber, with a heating rate of 1°C/minute.

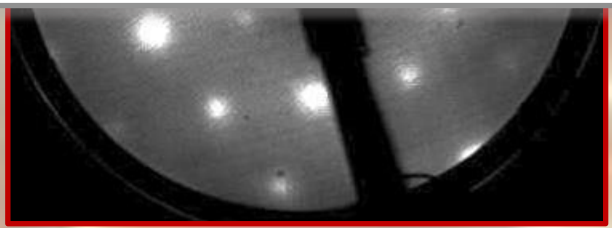


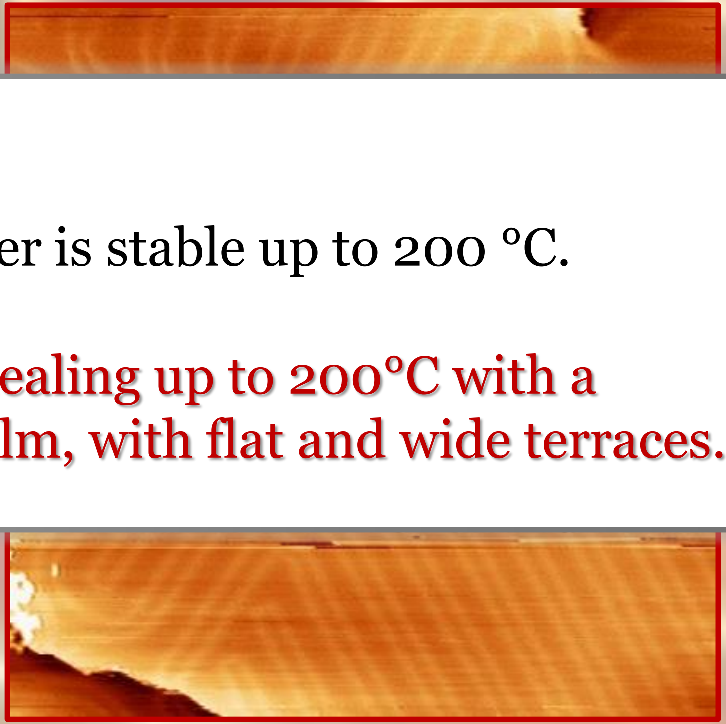
M5/M6-series: Au/mica

The annealing procedure up to 200 °C, performed in the UHV chamber, allows to obtain single crystalline films, [111] oriented.



Low Energy Electron





TO SUM UP…

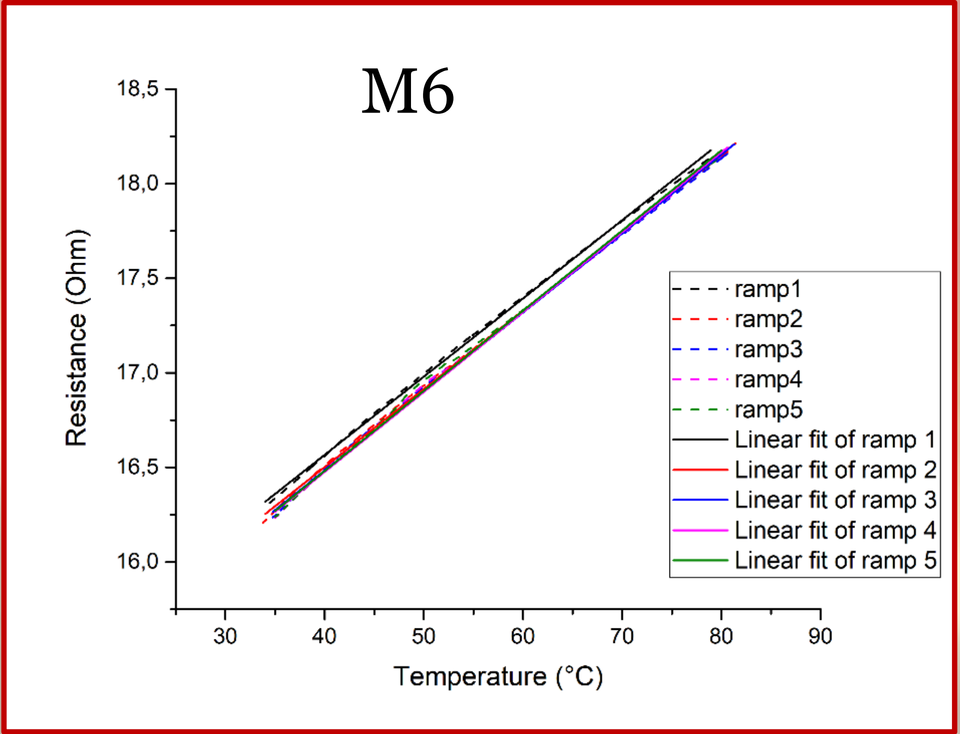
The STM measurements have demonstrated that the gold film thermometer is stable up to 200 °C.

The surface recostruction obtained with the M5/M6 samples after the annealing up to 200°C with a heating rate of 1°C/minute ensures a perfect recrystallization of the gold film, with flat and wide terraces.

Resistance vs Temperature

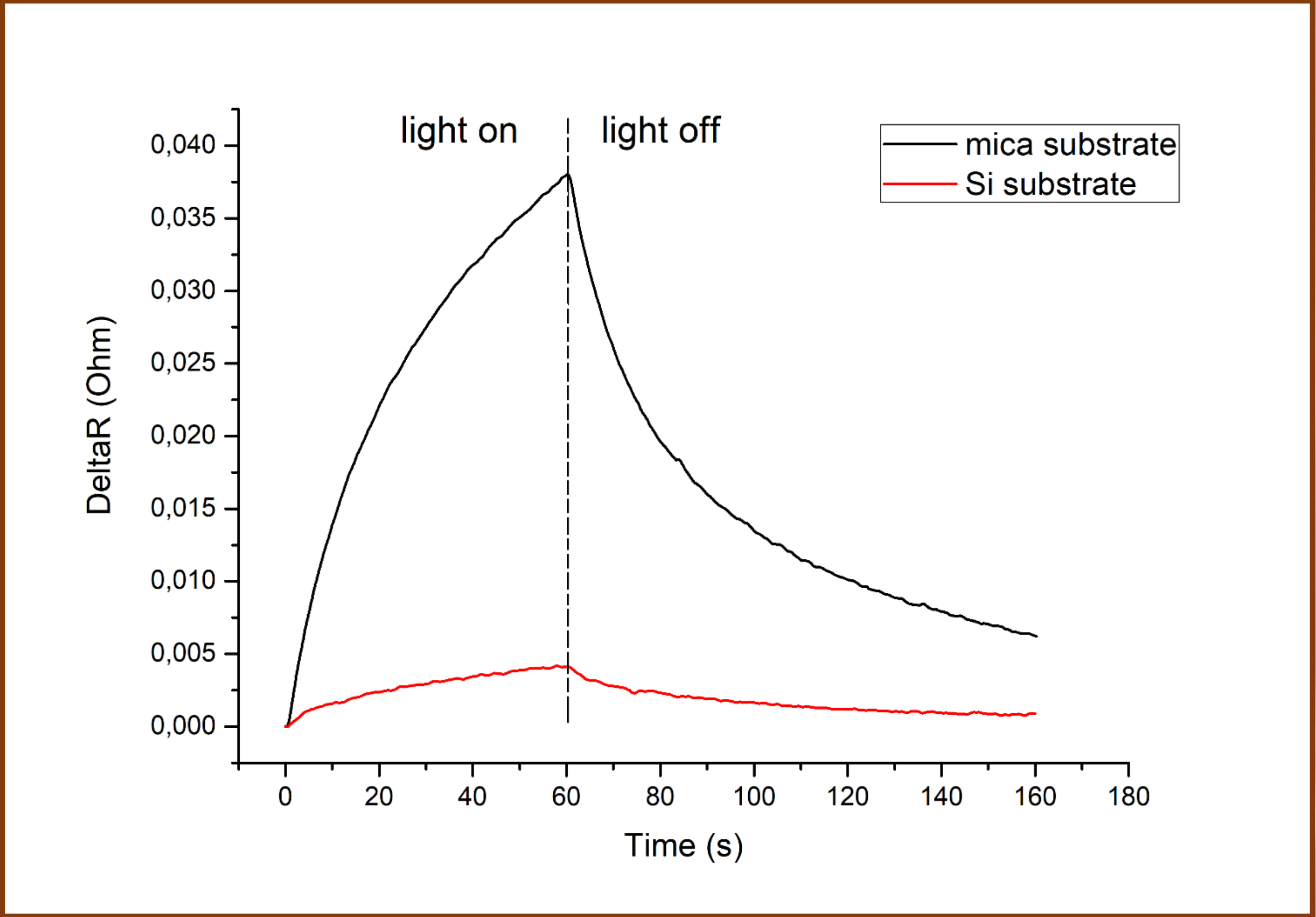
$$R(T) = R_0[1 + \alpha(T - T_0)]$$

→ resistance - temperature coefficient α (via linear fitting)



$$\alpha_{M5} = (3.1 \pm 0.3) \times 10^{-3}\ °C^{-1}$$
$$\alpha_{M6} = (2.8 \pm 0.1) \times 10^{-3}\ °C^{-1}$$

Heat transfer calibration – comparison



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

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

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

- The possibility to fully exploit the STM potentiality, due to the atomically flat thermometer surface

Outlook

- The STM measurements have demonstrated that the gold film thermometers are stable up to 200 °C. Stability range could be improved with a Ti layer.

- Simultaneous investigation of energy transfer mechanisms and surface physics on the same physical support.

- The atomically flat thermometer would allow a detailed study of 2D materials utilising STM and LEED probes.

- Mica properties make this sensors suitable to have a remarkable impact on flexible electronics.

Thank you for your attention!