UNIVERSITÀ DI PISA

An atomically flat gold film thermometer on mica for calorimetric applications

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Outline

State of The Art

- Calorimetry
- Nano-scale calorimetry
- Mica
- Au(111) herringbone reconstruction
- Gold thin films on mica

Au thermometer on mica

- Thermometer Fabrication
- Thermometer Calibration

Thermometer Application: atomic hydrogen adsorption

- Hydrogen adsorption on amorphous gold
- Hydrogen adsorption on Au(111)/mica

Conclusions and Outlook

Calorimetry

Calorimetric techniques are useful means to investigate the properties of matter by measuring the heat exchange during the system evolution. Indeed, an energy flux accopanies any evolution of a system, giving invaluable information on the processes underlying the evolution itself.

While the absolute amount of energy in a chemical system is difficult to measure or to calculate, the enthalpy variation is much easier to work with.

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

In case of exothermic heat release (with time-independent C_p):

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

IDEAL CASE

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In case of exothermic heat release (with time-independent C_p):

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

REAL CASE

Commercial calorimeters

A large number of commercial calorimeters can be found, specialized in studying solid or liquid samples, phase transitions and chemical reactions generally.
Usual requirements of commercial devices:

- sample mass in the mg range
- limited sensitivity (~mJ)

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

In this context, an original thermometric technique has been presented [1], and has been utilized to monitor the hydrogen storage in titanium-functionalized mono-layer graphene (Ti-MLG).

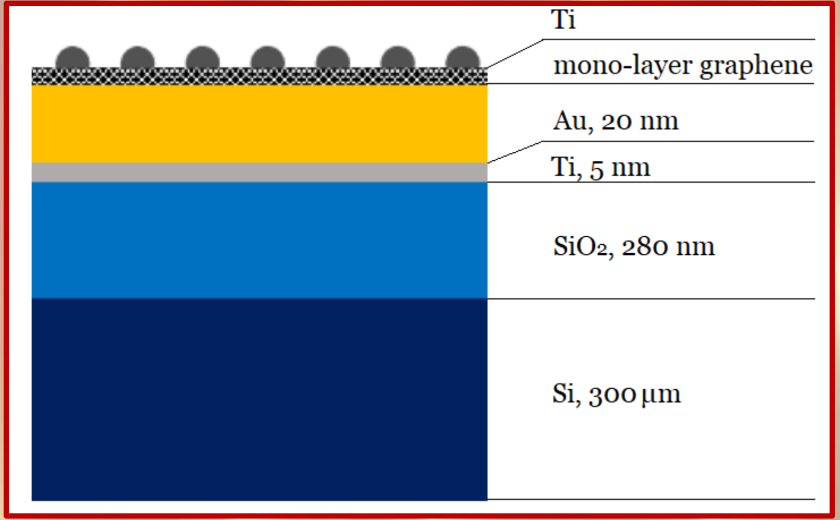
[1] L. Basta et al. A sensitive calorimetric technique to study energy (heat) exchange at the nanoscale. *Nanoscale*, 10:10079-10086, 2018.

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 $\Rightarrow$ α)
- MLG transfer
- Ti functionalization in situ (6.5 ML)
- Final calibration
- D_2 exposure (5 minutes, 1.0×10^{-7} mbar)

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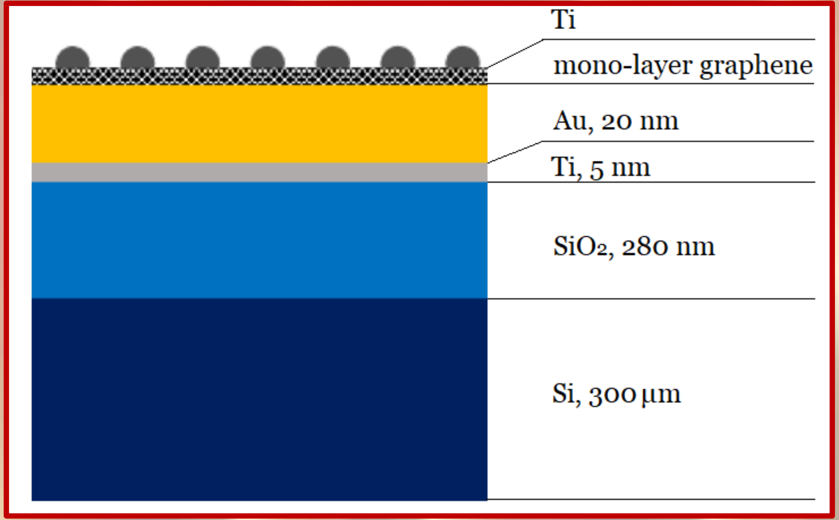


[1] L. Basta et al. *Nanoscale*, 10:10079-10086, 2018.

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)

Calorimetric analysis

THE THERMAL MODEL

- the thermometer is heated by the absorption of a thermal power $P(t) = \delta H_r/\delta t$
- at the same time it releases energy by heat losses towards the substrate

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

with $C_{sensor} = C_{MLG} + C_{Au} + C_{Ti} + C_{SiO2}$ heat capacity at constant pressure [1]

- point-by-point derivative of the measured $\Delta T(t)$ curve
- point-by-point integration of $\frac{\delta H_r}{\delta t}$
- experimental parameters C_{sensor} e λ

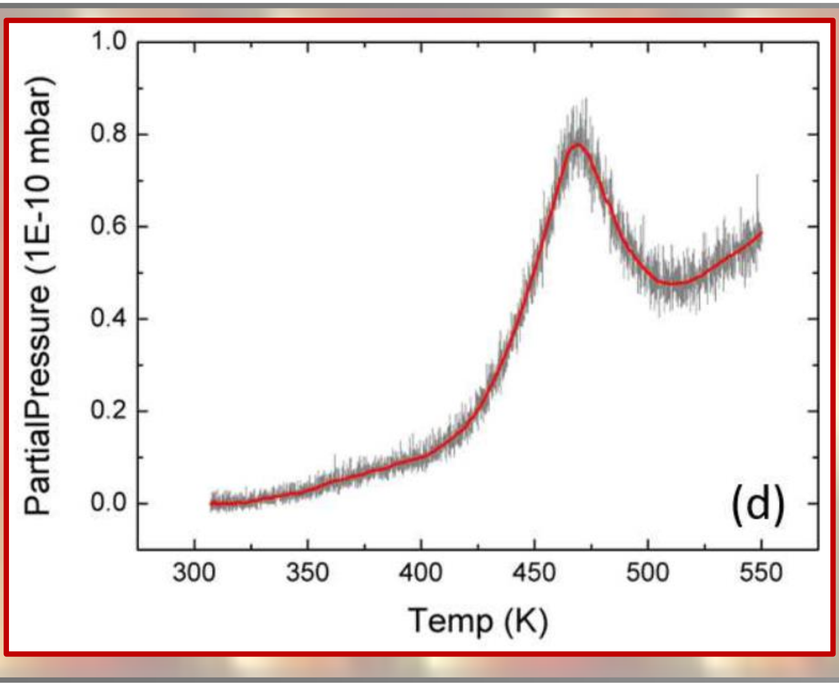
$$H_r \simeq (23 \pm 5)\ \mu J$$

[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 rapidly heating the sample, the adsorbed species are removed.

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



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

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

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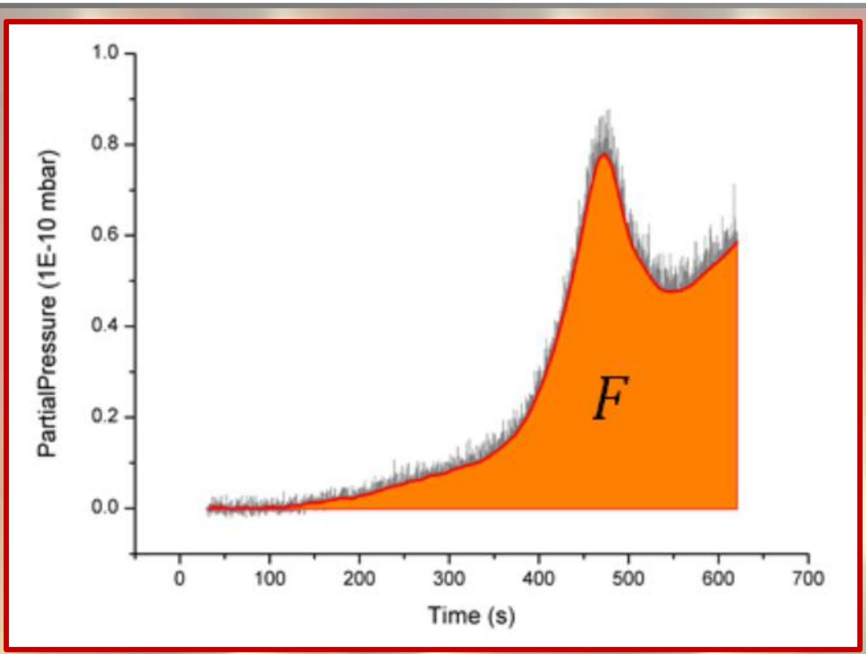


$$P \cdot V = F \cdot S = n \cdot R \cdot T \Longrightarrow n\,(\text{from } F,\ S \approx 300\ \text{L/s})$$

[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 rapidly heating the sample, the adsorbed species are removed.

- TDS Spectrum vs Temperature $\Longrightarrow$ binding energy $E_b = E_d$
- TDS Spectrum vs Time $\Longrightarrow$ desorbed moles n

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

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

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

Final remarks

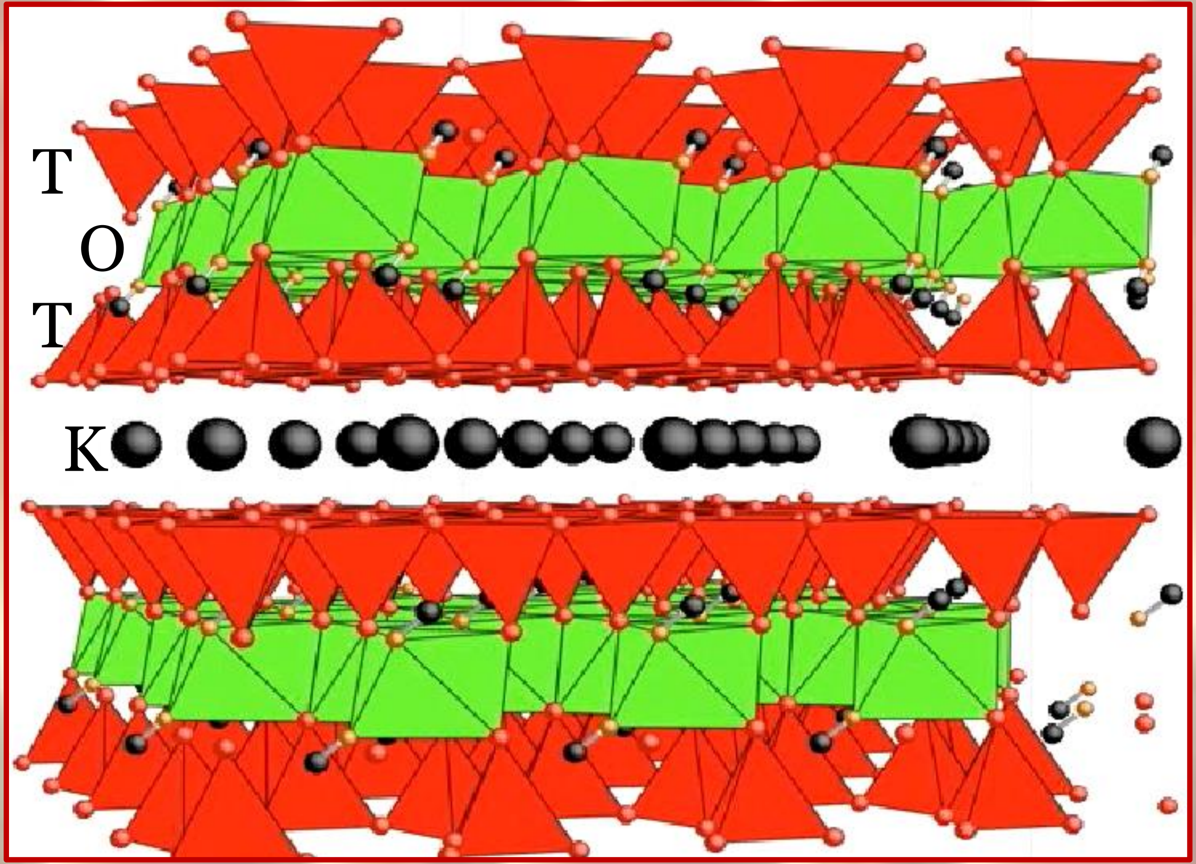
First direct measurement of the enthalpy released during an hydrogen adsorption process

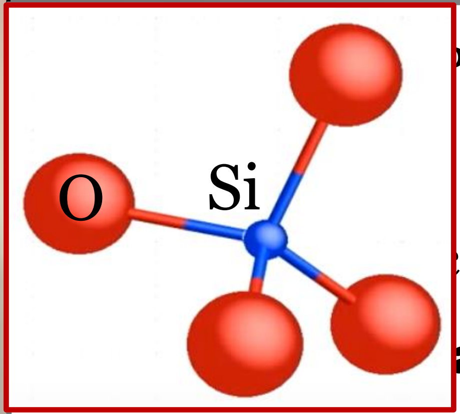
- resistance variation sensitivity of ~ 0.03 mΩ
- temperature variation sensitivity ~ 10 mK
- D_2 detected during adsorption ~ 0.2 ng or 10^{-10}mol
- corresponding to a released enthalpy $H_r \simeq (23 \pm 5)$ μJ
- in good agreement with TDS evaluation $H_r \simeq (22 \pm 1)$ μJ
- main advantage: the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

THERMOMETER WEAK POINT: its substrate!!!

[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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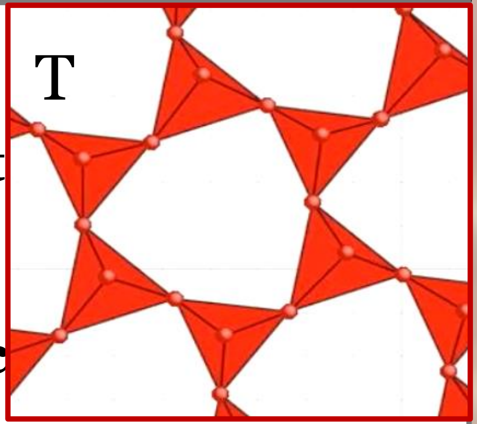

- **Capability to allow gold surface**

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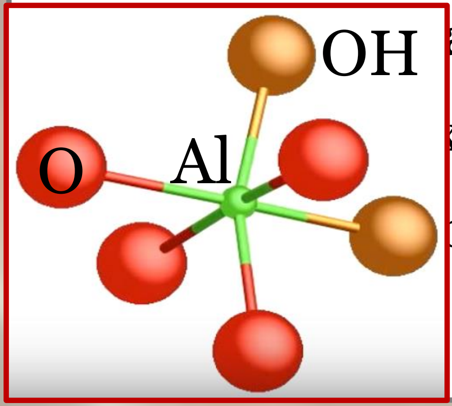
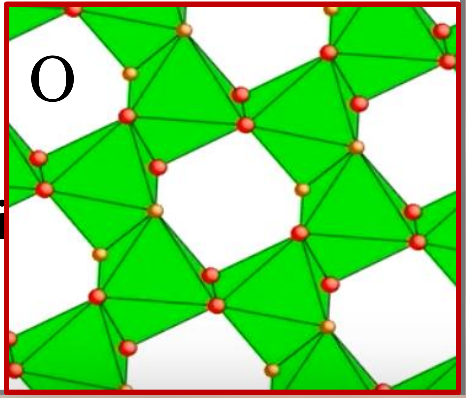
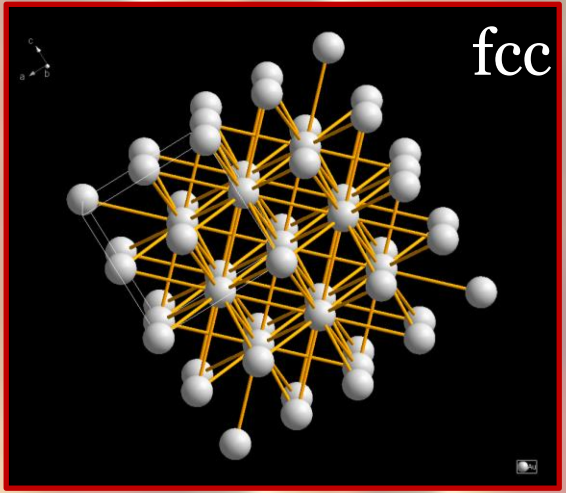
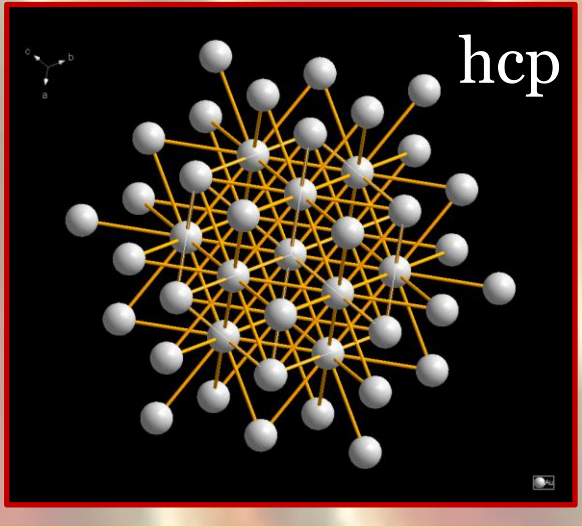
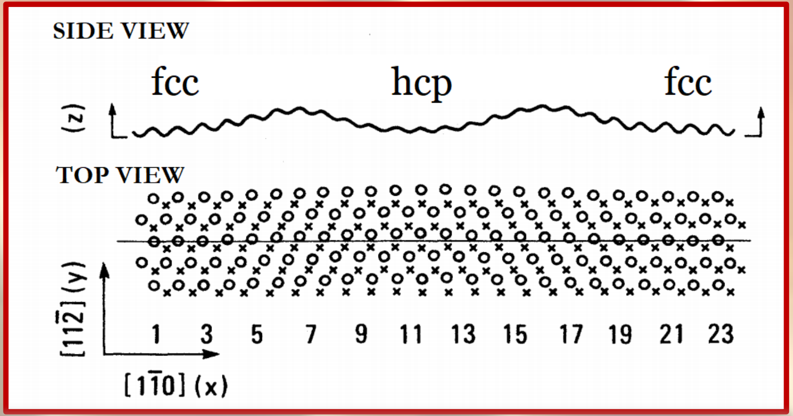




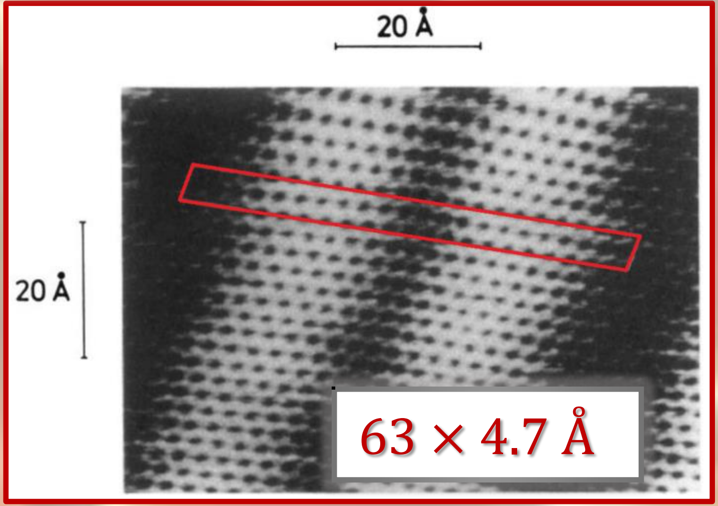
Au(111) herringbone reconstruction

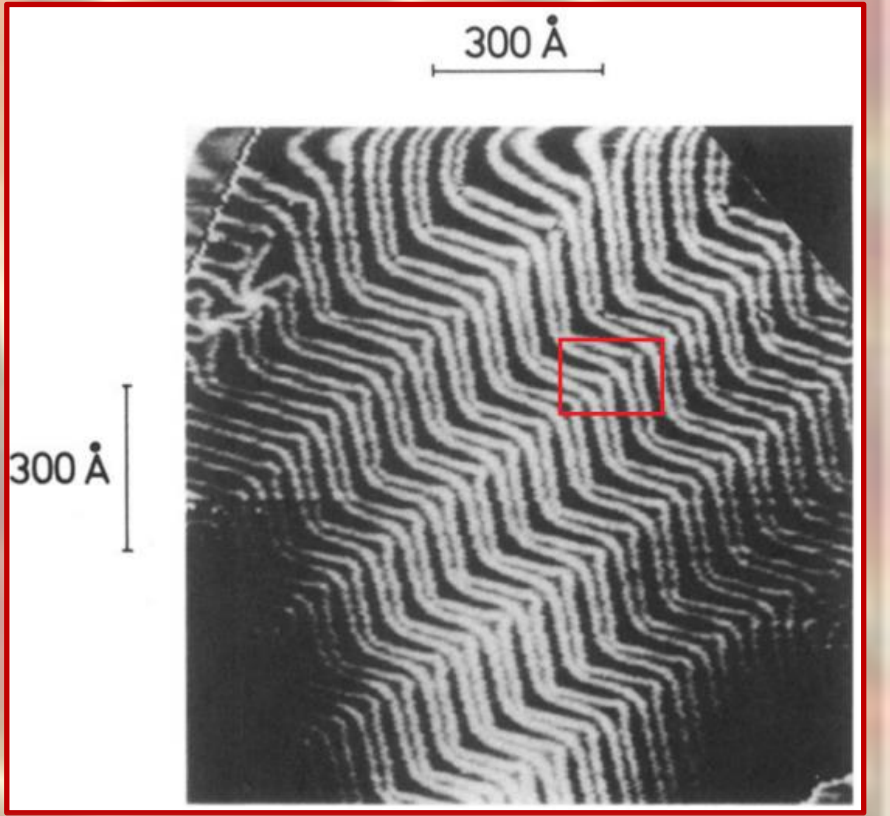






Ch. Wöll et al. *Phys. Rev. B*, 39:7988-91, 1989.





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

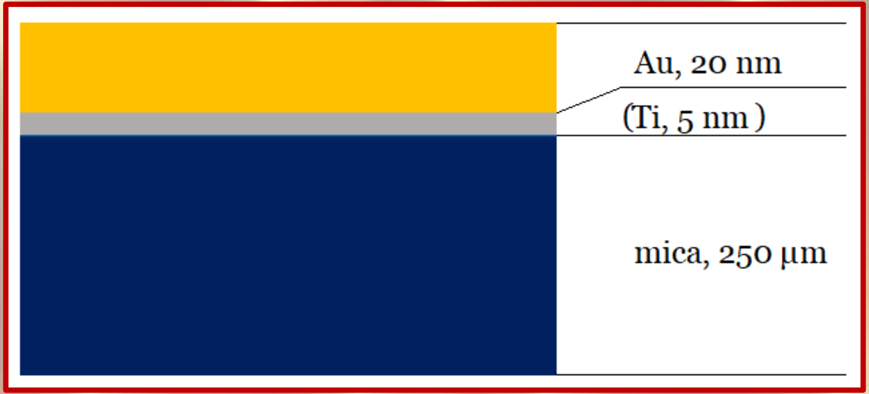
Gold thin films on mica

ESSENTIAL REQUIREMENTS FOR THE DEPOSITION OF GOLD THIN FILMS

- Best possible vacuum
- Clean chamber
- Smooth dry substrate (e.g. mica)
- Appropriate combination of substrate temperature and deposition rate

Gold deposition on a freshly cleaved, heated, mica substrate produces very large grains.
The annealing procedure allows to obtain crystalline films, [111] oriented.

Thermometer Fabrication - overview

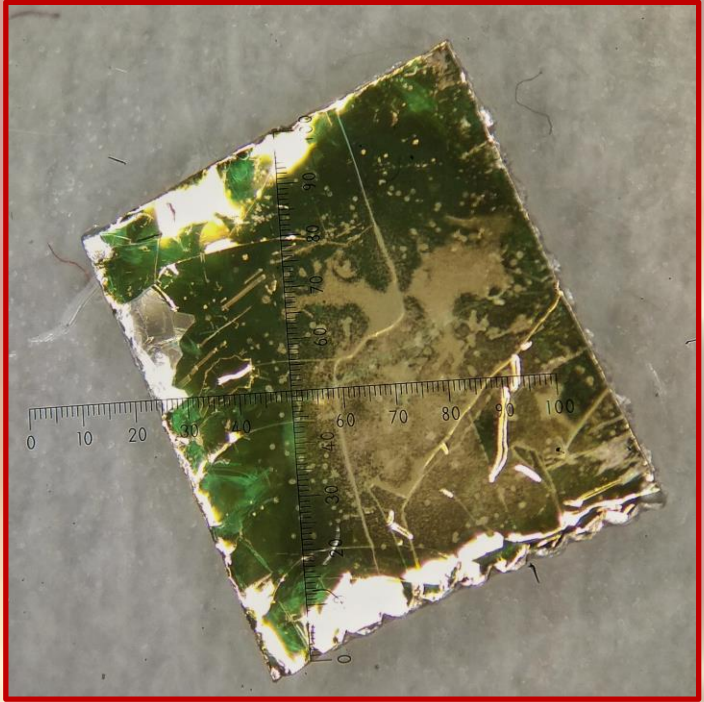


M2-series	M3-series	M4-series	M5/M6-series
Au/Ti/mica	Au/mica	Au/mica	Au/mica
• no substrate annealing • metal deposition at room temperature (RT)	• no substrate annealing • gold deposition at RT	• substrate annealing at 200°C • gold deposition at 200°C	• substrate annealing at 200°C • gold deposition at RT

M2-series: Au/Ti/mica

- No substrate annealing
- Metal deposition at RT, with a deposition rate of 1 Å/s

The annealing procedure, performed either with a butan torch or in the UHV chamber, allows to obtain crystalline films, [111] oriented.

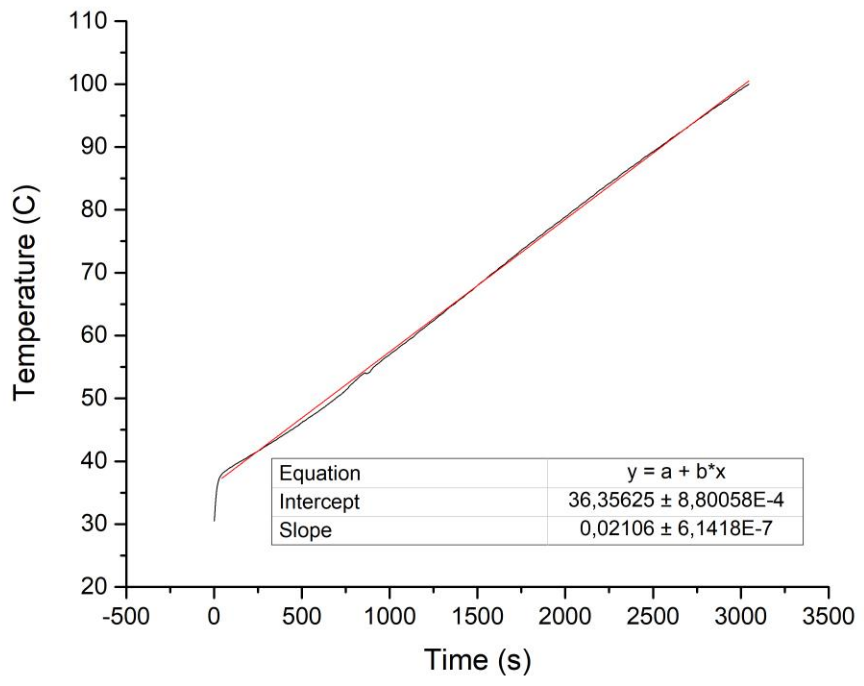


M2-series: Au/Ti/mica

- No substrate annealing
- Metal deposition at RT, with a deposition rate of 1 Å/s

The annealing procedure, performed either with a butan torch or in the UHV chamber, allows to obtain crystalline films, [111] oriented.

Several heating ramps, up to temperatures ranging from 100°C to 400°C have been performed in the UHV chamber, with a heating rate of 1°C/minute.



M2-series: Au/Ti/mica

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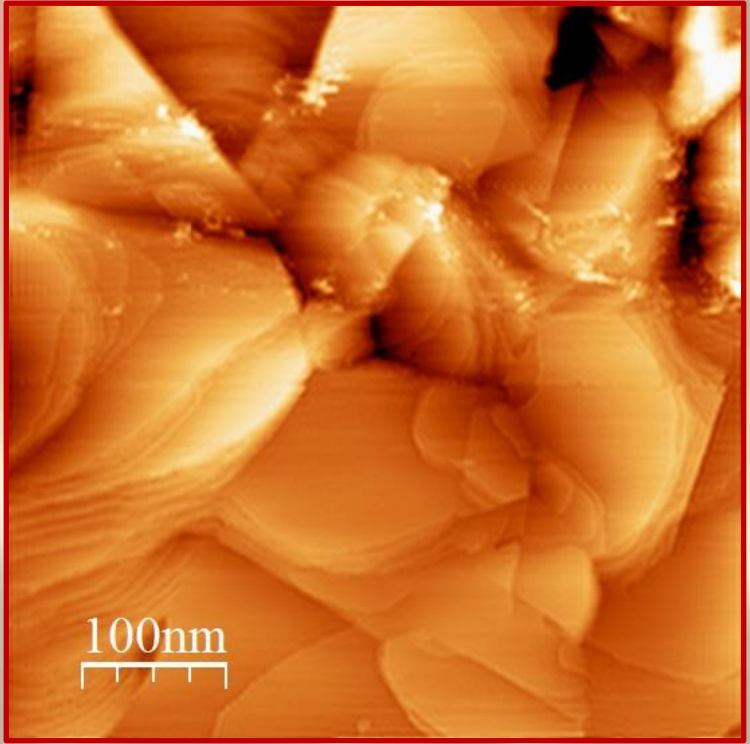
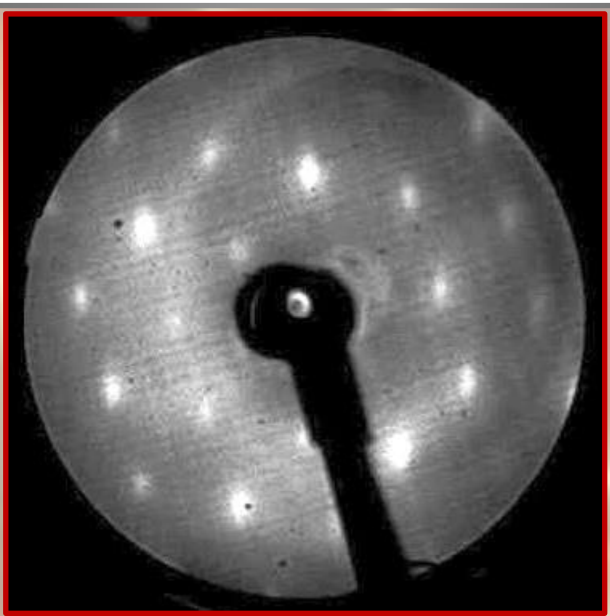
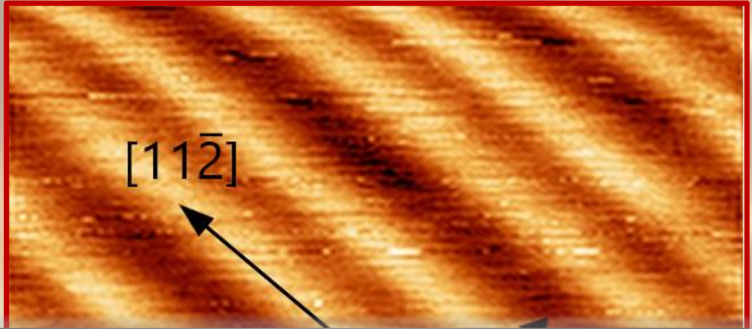
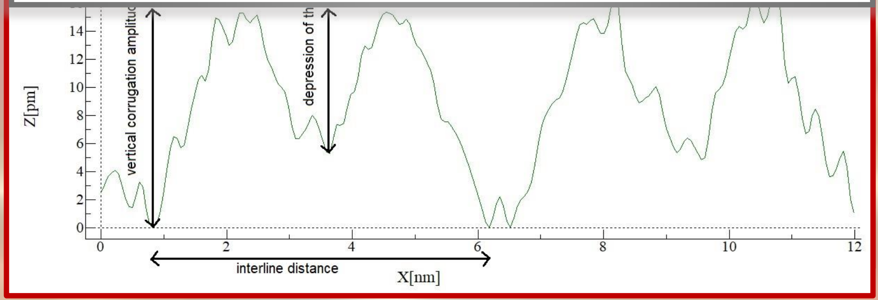


After the heating ramp up to 200°C…



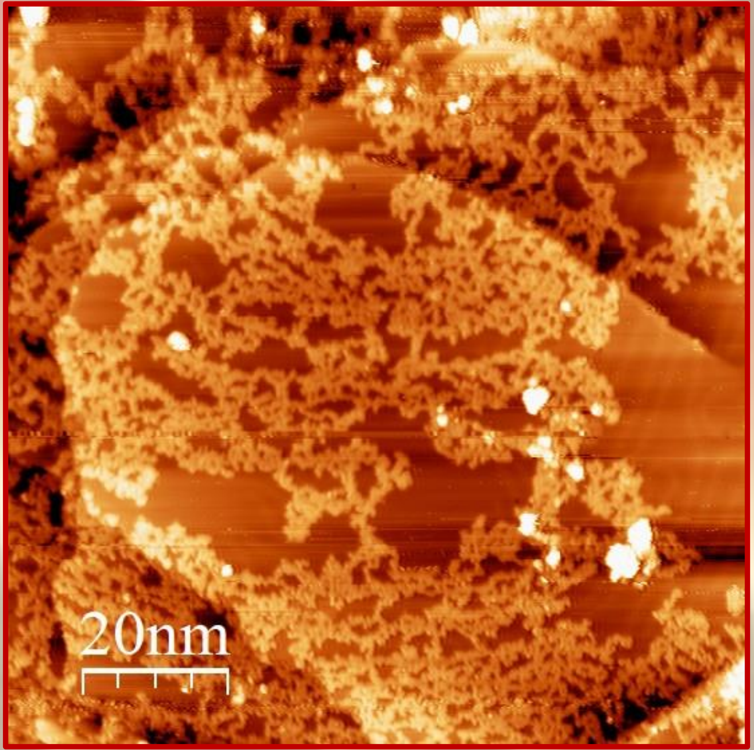


LOW ENERGY ELECTRON DIFFRACTION (LEED) PATTERN

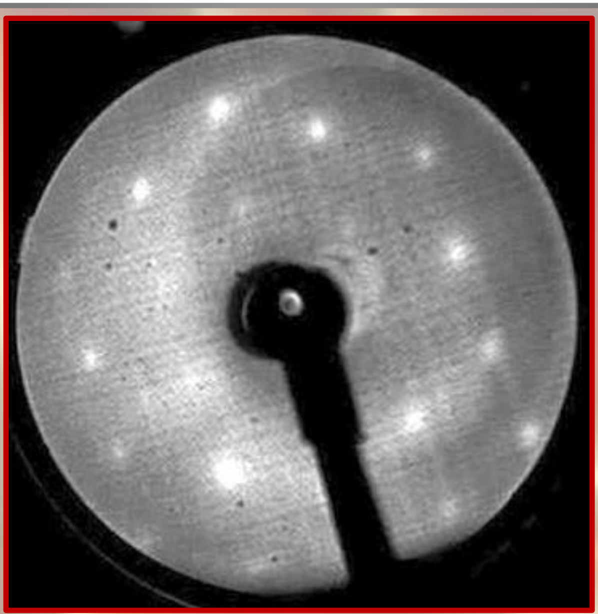


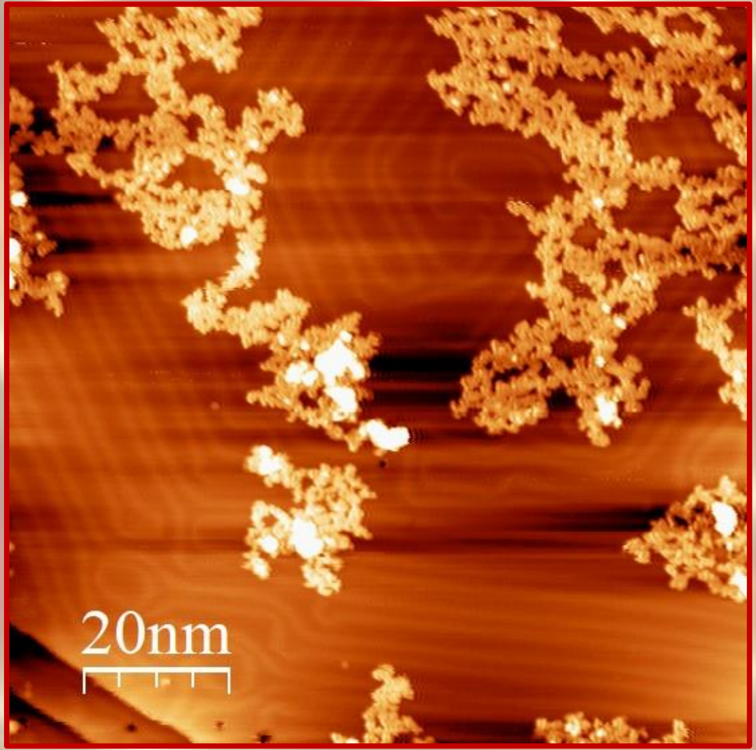
M2-series: Au/Ti/mica

- No substrate annealing
- Metal deposition at RT, with a deposition rate of 1 Å/s



After the heating ramp up to 300°C…





M2-series: Au/Ti/mica

- No substrate annealing
- Metal deposition at RT, with a deposition rate of 1 Å/s

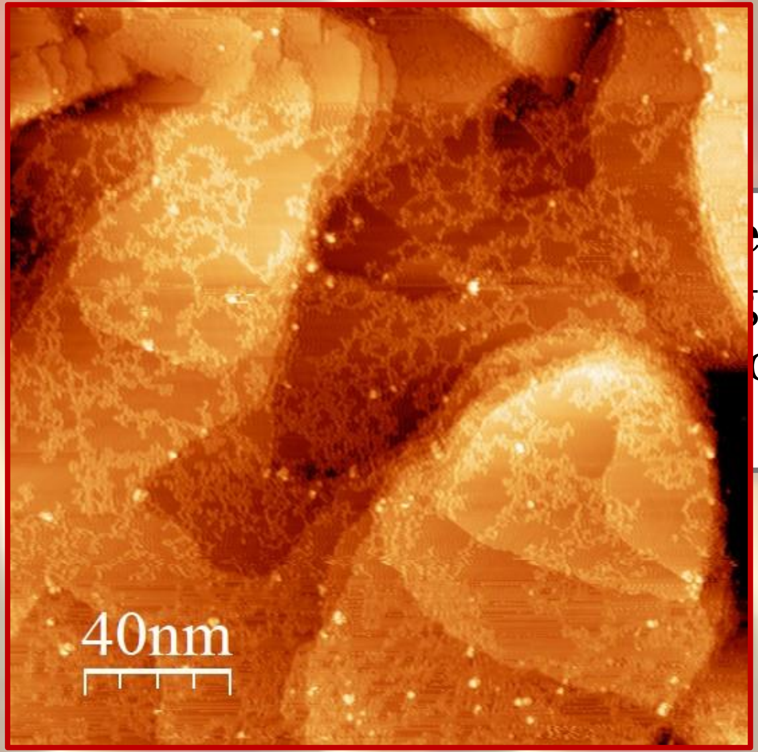
FIRST GUESS: Titanium diffusion in the gold thin film, induced by the temperature increase [2]

SOLUTION: M3-series, fabricated without using titanium as adhesion promoter between gold and mica

[2] W. E. Martinez et al. Titanium diffusion in gold thin films. *Thin Solid Films*, 518(10):2585-2591, 2010.

M3-series: Au/mica

- No substrate annealing
- Gold deposition at RT, with a deposition rate of 1 Å/s



Already after the heating ramp up to 200°C...

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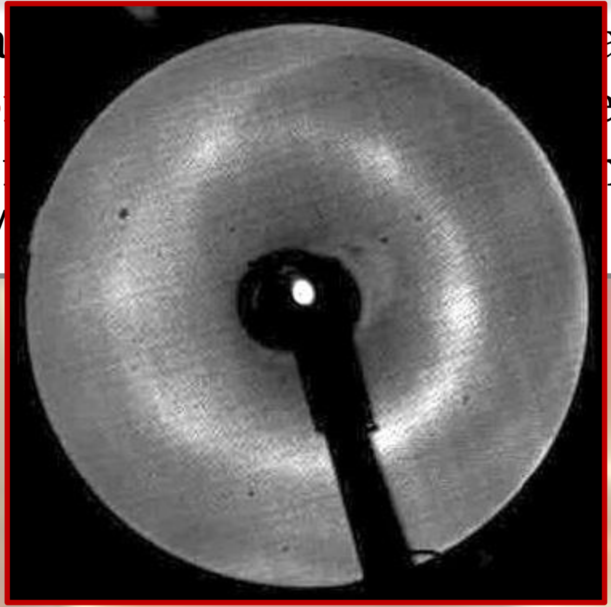
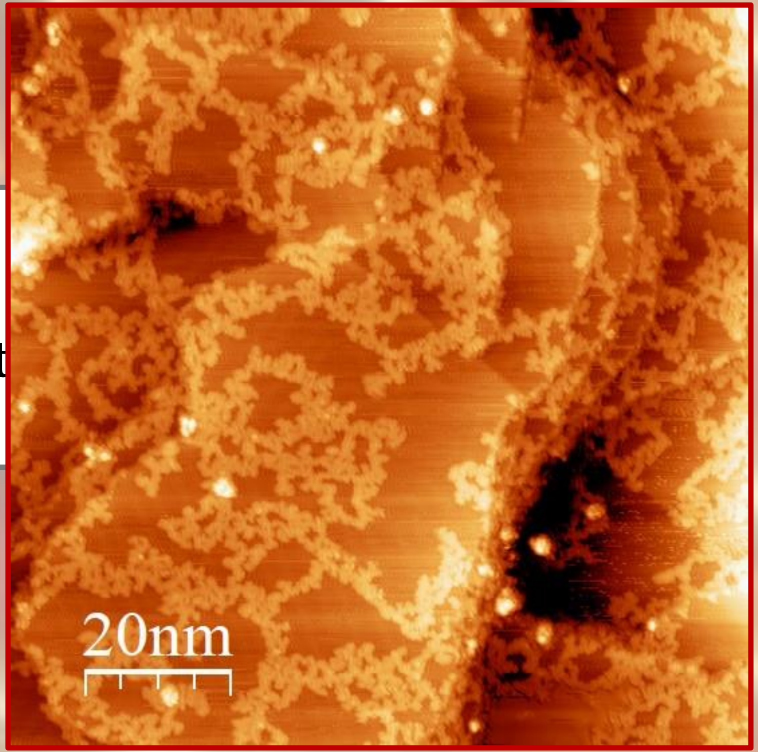
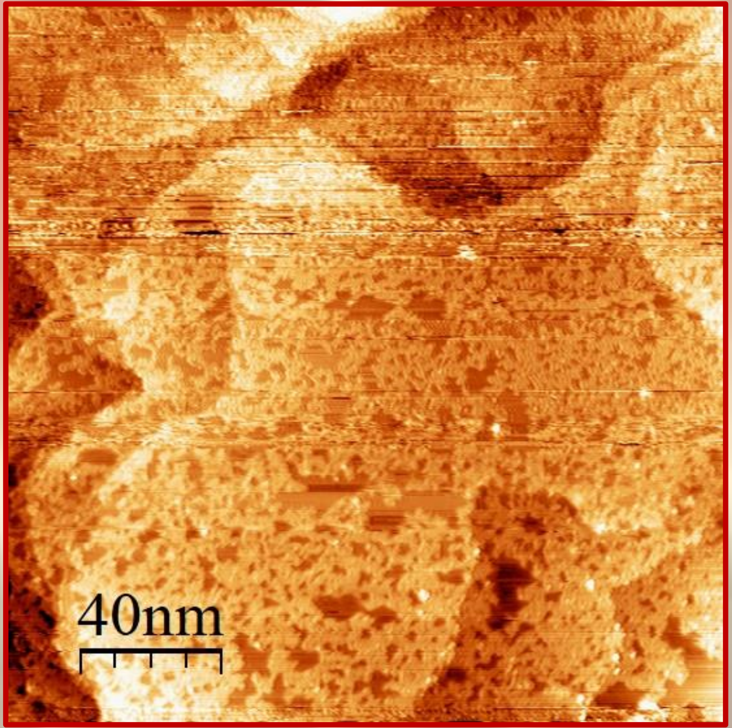


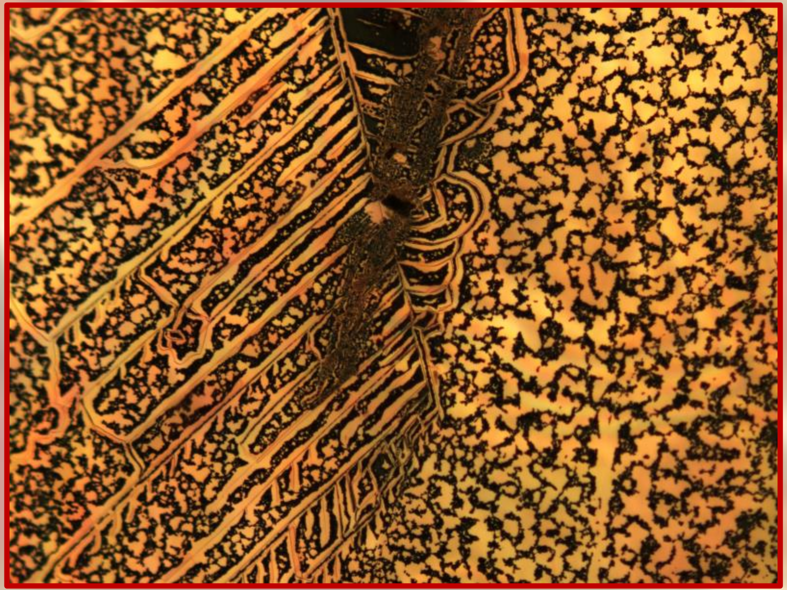


M3-series: Au/mica

- No substrate annealing
- Gold deposition at RT, with a deposition rate of 1 Å/s



After the heating ramp up to 450°C…



M3-series: Au/mica

- No substrate annealing
- Gold deposition at RT, with a deposition rate of 1 Å/s

SECOND GUESS: Water intercalated between the gold layer and the mica substrate

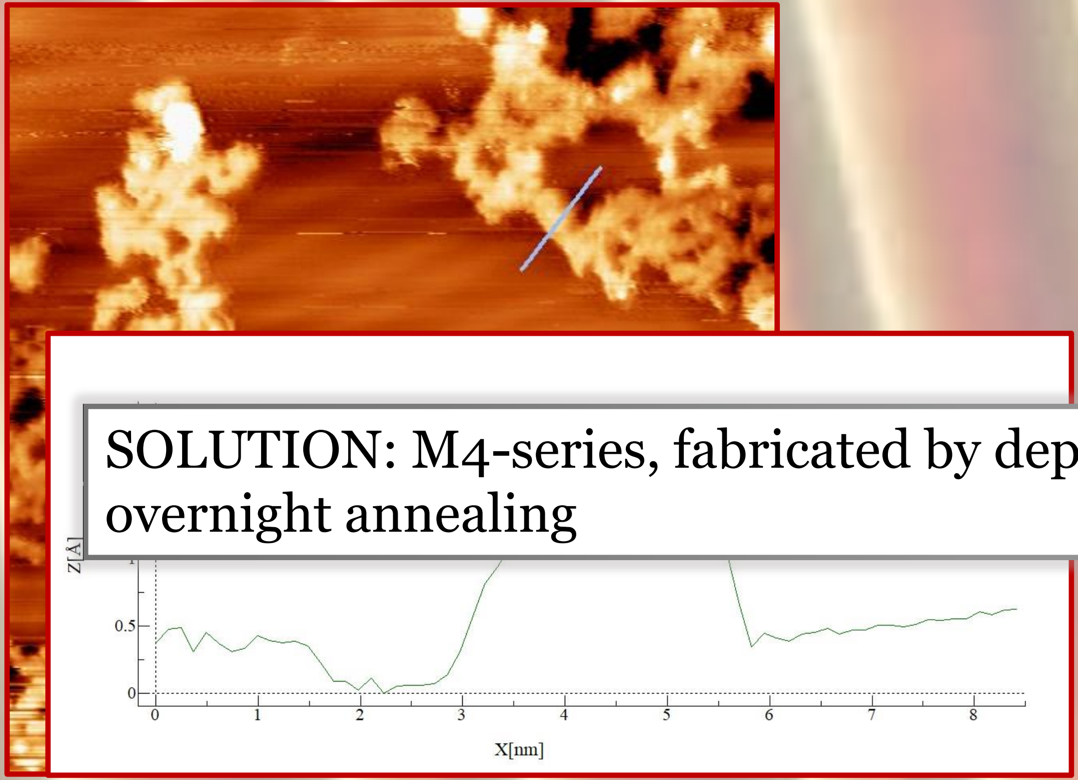
Scanning Polarization Force Microscopy (SPFM) [3] and the «graphene template technique» [4] have been used to study water films on mica.

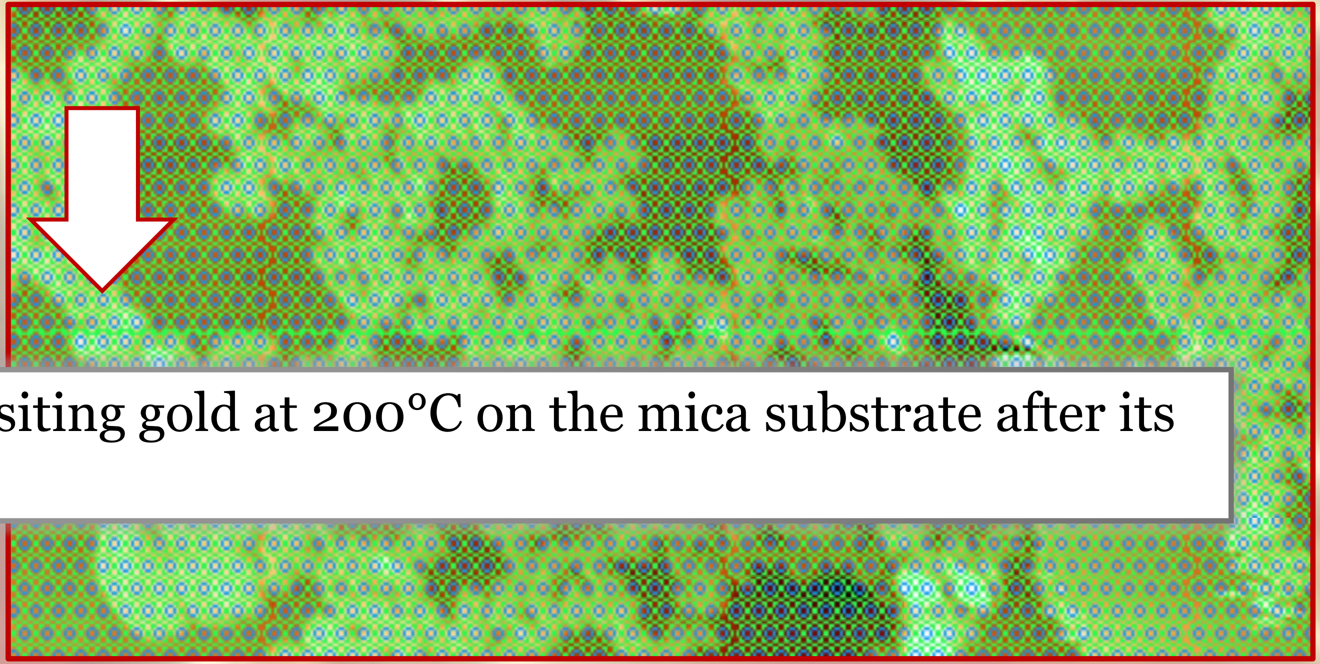
In the light of the results reported in these research works, the STM images relating to M3-samples have been analysed.

[3] J. Hu et al. Imaging the Condensation and Evaporation of Molecularly Thin Films of Water with Nanometer Resolution. *Science*, 268:267-9, 1995.
[4] K. Xu et al. Graphene Visualizes the First Water Adlayers on Mica at Ambient Conditions. *Science*, 329:1188-91, 2010.

M3-series: Au/mica

- No substrate annealing
- Gold deposition at RT, with a deposition rate of 1 Å/s





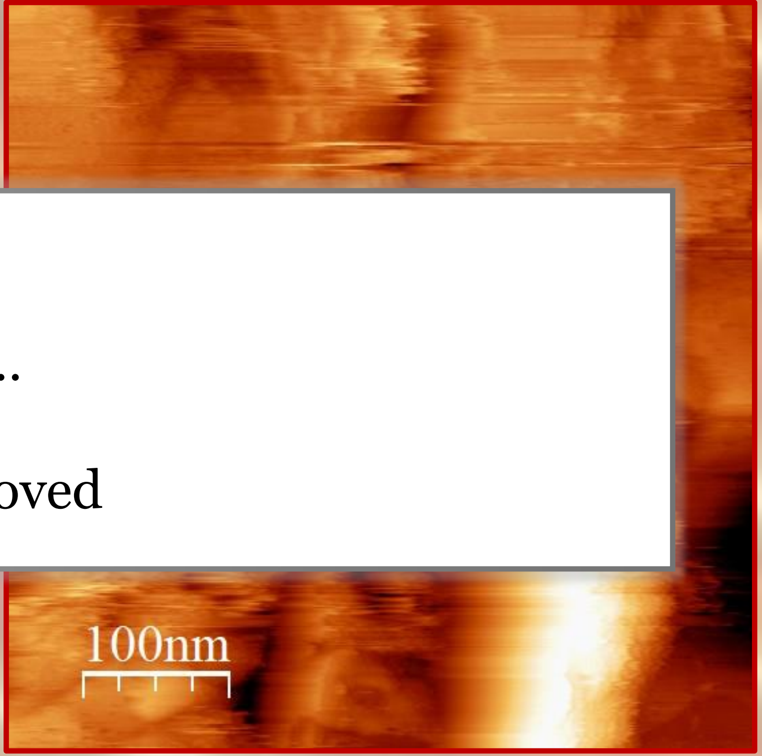
SOLUTION: M4-series, fabricated by depositing gold at 200°C on the mica substrate after its overnight annealing

M4-series: Au/mica

- Substrate annealing at 200°C
- Gold deposition at 200°C, with a deposition rate of 1 Å/s

Several heating ramps, up to temperatures ranging from

300°C...



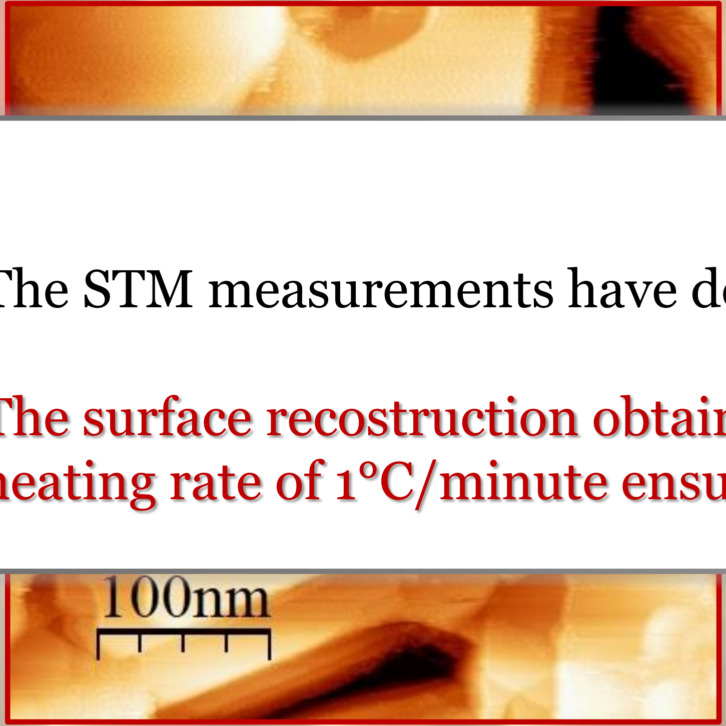
TO SUM UP...

The «water issue» has been solved, but...

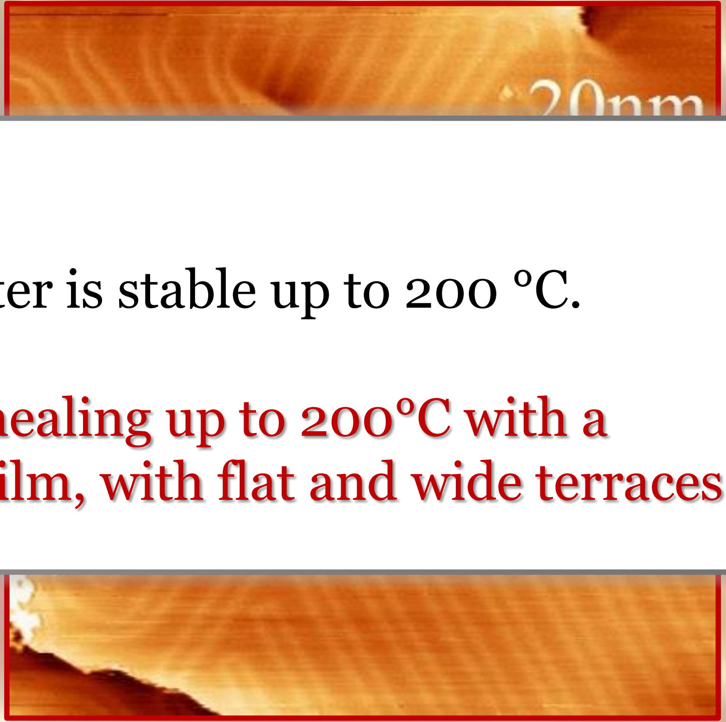
The deposition procedure needs to be improved

M5/M6-series: Au/mica

- Substrate annealing at 200°C
- Gold deposition at RT, with a deposition rate of 1 Å/s



After the heating ramp up to



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

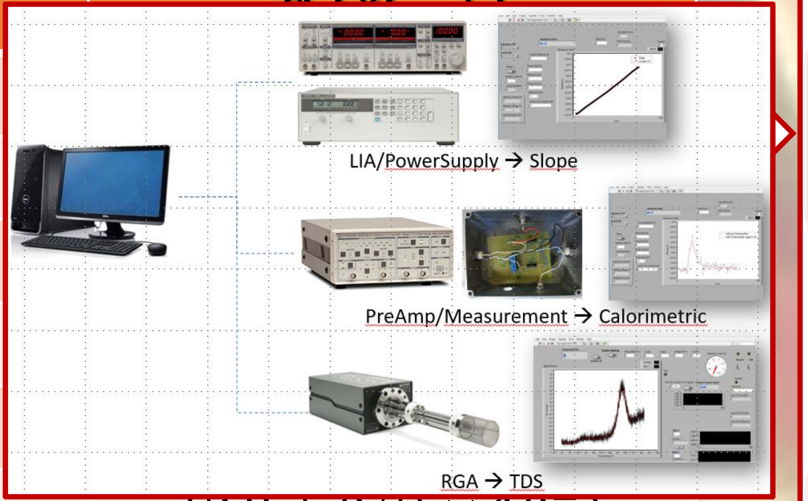
In order to properly calibrate the thermometer, several heating cycles have been performed, recording Resistance vs Temperature curves.

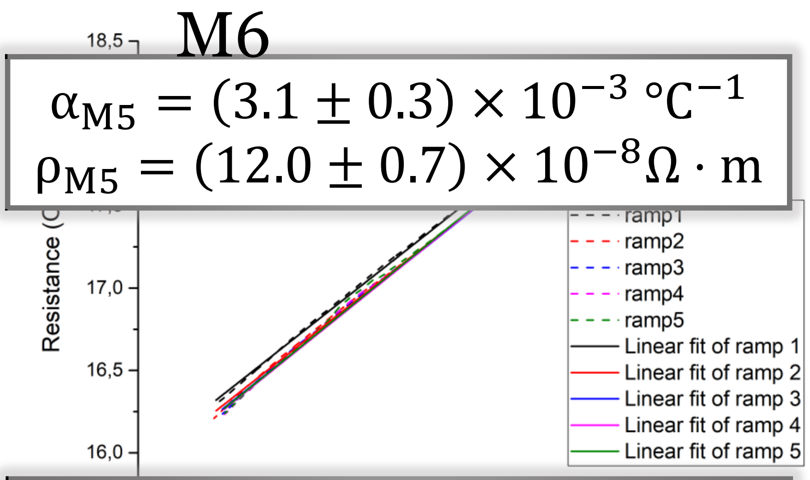
$$R(T) = R_0[1 + \alpha(T - T_0)]$$

⇨

resistance - temperature coefficient α (via linear fitting)
resistivity $\rho = R \times A/l$

Sample M5	Ramp	α (°C^{-1})
M5	1	
M5	2	
M6	1	
M6	2	
M6	3	
M6	4	$(2.9 \pm 0.7) \times 10^{-3}$
M6	5	$(2.9 \pm 1.0) \times 10^{-3}$





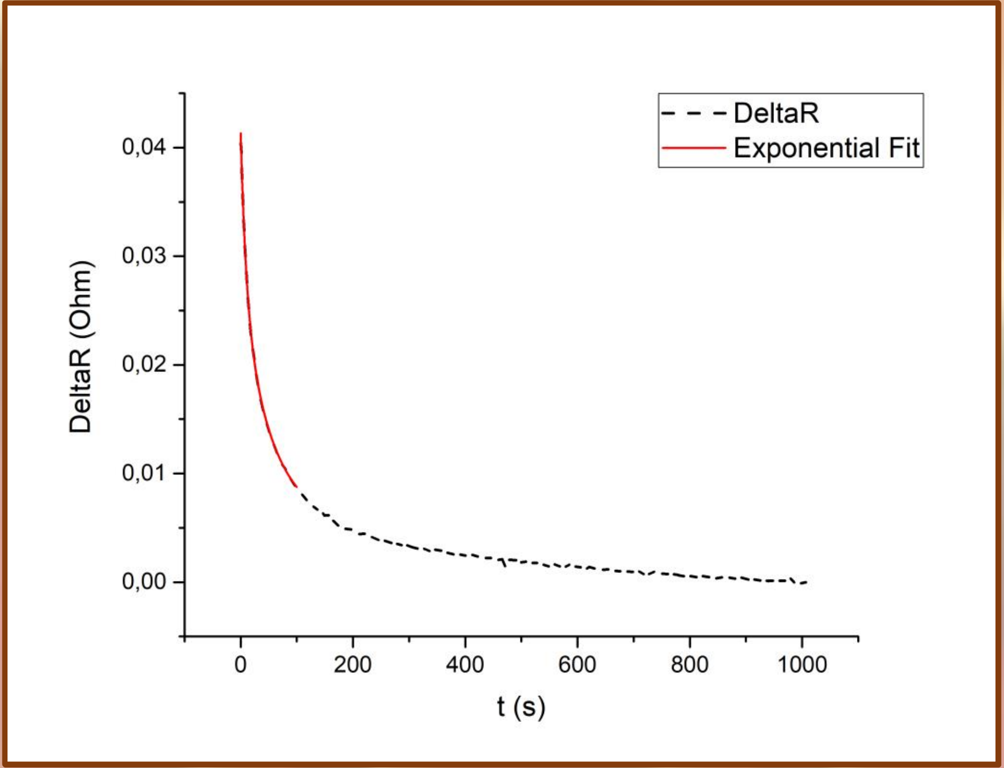
$$\alpha_{M5} = (3.1 \pm 0.3) \times 10^{-3}\ ^{\circ}C^{-1}$$
$$\rho_{M5} = (12.0 \pm 0.7) \times 10^{-8} \Omega \cdot m$$

⇨

$$\alpha_{M6} = (2.8 \pm 0.1) \times 10^{-3}\ ^{\circ}C^{-1}$$
$$\rho_{M6} = (14.7 \pm 0.8) \times 10^{-8} \Omega \cdot m$$

Heat transfer calibration

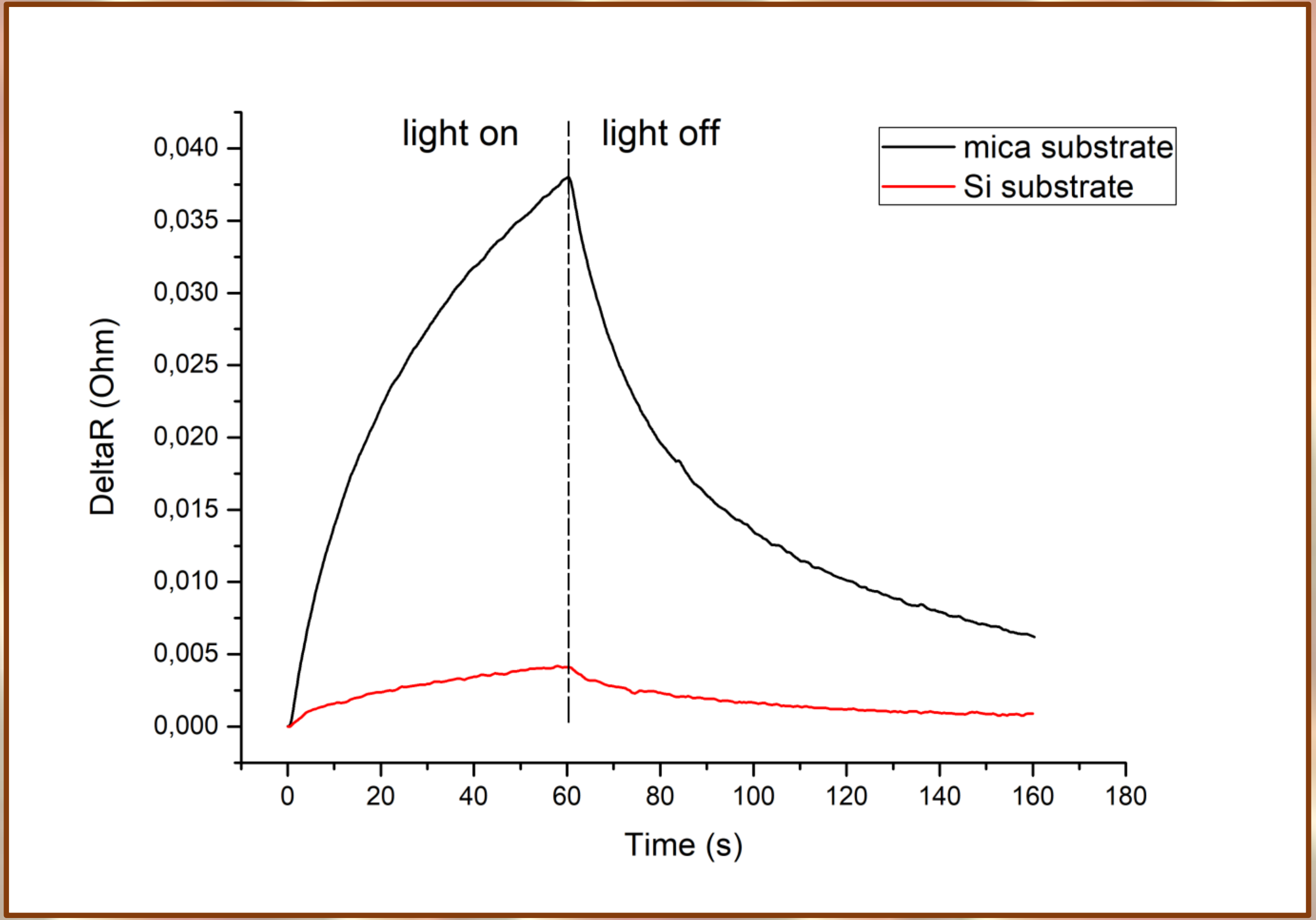
$$\Delta T(t) = \Delta T(0) + A_1\, exp\left(-\frac{t}{\tau_1}\right) + A_2\, exp\left(-\frac{t}{\tau_2}\right)$$



- $\tau_1 = (9.9 \pm 0.1)$ s
- $\tau_2 = (56 \pm 1)$ s

$$\lambda = C_{sensor}/\tau_1$$

Heat transfer calibration – comparison



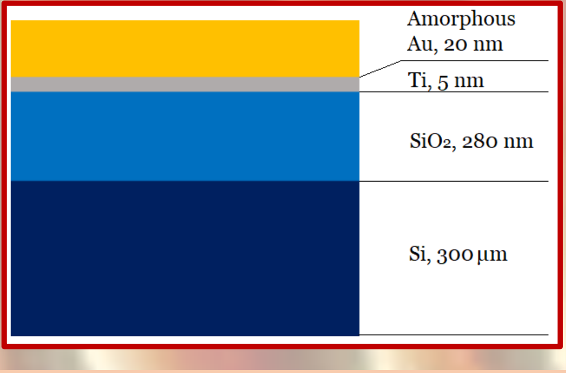
- $\Delta R_{mica} = 0.038\ \Omega$
- $\Delta R_{Si} = 0.004\ \Omega$

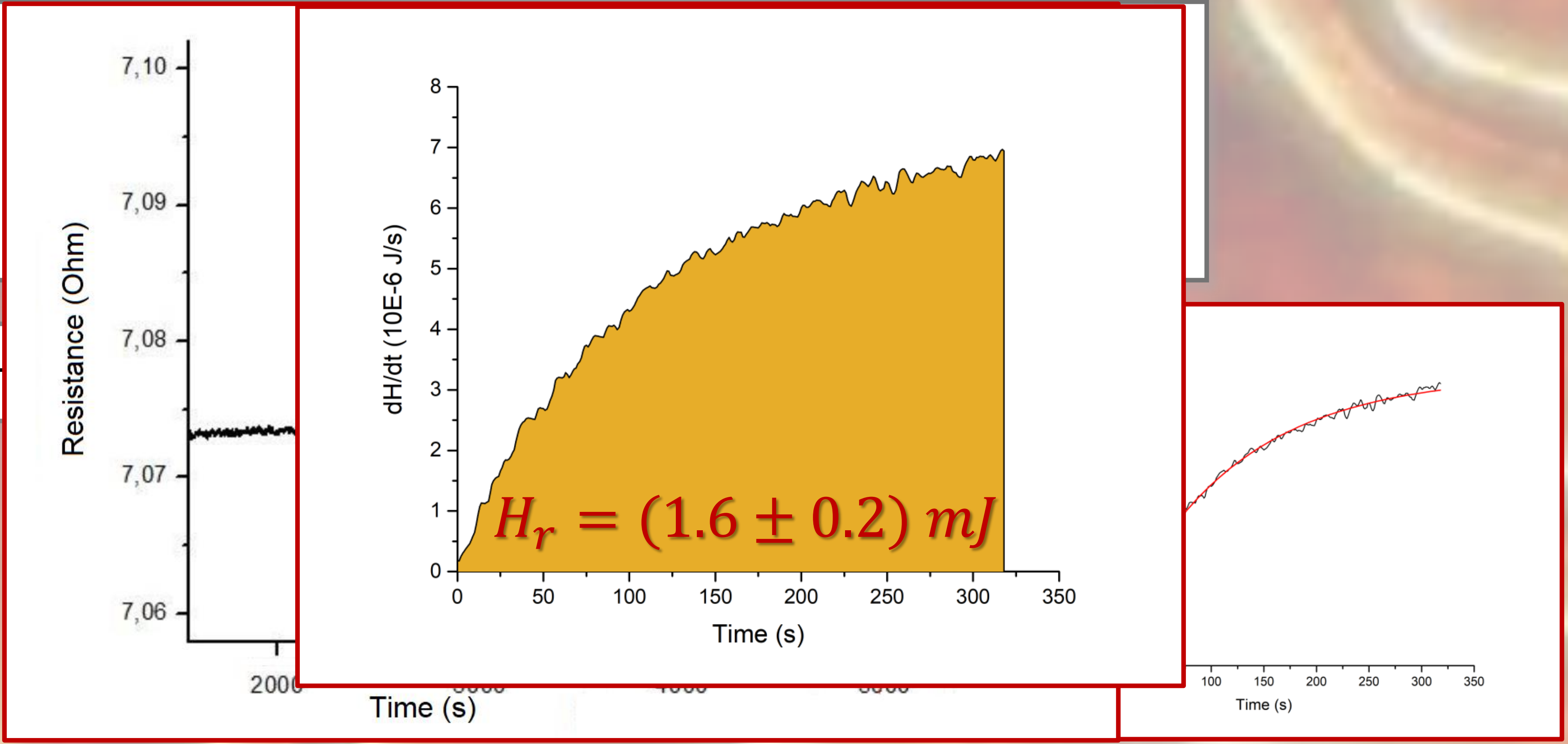
The new sensor is **10 times** more sensitive!

Hydrogen adsorption on amorphous gold: calorimetry

Atomic hydrogen exposure, 5 minutes, 1×10^{-7} mbar

$$C_{sensor} = C_{Au} + C_{Ti} +$$

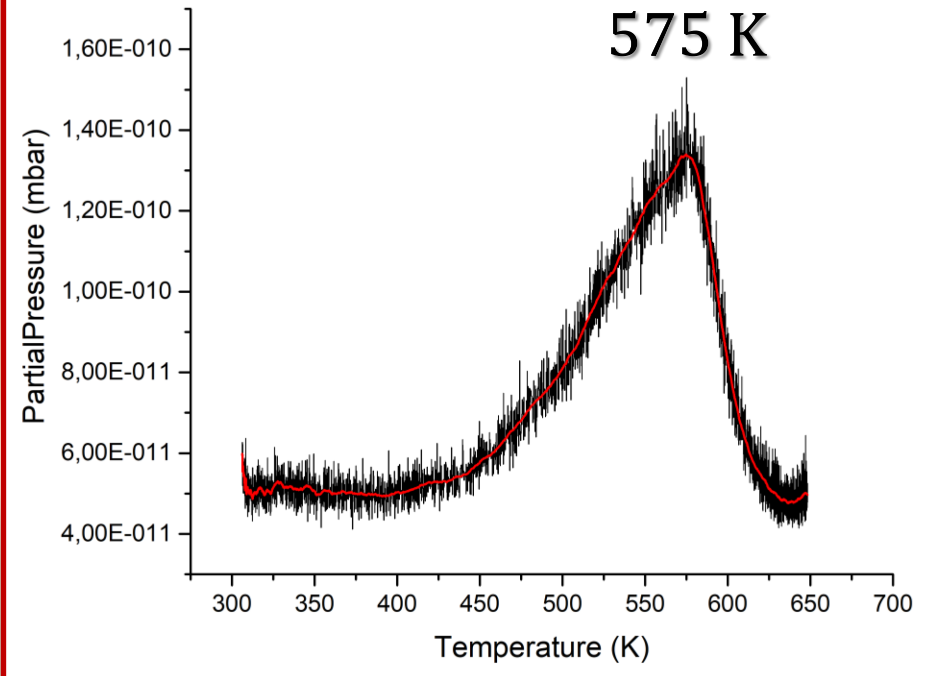




$H_r = (1.6 \pm 0.2)\ mJ$

Hydrogen adsorption on amorphous gold: TDS

Atomic hydrogen exposure, 5 minutes, 1×10^{-7} mbar



$P \cdot V = F \cdot S = n \cdot R \cdot T$

(from F, $S \approx 300$ L/s)

$\Rightarrow n = 2.2 \times 10^{-9}\ mol$

$E_b \simeq 3\ eV$

$E_d = (1.65 \pm 0.04)\ eV$

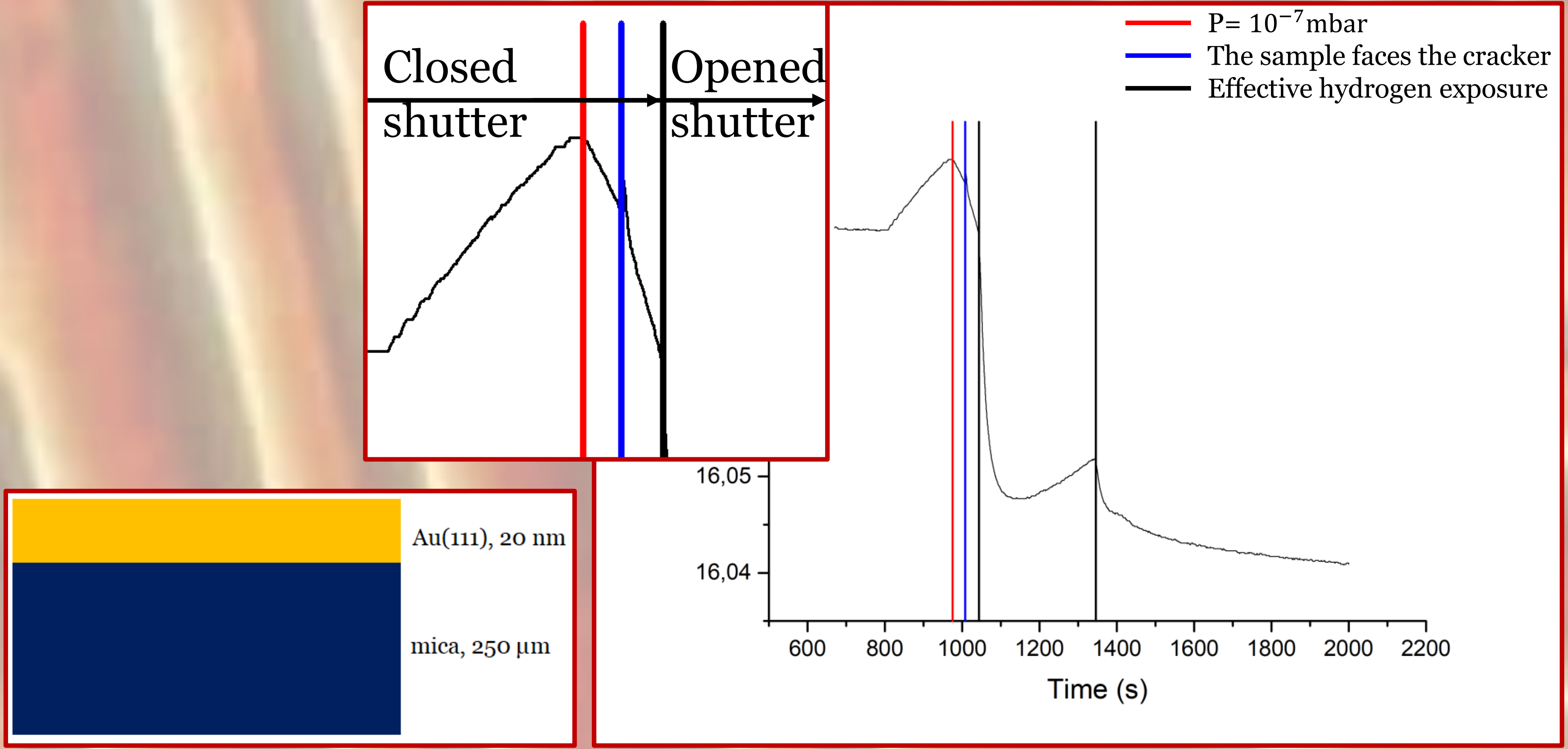
$H_r^{TDS} = nN_AE_b = (1.3 \pm 0.1)\ mJ$

eV

$H_r^{calorimetry} = (1.6 \pm 0.2)\ mJ$

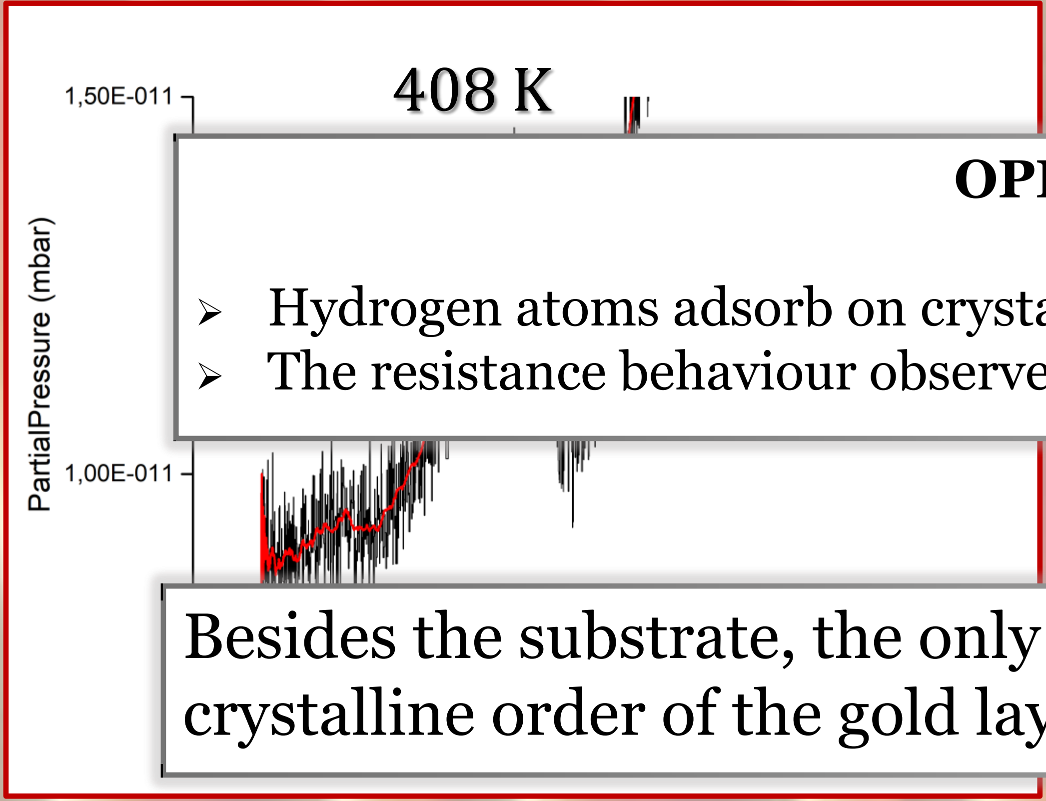
Hydrogen adsorption on Au(111)/mica: calorimetry

Atomic hydrogen exposure, 5 minutes, 1×10^{-7} mbar



Hydrogen adsorption on Au(111)/mica: TDS

Atomic hydrogen exposure, 5 minutes, 1×10^{-7} mbar



$$P \cdot V = F \cdot S = n \cdot R \cdot T$$

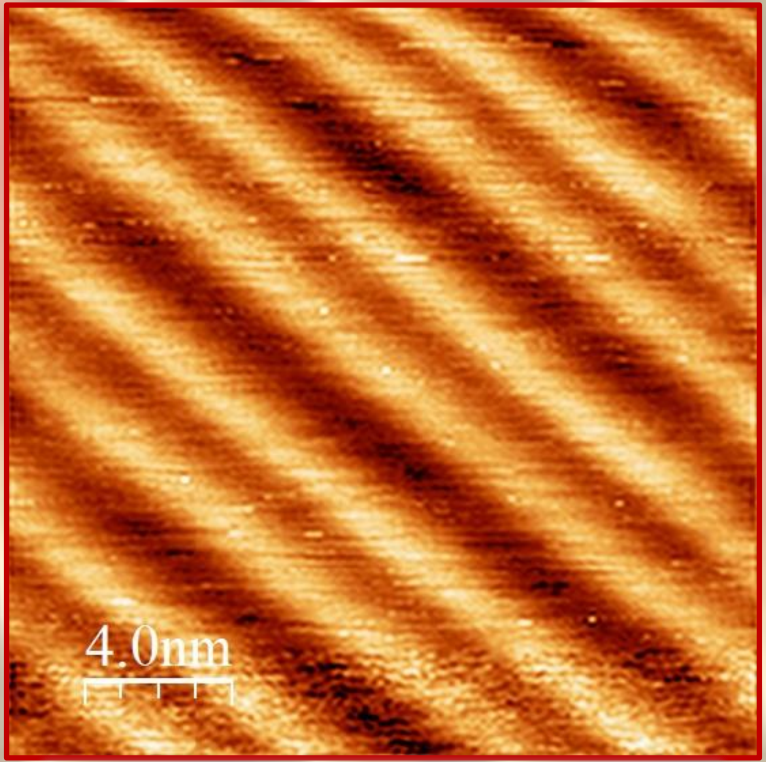
OPEN QUESTIONS

- Hydrogen atoms adsorb on crystalline gold, even in smaller amounts
- The resistance behaviour observed with Au(111) is completely different

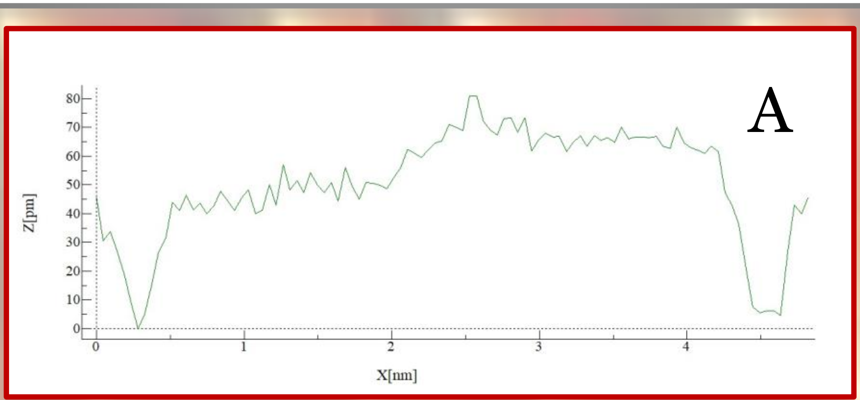
Besides the substrate, the only difference between the two sensors is the crystalline order of the gold layer.

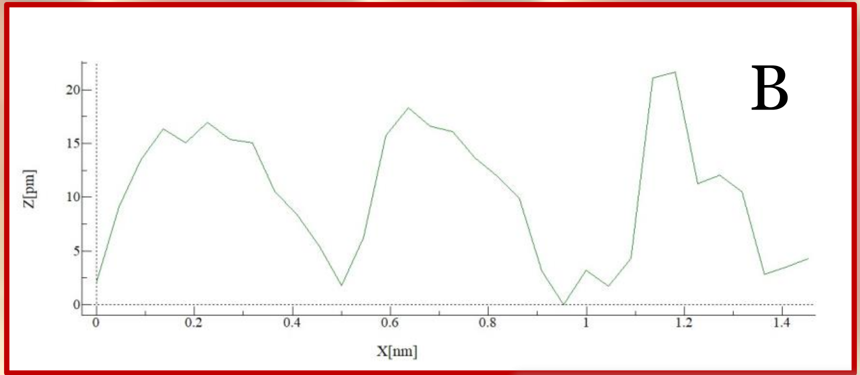
Hydrogen adsorption on Au(111)/mica: STM

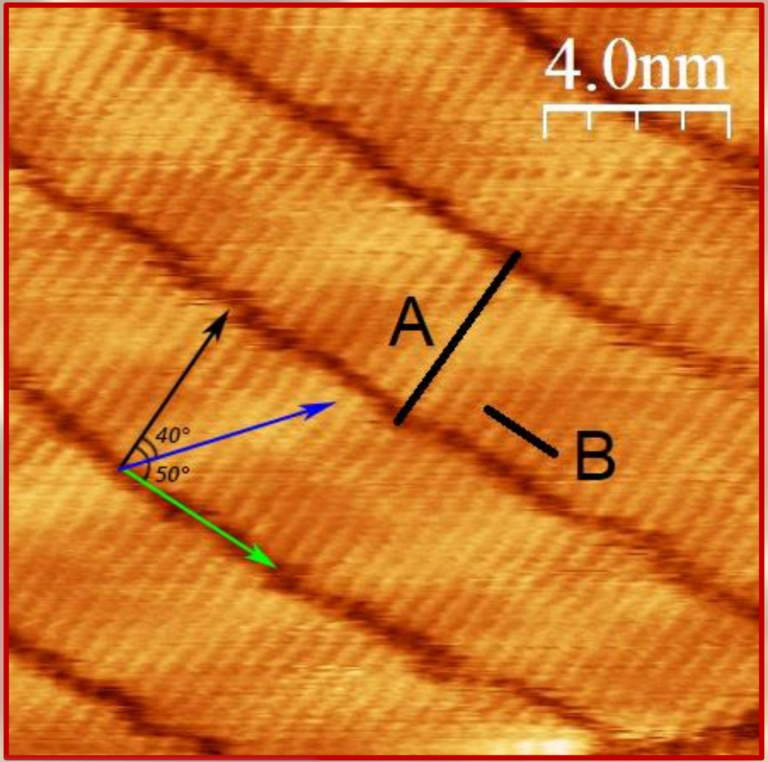
Atomic hydrogen exposure, 5 minutes, 1×10^{-7} mbar



Before hydrogenation







After hydrogenation

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 allowed to discover that atomic hydrogen behaves differently with amorphous and crystalline gold

Outlook

- The STM measurements have demonstrated that the gold film thermometers are stable up to 200 °C.
  A possible solution could be an additional Ti layer underneath gold.
- The hydrogen supply experiment could be repeated with further STM and LEED analysis.
- The atomically flat thermometer would allow a detailed study of 2D materials.
- Mica properties make this sensors suitable to have a remarkable impact on flexible electronics.

Thank you for your attention!