



# ***Materiale nanostructurate: aplicatii practice in nanomedicina si bio-senzoristica***

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21-24/09/2010



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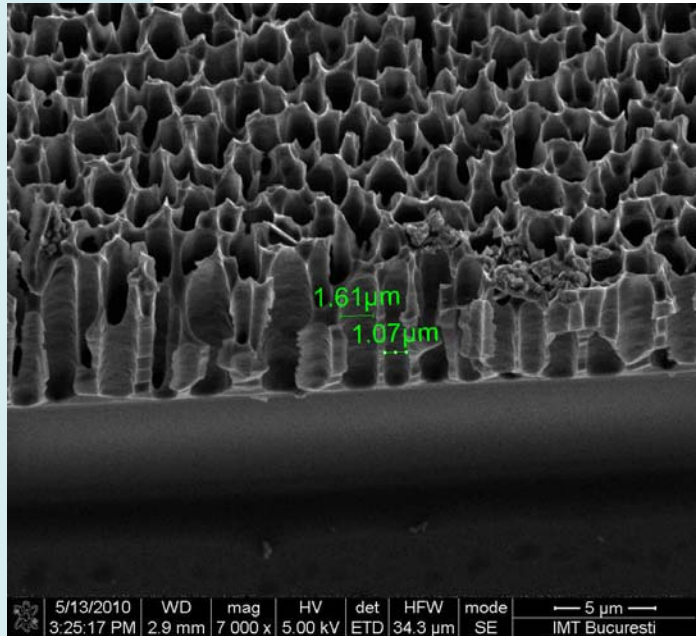
- Si – porous Si
- Au – Au (111)
- Graphene – metallic nanoparticles decorated
- Applications



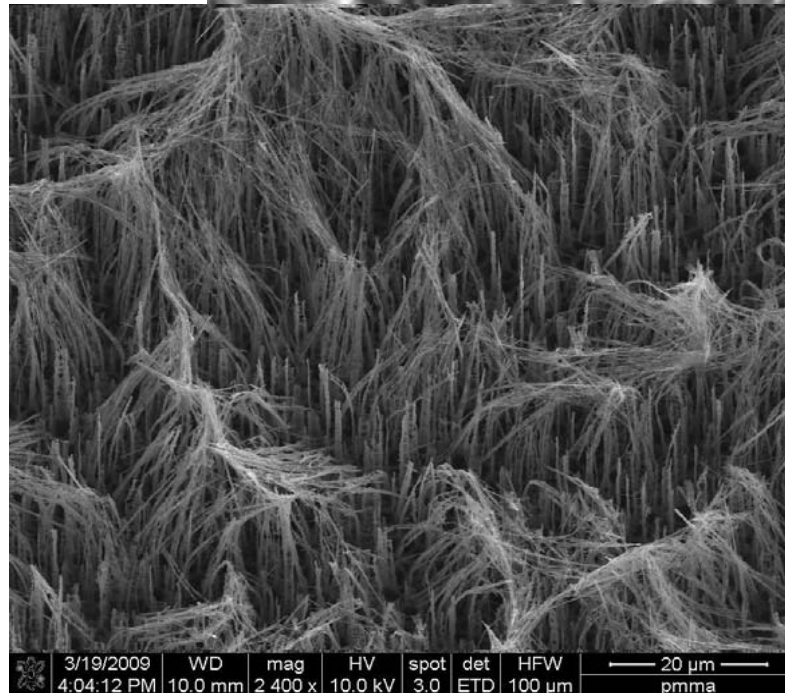
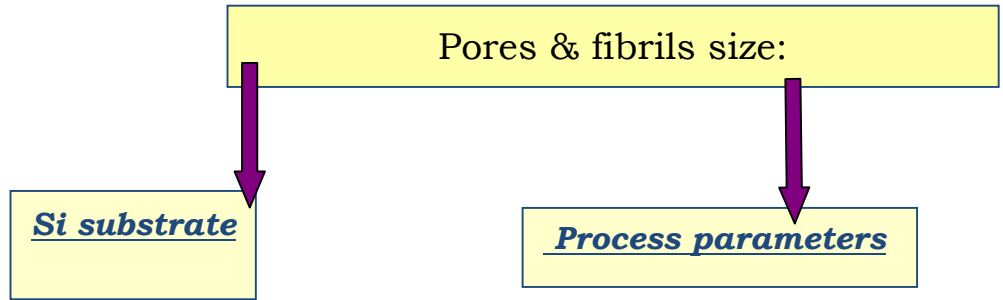
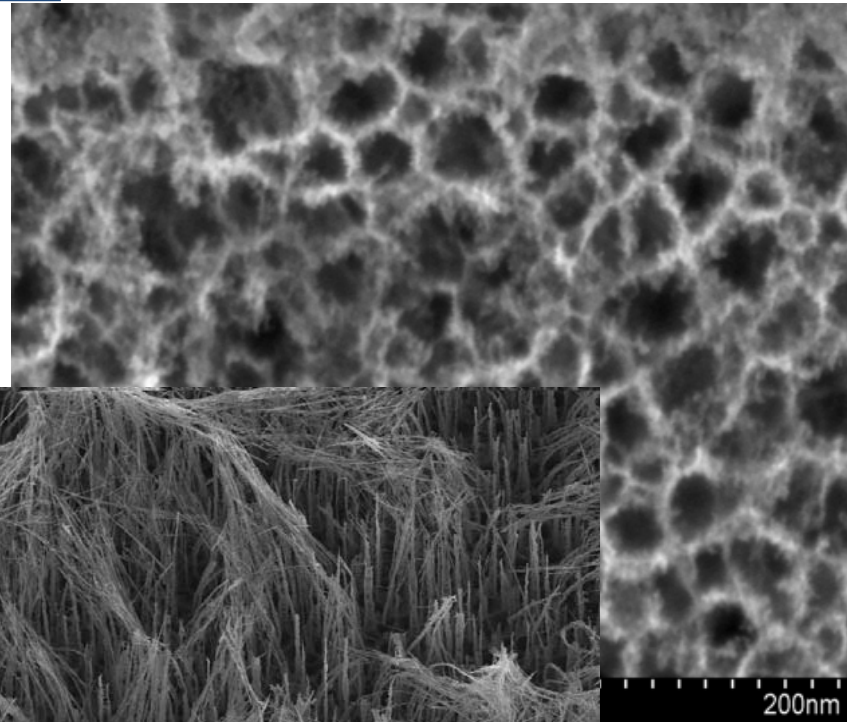
Si

# SEM - PS morphology

macro-PS (1- 2  $\mu\text{m}$ )

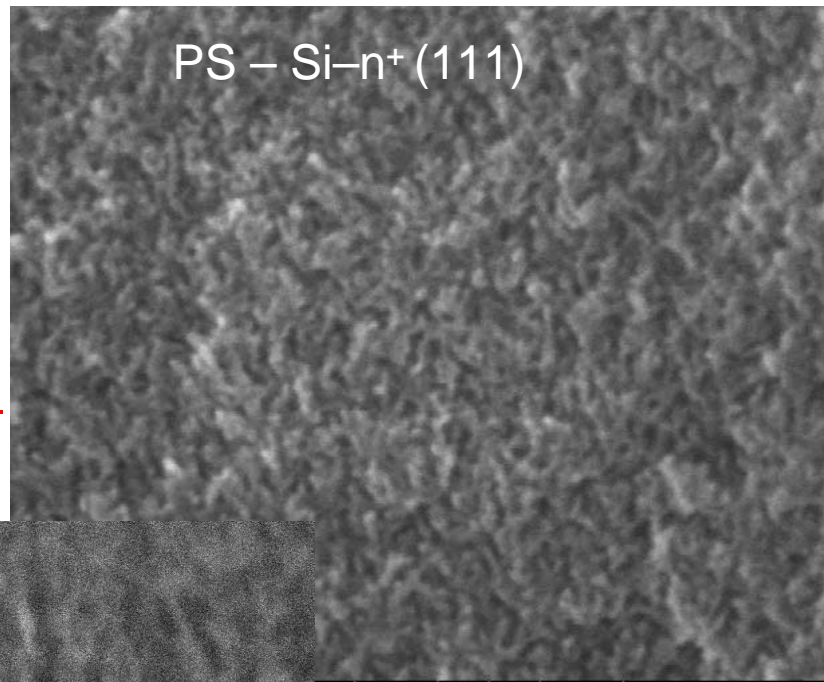
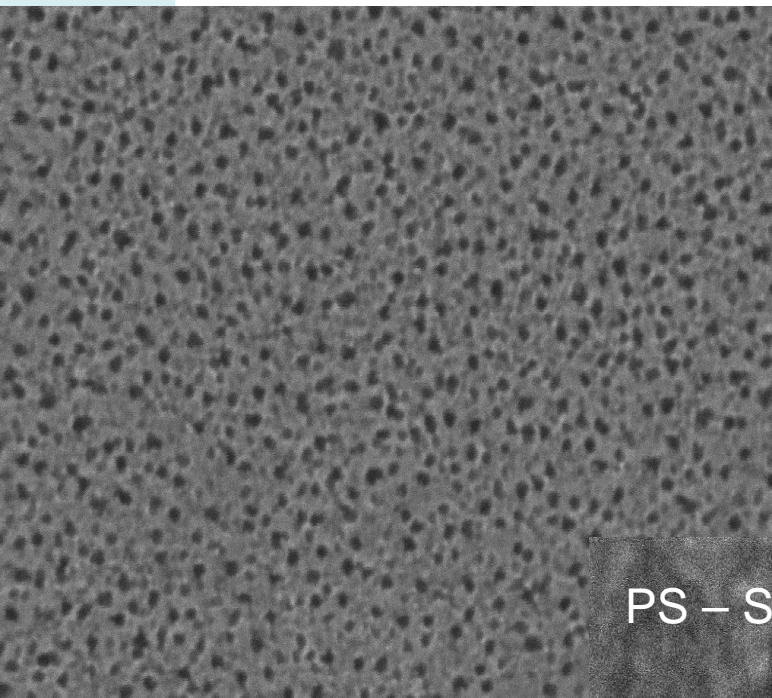


meso-PS  
(50 - 100 nm)

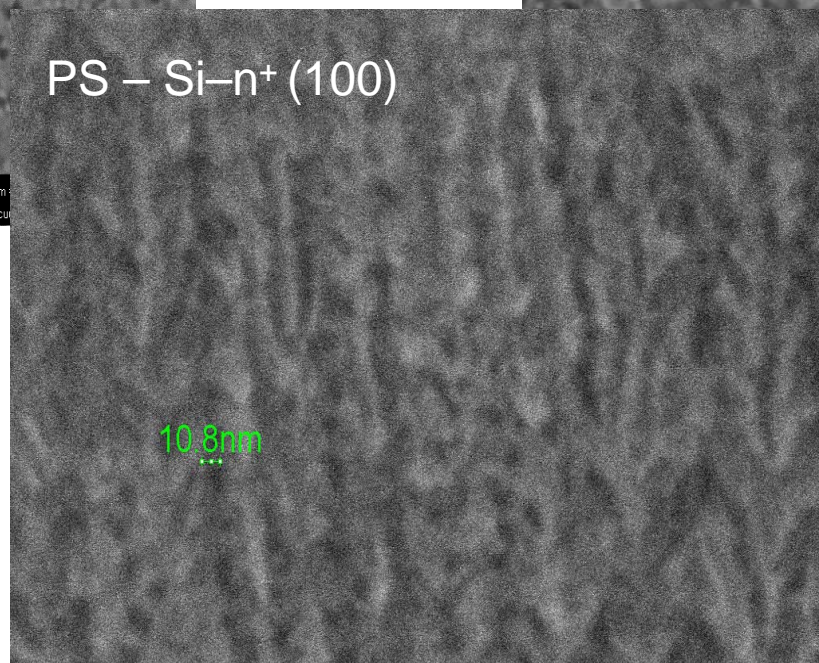




# SEM - PS morphology



**nano-PS**  
**(< 15 nm)**



SUPRA 35-29-87    Mag = 143.66 KX    EHT = 10.00 kV    Signal A = InLens    Gun Vacuum    100 x  
Ext. Scan Control = Off    20 nm    WD = 6.8 mm    Aperture Size = 30.00 µm    System Vacuum

100 x    HV 10.3 kV    spot 3.0    det TLD    HFW 480 nm    — 100 nm —

Si

3/19/2009    WD 5.6 mm    mag 500 000 x    HV 10.0 kV    spot 3.0    det TLD    HFW 480 nm    — 100 nm —  
3:13:47 PM    si po





**Si substrate**

- type and level of doping;
- crystallographic orientation

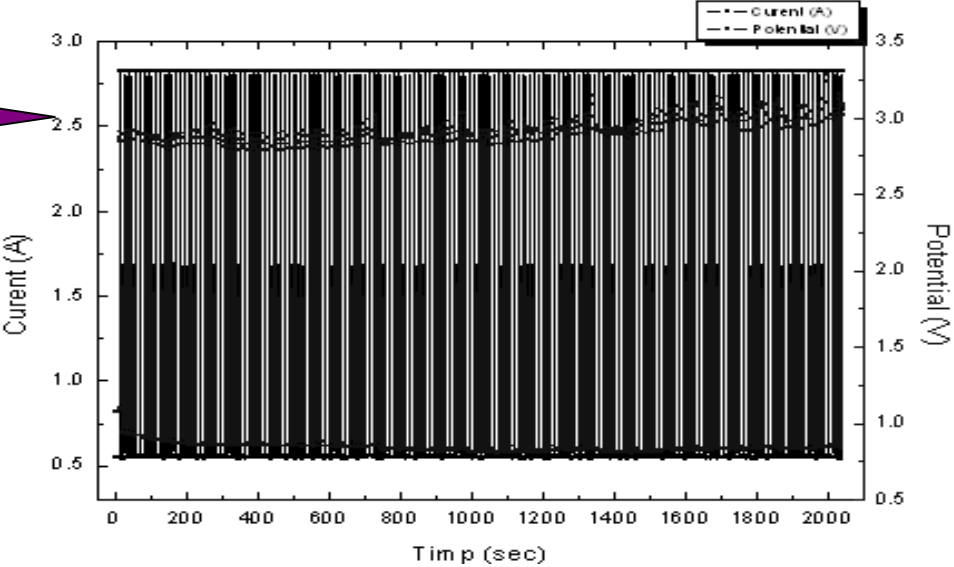
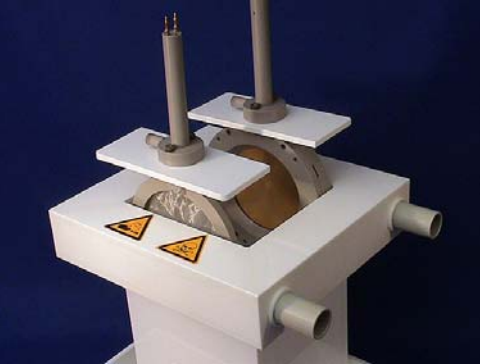
Pores & fibrils size depends on:

**Process parameters**

- electrolyte type / HF concentration;
- current density;
- illumination conditions.

*Porous silicon – PS - is obtained by electrochemical dissolution of silicon in HF*

**PS layers, have been obtained using the A.M.M.T etching system for 4” Si wafers with programmable power supply and dedicated software for time-based current profiles.**

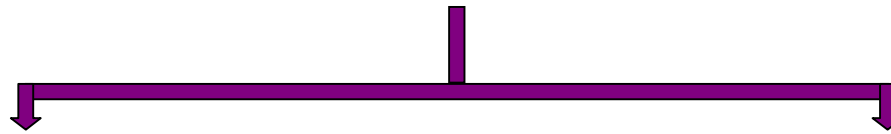


Current-potential-time diagram for 150 cycles (0.554 A, 10 sec, 2.825 A, 4 sec).

Si



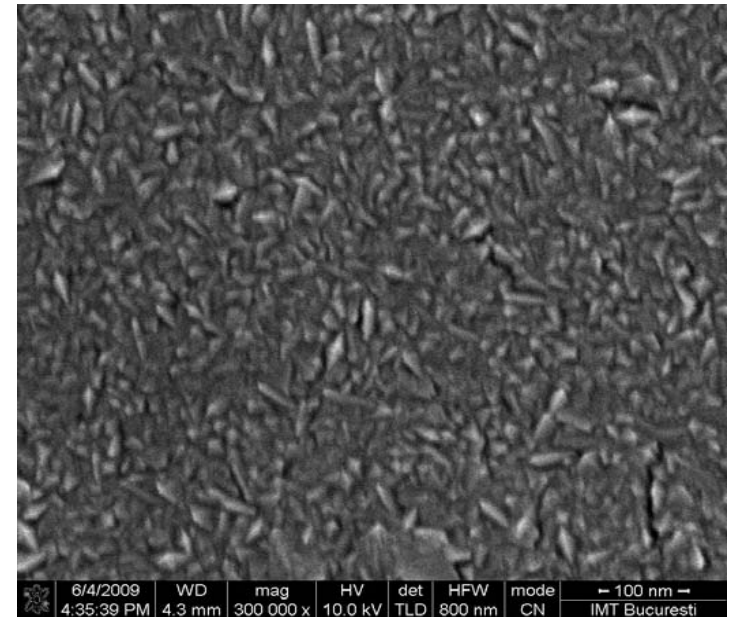
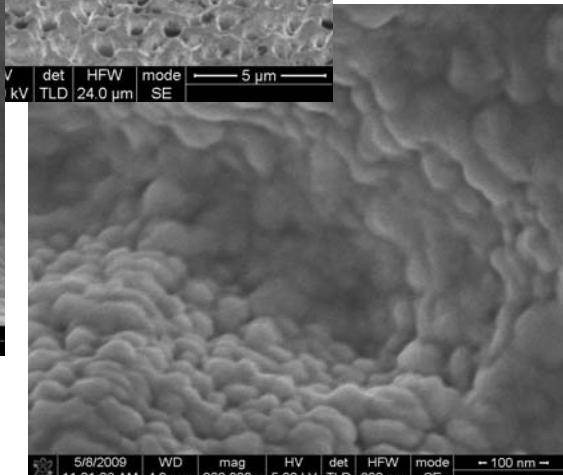
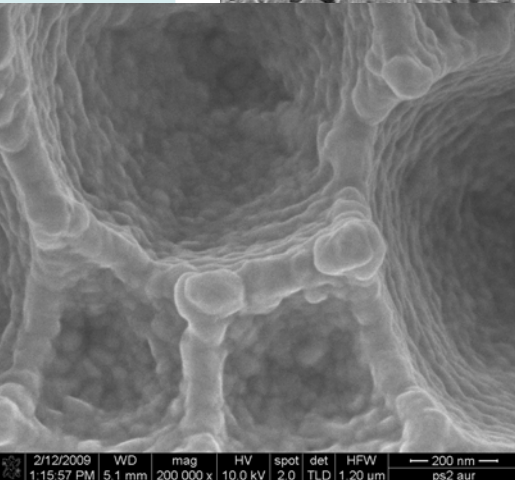
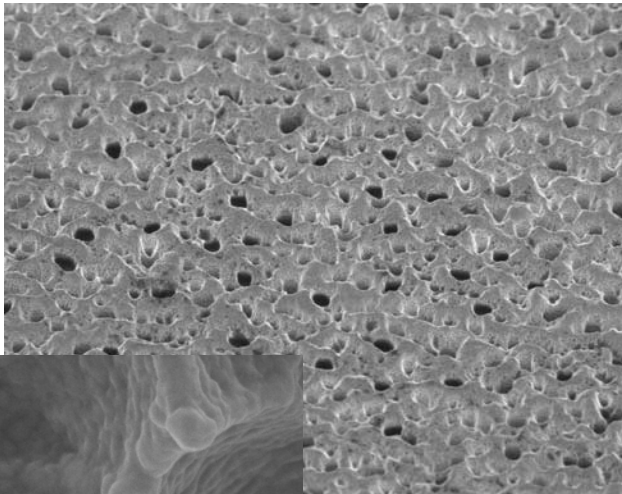
# Nano-structured metallic thin films (NP-PVD) on PS substrate



***Au thin films*** - 100 nm – cathodic sputtering system

***Pt thin films*** - 100 nm  
e-beam deposition system

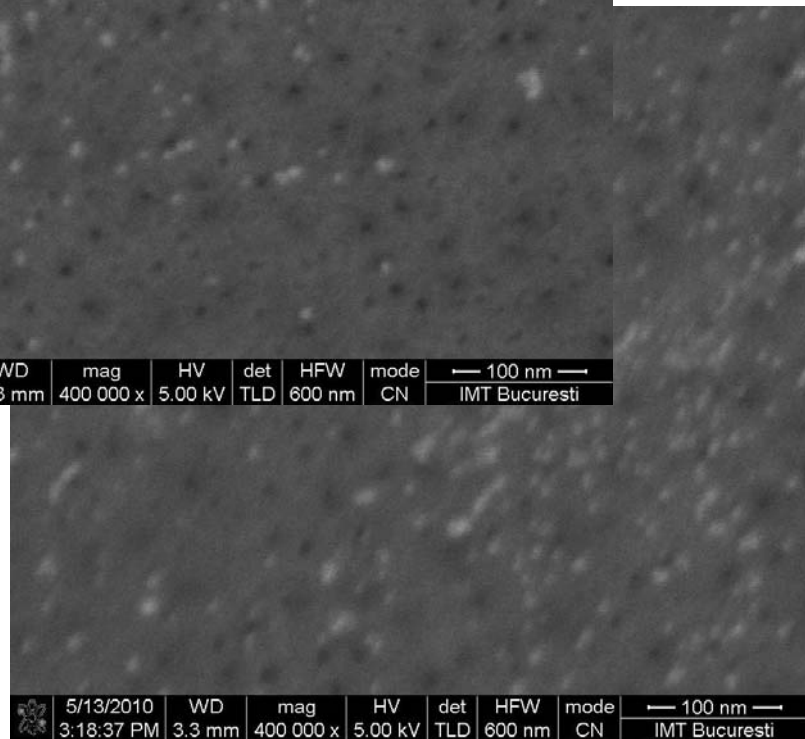
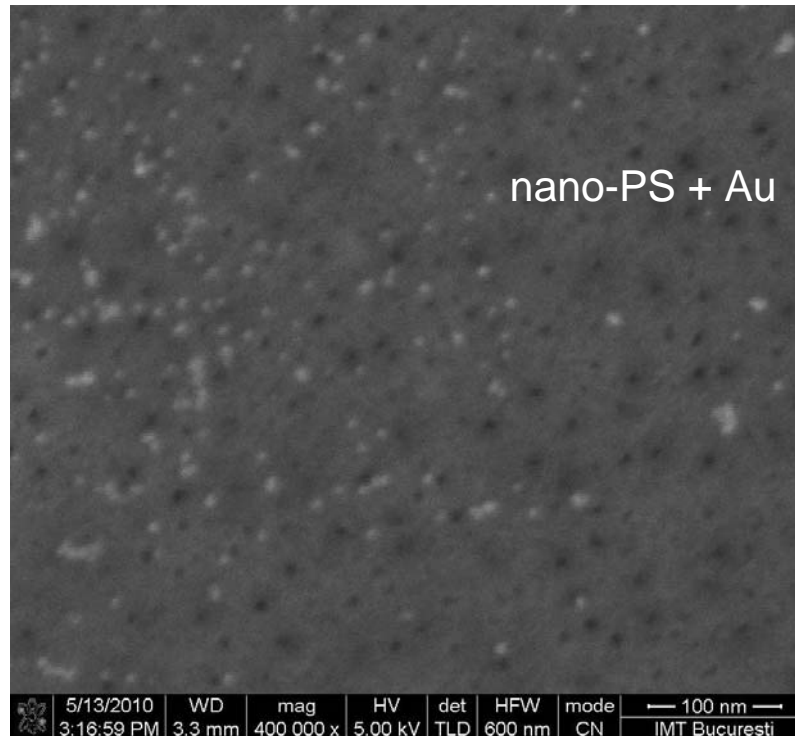
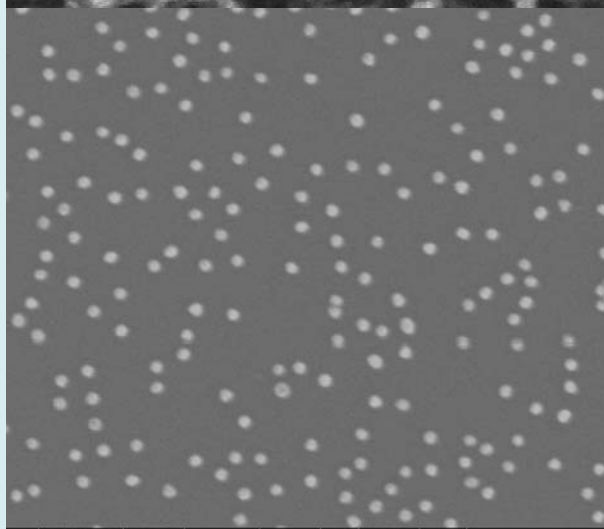
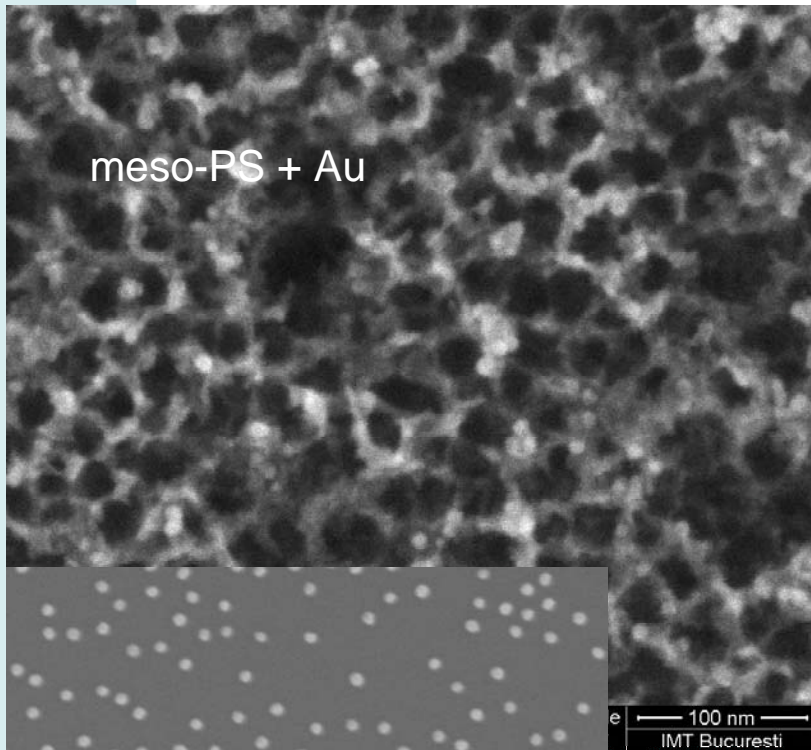
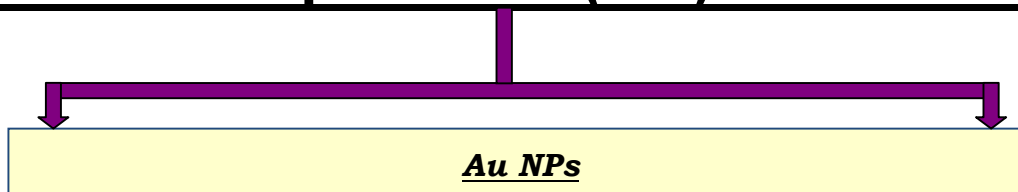
Si





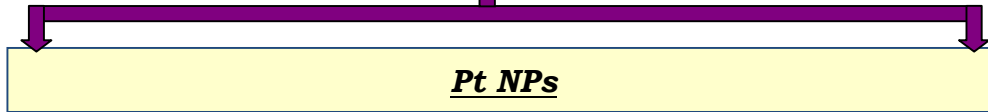
Si

# Metallic nanoparticles (NP) on PS substrate



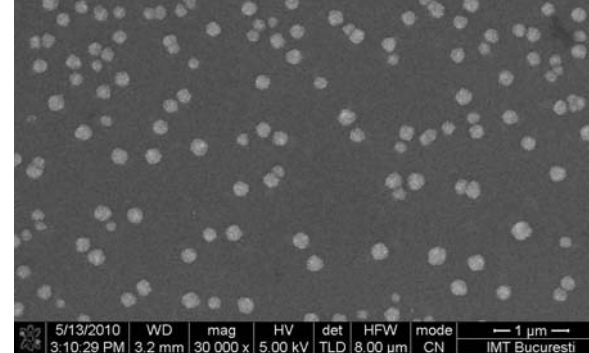
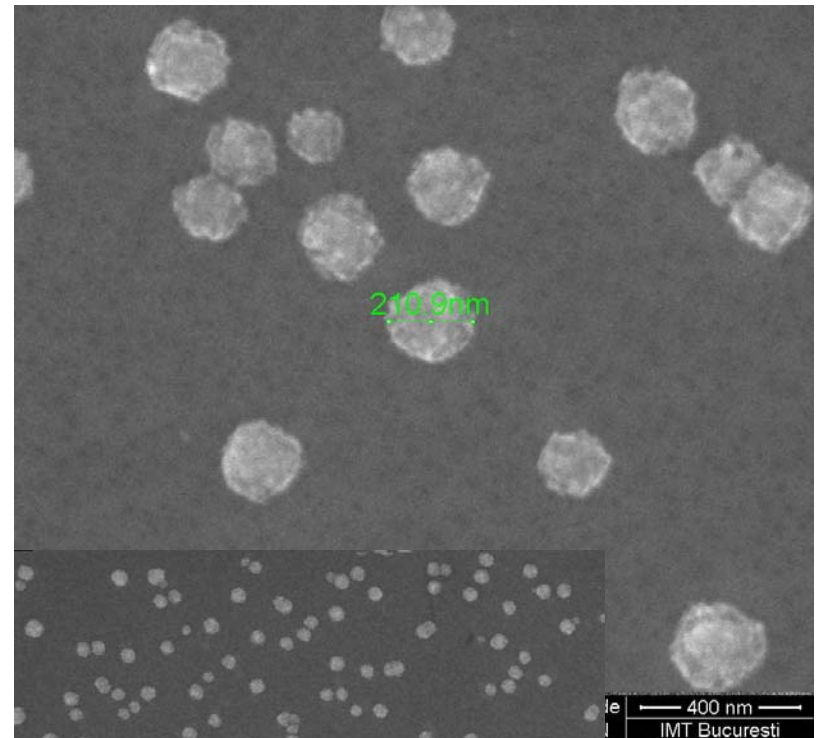
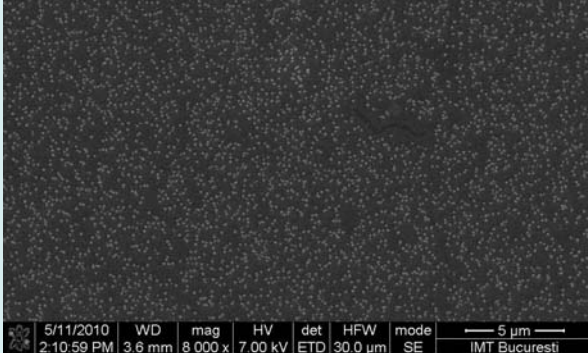
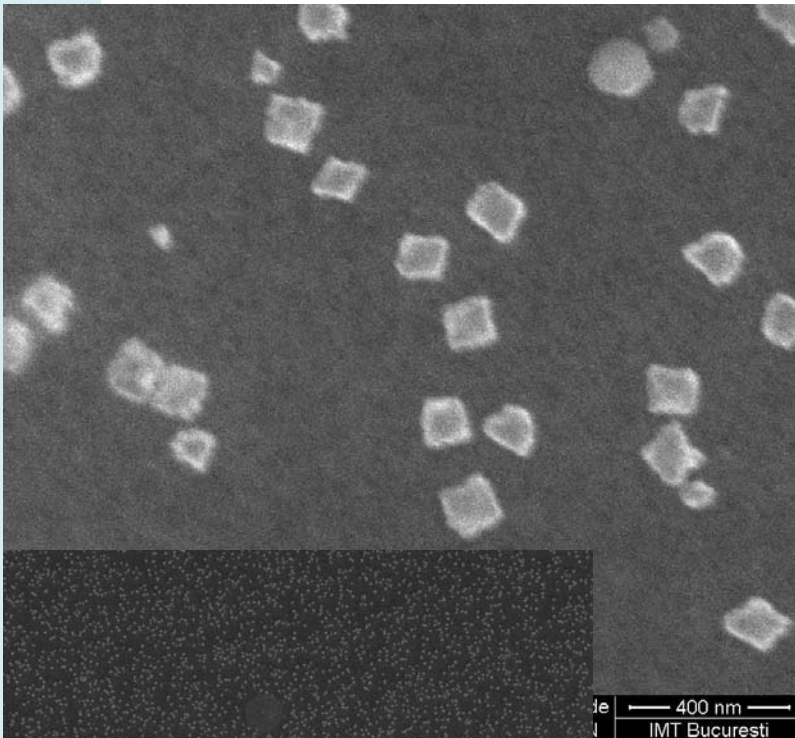


# Metallic nanoparticles (NP) on PS substrate



**nano-PS + Pt**

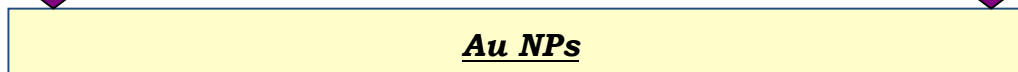
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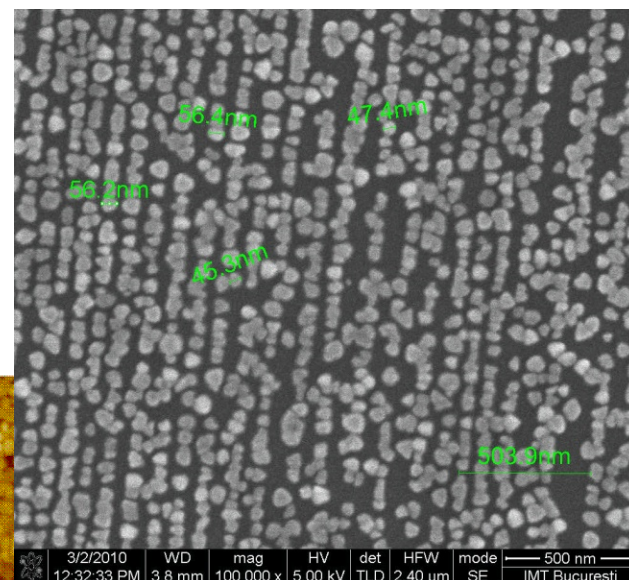


# Electrochemically deposited Au (NP) on Si substrate

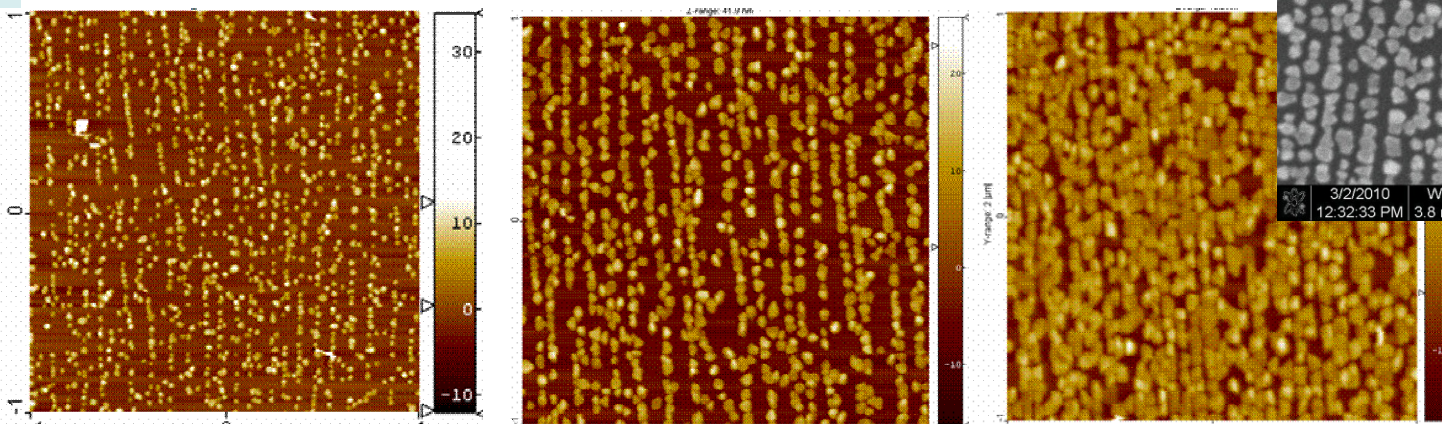
Si



Substrate preparation:  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 1:3$  v/v;  
Si(111)-H;  $(\text{NH}_4\text{F } 40\%)$ ;  $(\text{NH}_4)_2\text{SO}_3$ ; 15 min.  
Electrochemical deposition of gold nanoislands  
(0.1mM  $\text{KAu}(\text{CN})_2$ , 0.2mM NaCN, 2M NaOH,  
pH=14).



AFM images of gold-nano-islands on n-type silicon (111) substrates



**(a) 4s -2V and  
10s -1,5V**

I=10 nm  
D= 50 nm

**(b) 4s -2V and  
30s -1,5V**

I=50 nm  
D= 70 nm

**(c) 4s -2V and  
100s -1,5V**

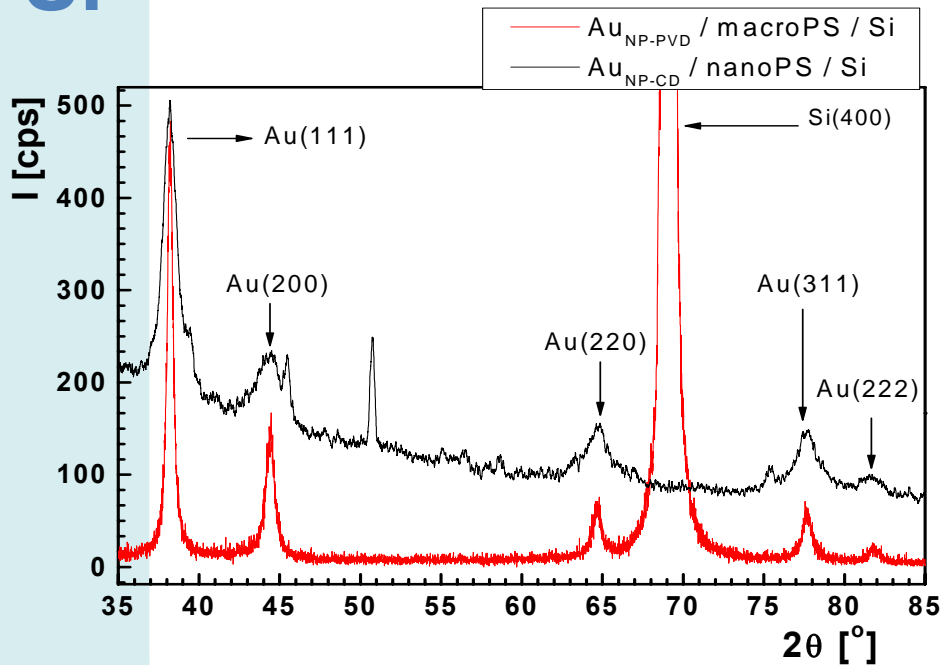
I=80 nm  
D= 100 nm

Au nano-islands are prepared by electrochemical deposition on silicon.

# X-ray diffraction

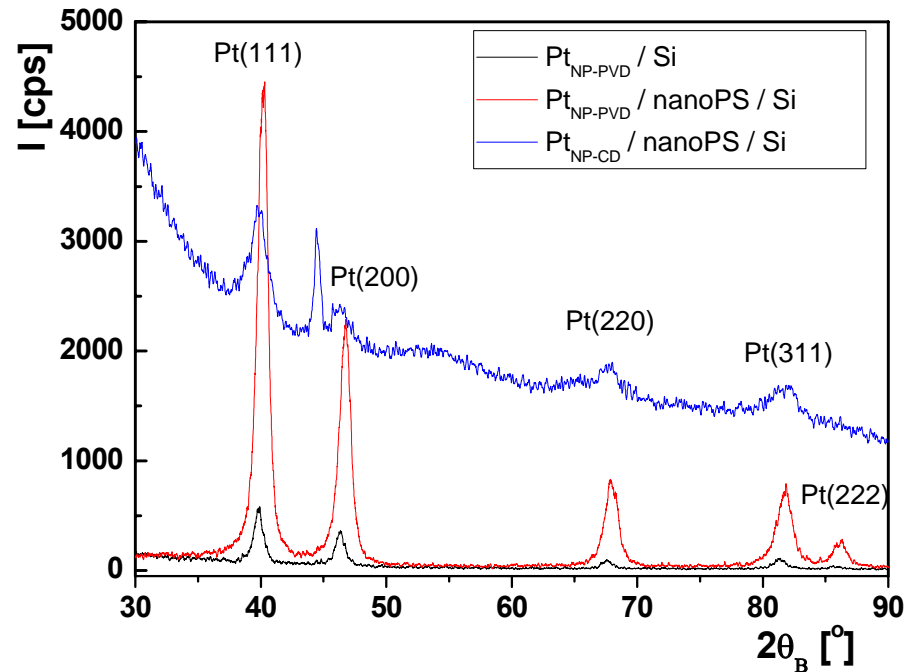
The microstructural characterisation of AuNP-PVD on macroPS and AuNP-CD on nanoPS.

Si



-XRD reveals the high intensity ratios between (111) diffraction pattern and the peaks assigned to (200), (220), (311), (222), and (400) reflections of fcc structure of gold, indicating that the faces of these nanoparticles were primarily composed of (111) planes.

GIXRD X-ray diffraction spectra ( $\omega = 0.35^\circ$ ) of samples as function of both deposition method and substrate nature



-  $Pt_{NP-PVD} / Si$  : no preferential texture;  
-  $Pt_{NP-PVD/CD} / PS / Si$  : indicates a better defined degree of crystallization with no preferential orientation.



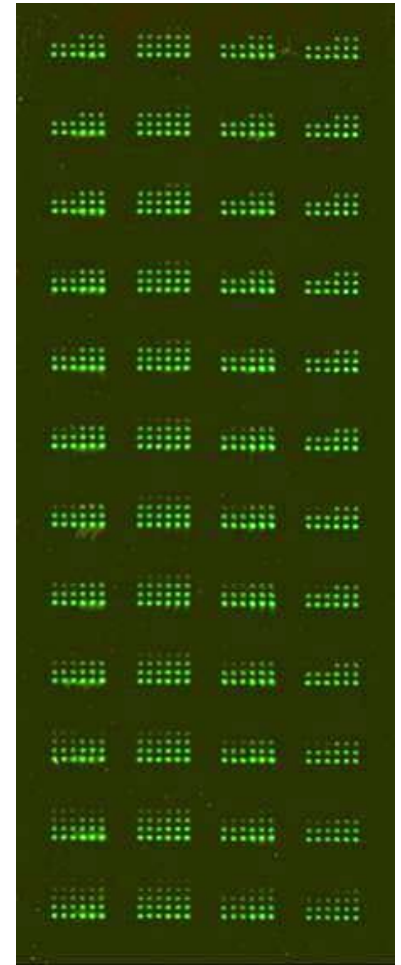
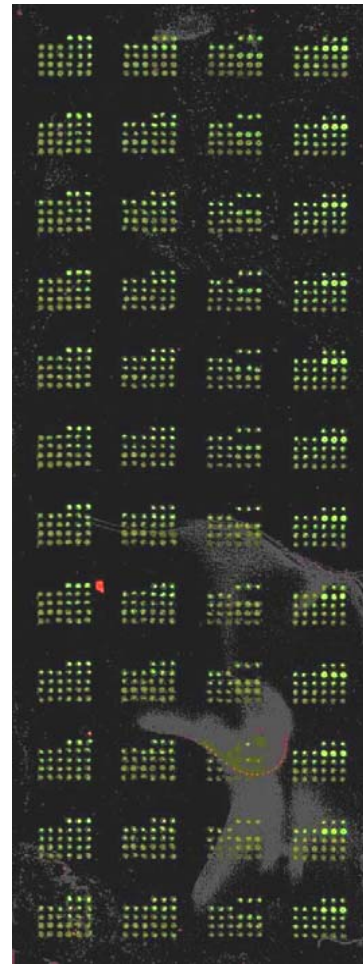
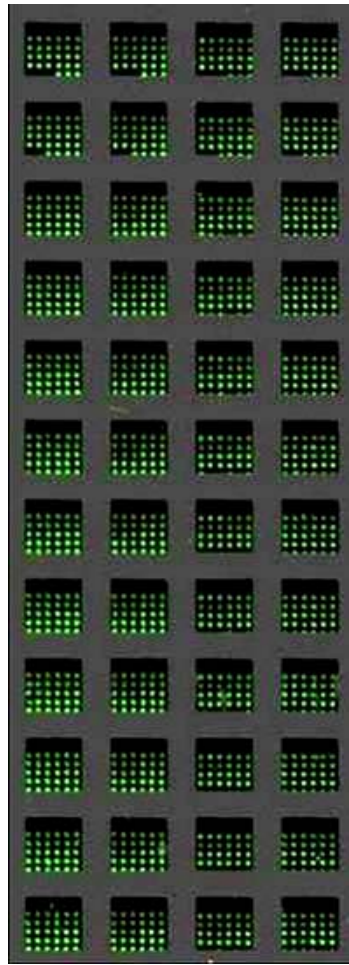
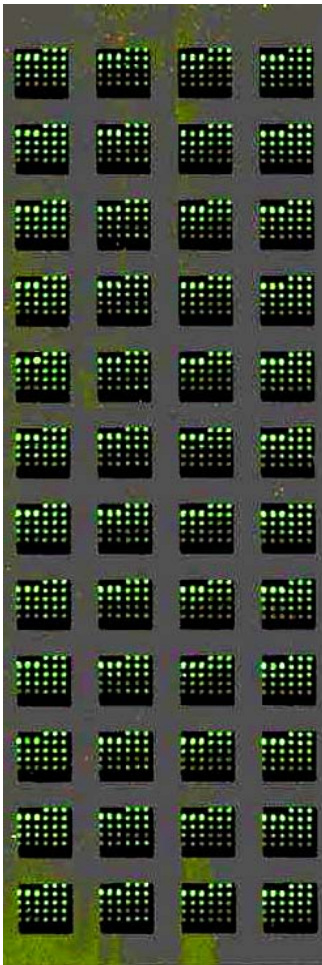
# Practical applications

## Microarray technology

Si

ALD -slides

p-L-lysine slides



GLASS

PS

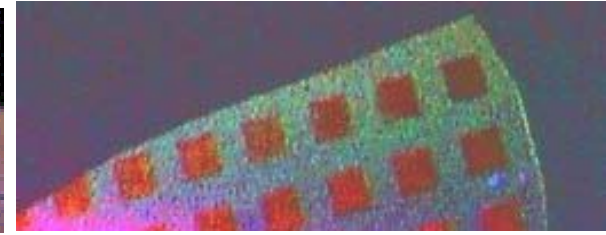
PS

GLASS

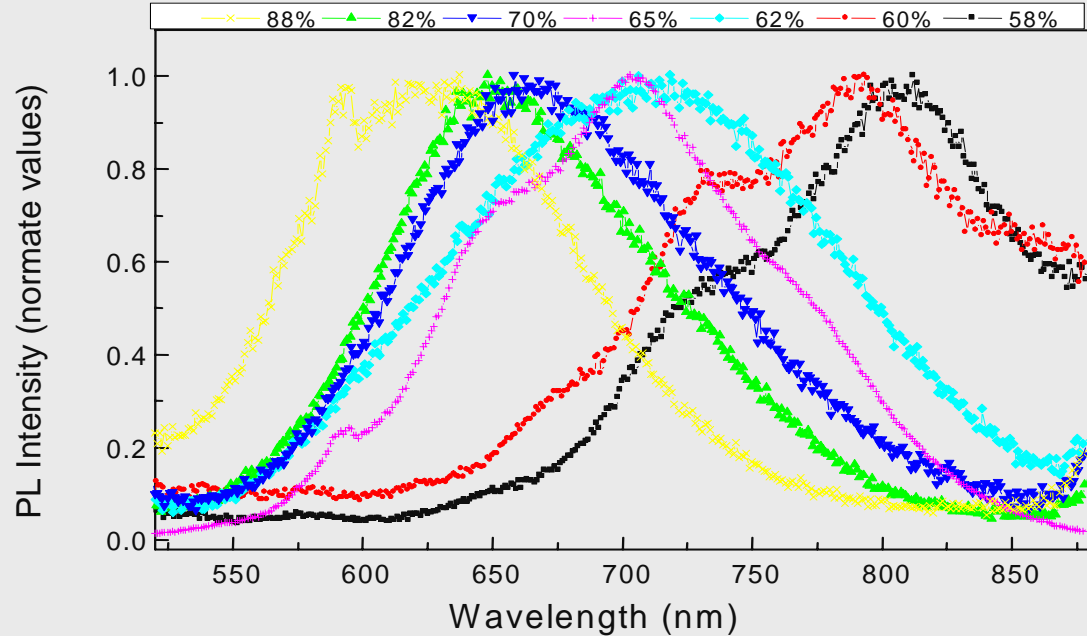


# Photoluminescence

The orange - red photoluminescence of nanoPS is clearly visible when the wafer illuminated by UV light.



No.	Concentration HF (%)	Current density (mA/cm <sup>2</sup> )	Time (min)	Porosity (%)
1	25	15	6	58
2	25	20	6	60
3	25	25	6	62
4	18	15	6	65
5	18	20	6	70
6	15	15	6	80
7	15	25	6	88



Photoluminescence spectra of PS / Si-p samples with different porosities (58% - 88%)

Si

- the PL peaks for high porosity PS samples are centred around 650-720 nm, in visible range due to quantum confinement and surface states effects;
- a shift of the PL peak position towards high photon energies with the increase of the PS porosity is observed;

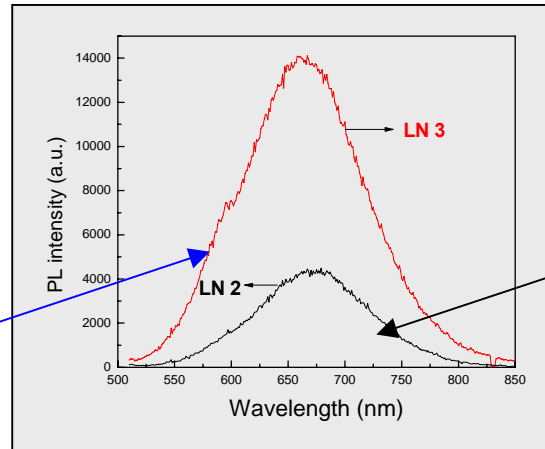
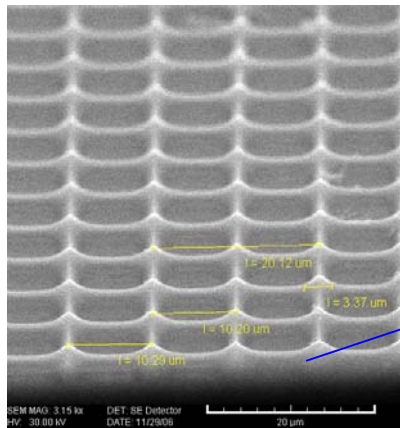
The PL emission from PS is observable at wavelengths ranging from the UV to the IR, the normalized spectra recorded for different experimental samples demonstrate the dependence on porosity.

# Si microstructuration and porosification

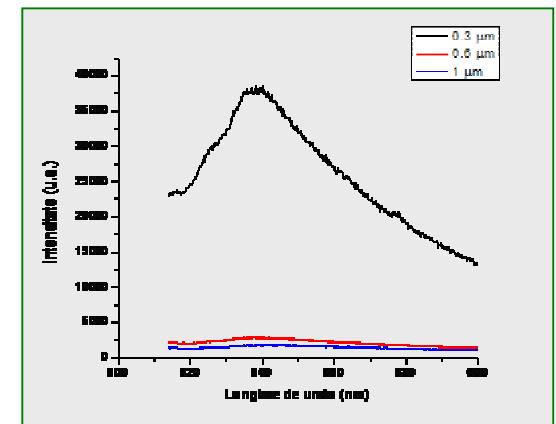
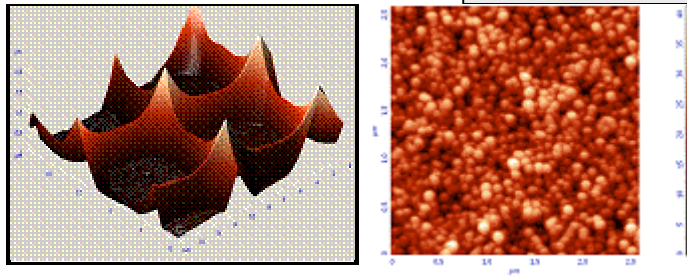
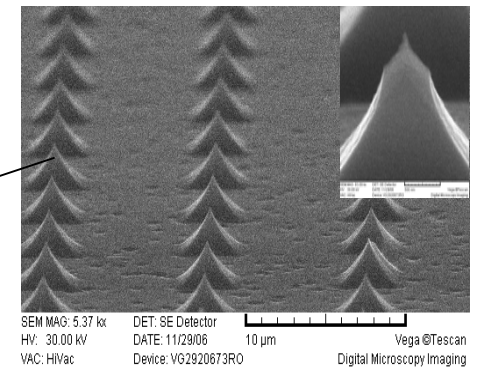
Si

Silicon substrate was micropatterned prior porosification process as:  
an **array of pyramids** (right) or as **semi-circular cavities** (left);

LN3 interconnected lines

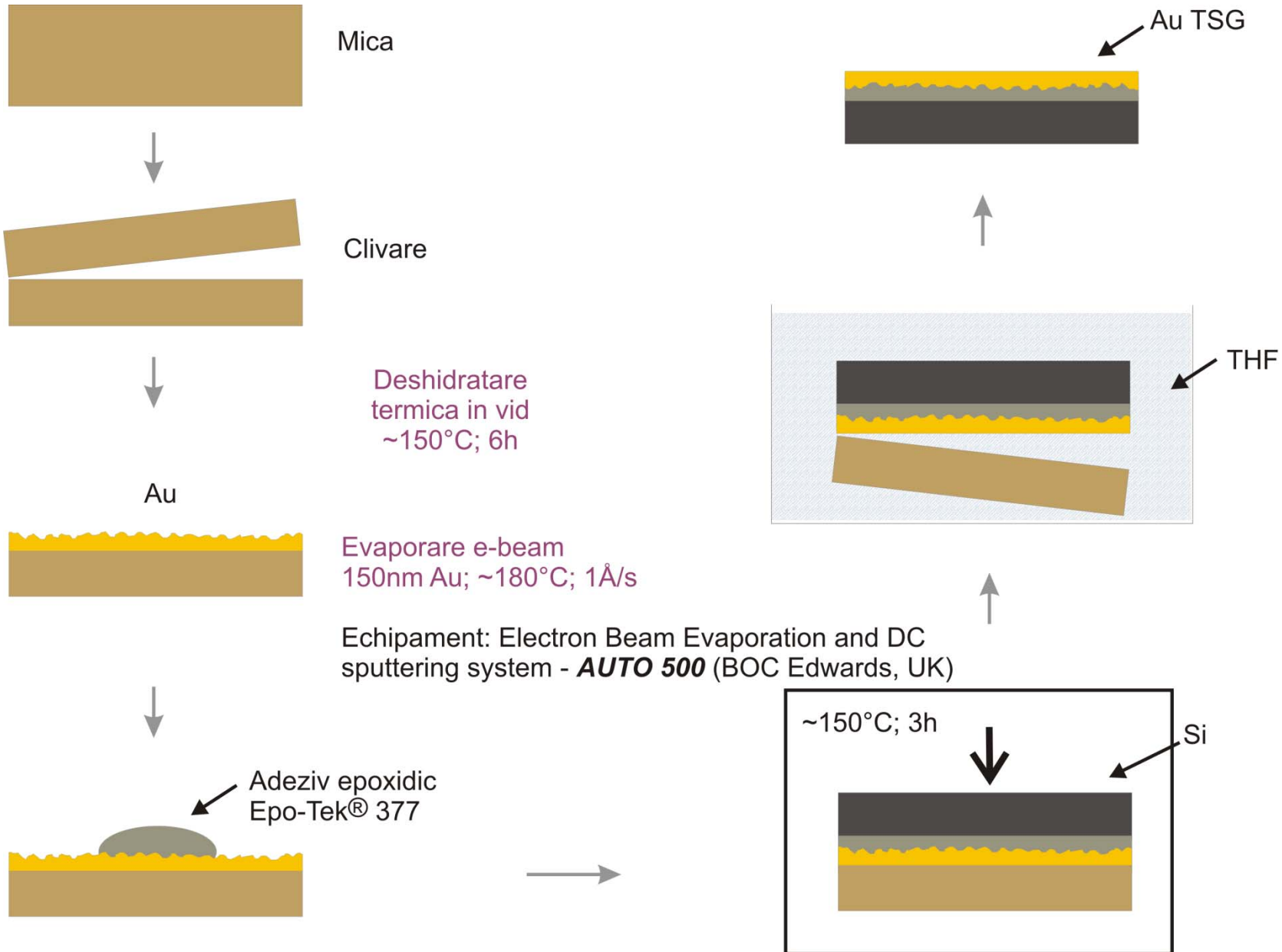


LN2 pyramidal structures



- **similar recording conditions were** (488 nm frequency of excitation and 87 mW nominal power)
- **the intensity of PL emission is three times larger in the case of semicircular microcavities** leading to an important improvement of detection.

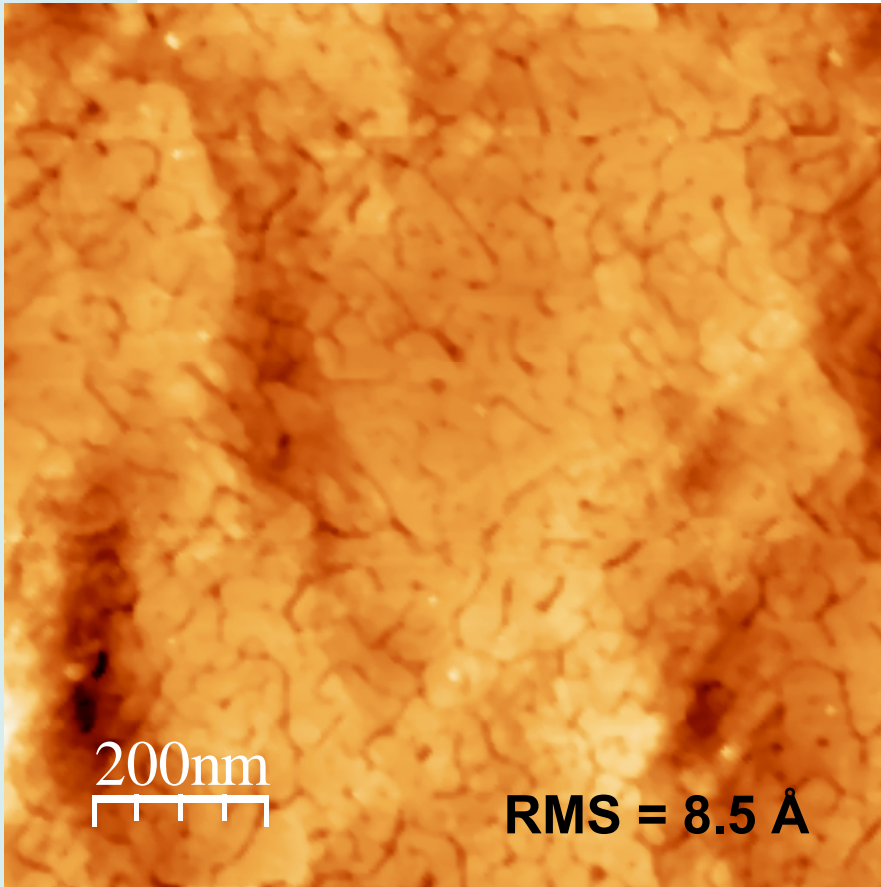
# TSG - "template stripped gold"



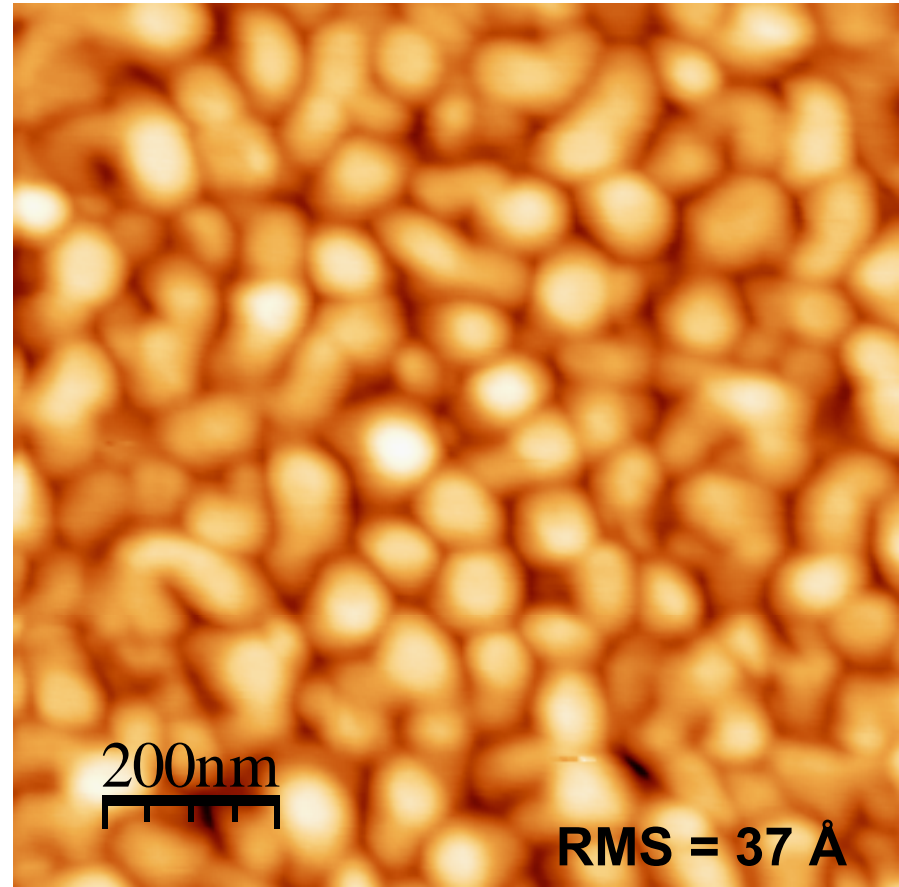




# STM – Scanning Tunneling Microscopy



Au/mica - *TSG*

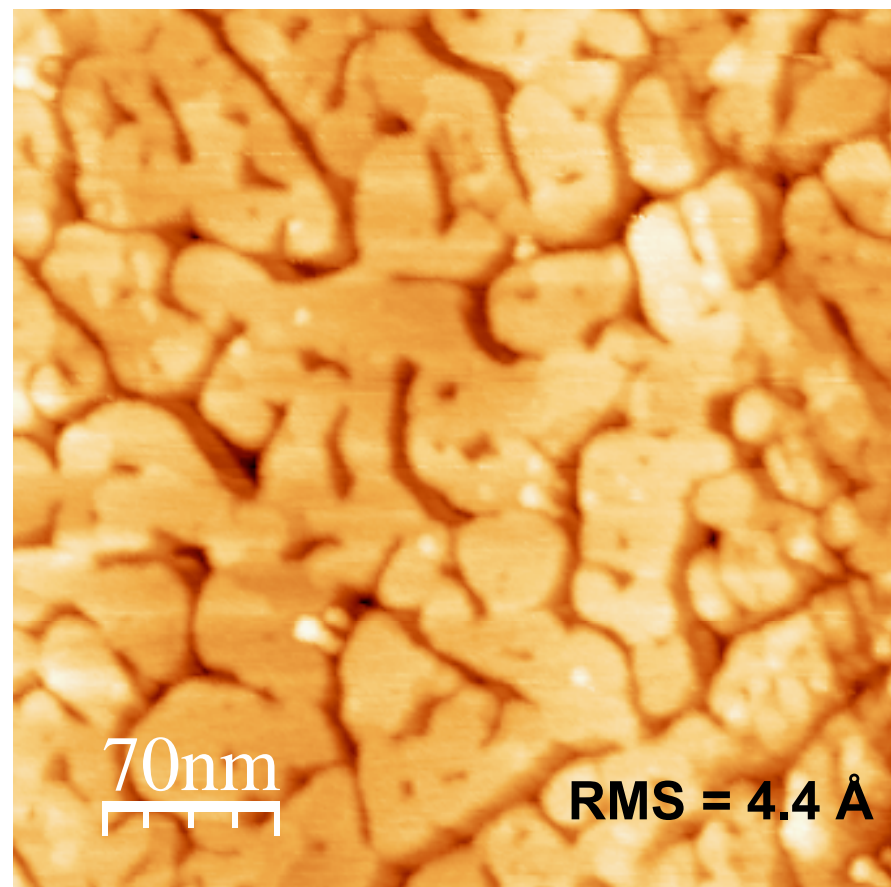
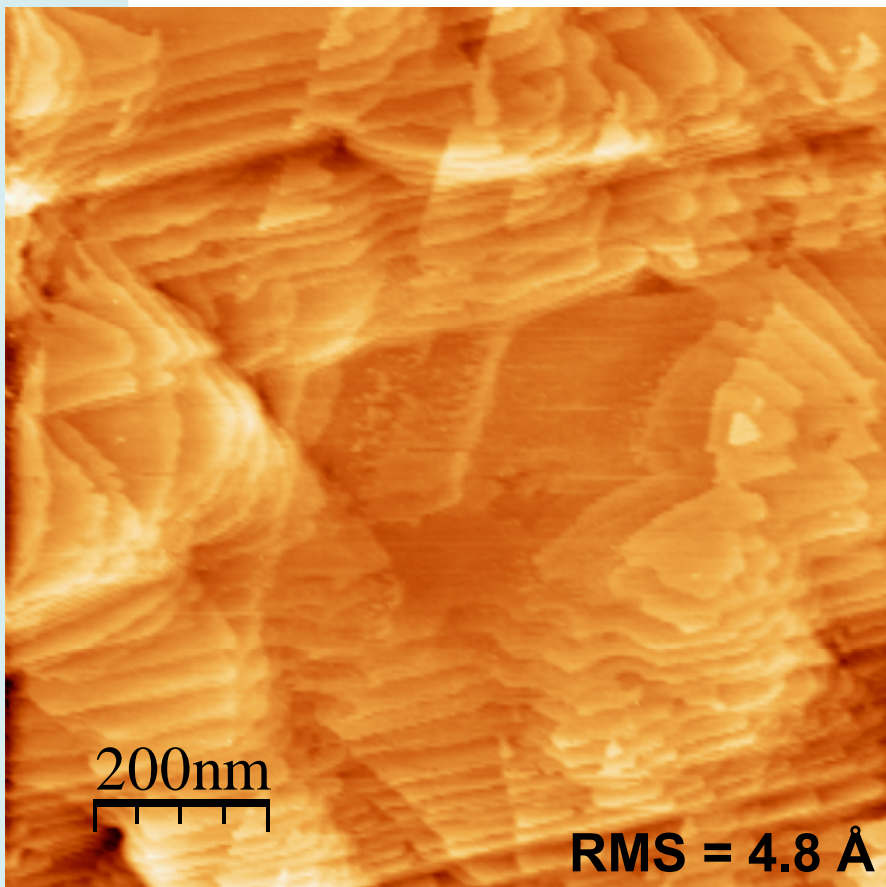
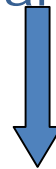


Au/Si

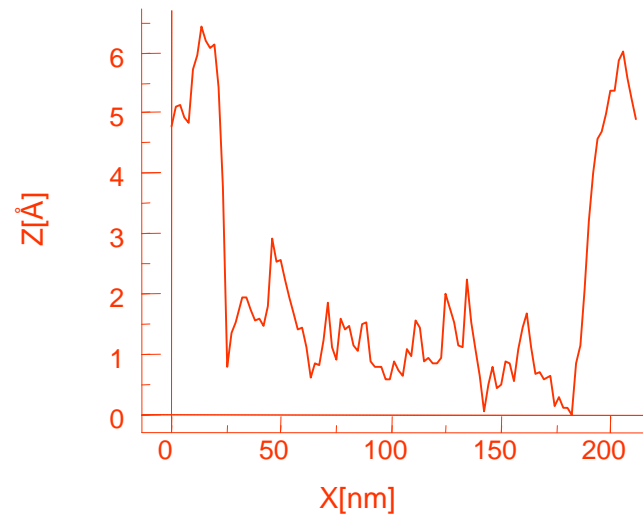
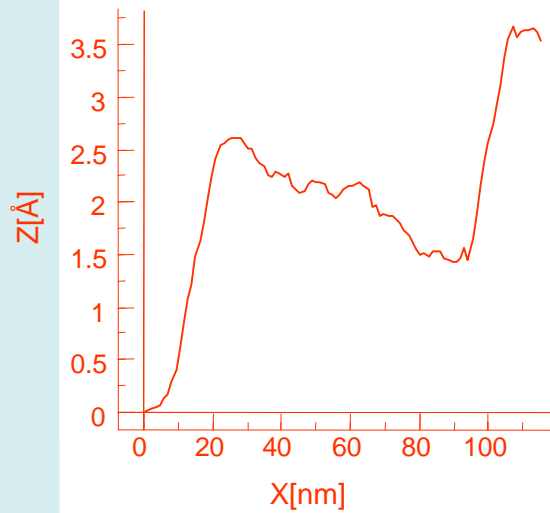
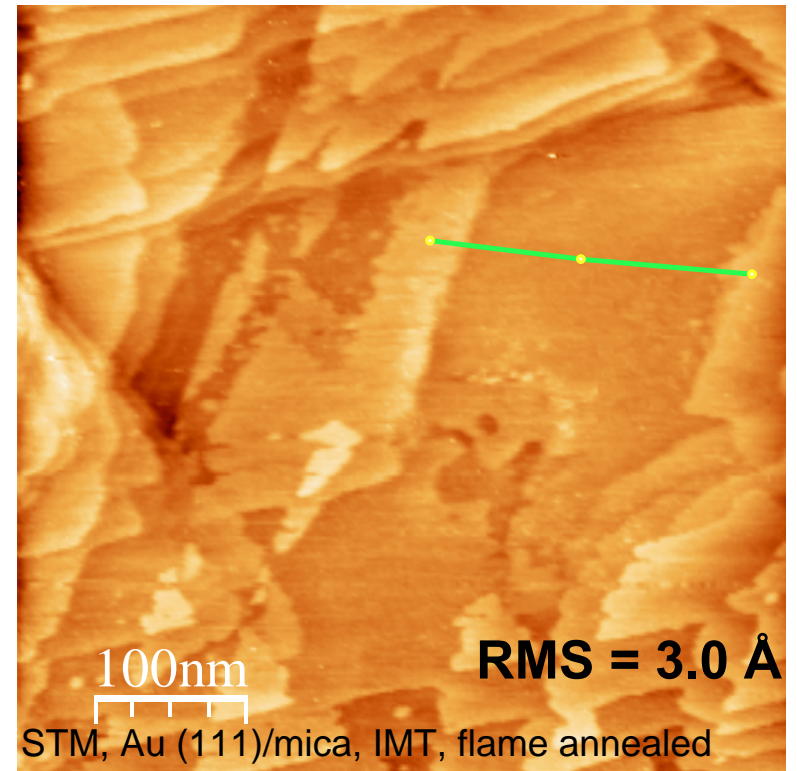
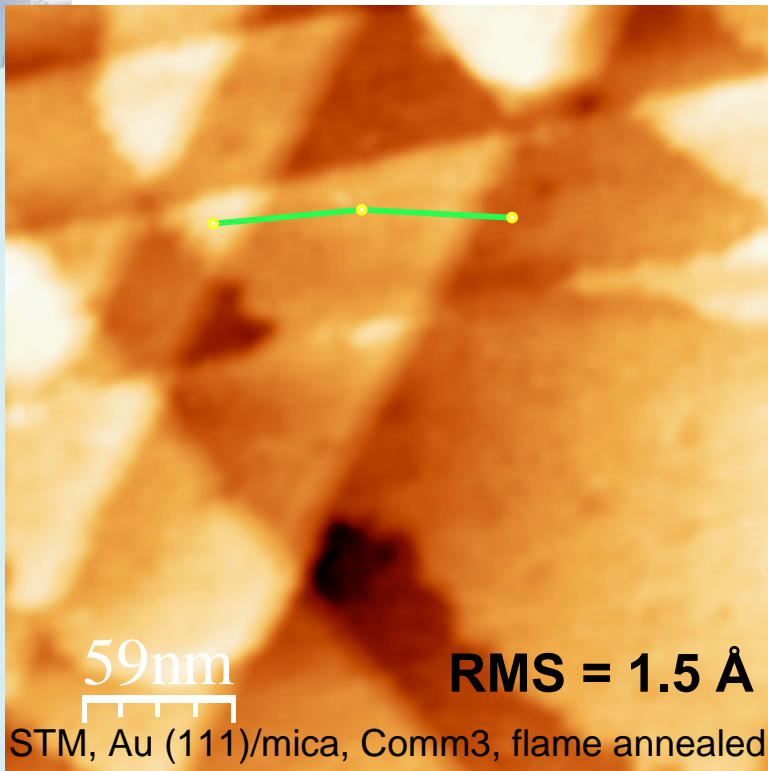


# STM, Au (111)/mica

Flame annealed vs. non-flame annealed



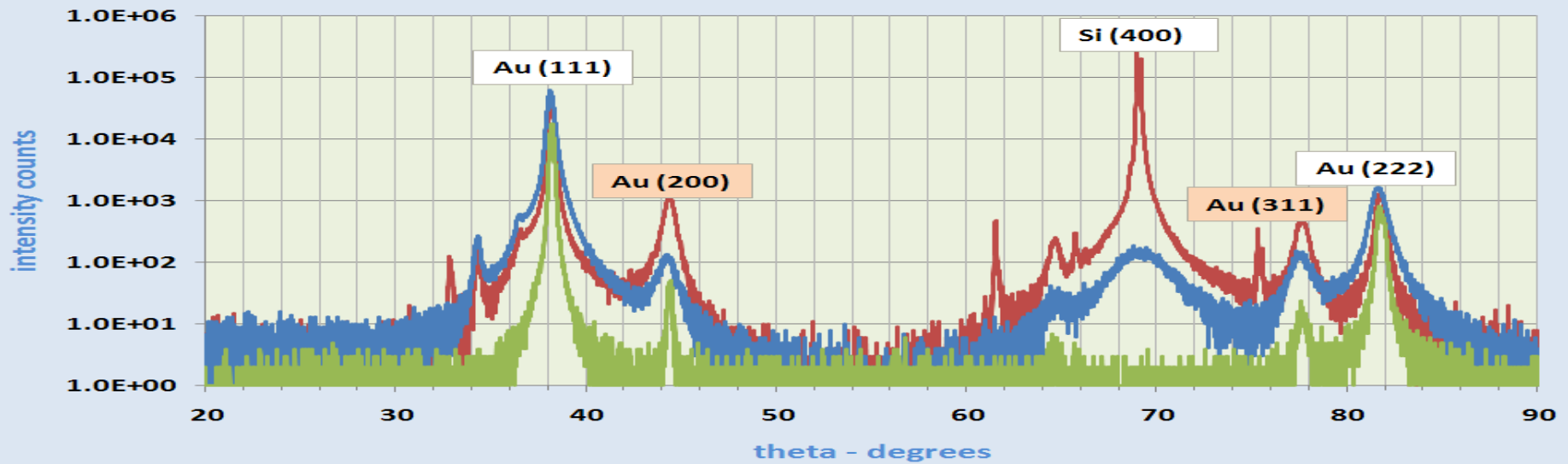
# STM, Au (111)/mica - flame annealed



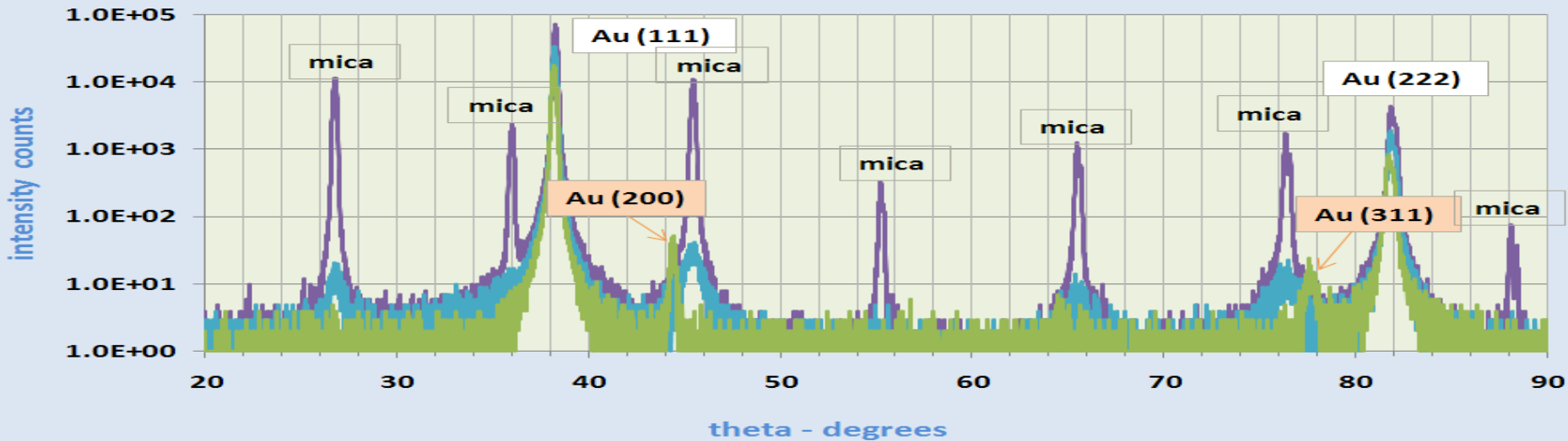




# XRD characterisation



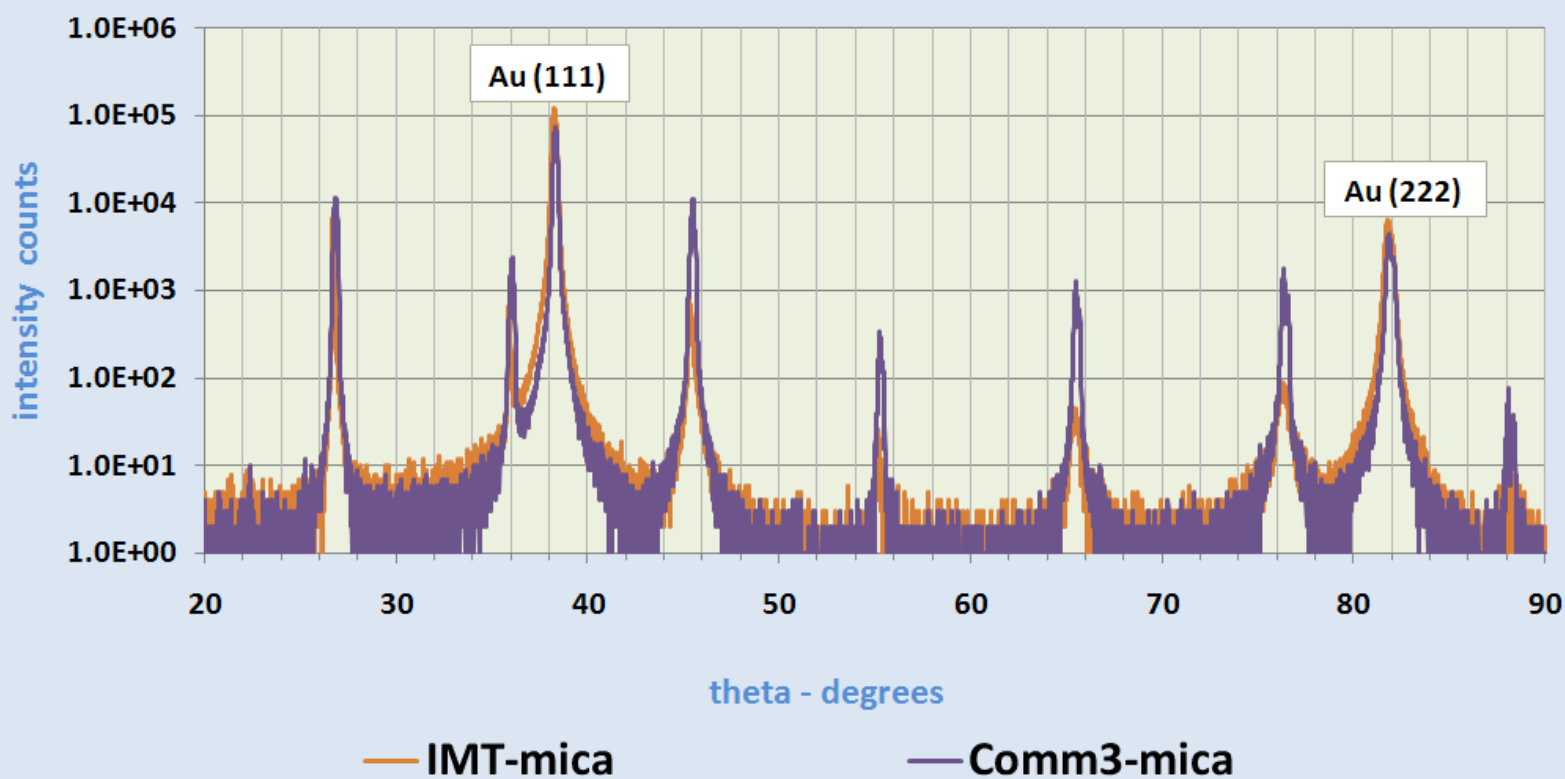
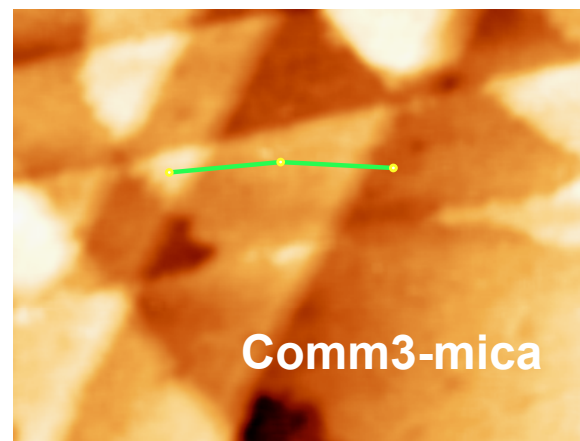
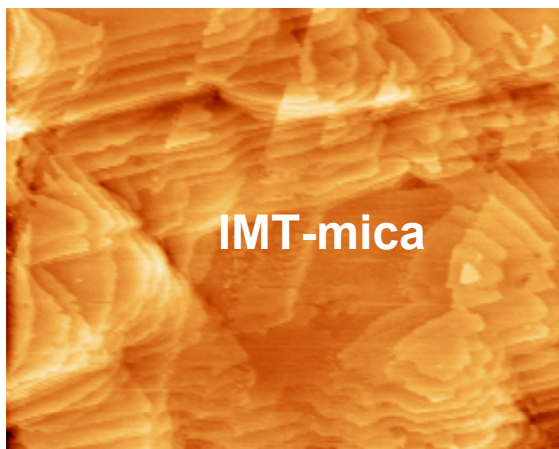
— IMT-Cr/Si      — Comm1-Cr/Si      — Comm2-Cr/boro.glass



— Comm3-mica      — Comm1-mica      — Comm2-Cr/boro.glass

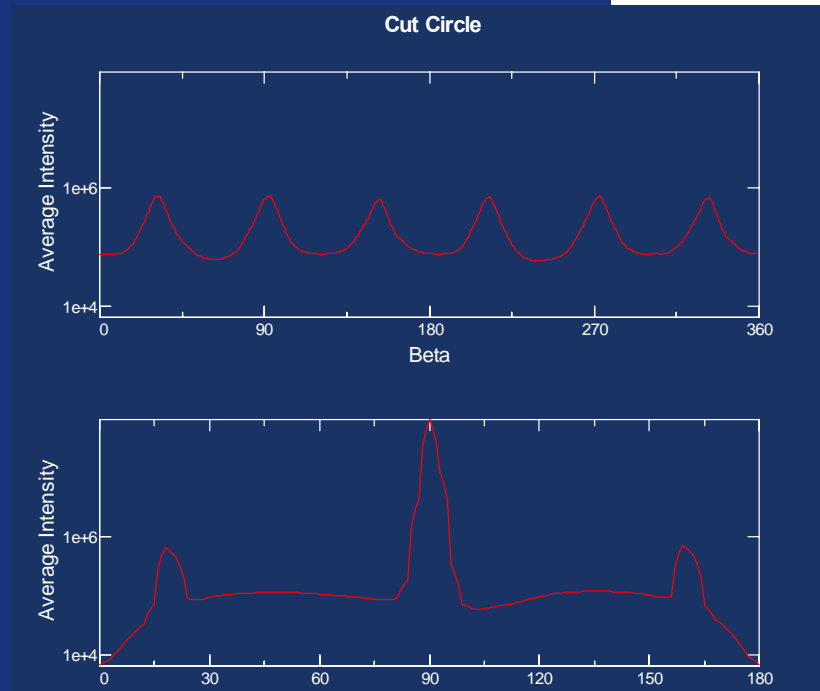
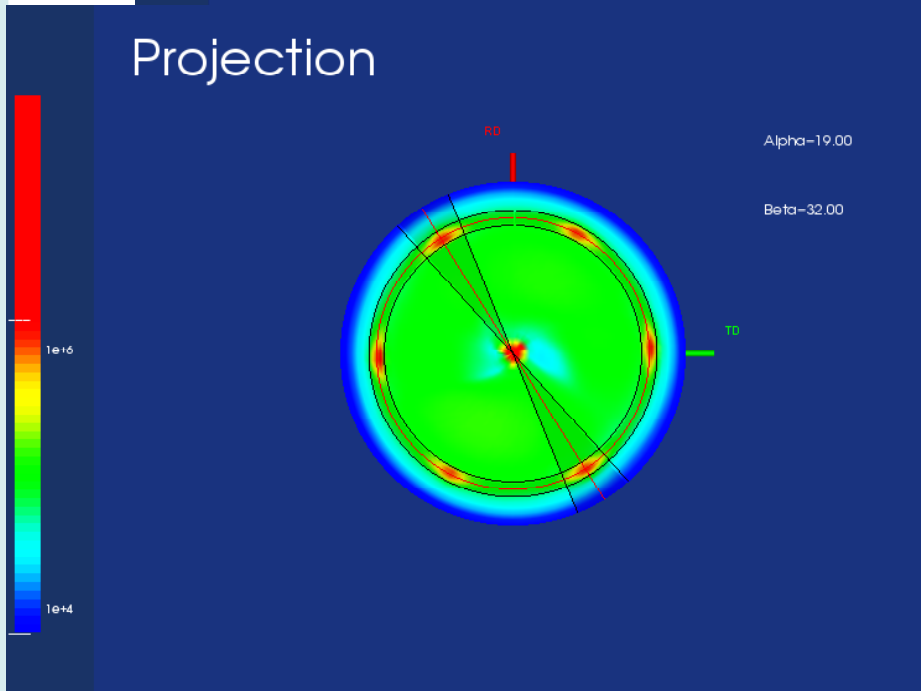
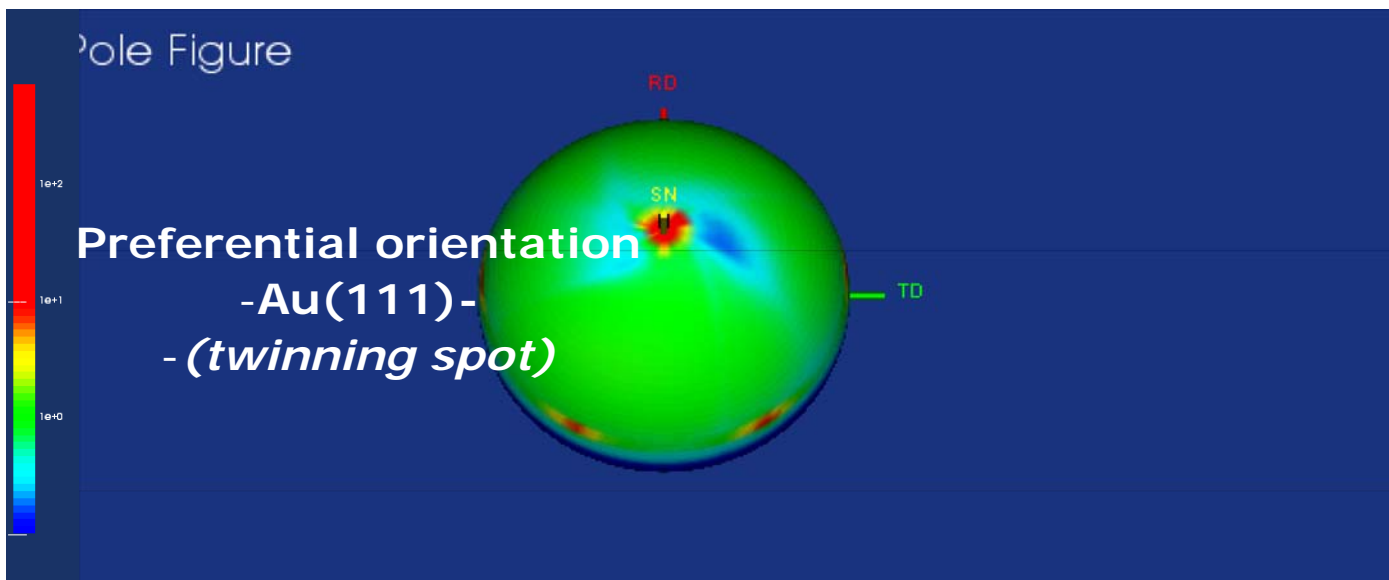


# XRD characterisation



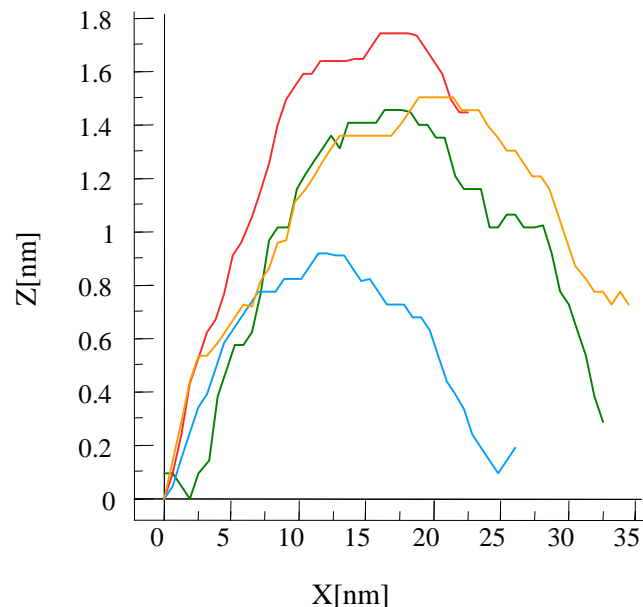
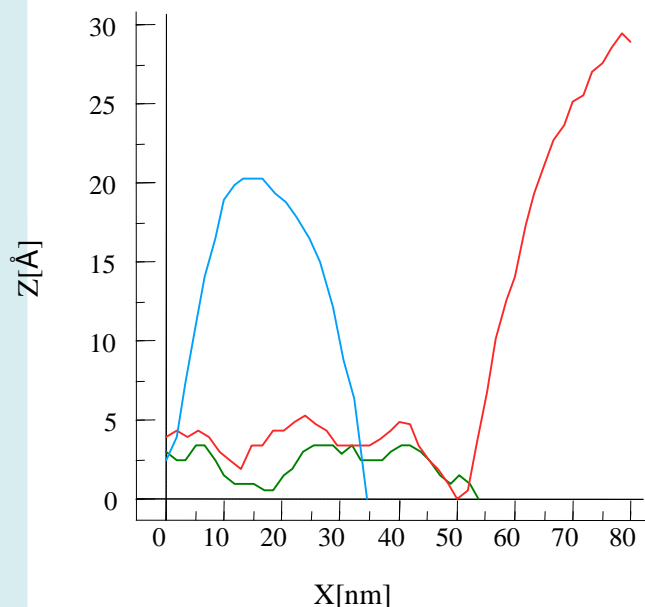
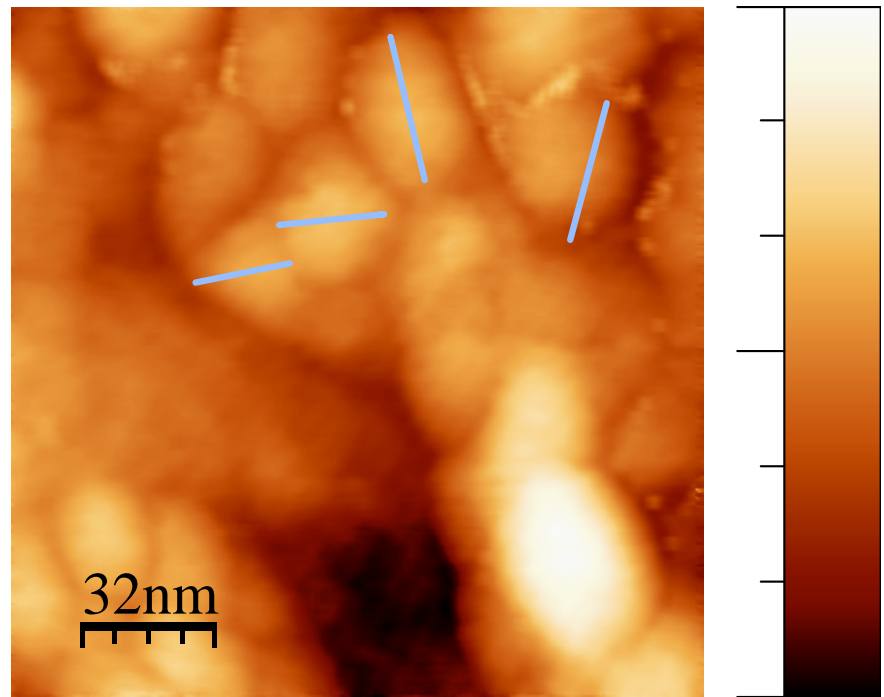
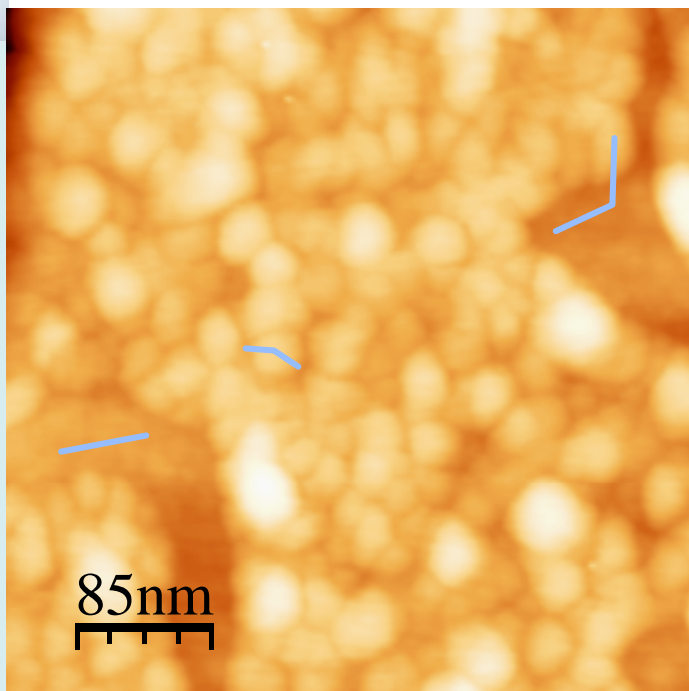


# XRD characterisation





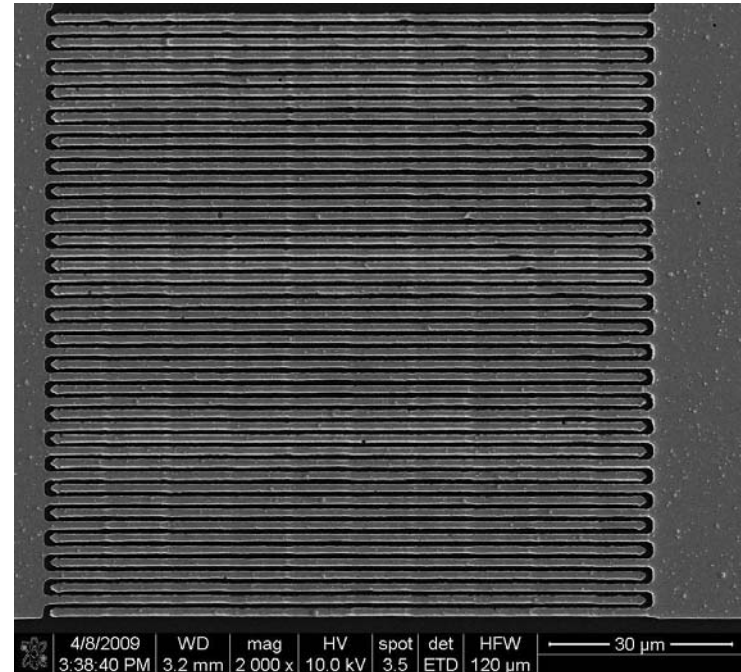
# Human Serum Albumine/Au (111)



•Graphene – metallic nanoparticles decorated

•Graphene decorated with:

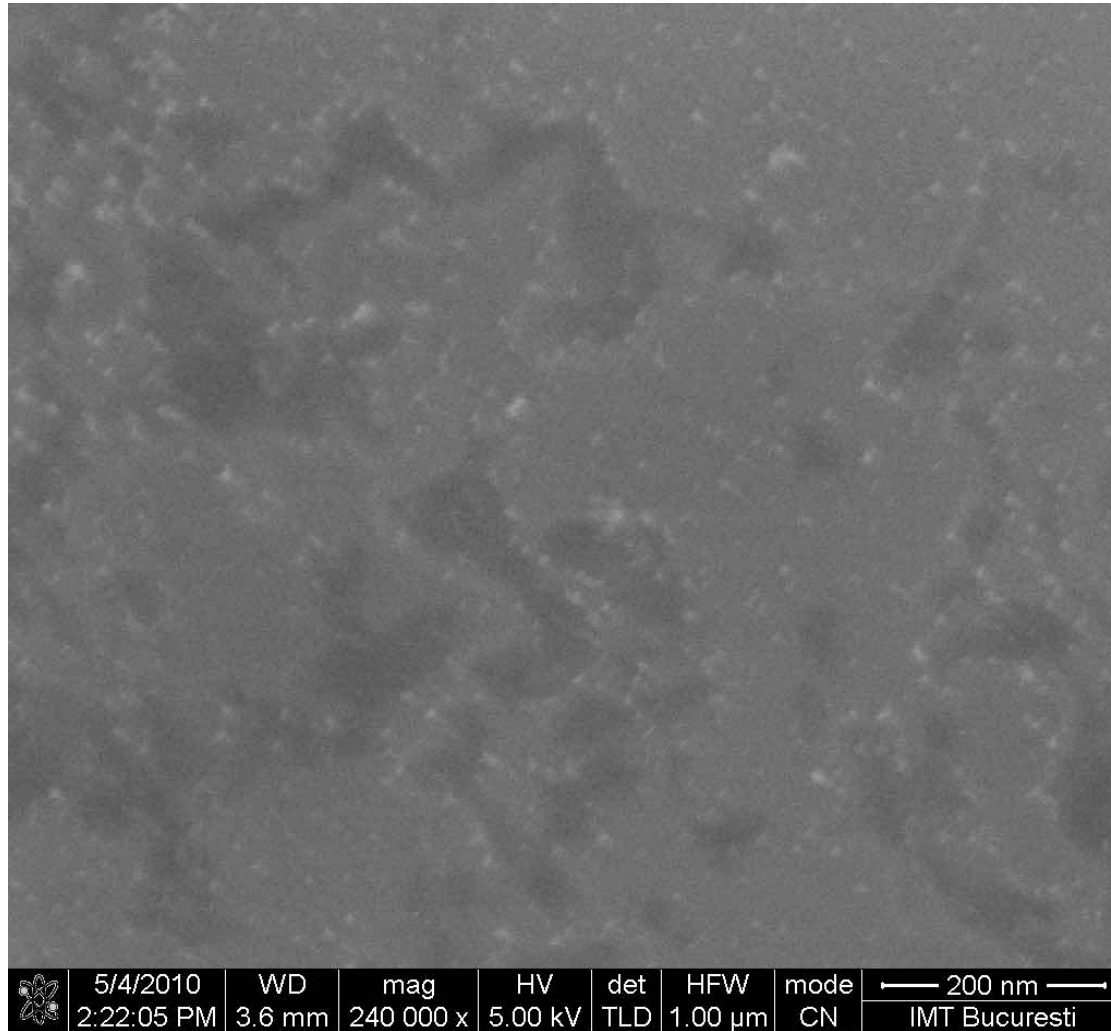
- Au nanoparticles
- Ag nanoparticles



***SEM - IDT***



- Graphene – Au nanoparticles decorated



**Graphene decorated with nanoAu**



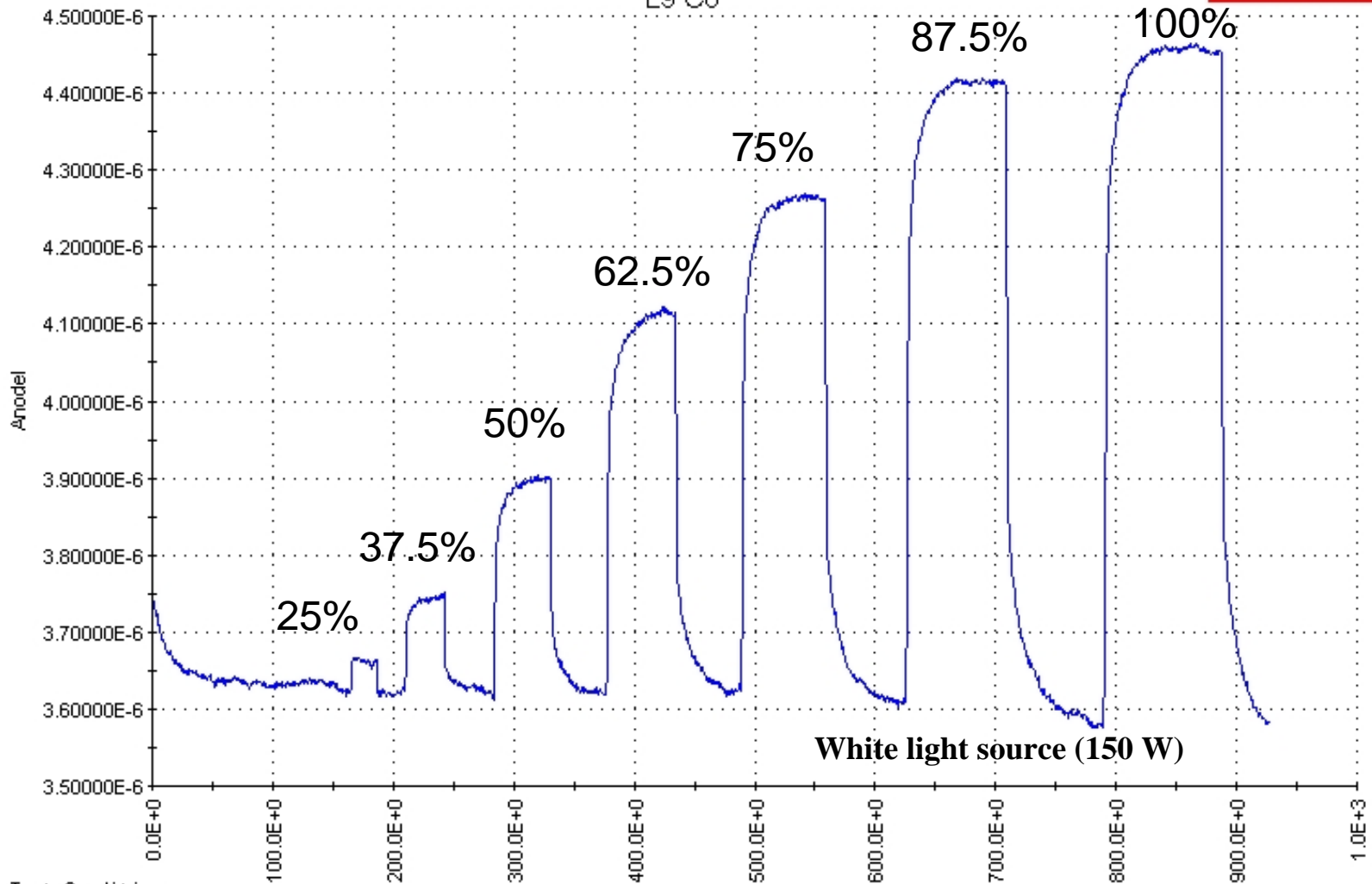


# Photocurrent Graphene – nanoAu

06/08/2010 15:20:13

L9 C8

KEITHLEY



Test Conditions  
Anode: V.Bias  
Bias: 0.1  
Cathode: V.Bias  
Bias: 0

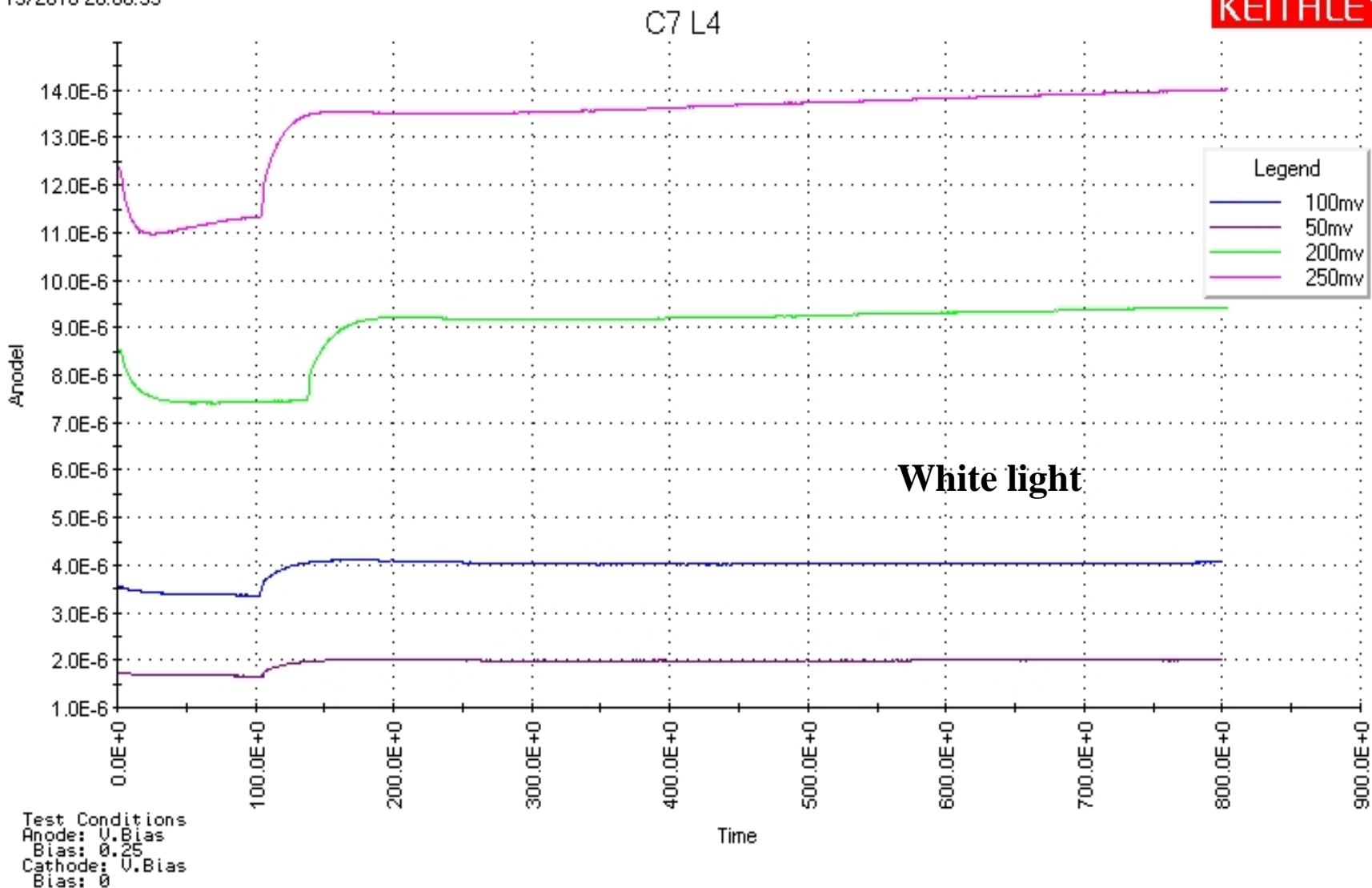
Time



# Photocurrent Graphene – nanoAg

07/19/2010 20:00:39

KEITHLEY



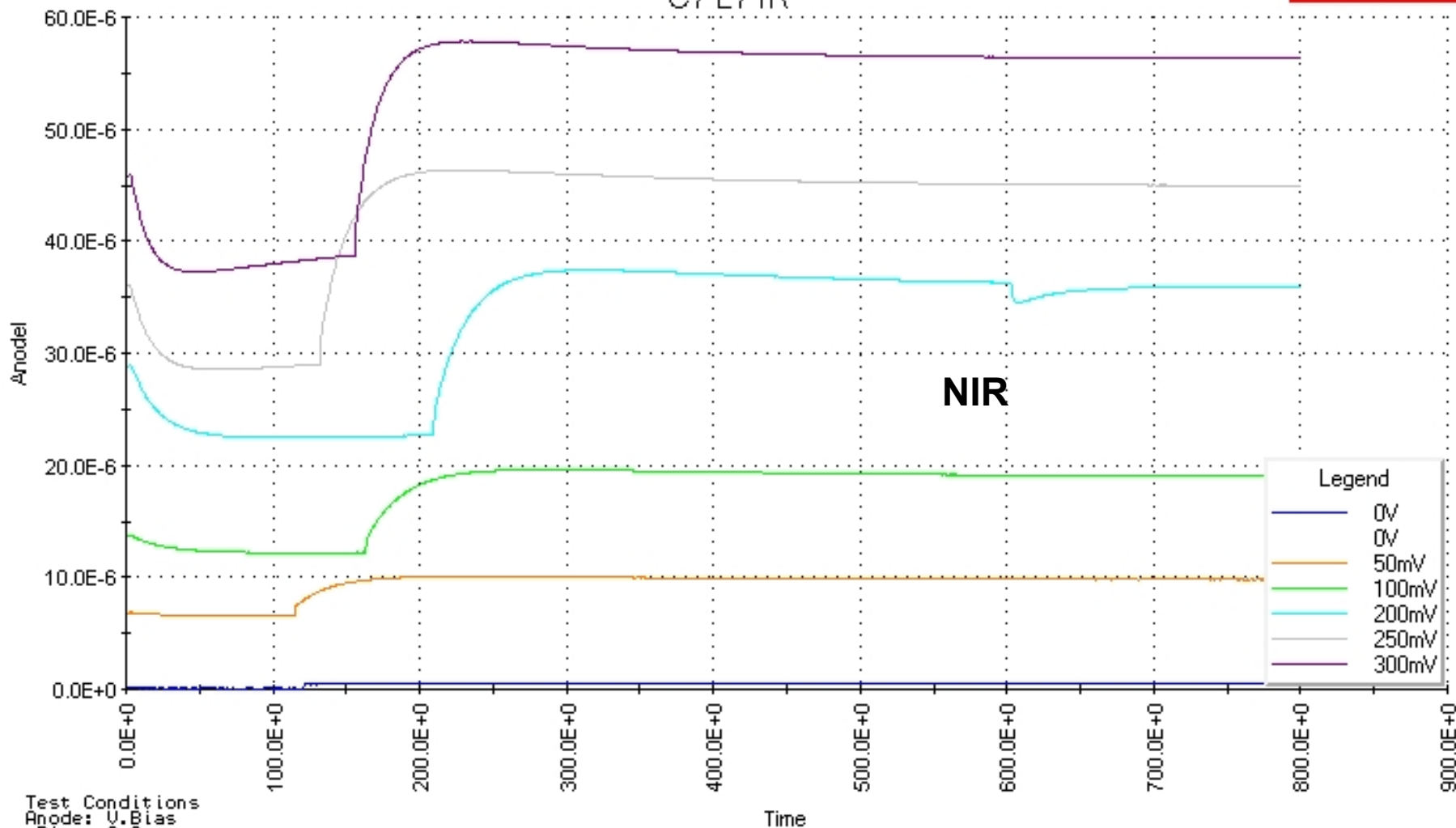


# Photocurrent Graphene – nanoAg

07/20/2010 04:05:18

KEITHLEY

C7 L7 IR



Test Conditions  
Anode: U.Bias  
Bias: 0.3  
Cathode: U.Bias  
Bias: 0

Time



