Daniele Passeri

Tecniche innovative di imaging e caratterizzazione alla nanoscala

EMINA lab
Electron Microscopies and Nanoscopies

EMiNa (**E**lectron **Mi**croscopy and **Na**noscopies)**-Lab**
Responsabile Scientifico: Marco Rossi

Dipartimento di Scienze di Base e Applicate per l'Ingegneria (SBAI)

SNN Lab
Sapienza Nanotechnology & Nanoscience Lab

Centro per le Nanotecnologie Applicate all'Ingegneria della Sapienza (CNIS)

A short description of EMiNa group

EMiNa group is committed with the use of **standard tools** and in the **development of innovative techniques** for the characterization of different materials at micro- and nano-scale, such as:

- Thin films, either crystalline or polymeric;
- Nanomaterials and nanostructures (e.g., carbon nanotubes, nadiamond, superparamagnetic nanoparticles…);
- Nanocomposites (e.g., polymers reinforced with nanomaterials);
- Biological micro- and nano-systems (e.g., bacteria, bacterial biofilms);

The used techniques are available at SBAI and/or at SNN-Lab (Sapienza Nanoscience and Nanotechnology Laboratory).

Beam techniques

The techniques are based on **electron beam** or **x-ray beam** methods as well as on **scanning probe** techniques.

Electron beam methods:

- Scanning electron microscopy (SEM)
- Transmission electron microscopy (TEM)
- Reflection high energy electron diffraction (RHEED)

X-ray beam methods:

- X-ray diffraction (XRD)
- Microanalysis

Probe techniques

Scanning probe techniques:

- Scanning tunneling microscopy (STM)
- Atomic force microscopy (AFM):
    - **Morphological** characterization
    - **Mechanical** characterization:
        - AFM quasi-static indentation
        - Atomic force acoustic microscopy (AFAM)
        - Torsional harmonic AFM (TH-AFM)
    - **Electric** characterization
    - **Magnetic** characterization
    - **Thermoacoustic** characterization

Approccio multidisciplinare

Marco Rossi
Dip. Scienze di Base e Appl. per l'Ing.
EMINA Lab
SNN Lab - CNIS
Univ. "La Sapienza"

Maria Letizia Terranova
Dip. Scienze e Tecnologie Chimiche
MINIMA Lab
Univ. Tor Vergata

D. Passeri
R. Matassa
F. Mura (SNN - Lab)
C. Dong
L. Angeloni

S. Orlanducci
E. Tamburri
V. Guglielmotti
V. Sessa
I. Cianchetta
S. Gay

TECNICHE DI SINTESI
e trattamenti post-sintesi

CARATTERIZZAZIONE
strutturale morfologica
composizionale funzionale

ENEA - Frascati
ENEA - Casaccia
INFN - LNF
INFN - Sezione di Milano
CNR - Bologna
CNR - Roma

Univ. di Lecce - Dip.to Scienza dei Materiali
ANL - Center for Nanoscale Materials - USA
Inst of Semiconductor Physics - Ukraine
Ioffe Institute, S. Pietroburgo, Russia
Dept of Materials, Oxford, UK
CSIRO, Australia

Synthesis and characterizations of C-based nanomaterial for technological applications

- *Electron Emission-based systems*
  X-Ray tubes *(EU 7thFP NANORAY project 2009-2011 & PRIN 2008)*

- *Electronics*
  Microcircuits, nanointerconnections, flexible electrodes, thermal management *(Contracts with SELEX-SI, Finmeccanica group, since 2004)*

- *Sensing*
  Gauge sensors, analytical sensors, Gas/vapor sensors
  (SENSATIONAL project, Industria 2015, Made in Italy, 2010-2012)

- *Energetics*
  Hydrogen storage *(start-up company* ***NanoShare Srl****, founded in 2010 with financial support of MIUR)*

Patent n° RM2007A000618
PCT/IT2008/000677)13
→
Project STOR-AGE
(2009, Art. 11 - DM 593/00)

Based on a Polymer-CNT nanocomposite exhibiting a reproducible and stable adsorption of about 4%*wt in suitable condition for a large use
(@ room temperature and @ 1 Atm)
**with a max of 8* not reproducible up-to-now*

The materials of our interest

Carbon-based materials and nanomaterials

- *Carbon nanotubes*
- *Onions, carbon cages*
- *Graphene oxides*
- *Fullerenes*
- *Diamond and diamond-like films*
- *Diamond/metals and diamond/Si films*
- *Nanodiamonds*

Nanocarbon-metals and -oxides materials

- *Nanotubes/*Ta_2O_5
- *Nanotubes/*TiO_2
- *Nanotubes/Ni*
- *Nanodiamond/Au*

Metallic nanoparticles

- *Nanoparticles and nanodispersions of: Au, Ag, Ni, Pt*

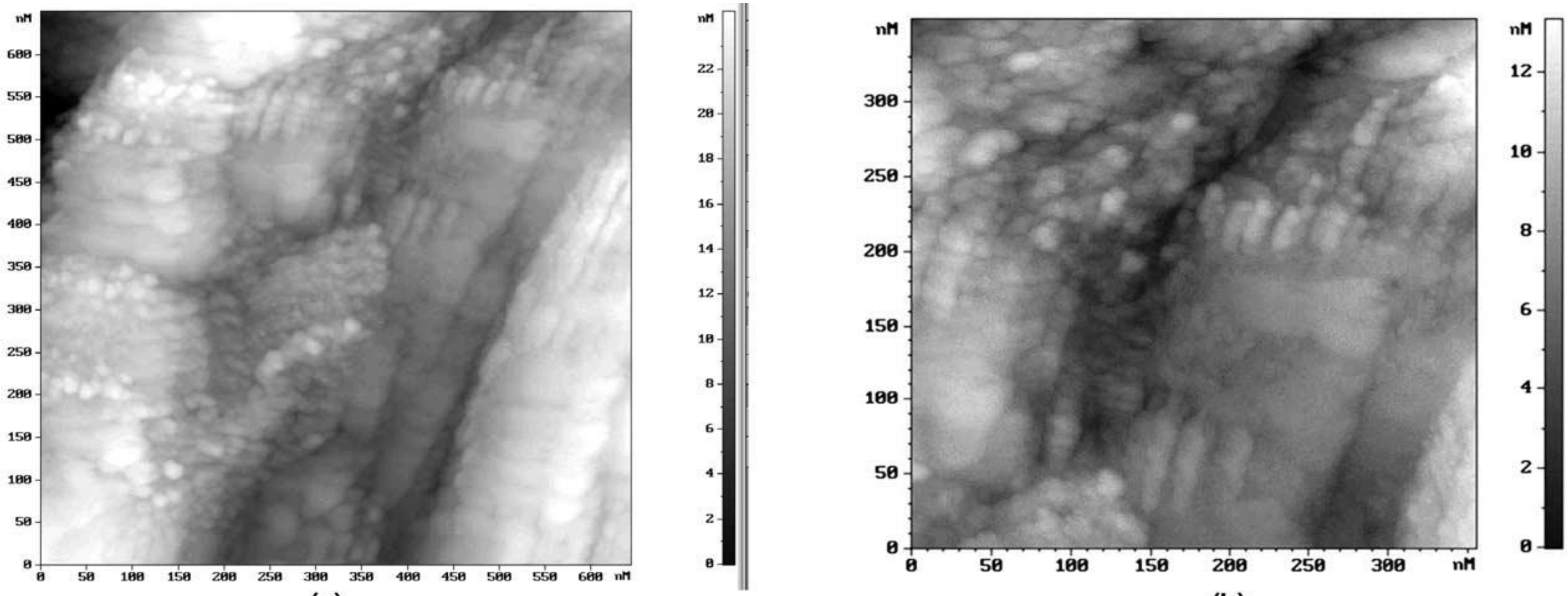
Polymeric materials and polymer-based nanocomposites

- *Conducting Polymers-nanotubes*
- *Conducting Polymers-nanodiamond*
- *Nylon-nanotubes*
- *Silicones-nanotubes*
- *Epoxy-nanotubes*
- *Liquid crystals-nanotubes*
- *Liquid crystals-nanodiamonds*
- *Polymers/*TiO_2

Other materials

- *Nanostructured Si*
- *Colloidal nanocrystals*
- *Nanoclays*
- *ZnO*

Scanning tunneling microscopy



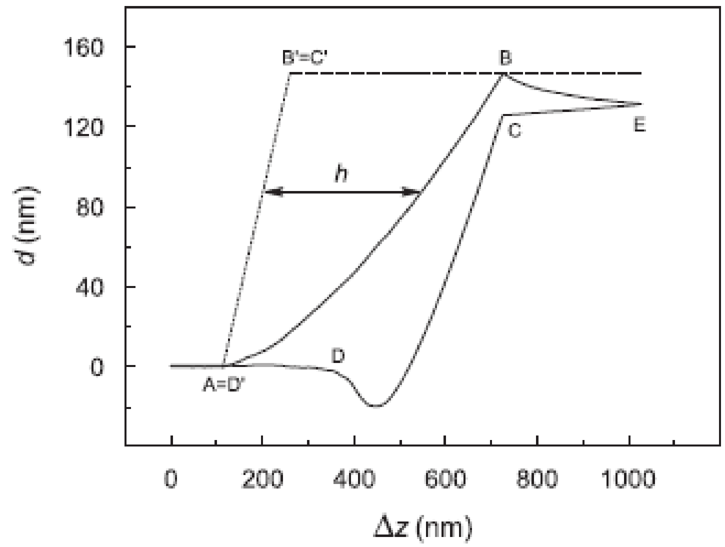
(a)

(b)

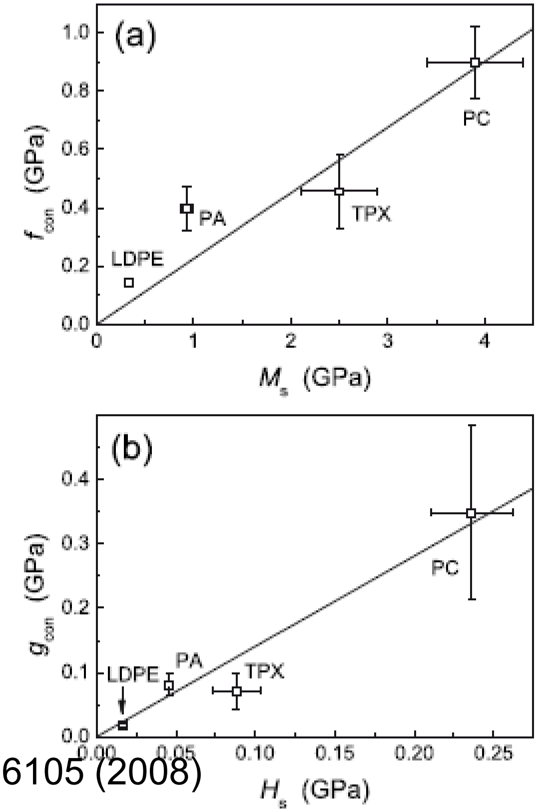
Single-walled carbon nanotubes (SWCNTs) in 1,8-diaminonaphthalene

E. Tamburri, M. Rossi, D. Passeri *et al.*, Carbon **43**, 1213 (2005)

Quasi-static indentation by AFM



D.Passeri *et al.*, Ultramicroscopy **109**, 1417 (2009)



D.Passeri, M. Rossi *et al.*, Rev. Sci. Instrum. **79**, 066105 (2008)

We developed a procedure to analyze the AFM deflection versus distance curves that allows the accurate determination of <u>indentation modulus</u> and <u>hardness</u> of soft samples (**polymers, biological matrices**) through a phenomenological calibration, which takes into account also samples viscoelastic properties.

Caratterizzazione delle proprietà MECCANICHE dei materiali

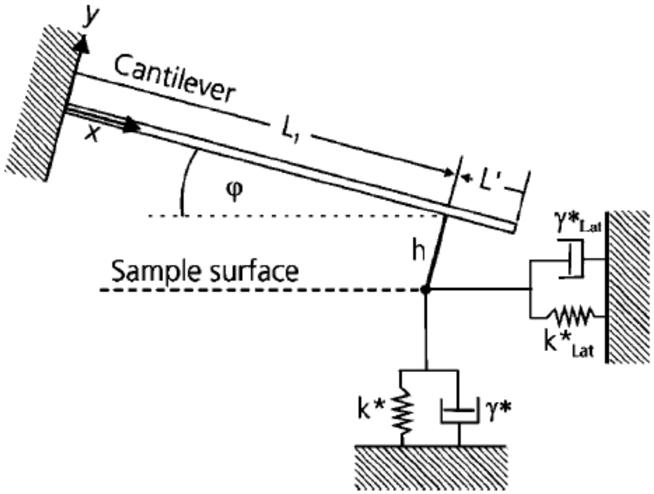
PROBLEMI

su scala micrometrica e nanometrica
con le tecniche convenzionali

- ***Svantaggi della micro- e nano- indentazione standard:***
  - *Limitata risoluzione*
  - *Effetto del substrato per film sottili*
  - *Distruttive (a queste scale)*

Soluzioni alternative basate su
Tecniche SPM

Atomic force acoustic microscopy



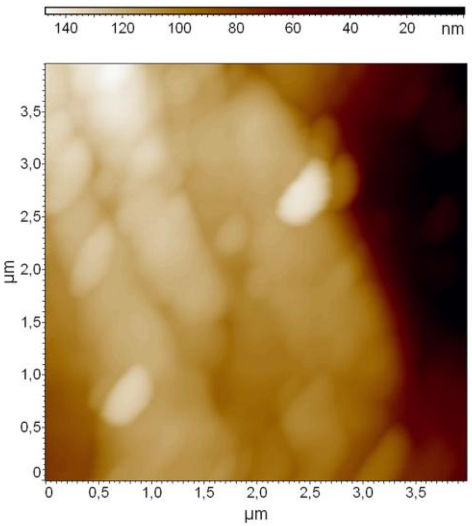
- An ultrasonic transducer is coupled to the back of the sample that sets into out-of-plane vibration the sample surface.
- Analyzing the contact resonance frequencies of the cantilever whose tip is in contact with the sample surface, the sample indentation modulus can be quantitatively evaluated (elastic samples).
- From resonance frequencies and quality factors sample storage and loss modulus can be determined (viscoelastic samples).

Sample	M_{exp} (GPa)	M_{lit} (GPa)	ν	E_{exp} (GPa)	E_{lit} (GPa)
GaAs	120 ± 12	117.5			
InP	93 ± 16	92.1			
Al	82 ± 11		0.35	72 ± 10	71
Pt	200 ± 30		0.39	170 ± 26	170

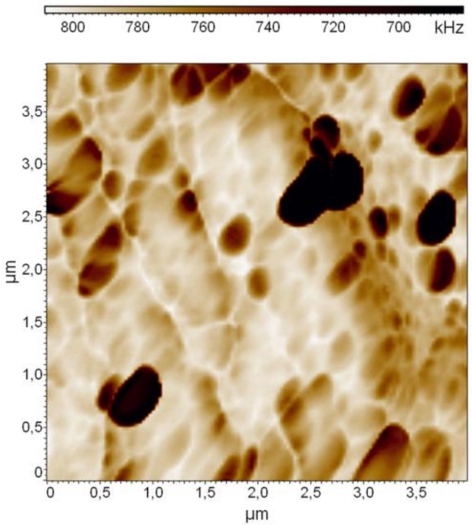
D.Passeri, M. Rossi *et al.*, Microelectr. Eng. **84**, 490 (2007)

Atomic force acoustic microscopy

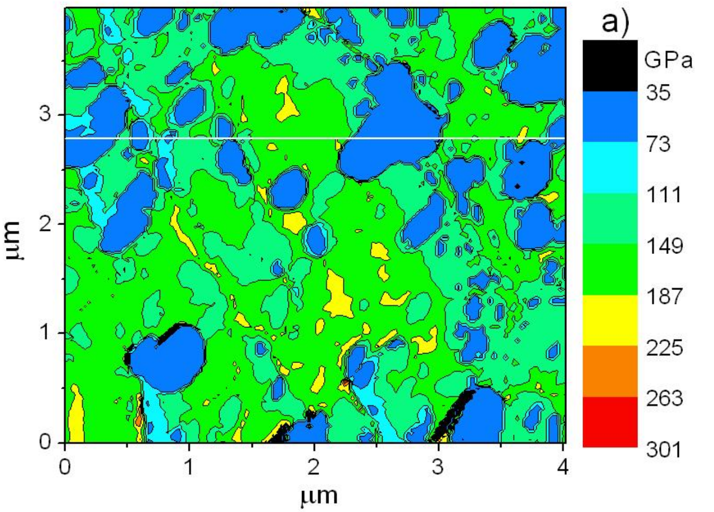
- AFAM contact resonance frequency (CRF) images can be analyzed to obtain quantitative maps of sample indentation modulus.
- As an example, diamond-like carbon (DLC) film deposited by laser ablation on a Molybdenum substrate from a glassy carbon (GC) target:



Topography



1st CRF

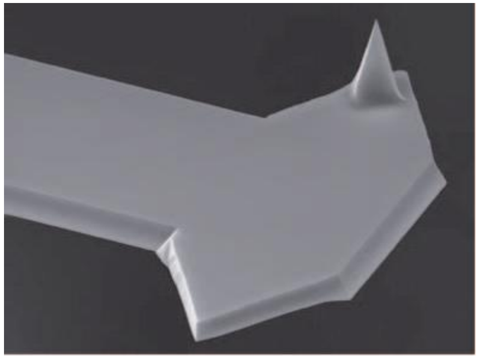


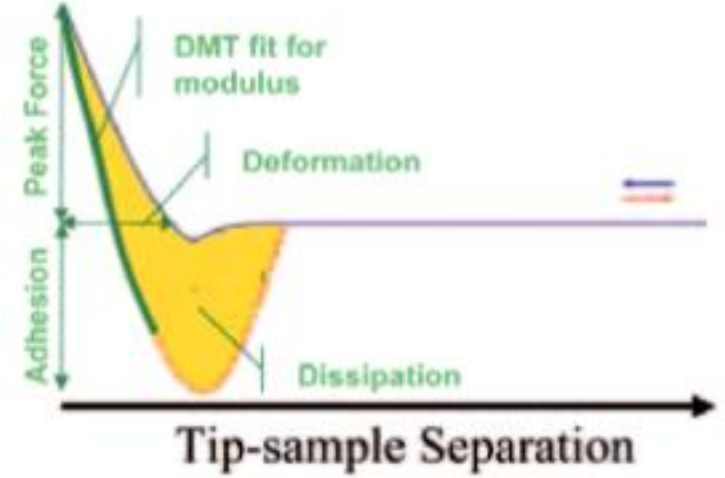
Indentation modulus map

D.Passeri, M. Rossi *et al.*, Appl. Phys. Lett. **88**, 121910 (2006)

Torsional harmonic AFM

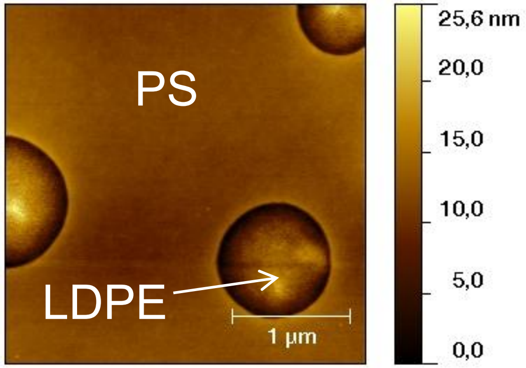
- Tapping mode using T-shaped cantilevers with out-of-axis tip.
- The tip periodically indents the sample surface.
- The cantilever torsional deflection signal is analyzed and used to obtain force versus distance curves by inverse Fourier transform of its spectrum.
- After calibration using a reference sample, simultaneously to topography quantitative maps are acquired of indentation modulus, peak force, tip-sample adhesion and dissipation on soft samples (polymers, biological matrices).



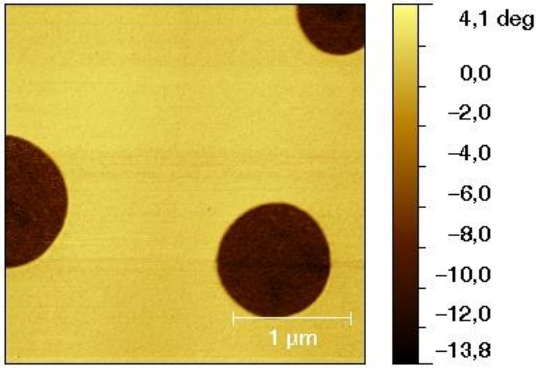


Torsional harmonic AFM

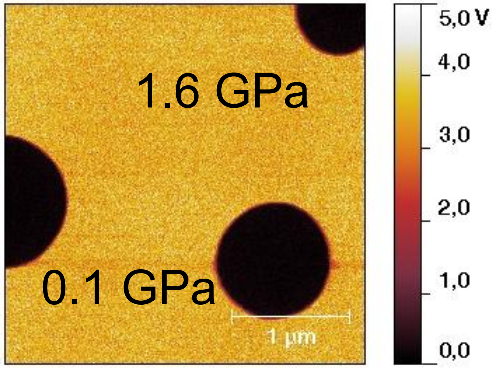
- As an example, the characterization of the polystyrene (PS)/low density polyethylene (LDPE) reference sample:



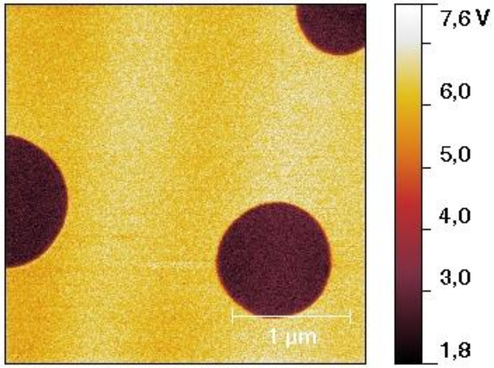
Height



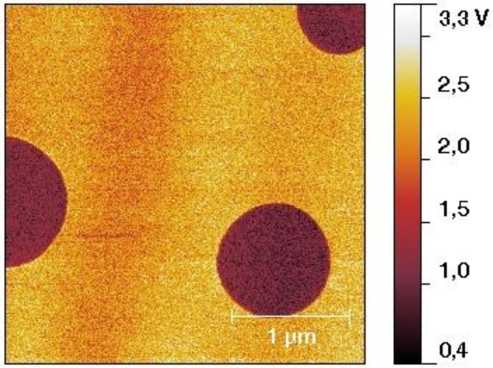
Phase



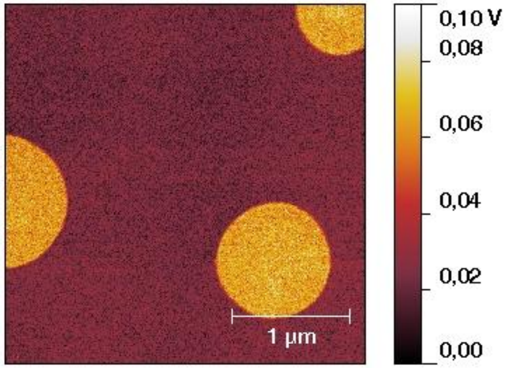
Elastic modulus



Peak force



Adhesion

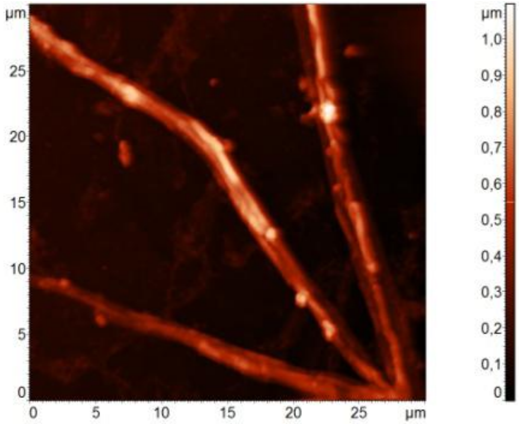


Dissipation

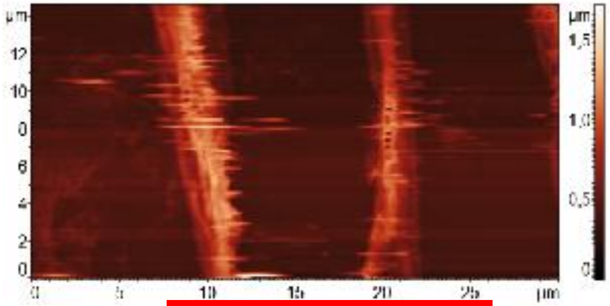
D.Passeri, M. Rossi *et al.*, Anal. Bioanal. Chem., 2012 (accepted).

Conductive AFM

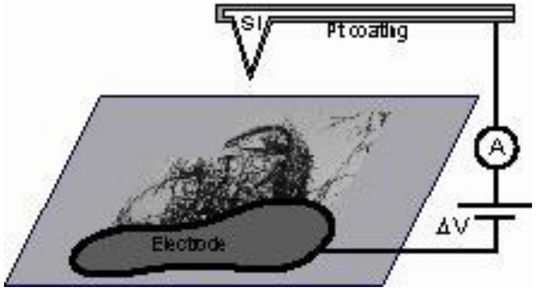
- To verify the conductivity of polyaniline (PANI)/nanodiamond (ND) fibers, an electrode has been realized at one end of the fibers, a dc voltage has been imposed between the electrode and the conductive cantilever, and the dc electric current between tip and sample has been recorded during the scanning.



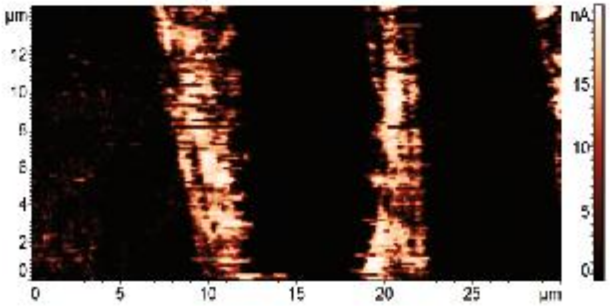
PANI/ND fibers



Topography



Sketch of the experimental configuration



Current image

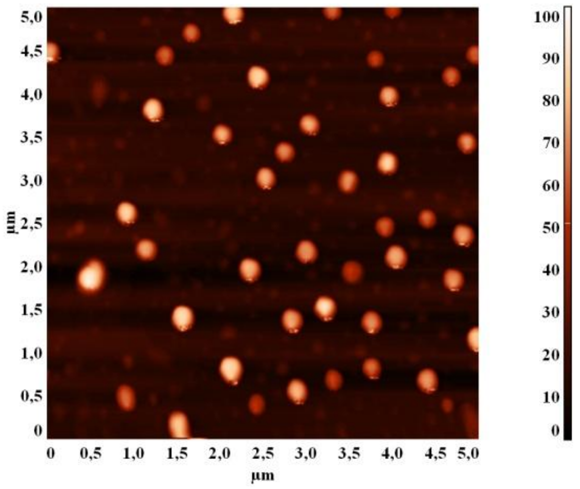
E. Tamburri, M. Rossi, D. Passeri *et al.*, Polymer (2012) accepted.

Magnetic force microscopy

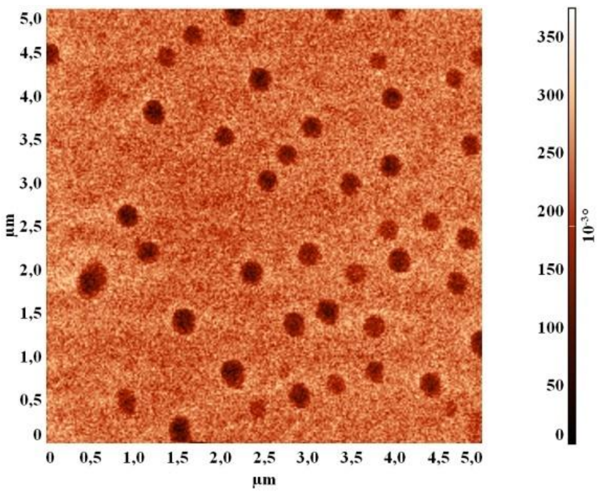
- Two-pass technique:

  1st pass: the topography is acquired;
  2nd pass: the tip is kept at fixed distance from the surface, the surface is scanned while the cantilever is oscillating and the phase is recorded, which depends on the tip-sample force. Using a magnetic film coated tip, the magnetic force is monitored.

- As an example, superparamagnetic nanoparticles Fe-Cu:



Topography



Magnetic image

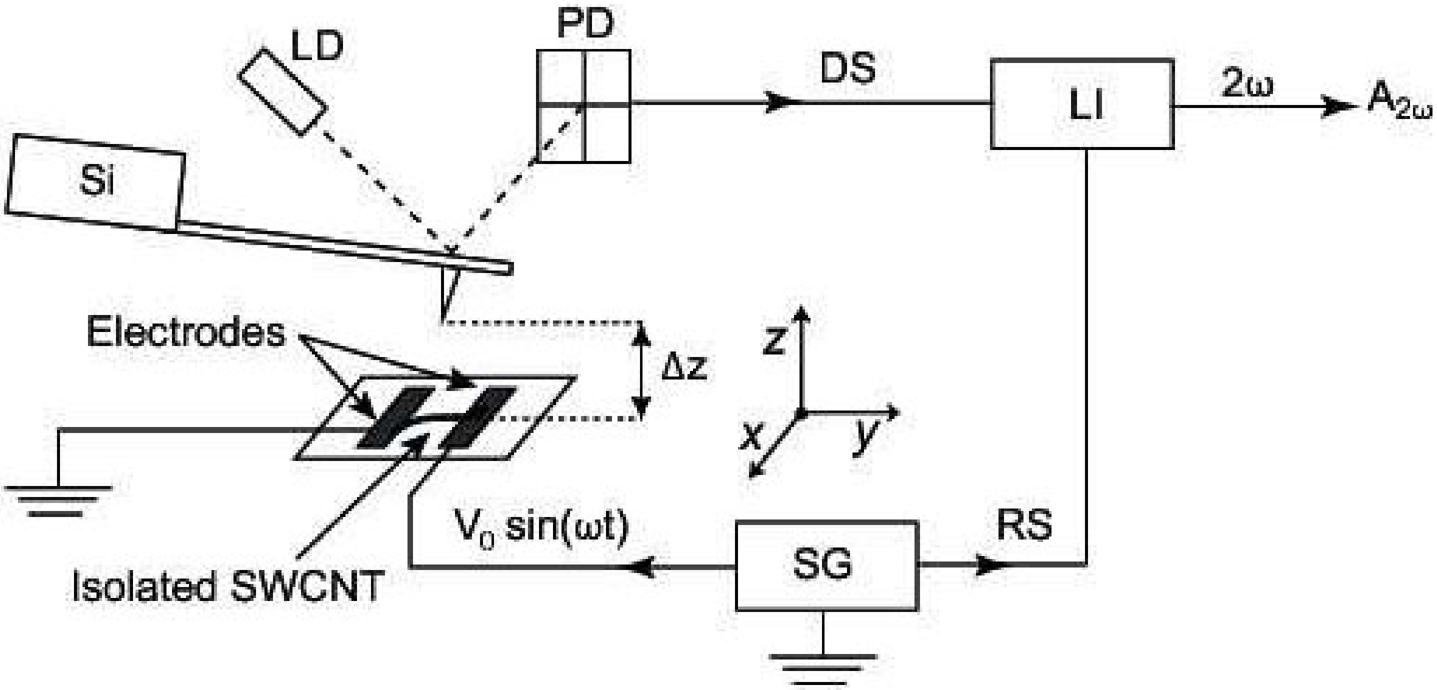
Thermoacoustic characterization

Thermoacoustic effect in wires or foils:

- An ac electric current at frequency *f* produces an oscillating heating of the conductor at frequency 2*f* due to Joule effect;
- This produces as oscillation in the temperature of a thin air film surrounding the conductor;
- The periodic oscillation of the volume of air produces an acoustic wave propagating in the medium.

Thermoacoustics from single SWCNTs

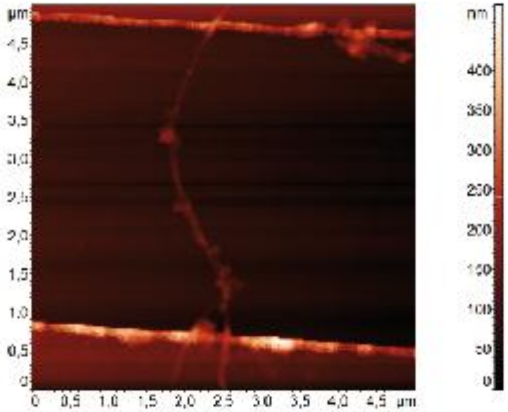
- AFM-based technique:



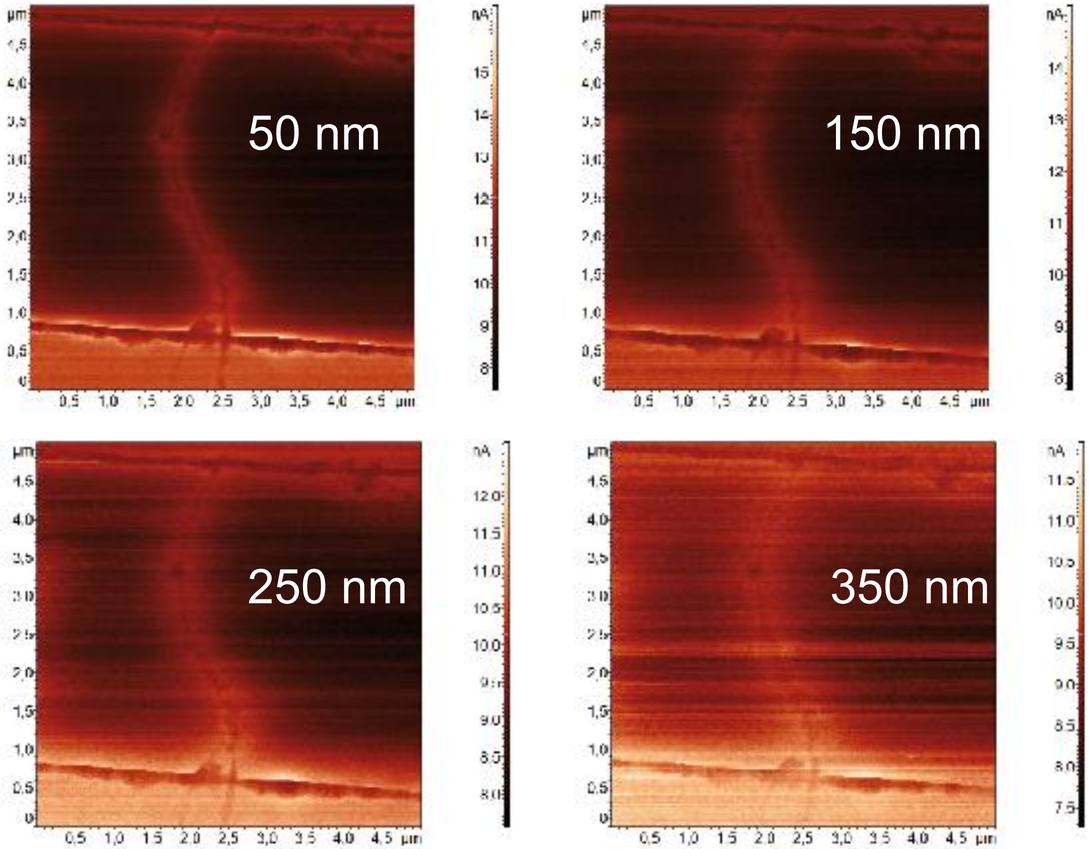
D.Passeri, M. Rossi *et al.*, Adv. Funct. Mater. in press (2012)

Thermoacoustics from SWCNTs

- Imaging of thermoacoustic emission from SWCNTs at different height from the surface:



Topography



D.Passeri, M. Rossi *et al.*, Adv. Funct. Mater. in press (2012)

GRAZIE PER L’ATTENZIONE

Roma, 13 giugno 2012