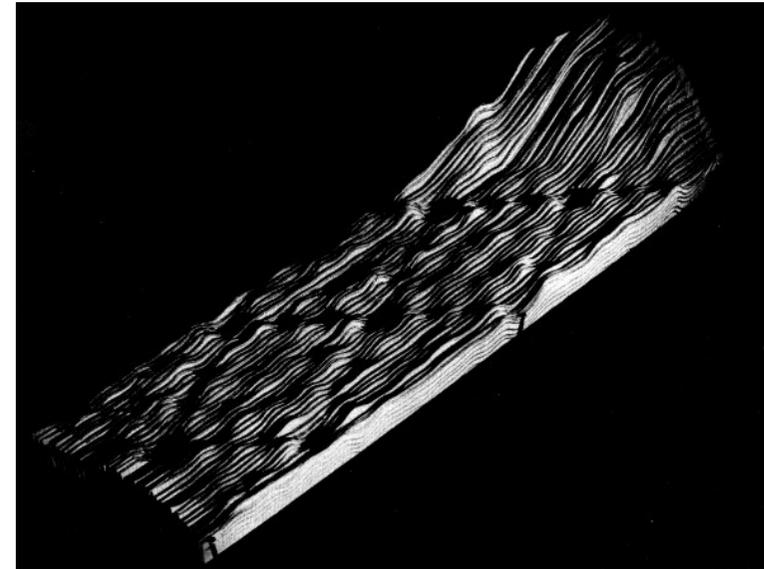


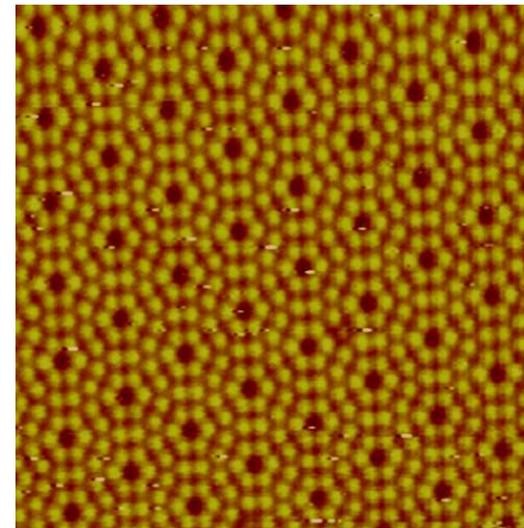
1982. Rohrer e Binnig pubblicano
dati STM della ricostruzione 7×7
del Si(111).

1986. Premio Nobel per la Fisica



Scanning Tunneling Microscopy
Scanning Probe Microscopy

STM e tecniche correlate (SPM, scanning probe
microscopy) forniscono informazioni legate allo
spazio diretto dei sistemi



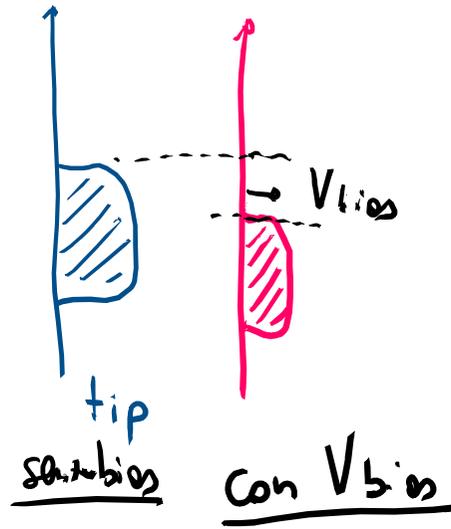
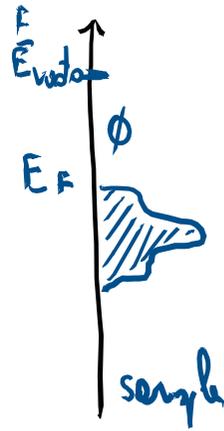
Wandelt, volume 1:

3.5 Scanning Probe Techniques | 427

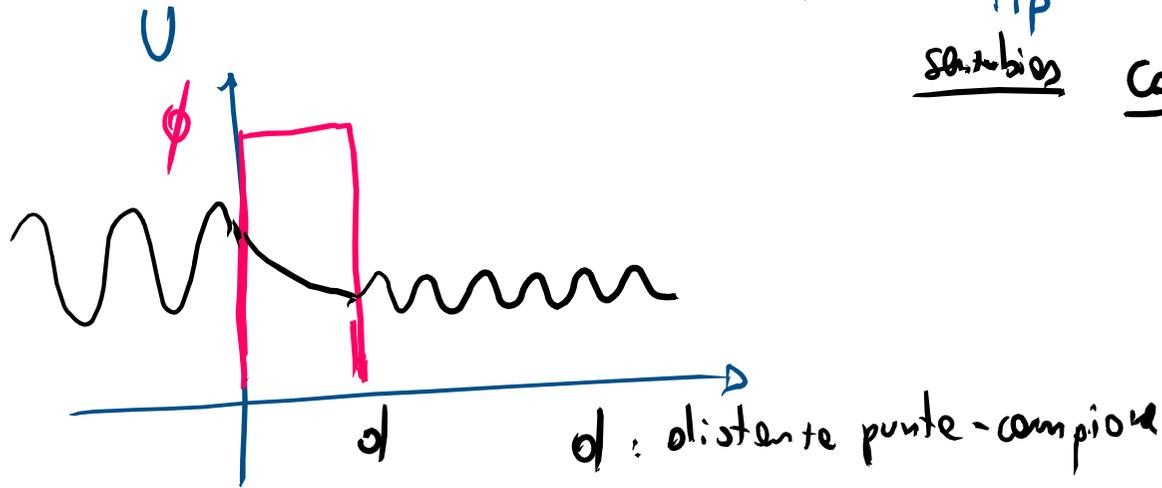
3.5

Scanning Probe Techniques

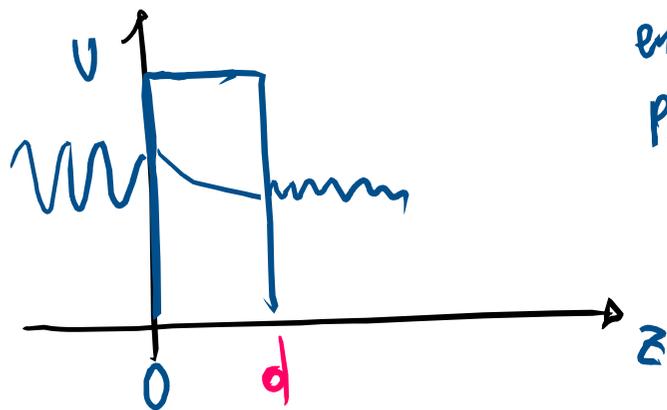
Angelika Kühnle and Michael Reichling



Considerazioni, per
semplicità
 $\phi_{\text{sample}} = \phi_{\text{tip}}$



Senza V_{bias} , la probabilità è paragonabile che un e^- passi da sample \rightarrow tip e viceversa, quindi non ho una netta corrente di tunneling.



energia dell' e^- : E
 Potenziale (altezza barriera) : U

$z=0$ punto di contatto
 in contatto

$$-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} \psi(z) + U(z) \psi(z) = E \psi(z)$$

$z < 0, z > d$

$$\psi(z) \approx \psi_0 e^{\pm ikz}$$

$$k = \frac{\sqrt{2m(E-U)}}{\hbar}$$

nel tunnel ($0 < z < d$)

$$\psi(z) = \psi_0 e^{-\tilde{k}z}$$

$$\tilde{k} = \frac{\sqrt{2m(U-E)}}{\hbar}$$

se $V_{bias} \sim e$ piccolo $U-E \sim \phi$

Qual è la corrente di tunneling?

$$I_{\text{tunneling}} \propto \sum_{E = E_F - V_{\text{bias}}}^{E_F} |\psi_n(0)|^2 e^{-\frac{2\sqrt{2m\phi}d}{\hbar}}$$

$\rightarrow |\psi|^2$

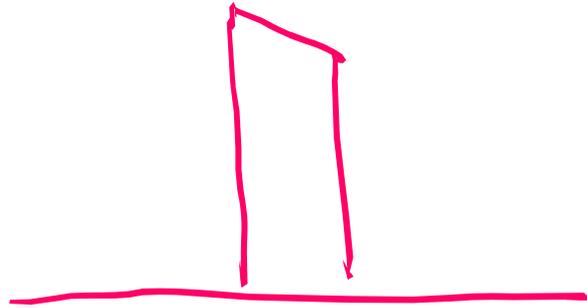
$$I_{\text{tunneling}} \propto (\text{DOS})_{\text{sample}} e^{-1.025 \sqrt{\phi} \cdot d}$$

$$\phi \approx 4 \text{ eV}$$

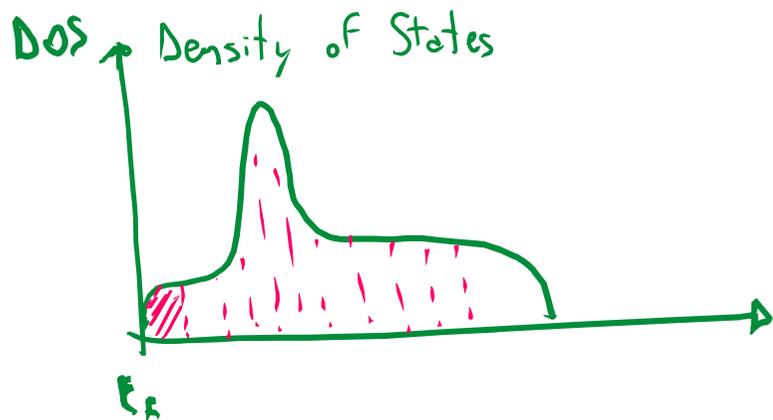
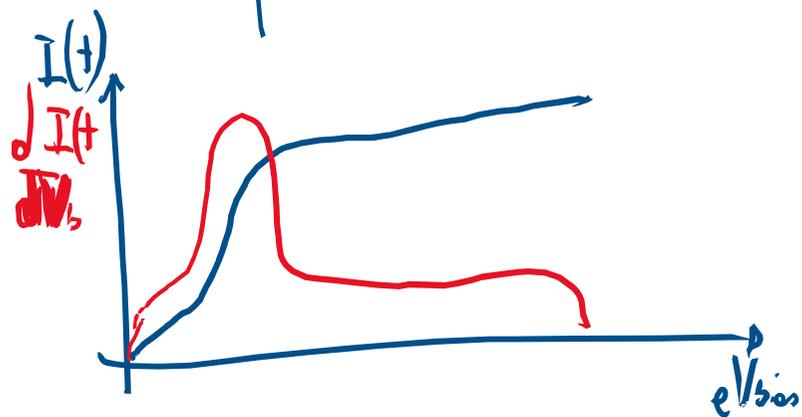
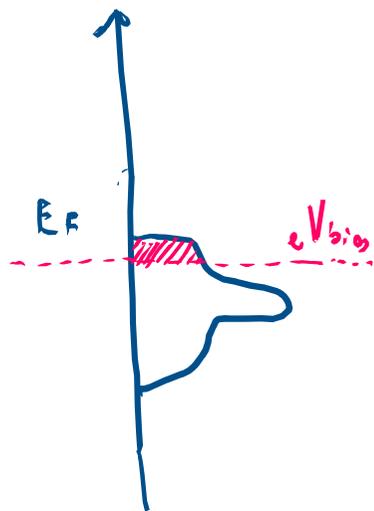
Se sposta la punta (cambia d) di $\sim 1 \text{ \AA}$ $\rightarrow I_{\text{tun}}$ cambia ~ 10 volte

\Rightarrow raggiungo riduzione di $\sim 0.1 \text{ \AA}$

Se $\phi_{\text{sample}} \neq \phi_{\text{tip}}$



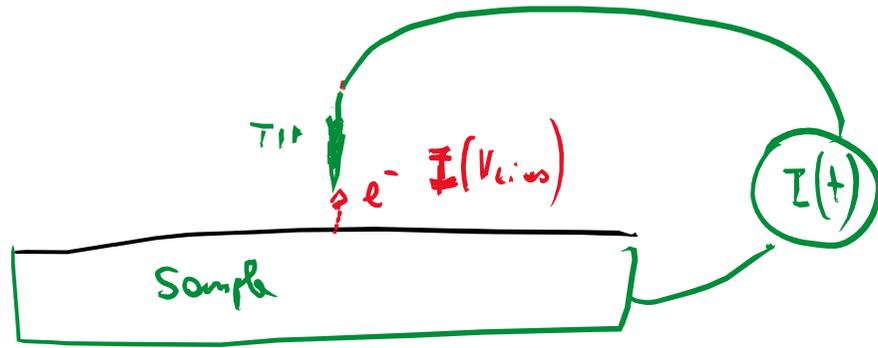
$e \cdot V_{bias}$ mi determina la porzione di elettroni in banda di valenza che possono fare tunneling



$I \rightarrow$ TOPOGRAFIA

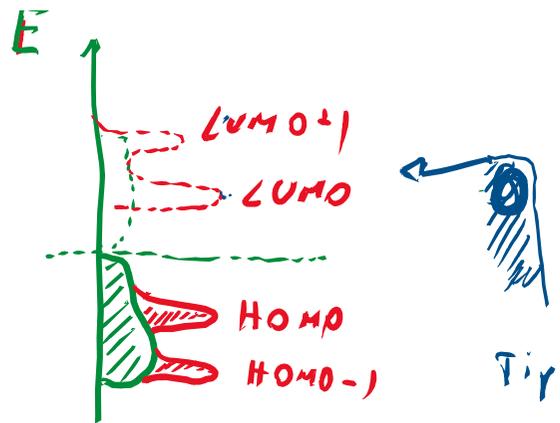
$\frac{dI}{dV} \rightarrow$ SPECTROSCOPIA
(STS Scanning Tunneling Spectroscopy)

La quantità $\frac{dI}{dV}$ è proporzionale alla DOS.

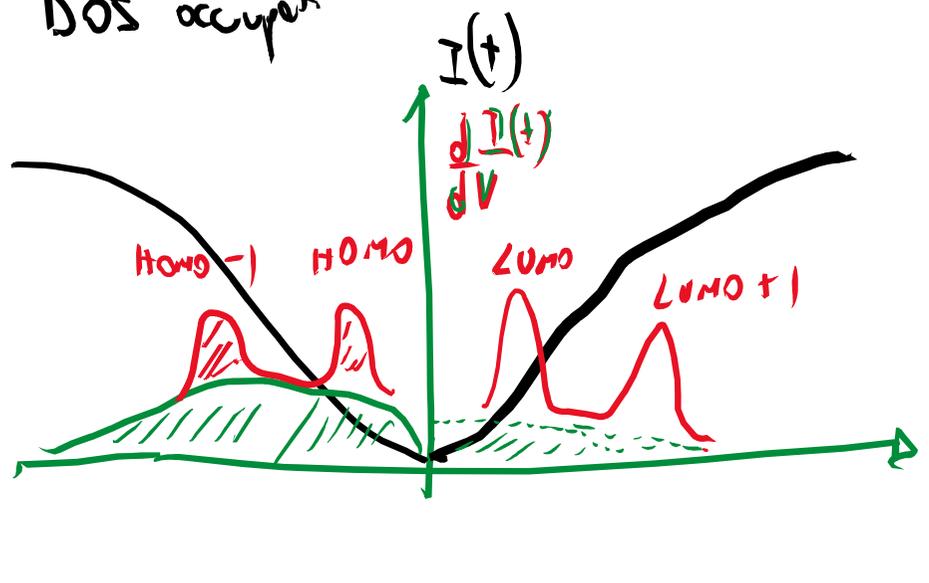


!!
punte e campione
operano a circuito elettrico

⇒ STM ↔ ip campione conoluce



DOS occupied

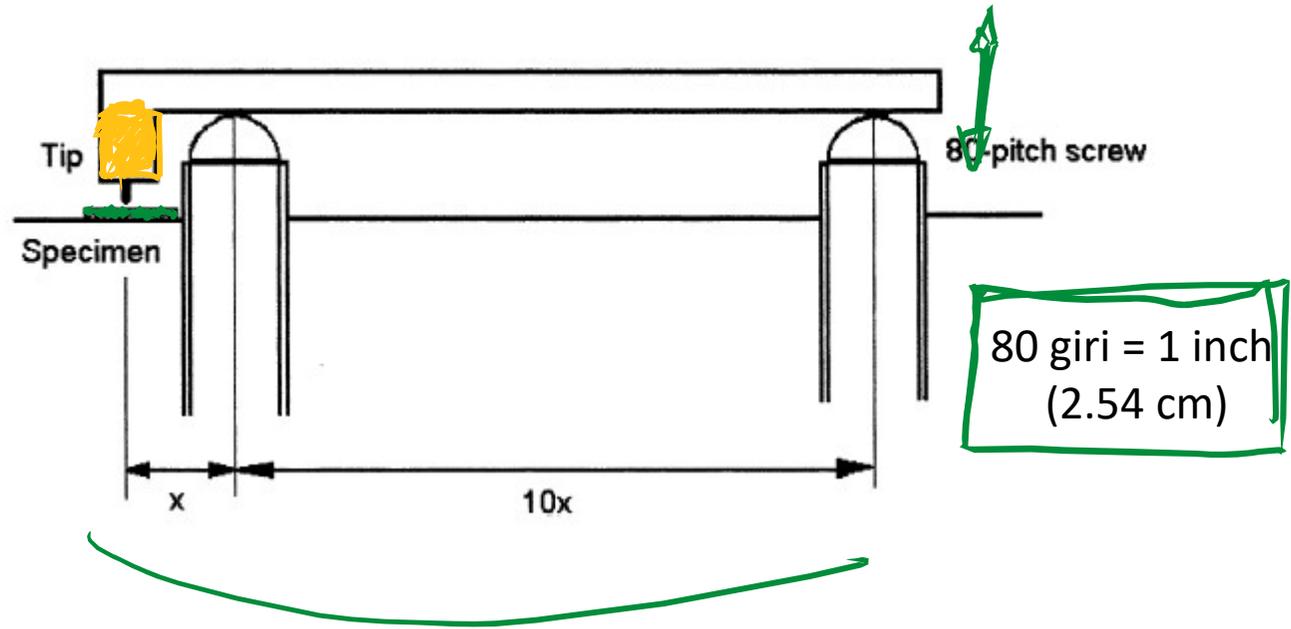


posso avere tunneling

tip \rightarrow sample e metallo
Bias opposto

Per convenzione $V_{bias} < 0 \rightarrow$ tunneling tip \rightarrow sample
 $> 0 \leftarrow$

Movimentazione *coarse*



Rotazione della vite di 1 grado: 880 nm

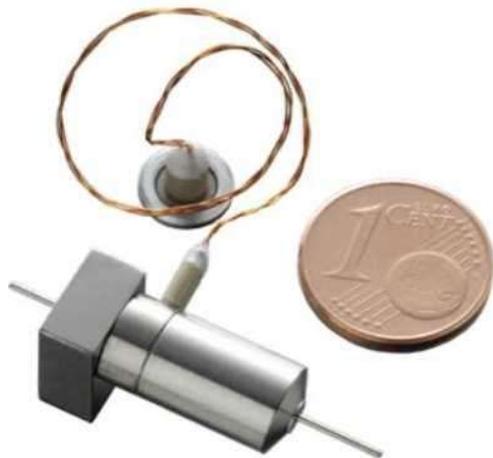
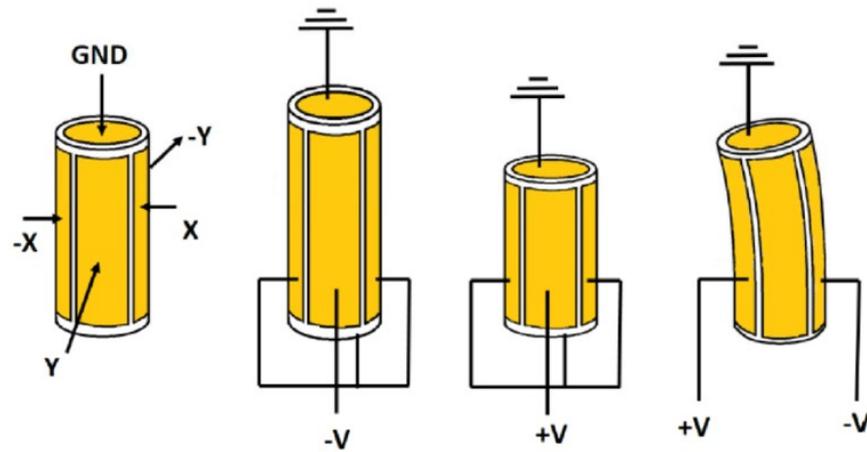
Cantilever 1/10: 88nm

Movimentazione *fine*

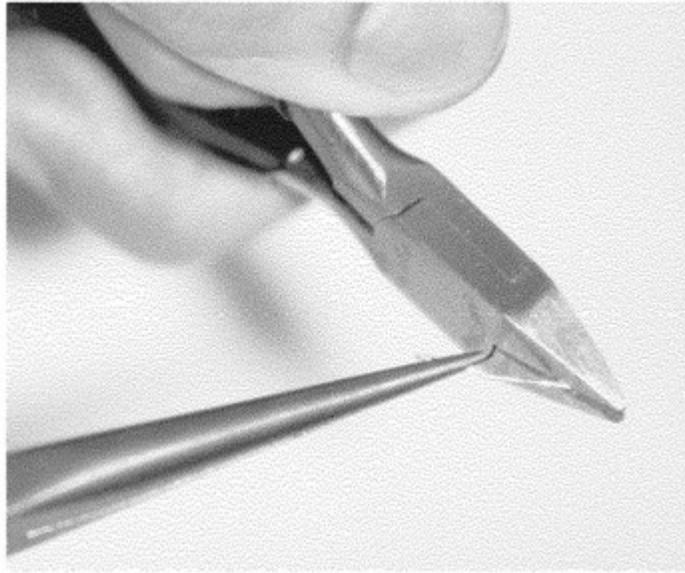


Materiale piezoelettrico

applied V → modifica la struttura



Piombo-zirconato di titanio
 $Pb [Zr_x Ti_{1-x}] O_3$

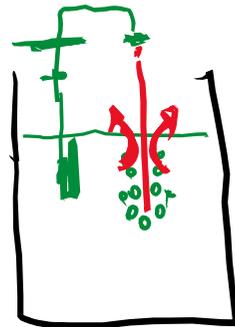


Punta: tungsteno, oro, PtIr

Diametro filo ~ 0.2 mm

1. avere fortuna (nel toplo)

2. chimice
(ETCHING)



Soluzione NaOH
(ca. 2M di NaOH)

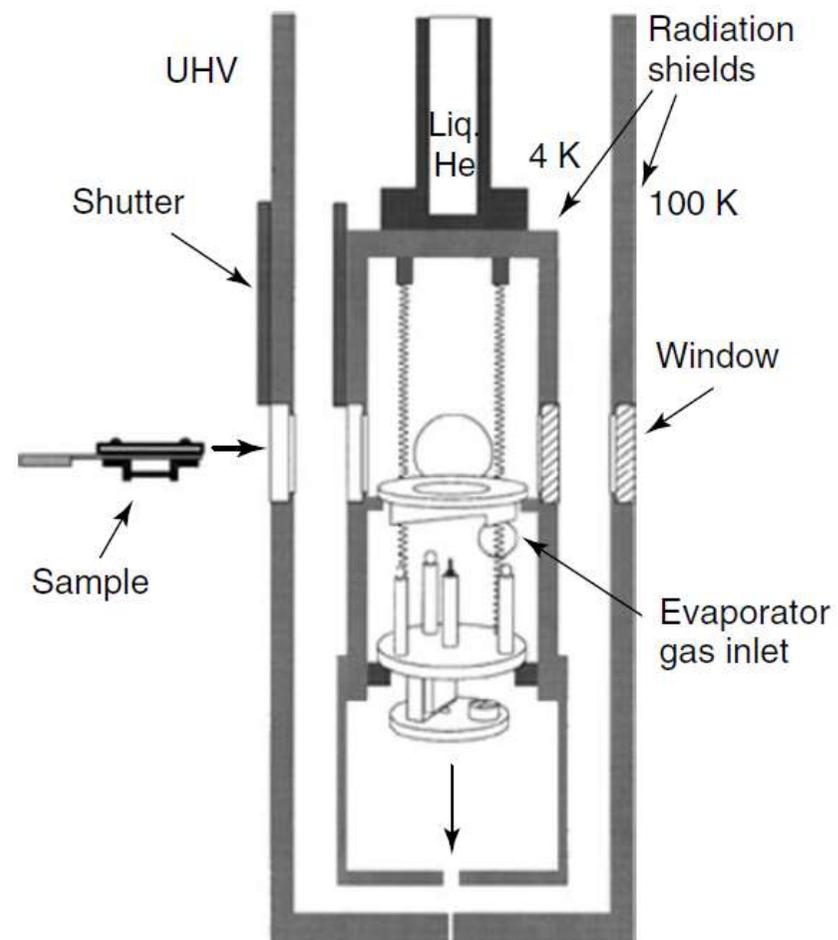
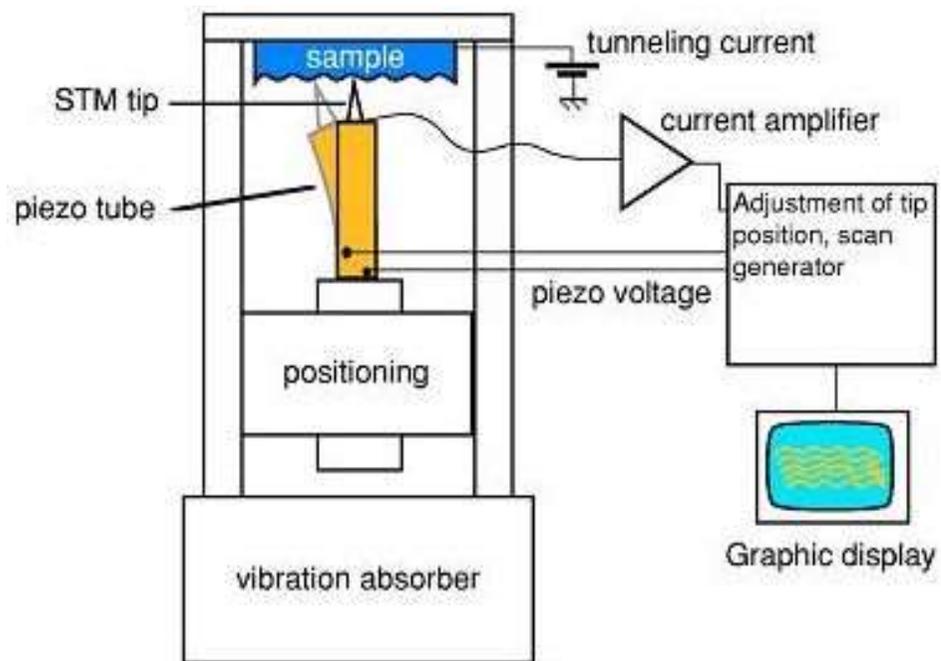
1 filo di W

corrosione del filo, formazione di ioni $\boxed{WO_4^{2-}}$

Nel meniscio con soluzione ho un'induzione

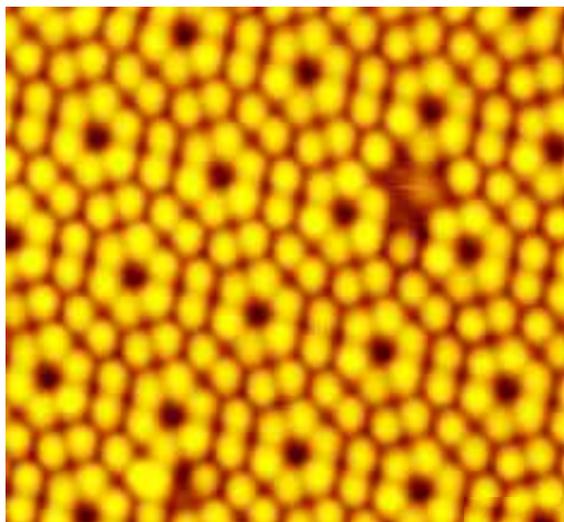


Raffreddamento e isolamento dalle vibrazioni

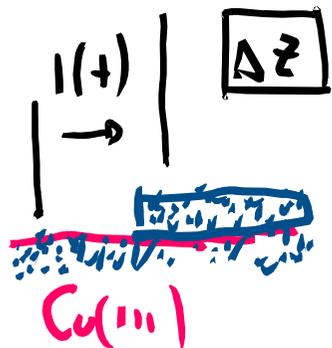


Imaging

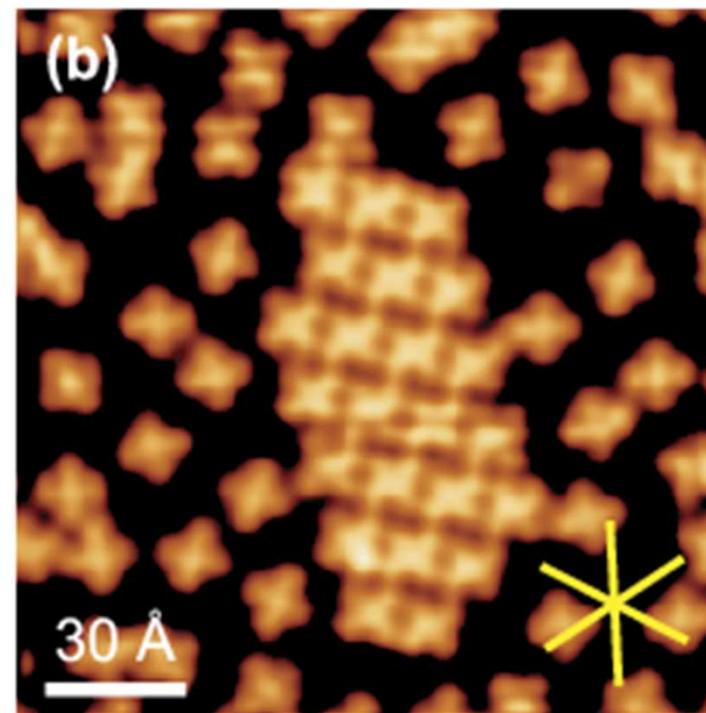
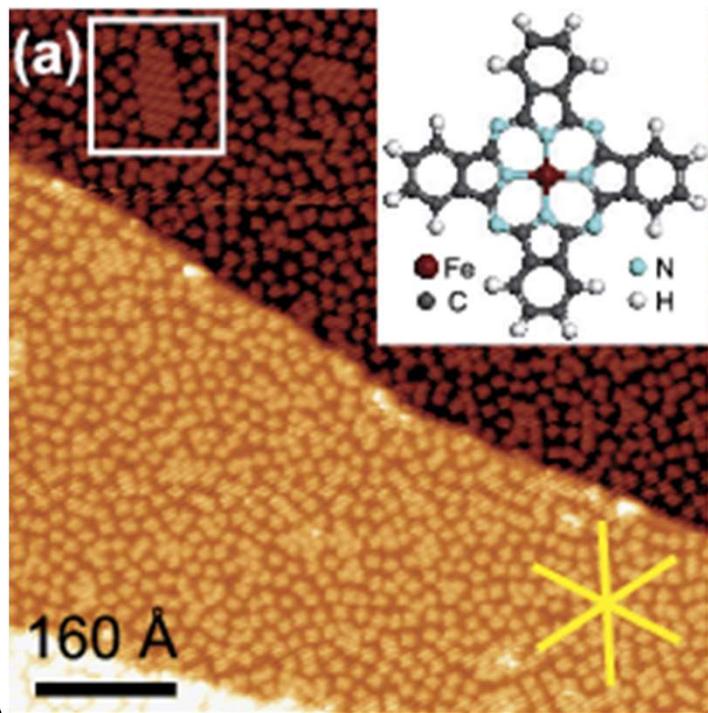
Si (111) 7x7



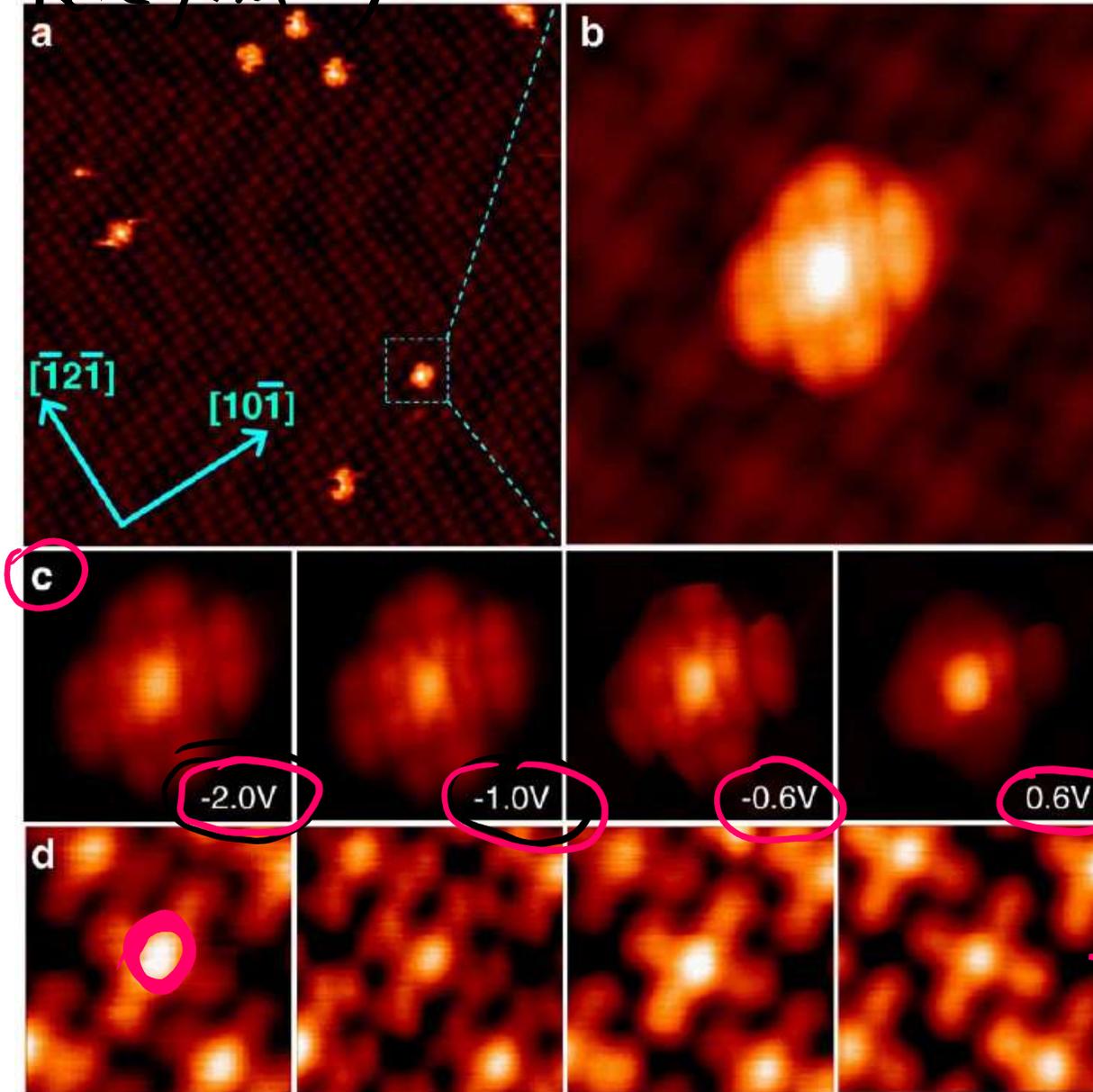
0.63 ML \pm 0.05 ML



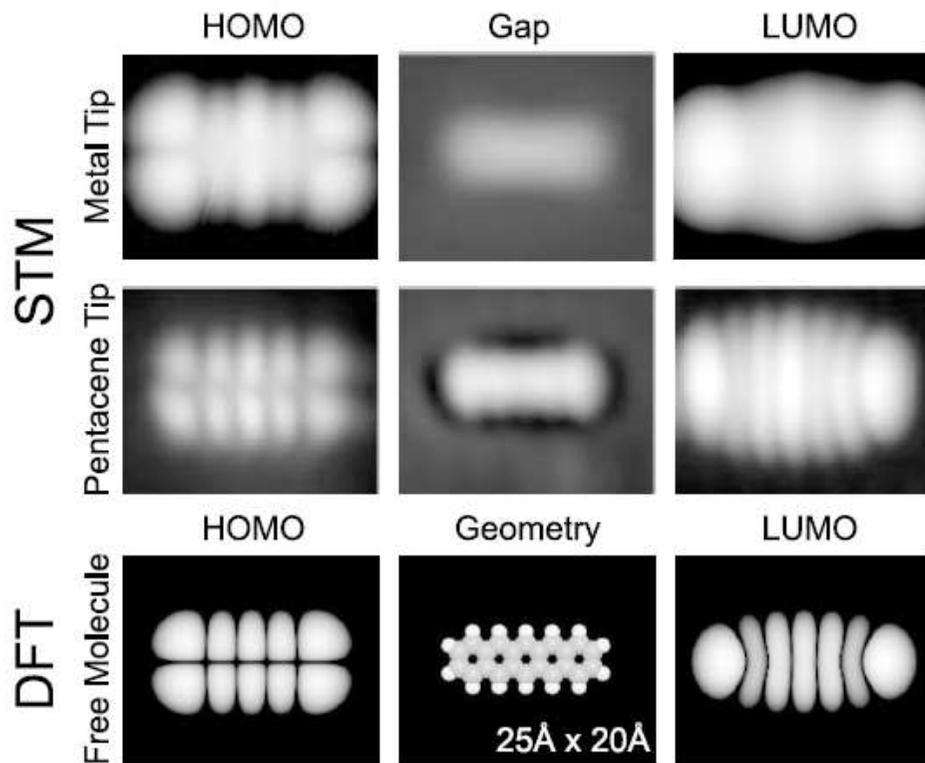
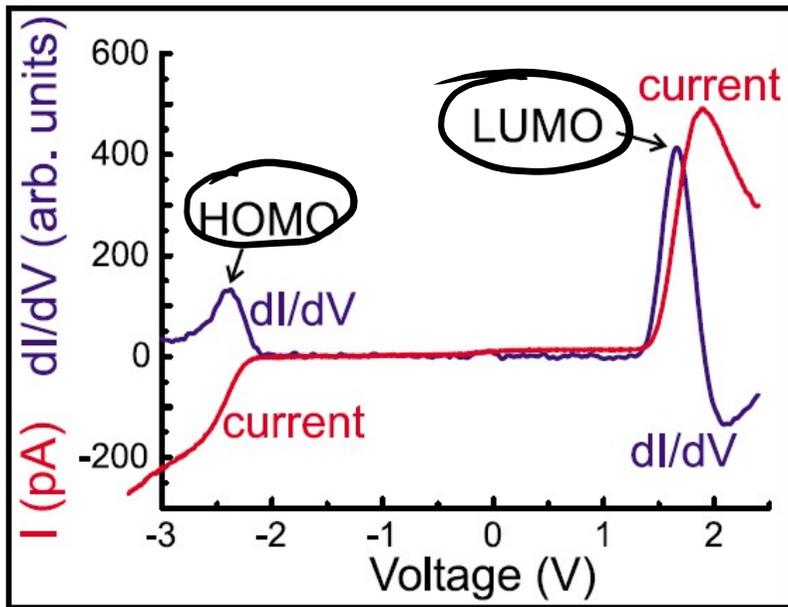
FePc/Cu(111)



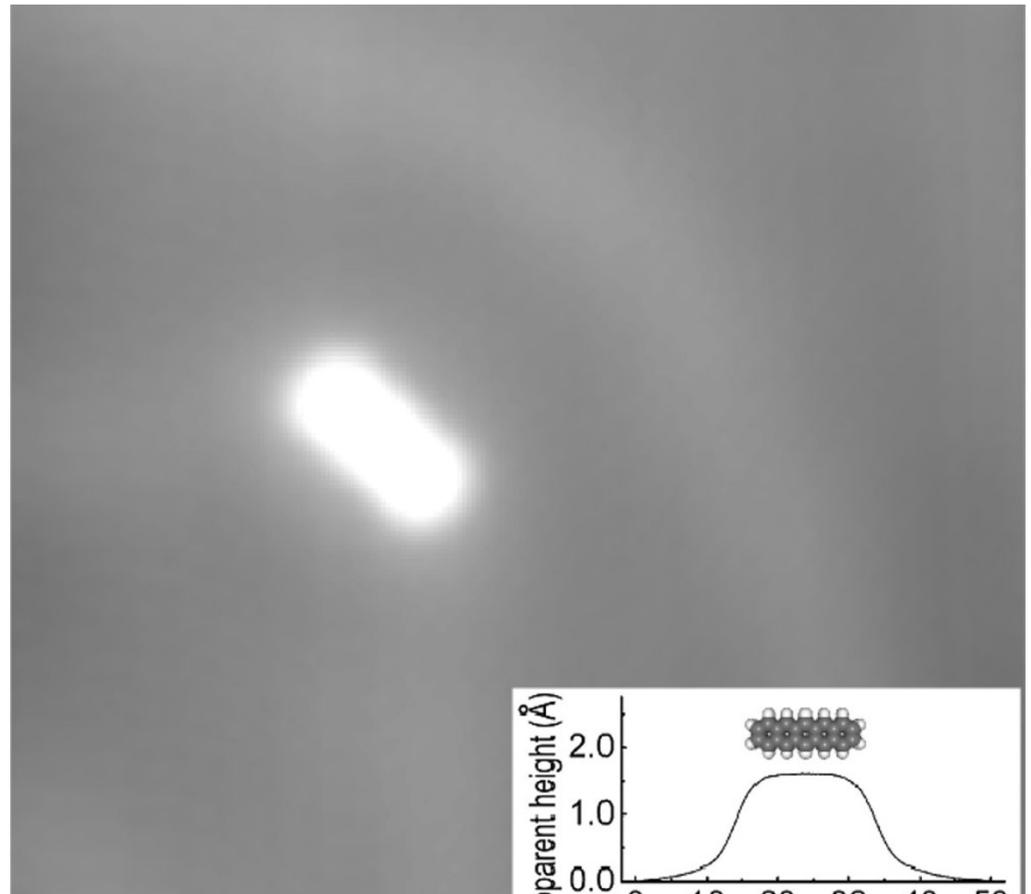
FePc / Au(111)



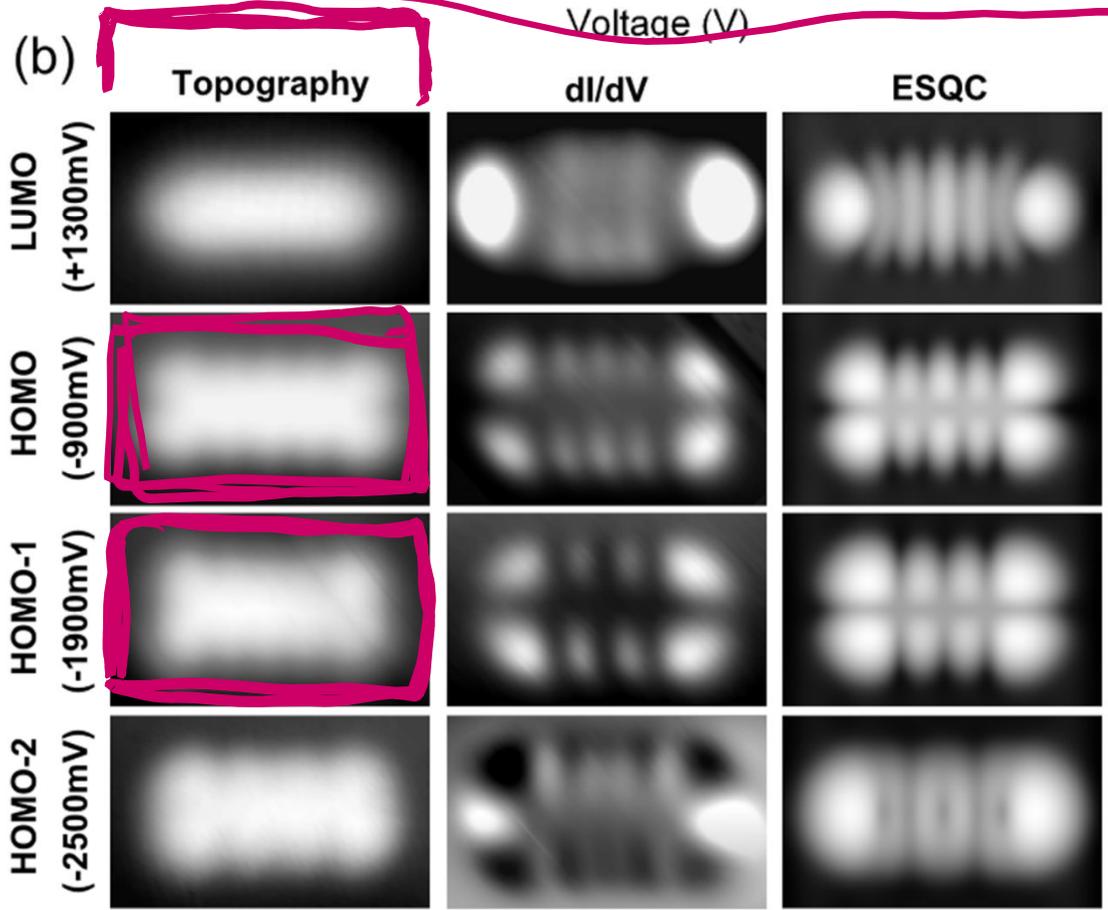
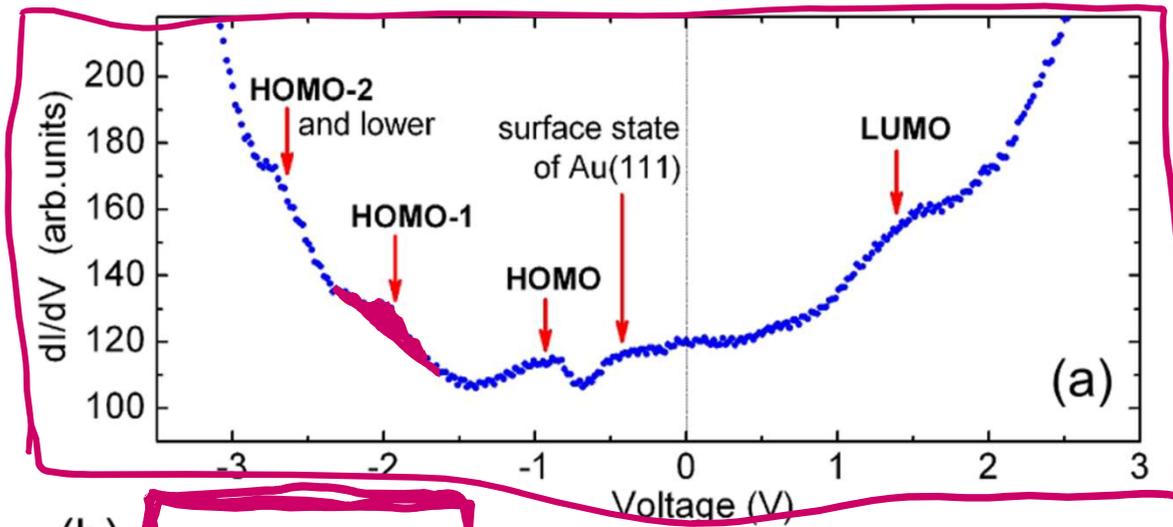
ibridizzazione
con il substrato



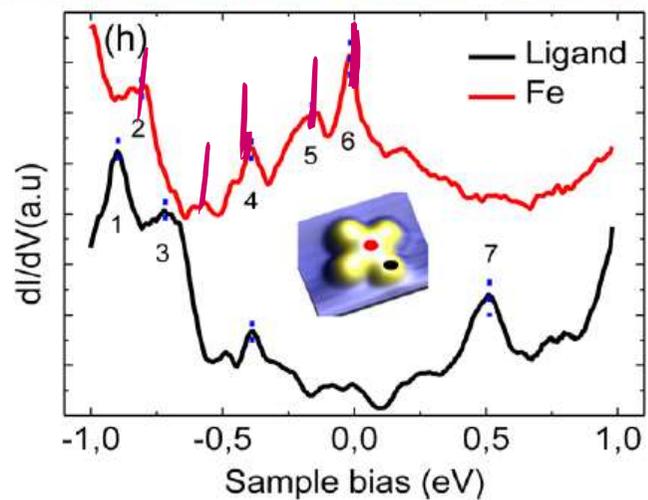
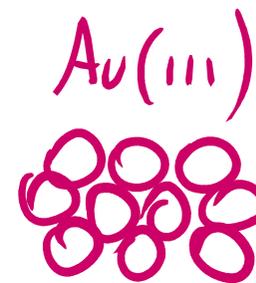
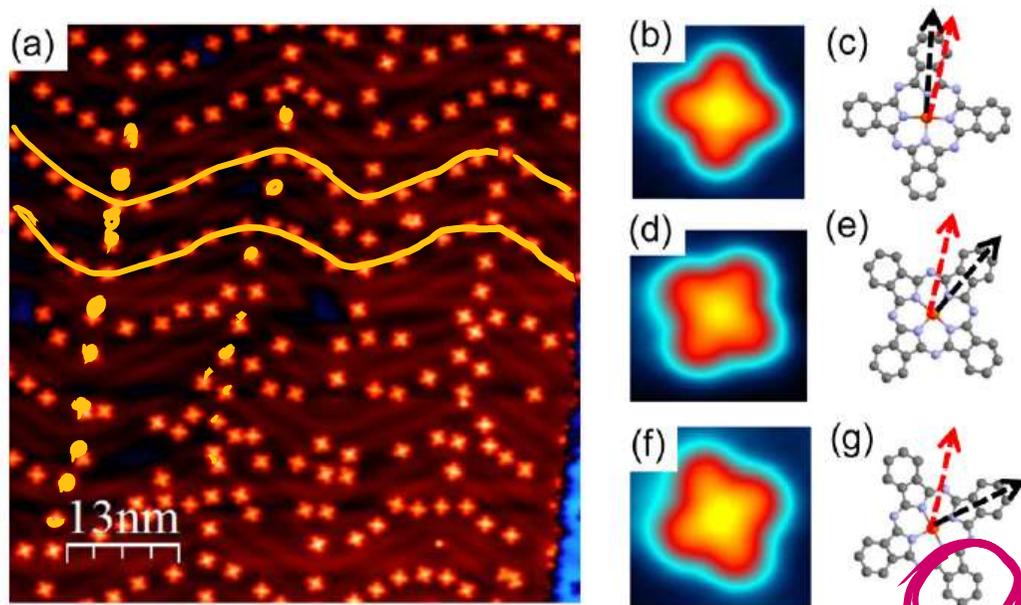
→ Tip functionalization:
functionaliser le pointe
con une molecule



PRL **102**, 176102 (2009)

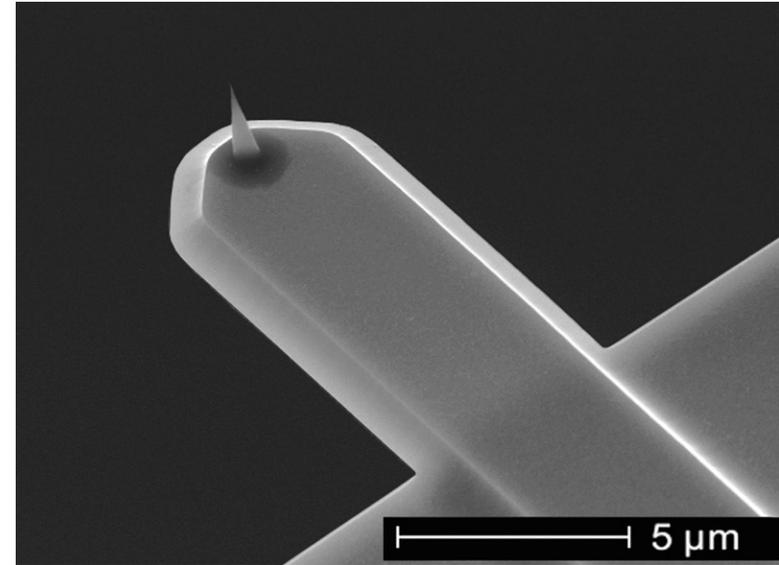
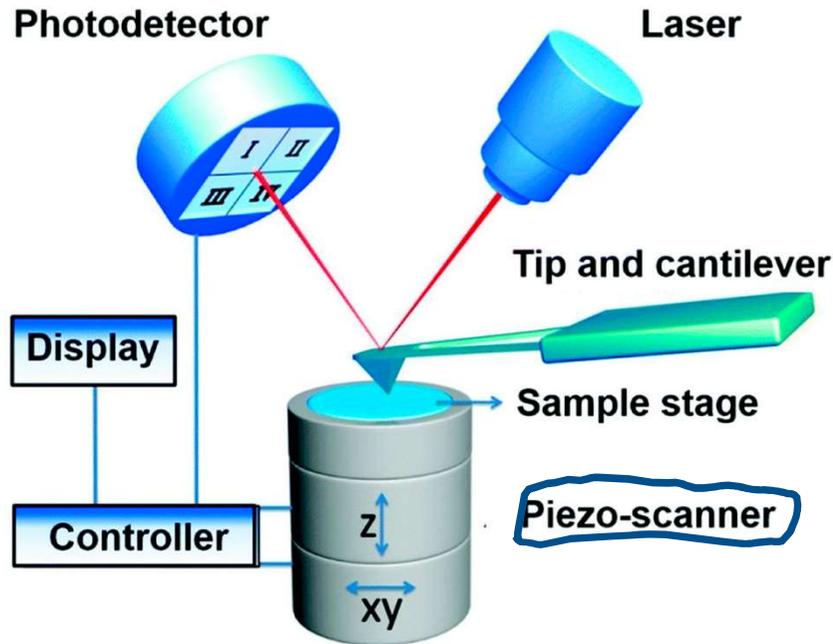


STS (Scanning Tunneling Spectroscopy)



J. Phys. Chem. Lett. 2014, 5, 3175–3182

AFM – Atomic Force Microscope



CONTACT MODE



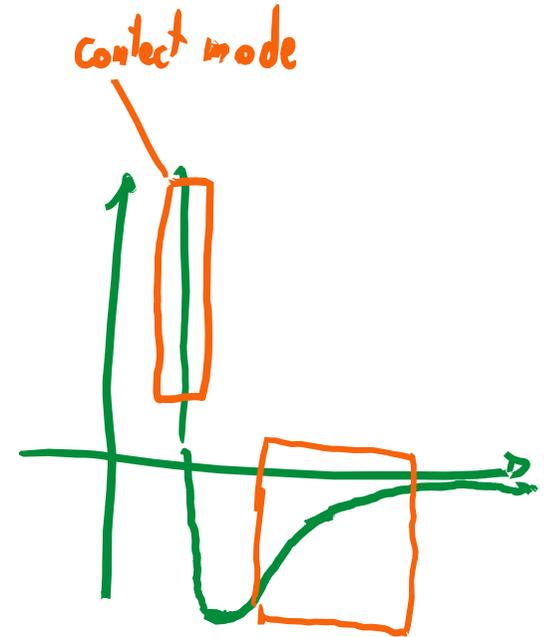
→ costruisco una mappa z

→ con un feedback
sulla posizione del raggio
riflesso
↓
correggo z con piezo elettrico

CONTACT MODE

→ rischio di modificare la superficie

NO-CONTACT MODE

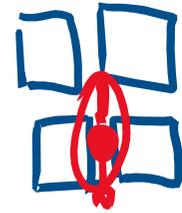
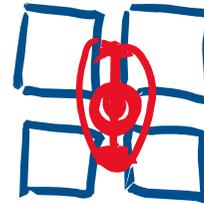


- Mettere il cantilever in oscillazione:

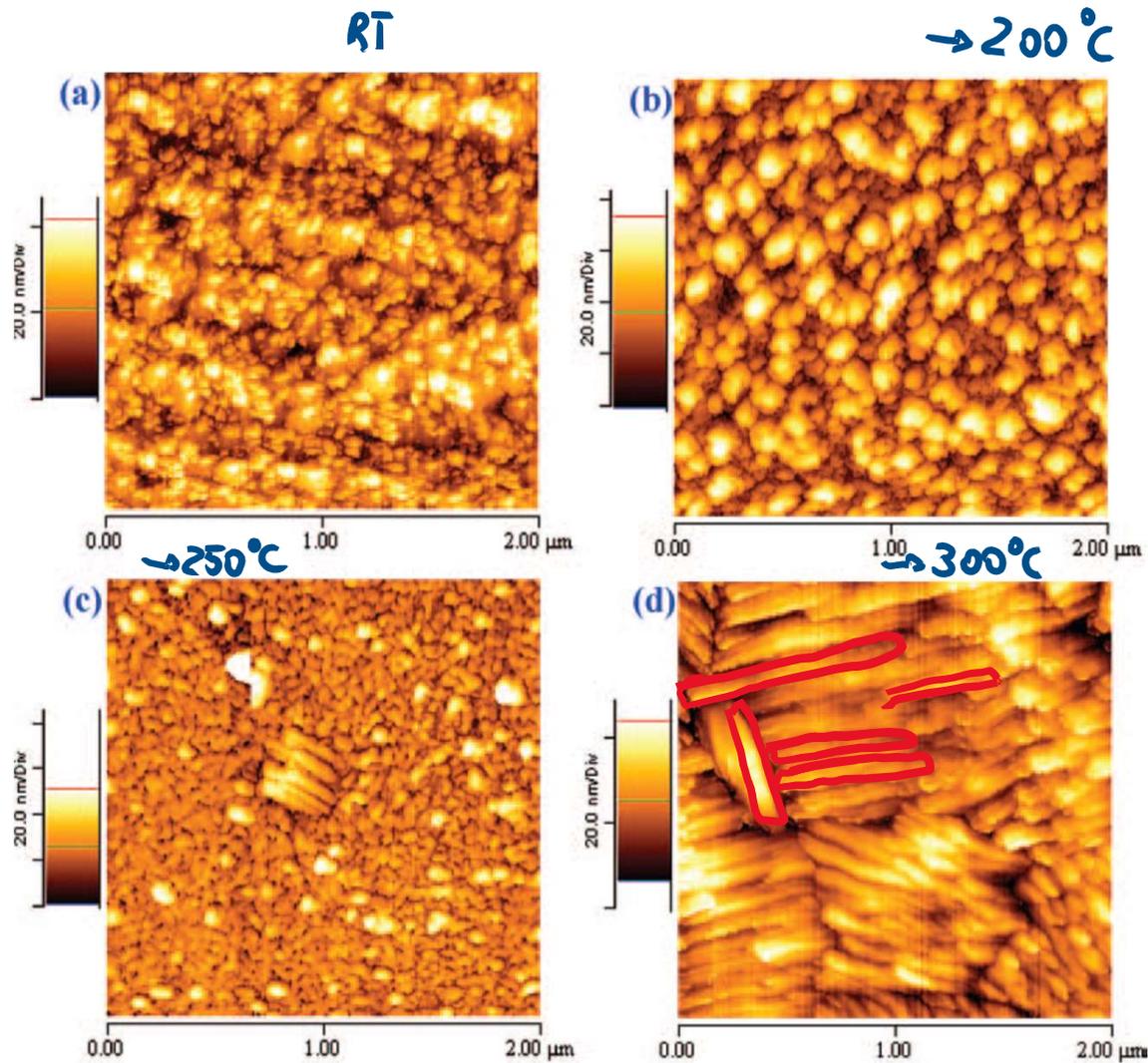


- Mi avvicino alla superficie

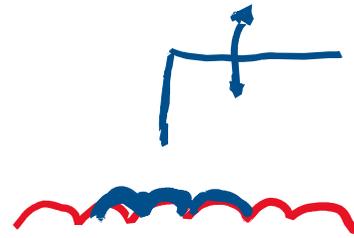
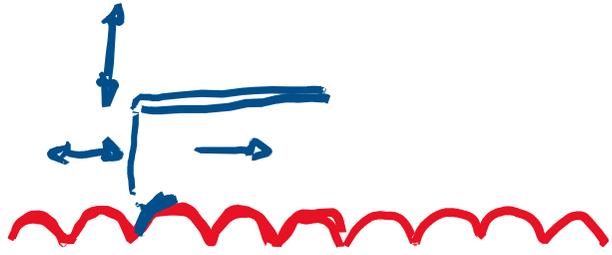
→ la punta sente attrazione



Contact AFM: morfologia di film organici



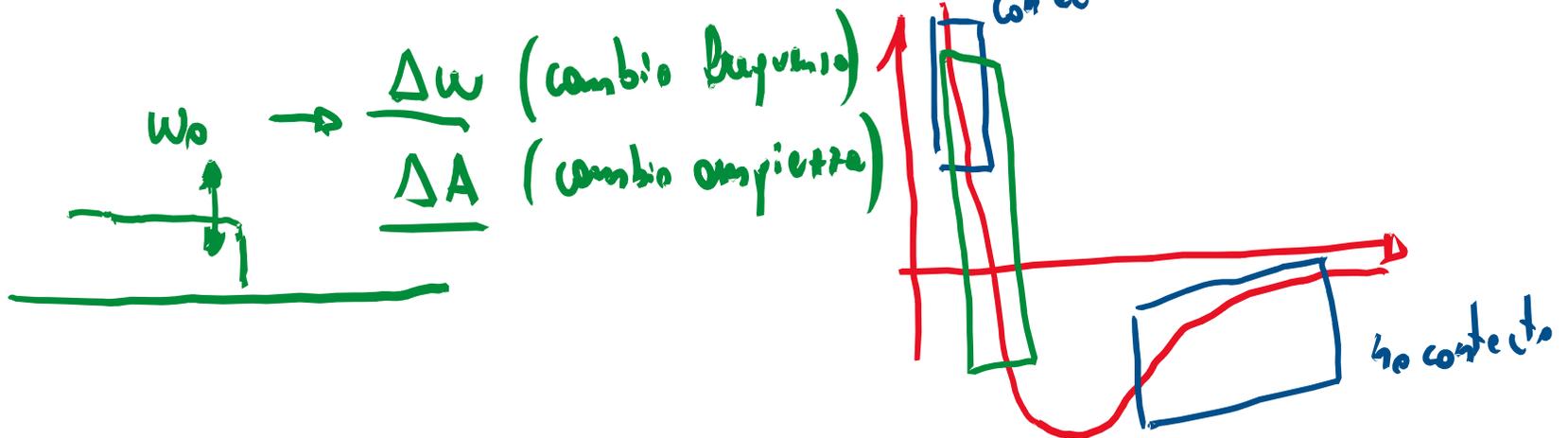
50 nm di ZnPc su Si(111).

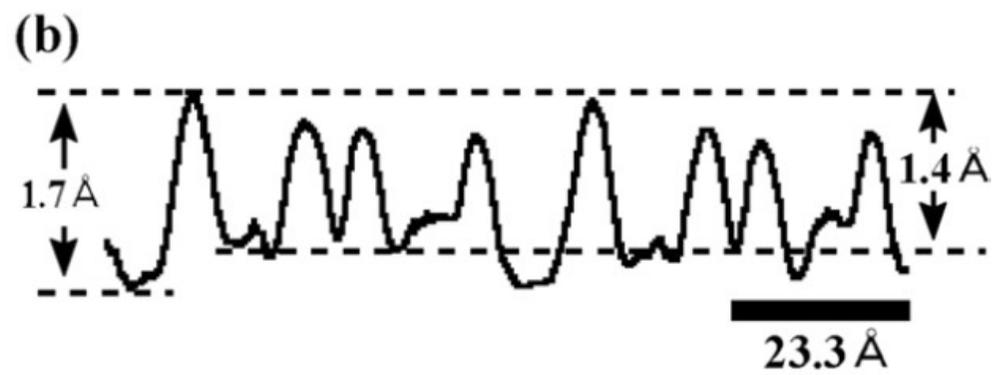
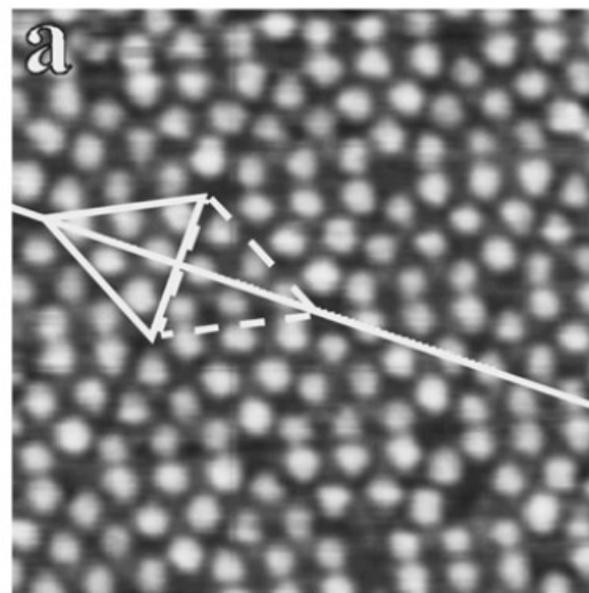
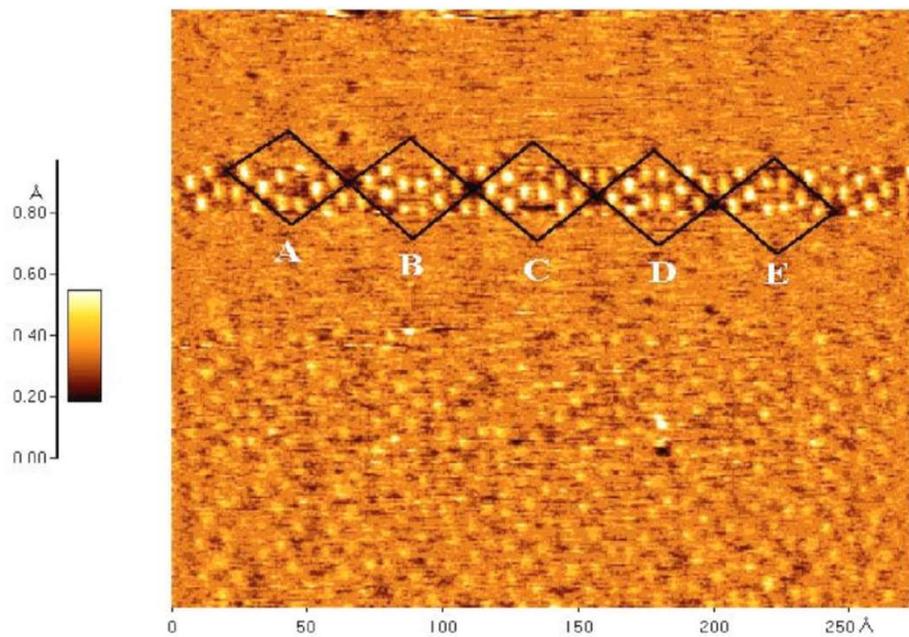


NON HO RISOLUZIONE ATOMICA

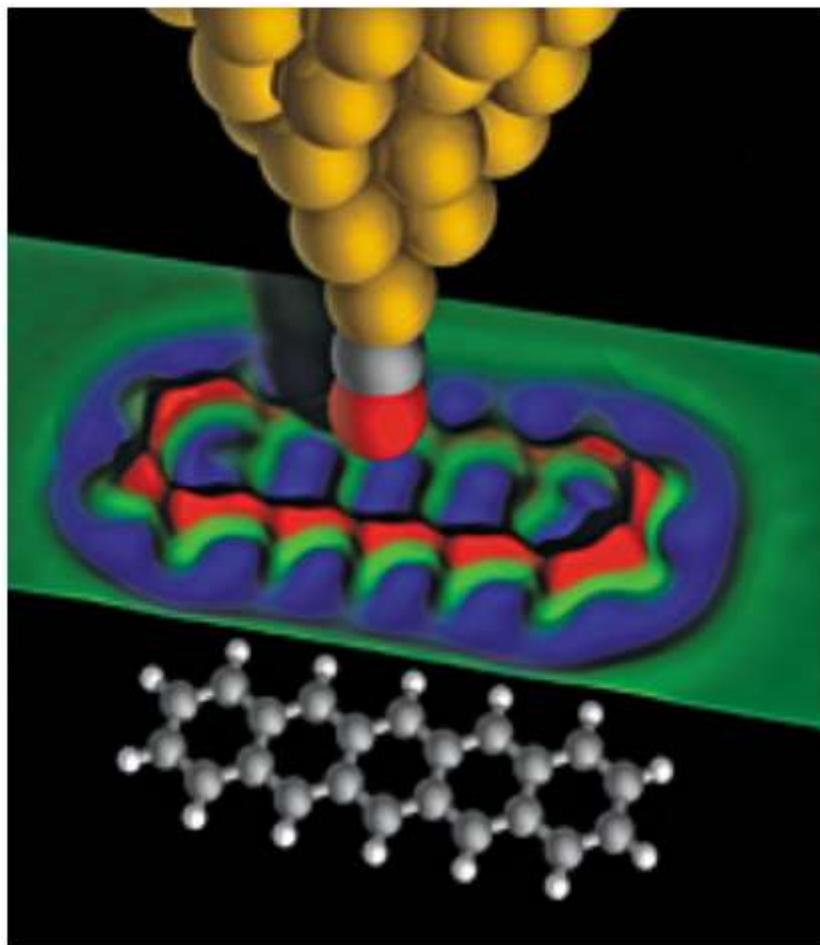
③ TAPPING MODE

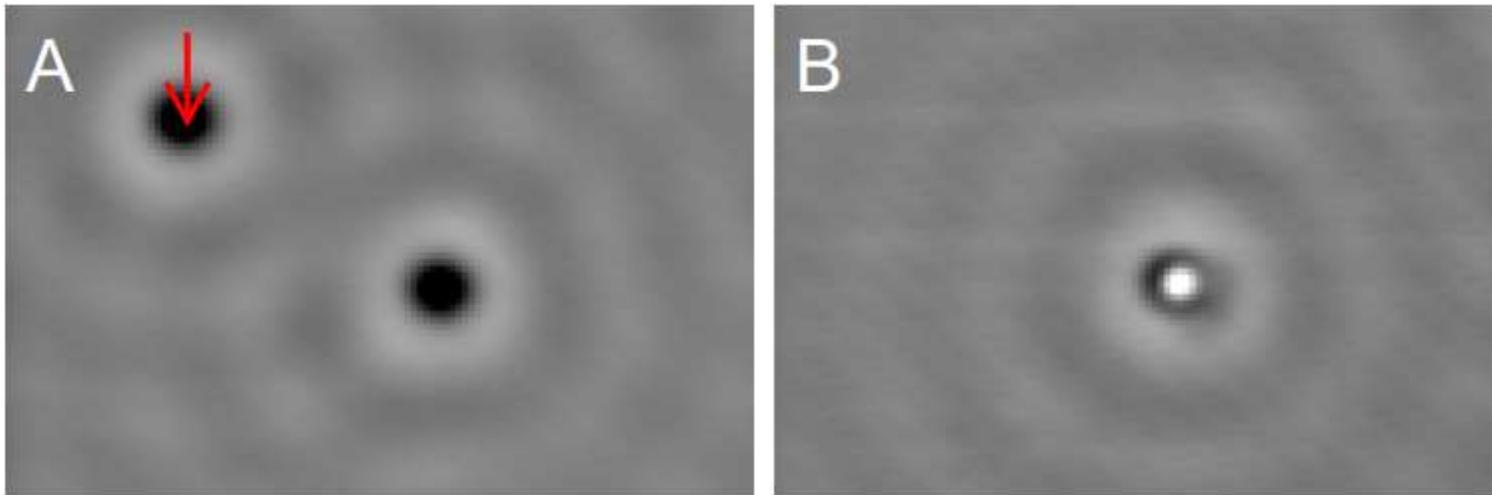
NO-CONTACT pro con contatto:



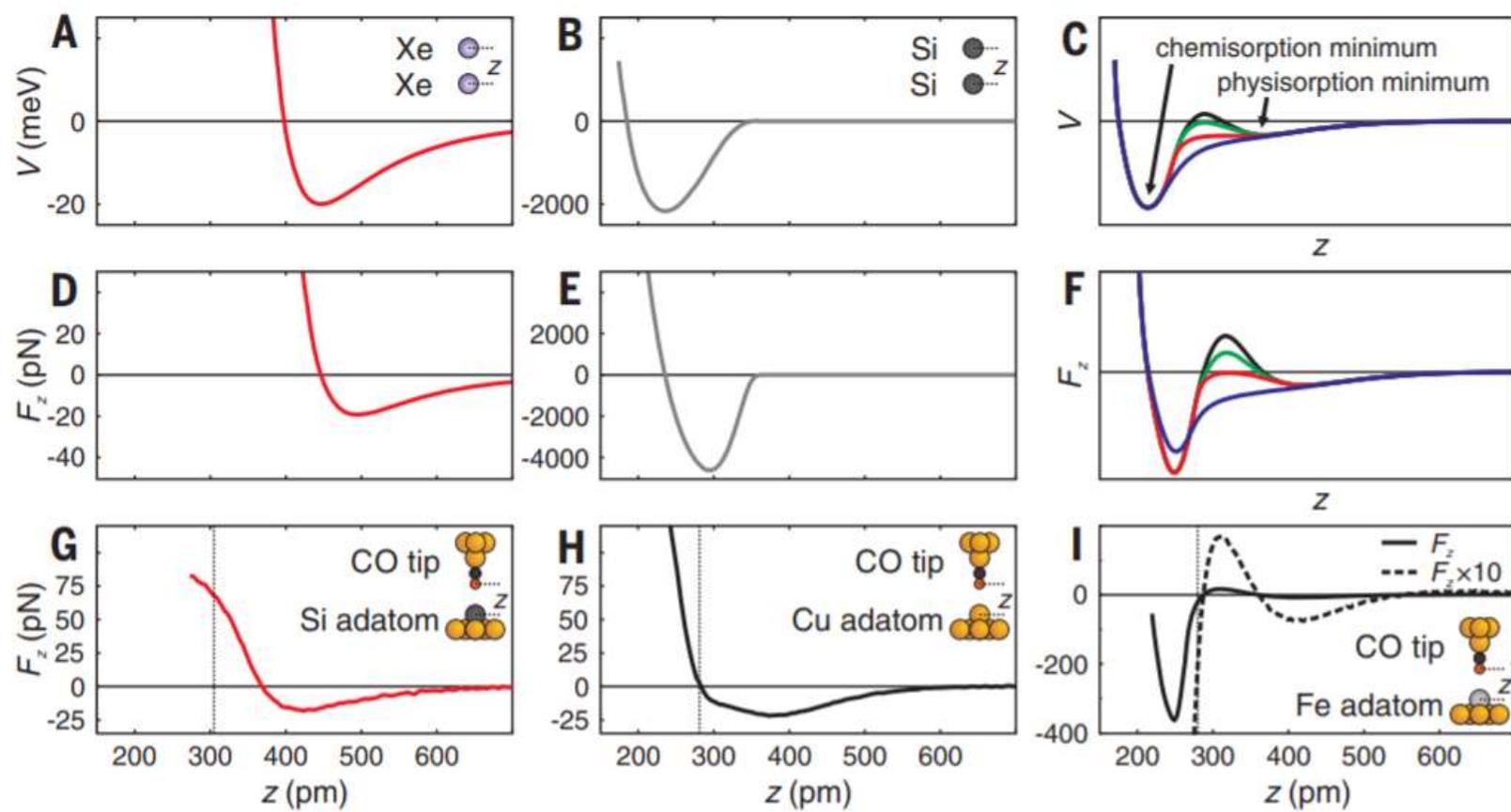


Per rendere l'interazione punta-campione il più possibile sensibile a minimi cambiamenti della struttura elettronica del campione, si funzionalizza la punta di un STM con una molecola di CO e si usa STM in modalità AFM, con una frequenza di oscillazione di cui si misurano le variazioni.



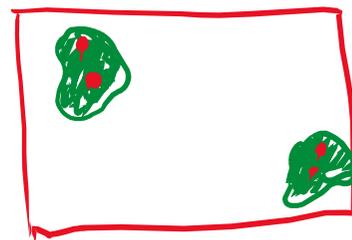


Gross et al., Science 2009, vol. 325, 1110-1113



Huber *et al.*, *Science* **366**, 235–238 (2019)

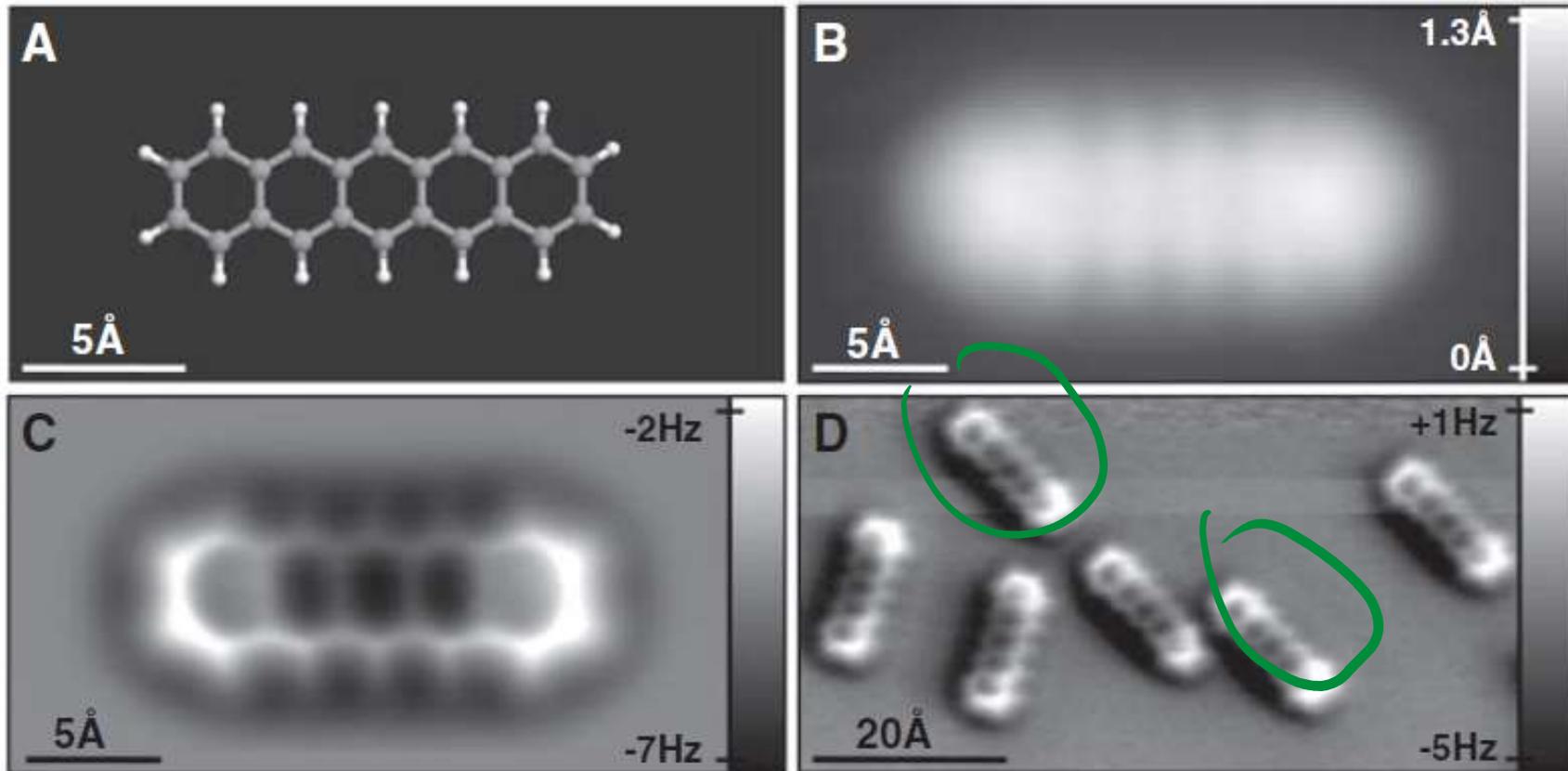
1. Creare delle isole NiCl sulle superficie



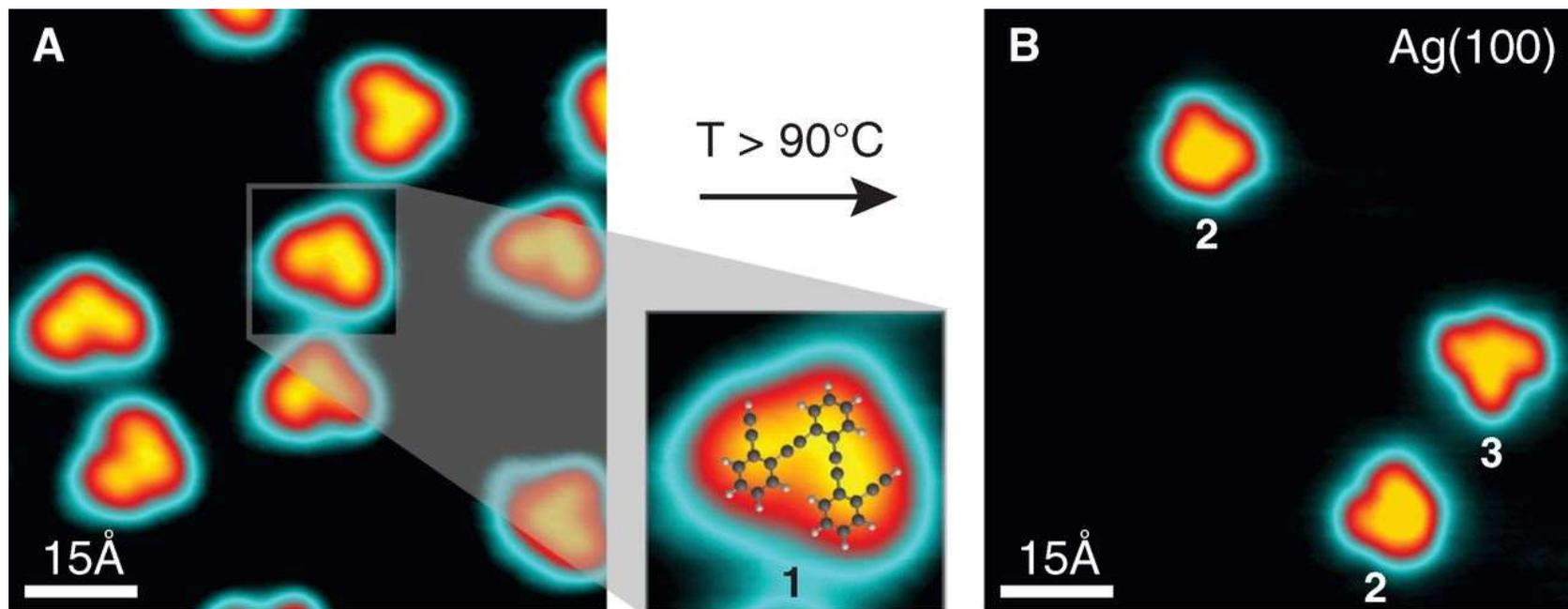
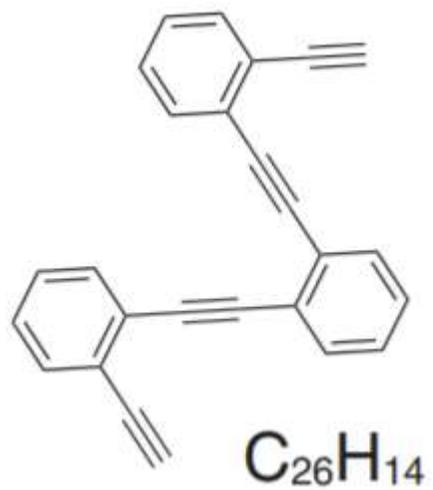
2. Deposito poche molecole di CO

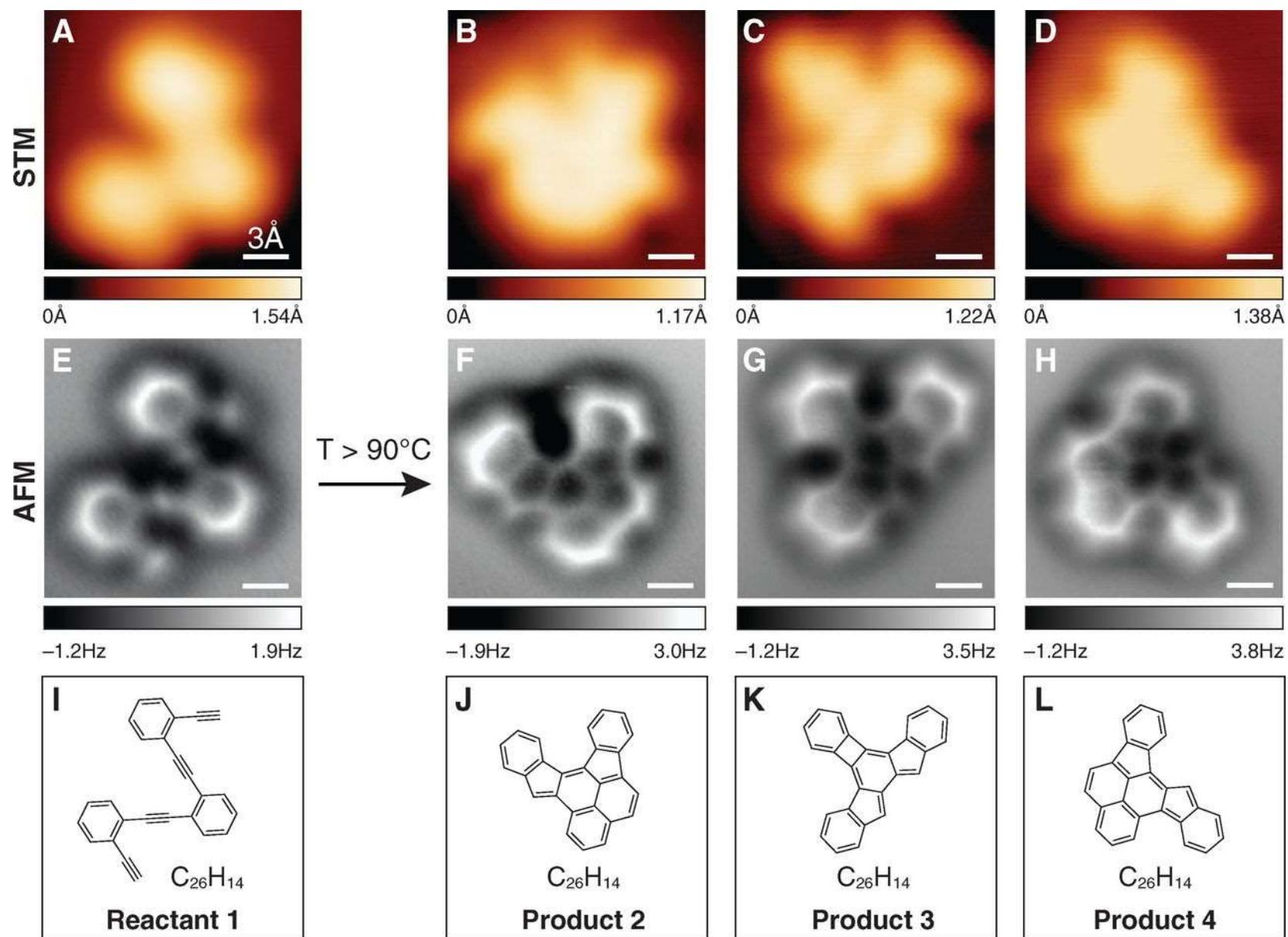
3. Recupero con la punta 1 molecola di CO (tip functionalization)

4. Deposito molecole che mi interessano e le guardo —



10.2 - 0.4 Å





Naphthalenetetracarboxylic diimide

NTCDI

