

Зондовые методы

За пределами топографии

Васильев Сергей Юрьевич

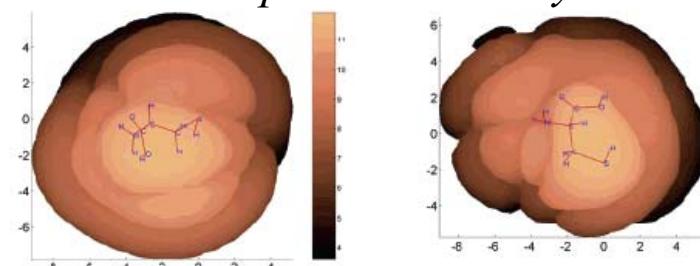
(wasq@elch.chem.msu.ru)



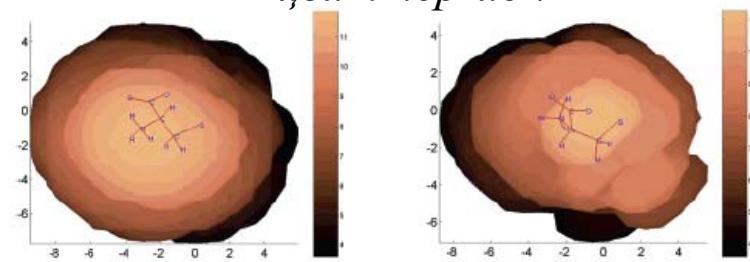
Презентация доступна в интернет:
<http://www.elch.chem.msu.ru/wasq/zond2.pdf>

Моделирование контрастов: цистеин/Au(111)

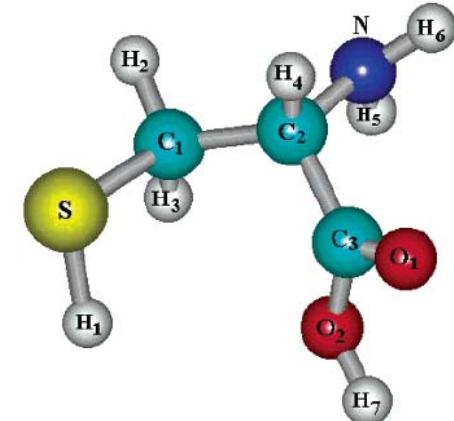
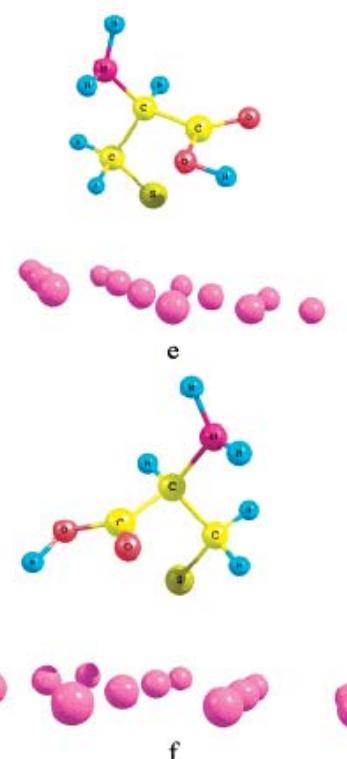
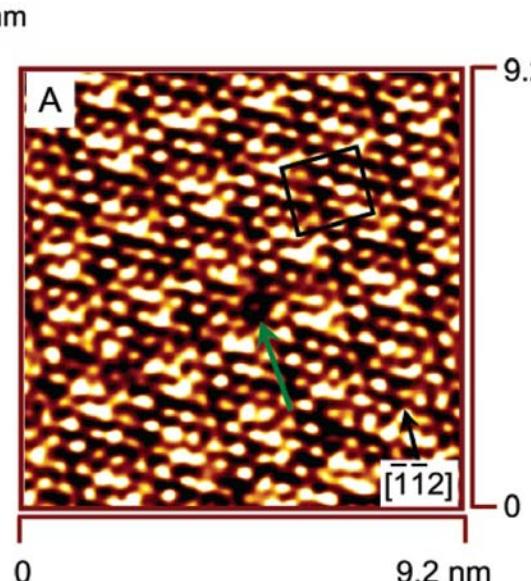
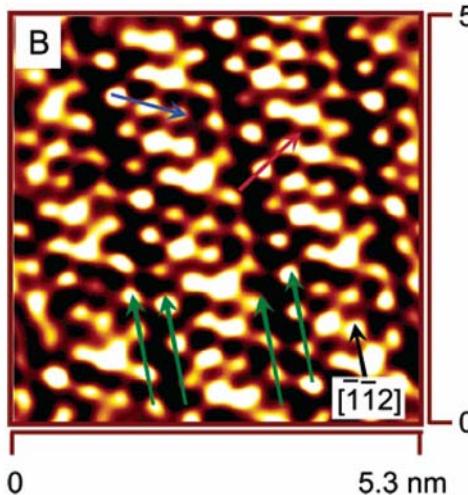
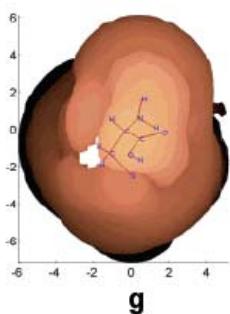
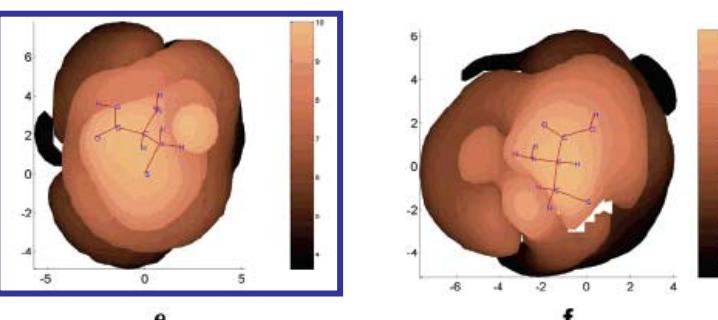
нейтральная молекула



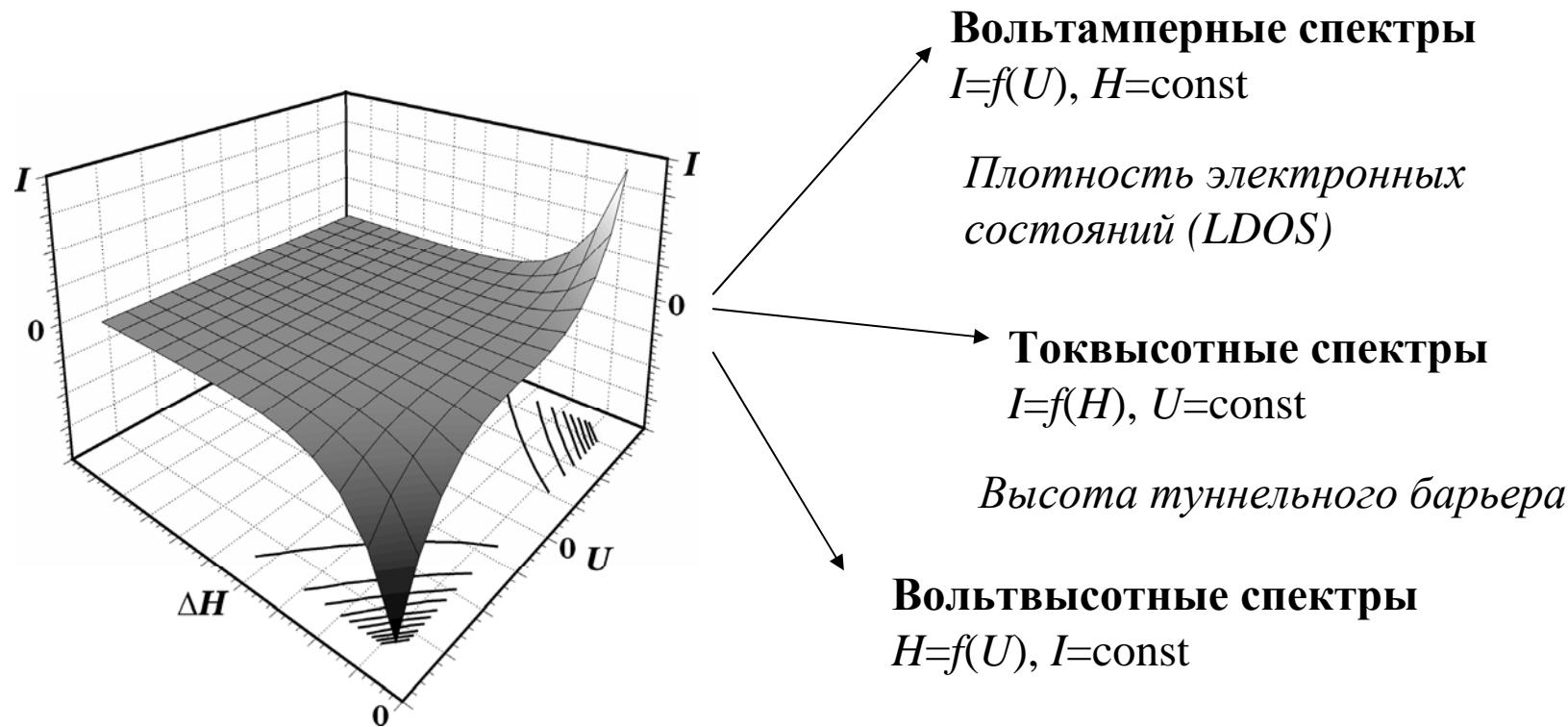
цвиттер-ион



радикал



СТМ: Локальные туннельные спектры

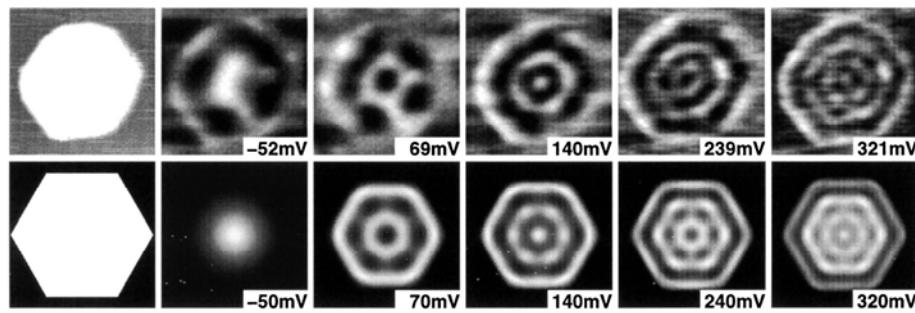


Спектроскопическое картирование

Ag/Ag(111)

Current imaging tunneling spectroscopy (CITS)

Дифференциальное картирование $dI/dU, dI/dH$

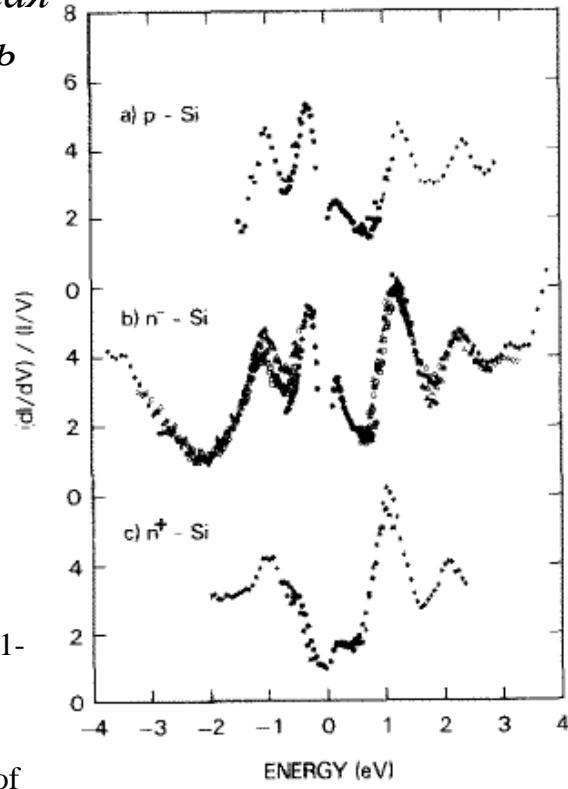


СТМ: Вольтамперные спектры

$$I(U) \propto \int_0^{eU} \rho_s(E) \rho_t(E - eU) T(E, U) dE$$

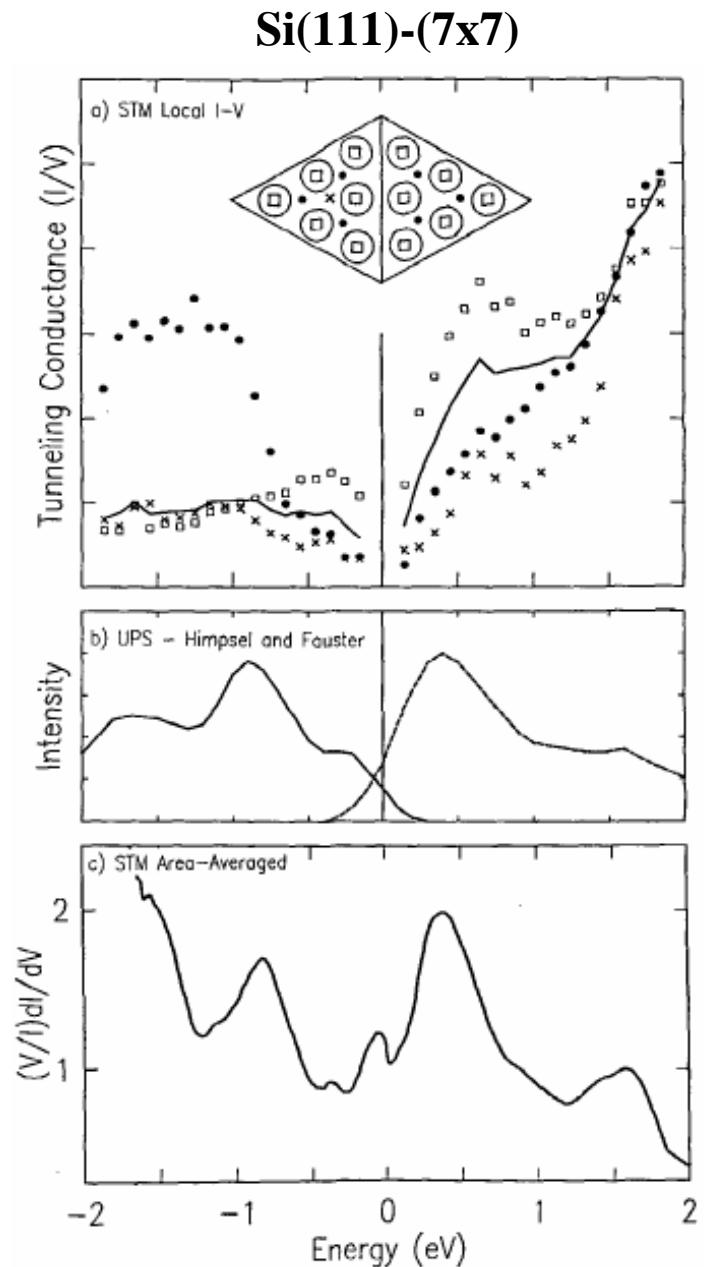
$$\frac{dI / dU}{I / U} = \frac{\rho_s(eU) \rho_t(0) + A(U)}{B(U)}$$

Нормализованная проводимость



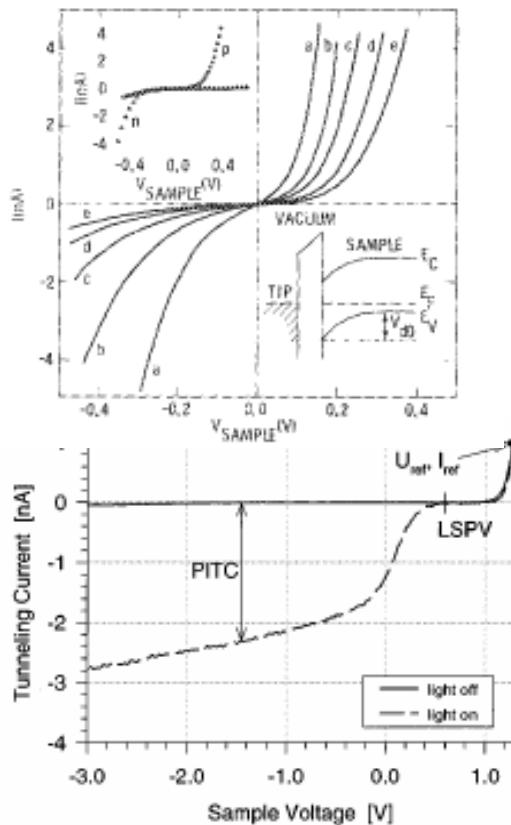
R.J.Hamers, Atomic-resolution surface spectroscopy with the scanning tunneling microscope, Annu.Rev.Phys.Chem. 40(1989)531-559

R.M.Feenstra, J.A.Stroscio, A.P.Fein, Tunneling spectroscopy of the Si(111)2x1 surface, Surf.Sci. 181(1987)295-306

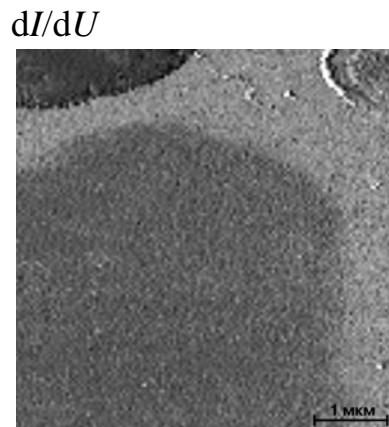
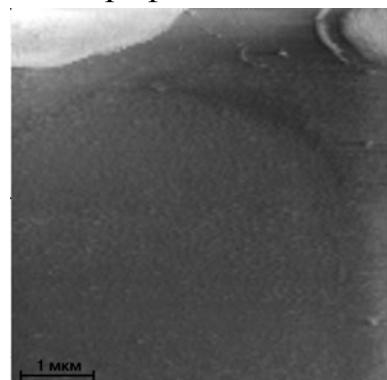


СТМ: Вольтамперные спектры: полупроводники

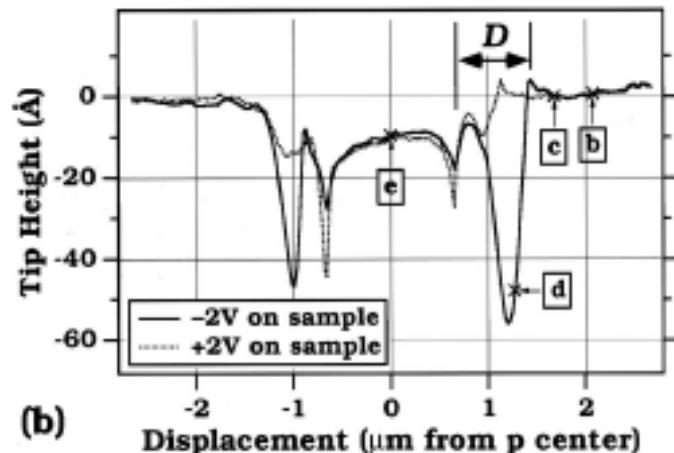
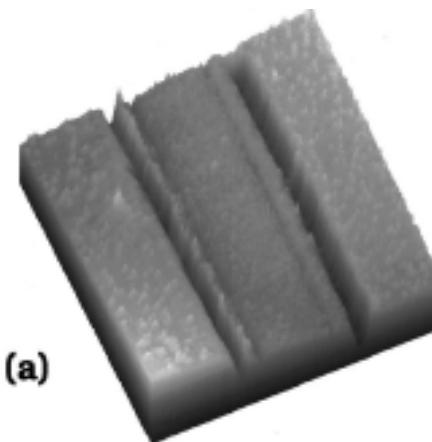
Гетероструктура металл/
изолятор/полупроводник (MIS)
Барьер Шоттки



Керамика SnO_2
топография



pn-переход



L.D.Bell, W.J.Kaiser, M.H.Hecht, F.J.Grunthaner, Direct control and characterization of a Schottky barrier by scanning tunneling microscopy, Appl.Phys.Lett. 52(1988)278-280

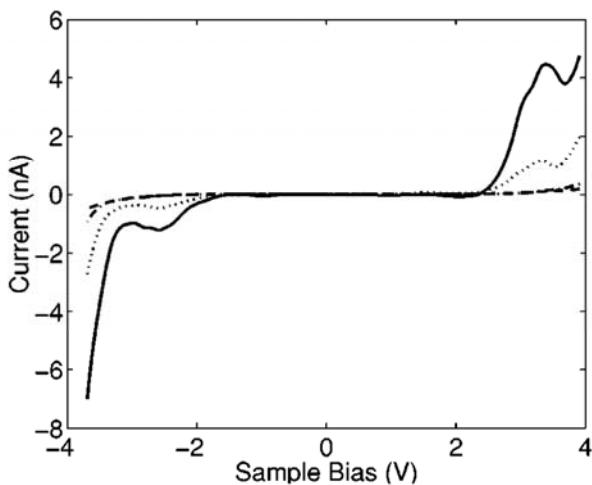
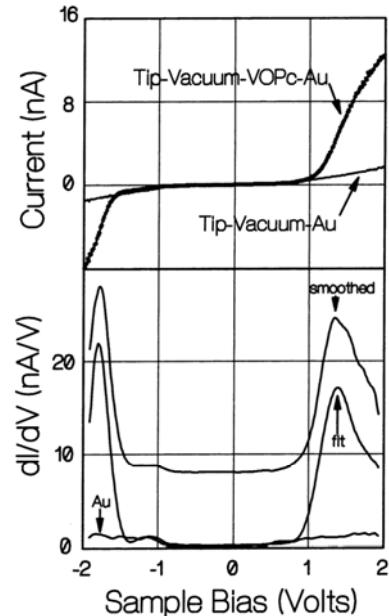
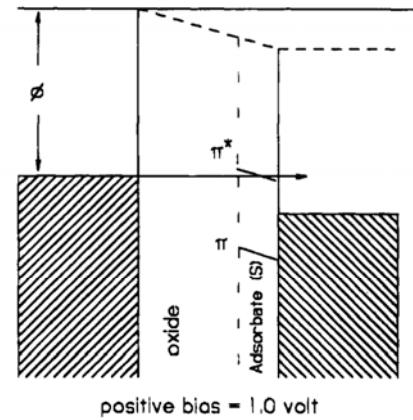
Ch.Sommerhalter, Th.W.Matthes, J.Boneberg, P.Leiderer, M.Ch.Lux-Steiner, Tunneling spectroscopy on semiconductors with a low surface state density, J.Vac.Sci.Technol.B 15(1997)1876-1883

M.L.Hildner, R.J.Phaneuf, E.D.Williams, Imaging the depletion zone in a Si lateral *pn* junction with scanning tunneling microscopy, Appl.Phys.Lett. 72(1998)3314-3316

СТМ: Вольтамперные спектры: частицы в зазоре

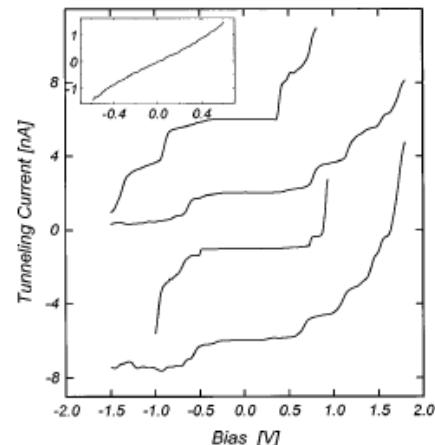
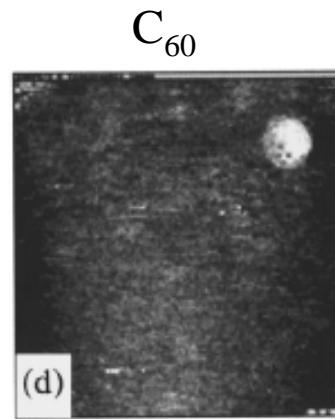
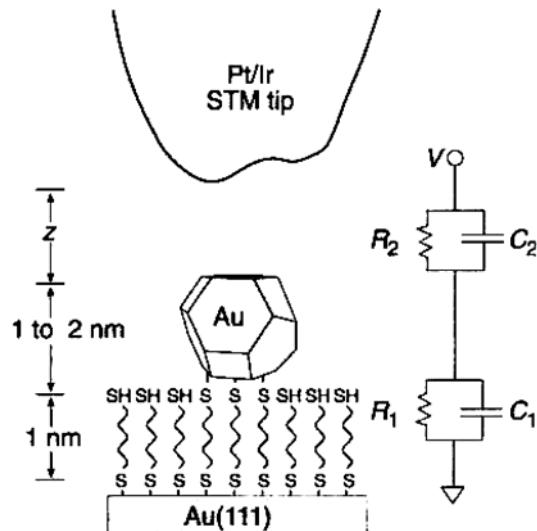
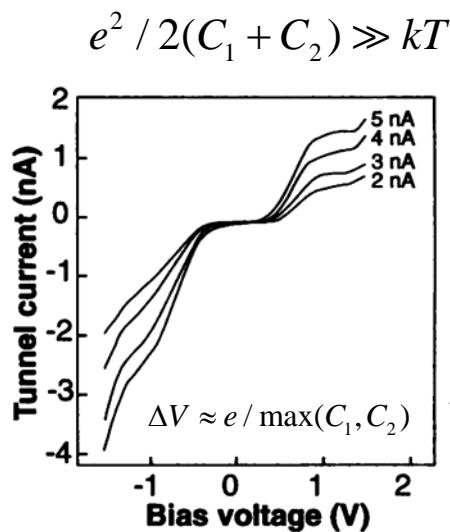
Молекулы

Orbital mediated tunneling
Negative differential resistance



Наночастицы

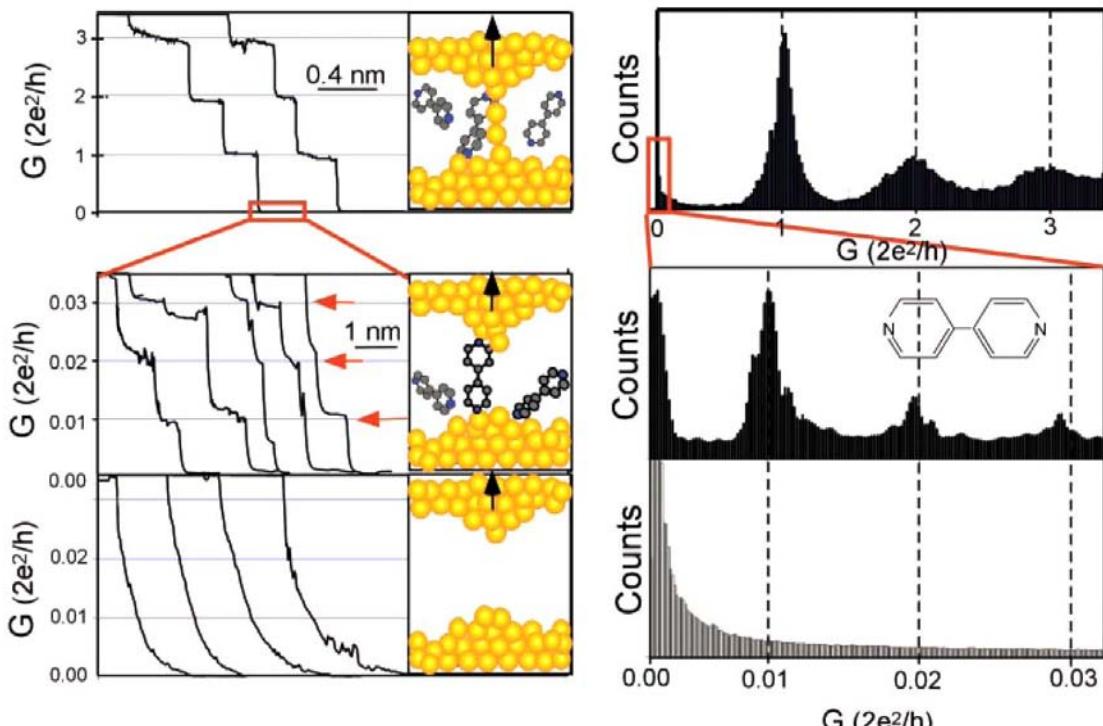
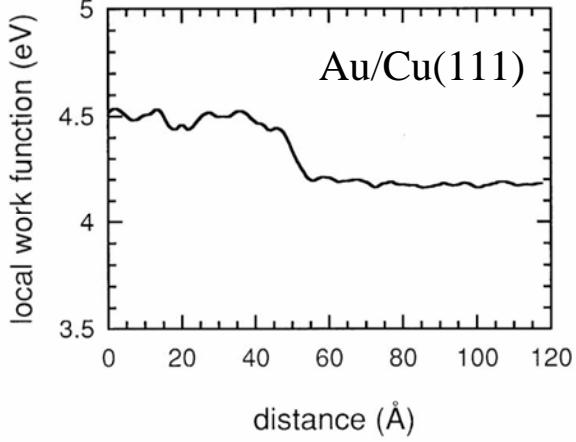
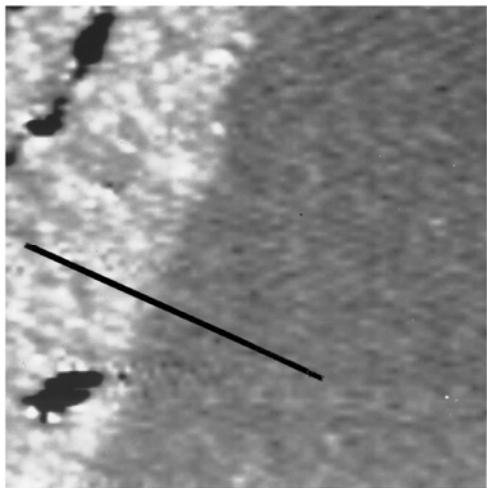
Coulomb blockade
Coulomb staircase



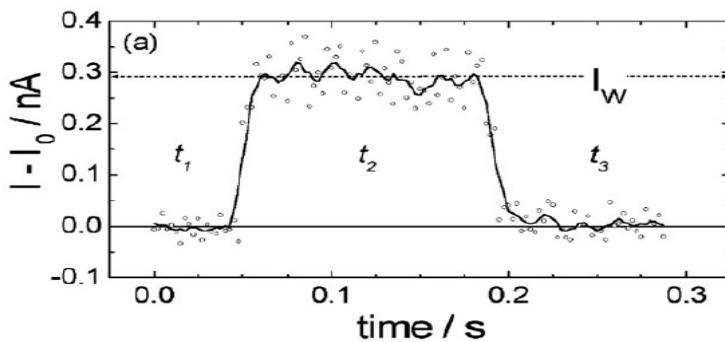
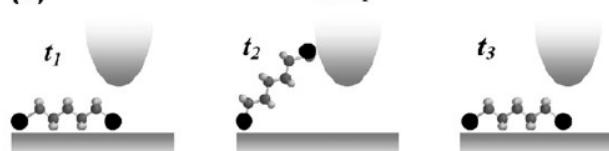
СТМ: Токвысотные спектры

$$G = \frac{I}{U} \propto \exp(-1.025\sqrt{\phi}H)$$

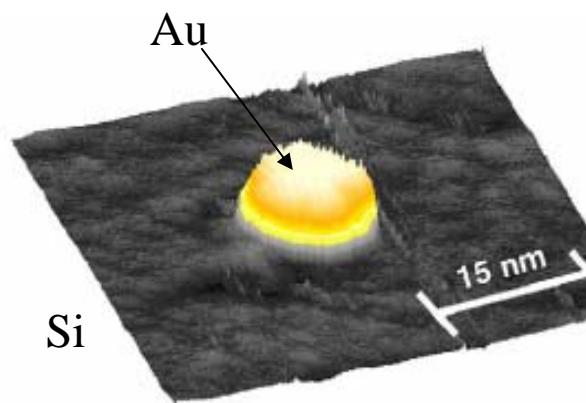
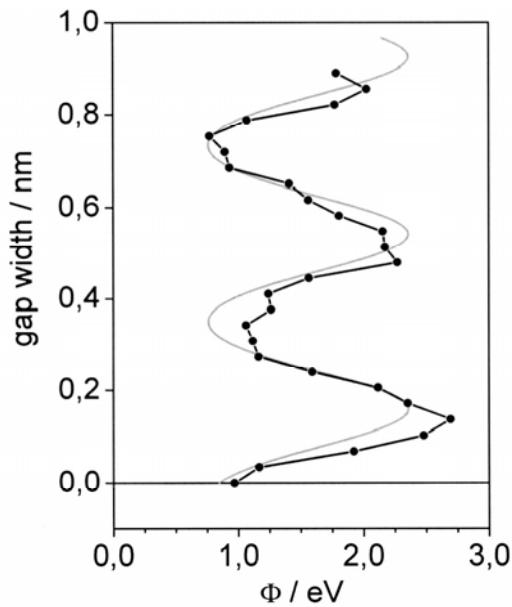
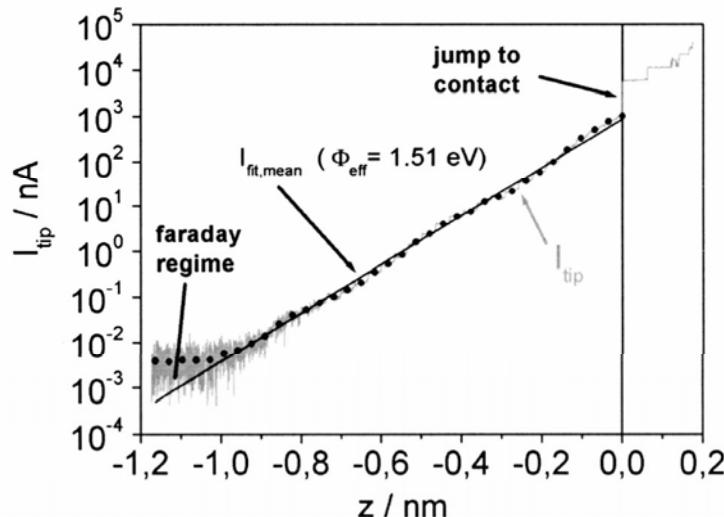
$$\phi = \left(\frac{1}{1.025} \frac{d \ln G}{d H} \right)^2 = \left(\frac{1}{1.025} \left(\frac{d \ln I}{d H} \right)_{U=\text{const}} \right)^2$$



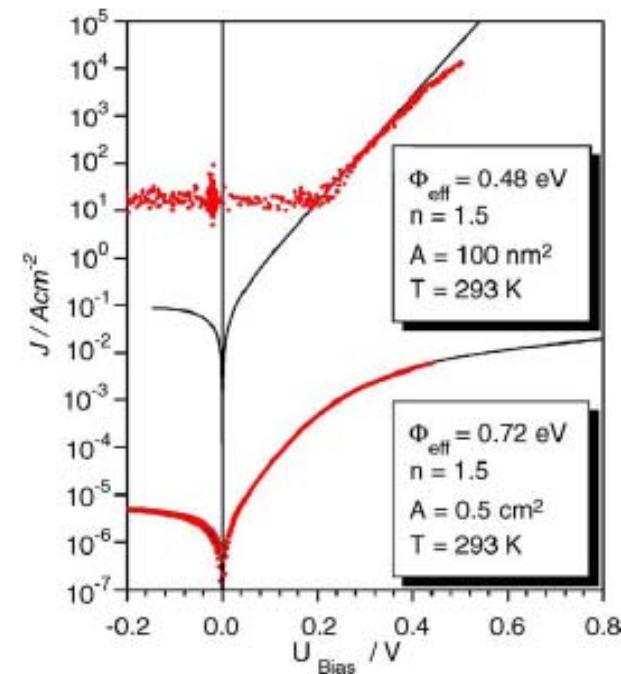
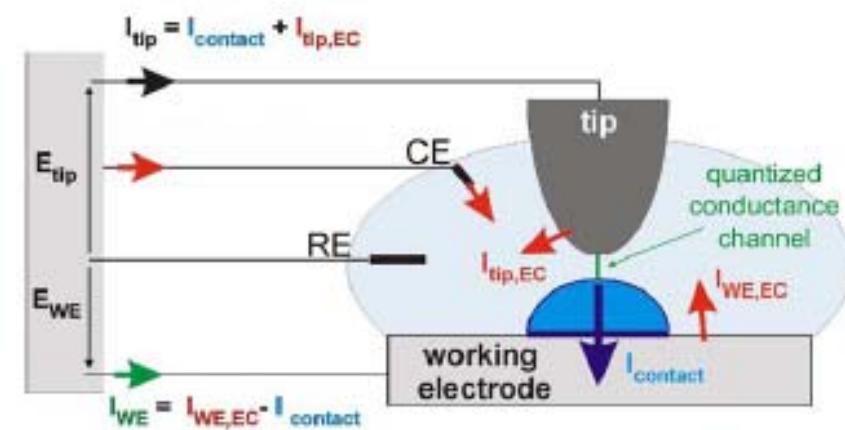
(b)



СТМ: Токвысотные спектры

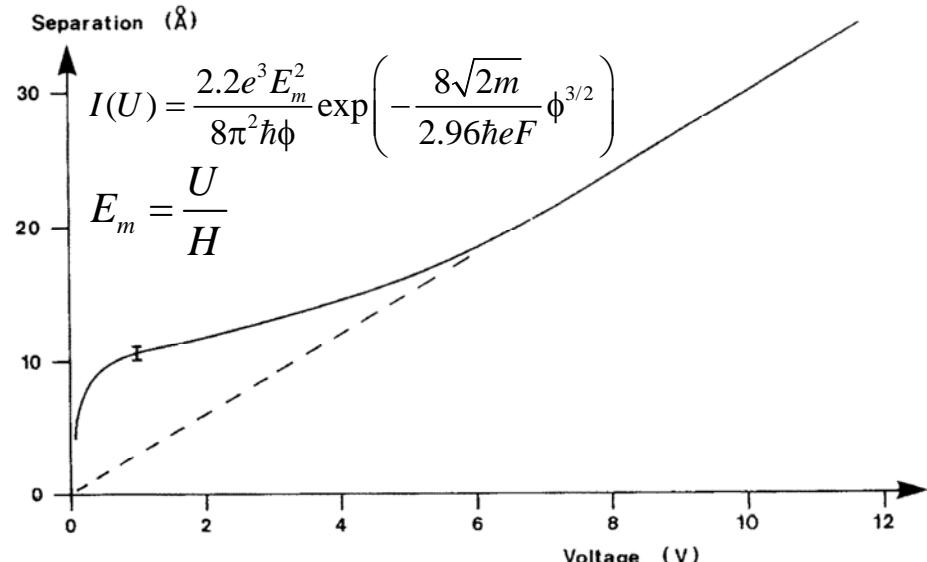
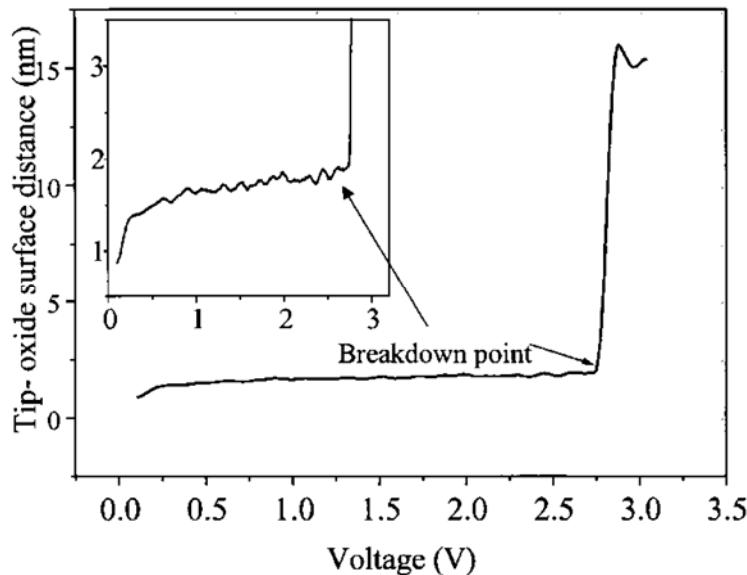


СТМ: Локальный контакт



СТМ: Вольтвысотные спектры

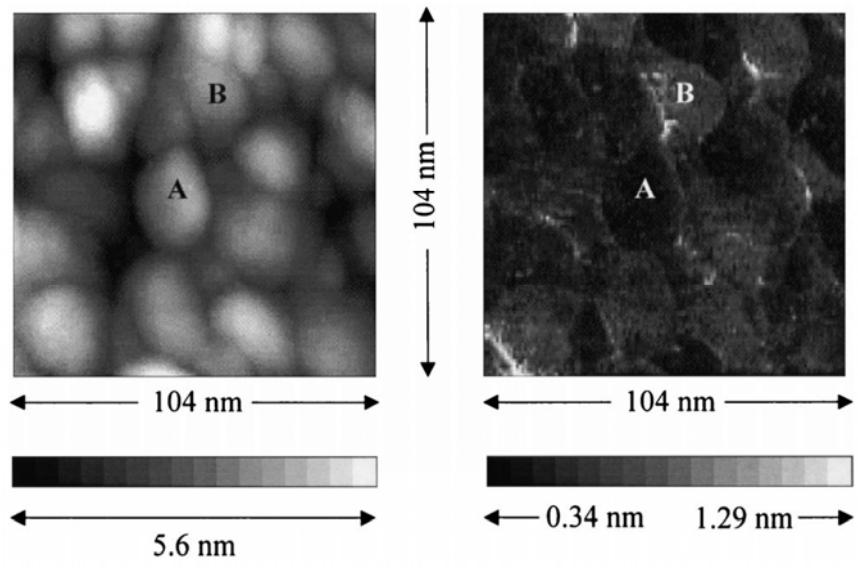
$$I \propto U \cdot \exp\left(\frac{\sqrt{2m\phi}}{\hbar} H\right) \quad \left(\frac{d \ln U}{dH}\right)_{I=\text{const}} = 2 \frac{\sqrt{2m\phi}}{\hbar}$$



N.P.Magtoto, C.Niu,B.M.Ekstrom, S.Addepalli, J.A.Kelber,
Dielectric breakdown of ultrathin aluminum oxide films induced by
scanning tunneling microscopy, Appl.Phys.Lett. 77(2000)2228-2230

M.D.Pashley, J.B.Pethica, J.Coombs, Scanning Tunneling
Microscope Studies, Surf.Sci. 152/153 (1985) 27-32

G.Seine, R.Coratger, A.Carladous, F.Ajustron, R.Pechou,
J.Beauvillain, Imaging using tip-surface distance variations vs.
voltage in scanning tunneling microscopy, Surf.Sci.
465(2000)219-226

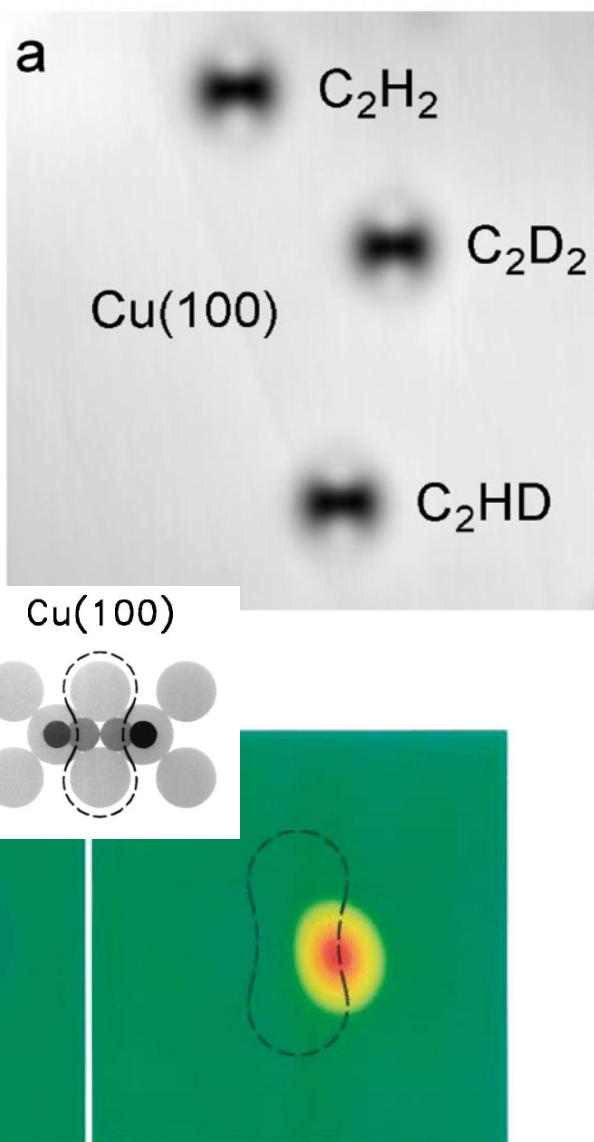
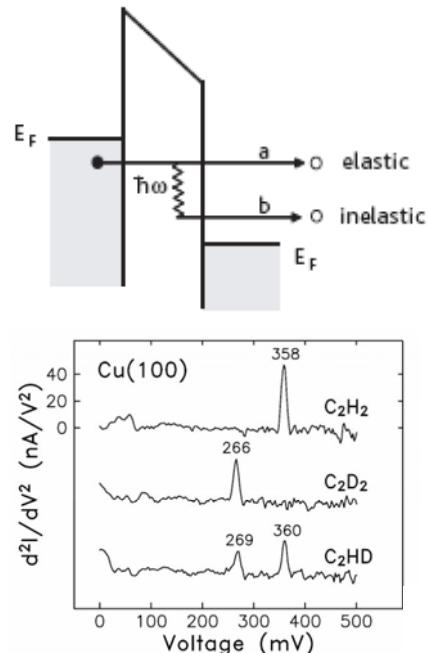
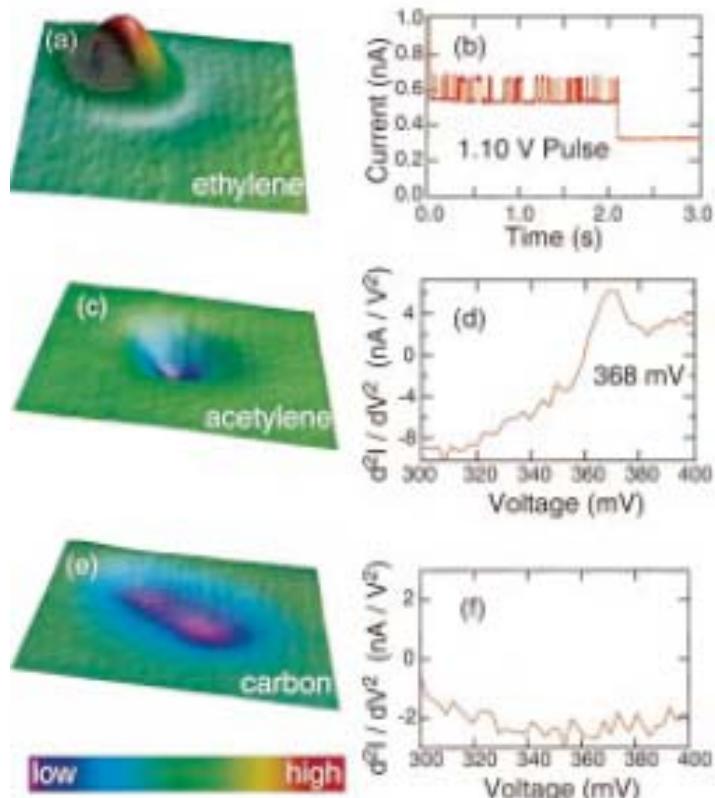


СТМ: Неупругое туннелирование (d^2I/dU^2)

inelastic tunneling spectroscopy, IETS

R.C.Jaklevic, J.Lambe, Molecular Vibration Spectra by Electron Tunneling, Phys.Rev.Lett. 17(1966)1139-1140

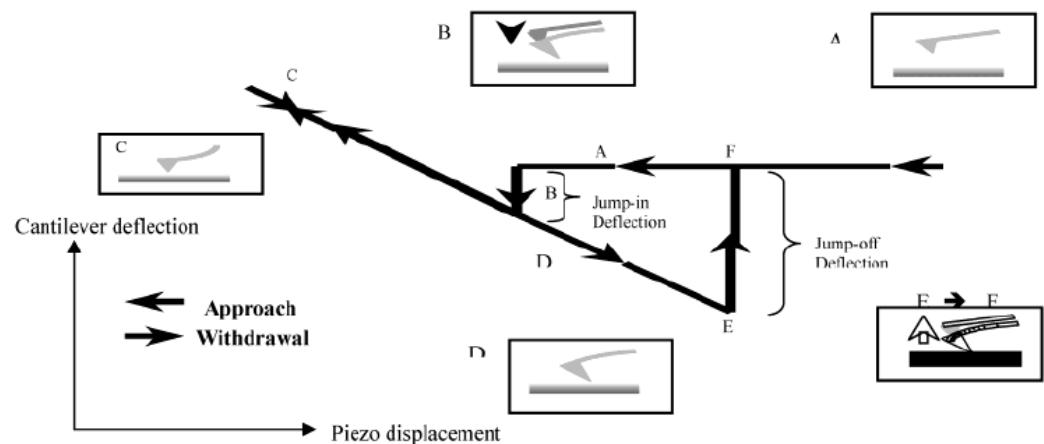
G.Binnig, N.Garcia, H.Rohrer, Conductivity sensitivity of inelastic scanning tunneling microscopy, Phys.Rev.B 32(1985)1336-1338



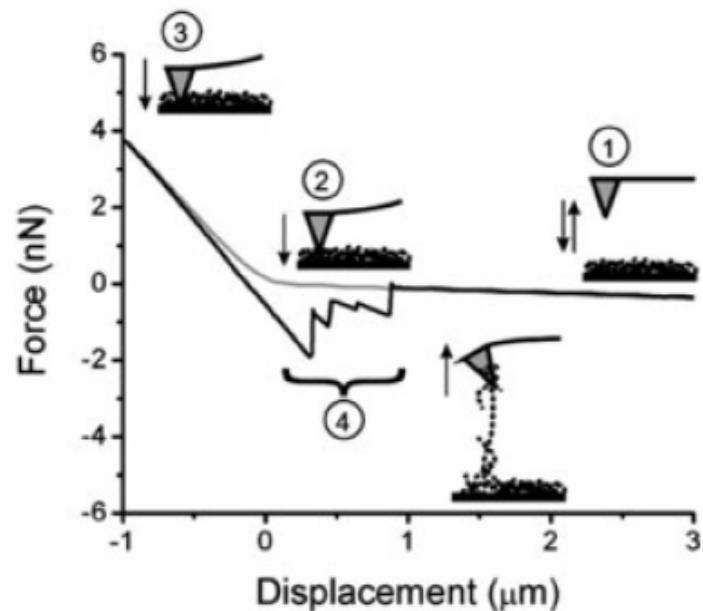
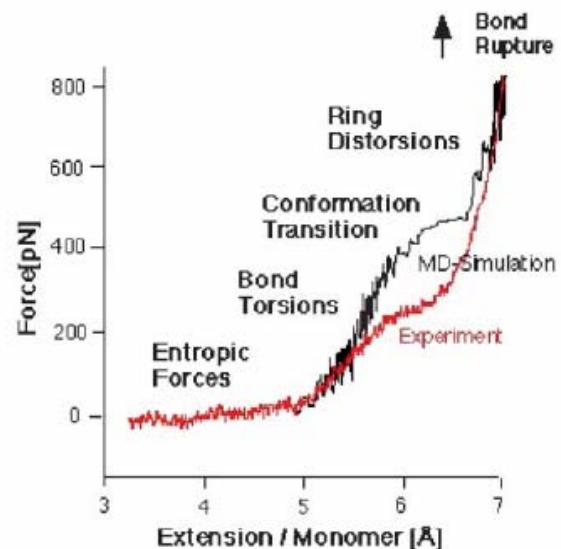
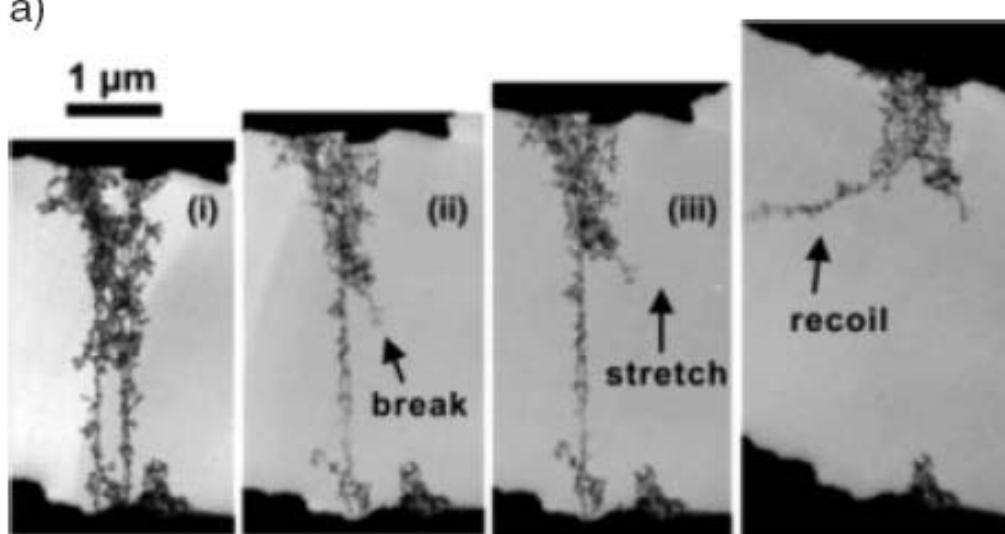
J.Gaudioso, H.J.Lee, W.Ho, Vibrational Analysis of Single Molecule Chemistry: Ethylene Dehydrogenation on Ni(110), J.Am.Chem.Soc. 121(1999)8479-8485

B.C.Stipe, M.A.Rezaei, W.Ho, Localization of Inelastic Tunneling and the Determination of Atomic-Scale Structure with Chemical Specificity, Phys.Rev.Lett. 82(1999)1724-1727

ACM: Силовые кривые

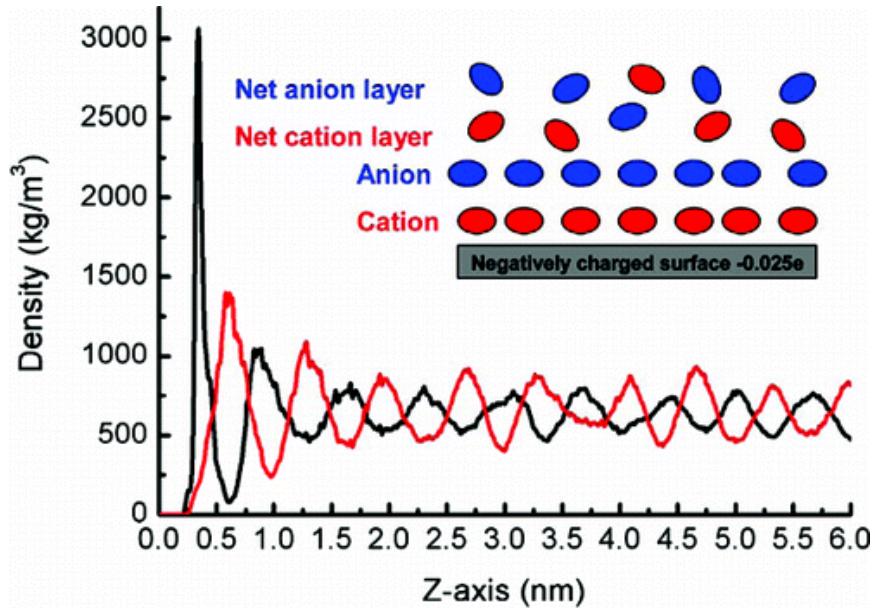


a)

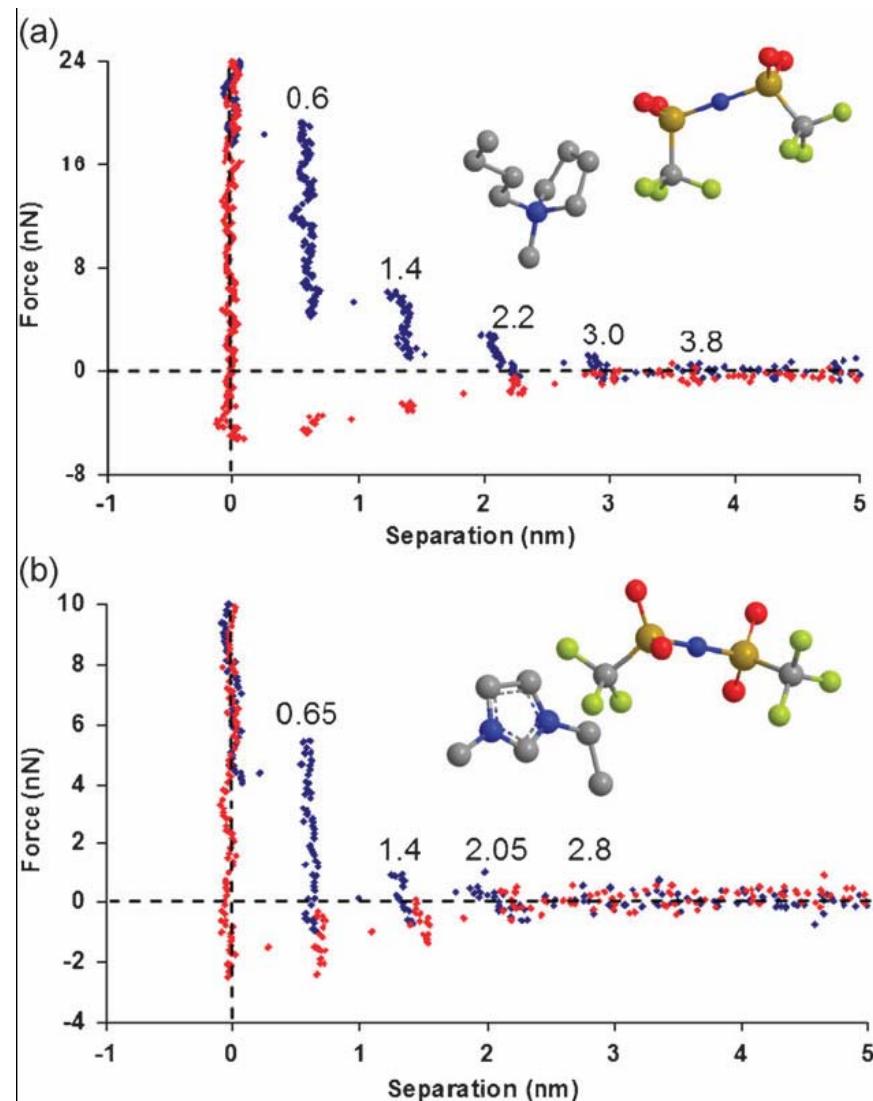
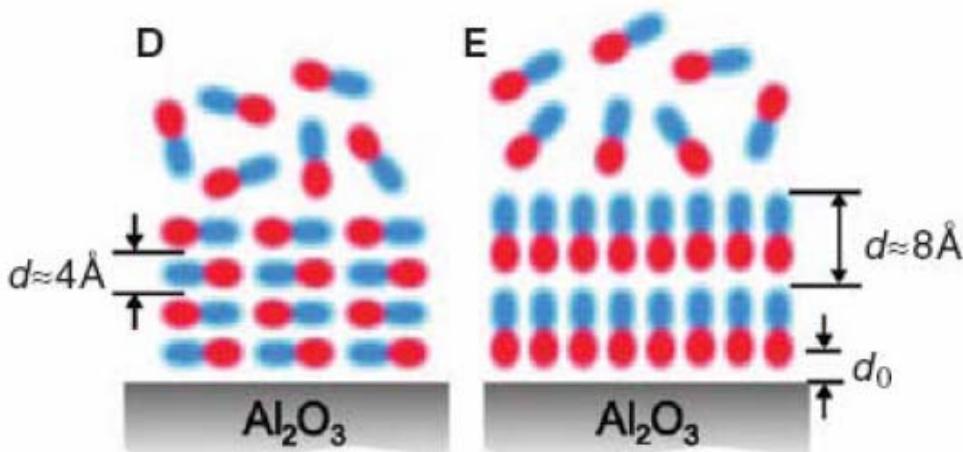


ACM: Силовые кривые

Строение межфазных границ,



Langmuir, 2010, 26 (15), pp 12667–12672



Phys. Chem. Chem. Phys., 2010, 12, 1724–1732

АСМ: Локальное сопротивление

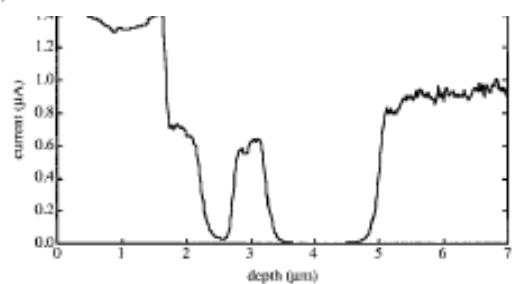
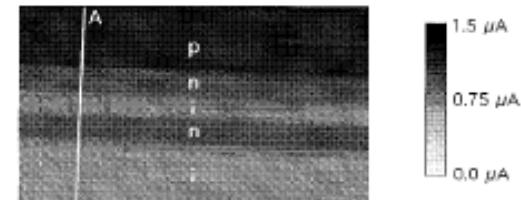
conducting atomic force microscopy (C-AFM)

current-sensing atomic force microscopy

tunneling atomic force microscopy (TUNA)

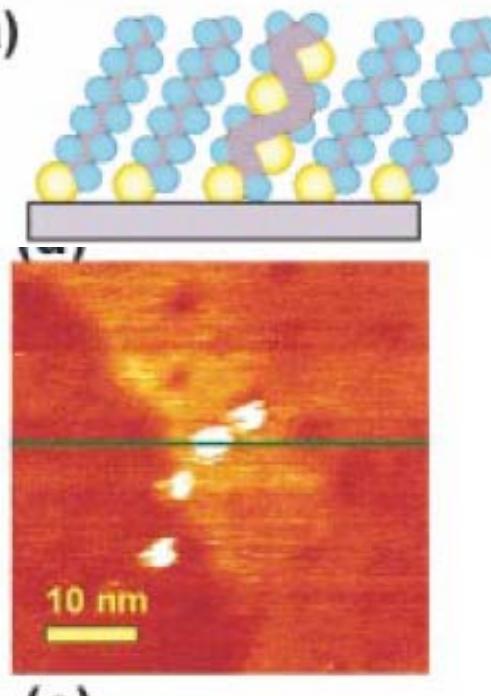
scanning spreading resistance microscopy (SSRM)

Гетероструктуры

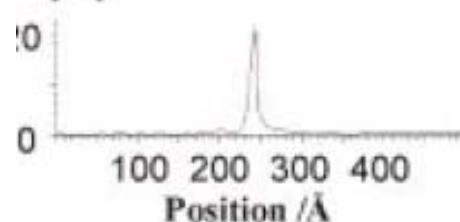


P.DeWolf, M.Geva, T.Hantschel,
W.Vandervorst, R.B.Bylsma, Two-dimensional carrier profiling of InP
Structures using scanning spreading
resistance microscopy,
Appl.Phys.Lett. 73(1998)2155

(a)



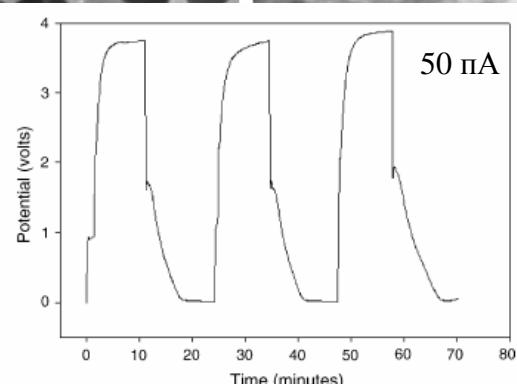
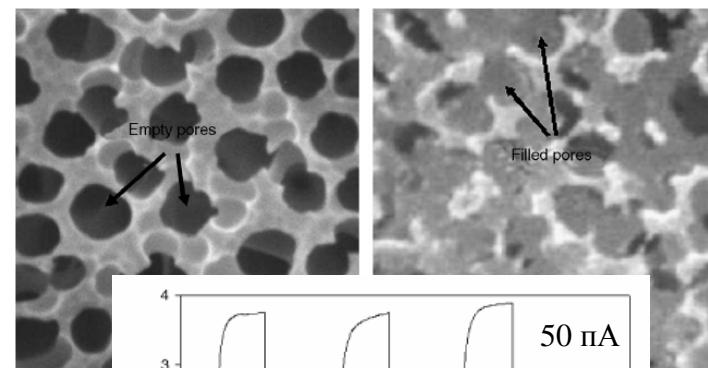
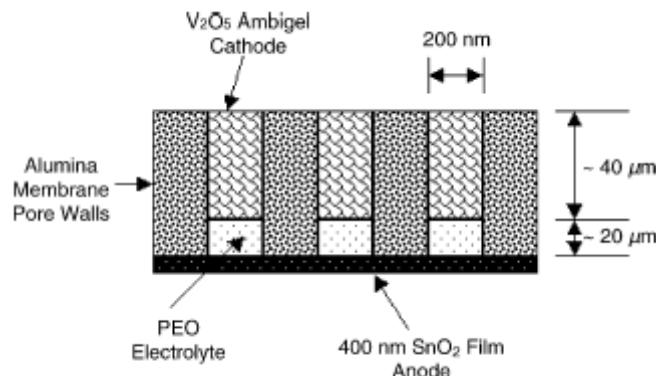
(e)



H.Sakaguchi, A.Hirai, F.Iwata, A.Sasaki, T.Nagamura, E.Kawata,
S.Nakabayashi, Determination of performance on tunnel conduction through
molecular wire using a conductive atomic force microscope, Appl.Phys.Lett.
79(2001)3708

Молекулярная проводимость

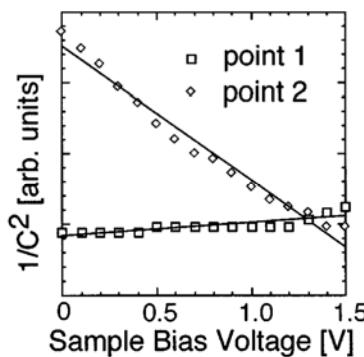
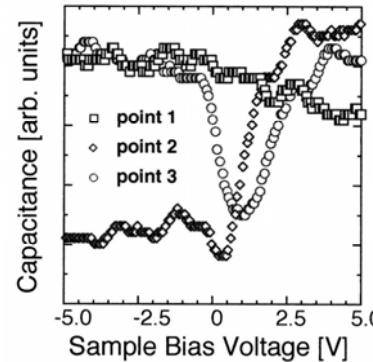
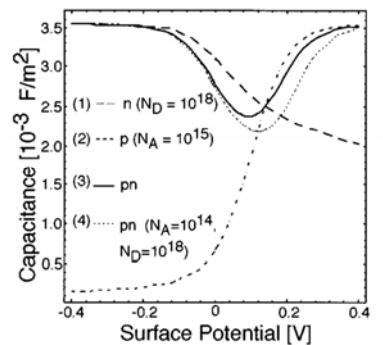
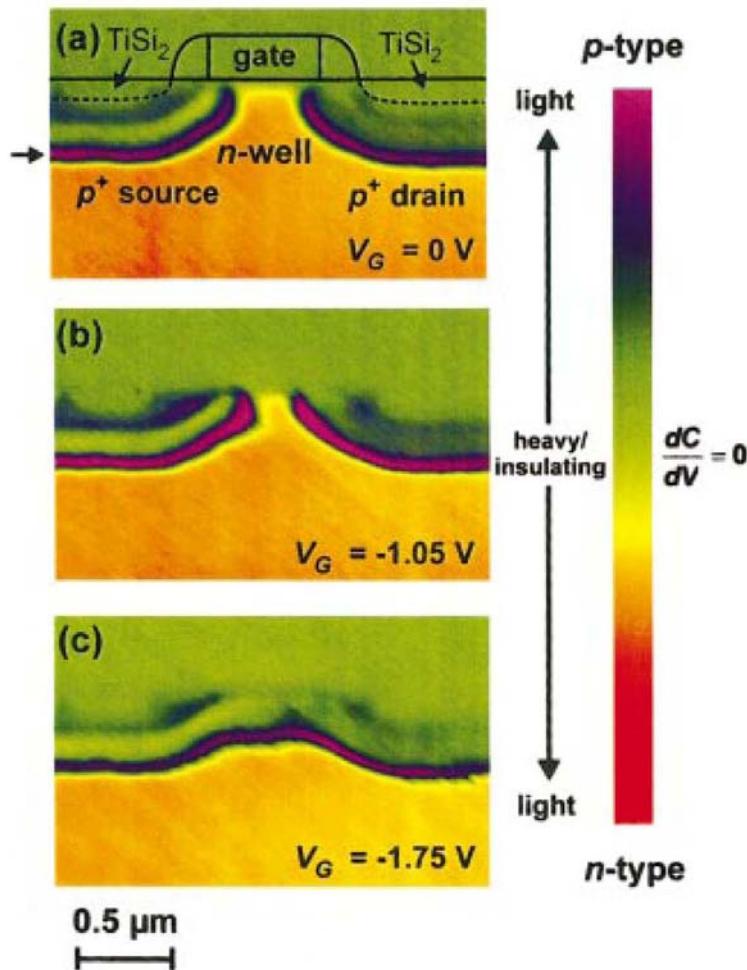
Наноизделия



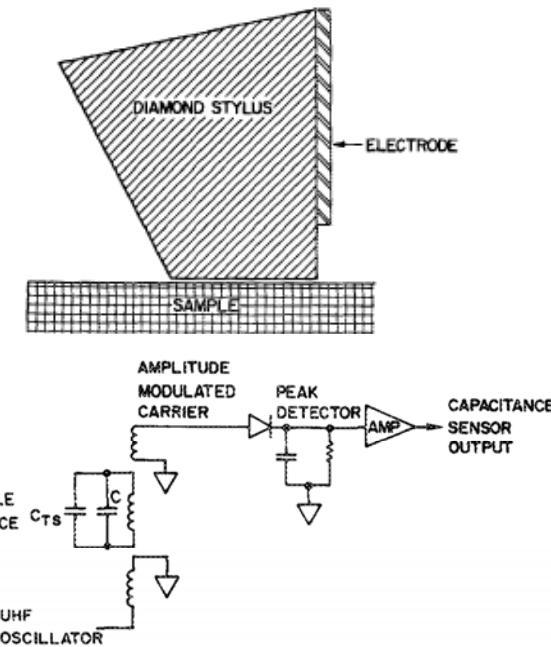
F.Vullum, D.Teeters, Investigation of lithium battery
nanoelectrode arrays and their component nanobatteries,
J.Power Sources 146(2005)804

АСМ: Локальная емкость

Scanning capacitance microscopy (SCM)

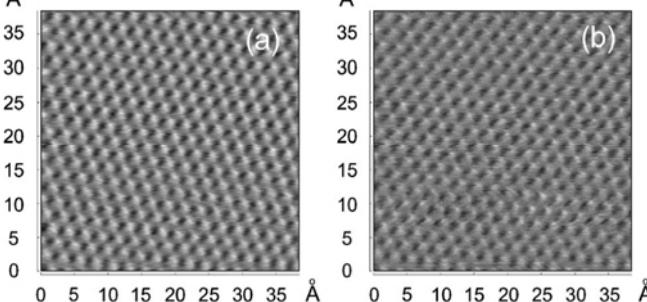


J.R.Matey, J.Blanc, Scanning capacitance microscopy, J.Appl.Phys. 57(1985)1437-1444



Alternating-current scanning tunneling microscopy (AC-STM)

Scanning surface harmonic microscopy (SSHM)



J.Schmidt, D.H.Rapoport, H.J.Frohlich, Rev.Sci.Instrum., 70(1999)3377-3380

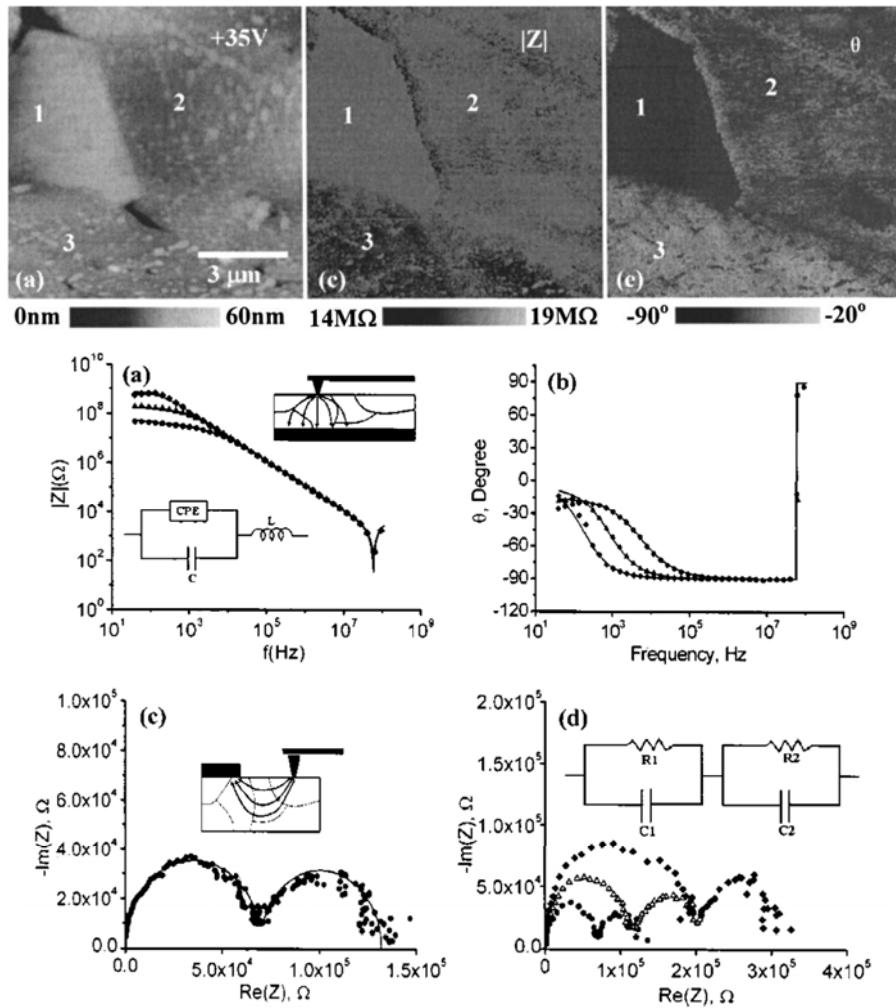
C.Y.Nakakura, P.Tangyunyong, D.L.Hetherington, M.R.Shaneyfelt, Method for the study of semiconductor device operation using scanning capacitance microscopy, Rev.Sci.Instrum. 74(2003)127-133

H.Tomiye, T.Yao, H.Kawami, T.Hayashi, Nanometer-scale characterization of SiO₂/Si with a scanning capacitance microscope, Appl.Phys.Lett. 69(1996)4050-4052

ACM: Локальный импеданс

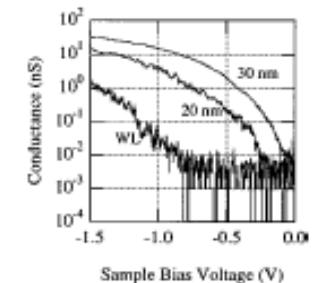
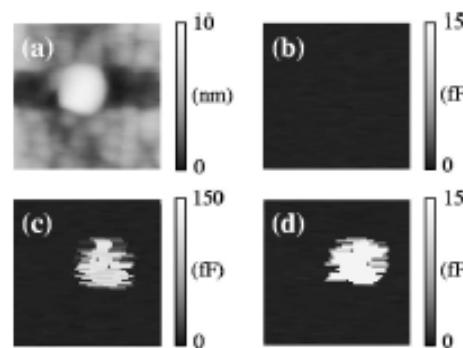
Nanoscale impedance microscopy (NIM)

Керамические материалы



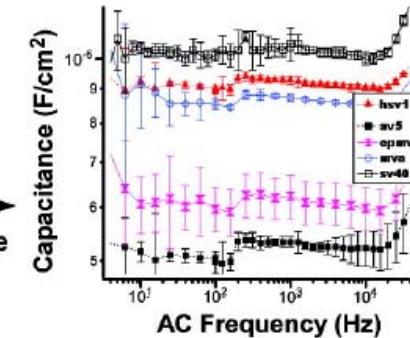
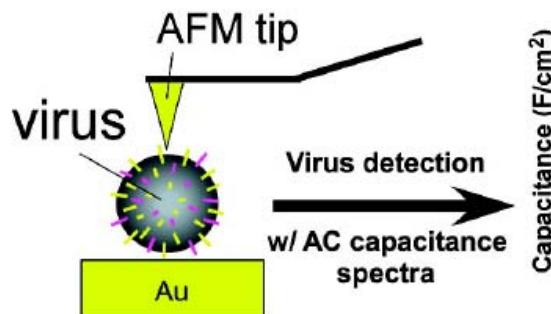
R.Shao, S.V.Kalinin, D.A.Bonnell, Local impedance imaging and spectroscopy of polycrystalline ZnO using contact atomic force microscopy, Appl.Phys.Lett. 82(2003)1869-1871

Квантовые точки



H.Yamamoto, T.Takahashi, I.Kamiya,
Local capacitance measurements on
InAs dot-covered GaAs surfaces by
scanning capacitance microscopy,
Appl.Phys.Lett. 77(2000)1994-1996

Вирусы



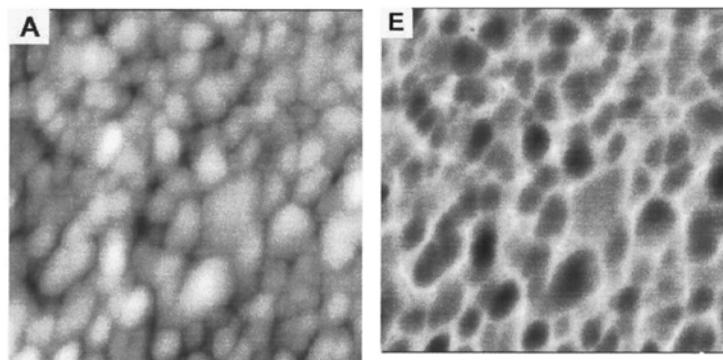
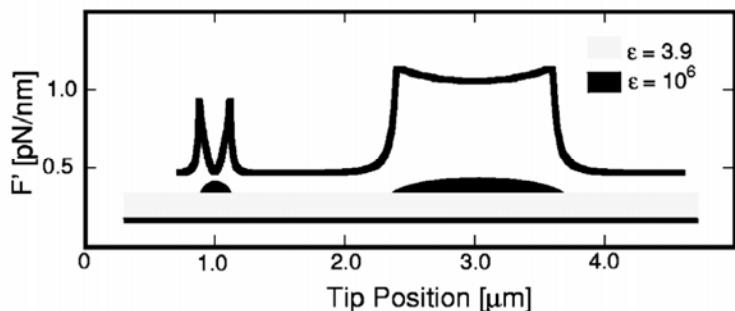
R.I.MacCuspie, N.Nuraje, S.Y.Lee, A.Runge, H.Matsui, Comparison of Electrical Properties of Viruses Studied by AC Capacitance Scanning Probe Microscopy, J.Am.Chem.Soc. 130(2008)887

АСМ: Электростатика

electrostatic force microscopy (EFM)

scanning surface potential microscopy (SSPM)

Kelvin probe force microscopy (KFM, KPFM)

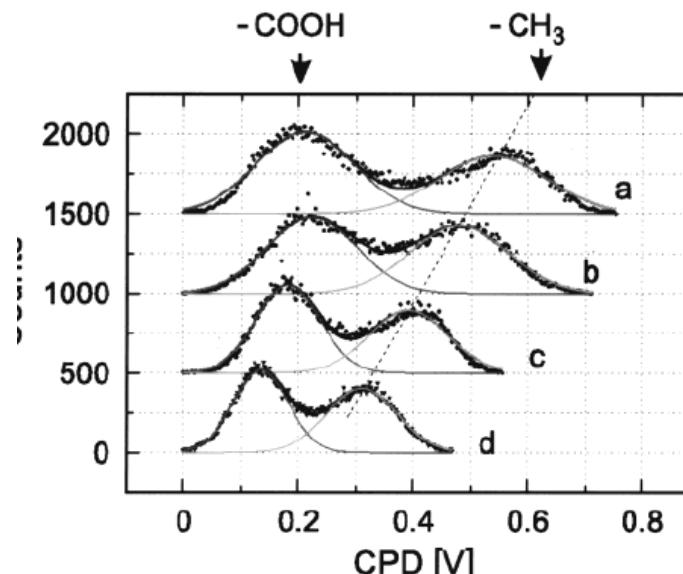
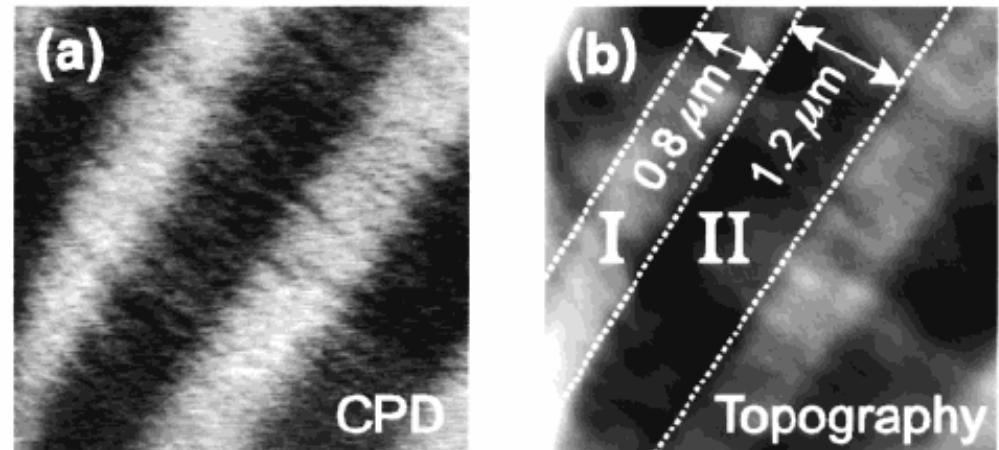


A.Efimov, S.R.Cohen, Simulation and correction of geometric distortions in scanning Kelvin probe microscopy, J.Vac.Sci.Technol.A 18(2000)1051-1055

E.Tevaarwerk, D.G.Keppel, P.Rugheimer, M.G.Lagally, M.A.Eriksson, Quantitative analysis of electric force microscopy: The role of sample geometry, Rev.Sci. Instrum. 76(2005)053707

$$F_E = \frac{1}{2} \cdot \frac{\partial C}{\partial H} \cdot (U_{surf} - U_0)^2$$

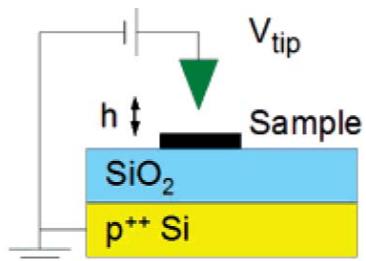
$$F_E = \frac{1}{2} \cdot \frac{\partial C}{\partial H} \left(\Delta U^2 + \frac{U_{ac}^2}{2} \right) + \frac{\partial C}{\partial H} \cdot \Delta U \cdot U_{ac} \cos(\omega t) - \frac{\partial C}{\partial H} \frac{U_{ac}^2}{4} \cos(2\omega t)$$



J.Lu, E.Delamarche, L.Eng,
R.Bennewitz, E.Meyer,
H.J.Guntherodt, Langmuir
15(1999)8184

ACM: Электростатика

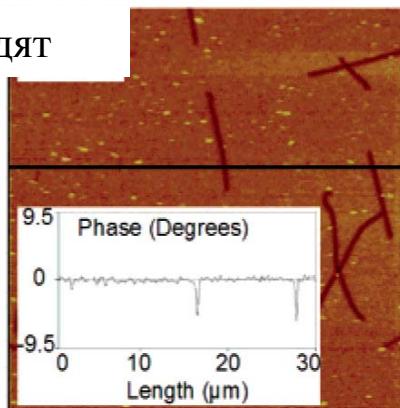
scanning conductance microscopy



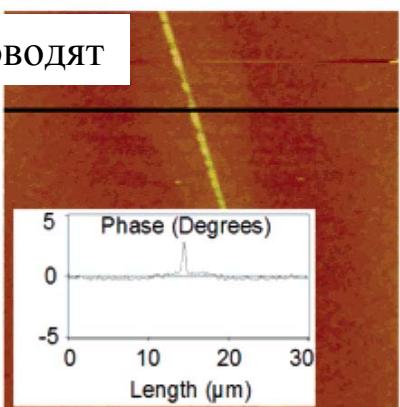
scanning polarization force microscopy (SPFM)



проводят



не проводят



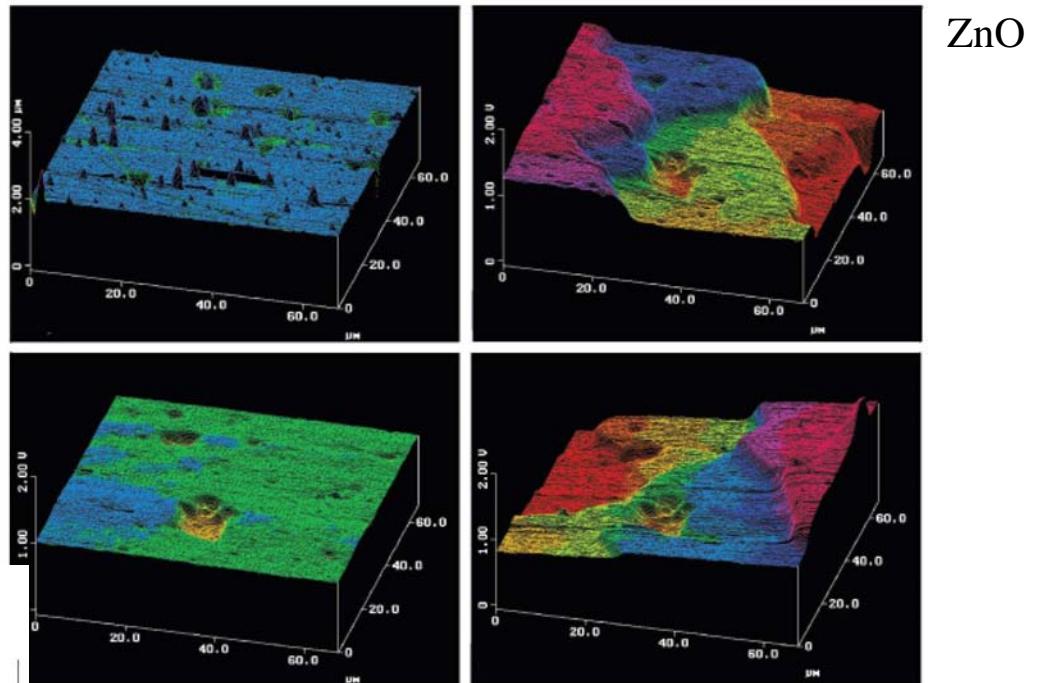
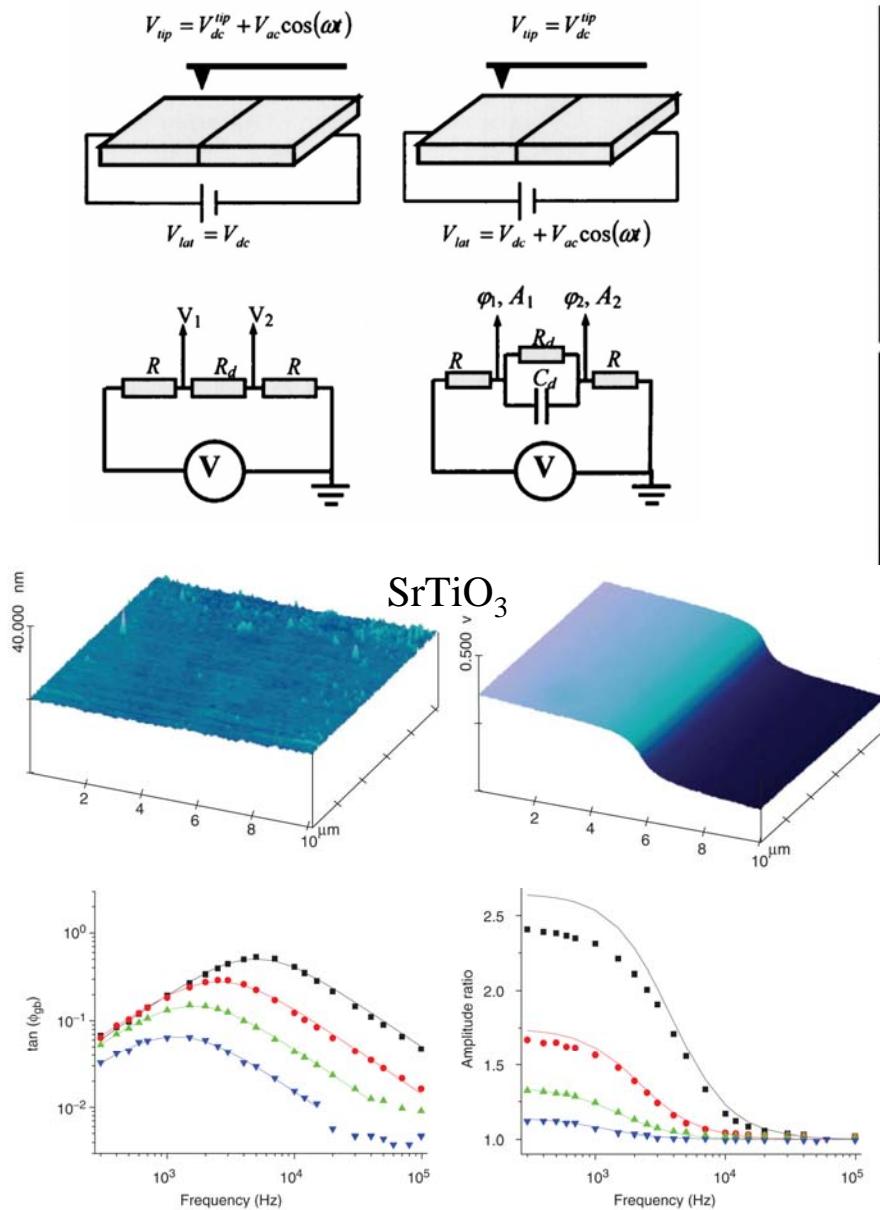
C.Staii, A.T.Johnson Jr., N.J.Pinto, Quantitative Analysis of Scanning Conductance Microscopy, Nanolett. 4(2004)859-862

J.Hu, X.D.Xiao, M.Salmeron, Scanning polarization force microscopy: A technique for imaging liquids and weakly adsorbed layers, Appl.Phys.Lett. 67(1995)476-478

пленка воды на слюде

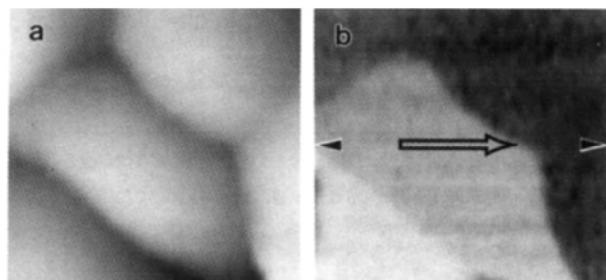
АСМ: Электростатика

scanning impedance microscopy (SIM)



S.V.Kalinin, R.Shao, D.A.Bonnell, Local Phenomena in Oxides by Advanced Scanning Probe Microscopy, J.Am.Ceram.Soc. 88(2005)1077

Scanning tunneling potentiometry



$\text{Au}_{60}\text{Pd}_{40}$

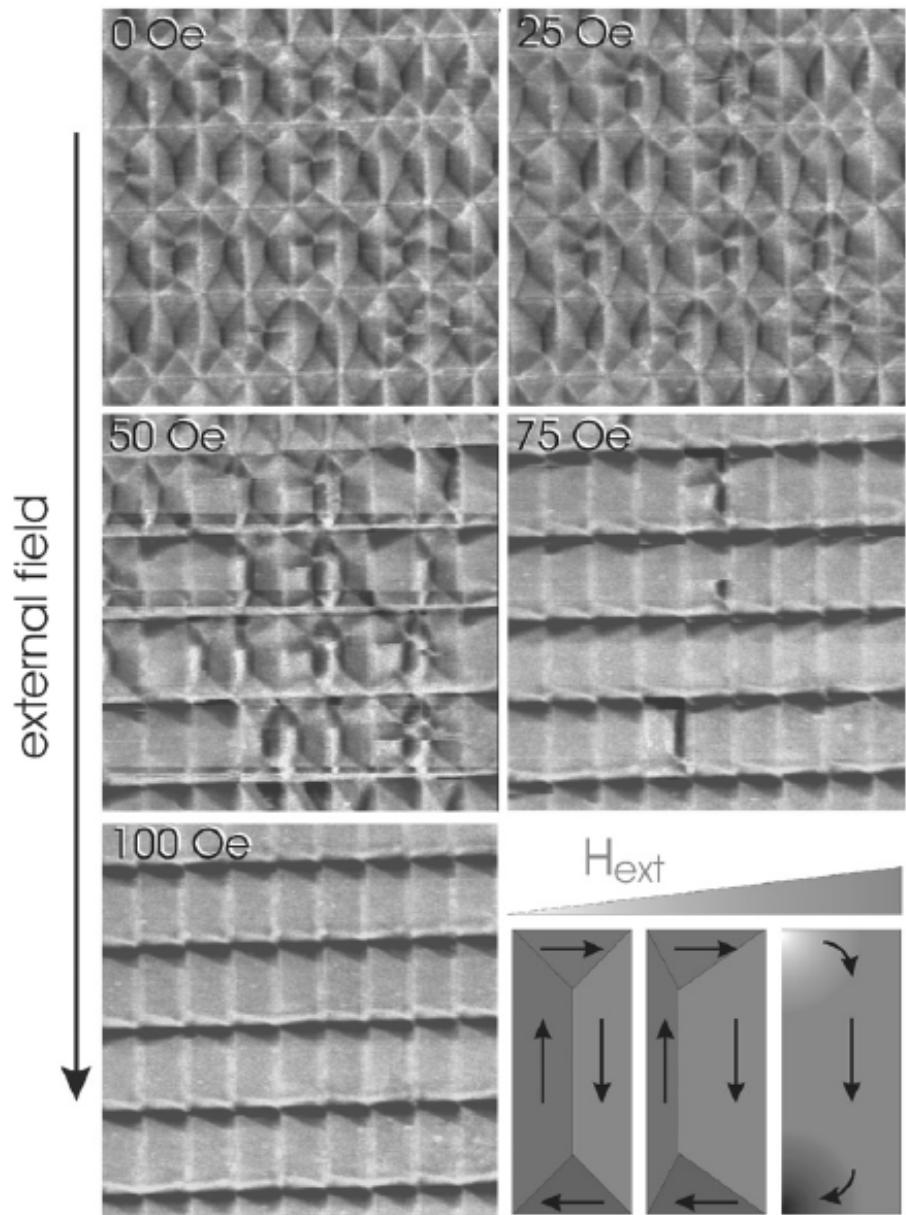
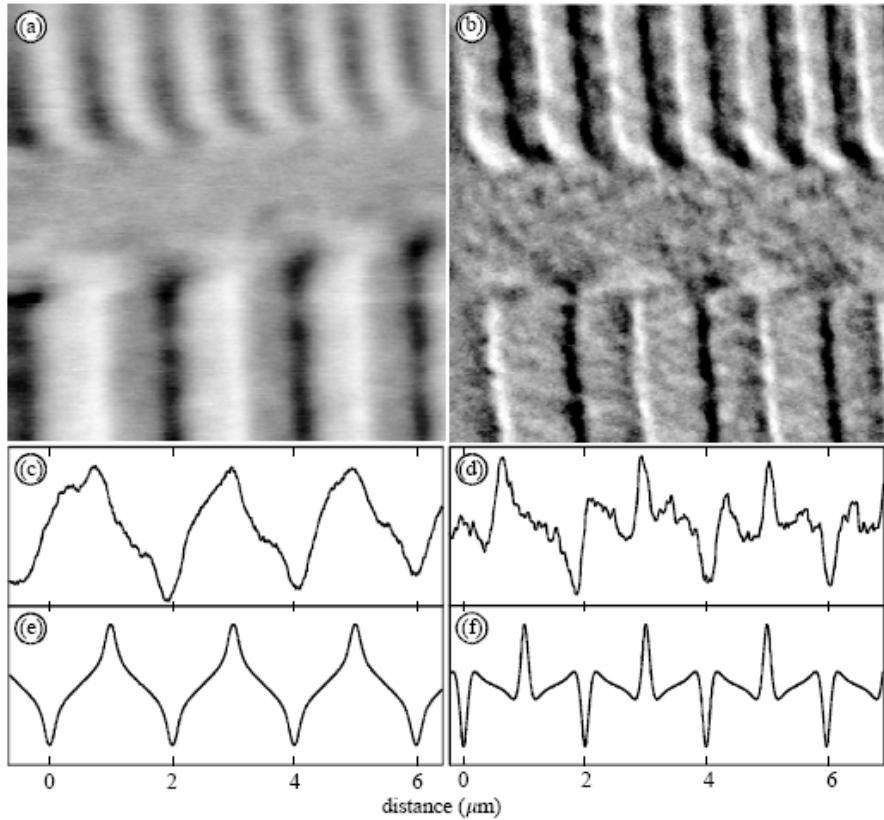
J.R.Kirtley, S.Washburn, M.J.Brady, Direct Measurement of Potential Steps at Grain Boundaries in the Presence of Current Flow, Phys.Rev.Lett. 60(1988)1546-1549

АСМ: Магнитные взаимодействия

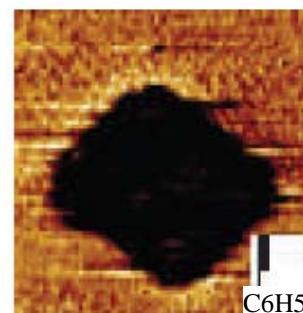
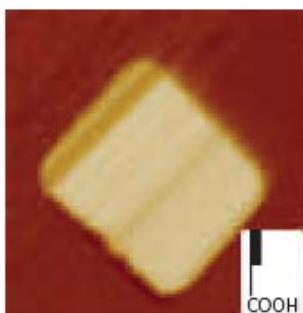
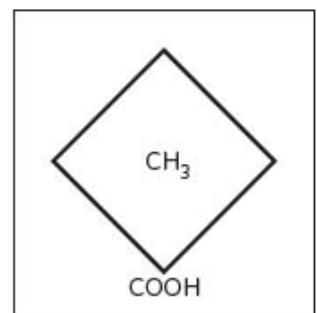
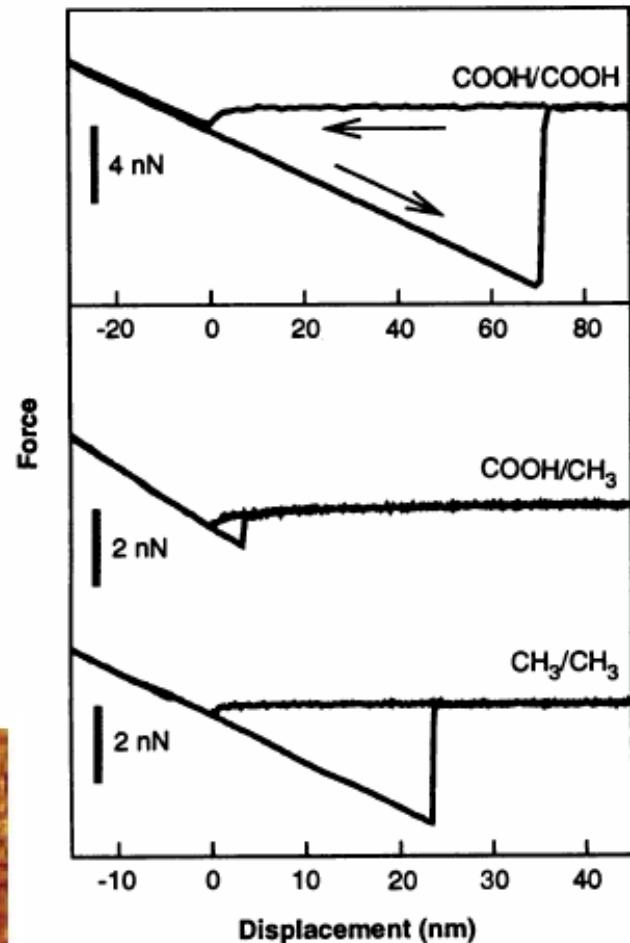
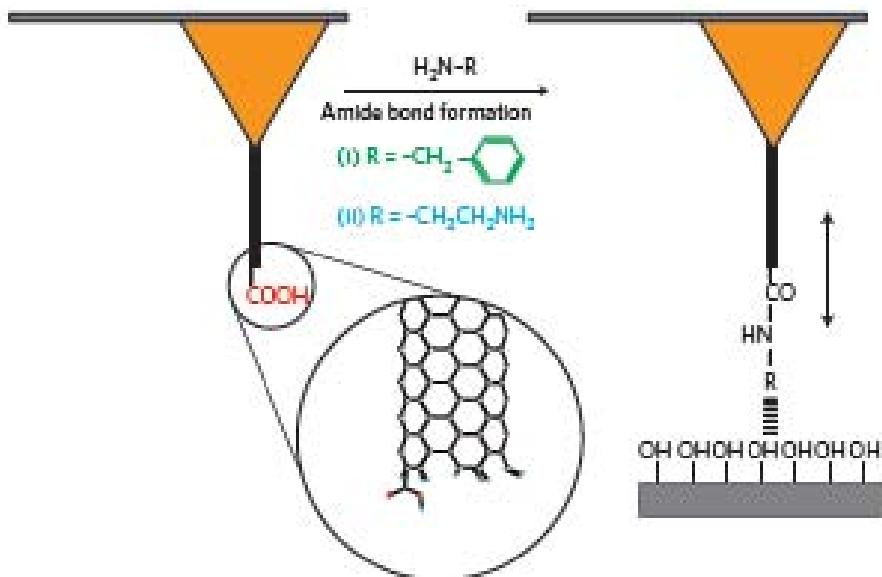
magnetic force microscopy (MFM)

Пермалloy

HDD

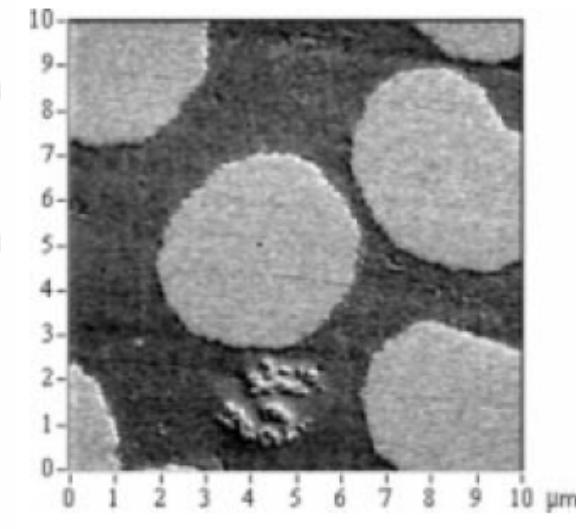
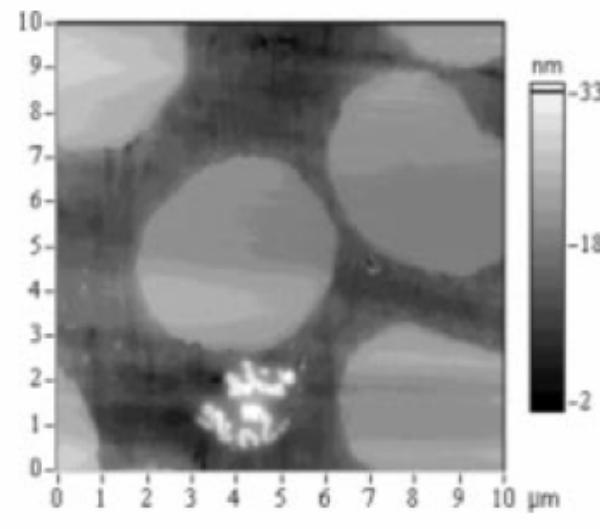
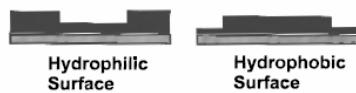
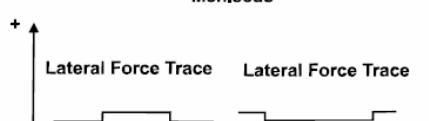
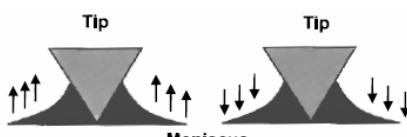
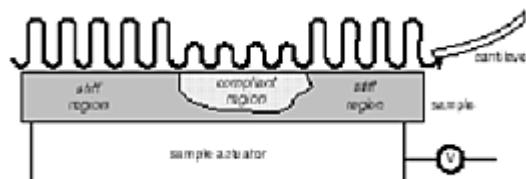
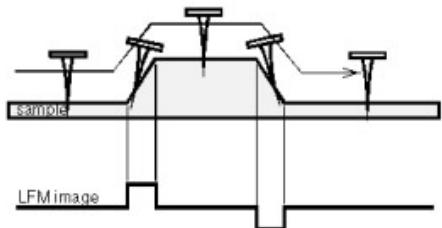
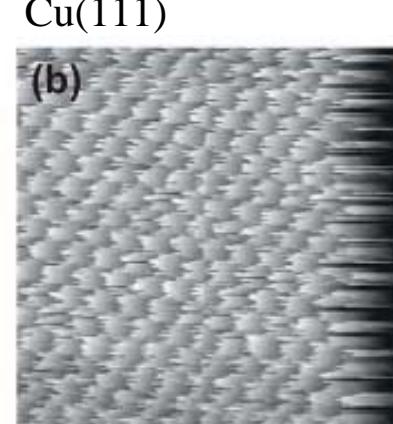
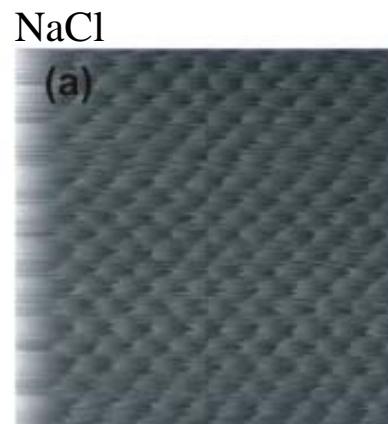
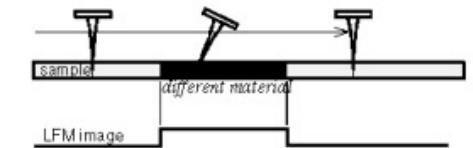


АСМ: Химическая природа объекта *chemical force microscopy (CFM)*



ACM: Механические свойства

lateral force microscopy (LFM)
friction force microscopy (FFM)
force modulation microscopy (FMM)



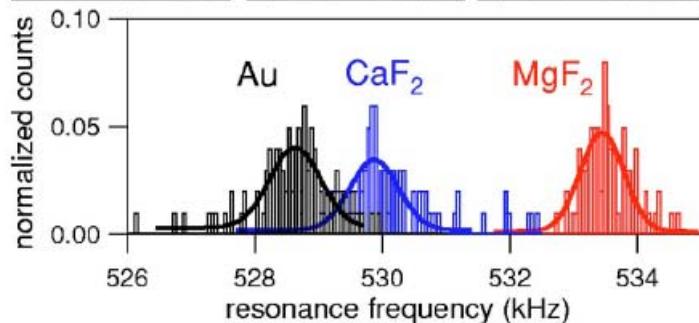
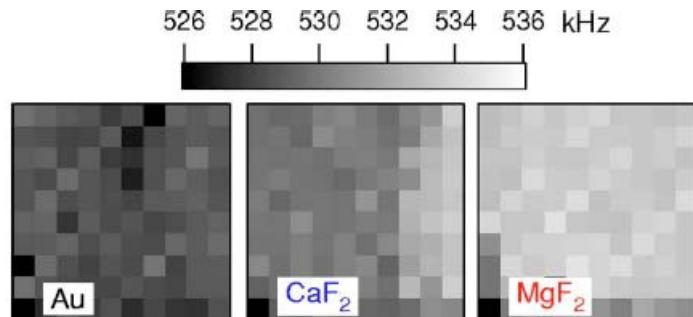
R.Bennewitz, Friction force microscopy, Materials Today, (2005)42

P.E.Mazeran, J.L.Loubet, Normal and lateral modulation with a scanning force microscope, an analysis: implication in quantitative elastic and friction imaging, Tribology Letters 7(1999)199

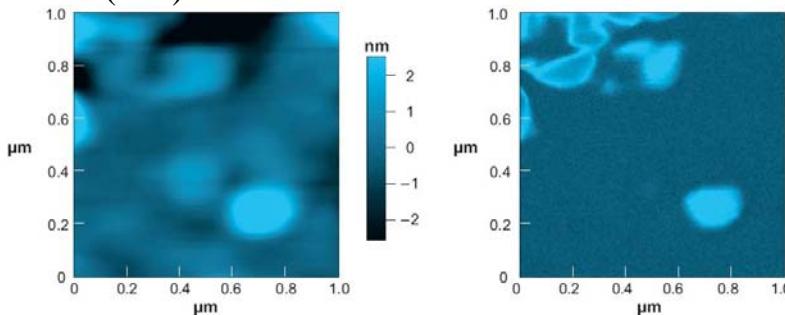
ACM: Механический отклик

Atomic force acoustic microscopy (AFAM)

Ultrasonic force microscopy (UFM)



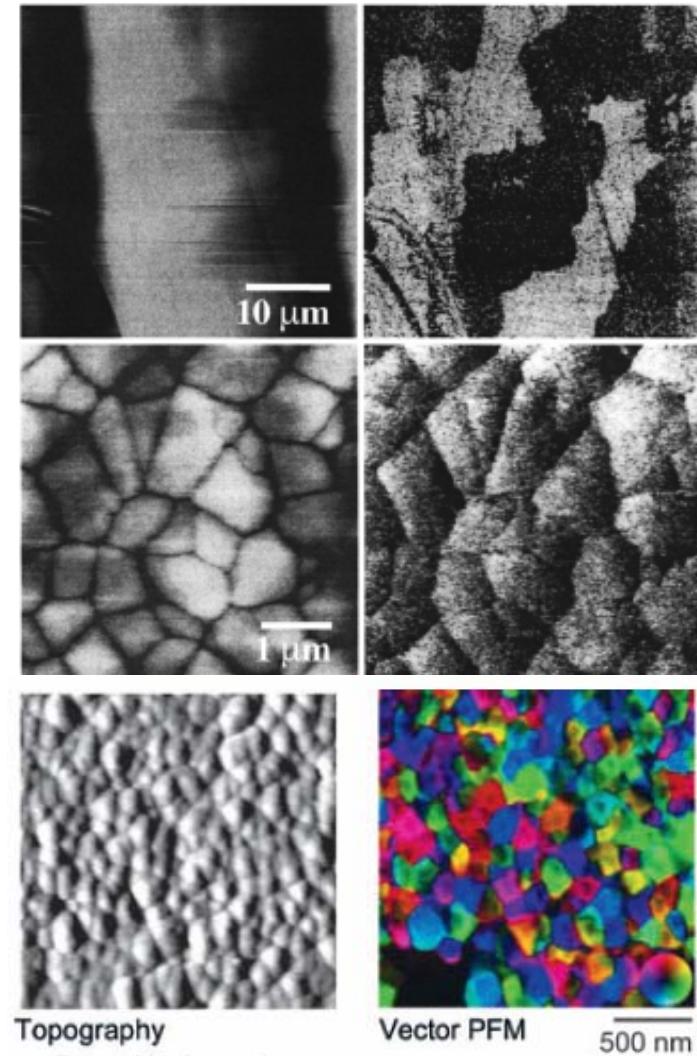
Au/Si(111)



G.Stan, W.Price, Quantitative measurements of indentation moduli by atomic force acoustic microscopy using a dual reference method, Rev.Sci.Instrum. 77(2006)103707

B.D.Huey, AFM and Acoustics: Fast, Quantitative Nanomechanical Mapping, Annu.Rev.Mater.Res. 37(2007)351

Piezoresponse force microscopy (PFM)



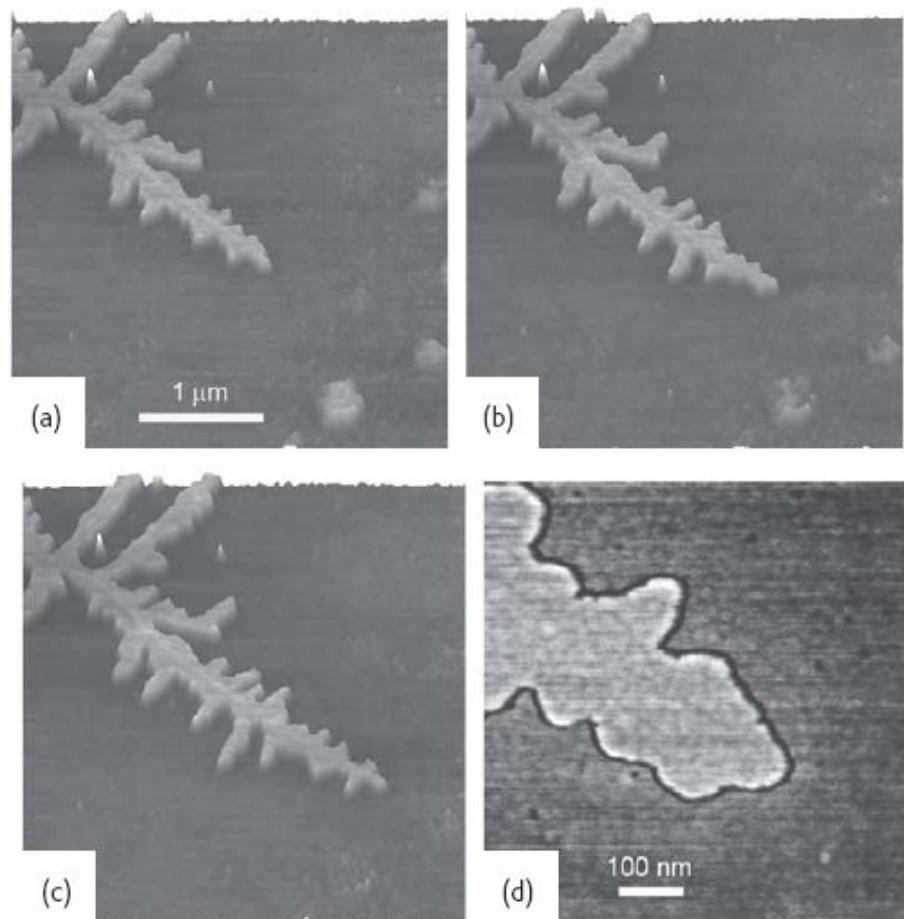
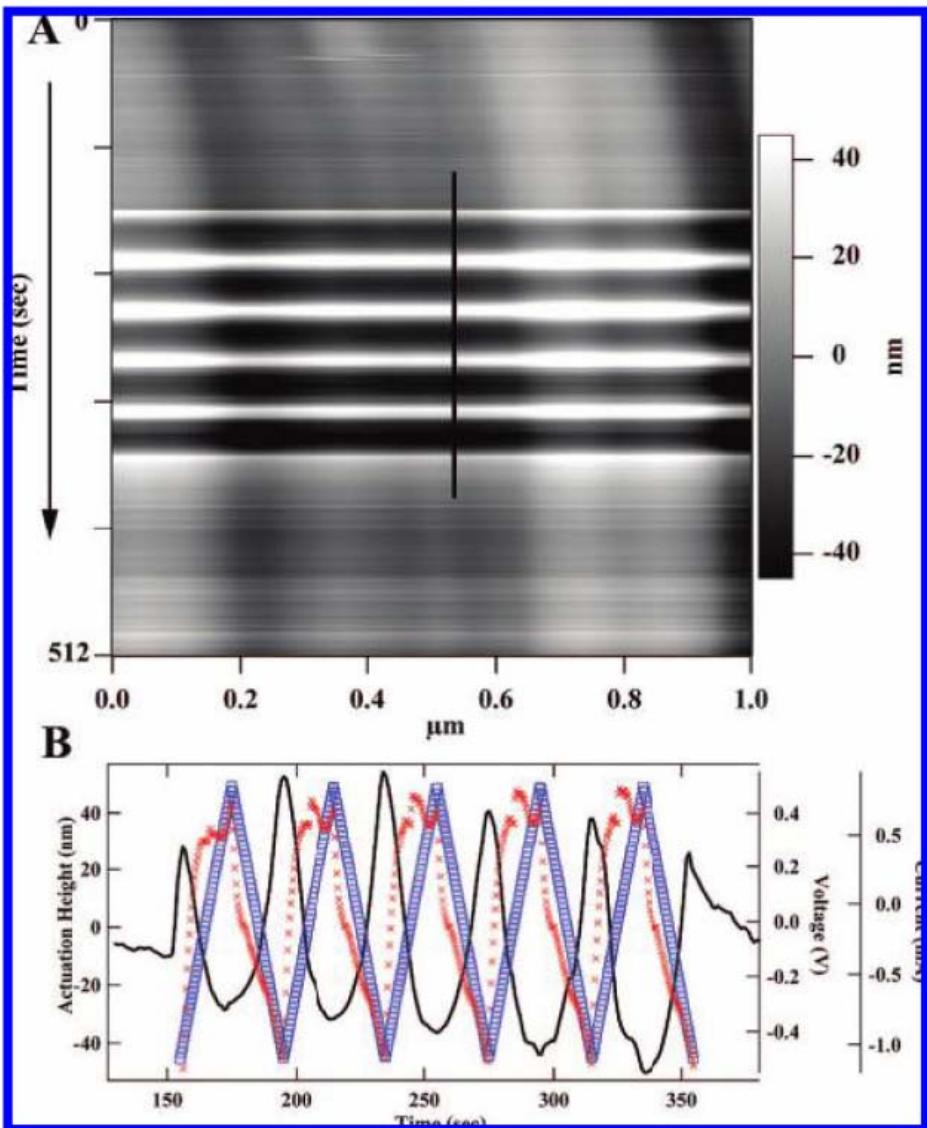
S.V.Kalinin, D.A.Bonnell, Imaging mechanism of piezoresponse force microscopy of ferroelectric surfaces, Phys.Rev.B. 65(2002)125408

S.V.Kalinin, B.J.Rodriguez, S.Jesse, E.Karapetian, B.Mirman, E.A.Eliseev, A.N.Morozovska, Nanoscale Electromechanics of Ferroelectric and Biological Systems: A New Dimension in Scanning Probe Microscopy, Annu.Rev.Mater.Res. 37(2007)189

СТМ/АСМ: Мониторинг процессов

В объеме

На поверхности

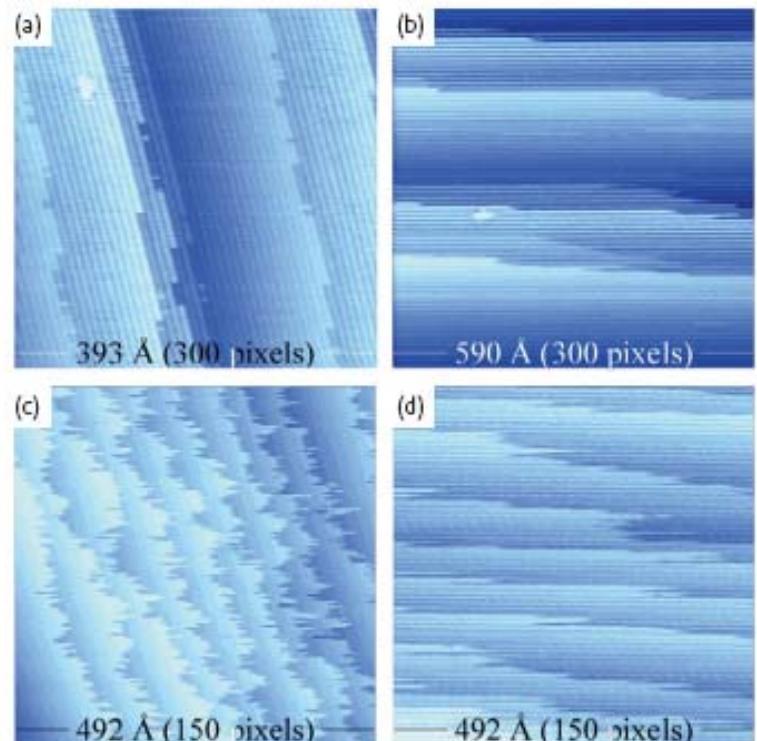


J.K.Hobbs, N.Mullin, C.H.M.Weber, O.E.Farrance, C.Vasilev,
'Watching' processes in soft matter with SPM, Materials Today,
12(2009)26

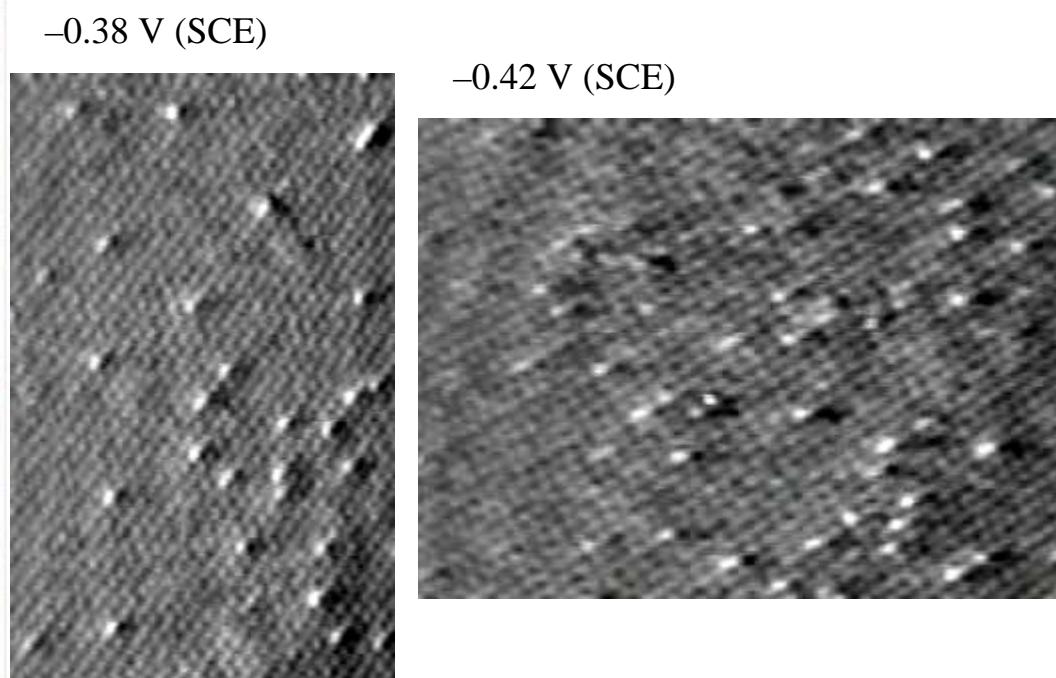
СТМ/АСМ: Мониторинг процессов

	Video-rate SPM	High-speed SPM	Intermediate speed
Pixel resolution	256 x 256 pixel	256 x 256 pixel	100 x 100 pixel
Frame rate	25 frames/s	10 frames/s	10 frames/s
Scan requirements			
Z-direction	3.3 MHz	1.3 MHz	200 kHz
X-direction	6.4 kHz	2.6 kHz	1 kHz
Y-direction	12.5 Hz	5 Hz	5 Hz

Au(110)



S²⁻/Cu(100)



Возможности метода

- 1) **Метрологическая характеристика:** размер частиц, толщина слоя, размерное распределение, локализация на поверхности.....
- 2) **Электрические параметры:** проводимость, тип и число носителей заряда, полупроводниковые свойства, электрическая емкость, диэлектрическая проницаемость, работа выхода, поверхностный потенциал, строение межзеренных границ.....
- 3) **Механические параметры:** трение, упругость, эластичность, твердость.....
- 4) **Молекулярная характеристика:** идентификация молекул, электронная структура, колебательная спектроскопия, проводимость, энергия химической связи, манипулирование отдельными молекулами.....
- 5) **Магнитная структура**
- 6) **Электромеханические свойства**
- 7) **Кинетика различных процессов**
- 8) **Локальная модификация поверхности, нанолитография**

И многое, многое другое.....