

Зондовые методы

За пределами топографии

Васильев Сергей Юрьевич

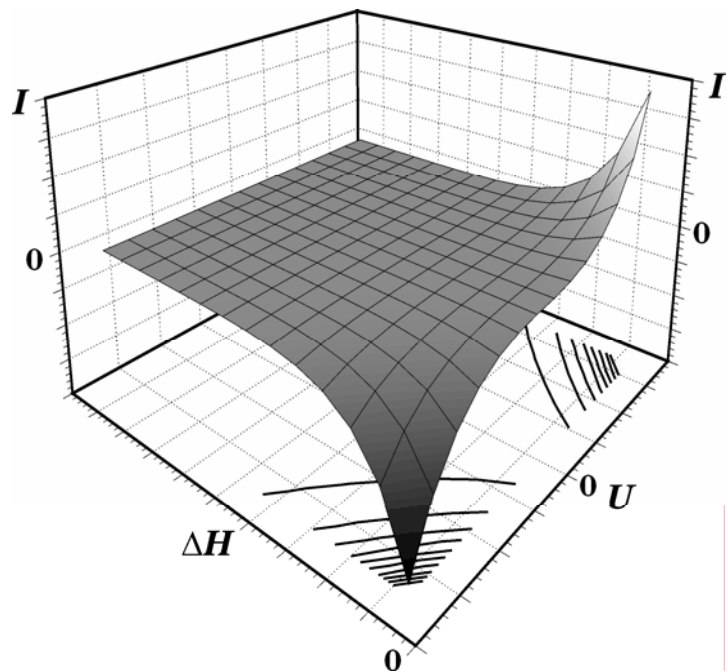
(wasq@elch.chem.msu.ru)



Презентация доступна в интернет:

<http://www.elch.chem.msu.ru/wasq/zond2.pdf>

СТМ: Локальные туннельные спектры



Вольтамперные спектры

$$I=f(U), H=\text{const}$$

Плотность электронных состояний (LDOS)

Токвысотные спектры

$$I=f(H), U=\text{const}$$

Высота туннельного барьера

Вольтвысотные спектры

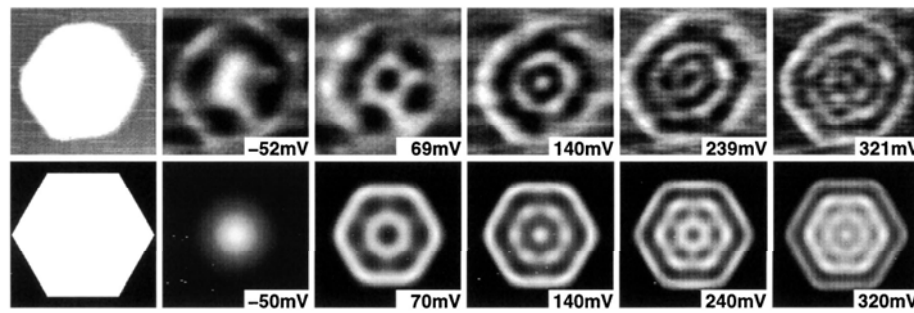
$$H=f(U), I=\text{const}$$

Спектроскопическое картирование

Ag/Ag(111)

Current imaging tunneling spectroscopy (CITS)

Дифференциальное картирование dI/dU , dI/dH



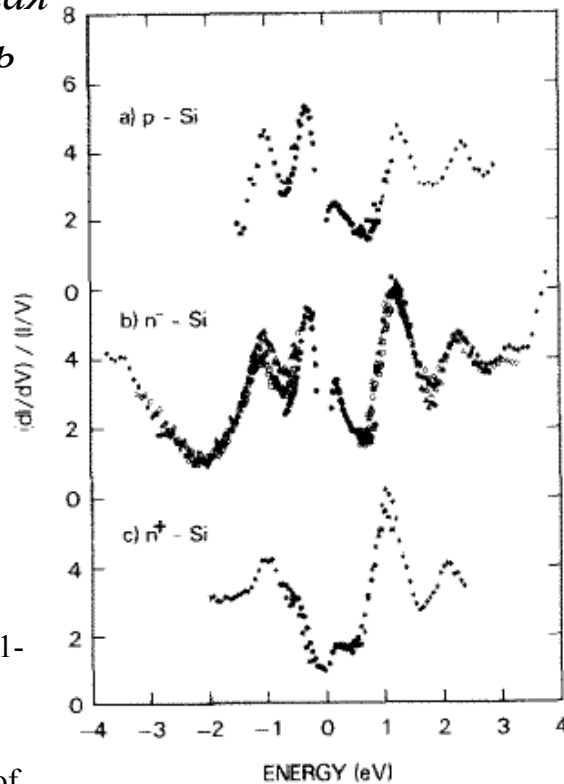
СТМ: Вольтамперные спектры

Si(111)-(7x7)

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

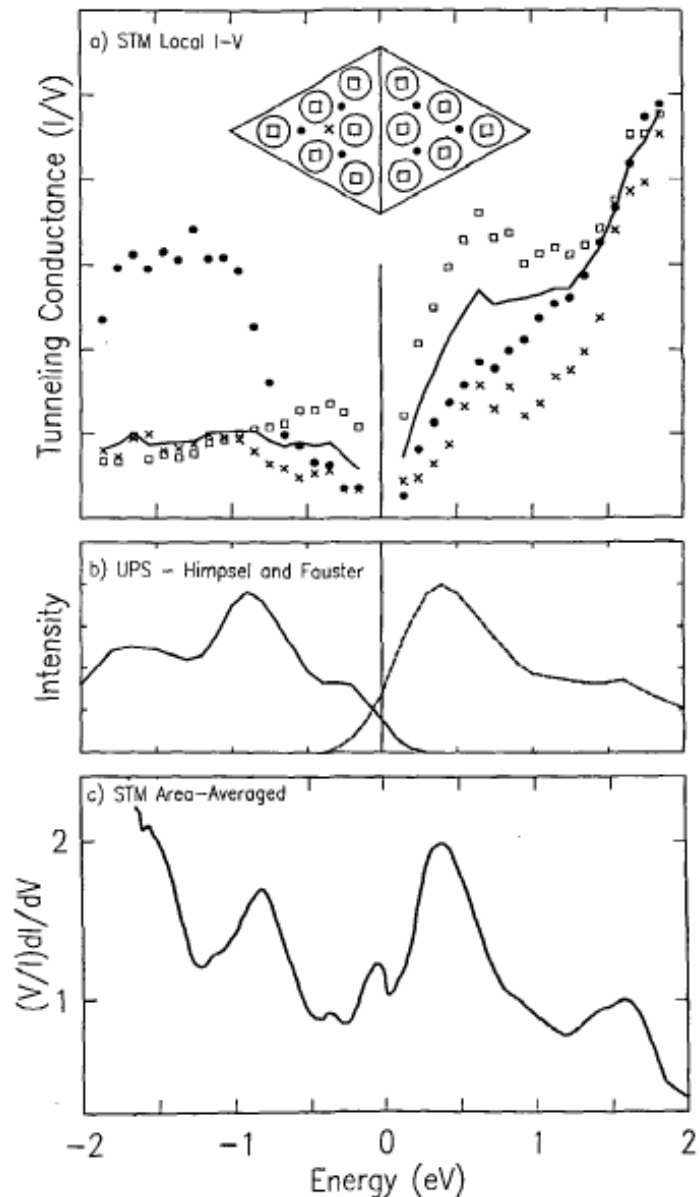
$$\frac{dI/dU}{I/U} = \frac{\rho_s(eU) \rho_t(0) + A(U)}{B(U)}$$

Нормализованная
проводимость



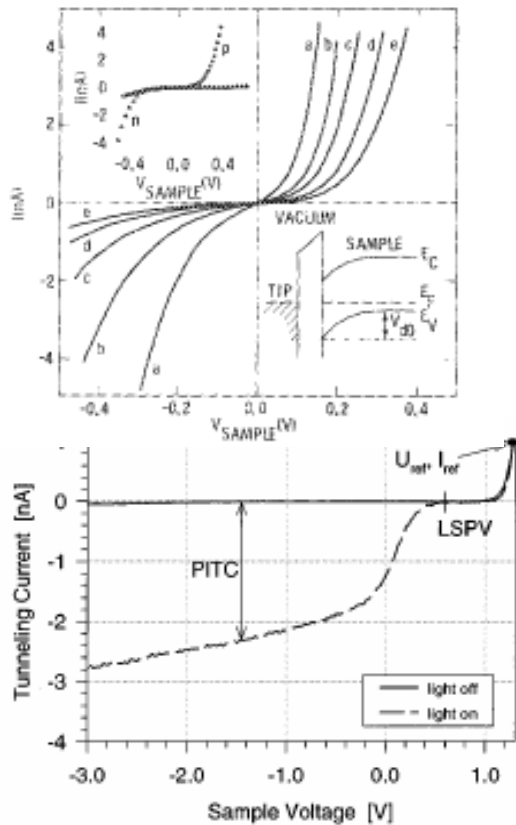
R.J.Hamers, Atomic-resolution surface spectroscopy with the scanning tunneling microscope, Annu.Rev.Phys.Chem. 40(1989)531-559

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



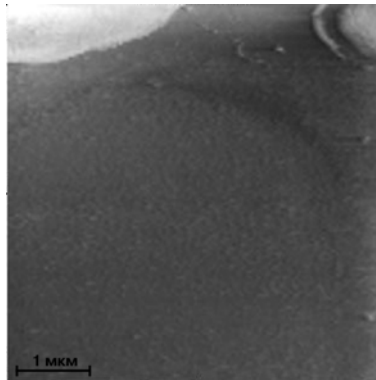
СТМ: Вольтамперные спектры: полупроводники

Гетероструктура металл/
изолятор/полупроводник (MIS)
Барьер Шоттки

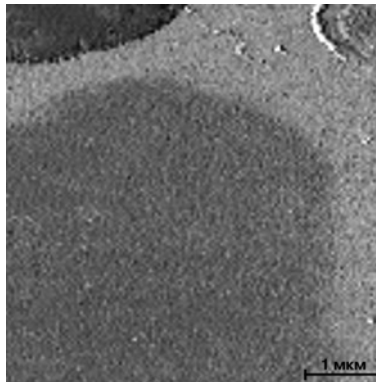


Керамика SnO_2

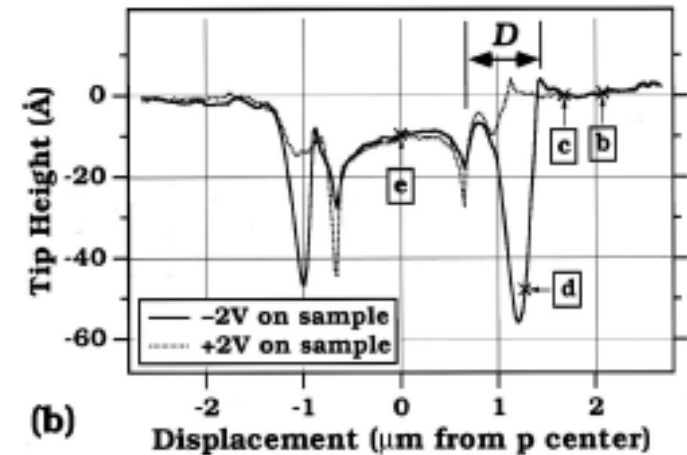
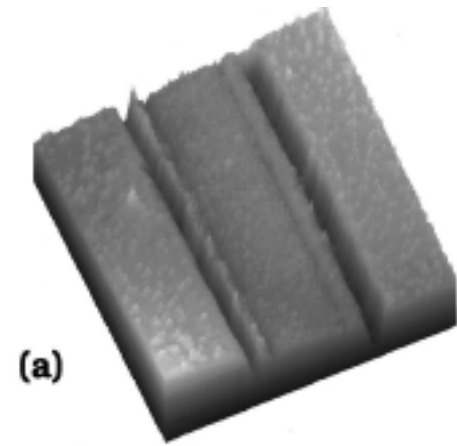
топография



dI/dU



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

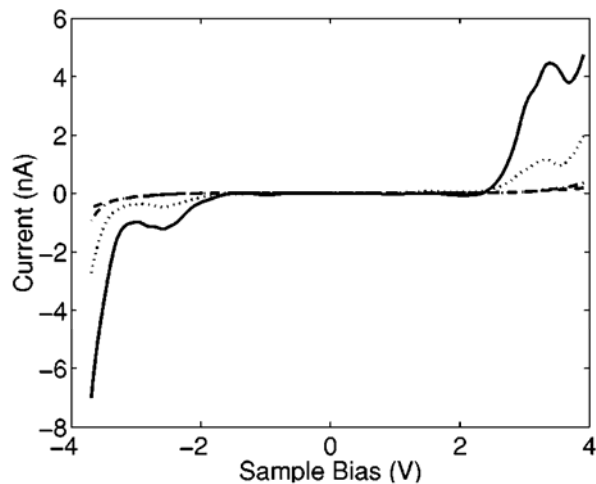
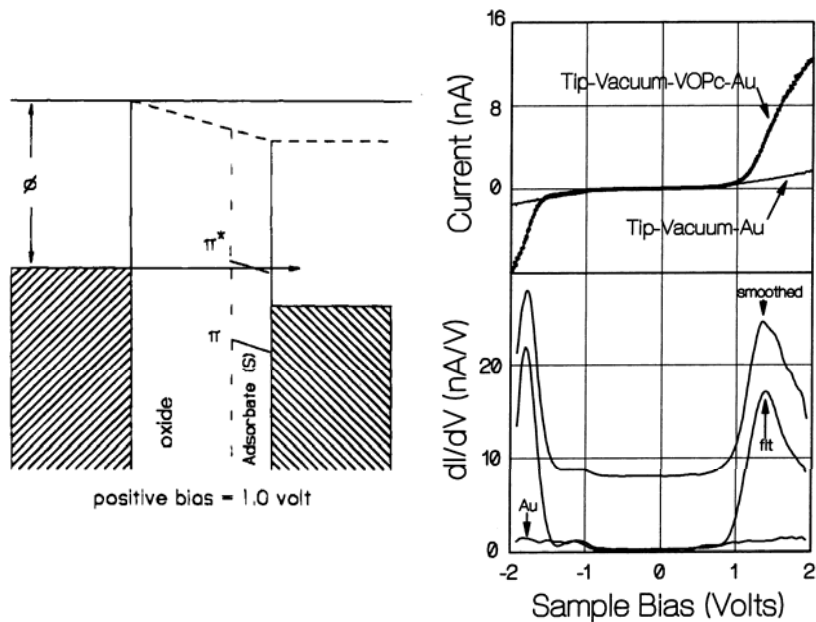
Ch.Sommerhalter, Th.W.Matthes, J.Boneberg, P.Leiderer, M.Ch.Lux-Steiner, Tunneling spectroscopy on semiconductors with a low surface state density, J.Vac.Sci.Technol.B 15(1997)1876-1883

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

STM: Вольтамперные спектры: частицы в зазоре

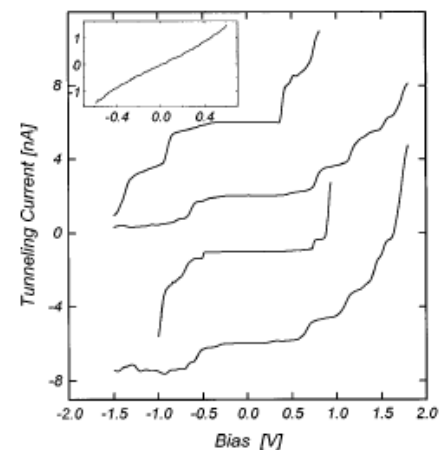
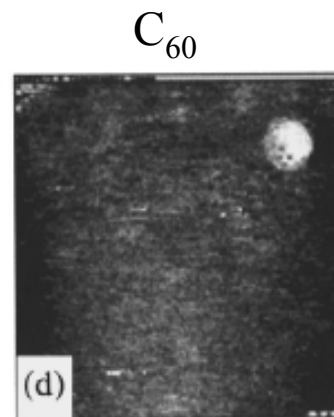
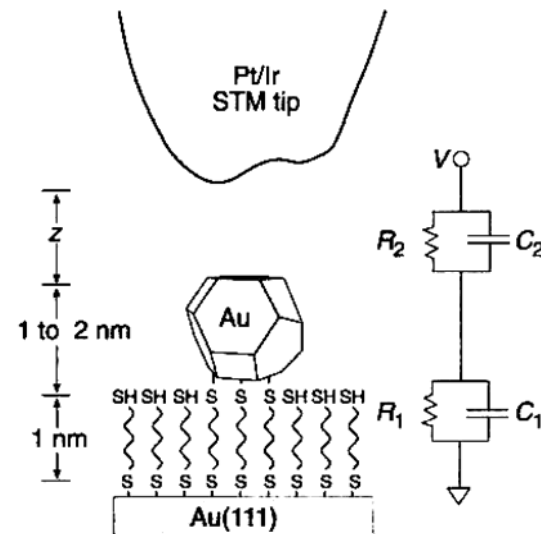
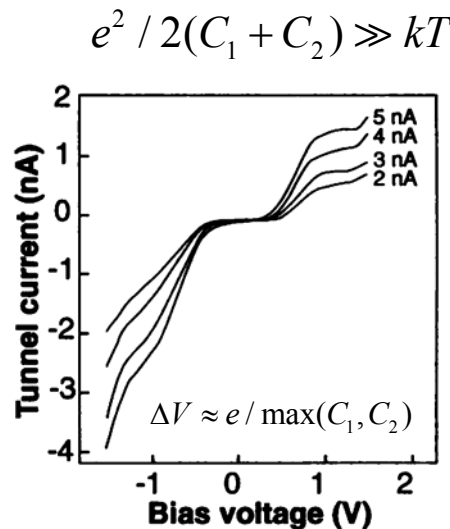
Молекулы

Orbital mediated tunneling
Negative differential resistance



Наночастицы

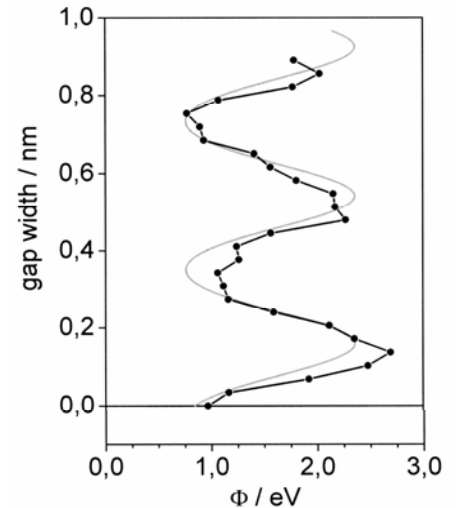
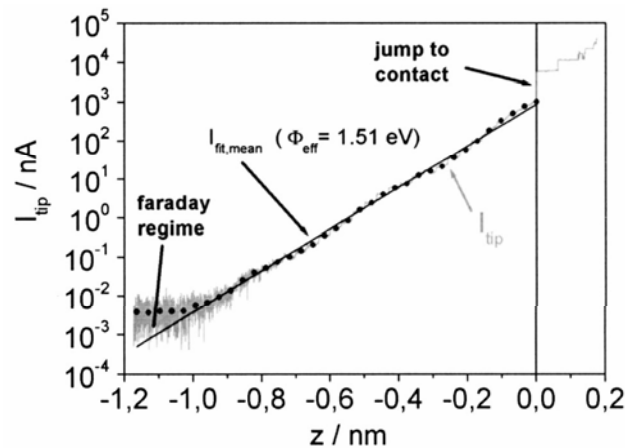
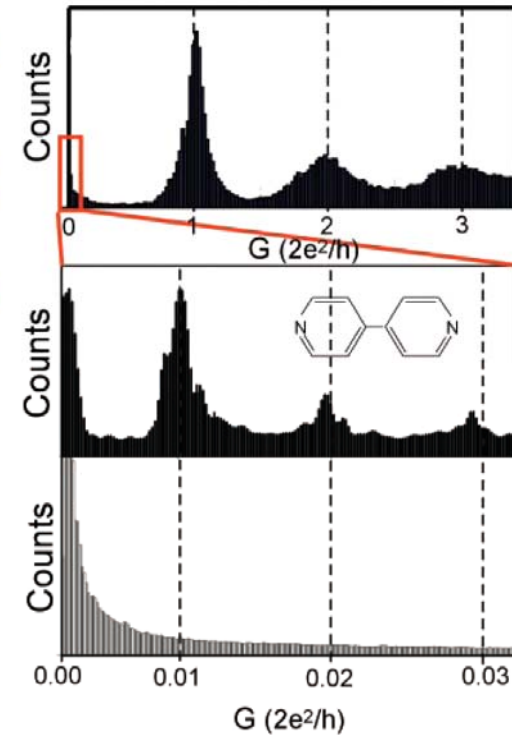
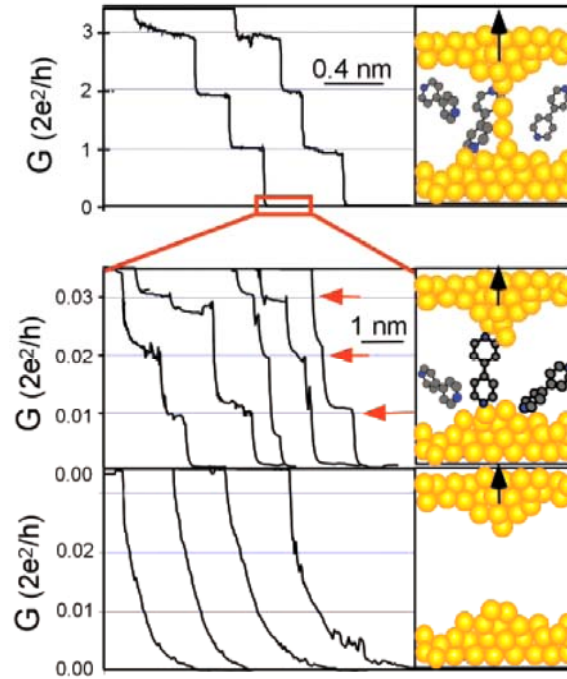
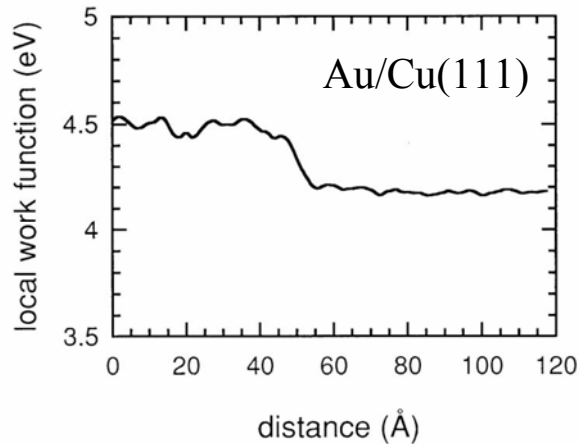
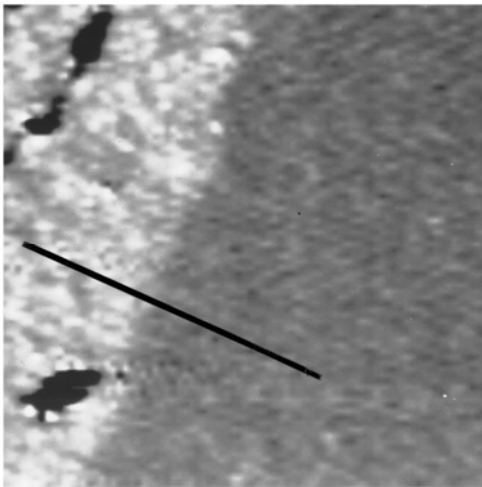
Coulomb blockade
Coulomb staircase



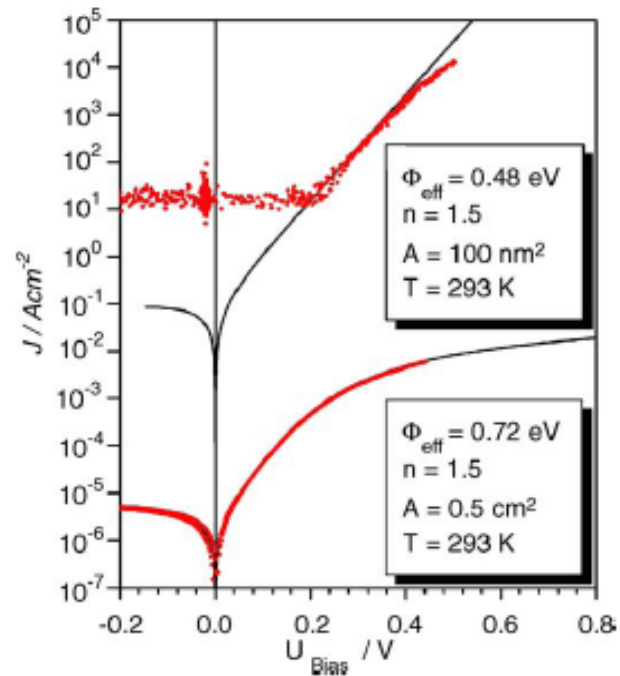
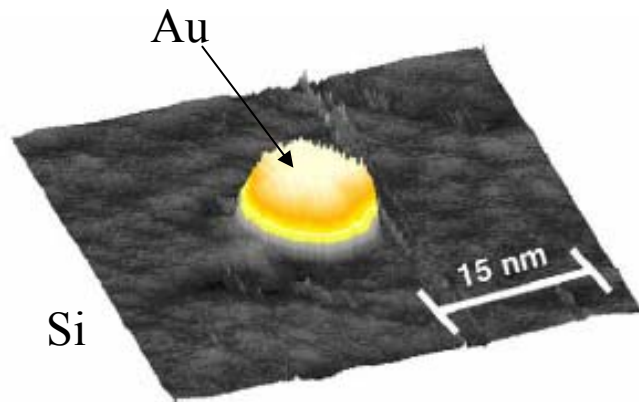
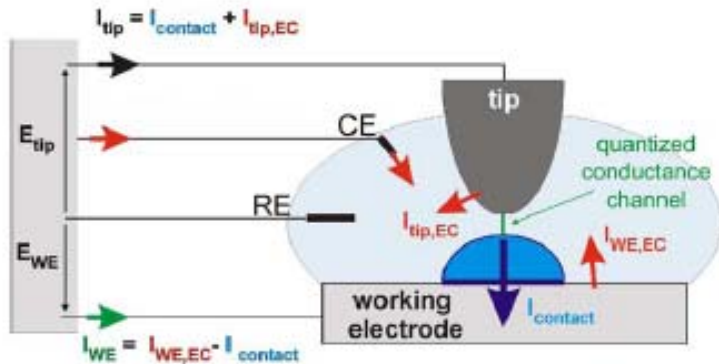
СТМ: Токвысотные спектры

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

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

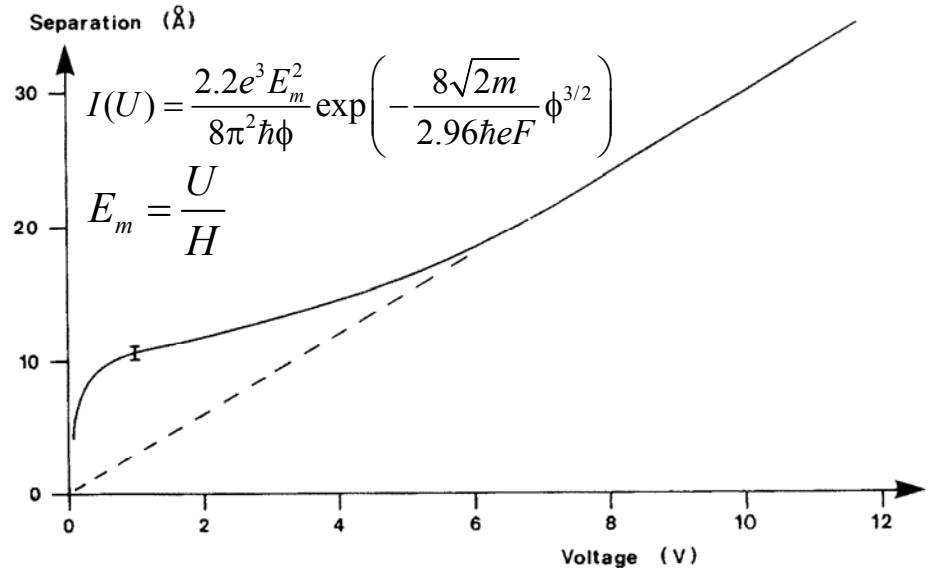
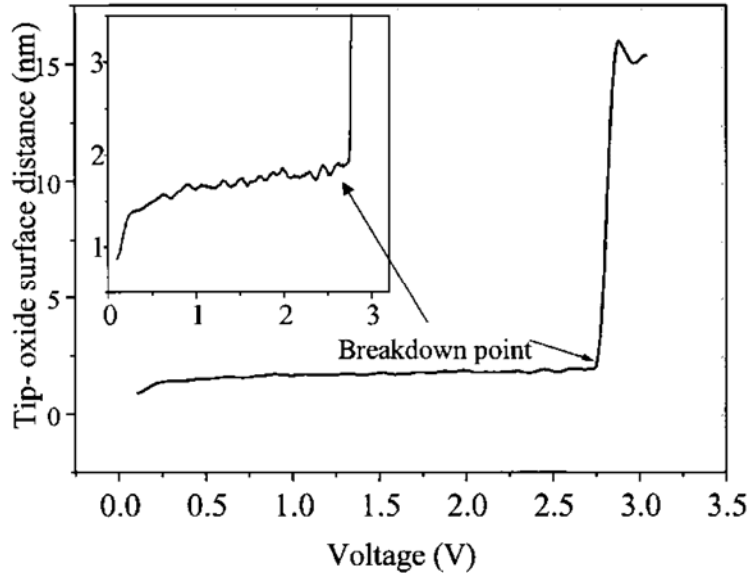


СТМ: Локальный контакт



СТМ: Вольтвысотные спектры

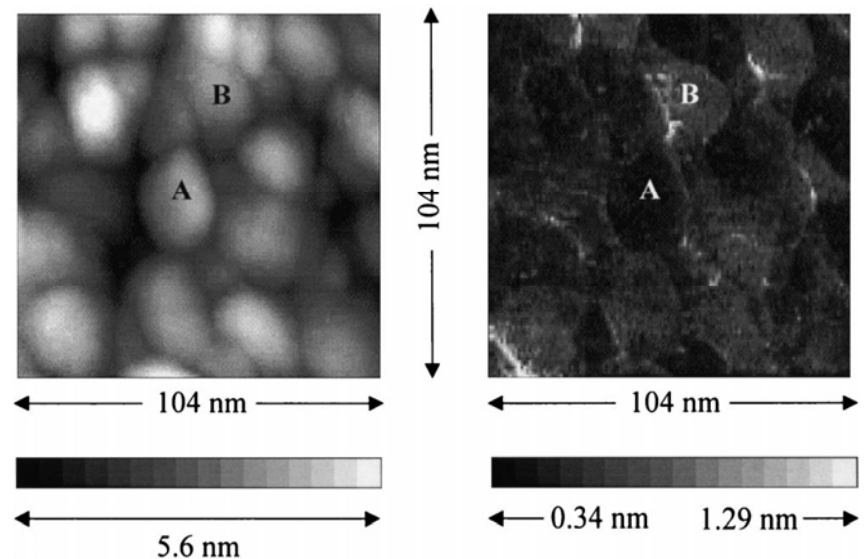
$$I \propto U \cdot \exp\left(\frac{\sqrt{2m\phi}}{\hbar} H\right) \left(\frac{d \ln U}{dH}\right)_{I=\text{const}} = 2 \frac{\sqrt{2m\phi}}{\hbar}$$



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

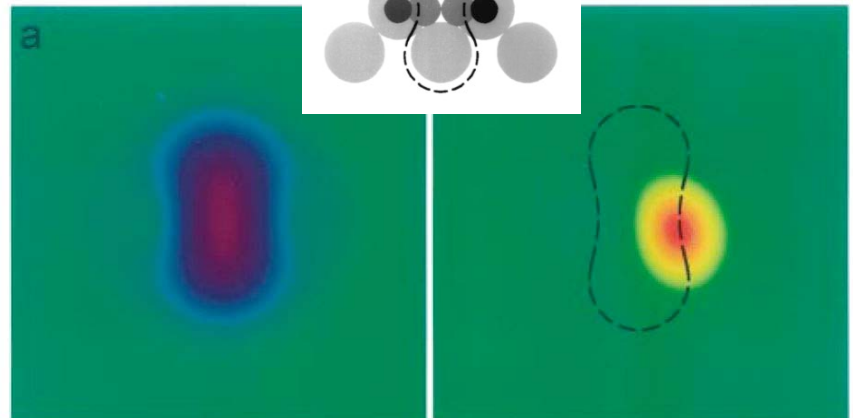
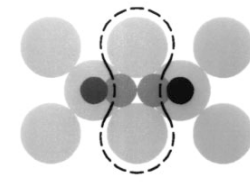
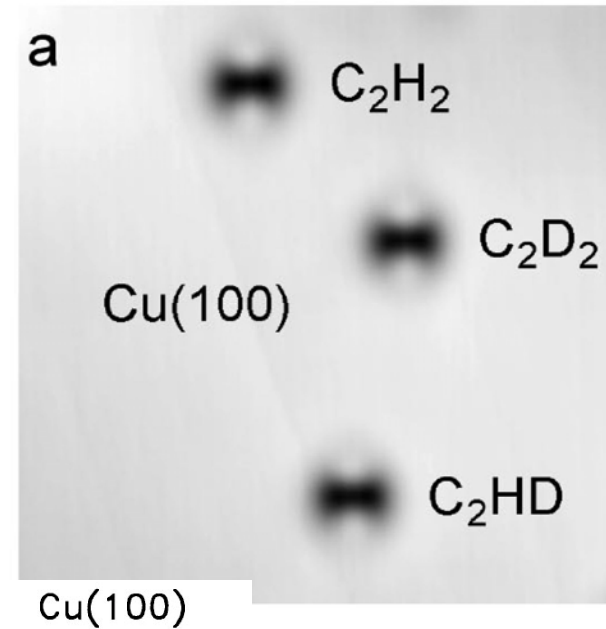
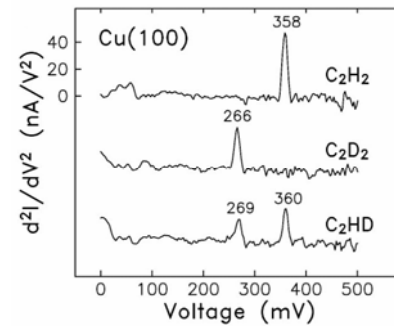
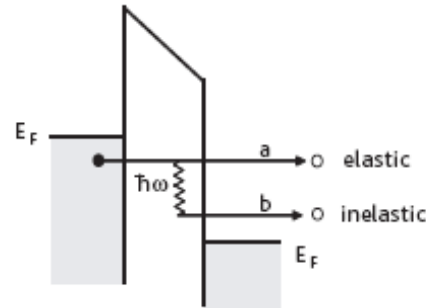
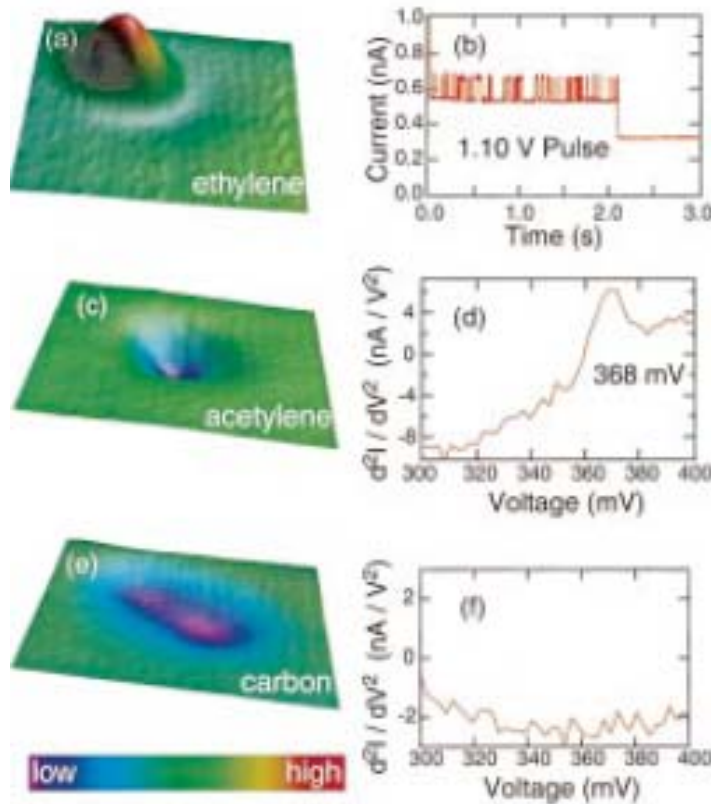


СТМ: Неупругое туннелирование (d^2I/dU^2)

inelastic tunneling spectroscopy, IETS

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

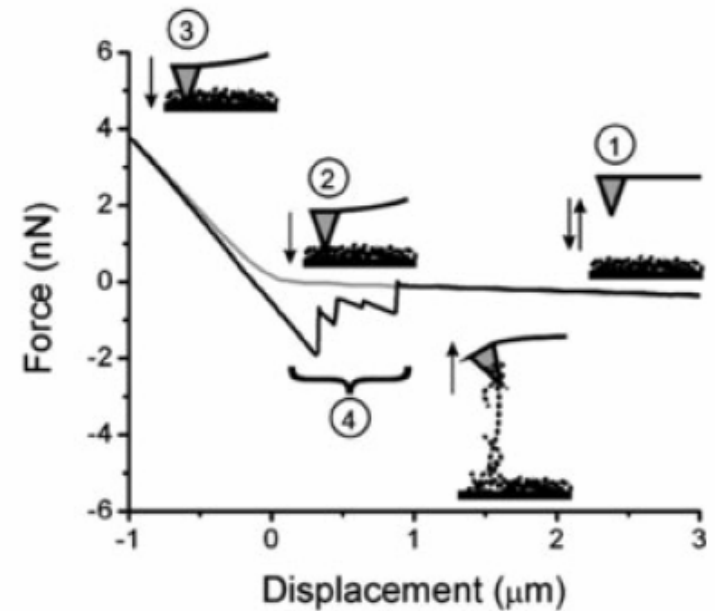
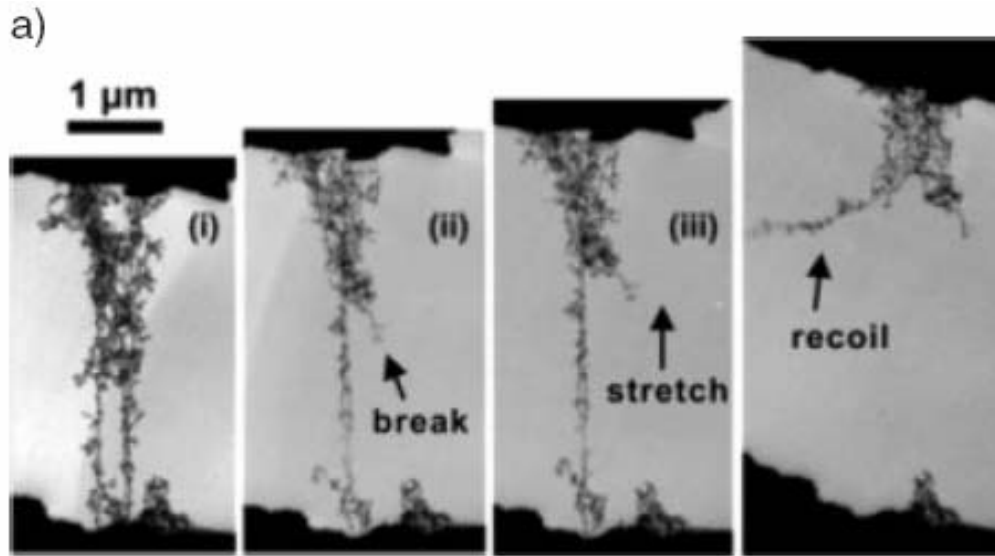
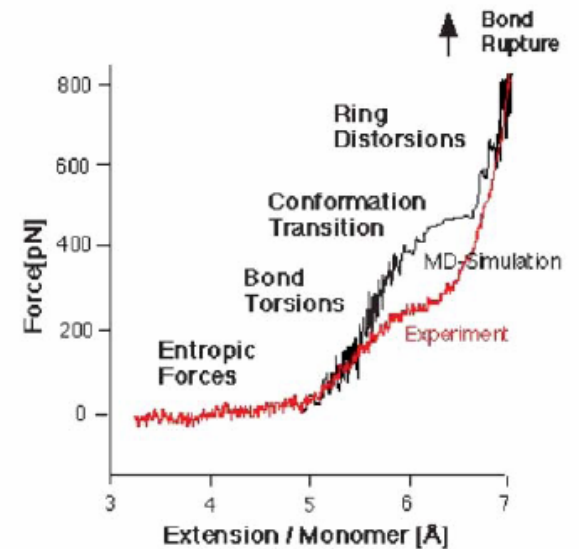
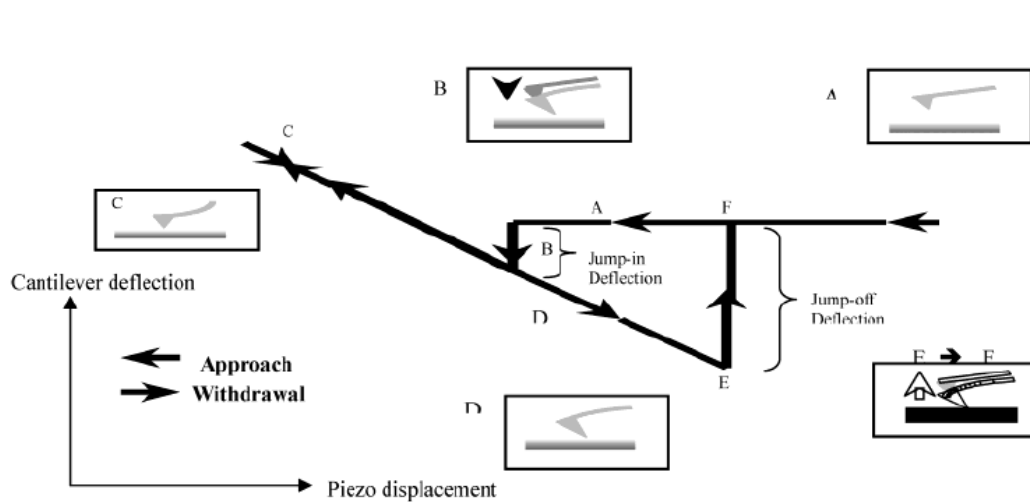
G.Binnig, N.Garcia, H.Rohrer, Conductivity sensitivity of inelastic scanning tunneling microscopy, Phys.Rev.B 32(1985)1336-1338



J.Gaudio, 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

АСМ: Силовые кривые



АСМ: Локальное сопротивление

conducting atomic force microscopy (C-AFM)

current-sensing atomic force microscopy

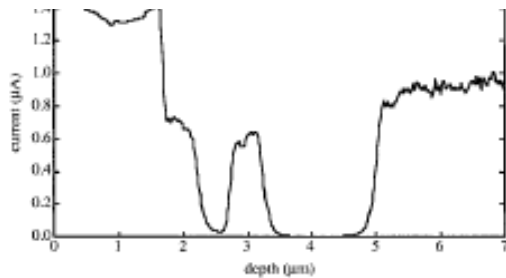
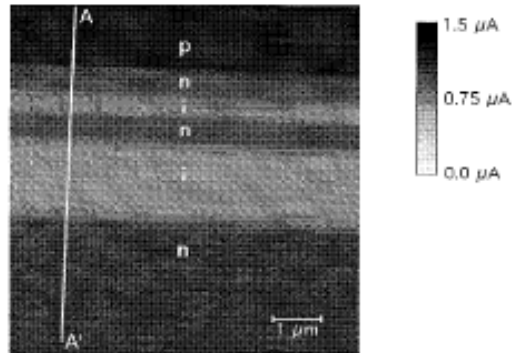
tunneling atomic force microscopy (TUNA)

scanning spreading resistance microscopy (SSRM)

**Молекулярная
проводимость**

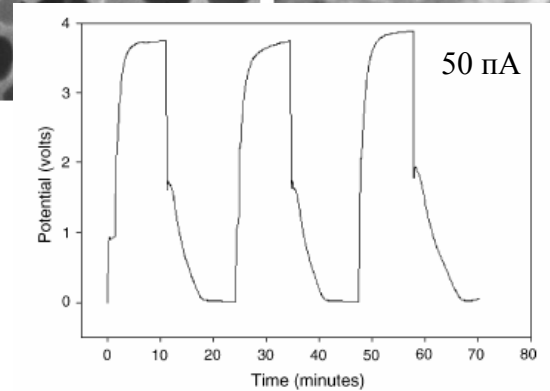
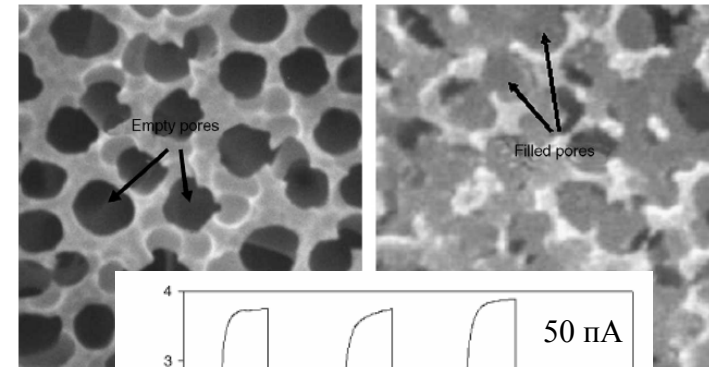
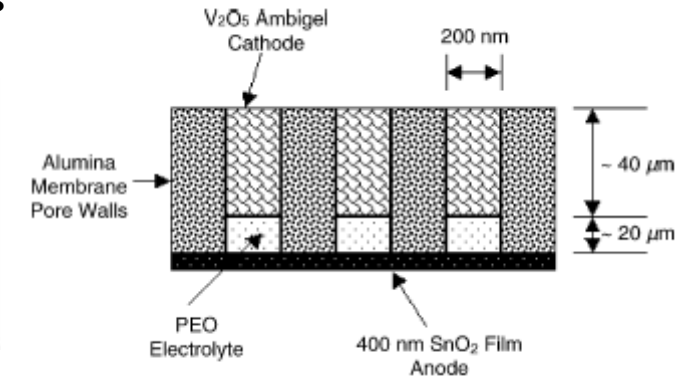
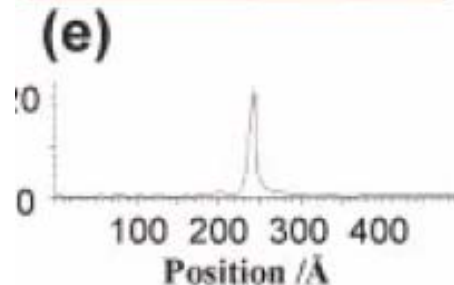
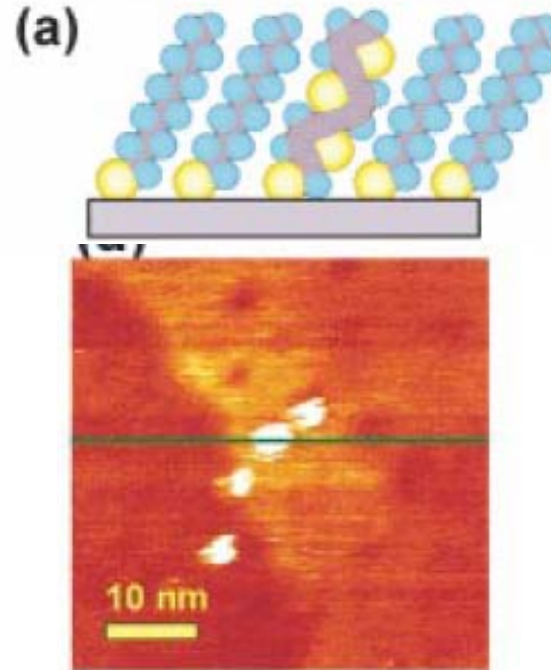
Наноизделия

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

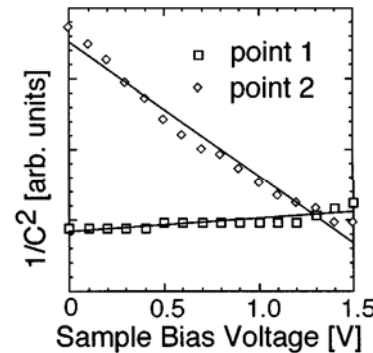
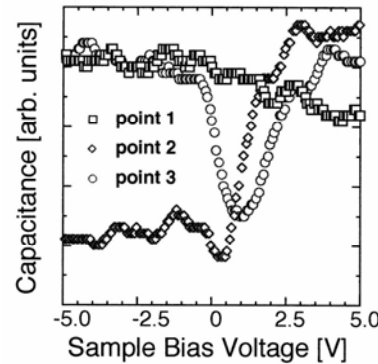
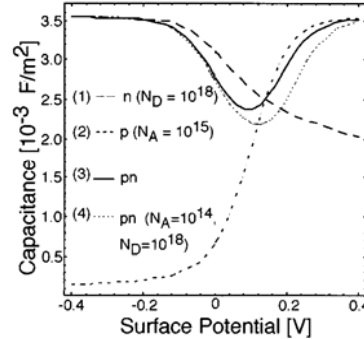
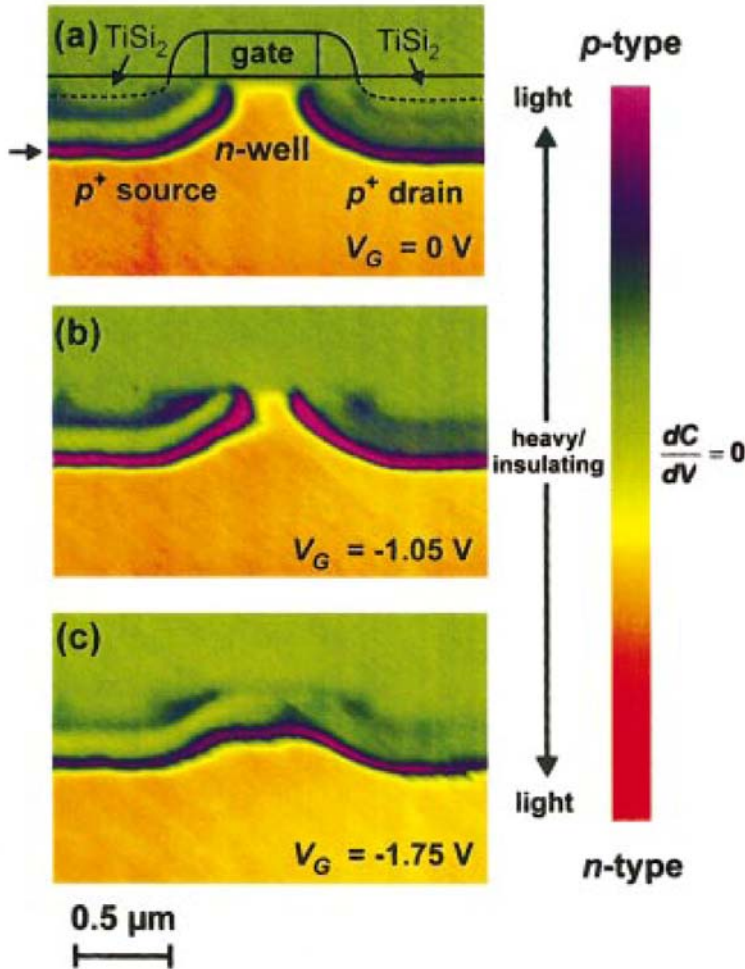
H.Sakaguchi, A.Hirai, F.Iwata, A.Sasaki, T.Nagamura, E.Kawata, S.Nakabayashi, Determination of performance on tunnel conduction through molecular wire using a conductive atomic force microscope, Appl.Phys.Lett. 79(2001)3708



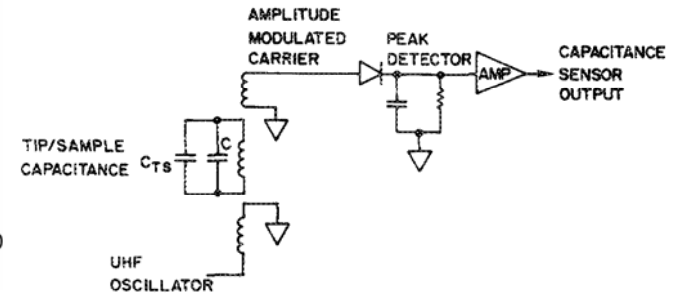
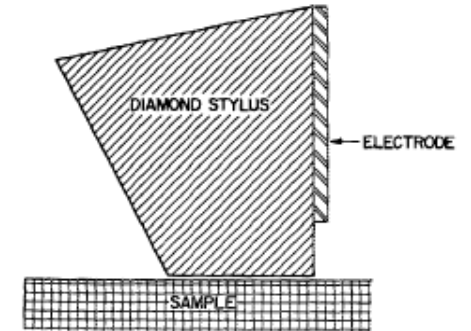
F.Vullum, D.Teeters, Investigation of lithium battery nanoelectrode arrays and their component nanobatteries, J.Power Sources 146(2005)804

АСМ: Локальная емкость

Scanning capacitance microscopy (SCM)

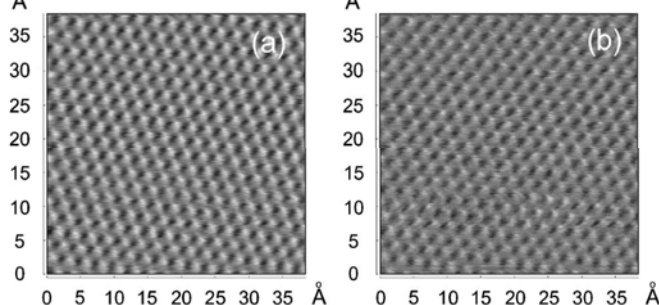


J.R.Matey, J.Blanc, Scanning capacitance microscopy, J.Appl.Phys. 57(1985)1437-1444



Alternating-current scanning tunneling microscopy (AC-STM)

Scanning surface harmonic microscopy (SSHM)



C.Y.Nakakura, P.Tangyonyong, 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

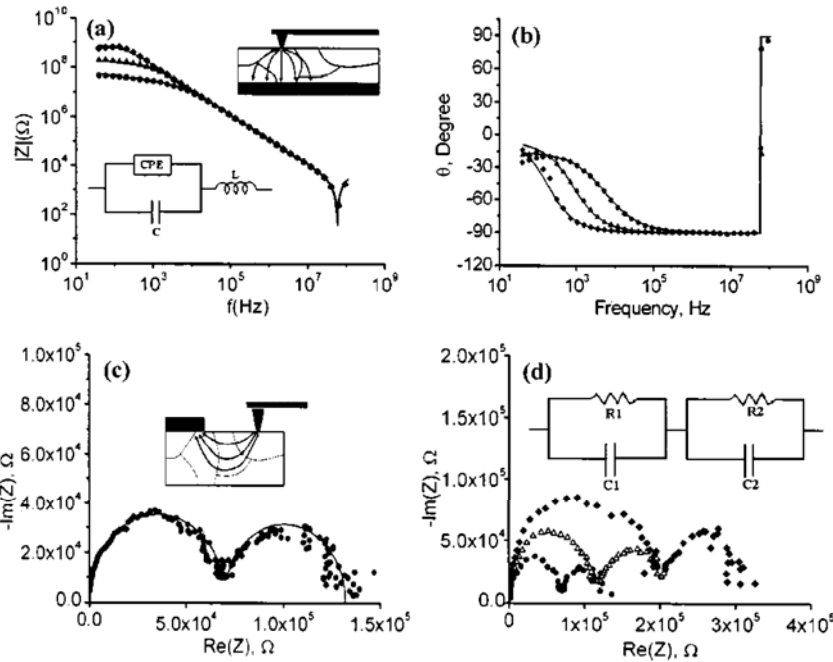
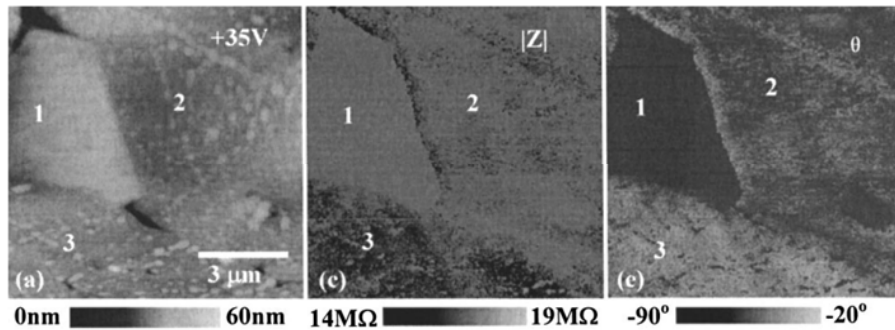
H.Tomiye, T.Yao, H.Kawami, T.Hayashi, Nanometer-scale characterization of SiO₂/Si with a scanning capacitance microscope, Appl.Phys.Lett. 69(1996)4050-4052

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

АСМ: Локальный импеданс

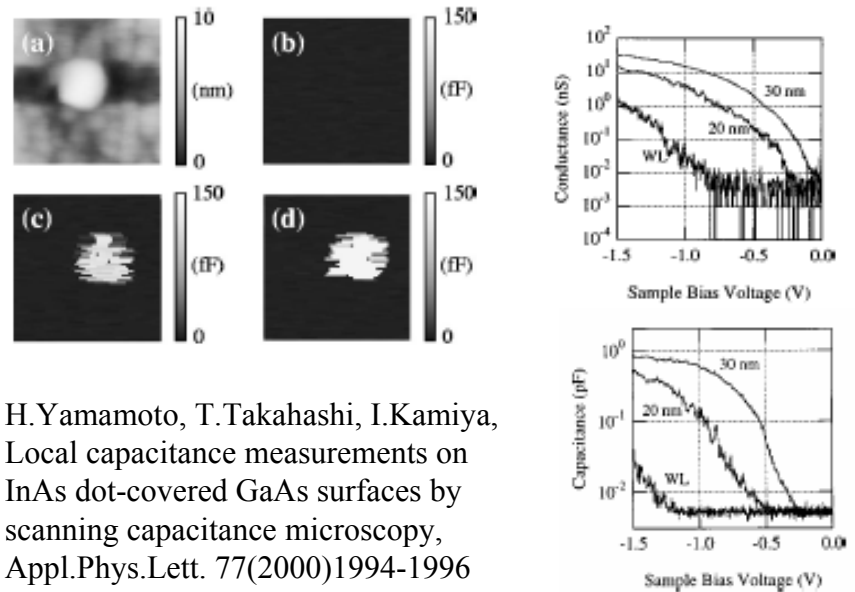
Nanoscale impedance microscopy (NIM)

Керамические материалы



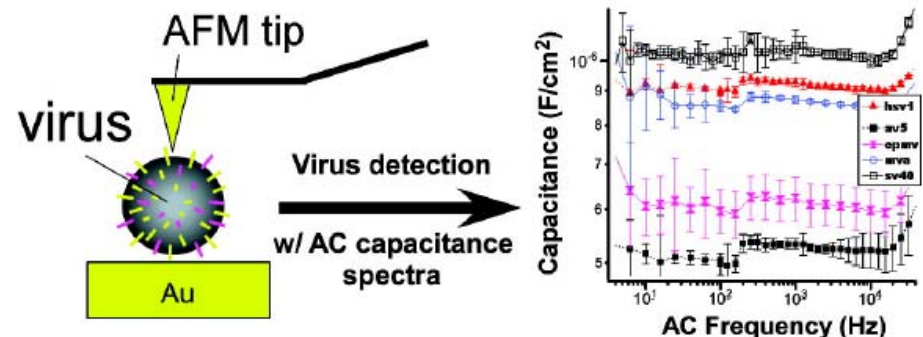
R. Shao, S.V. Kalinin, D.A. Bonnell, Local impedance imaging and spectroscopy of polycrystalline ZnO using contact atomic force microscopy, *Appl. Phys. Lett.* 82(2003)1869-1871

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

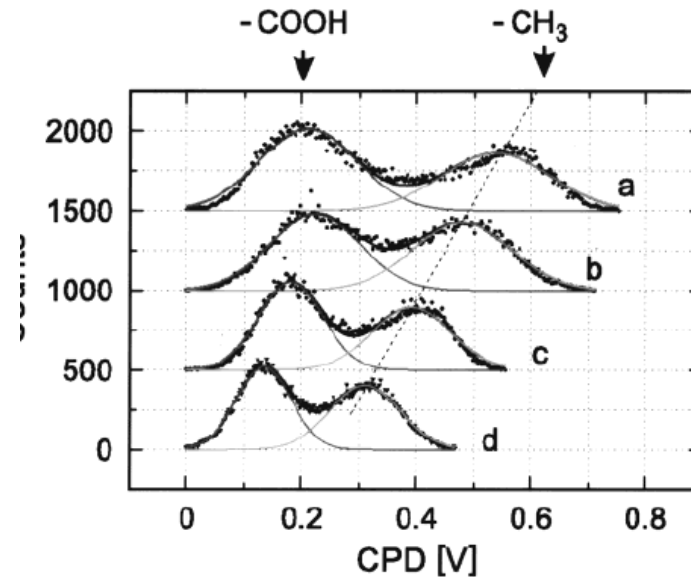
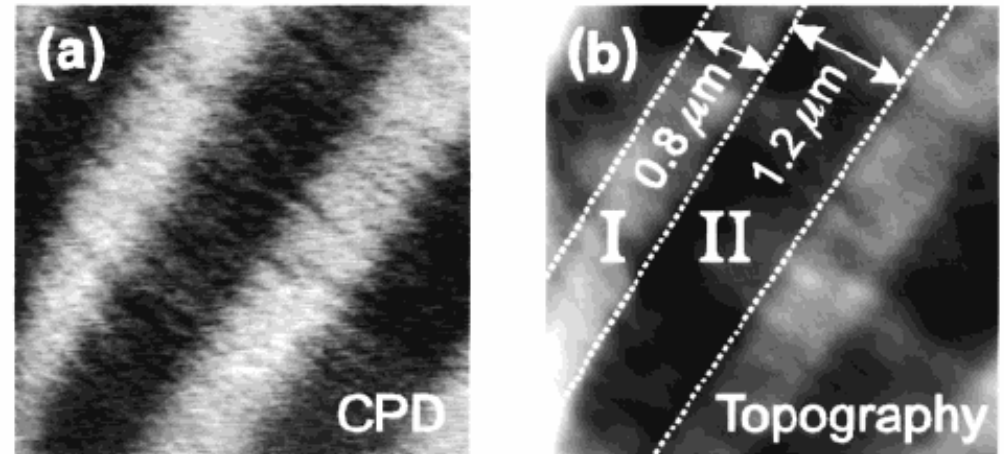
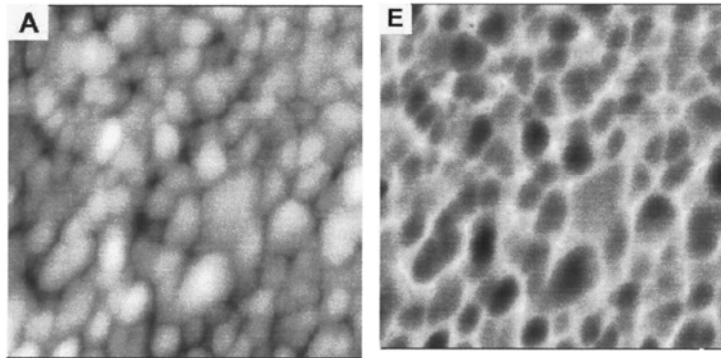
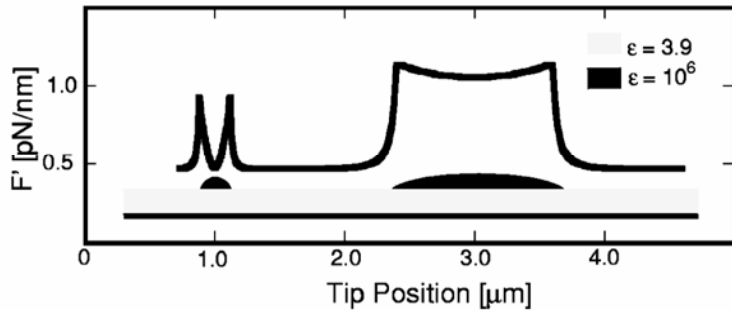
electrostatic force microscopy (EFM)

scanning surface potential microscopy (SSPM)

Kelvin probe force microscopy (KFM, KPFM)

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

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



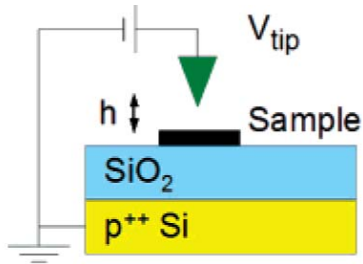
J.Lu, E.Delamarche, L.Eng,
R.Bennewitz, E.Meyer,
H.J.Guntherodt, Langmuir
15(1999)8184

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

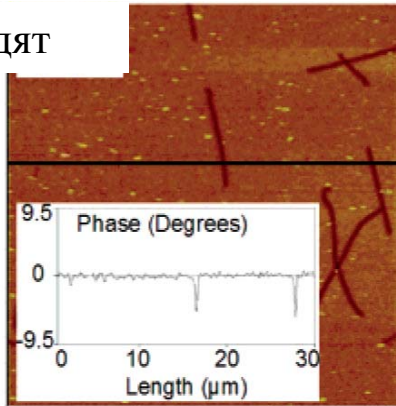
АСМ: Электростатика

scanning conductance microscopy

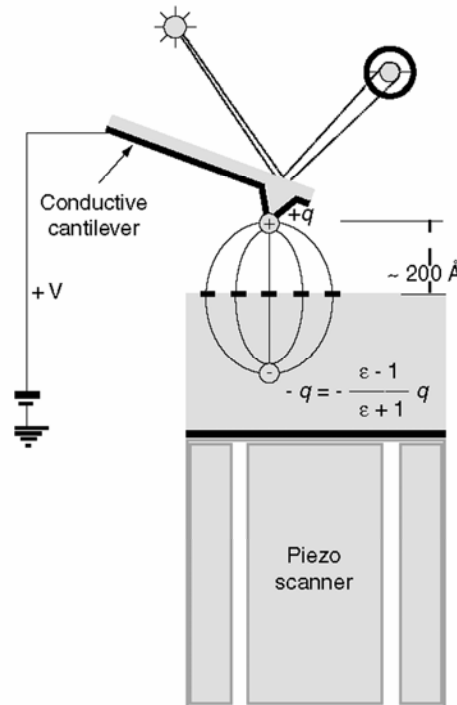
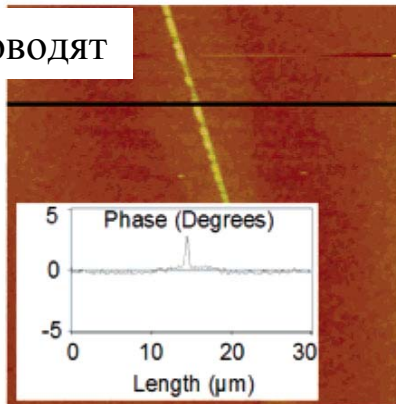


scanning polarization force microscopy (SPFM)

проводят



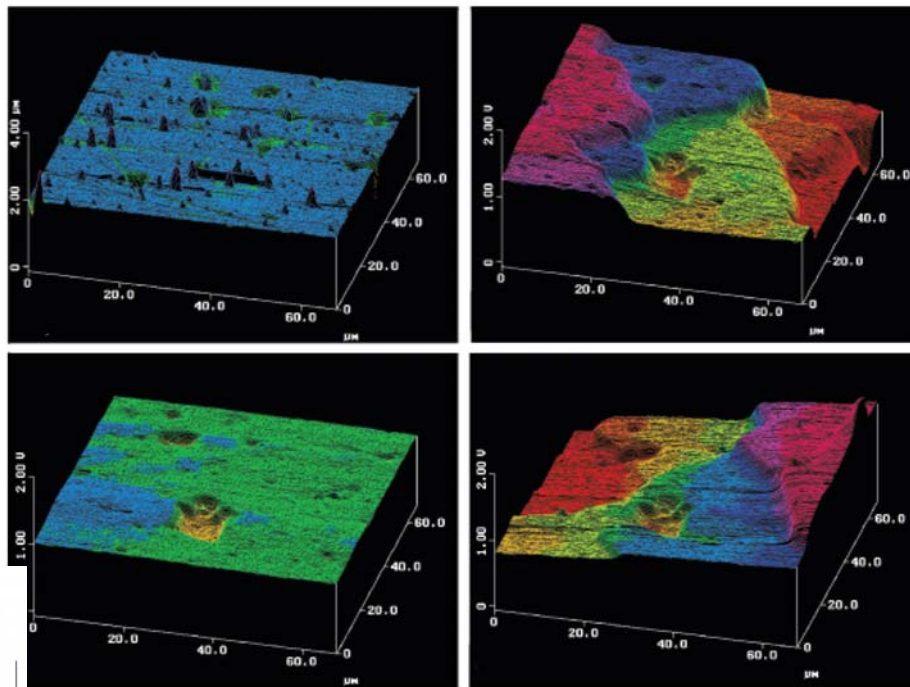
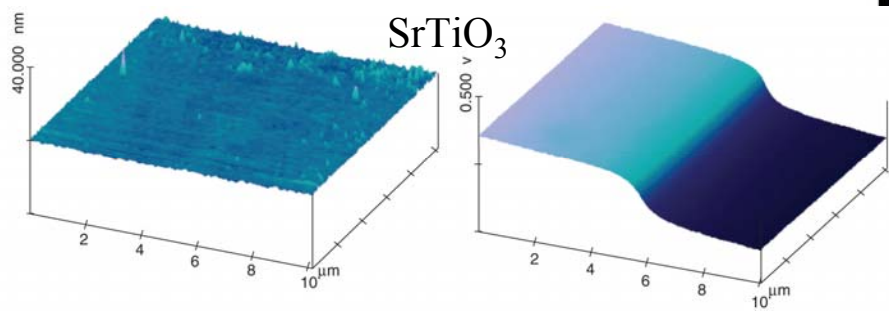
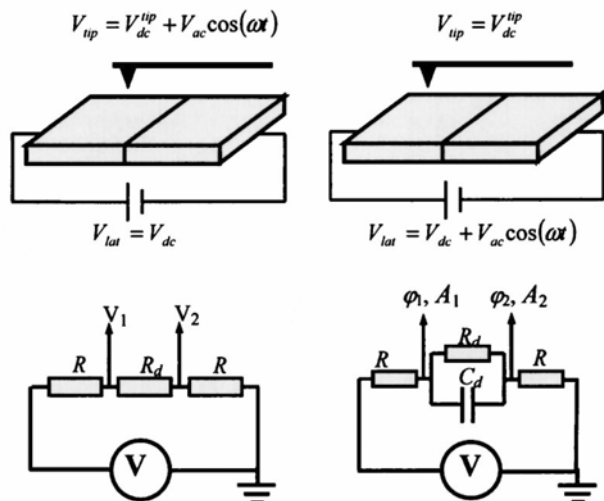
не проводят



пленка воды на слюде

АСМ: Электростатика

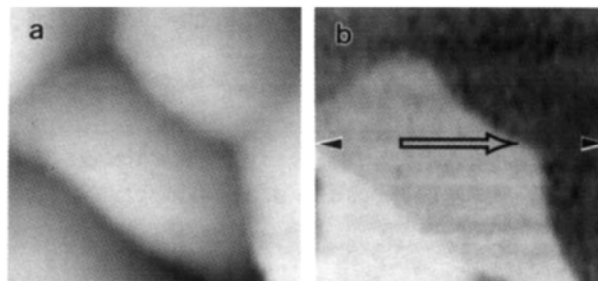
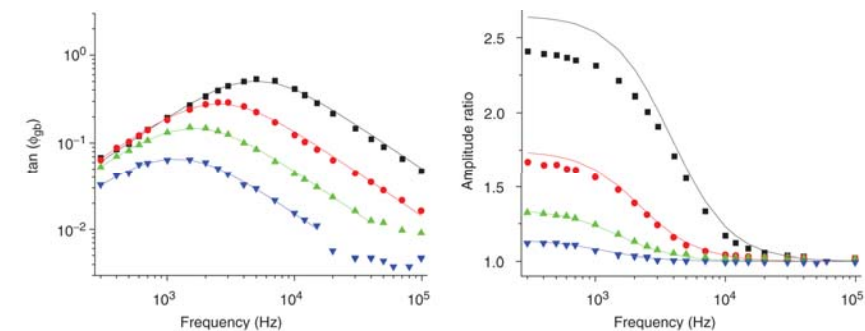
scanning impedance microscopy (SIM)



ZnO

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



Au₆₀Pd₄₀

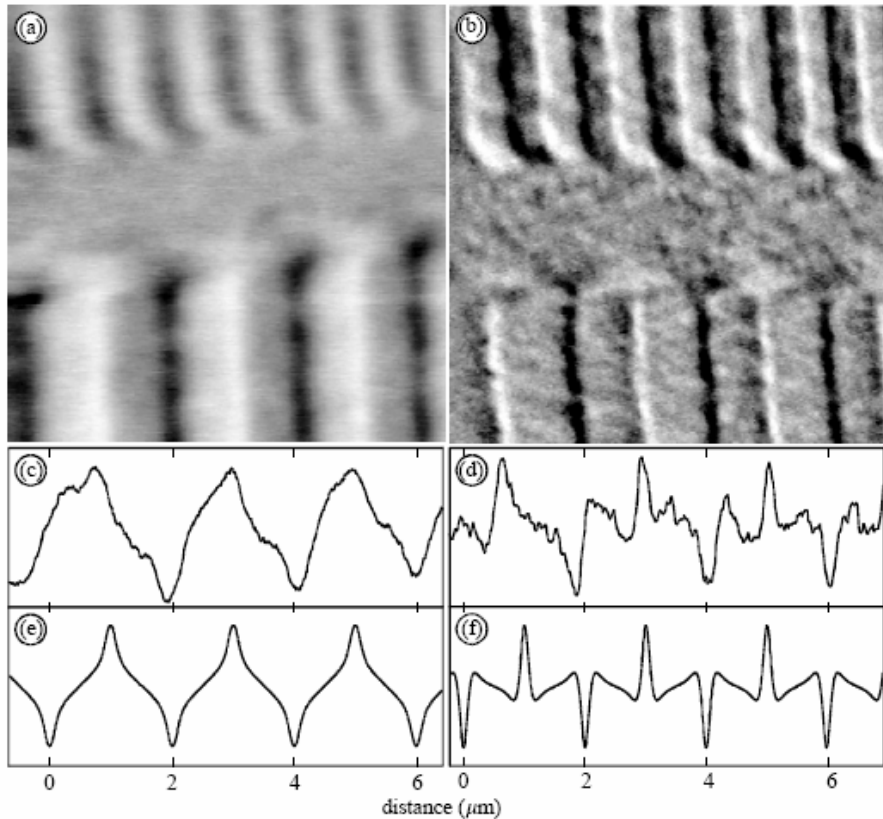
J.R.Kirtley, S.Washburn, M.J.Brady, Direct Measurement of Potential Steps at Grain Boundaries in the Presence of Current Flow, Phys.Rev.Lett. 60(1988)1546-1549

АСМ: Магнитные взаимодействия

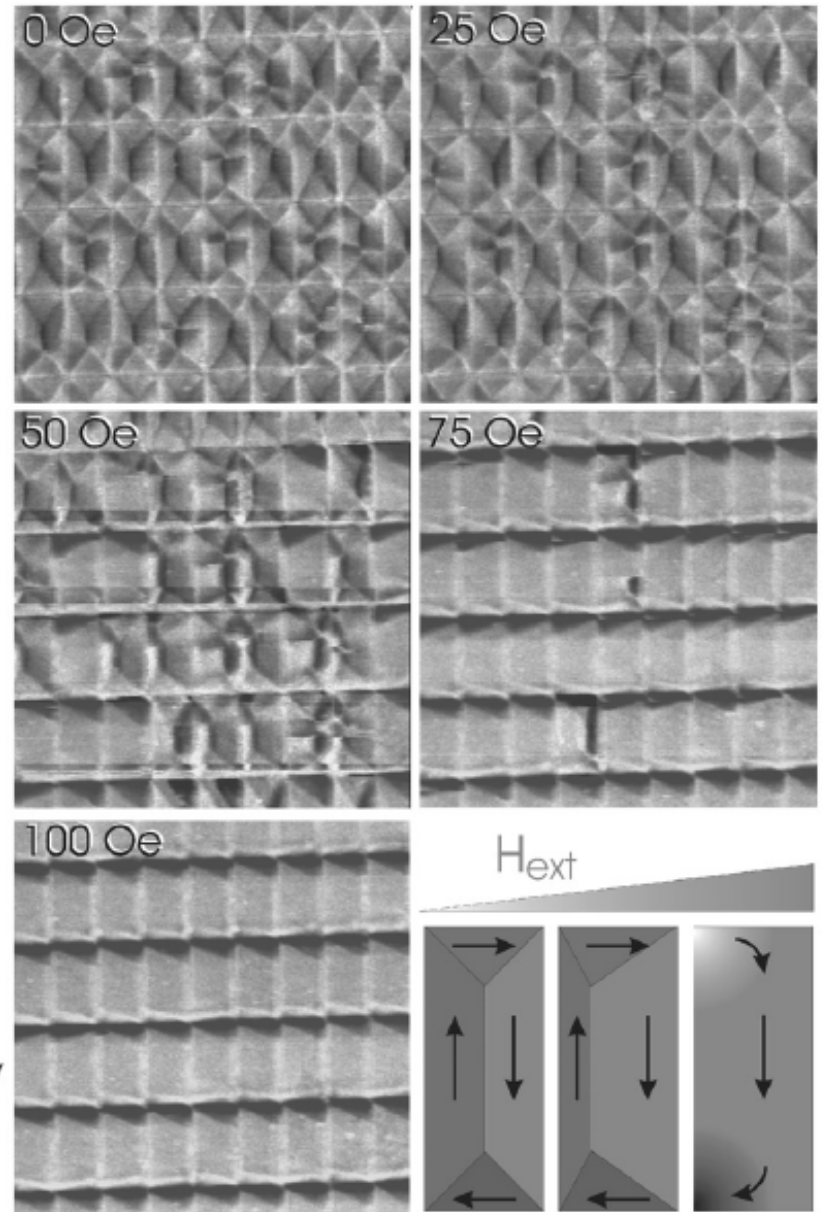
magnetic force microscopy (MFM)

Пермаллой

HDD

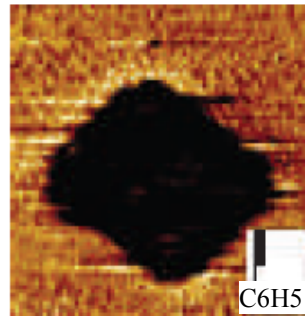
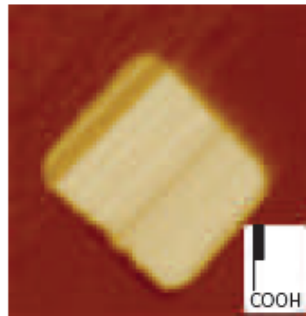
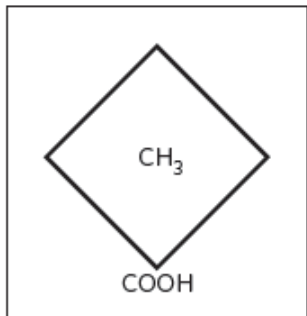
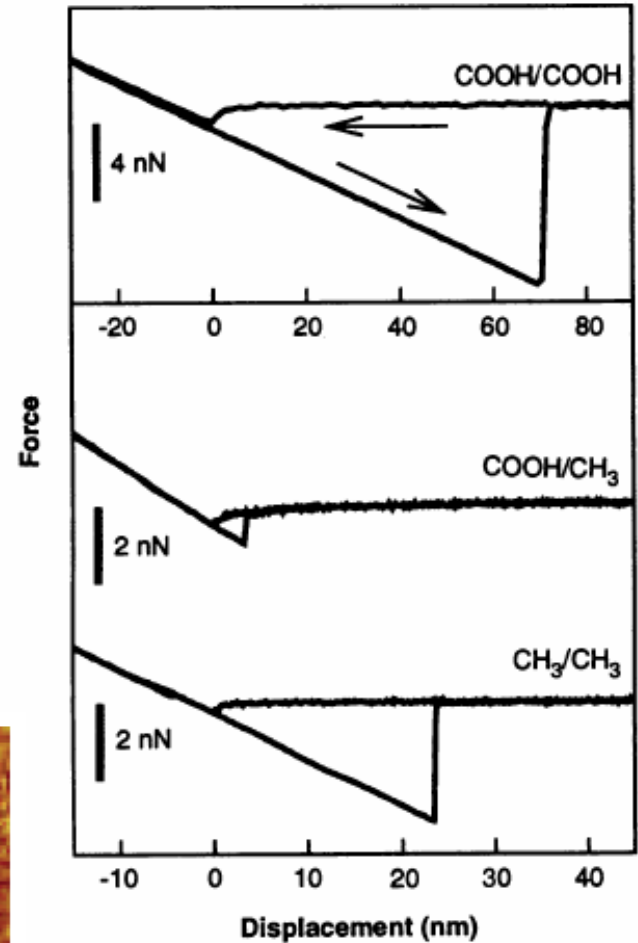
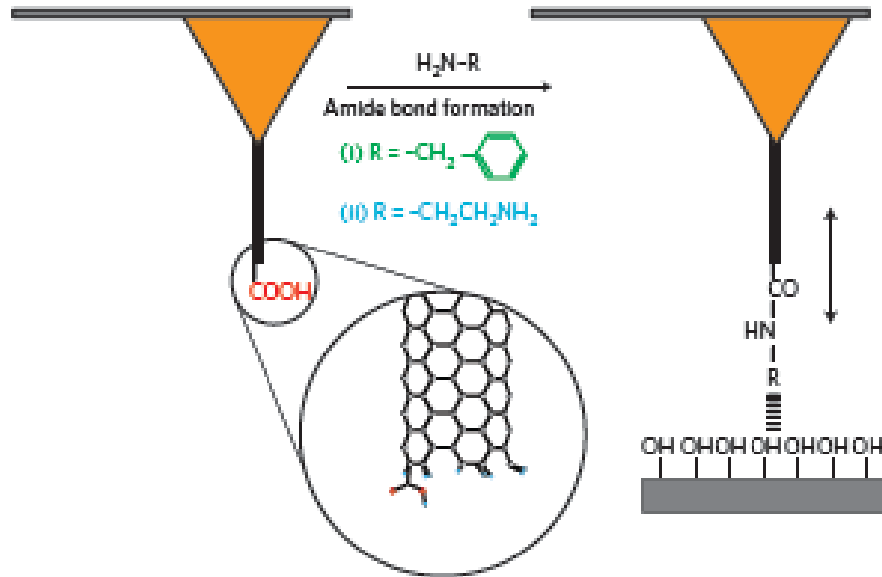


external field



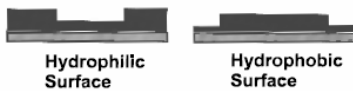
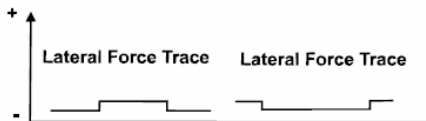
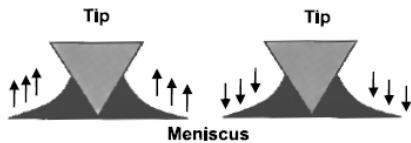
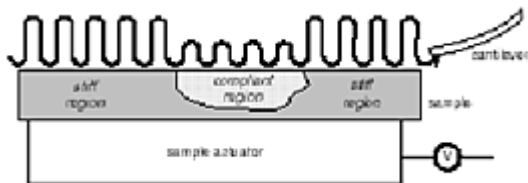
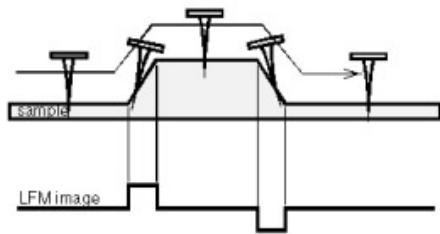
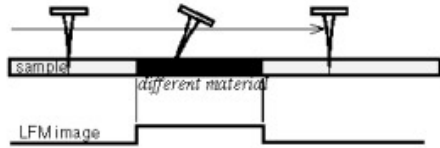
АСМ: Химическая природа объекта

chemical force microscopy (CFM)

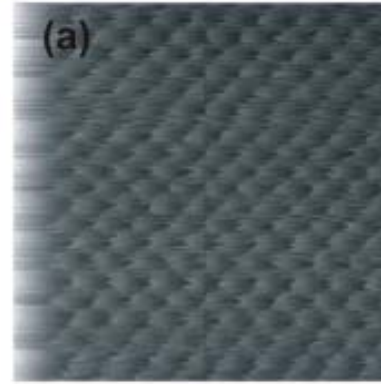


АСМ: Механические свойства

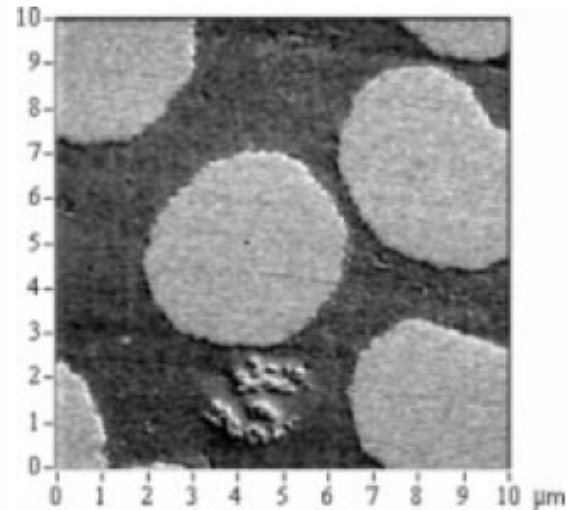
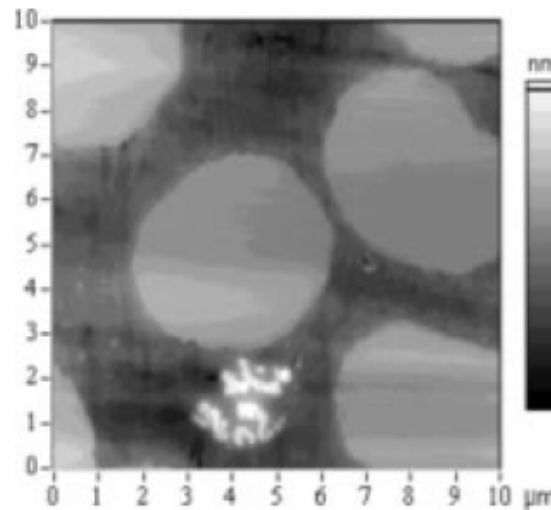
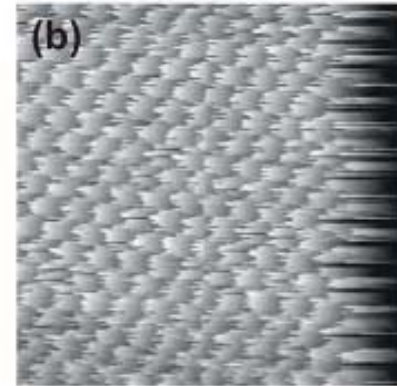
lateral force microscopy (LFM)
friction force microscopy (FFM)
force modulation microscopy (FMM)



NaCl



Cu(111)



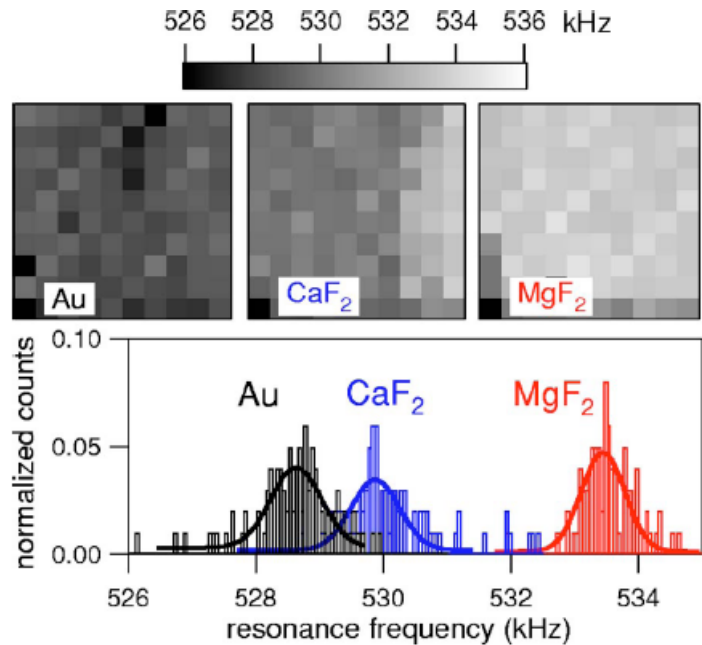
R.Bennewitz, Friction force microscopy, Materials Today, (2005)42

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

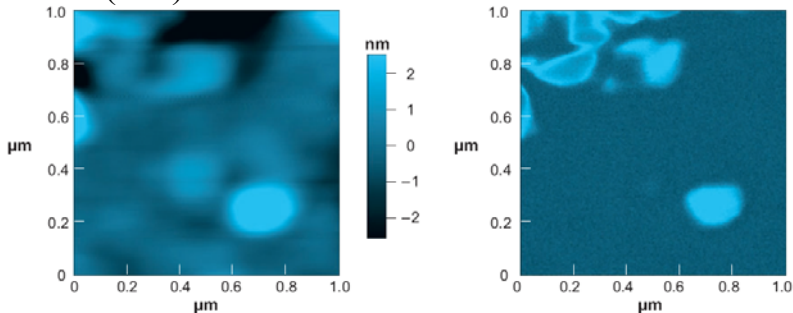
АСМ: Механический отклик

Atomic force acoustic microscopy (AFAM)

Ultrasonic force microscopy (UFM)



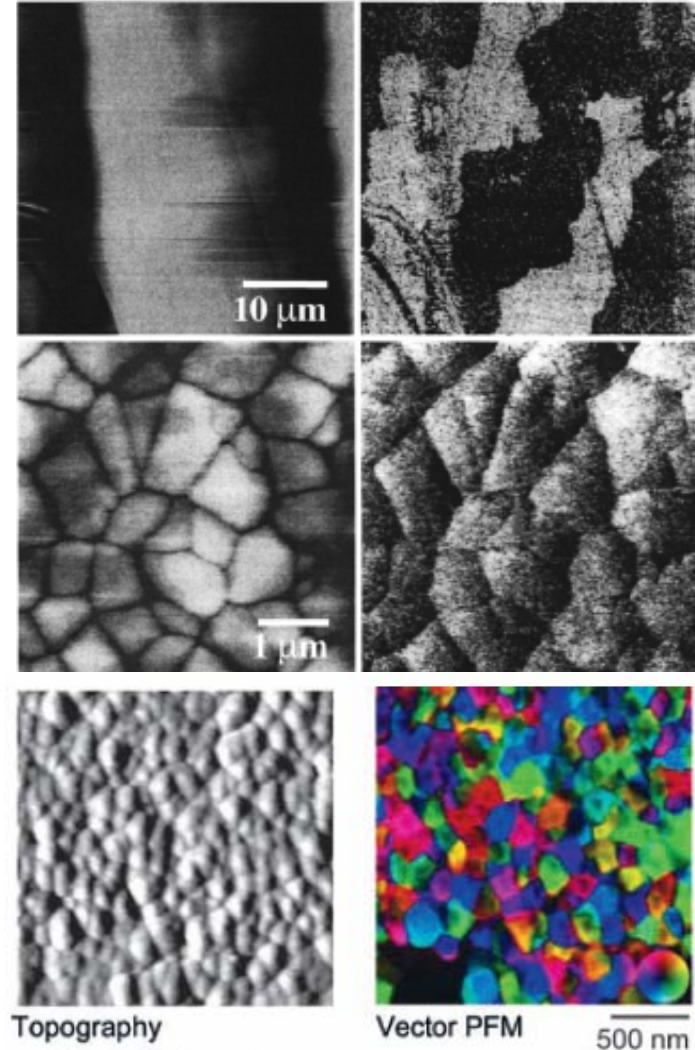
Au/Si(111)



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)



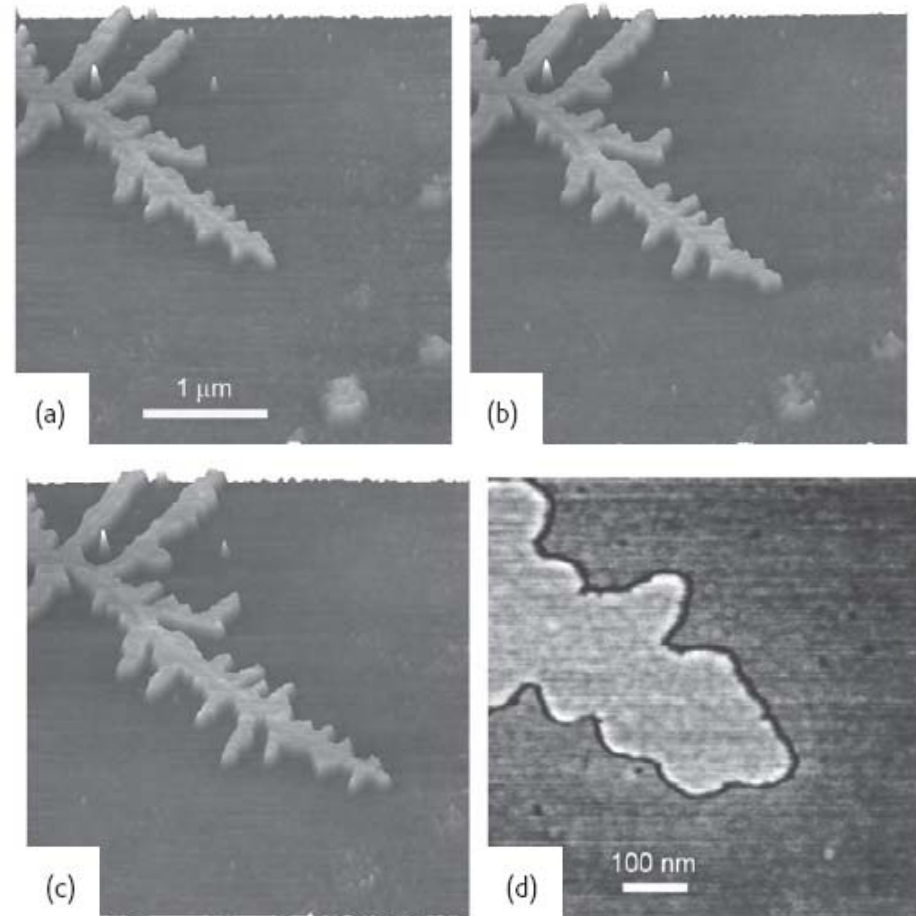
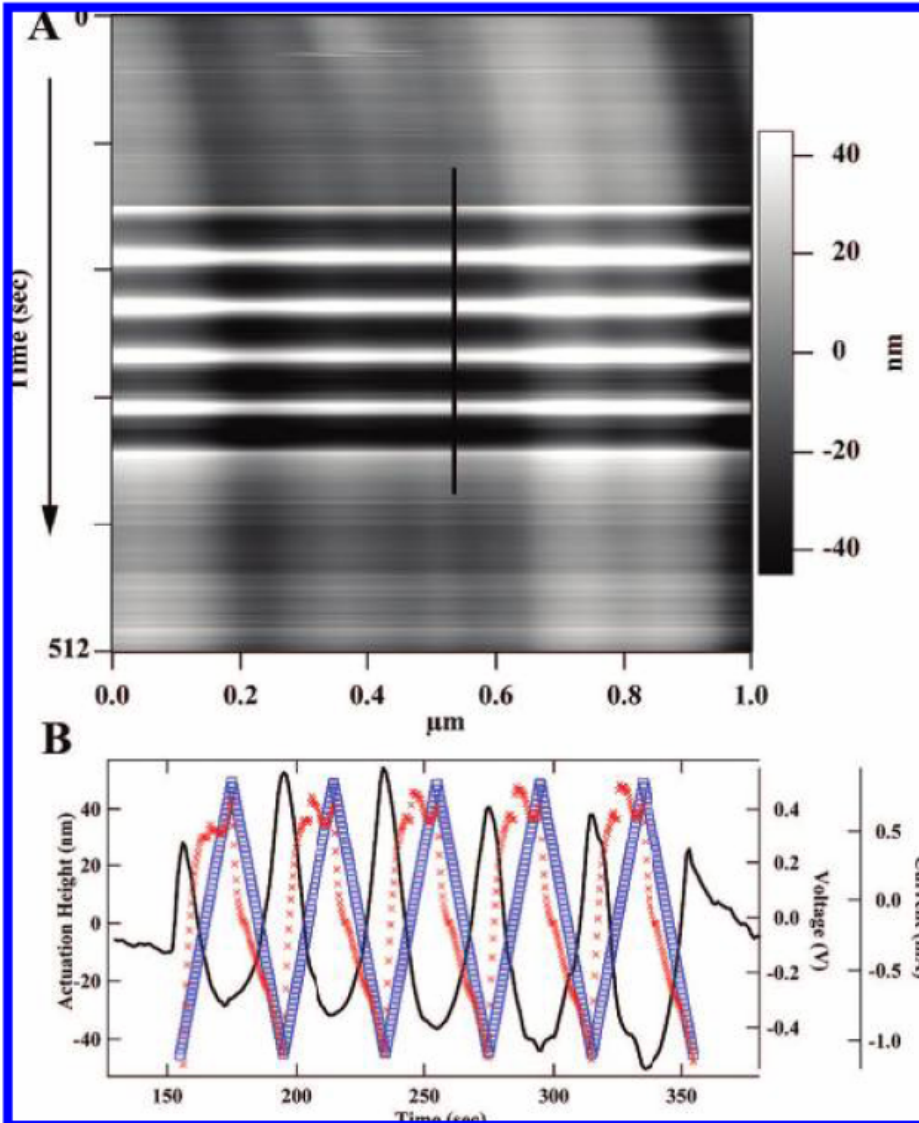
S.V.Kalinin, D.A.Bonnell, Imaging mechanism of piezoresponse force microscopy of ferroelectric surfaces, Phys.Rev.B. 65(2002)125408

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



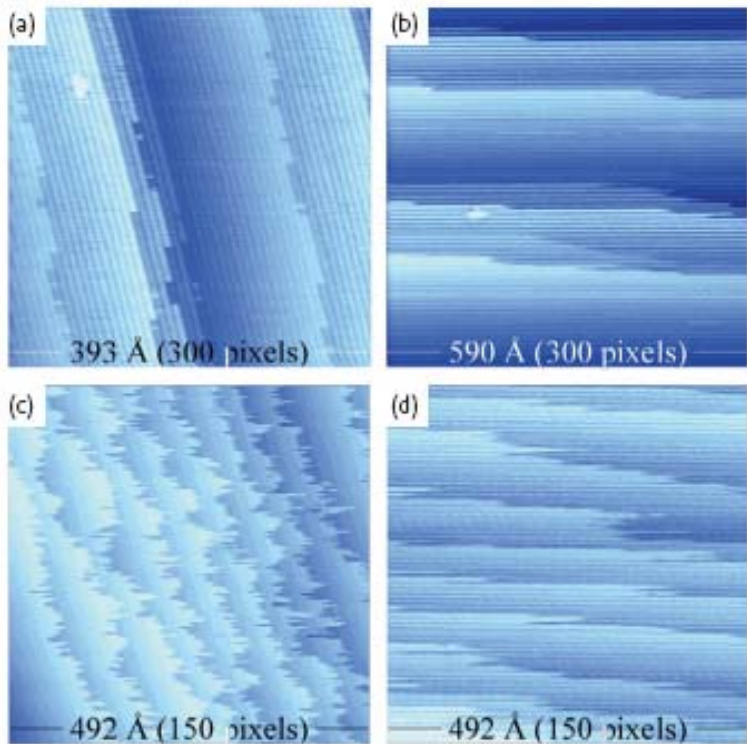
J.K.Hobbs, N.Mullin, C.H.M.Weber, O.E.Farrance, C.Vasilev, 'Watching' processes in soft matter with SPM, Materials Today, 12(2009)26

STM/АСМ: Мониторинг процессов

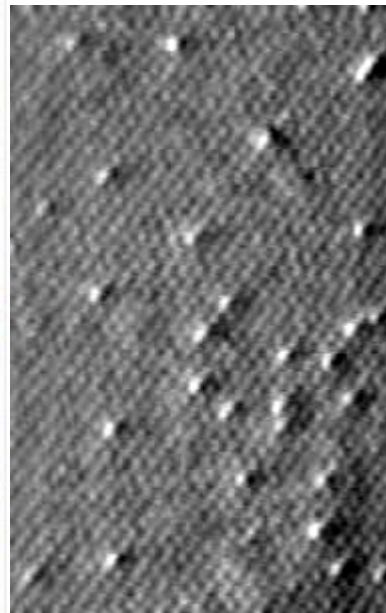
	Video-rate SPM	High-speed SPM	Intermediate speed
Pixel resolution	256 x 256 pixel	256 x 256 pixel	100 x 100 pixel
Frame rate	25 frames/s	10 frames/s	10 frames/s
Scan requirements			
Z-direction	3.3 MHz	1.3 MHz	200 kHz
X-direction	6.4 kHz	2.6 kHz	1 kHz
Y-direction	12.5 Hz	5 Hz	5 Hz

Au(110)

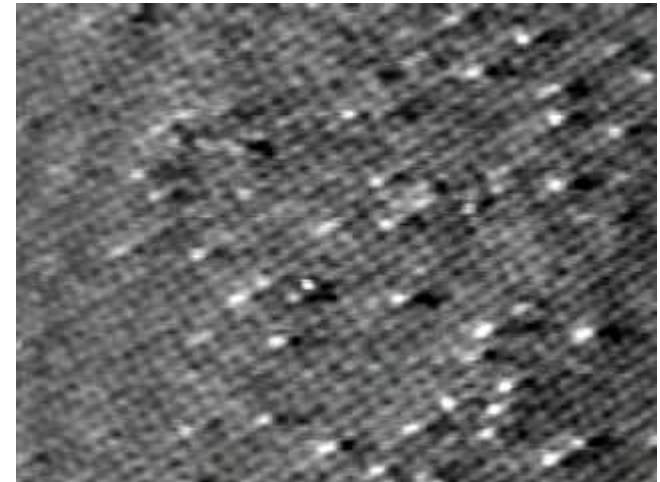
S²⁻/Cu(100)



–0.38 V (SCE)



–0.42 V (SCE)



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.....