Атомно-силовой микроскоп



Сканирование зондом



АСМ для исследования рельефа

Контактная методика

Lateral force imaging, force modulation, contact resonance, PFM

Осцилляционные резонансные

методики

Amplitude modulation with phase and frequency imaging, frequency modulation, single- and double pass methods

Осцилляционные ненезонансные методики Jumping mode, HybriD™ mode, etc









АМ-АСМ (полуконтакт)



Possible names:

- Tapping Mode
- Amplitude Modulation AFM
- Semicontact Mode
- Intermittent Contact Mode
- AC-Mode
- Non-Contact Mode
- etc...



Исследования морфологии фибрил RADA-16-I and RLDL-16-I



AFM images of RADA-16-I and RLDL-16-I fibrils. (a) AFM image of RADA-16-I fibrils deposited on mica, (b) AFM image of RLDL-16-I fibrils deposited on mica (c) Histogram of RADA-16-I fibrils height distribution showing 1.8 nm gap between the peaks, (d) histogram of RLDL-16-I fibrils height distribution showing 2.4 gap between the peaks

D. Bagrov, Y. Gazizova, V. Podgorsky, I. Udovichenko, A. Danilkovich, K. Prusakov and D. Klinov, "Morphology and aggregation of RADA-16-I peptide Studied by AFM, NMR and molecular dynamics simulations", *Biopolymers*, vol. 106, no. 1, pp. 72-81, 2016.



Исследования молекул ДНК, заполненных серебром (E-DNA)



Tentative scheme of A) E-DNA formation and B) AFM imaging of an intermediate stage of E-DNA formation. A) (1) The AgNP binds to DNA and donates its atoms to the nucleic acid. As a result, silver atoms and few atoms clusters are positioned within or on the DNA molecules. (2) The NP dissociates, leaving some of its atoms bound to the DNA. (3) A number of binding–dissociation cycles yield E-DNA. B) The DNA was incubated with AgNPs for 20 h and imaged by AFM. AgNPs bound to the DNA molecules are indicated by the arrows.

Eidelshtein, G., Fardian-Melamed, N., Gutkin, V., Basmanov, D., Klinov, D., Rotem, D., Levi-Kalisman, Y., Porath, D. & Kotlyar, A. DNA-Metalization: Synthesis and Properties of Novel Silver-Containing DNA Molecules (Adv. Mater. 24/2016). *Advanced Materials* 28, 4944-4944 (2016).



Исследования перфорированных пленок гидрогеля



(a) AFM micrographs of the structured poly(NIPAm-co-10%MABP) + DR1 hydrogel film with a 2 μ m period for different irradiation times. The pore diameter decreases and the pore spacing increases with increasing irradiation time. The depth of the pores is about 280 nm. (b) The dependence of the pore size on irradiation time at different periodicities of the interference pattern.

Jelken, J., Pandiyarajan, C., Genzer, J., Lomadze, N. & Santer, S. Fabrication of Flexible Hydrogel Sheets Featuring Periodically Spaced Circular Holes with Continuously Adjustable Size in Real Time. *ACS Applied Materials & Interfaces* 10, 30844-30851 (2018).









ScanTronic[™]



Straightforward for beginners Helpful for experts

NT-MDT

Количественные измерения механических свойств с использованием силовых кривых (QNM)







Коричневый отшельник







Наномеханические измерения паутины коричневого отшельника



a) Top view of the mechanical testing setup (optical micrograph). Scale bar: 200 μ m. b) Schematic of the setup: a Loxosceles fiber (rose) was suspended over a gap in a glass substrate (light blue) and secured with cyanoacrylate glue (amber). A blunted AFM probe (grey) strained the silk via vertical defl ection, while simultaneously measuring the vertical component F vert of the fiber tensile force F T function of the probe as а indentation height h.

c) Obtained force curves (various colors) and the fitted model (black). d) AFM tapping-mode phase image of a silk ribbon suspended over a 1 μ m-diameter hole in a silicon nitride substrate. The ribbon covers the hole and can sustain forces exerted by the AFM probe. Phase imaging reveals the position of the hole since the ribbon deflects in the suspended area (scale bar: 1 μ m).

H. Schniepp, S. Koebley and F. Vollrath, "Brown Recluse Spider's Nanometer Scale Ribbons of Stiff Extensible Silk", *Advanced Materials*, vol. 25, no. 48, pp. 7028-7032, 2013.



Наномеханические измерения паутины коричневого отшельника



Breaking strength of a single nanofibril is ~120 nN

Wang, Q. & Schniepp, H. Strength of Recluse Spider's Silk Originates from Nanofibrils. *ACS Macro Letters* 7, 1364-1370 (2018).



Методика HybriD™

•HybriD mode (HD mode) – scanning technique based on fast forcedistance curves measurements with real-time processing of the tip response.



S. Magonov, S. Belikov, J. D. Alexander, C. G. Wall, S. Leesment, and V. Bykov, "Scanning probe based apparatus and methods for low-force profiling of sample surfaces and detection and mapping of local mechanical and electromagnetic properties in non-resonant oscillatory mode," US9110092B1.

Морфологические и механические исследования

полимерных смесей

Topography

Adhesion





Scan Size: $3 \times 3 \mu m$





Polyethylene blobs on polystyrene spheres

E Modulus overlaid over topography



HybriD в вакууме



WS₂ monolayers grown on epitaxial graphene measured in vacuum with use of HD and AM modes. The influence of electrostatic forces is demonstrated. Scan size: 14×14 µm

Vacuum setup of **NTEGRA AFM**

Sample courtesy:



Set-point calculation principle eliminating electrostatic force gradient



Измерение проводимости (C-AFM)





NT-MDT Spectrum Instruments

Измерения проводимости границ зерен солнечных батарей Cu2ZnSnSe4



(a) AFM topography of the top surface of a CZTSe device. (b) Zero biased photocurrent mapping, under illumination of a defocused 532 nm continuous wave laser with total power of 1mW. The photocurrent mapping is superimposed on the topography in (a) to illustrate the correlation between the position of the photo current and that of the GBs

M. Xu, B. Liu, G. Graham and X. Pan, "High resolution characterization of grain boundaries in Cu 2 ZnSnSe4 solar cells synthesized by nanoparticle selenization", *Solar Energy Materials and Solar Cells*, vol. 157, pp. 171-177, 2016.



Измерение проводимости при помощи методики HybriD





Измерение проводимости серебряных нанотрубок



Sample courtesy: Prof. D. Klinov, FMBA, Moscow, Russia



Электрические и механические измерения нанотрубок при помощи HD-CAFM



HD C-AFM study of coupled carbon and peptide Nanotubes. Sample courtesy: Dr. J. Montenegro, University Santiago de Compostela. Scan size: 3×3 μm¹.

¹ J. Montenegro, C. Vázquez-Vázquez, A. Kalinin, K.E. Geckeler, J.R. Granja, Coupling of carbon and peptide nanotubes, *J. Am. Chem. Soc.* 136 (2014) 2484–2491

Атомно-силовая микроскопия пьезоотклика (PFM)









Пьезоэлектрические измерения керамики Bio.9Lao.1FeO3



Vertical PFM images of the Bi0.9La0.1Fe1xNbxO3+x ceramics. An A cos ϕ signal was recorded. Here, A is the amplitude of the measured vibration proportional to the effective longitudinal piezoelectric coefficient and ϕ is the phase shift determining the direction of polarization (the bright and dark regions correspond to polarization vectors directed to the free surface and to the bottom electrode, respectively)

PFM Studies confirm the effect of Effect of Nb doping

B. Stojadinović, B. Vasić, D. Stepanenko, N. Tadić, R. Gajić and Z. Dohčević-Mitrović, "Variation of electric properties across the grain boundaries in BiFeO3film", *Journal of Physics D: Applied Physics*, vol. 49, no. 4, p. 045309, 2015.



HD PFM

In HD PFM an AC voltage is applied to the conductive coating of the AFM cantilever when the tip comes in contact with the sample during each fast force spectroscopy cycle.



•HD PFM working principle: a) an idealized temporal deflection curve during an
•oscillatory cycle, b) tip-sample interaction in "time window", c) measurement scheme











Molecular structure of diphenylalanine peptide nanotubes¹

• Contact PFM image²

¹Kholkin, A., Amdursky, N., Bdikin, I., Gazit, E., & Rosenman, G. (2010) ACS nano, 4(2), 610-614. ²Ivanov, M., Kopyl, S., Tofail, S. A., Ryan, K., Rodriguez, B. J., Shur, V. Y., & Kholkin, A. L. (2016) In Electrically Active Materials for Medical Devices (pp. 149-166).

Электромеханические исследования нанотрубок дифенилаланина

For the first time HD PFM mode allowed non-destructive piezoresponse study of diphenylalanine peptide nanotubes – a very prospective material for biomedical applications.



Non-destructive electromechanical study of diphenylalanine peptide nanotubes. Scan size: $8 \times 8 \mu m$, nanotubes diameter: $30 \div 150 nm$. Sample courtesy: Dr. A. Kholkin, University of Aviero

A. Kalinin, V. Atepalikhin, O. Pakhomov, A. Kholkin and A. Tselev, "An atomic force microscopy mode for nondestructive electromechanical studies and its application to diphenylalanine peptide nanotubes", *Ultramicroscopy*, vol. 185, pp. 49-54, 2018.

Электромеханические исследования нанотрубок дифенилаланина

 For the first time HD PFM mode allowed non-destructive piezoresponse study of diphenylalanine peptide nanotubes – a very prospective material for biomedical applications.



- Non-destructive electromechanical study of diphenylalanine peptide nanotubes. Scan size: 7×7 μm, nanotubes diameter: 70÷100 nm¹. Sample courtesy: Dr. A. Kholkin, University of Aviero
- A. Kalinin, V. Atepalikhin, O. Pakhomov, A. Kholkin and A. Tselev, "An atomic force microscopy mode for nondestructive electromechanical studies and its application to diphenylalanine peptide nanotubes", *Ultramicroscopy*, vol. 185, pp. 49-54, 2018.

Электромеханические исследования фазового перехода триглицисульфата при нагреве в режиме реального времени



In-situ HD PFM study of second-order phase transition of triglycine sulfate crystal. Scan size 15×15 µm. Sample courtesy: Dr. R. Gainutdinov, IC RAS



HD PFM

Continuous PFM studies under variable temperature >0.1 °C/sec temperature change



In-situ HD PFM study of second-order phase transition of triglycine sulfate crystal. Scan size 15×15 µm. Sample courtesy: Dr. R. Gainutdinov, IC RAS www.ntmdt-si.com

Spectrum Instruments

Кельвин-зондовая микроскопия



$$\begin{split} F_{z} &= F_{z,DC} + F_{z,\omega} + F_{z,2\omega} \\ F_{z,DC} &= - \bigg[\frac{1}{2} \times \bigg((U_{0} - \varphi(x, y))^{2} + \frac{1}{2} \times U_{1}^{2} \bigg) \bigg] \times \frac{\partial C}{\partial Z} \\ F_{z,\omega} &= - \bigg[(U_{0} - \varphi(x, y)) \times U_{1} \times \sin(\omega t) \bigg] \times \frac{\partial C}{\partial Z} \\ F_{z,2\omega} &= \bigg[\frac{1}{4} \times U_{1}^{2} \times \cos(2\omega t) \bigg] \times \frac{\partial C}{\partial Z} \end{split}$$



Исследования работы выхода графена при различной влажности



C. Melios, A. Centeno, A. Zurutuza, V. Panchal, C. Giusca, S. Spencer, S. Silva and O. Kazakova, "Effects of humidity on the electronic properties of graphene prepared by chemical vapour deposition", *Carbon*, vol. 103, pp. 273-280, 2016.



Магнитно-силовая микроскопия (MFM)







МСМ исследования нанотрубок Co/Pt при приложении разных магнитных полей



NTEGRA AFM Setup with in-plane external magnet



The sequential stages of remagnetization for Co/Pt NWs partly covered by Co capping layer. (a) The AFM image of the sample with Co/Pt NWs. The area below line A-B is covered by Co (1.3 nm) The frame sizes are $1.5 \ \mu m \times 1.5 \ \mu m$. The MFM contrast is normalized to the maximum. The border of Co capping layer is shown by arrows and dashed line; (b) The MFMimage of up-magnetized sample; (c) The MFM image of partly remagnetized NWs after applying of 150 Oe reversed magnetic field; (d) The MFM image of down-magnetized NWs in the field of 200 Oe. The frame sizes are $1.5 \ \mu m \times 1.5 \ \mu m$. The MFM contrast is normalized to the maximum.

O. Ermolaeva, N. Gusev, E. Skorohodov, Y. Petrov, M. Sapozhnikov and V. Mironov, "Magnetic Force Microscopy of Nanostructured Co/Pt Multilayer Films with Perpendicular Magnetization", *Materials*, vol. 10, no. 9, p. 1034, 2017.



Нанолитография





Нанолитография на монослоях октадецлтрихлорсилана



Experimental results obtained with the ion-conducting macro-micro-nano-channel.

AFM images of the OTSeo@OTS nano-micro-channel constriction connecting two large OTSeo@OTS macro-channels with a total area of 2.27 cm² taken after the acquisition of all electrical data from this specimen.

J. Berson, D. Burshtain, A. Zeira, A. Yoffe, R. Maoz and J. Sagiv, "Single-layer ionic conduction on carboxyl-terminated silane monolayers patterned by constructive lithography", *Nature Materials*, vol. 14, no. 6, pp. 613-621, 2015.



Обратимая нанолитография на полипирролловых пленках



Comparison of the writing and erasing processes using different operation times. The size of each image is $1 \ \mu m \times 1 \ \mu m$. potentiostatically

H. Liu, S. Hoeppener and U. Schubert, "Reversible Nanopatterning on Polypyrrole Films by Atomic Force Microscope Electrochemical Lithography", *Advanced Functional Materials*, vol. 26, no. 4, pp. 614-619, 2015.





Комбинация АСМ с оптическими методиками



Комбинация АСМ с оптическими методиками

NTEGRA SPECTRA 1998-2018 более **20** лет опыта





100x high NA objective Apertured cantilever



Spectrum Instruments

ИНТЕГРА СПЕКТРА II





Комбинация АСМ с рамановской спектроскопией



AFM: Force modulation (elastic properties)



AFM: Electrostatic force (charge distribution)



AFM: Kelvin probe microscopy (surface potential)



AFM: Lateral force (friction)



Rayleigh light intensity (473 nm laser)



Confocal Raman map: G-band intensity



Confocal Raman map: 2D (G') band mass center



AFM: Height (topography) Size: 30×30 μm. Substrate: gold



Зондово-усиленное комбинационное рассеяние света (TERS)

Raman/Fluorescence microscopy with subwavelength spatial resolution



Localized surface plasmon at the end of nanoantenna





Дефекты в графене с разрешением лучше диффракционного предела





(a) TERS maps of single layer CVD Graphene on copper substrate. Green color: areas of pristine graphene (2D band intensity). Blue color: CH-terminated graphene areas (CHbands intensity). (b) TERS map of mechanically exfoliated single layer graphene on Au substrate. Green color: 2D band intensity. Red color: Dband intensity (areas with strong defects). Resolution of all Raman maps is <12 nm.

J. Stadler, T. Schmid, and R. Zenobi, Nano Letters (2010), 10, 4514-4520.



NTEGRA Nano IR: ИК p-СБОМ



- IR s-SNOM microscopy and spectroscopy with 10 nm spatial resolution
- Wide spectral range of operation: 3-12 μm
- Incredibly low thermal drift and high signal stability
- Versatile AFM with advanced modes: SRI (conductivity), KPFM (surface potential), SCM (capacitance), MFM (magnetic properties), PFM (piezoelectric forces)
- HybriD Mode[™] quantitative nanomechanical mapping
- Integration with microRaman (optional)



ИК p-СБОМ исследования фазового перехода метаматериала VO₂





Temperature-dependent infrared near-field images of patterned VO2/TiO2 at 11 μ m, revealing area-dependent insulator-to- metal phase transitions. The metallic phase is shown in cyan and the insulating phase in red

Gilbert Corder, S. et al. Controlling phase separation in vanadium dioxide thin films via substrate engineering. *Physical Review B* 96, (2017).



ИК p-СБОМ исследования фазового перехода метаматериала VO₂



IR s-SNOM Reflection

- Superior high temperature performance: under 1 hour needed to acquire images 40C apart. Compare to days on competitor's system
- Low drift and high signal stability: <1um XY drift from 27 to 67C, no realignment of nanoReflection
 optics needed

Sample courtesy to prof. Liu (Stony Brook University, New York, USA)



Высокие разрешение и чувствительность методики ИК р-СБОМ на примере исследования монослоев олиготиофенов



IR reflection contrast of thin and soft structures easily detectable. Each of five 3.4 nm steps is resolved. Spatial resolution is better than $\lambda/1000$.

Sample courtesy to Dr. A. Mourran (DWI, Aachen, Germany). Measured by Dr. G. Andreev (EVS Co)



Продуктовая линейка НТ-МДТ Спектрум Инструментс

AFM

AFM-Raman / IR / TERS



HybriD Mode[™]

Ссылки на использованные публикации

- D. Bagrov, Y. Gazizova, V. Podgorsky, I. Udovichenko, A. Danilkovich, K. Prusakov and D. Klinov, "Morphology and aggregation of RADA-16-I peptide Studied by AFM, NMR and molecular dynamics simulations", *Biopolymers*, vol. 106, no. 1, pp. 72-81, 2016.
- Eidelshtein, G., Fardian-Melamed, N., Gutkin, V., Basmanov, D., Klinov, D., Rotem, D., Levi-Kalisman, Y., Porath, D. & Kotlyar, A. DNA-Metalization: Synthesis and Properties of Novel Silver-Containing DNA Molecules (Adv. Mater. 24/2016). *Advanced Materials* 28, 4944-4944 (2016).
- Jelken, J., Pandiyarajan, C., Genzer, J., Lomadze, N. & Santer, S. Fabrication of Flexible Hydrogel Sheets Featuring Periodically Spaced Circular Holes with Continuously Adjustable Size in Real Time. *ACS Applied Materials & Interfaces* 10, 30844-30851 (2018).
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- Wang, Q. & Schniepp, H. Strength of Recluse Spider's Silk Originates from Nanofibrils. *ACS Macro Letters* 7, 1364-1370 (2018).
- S. Magonov, S. Belikov, J. D. Alexander, C. G. Wall, S. Leesment, and V. Bykov, "Scanning probe based apparatus and methods for low-force profiling of sample surfaces and detection and mapping of local mechanical and electromagnetic properties in non-resonant oscillatory mode," US9110092B1.
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- Kholkin, A., Amdursky, N., Bdikin, I., Gazit, E., & Rosenman, G. (2010) ACS nano, 4(2), 610-614.
- Ivanov, M., Kopyl, S., Tofail, S. A., Ryan, K., Rodriguez, B. J., Shur, V. Y., & Kholkin, A. L. (2016) In Electrically Active Materials for Medical Devices (pp. 149-166).
- A. Kalinin, V. Atepalikhin, O. Pakhomov, A. Kholkin and A. Tselev, "An atomic force microscopy mode for nondestructive electromechanical studies and its application to diphenylalanine peptide nanotubes", *Ultramicroscopy*, vol. 185, pp. 49-54, 2018.
- M. Konečný et al. "Kelvin Probe Force Microscopy and Calculation of Charge Transport in a Graphene/Silicon Dioxide System at Different Relative Humidity", ACS Applied Materials & Interfaces, vol. 10, no. 14, pp. 11987-11994, 2018.
- O. Ermolaeva, N. Gusev, E. Skorohodov, Y. Petrov, M. Sapozhnikov and V. Mironov, "Magnetic Force Microscopy of Nanostructured Co/Pt Multilayer Films with Perpendicular Magnetization", *Materials*, vol. 10, no. 9, p. 1034, 2017.
- J. Berson, D. Burshtain, A. Zeira, A. Yoffe, R. Maoz and J. Sagiv, "Single-layer ionic conduction on carboxylterminated silane monolayers patterned by constructive lithography", *Nature Materials*, vol. 14, no. 6, pp. 613-621, 2015.
- H. Liu, S. Hoeppener and U. Schubert, "Reversible Nanopatterning on Polypyrrole Films by Atomic Force Microscope Electrochemical Lithography", *Advanced Functional Materials*, vol. 26, no. 4, pp. 614-619, 2015.
- J. Stadler, T. Schmid, and R. Zenobi, Nano Letters (2010), 10, 4514-4520
- Gilbert Corder, S. et al. Controlling phase separation in vanadium dioxide thin films via substrate engineering. *Physical Review B* 96, (2017).

Благодарности

Быков В.А., д.т.н. Поляков В.В., к.т.н. Бобров Ю.А., к.ф.-м.н. Калинин А.С., к.ф.-м.н. Шелаев А.В., к.ф.-м.н. Дорожкин П.И., к.ф.-м.н. Магонов С.Н., к.ф.-м.н. Нестеров С.И.



Спасибо за внимание!

