

ИССЛЕДОВАНИЕ УГЛЕРОДНЫХ МАТЕРИАЛОВ МЕТОДАМИ СКАНИРУЮЩЕЙ ЗОНДОВОЙ МИКРОСКОПИИ И СПЕКТРОСКОПИИ ВЫСОКОГО ПРОСТРАНСТВЕННОГО РАЗРЕШЕНИЯ 09 Августа 2019

В.А. Быков Группа компаний НТ-МДТ Спектрум Инструментс, Москва

> NT-MDT-Spectral Instruments, 124460, Russia, Moscow, Zelenograd, Proezd 4922, 4/3 <u>www.ntmdt-si.com</u>, <u>spm@ntmdt-si.ru</u> Нанотехнологическое общество России <u>www.rusnor.org</u> Moscow Institute of Physics and Technology, 141701, Russia, Moscow6 Dolgoprudny, 9 Institutskiy per.





Scanning Probe Microscopy (SPM)



1966 - 1981 – Изобретение СТМ, Рассел Янг (1966), Герд Бинниг, Герберд Рорер (1979), Эрнст Руска (ЭМ) Нобелевская премия за изобретение туннельной и электронной микроскопии 1986) 1986 – Изобретение АСМ (Герд Биниг, Кристофер Гербер, Кельвин Куэйт)

In 1987, while on sabbatical, Vergil Elings co-founded Digital Instruments (DI), which bec the world's leader in the design and manufacture of Scanning Probe Microscopes (SPMs



Global Atomic Force Microscopes (AFM) Market Insights, Forecast from 2018 to 2025

Chapter Eight Manufacturers Profiles 8.1 Bruker Corporation **8.2 JPK Instruments 8.3 NT-MDT SI 8.4 Keysight Technologies 8.5 Park Systems** 8.6 Witec **8.7 Asylum Research(Oxford Instruments) 8.8** Nanonics Imaging 8.9 Nanosurf 8.10 Hitachi High-Technologies 8.11 Anasys Instruments 8.12 RHK Technology 8.13 A.P.E. Research



Spectrum Instruments HT-МДТ Спектрум Инструментс



Коллектив разработчиков – самый опытный на мировом рынке – опыт работы с 1989 года



In modern SPM more than 40 different modes of studying the surface



Scanning Force spectroscopy – Hybrid (PeakForce) mode

Research environments: Air, controlled atmosphere, liquids, electrolytes, vacuum from 10⁻³ to 10⁻¹¹ torr

Spectrum Instruments

- Туннельная микроскопия и спектроскопия;
- Профиль поверхностных структур и его зависимость от давления прижима;
- Неоднородность силы трения в системе зонд поверхность;
- Неоднородность адгезионных сил;
- Распределение поверхностного потенциала (Кельвин-мода);
- Распределение электрической емкости в системе кантилевер поверхность;
- Распределение теплопроводности;
- Распределение модуля Юнга;
- Диагностика пределов упругой деформации;
- Распределение магнитных сил;
- Распределение пьезоэлектрических характеристик поверхностных структур;
- Распределение оптических свойств поверхности в видимой (спектроскопия комбинационного рассеяния с пространственным разрешением до 10 нм) и ИК области спектра с разрешением значительно превышающим дифракционные ограничения (ближнепольная беаппертурная оптическая микроскопия);
- Безапертурная ИК и терагерцовая спектроскопия с пространственным разрешением до 10 нм качественный анализ поверхности;
- Возможность модификации поверхности с созданием и исследованием свойств наноструктур

NT-MDT Spectrum Instruments Product Line





Образовательный проект СТАРТ



15-03-1930 - 01-03-2019

Инициатором проекта по использованию сканирующих зондовых микроскопов в школах, колледжах, высших учебных заведениях был лауреат Нобелевской премии по физике Жорес Иванович Алферов. Идея оказалась жизнеспособной и популярной.

> Разработки приборов начались с 2002 года. Последовательно было выпущено три поколения приборов этого типа. Уже вторая версия приборов – НАНОЭДЬЮКАРОР-II вошла в сотню лучших мировых разработок.

Учебно-исследовательский лабораторный комплекс НАНОЭДЮКАТОР

установлен в более чем 80 ВУЗах, и 320 школах в России и за рубежом.



В настоящее время создан 3-й вариант этих приборов с мощным интеллектуальным наполнением на базе алгоритмов искусственного интеллекта, позволяющий сосредоточить внимание учащихся не на методике и приборе, а на предмете исследования исследования – биологических препаратах клеток, вирусов, молекул. На свойствах исследуемых материалов.



Солвер-НАНО — новая генерация НАНОЭДЬЮКАТОРА -Бюджетный сканирующий зондовый микроскоп с развитыми опциями туннельной и атомно-силовой микроскопии



Оптика высокого разрешения (0,5 мкм).



NT-MDT

Spectrum Instruments

Human erythrocytes, AFM scan size 50×50 µm



IC, AFM scan size 30×30 μm



HOPG, atomic resolution, STM scan size 2×2 nm







Атомная решетка ВОПГ. Размер скана 4 ×4 HM. Контактная латеральная АСМ



Атомные слои на графите. Размер скана 1.8×1.8 мкм. AM ACM



Размер скана

50 x50 мкм.

AM ACM



Магнитные домены НЖМД. Размер скана 30 х 30 мкм. AM MCM



Серебряные

проволоки.

4 ×4 мкм.

AM ACM

Размер скана

Смесь полистиренполиэтилена. Размер скана 20×20 МКМ. HybriD метод ACM

Получено на приборах СОЛВЕР-НАНО



Флуороалканы. Размер скана 500 ×500 нм. AM ACM



С60Н122 на ВОПГ. Размер скана 250 × 250 нм. AM ACM









5x5 nm, HOPG



VEGA – АСМ для больших образцов.













diphenylalanine peptide nanotubes Пептидные нанотрубки дифенилаланина, 8×8 мкм. Распределение диэлектрической проницаемости

Специально разработанная оптическая обладает схема самым низкого спектральной уровня значения плотности шума (25 фм/√Гц) датчика оптической системы регистрации

ATOMIC FORCE MICROSCOPY



Piezoceramic elements for sub nanometer displacements, but CREEP and HISTERESIS!!!

www.ntmdt-si.com



Инструментальные артефакты, связанные с конструкцией сканера

Крип

Собственная нелинейность сканера



В плоскости ХУ собственная нелинейность проявляется в неравномерности шага сканирования. В Z направлении собственная нелинейность будет приводить к погрешностям при измерении высоты микрорельефа поверхности.

Термический дрейф компонентов АСМ

В плоскости ХУ крип проявляется при перемещении или масштабировании области сканирования.



http://afmhelp.com/

Искажение АСМ-изображения бактерии из-за дрейфа

DECISION – 3D High accuracy capacitance sensors !!!



Нелинейность, ХҮ (с датчиками обратной связи)		≤0.1%	≤0.15%
Уровень шума, Z (СКВ в полосе 1000 Гц)	С датчиками	0.04 нм (типично), 0.06 нм	0.06 нм (типично), 0.07 нм
	Без датчиков	0.03 нм	0.05 нм



Closed-loop control as used for nanolithography, scan size 1.9x1.9 μ m





Closed-loop operation off

Closed-loop operation on

High resolution AFM and STM of graphite structures



The high-resolution AFM image showing an assembly of single-layer, functionalized Graphene sheets.

Some of the sheets are many square micrometers large. The thickness of each sheet is less than 1 nm.

Atomic resolution STM image of graphite (HOPG)

Image courtesy: Dr. Hannes Schniepp (The College of William & Mary, USA) Graphene in different atmospheric conditions

AFM topography



In ambient conditions

After heating above 100 °C

In toluene vapour

D.W. Horsell, P.J. Hale and A.K. Savchenko, Microscopy and Analysis 25(1), 15 (2011),

Nanomanipulation of graphene flake by AFM



Successive steps in multilayer graphene folding

Graphene (multilayer) folded in successive steps (image 3, scans a-d) by an AFM cantilever. The graphene is attached to a silica / silicon substrate. The degenerately doped silicon is separated from the graphene by 300 nm silica. Between each fold, 10 V is applied between the silicon and the tip held at the centre of the graphene crystal. After folding, a 'ghost' of the graphene is left behind (see white highlighted region in scan (d). This is from charge built up in the silica from the applied voltage: charge from the tip is dispersed across the conductive graphene crystal then charges impurities in the silica. Even in ambient conditions, this effect lasts for several hours.

D.W. Horsell, P.J. Hale and A.K. Savchenko, Microscopy and Analysis 25(1), 15 (2011),

Basics of the Hybrid Mode



Temporal Deflection Plot - The Bank of the Local Properties!

Predecessors

H. Becker, et al "Stylus profiler featuring an oscillating probe" US Patent 2728222, 1955.

V. Elings, & J. Gurley "Jumping probe microscope" US Patent 5,229,606, 1993.

Pulsed Force (Witec), Jumping Mode (NanoTech), Peak Force (Bruker), Anasys

Real-time Wavelet Filtering





www.ntmdt.com



HybriD Mode: loose CNT conductivity



1x1um Complex study of "loose" carbon nanotubes on SIO₂











Cantilevers for thermoconductivity

measurements

SThM Probes		
	Conventional Technology	APPNANO
Tip ROC (nm)	100 nm	> 50nm
Lateral Thermal Resolution	100 nm	up to 20nm
Thermal Sensor	Thermistor	Thermocouple
Location	Near the Apex	At the Apex
Maximum Temperature	160° C	∖ \ 700° C plus //
Thermistor	Heater	Thermocouple



HybriD Scanning Thermal Microscopy

HD Scanning Thermal Microscopy (HD SThM) allows studying local thermal properties – temperature and thermal conductivity – simultaneously with QNM measurements.



SEM image of AppNano VertiSenseTM thermocouple probe and comparison of HD SThM and AM SThM techniques. Scan size: $17 \times 17 \ \mu m$.



HD SThM study of PS-LDPE. Scan size: 10×10 µm.

Thermal conductivity measurements of supported and suspended graphene single- and multilayers



Special SThM tip works al local heater and temperature sensor



Thermal conductivity map (sensor tip temperature)



Thermal resistance profiles: supported and suspended bilayer graphene, supported biand single layer graphene.

Direct Nanoscale Imaging of Ballistic and Diffusive Thermal Transport in Graphene Nanostructures

Manuel E. Pumarol,[†] Mark C. Rosamond,[‡] Peter Tovee,[†] Michael C. Petty,[‡] Dagou A. Zeze,[‡] Vladimir Falko,[†] and Oleg V. Kolosov^{†,*}

[†]Physics Department, Lancaster University, Lancaster, LA1 4YB, United Kingdom [‡]School of Engineering and Computing Sciences, Durham University, Durham DH1 3LE, United Kingdom

Nano Lett. 2012, 12, 2906-2911







But to use it correctly to have perfect results it need you need to optimize at least 4 parameters:

- > Amplitude of probe oscillation (A₀);
- Feedback set point (SP);
- Integral feedback coefficient (k_i)
- Speed of scanning (V_x);

And 2 additional parameters:

- LP Low Pass filter band;
- k_p proportional feedback gain



ScanTronicTM -

Artificial Intelligence to AFM



Straightforward for beginners Helpful for experts

www.ntmdt-si.com

Selection of initial parameters for optimization

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Факторы и параметры, влияющие на выбор зонда и параметров





Scan Tronic: Examples of application



Al₂O₃ - "Grater" sample for tips. Left – topography, ScanTronic used, right – manual attempt to adjust scanning parameters

AI – ScanTronic!!!



Si₃N_{4,} 2x2 mkm



AI – ScanTronic!!

Cu/CuO, 5x5 mkm Topography in fashion in semicontact mode in ScanTronic mode

AI – ScanTronic!!!





4x4 mkm

15x15 mkm

Cubic red dye on mica, Topography in fashion in semi-contact mode in ScanTronic mode







5x5x1,7 um



2x2x0,3 um

Collagen is the main building material for connective tissues. On these images you can see the bunch of rabbit collagen fibers. On right image we can clearly see the periodic structure of these nano-ropes. Period size is ~50 nm. Image was done in liquid conditions by means of HybriD Mode. Image by Craig Wall, NT-MDT America

Fast Scan

Fastest Scaner.

Max Scan Size XY/Z, μ m: 90×90×4 ±10%

Line speed: 2 mm/sec





Scan size 90 * 90 * 0,5µm



NTEGRA Spectra in Upright, Inverted and Side illumination

configuration



Принцип работы



- True confocal design. Motorized confocal pinhole.
- Diffraction limited resolution guaranteed (e.g. 200 nm for blue laser, immersion optics)
- Extremely high optical throughput (~70-80 % for spectrometer, ~40-50% sample-to-detector)
- Fully motorized laser change (up to 3 / 5 lasers). UV VIS IR region
- Fully motorized: polarization optics, zoom beam expander, pinhole, 4 gratings
- Can be equipped by fastest and most sensitive detectors available (FI/BI CCD, EMCCD, DD-CCD etc.)
- Zoom beam expander to guarantee diffraction limited laser spot to every objective
- Three optical ports for detectors: two in monochromator, one in separate channel

Sample: SWCNTs, Raman spectrum of nanotube bundle





Integration time: 100 ms / point. 50*150 points.

Total spectrum was acquired at each point of the scan. After measurement, different Raman bands are chosen and their intensity distribution is analyzed. <u>All the images (AFM + all Raman maps) can be obtained simultaneously, in a single experiment, without any moving of the sample or objective</u>

Nitrogen vacancy color centers in nanodiamonds



Observation of nitrogen-vacancy (NV) color centers in *discrete* detonation nanodiamonds (a) AFM topography image; smallest particles observed are discrete isolated nanodiamonds of ~5 nm size. (b) Confocal fluorescence map of the same sample area; nitrogen-vacancy luminescence from isolated nanodiamonds is clearly seen. (c) Luminescence spectrum of individual NV center in a 5 nm crystal host.

C. Bradac et al., Nature Nanotechnology 5, 345 - 349 (2010)

Image Credit: A/Prof. James Rabeau, Quantum Materials and Applications group, Department of Physics and Astronomy, Macquarie University (Sydney, Australia)

Wavelength dependence of TERS enhancement,

graphene on SiO2



Graphene, AFM + Raman spectroscopy of Raman scattering A single scan - a lot of data



Lateral Force Microscopy (friction)



Capacitance Microscopy



Electrostatic Force Microscopy (charge distribution)

I layer2 layers



AFM Topography Size: 30*30 µm



Raman Map, 2D Band position



Confocal Rayleigh Microscopy



Force Modulation Microscopy (elasticity)



Scanning Kelvin Probe Microscopy (surface potential)



Raman Map, G-band Intensity

Graphene scales on Si/SiO₂

Чешуйки графена на Si/SiO₂



Topography



Инденсивность 2D полосы The intensity of the 2D-band



The intensity of the G-band







Graphene on SiO2/Si: AFM topography and single point Raman spectrum



30x30 um AFM (topography) and Raman spectra.

512x512 points. Laser power ~8 mW. 473 nm laser. 0.3s exposure time

Graphene flakes: AFM & Raman microscopy



Raman spectroscopy of graphene flakes



TERS on Graphene Oxide AFMTERS cantilevers, HYBRID regime





Typical resolution we obtain: $\sim 10 - 40$ nm.

TERS of Carbone Nanotubes



Chan K.L., Kazarian S.G., Nanotechnology 22, 175701 (2011)

Spectrum Instruments



S. Kharintsev, G. Hoffmann, A. Fishman. & M. Salakhov J. Phys. D: Appl. Phys. 46 **(2013)** 145501



Chan K.L., Kazarian S.G., Nanotechnology 21, 445704 **(2010)**



M. Zhang, J. Wang, Q. Tian, Optics Communications 315, 164 **(2014)**

Resolution: < I



Sample provided by Xu Du (SBU), measured on nR/NTMDT, lab of Prof. Liu, (SBU)



Carbon nanotubes degraded by neutrophil myeloperoxidase induce less pulmonary inflammation

Valerian E. Kagan¹*, Nagarjun V. Konduru¹, Weihong Feng¹, Brett L. Allen², Jennifer Conroy³, Yuri Volkov³, Irina I. Vlasova¹, Natalia A. Belikova¹, Naveena Yanamala⁴, Alexander Kapralov¹, Yulia Y. Tyurina¹, Jingwen Shi⁵, Elena R. Kisin⁶, Ashley R. Murray⁶, Jonathan Franks⁷, Donna Stolz⁷, Pingping Gou², Judith Klein-Seetharaman⁴, Bengt Fadeel⁵, Alexander Star² and Anna A. Shvedova⁶



Figure 4 | **Biodegradation of nanotubes in neutrophils evaluated by infrared and Raman spectroscopy. a**, Vis-NIR spectra showing biodegradation of nanotubes and IgG-nanotubes by human neutrophils after 0, 6 and 12 h. O.D., optical density. **b**,**c**, Raman spectra (excitation, 473 nm) recorded from different areas of neutrophils containing IgG-nanotubes at 2 h (**b**) and 8 h (**c**). Inset shows bright-field image of the neutrophils with engulfed IgG-nanotubes. The Raman spectra (red lines) with their corresponding G- and D-bands recorded from different areas of neutrophils are indicated by the cross-wire on the bright-field images.

Aperture Less Nearfield Optical Microscope Head (s-SNOM Head) with IR lens









- IR microscopy and spectroscopy with 10 nm resolution
- Wide spectral range of operation: $3-12 \ \mu m$
- Incredibly low thermal drift and high signal stability
- Versatile AFM with advanced modes: SRI (conductivity),

KPFM (surface potential), SCM (capacitance), MFM (magnetic

NTEGRA IR

properties), PFM (piezoelectric forces)

- HybriD Mode quantitative nanomechanical mapping
- Integration with Raman (optionally)

Bipolar transistor (Si) Skew plate with a planar p-n-p transistor









FastSpectra: Reverse Osmosis Membrane







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География поставок оборудования по России и миру



NT-MDT Spectrum Instruments