Institute of Physics

National academy of sciences of Ukraine

International Summer School
"NANOTECHNOLOGY: from fundamental
research to innovations”

LASER NANOMETROLOGY

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Bukovel

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Nanometrology is the science of measurement at the nanoscale
(1 nm to 100 nm).

It has a crucial role in the production of nanomaterials and the manufacturing of nanoscale devices with a high degree of accuracy and reliability.

Co-Nanomet

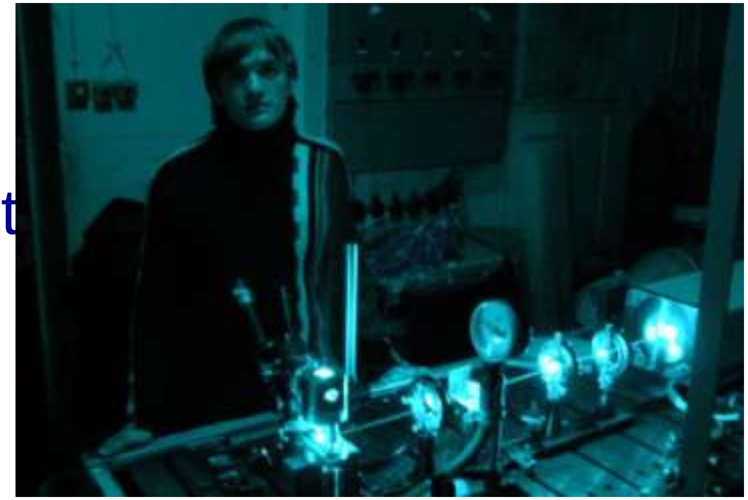
Co-ordination of Nanometrology in Europe

European
Nanometrology 2020

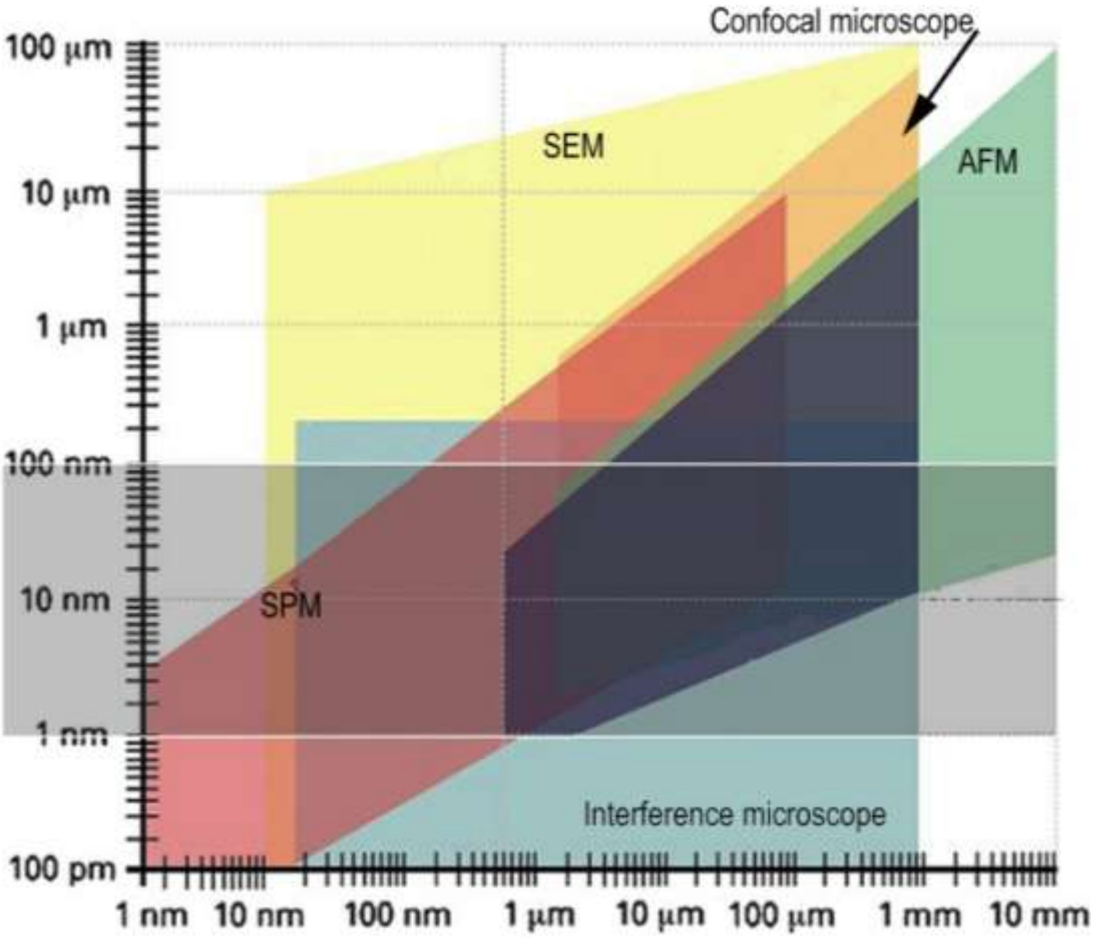
- **Dimensional nanometrology**
- **Chemical nanometrology**
- **Thin film nanometrology**
- **Mechanical nanometrology**
- **Metrology for nanostructured materials**
- **Electrical nanometrology**
- **Biological nanometrology**
- **Modelling and simulations for nanometrology**

LASER BASED MESUREMENT TECHNIQUES

- AFM, STM traceable to the national standards
- Laser interferometry
- Microscopy, confocal microscopy
- Laser spectroscopy, Raman, FTIR
- Polarimetry
- Light scattering and diffraction
- Laser tweezer, force measurement
- etc...

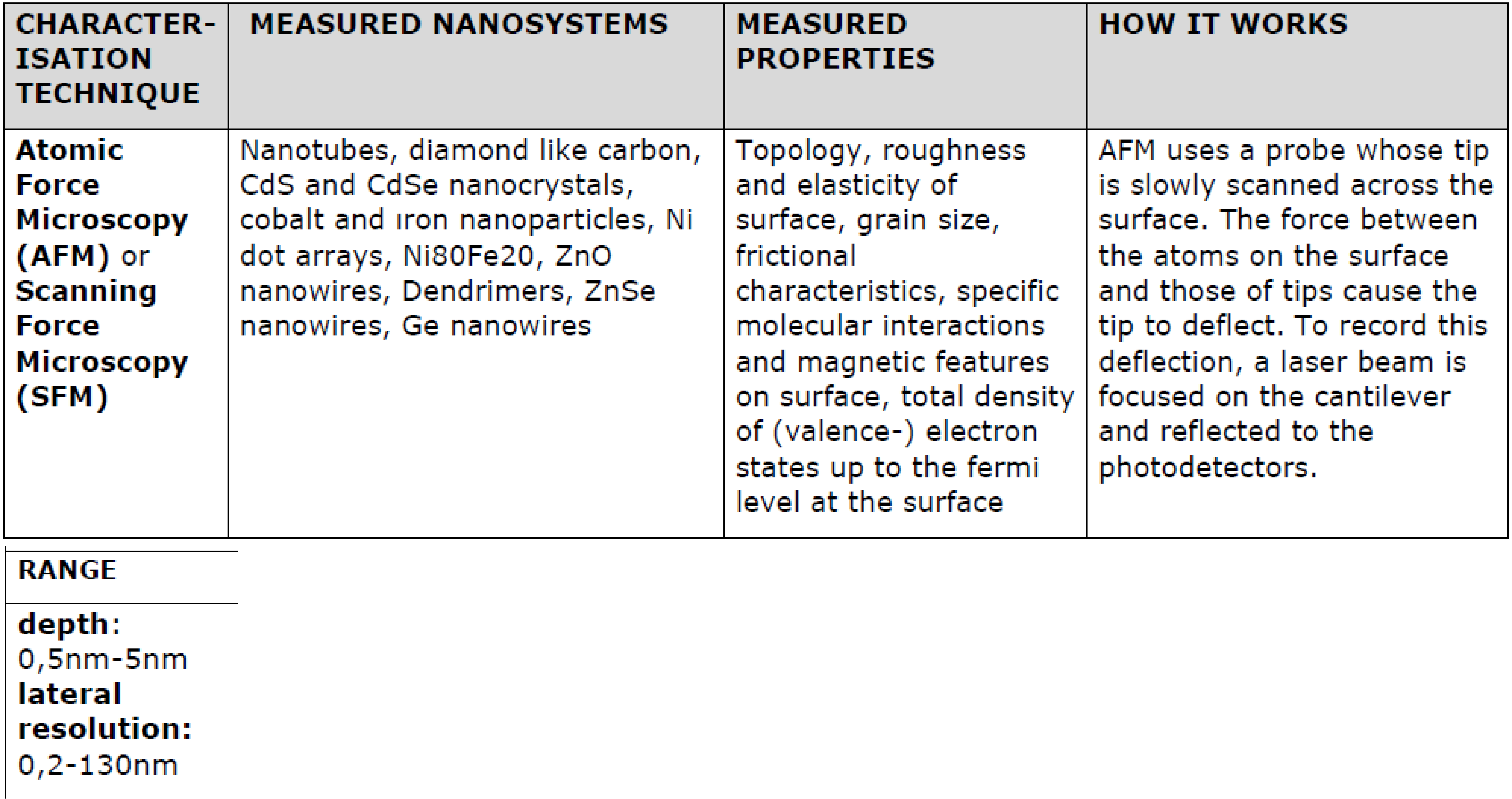


Dimensional Nanometrology



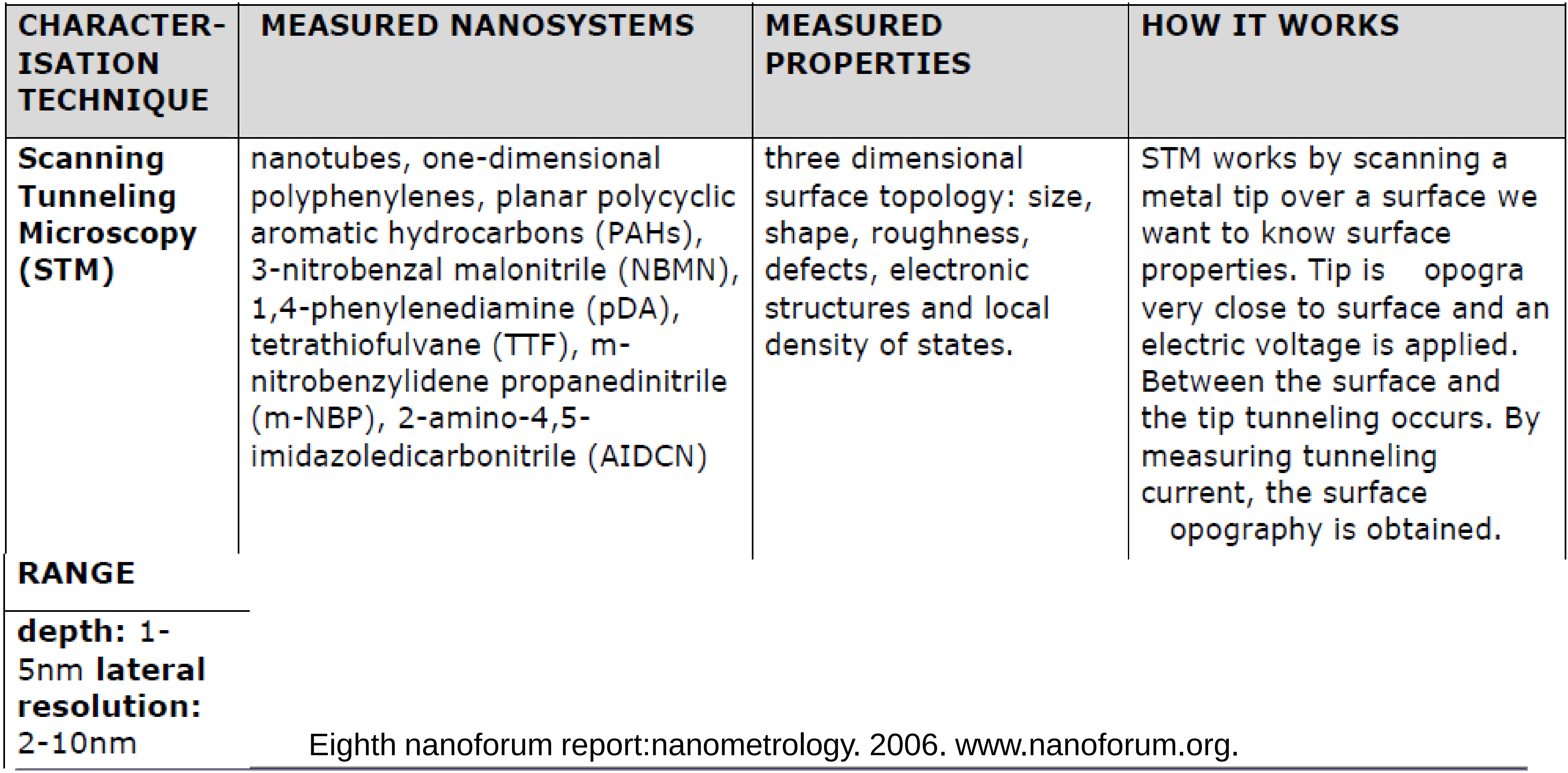
SEM: Scanning Electron Microscope; **SPM**: Scanning Probe Microscop; **AFM**: Atomic Force Microscope.

The grey box displays the dimensional range of nanomaterials.



CHARACTER-ISATION TECHNIQUE	MEASURED NANOSYSTEMS	MEASURED PROPERTIES	HOW IT WORKS	RANGE
Atomic Force Microscopy (AFM) or **Scanning Force Microscopy (SFM)**	Nanotubes, diamond like carbon, CdS and CdSe nanocrystals, cobalt and iron nanoparticles, Ni dot arrays, Ni80Fe20, ZnO nanowires, Dendrimers, ZnSe nanowires, Ge nanowires	Topology, roughness and elasticity of surface, grain size, frictional characteristics, specific molecular interactions and magnetic features on surface, total density of (valence-) electron states up to the fermi level at the surface	AFM uses a probe whose tip is slowly scanned across the surface. The force between the atoms on the surface and those of tips cause the tip to deflect. To record this deflection, a laser beam is focused on the cantilever and reflected to the photodetectors.	**depth**: 0,5nm-5nm **lateral resolution:** 0,2-130nm

Eighth nanoforum report:nanometrology. 2006. www.nanoforum.org.

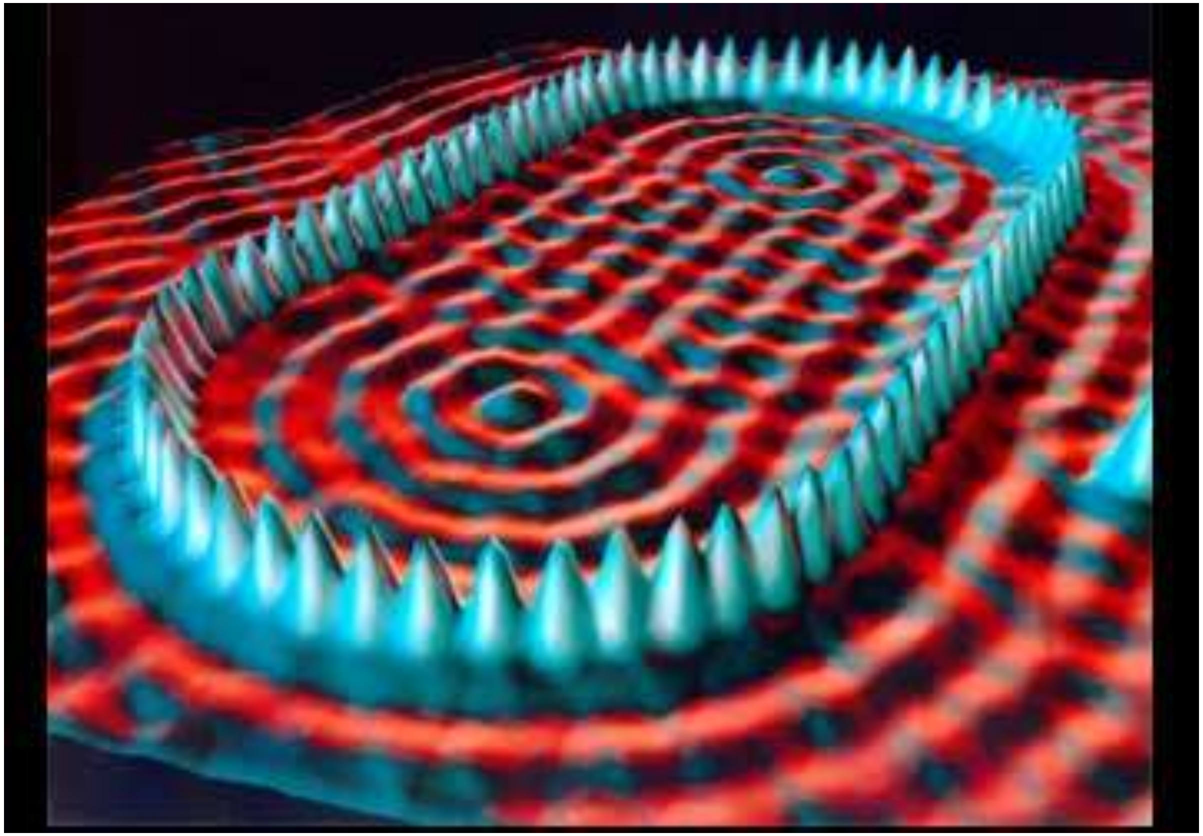


CHARACTER-ISATION TECHNIQUE	MEASURED NANOSYSTEMS	MEASURED PROPERTIES	HOW IT WORKS	RANGE
Scanning Tunneling Microscopy (STM)	nanotubes, one-dimensional polyphenylenes, planar polycyclic aromatic hydrocarbons (PAHs), 3-nitrobenzal malonitrile (NBMN), 1,4-phenylenediamine (pDA), tetrathiofulvane (TTF), m-nitrobenzylidene propanedinitrile (m-NBP), 2-amino-4,5-imidazoledicarbonitrile (AIDCN)	three dimensional surface topology: size, shape, roughness, defects, electronic structures and local density of states.	STM works by scanning a metal tip over a surface we want to know surface properties. Tip is opogra very close to surface and an electric voltage is applied. Between the surface and the tip tunneling occurs. By measuring tunneling current, the surface opography is obtained.	**depth:** 1-5nm **lateral resolution:** 2-10nm

Eighth nanoforum report:nanometrology. 2006. www.nanoforum.org.

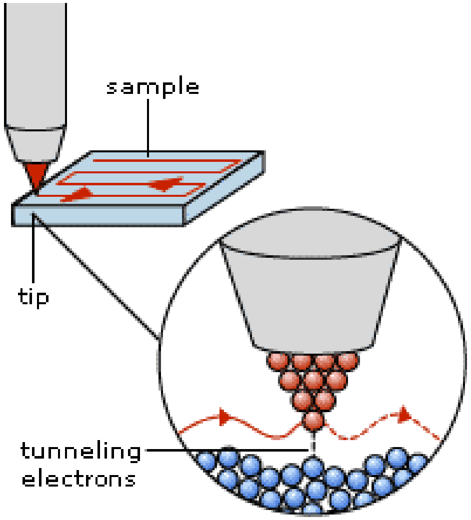
The Scanning Tunneling Microscope

The scanning tunneling microscope (STM) is a type of electron microscope that shows three-dimensional images of a sample. In the STM, the structure of a surface is studied using a stylus that scans the surface at a fixed distance from it.



A stadium shaped corral made by iron atoms on a copper surface.

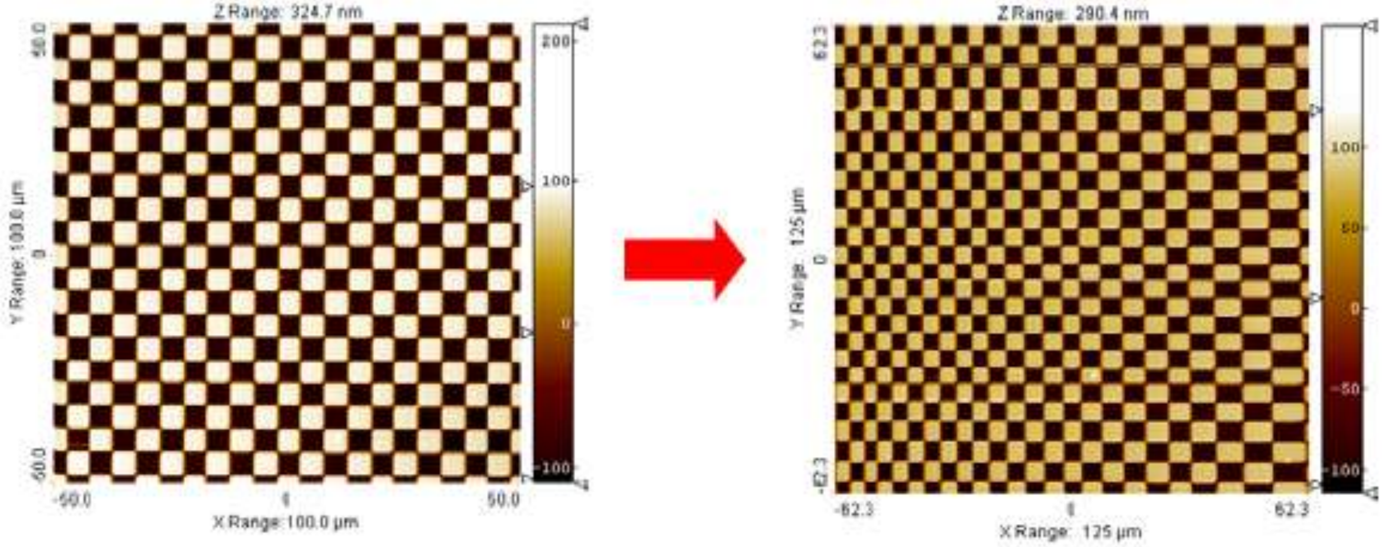
www.nobelprize.org/educational/physics/microscopes/scanning/gallery/9.httml



Nanometer Scale Dimensional Metrology: Calibrated Atomic Force Microscope

The semiconductor and nanotechnology industries have rapidly increasing dimensional metrology requirements in regimes where traceability to the SI unit of length is not always readily available.

Uncalibrated AFM - a false image device

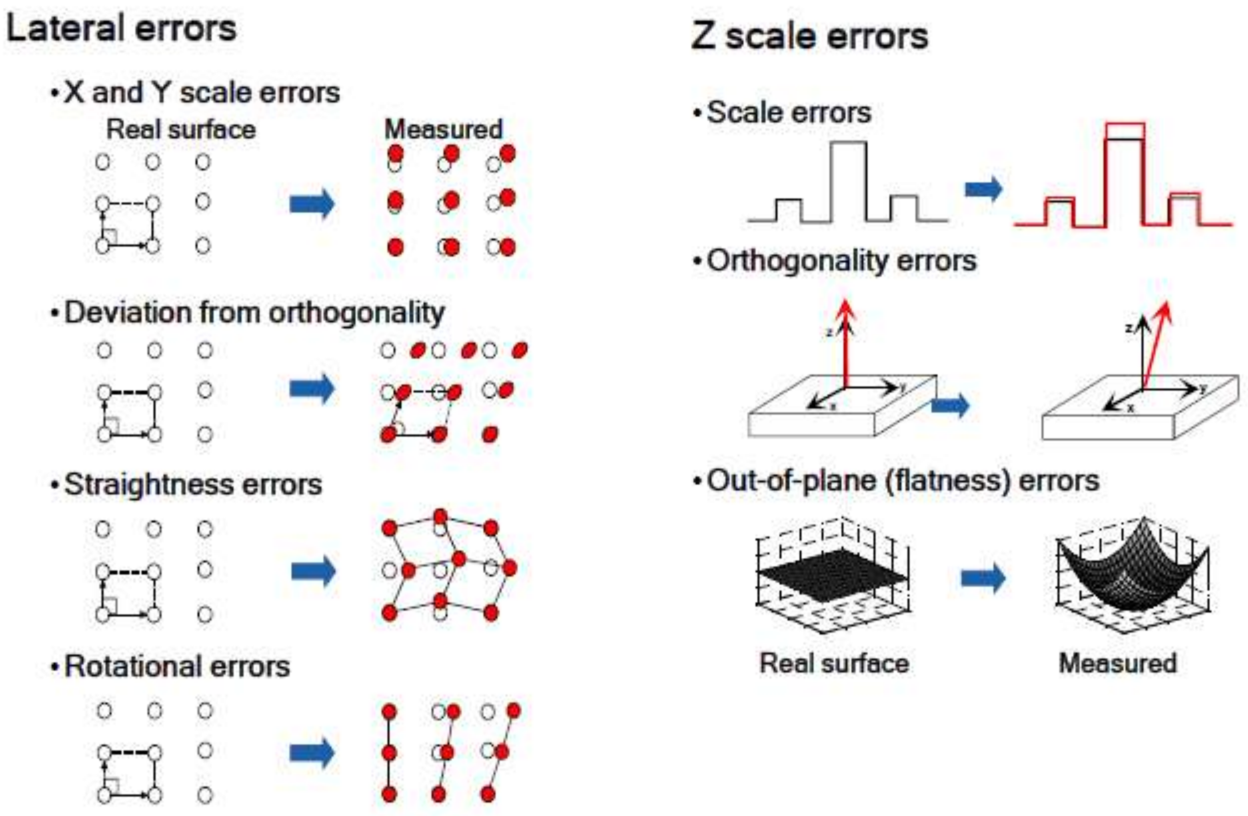


Real structure

Measured structure

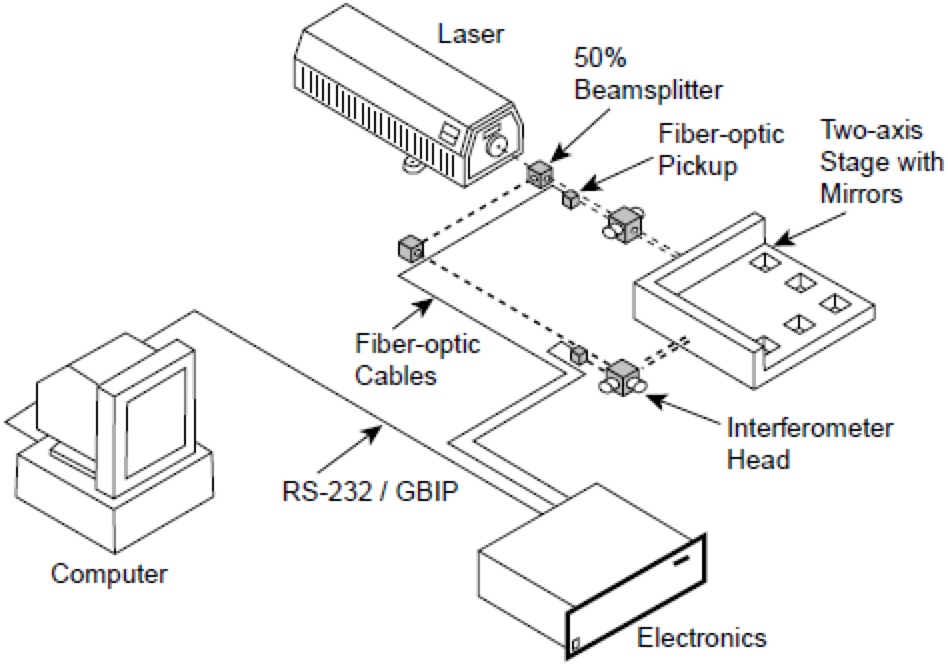
https://noppa.aalto.fi/noppa/.../Tfy-125_4008_nano**metrology**.pdf

Scanner errors



https://noppa.aalto.fi/noppa/.../Tfy-125_4008_nano**metrology**.pdf

Traditional Heterodyne
Displacement Measuring Interferometer (DMI)



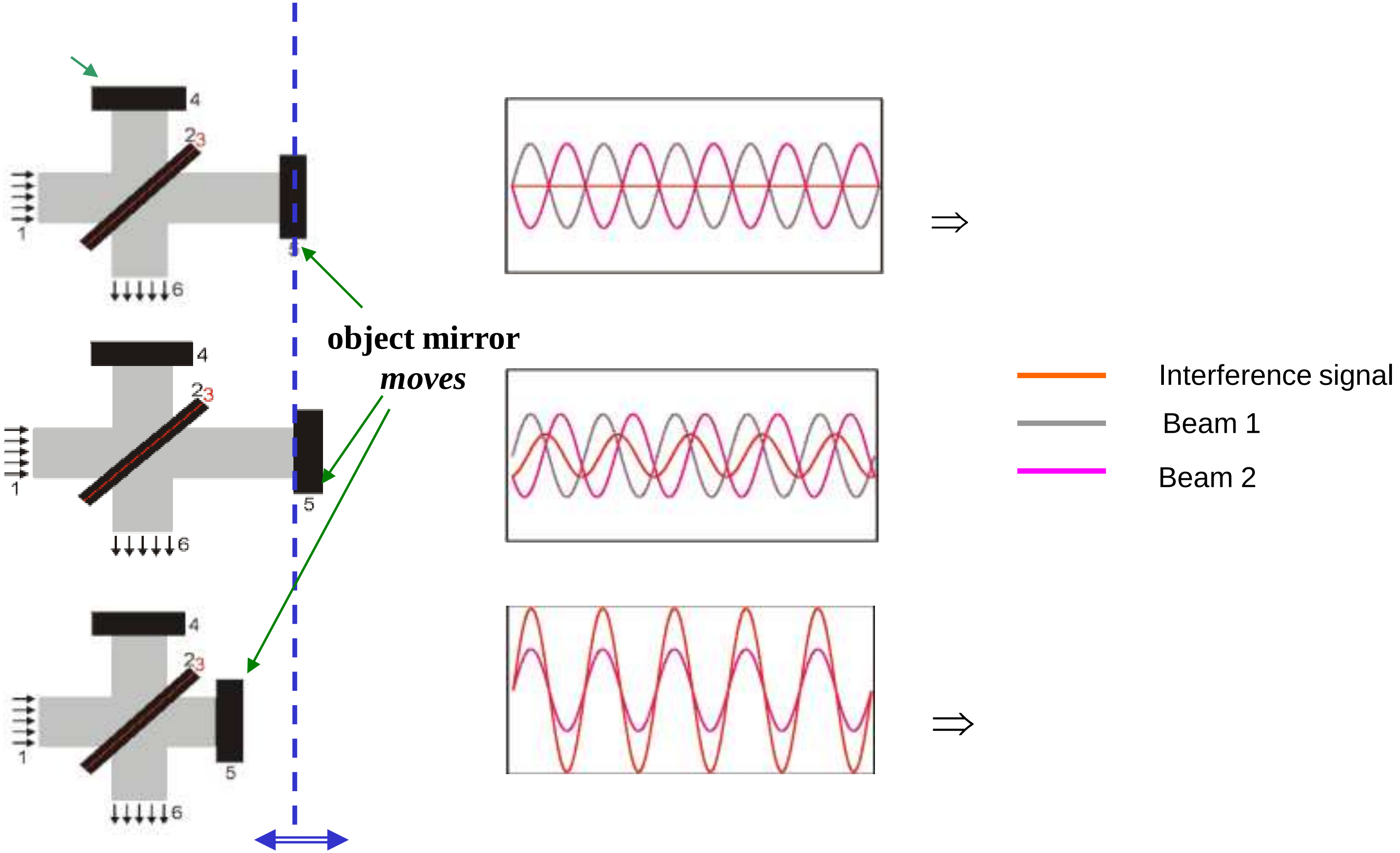
DMI Limitations

Moving arms create
time-dependant cosine,
Abbe, diffraction
& other path errors.

Air paths introduce large
errors due to atmospheric
disturbances:
-> Temperature, Pressure
-> Humidity, Turbulence

System is bulky
and expensive.

Heavy stage mirrors
limit stage scanning
speed & accuracy.



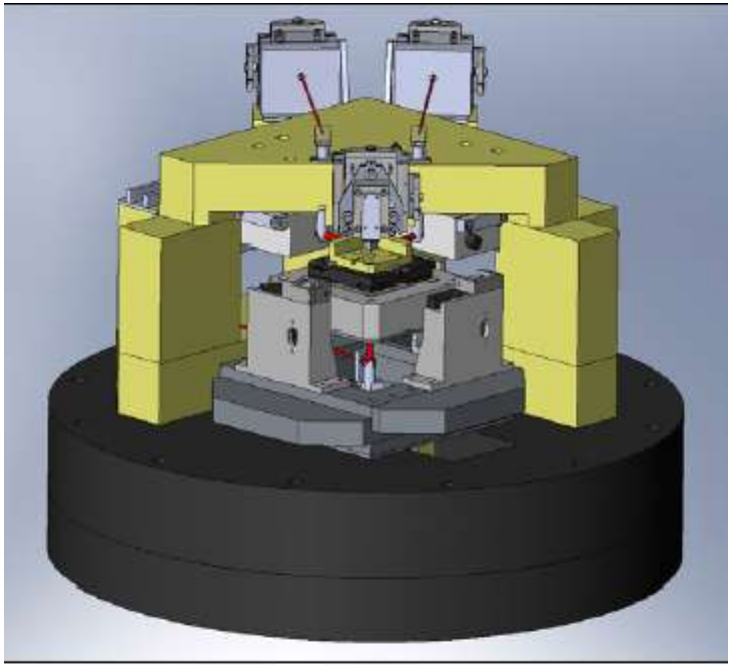
object mirror
moves

Moving an object mirror by half of a wavelength (λ/2)
produces a full cycle of the interference signal

A Coordinate Measuring Mashine works at the nanoscale and provide the necessary stiffness and stability to achieve nanoscale uncertainties in x,y and z directions.

The probes for such a machine need to be small to enable a 3-D measurement of nanometre features from the sides and from inside like nanoholes. Also for accuracy laser interferometers need to be used. NIST has developed a surface measuring instrument, called the Molecular Measuring Machine. This instrument is basically an STM. The x- and y-axes are read out by laser interferometers. The molecules on the surface area can be identified individually and at the same time the distance between any two molecules can be determined. For measuring with molecular resolution, the measuring times become very large for even a very small surface area.

Design of a large measurement-volume metrological atomic force microscope (AFM)



The design of a long-range metrological atomic force microscope has been presented. The goal of the described instrument is to achieve a 1 nm positioning uncertainty for a measurement volume of 40 mm × 40 mm × 6 mm. The

Brian J Eves, Meas. Sci. Technol. **20 (2009) 084003 (5pp)**

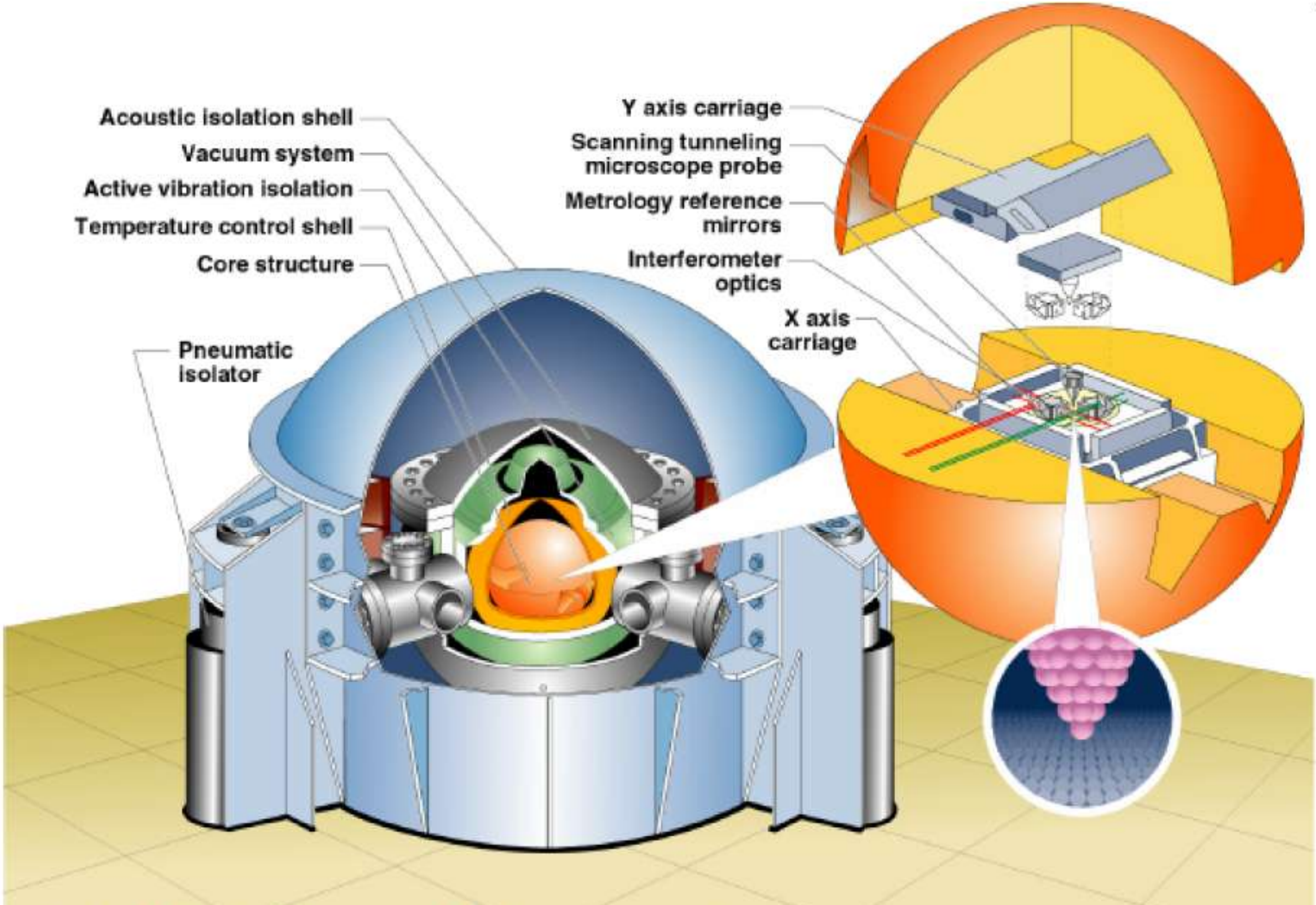


Fig. 1 Molecular Measuring Machine cut-away drawing.

LASER LINE WIDTH: SCHAWLOW-TOWNES LIMIT

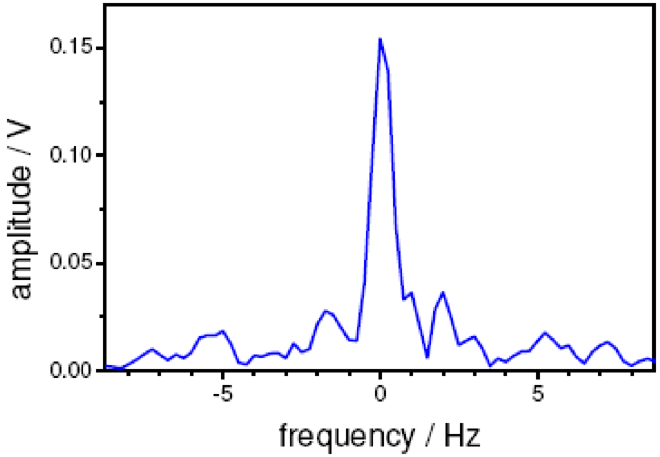
$$\Delta\omega_{osc} \le \frac{\hbar\omega}{2P_{out}} \frac{\Delta\omega_{gain}{}^{2}\,\Delta\omega_{cav}^{2}}{\left(\Delta\omega_{gain}+\Delta\omega_{cav}\right)^{2}}$$

For $\lambda=0,6328$ мкм $\hbar\omega \approx 1,96$ еВ $\approx 3,1\ 10^{-19}$ Дж

$2P_{out} / \hbar\omega \approx 0,65\ 10^{16}$ for $P_{out} = 1$ mW

$\Delta\omega_{cav} << \Delta\omega_{gain}$ $\Delta\omega_{cav} \approx 10^{6}$ Гц $\Delta\omega_{osc} \approx 10^{-4}$ Гц

LASER LINE WIDTH: STATE-OF-ART



Beat between two Nd:YAG beams stabilised to independent ULE cavities (NPL)

$\Delta\omega_{osc}$ ~ 0,2 Hz, frequency stabilized dye laser, relative frequency instability 10^{-16} for 1 s

~ 0,4 Hz, Nd:YAG laser (NPL, JILA)

~ 0,4 – 1 Гц diode laser (PTB, NIST, NPL…),

LASER MICHELSON INTERFEROMETER RESOLUTION

Laser shot noise

$$dx_{\text{quantum}} \simeq \frac{1}{4\pi}\sqrt{\frac{2hc\lambda B}{\eta P}}.$$

Detector noise

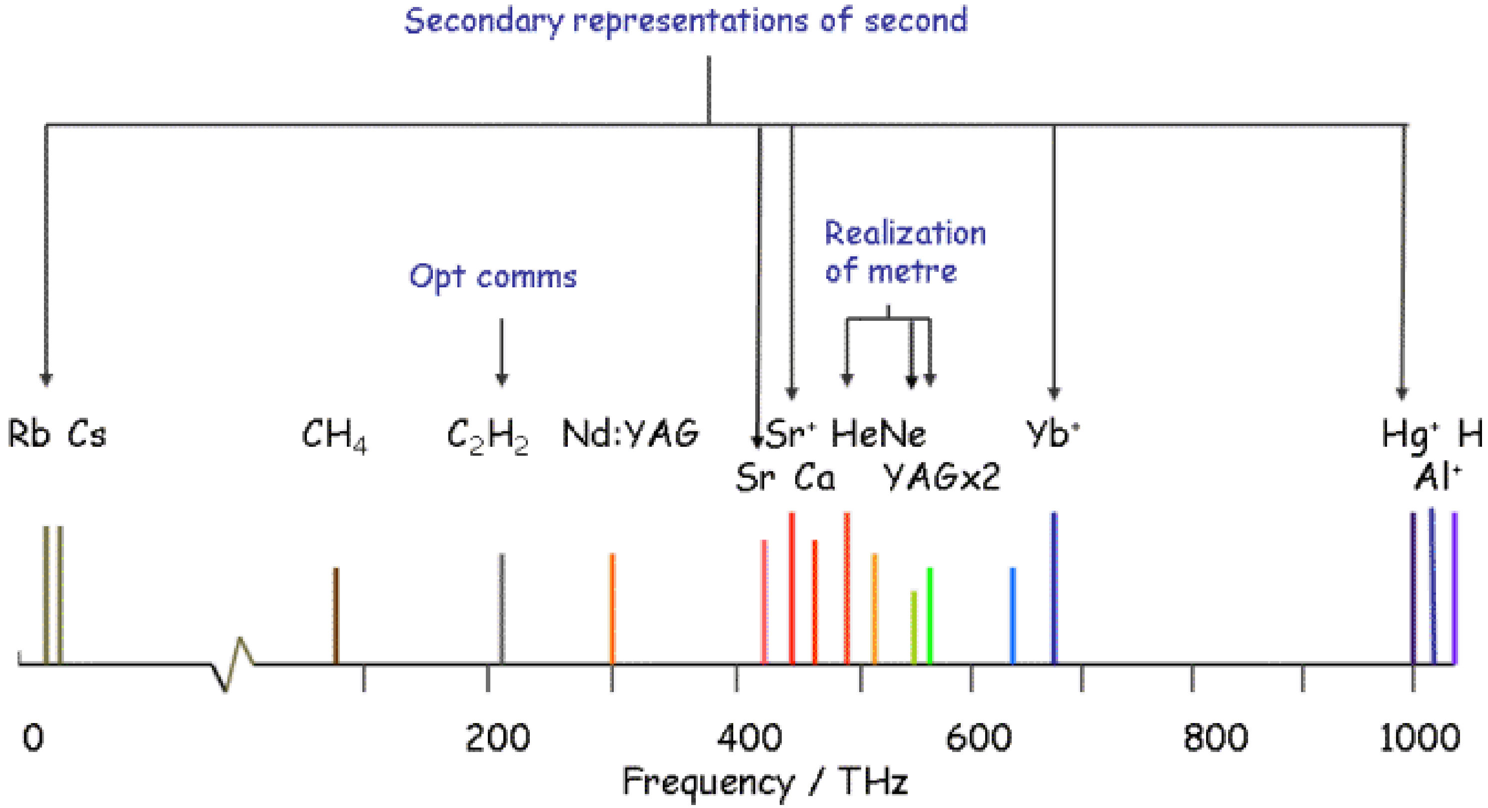
$$dx_{\text{classical}} \simeq \frac{\lambda}{4\pi}\frac{\text{NEP}\sqrt{B}}{P}.$$

For laser power P=100 μW, measurement bandwidth 10 kHz, uncertainty dx_{quant} = 0,44 pm, $dx_{classical}$ =0,36 pm, total uncertainty 0,57 pm corresponding to fringe interpolation of one part in 555 000.

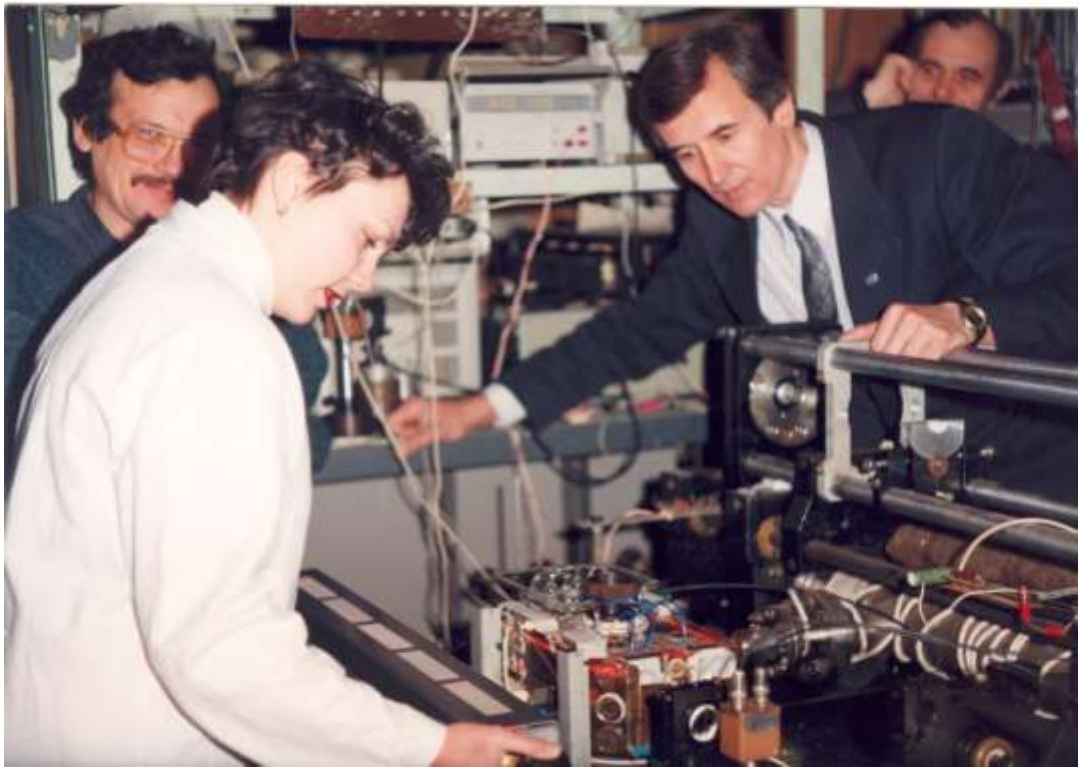
Digital signal processing make rapid phase measurements with resolution $0,01^0$ (one part in 36 000), for wavelength 633 nm this corresponds to a resolution 9 pm.

J. Lawall, E. Kessler, Rev. Sci. Instrum., v.71,no.7 (2000)

THE PRACTICAL REALIZATION OF THE METRE WITH LASER RADIATIONS



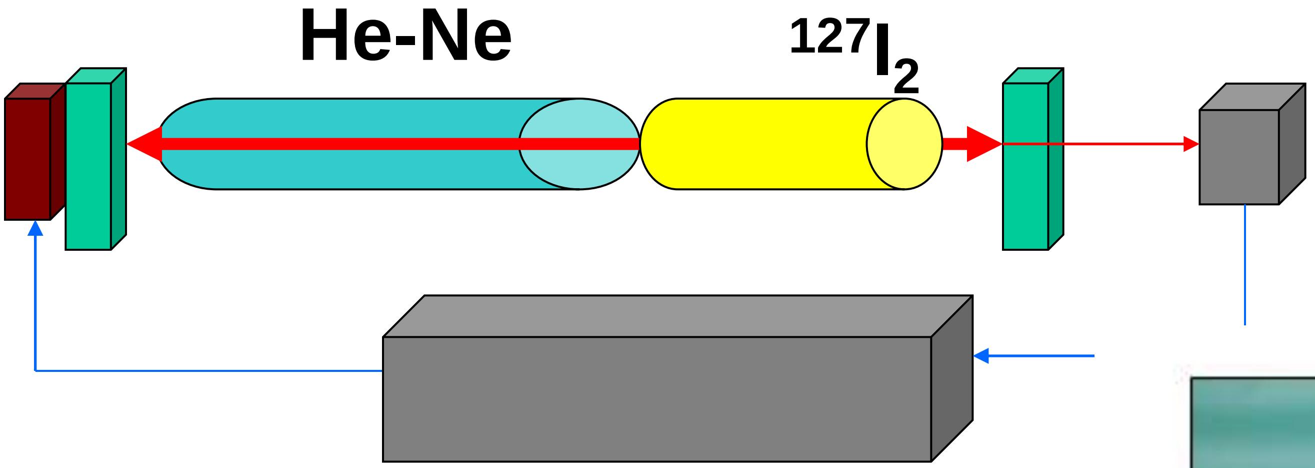
FREQUENCY-STABILIZED HE-NE LASER



633 nm, relative instability 10^{-12}

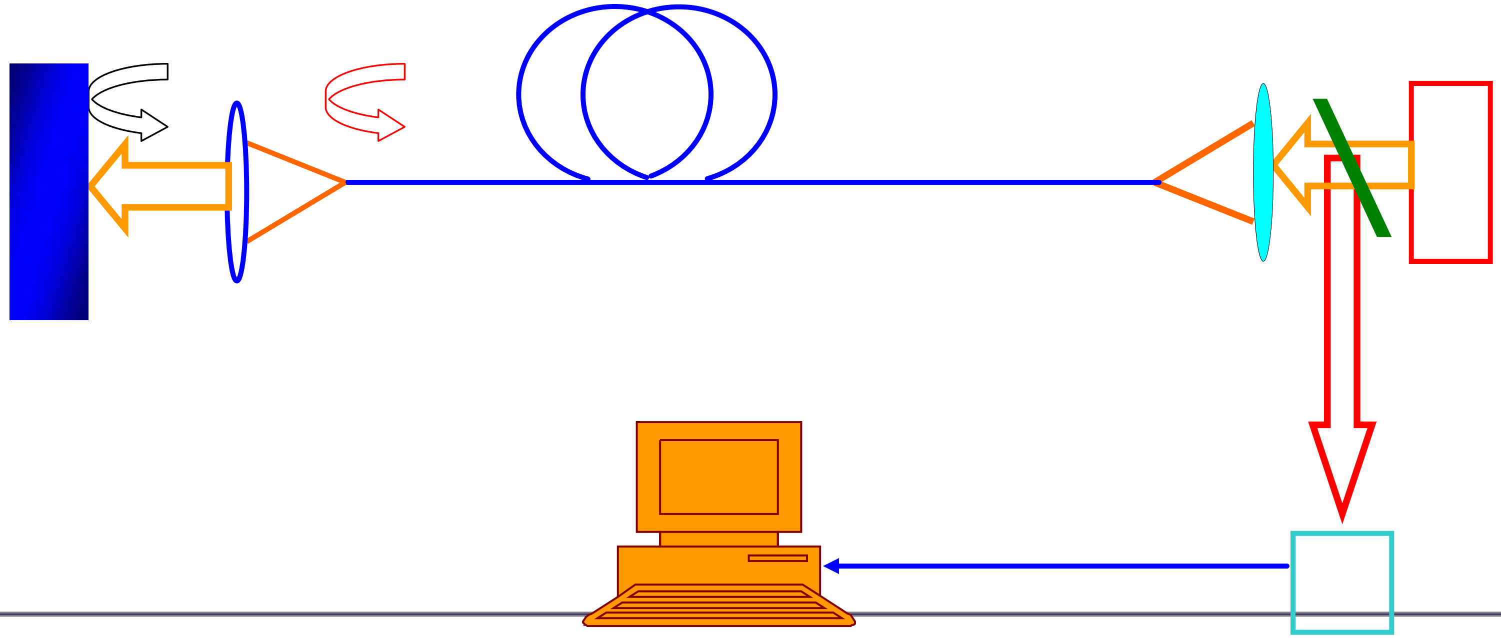
3,39 µm, relative instability $5\ 10^{-14}$

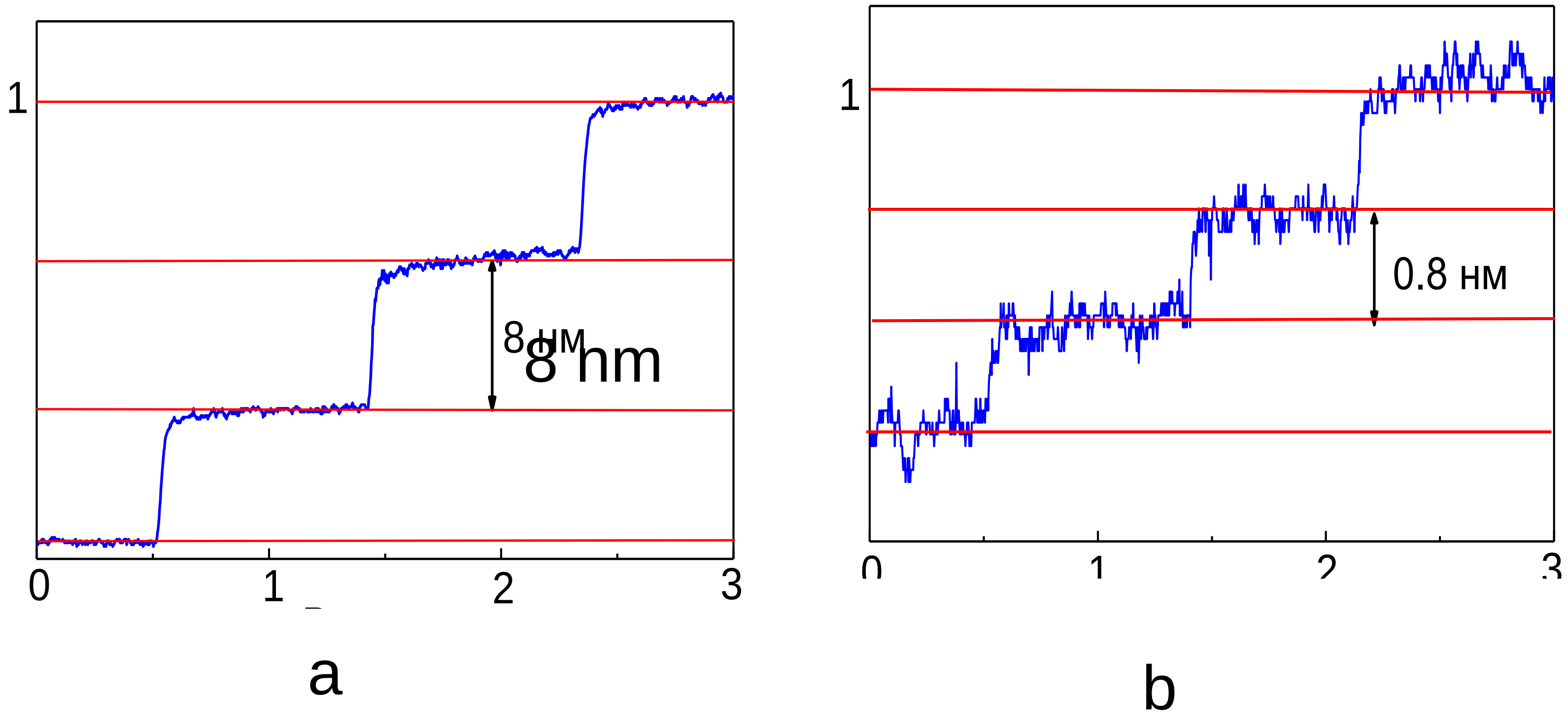
IODINE-STABILIZED METROLOGICAL LASER



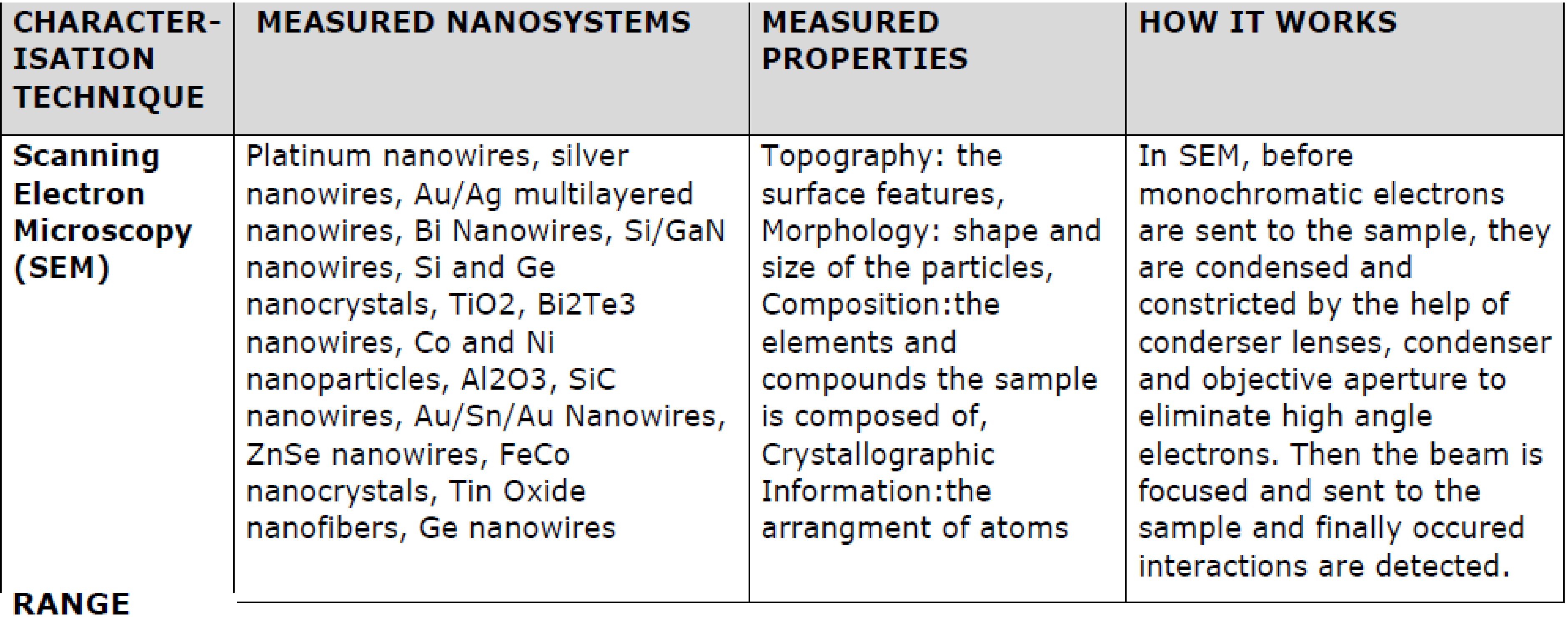
633 nm iodine-stabilized
helium-neon laser

Diode laser interferometer of small displacement

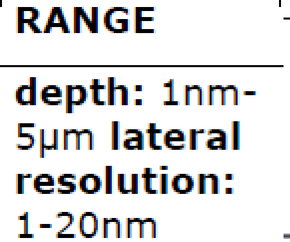




Measurement of the reference mirror shifts:
a –step 8 nm, b – 0,8 nm



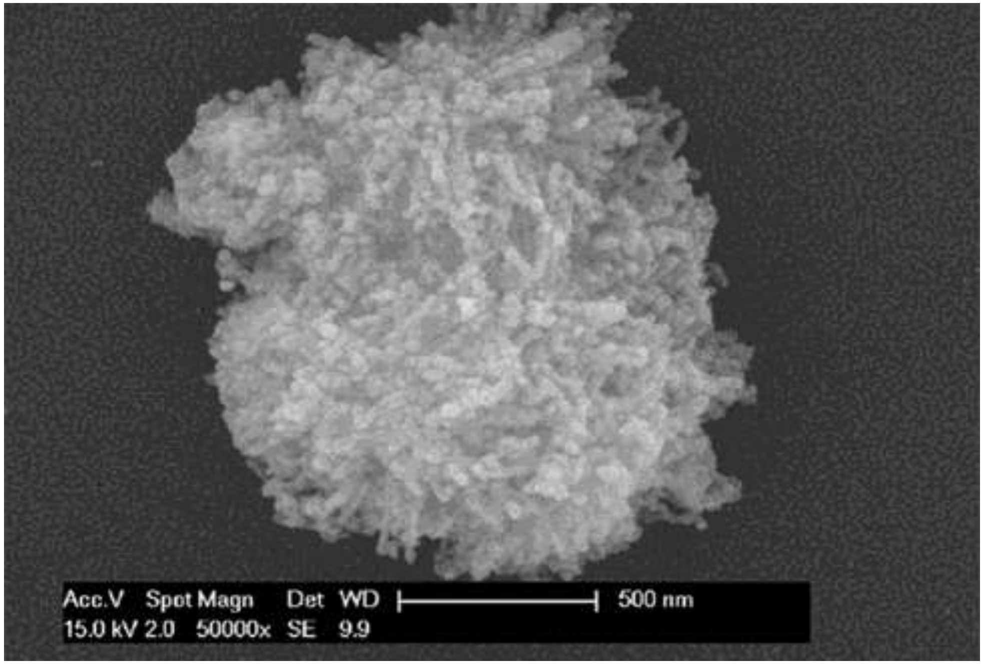
CHARACTER-ISATION TECHNIQUE	MEASURED NANOSYSTEMS	MEASURED PROPERTIES	HOW IT WORKS
Scanning Electron Microscopy (SEM)	Platinum nanowires, silver nanowires, Au/Ag multilayered nanowires, Bi Nanowires, Si/GaN nanowires, Si and Ge nanocrystals, TiO2, Bi2Te3 nanowires, Co and Ni nanoparticles, Al2O3, SiC nanowires, Au/Sn/Au Nanowires, ZnSe nanowires, FeCo nanocrystals, Tin Oxide nanofibers, Ge nanowires	Topography: the surface features, Morphology: shape and size of the particles, Composition:the elements and compounds the sample is composed of, Crystallographic Information:the arrangment of atoms	In SEM, before monochromatic electrons are sent to the sample, they are condensed and constricted by the help of conderser lenses, condenser and objective aperture to eliminate high angle electrons. Then the beam is focused and sent to the sample and finally occured interactions are detected.



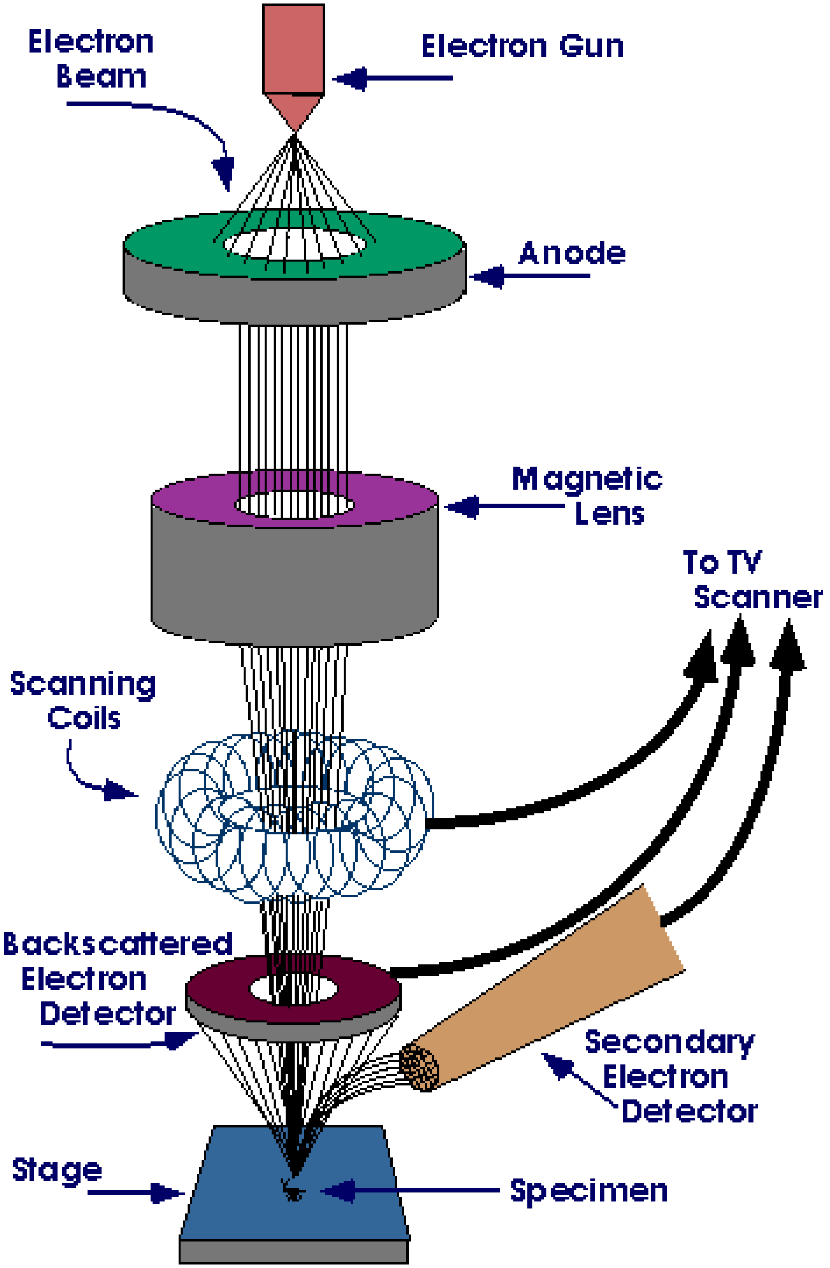
RANGE
depth: 1nm-5µm **lateral resolution:** 1-20nm

Eighth nanoforum report:nanometrology. 2006. www.nanoforum.org.

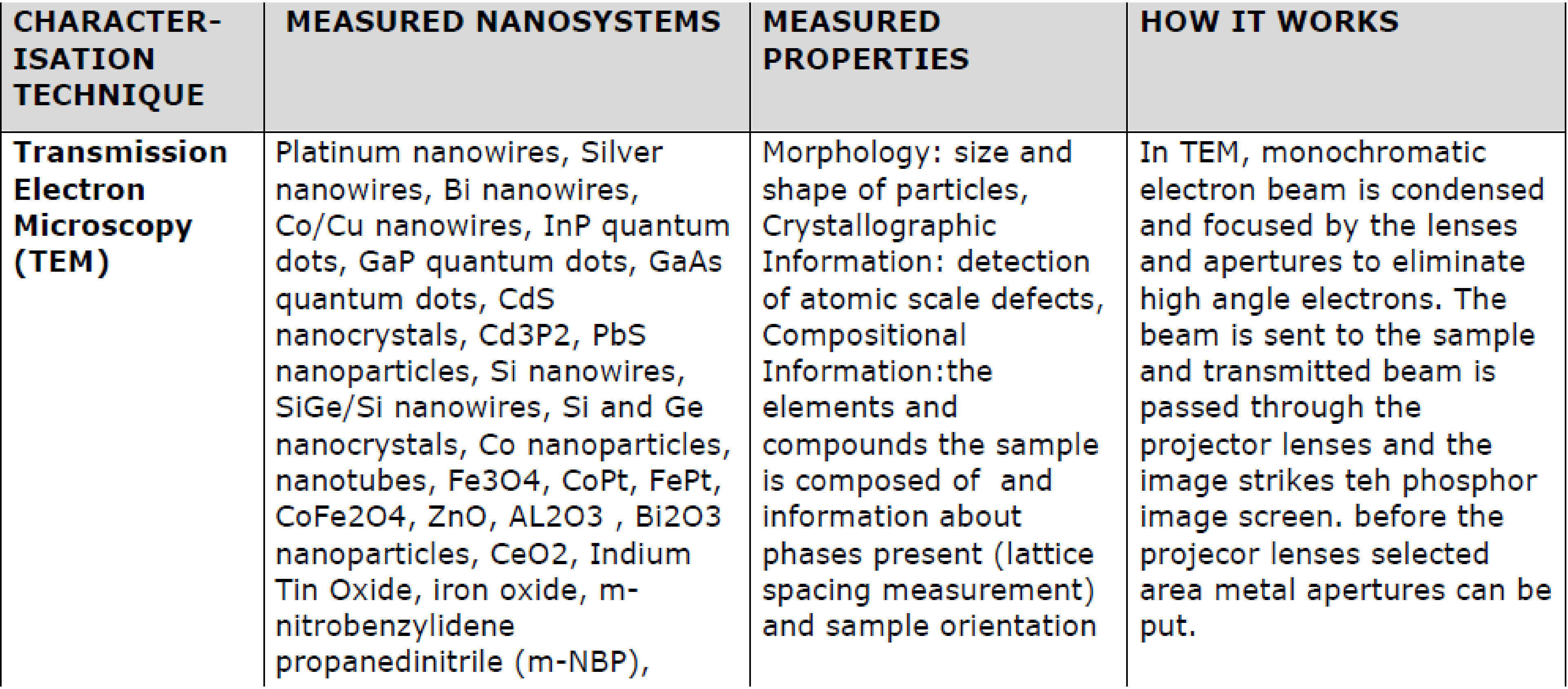
SEM: Scheme



SEM image of Co_3O_4 nanoparticles in cluster



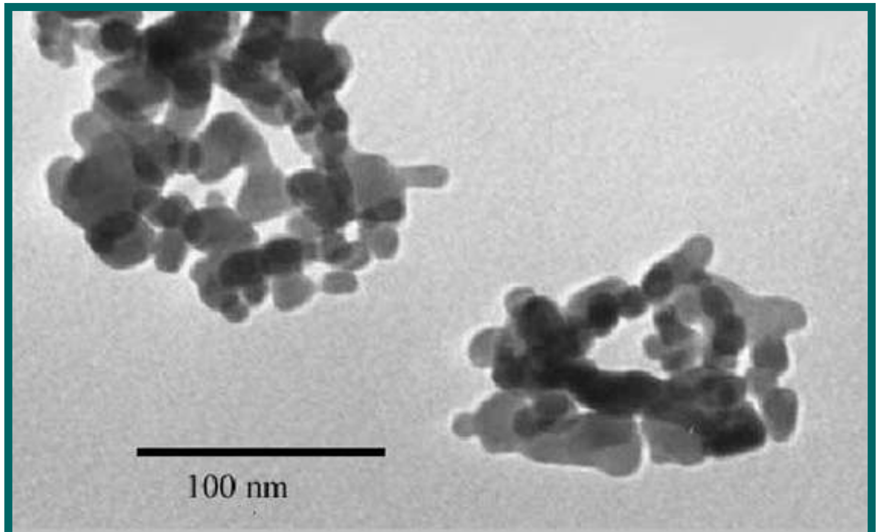
http://www-archive.mse.iastate.edu/microscopy/path2.html



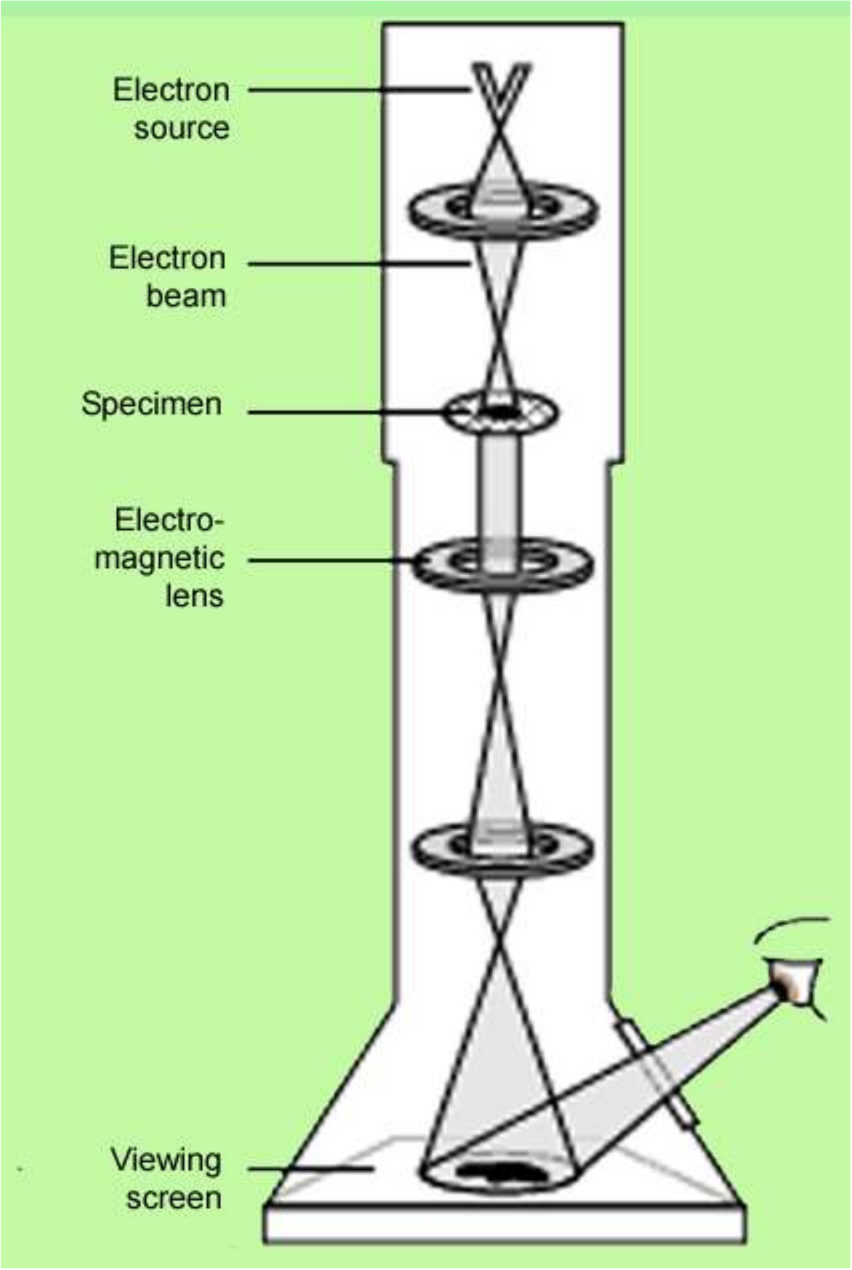
CHARACTER-ISATION TECHNIQUE	MEASURED NANOSYSTEMS	MEASURED PROPERTIES	HOW IT WORKS
Transmission Electron Microscopy (TEM)	Platinum nanowires, Silver nanowires, Bi nanowires, Co/Cu nanowires, InP quantum dots, GaP quantum dots, GaAs quantum dots, CdS nanocrystals, Cd3P2, PbS nanoparticles, Si nanowires, SiGe/Si nanowires, Si and Ge nanocrystals, Co nanoparticles, nanotubes, Fe3O4, CoPt, FePt, CoFe2O4, ZnO, AL2O3 , Bi2O3 nanoparticles, CeO2, Indium Tin Oxide, iron oxide, m-nitrobenzylidene propanedinitrile (m-NBP),	Morphology: size and shape of particles, Crystallographic Information: detection of atomic scale defects, Compositional Information:the elements and compounds the sample is composed of and information about phases present (lattice spacing measurement) and sample orientation	In TEM, monochromatic electron beam is condensed and focused by the lenses and apertures to eliminate high angle electrons. The beam is sent to the sample and transmitted beam is passed through the projector lenses and the image strikes teh phosphor image screen. before the projecor lenses selected area metal apertures can be put.

Eighth nanoforum report:nanometrology. 2006. www.nanoforum.org.

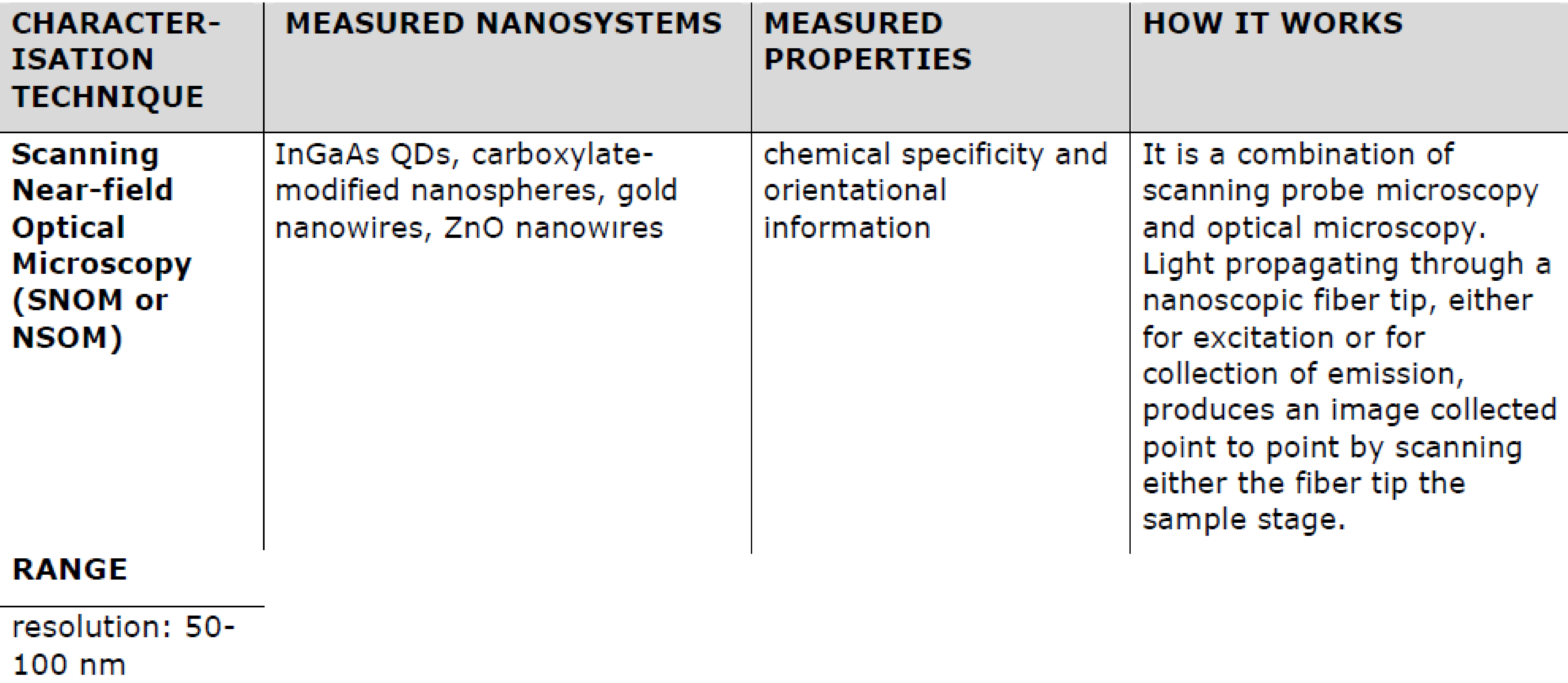
TEM: scheme



TEM image of Co3O4 nanoparticles.

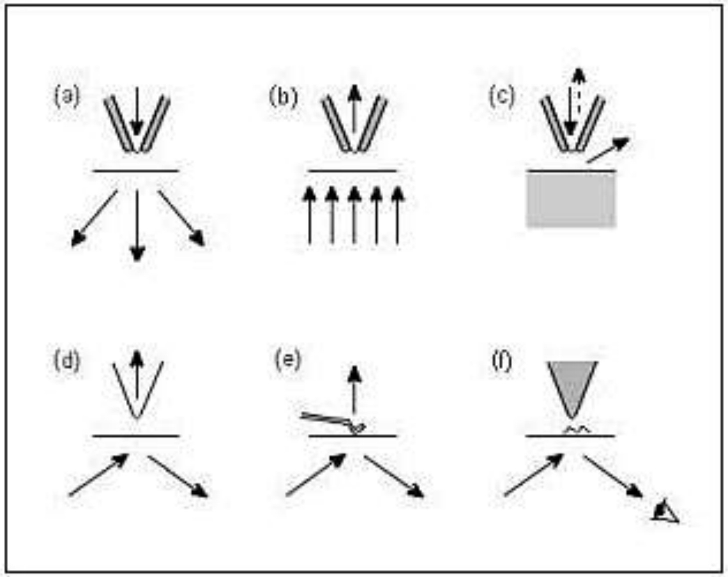


http://www.nobelprize.org/educational/physics/microscopes/tem/index.html

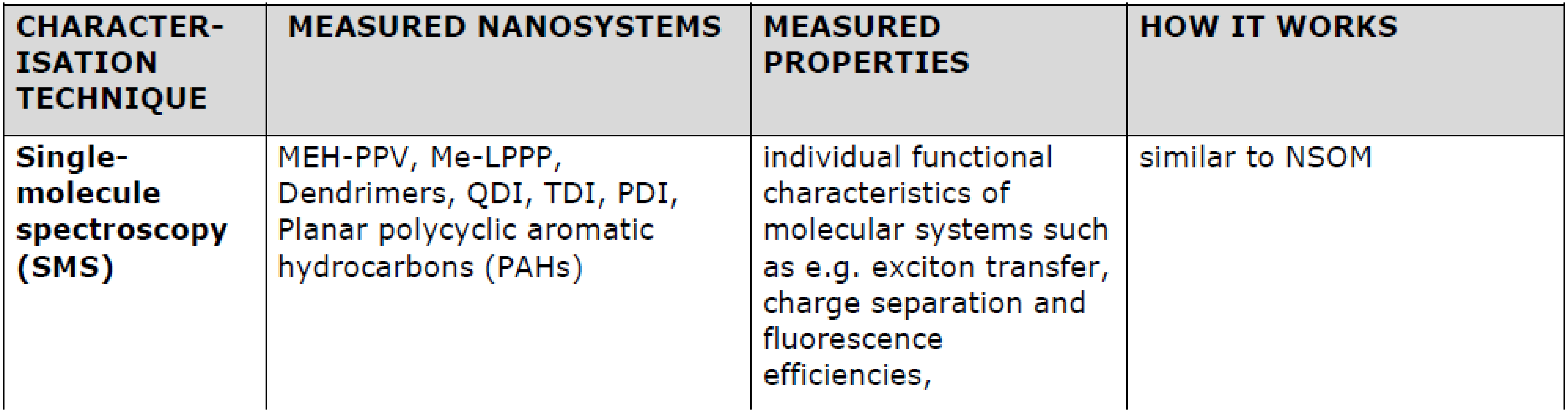


CHARACTER-ISATION TECHNIQUE	MEASURED NANOSYSTEMS	MEASURED PROPERTIES	HOW IT WORKS
Scanning Near-field Optical Microscopy (SNOM or NSOM)	InGaAs QDs, carboxylate-modified nanospheres, gold nanowires, ZnO nanowires	chemical specificity and orientational information	It is a combination of scanning probe microscopy and optical microscopy. Light propagating through a nanoscopic fiber tip, either for excitation or for collection of emission, produces an image collected point to point by scanning either the fiber tip the sample stage.
RANGE			
resolution: 50-100 nm			

Eighth nanoforum report:nanometrology. 2006. www.nanoforum.org.


(a)
(b)
(c)
(d)
(e)
(f)


Near-Field Scanning Optical Microscope Configuration
NSOM Head
ECU Interface Connection
Electronic Control Unit (ECU)
Figure 1
Photo Tube
CPU
Olympus IX71 Inverted Optical Microscope
External Laser
Keyboard
Monitor



CHARACTER-ISATION TECHNIQUE	MEASURED NANOSYSTEMS	MEASURED PROPERTIES	HOW IT WORKS
Single-molecule spectroscopy (SMS)	MEH-PPV, Me-LPPP, Dendrimers, QDI, TDI, PDI, Planar polycyclic aromatic hydrocarbons (PAHs)	individual functional characteristics of molecular systems such as e.g. exciton transfer, charge separation and fluorescence efficiencies,	similar to NSOM

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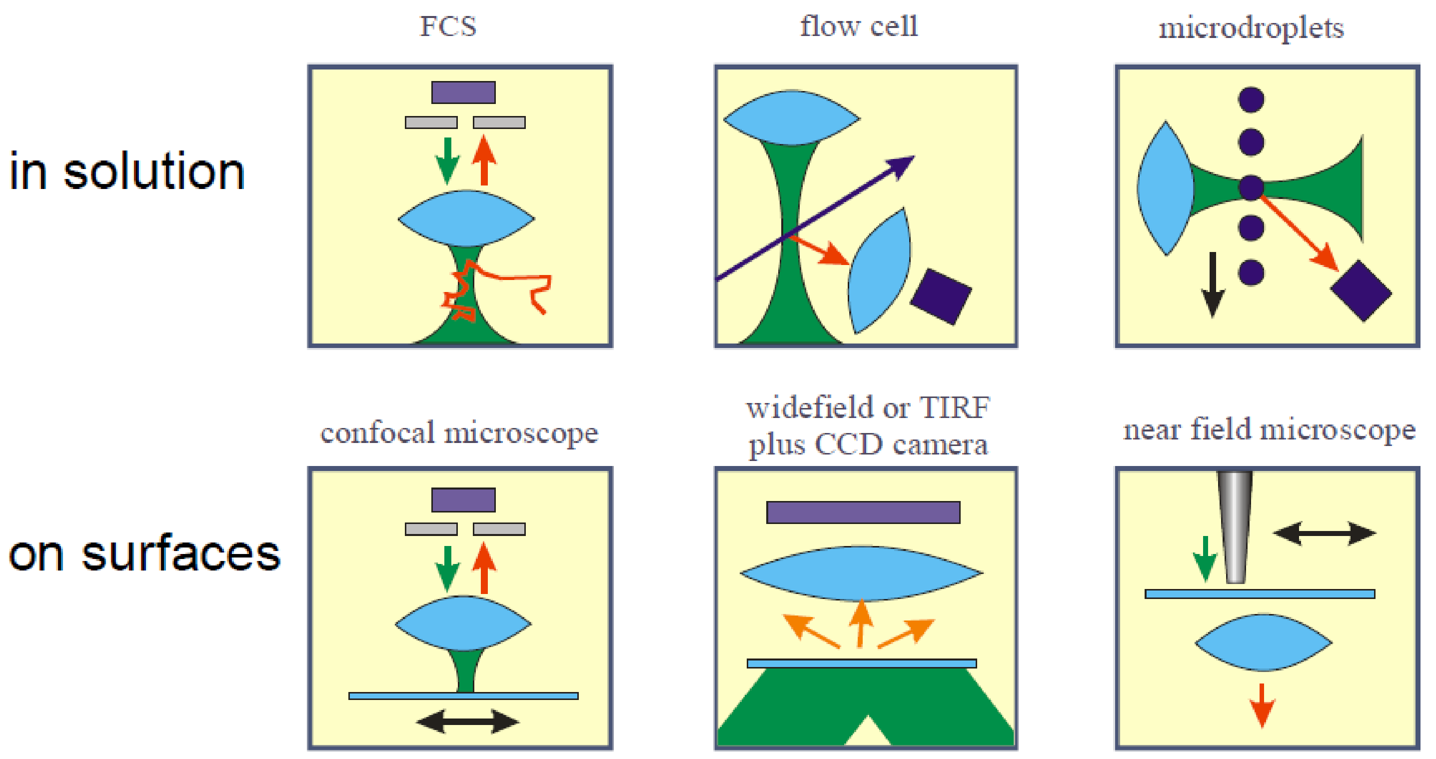
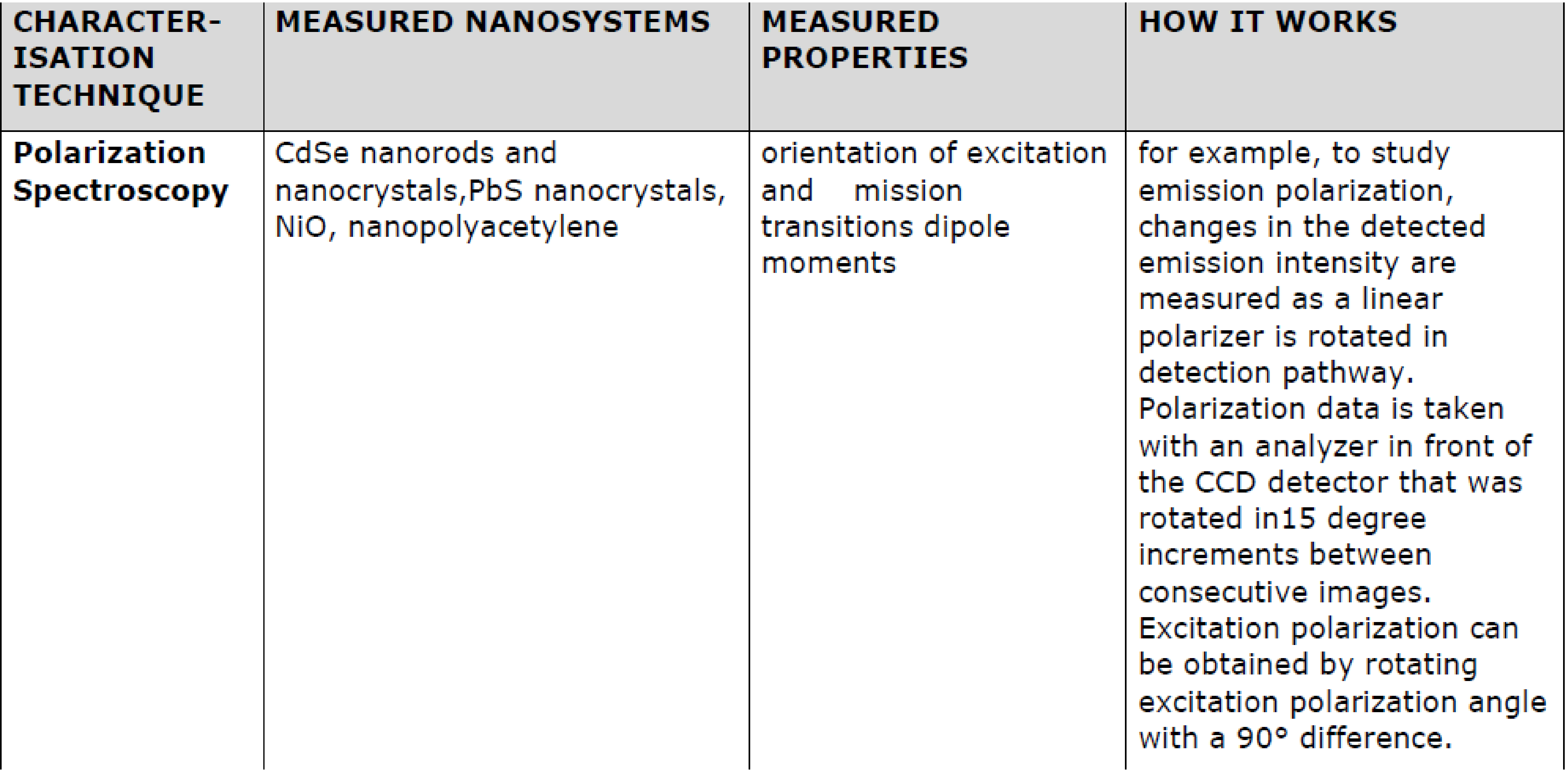
methods for SMD

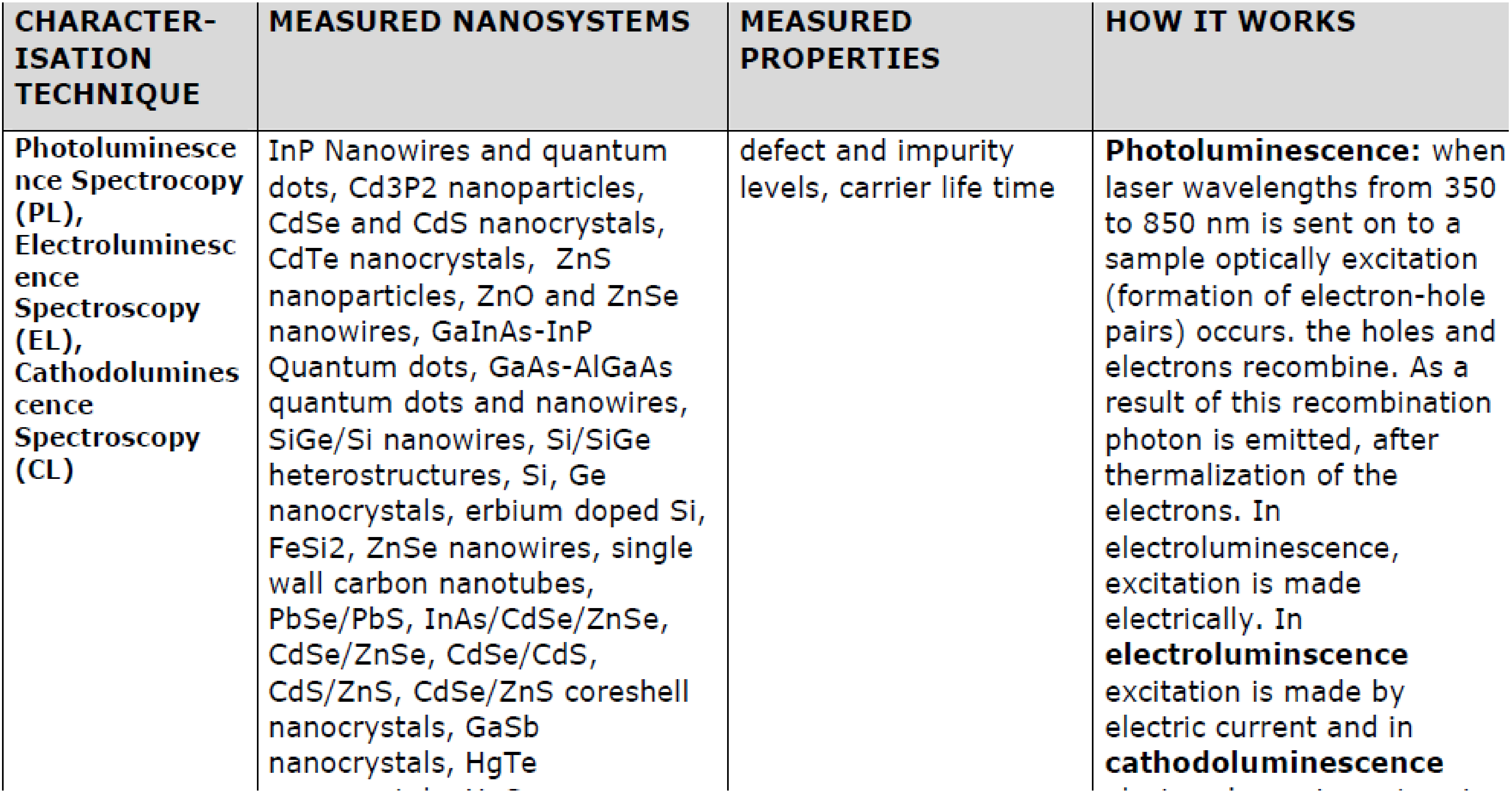


Courtesy: Jörg Enderlein, 1999. Forschungszentrum Jülich

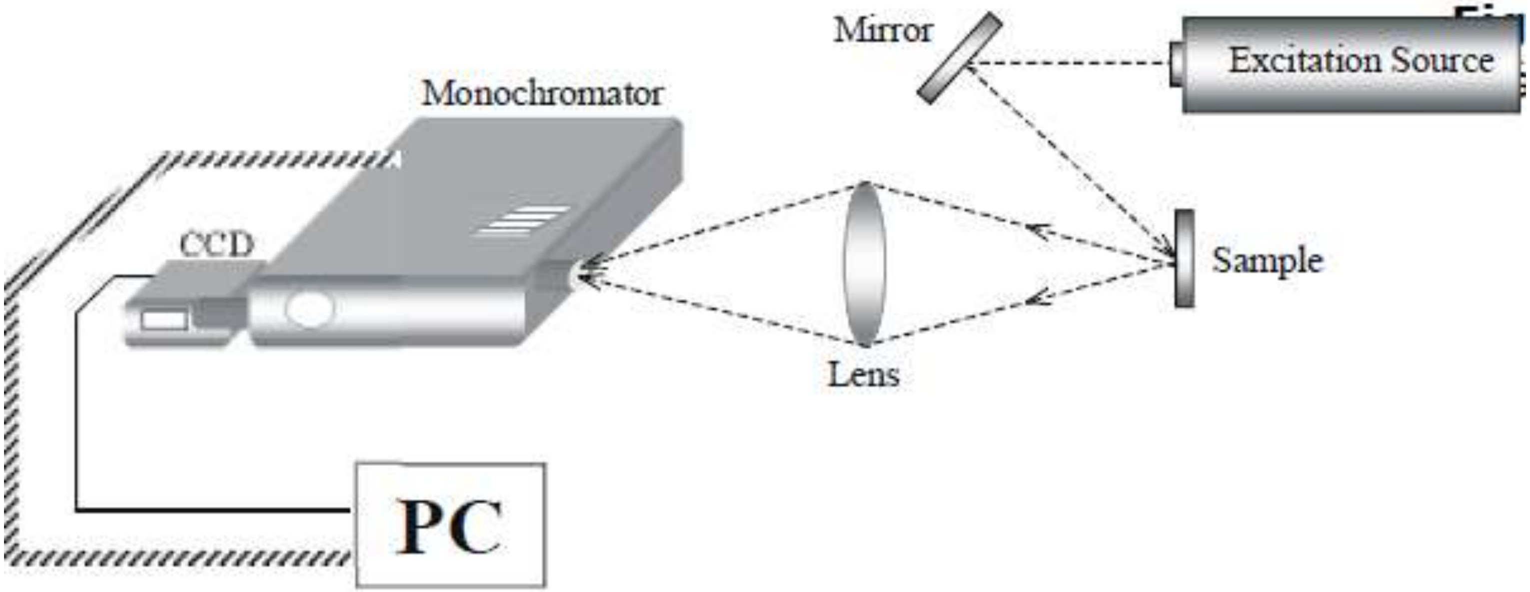


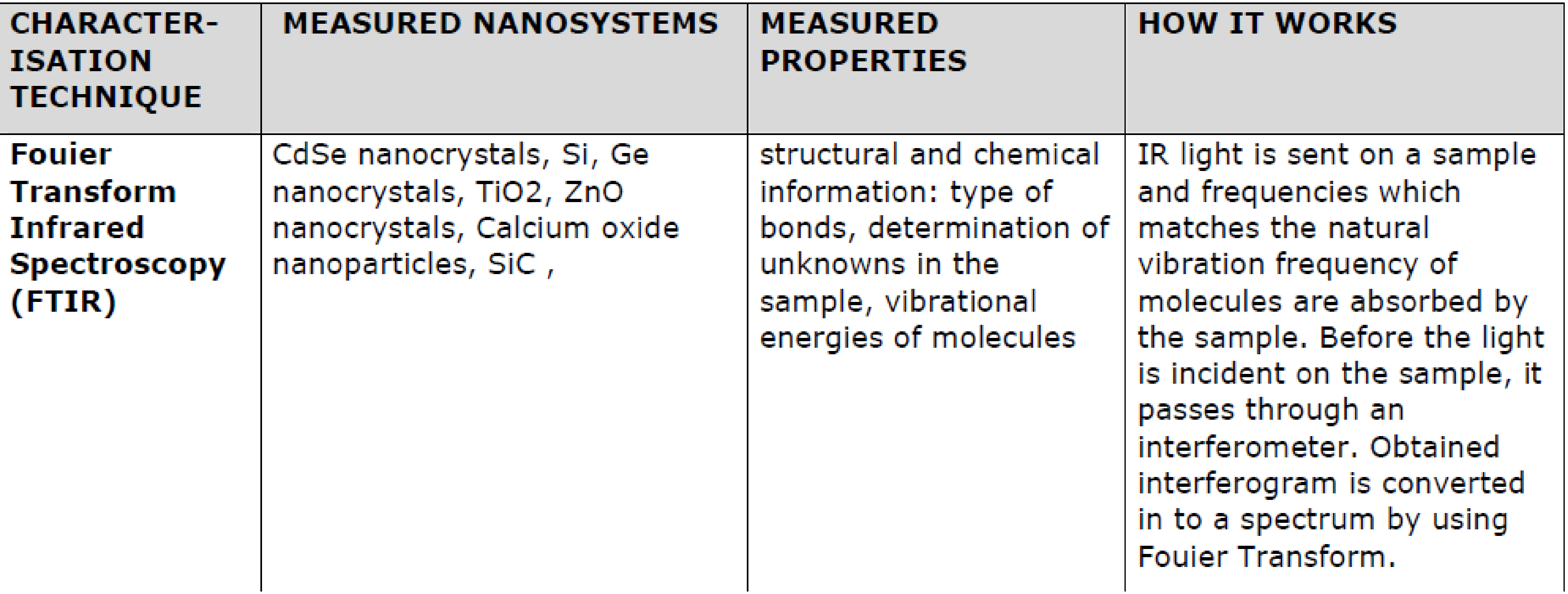
CHARACTER-ISATION TECHNIQUE	MEASURED NANOSYSTEMS	MEASURED PROPERTIES	HOW IT WORKS
Polarization Spectroscopy	CdSe nanorods and nanocrystals,PbS nanocrystals, NiO, nanopolyacetylene	orientation of excitation and mission transitions dipole moments	for example, to study emission polarization, changes in the detected emission intensity are measured as a linear polarizer is rotated in detection pathway. Polarization data is taken with an analyzer in front of the CCD detector that was rotated in15 degree increments between consecutive images. Excitation polarization can be obtained by rotating excitation polarization angle with a 90° difference.

Eighth nanoforum report:nanometrology. 2006. www.nanoforum.org.



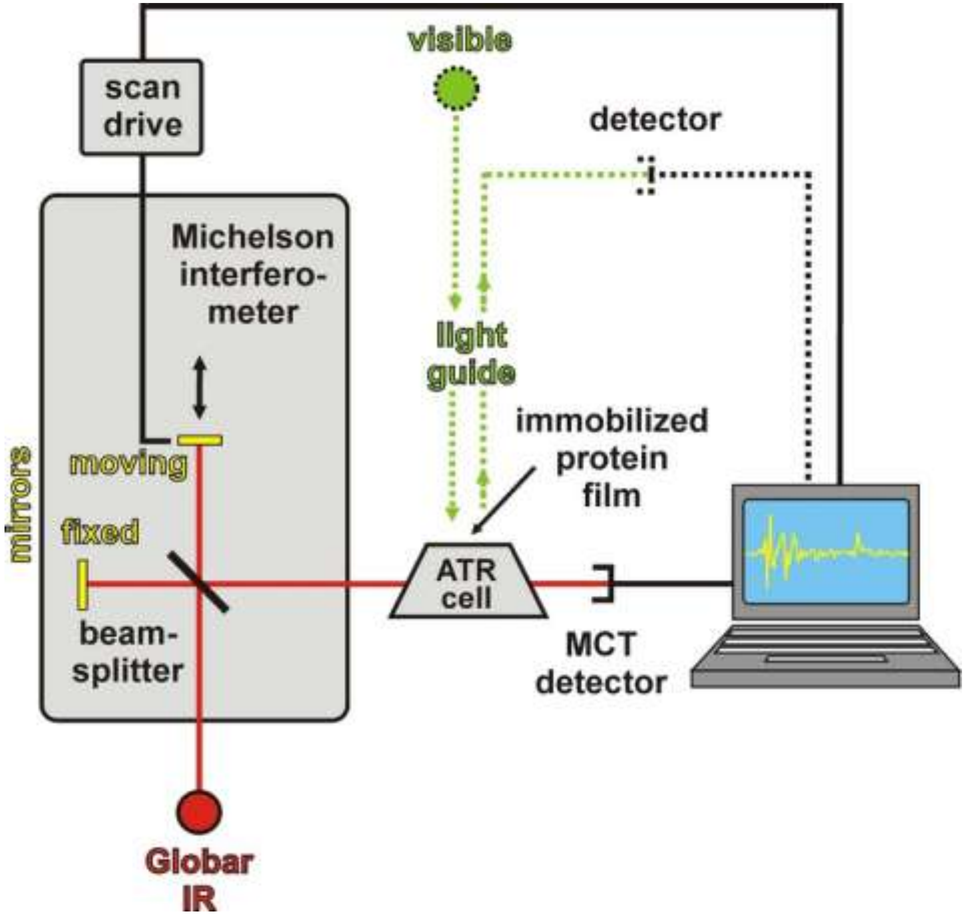
CHARACTER-ISATION TECHNIQUE	MEASURED NANOSYSTEMS	MEASURED PROPERTIES	HOW IT WORKS
Photoluminescence Spectrocopy (PL), Electroluminescence Spectroscopy (EL), Cathodoluminescence Spectroscopy (CL)	InP Nanowires and quantum dots, Cd3P2 nanoparticles, CdSe and CdS nanocrystals, CdTe nanocrystals, ZnS nanoparticles, ZnO and ZnSe nanowires, GaInAs-InP Quantum dots, GaAs-AlGaAs quantum dots and nanowires, SiGe/Si nanowires, Si/SiGe heterostructures, Si, Ge nanocrystals, erbium doped Si, FeSi2, ZnSe nanowires, single wall carbon nanotubes, PbSe/PbS, InAs/CdSe/ZnSe, CdSe/ZnSe, CdSe/CdS, CdS/ZnS, CdSe/ZnS coreshell nanocrystals, GaSb nanocrystals, HgTe	defect and impurity levels, carrier life time	**Photoluminescence:** when laser wavelengths from 350 to 850 nm is sent on to a sample optically excitation (formation of electron-hole pairs) occurs. the holes and electrons recombine. As a result of this recombination photon is emitted, after thermalization of the electrons. In electroluminescence, excitation is made electrically. In **electroluminscence** excitation is made by electric current and in **cathodoluminescence**


Mirror
Excitation Source
Monochromator
CCD
Sample
Lens
PC

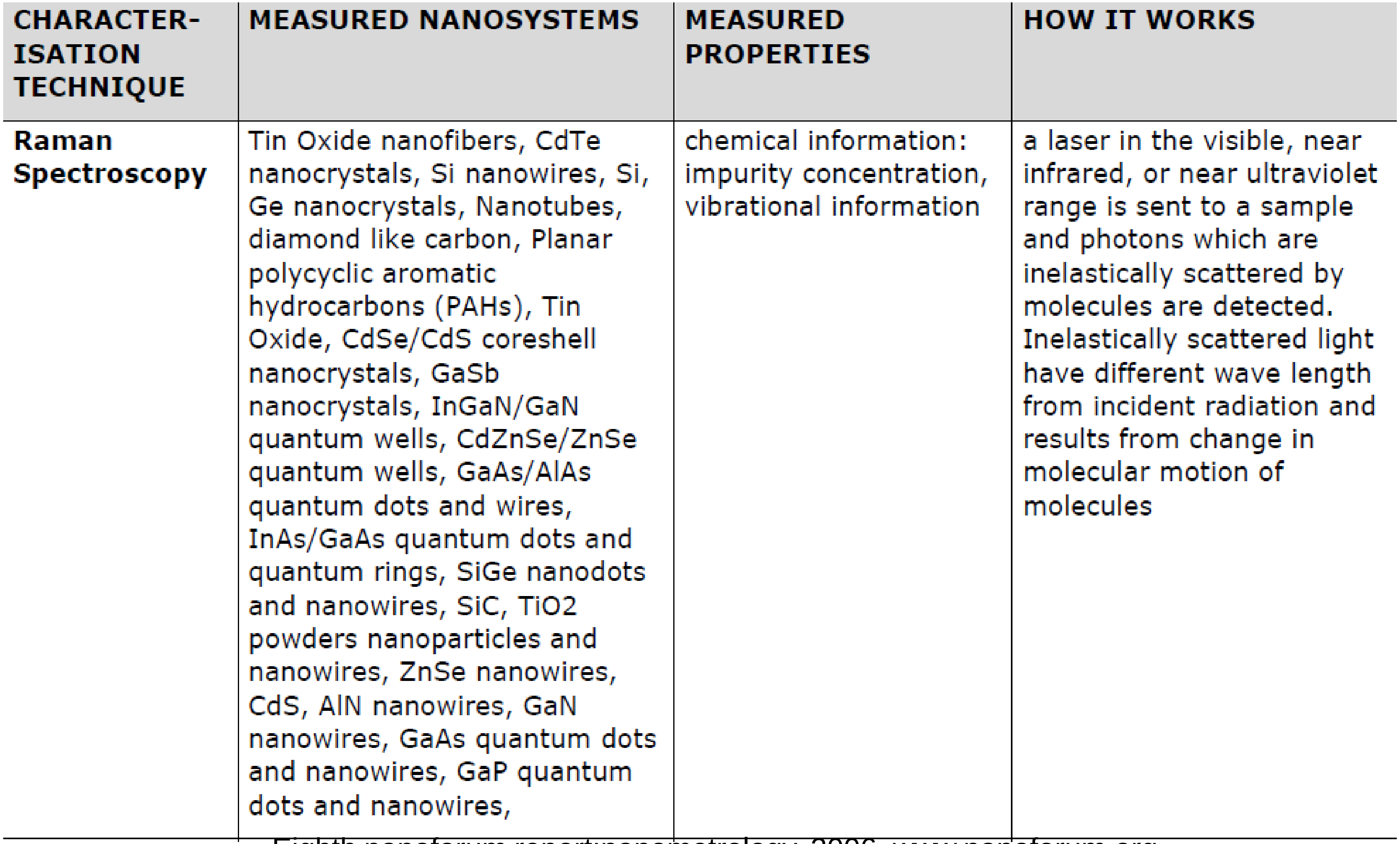


CHARACTER-ISATION TECHNIQUE	MEASURED NANOSYSTEMS	MEASURED PROPERTIES	HOW IT WORKS
Fouier Transform Infrared Spectroscopy (FTIR)	CdSe nanocrystals, Si, Ge nanocrystals, TiO2, ZnO nanocrystals, Calcium oxide nanoparticles, SiC ,	structural and chemical information: type of bonds, determination of unknowns in the sample, vibrational energies of molecules	IR light is sent on a sample and frequencies which matches the natural vibration frequency of molecules are absorbed by the sample. Before the light is incident on the sample, it passes through an interferometer. Obtained interferogram is converted in to a spectrum by using Fouier Transform.

Eighth nanoforum report:nanometrology. 2006. www.nanoforum.org.

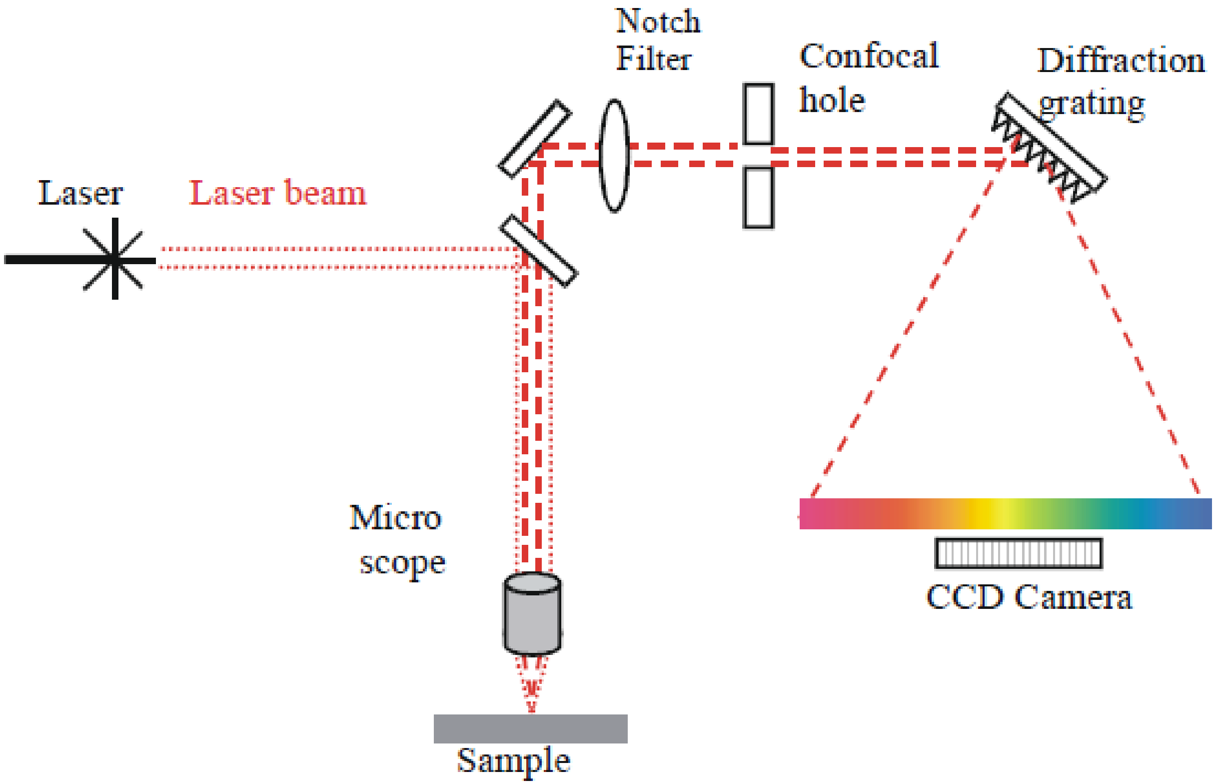


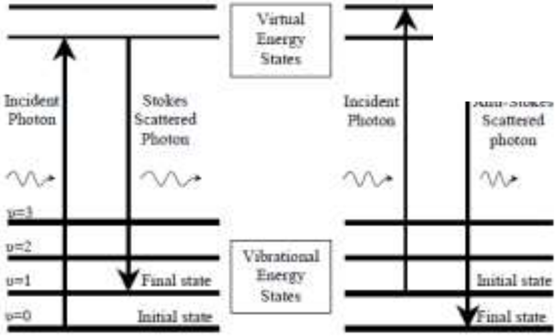
http://withfriendship.com/user/sathvi/ftir.php



CHARACTER-ISATION TECHNIQUE	MEASURED NANOSYSTEMS	MEASURED PROPERTIES	HOW IT WORKS
Raman Spectroscopy	Tin Oxide nanofibers, CdTe nanocrystals, Si nanowires, Si, Ge nanocrystals, Nanotubes, diamond like carbon, Planar polycyclic aromatic hydrocarbons (PAHs), Tin Oxide, CdSe/CdS coreshell nanocrystals, GaSb nanocrystals, InGaN/GaN quantum wells, CdZnSe/ZnSe quantum wells, GaAs/AlAs quantum dots and wires, InAs/GaAs quantum dots and quantum rings, SiGe nanodots and nanowires, SiC, TiO2 powders nanoparticles and nanowires, ZnSe nanowires, CdS, AlN nanowires, GaN nanowires, GaAs quantum dots and nanowires, GaP quantum dots and nanowires,	chemical information: impurity concentration, vibrational information	a laser in the visible, near infrared, or near ultraviolet range is sent to a sample and photons which are inelastically scattered by molecules are detected. Inelastically scattered light have different wave length from incident radiation and results from change in molecular motion of molecules

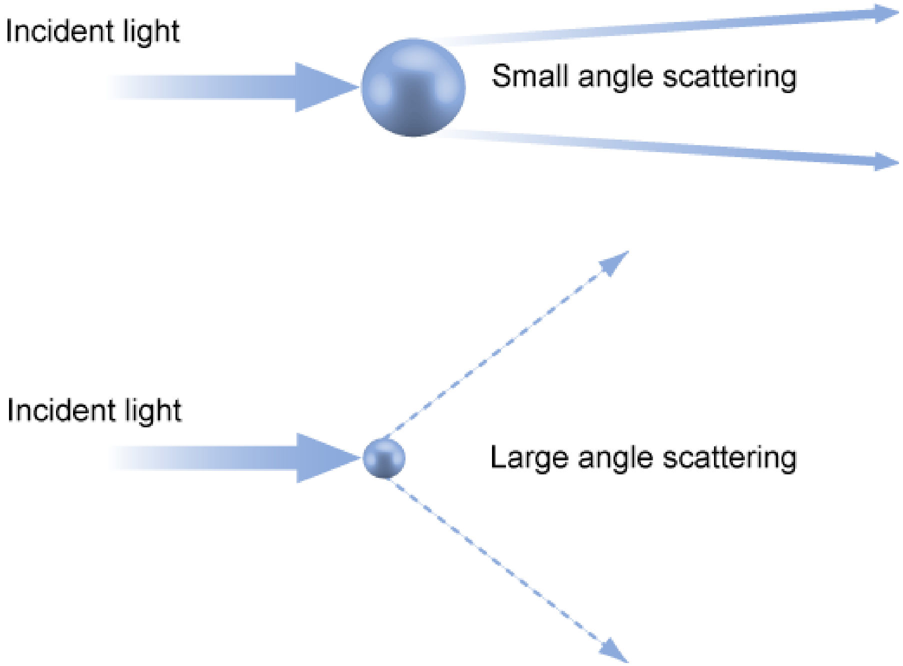
Eighth nanoforum report:nanometrology. 2006. www.nanoforum.org.


Notch Filter
Confocal hole
Diffraction grating
Laser
Laser beam
Micro scope
CCD Camera
Sample


Virtual Energy States
Incident Photon
Stokes Scattered Photon
υ=3
υ=2
υ=1
υ=0
Final state
Initial state
Vibrational Energy States
Incident Photon
Anti-Stokes Scattered photon
Initial state
Final state

0.01 - 3500 µm

LASER DIFFRACTION



Mastersizer 3000

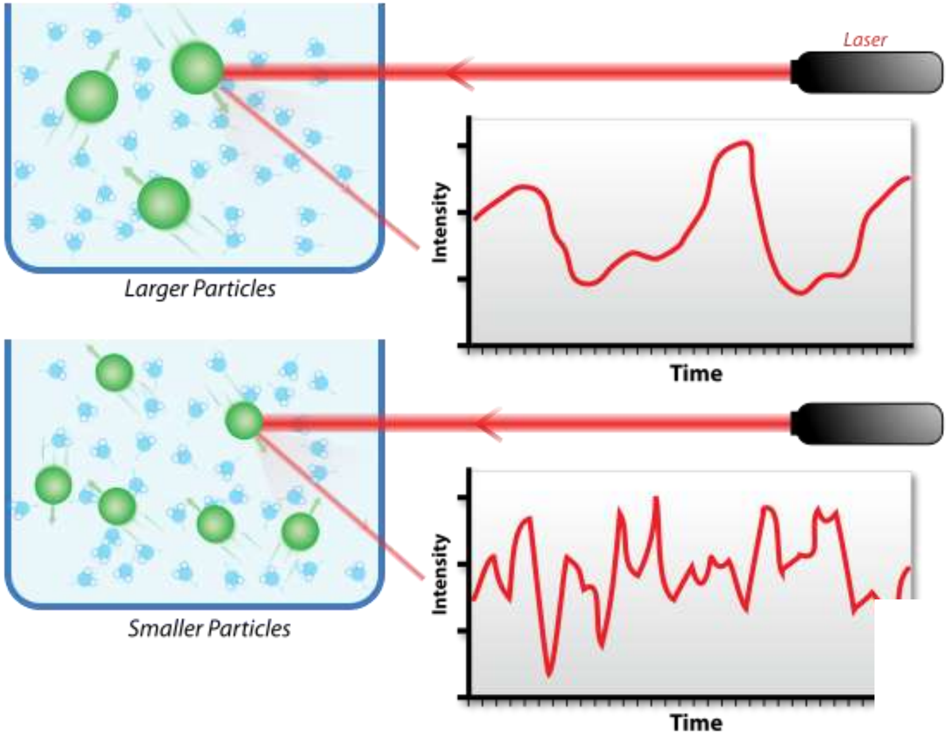
Smarter particle sizing

Size range: 0,01 – 3500 µm

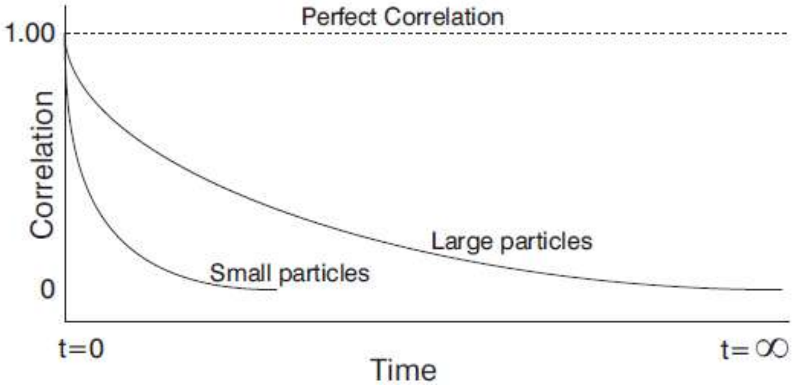
www.malvern.com/labeng/products/mastersizer3000.htm

0.01 - 3500 µm

Dynamic Light Scattering (also known as **PCS - Photon Correlation Spectroscopy) measures Brownian motion and relates this to the size of the** particles. It does this by illuminating the particles with a laser and analysing the intensity fluctuations in the scattered light.

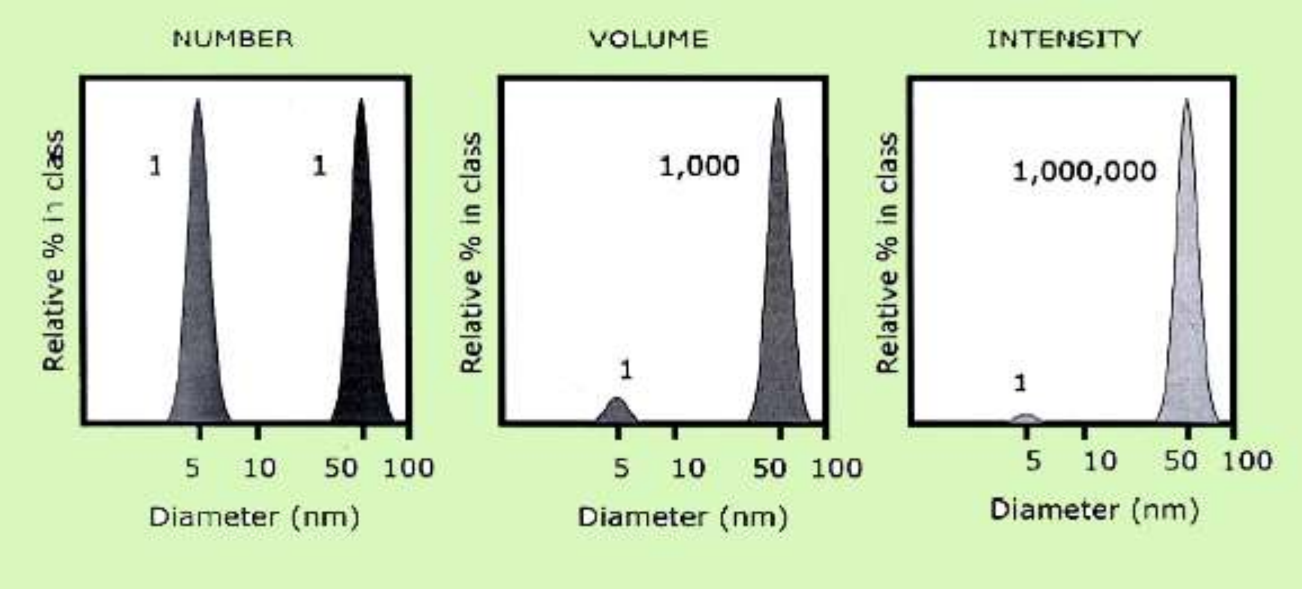


Specle pattern



Scatterometry is the investigation of micro- or nanostructured surfaces regarding their geometry and dimension by measurement and analysis of light diffraction from these surfaces. In contrast to optical methods, non-imaging metrology methods like scatterometry are not diffraction limited. They give access to the geometrical parameters of periodic structures like structure width (CD), pitch, side-wall angle or line height. However, scatterometry requires *apriori information about the surface structure. The inverse diffraction problem has to be solved to determine the structure parameters from a measured diffraction pattern. Proper scatterometric measurements require an intense effort regarding modeling, simulation and inverse methods.*

Dynamic Scatter Light: in the exemple the powder contains 50% of nanparticles sized 5 nm and 50% of their aggregates, sized 50nm. The number and the volume of particles, and the intensity of the scattered light are shown. Note that for particles of larger size the intensity is greater: in fact, smaller particles move faster, causing a rapid decay of scattering.



Eighth nanoforum report:nanometrology. 2006. www.nanoforum.org.

Co-Nanomet

Co-ordination of Nanometrology in Europe

SEVENTH FRAMEWORK
PROGRAMME

In the next decade, nanotechnology can be expected to approach maturity, as a major enabling technological discipline with widespread application. The principal drivers for its development are likely to shift from an overarching focus on the ‘joy of discovery’ towards the requirement to fulfil societal needs.

Thanks for your attention