Characterization

CHEM-E5125 Thin Films Technology

2023

Jari Koskinen

Contents

- Thin film properties
- Wealth of methods – MATRIX
- Scattering
- Thickness - profilometry
- Composition – EDS, WDS, SIMS, RBS, ERDA, GDOES
- Microstructure –XRD, TEM
- Bonding – ESCA, RAMAN
- Topography - ADM
- Electrical conductivity – four point probe
- Mechanical properties - indentation
- Optical transmittance

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Feature-Problem-Analysis-Tools
Visual Guide to Selecting Tools for Chemical Analysis*

Legend
- Range of Elements Detected
- Depth of Info
- Analysis in UHV or air
- Quantification Accuracy
- Li - U
- 1-5 nm
- Tool
- UHV
- ±30%
- 0.1 atom%
- Ultimate Detection Limit

Bulk Info

FT-IR — Molecular Bonding, 0.5-2.0 µ, in air, ±10%, 0.1 wgt%
- Contamination, QC
- Organics, Silicon
- Fingerprint Identification
- Film Thicknesses
- AT-FT-IR for Surface films
- Not for metals or alloys

XRF — Al - U, 0.1-0.5 µ, in air, ±10%, PPM
- Bulk Analysis, Alloy ID
- Film Thicknesses (1-5 µ)
- No Chemical States

LA-ICP-MS — Li - U, ~1µ, UHV, ±50%, PPB
- Contamination, Unknowns, FA
- Conductors, Semicon, Insulators
- Measured Elemental Ions
- ~ 1 micron per laser pulse
- No Chemical States

Depth Profiling Info

D-SIMS — Li - U, 5-20 Å, UHV, ±50%, PPM
- Isotope analysis, Dopant Profiles
- Semiconductor Films
- Element versus Depth info
- Profile Speed: <0.01 micron/min
- Usually 5-20 elements per profile
- Etch Depth Resolution 5-10 Å
- Molecular fragments

GD-OES — H - U, 2-10 Å, 1 torr, ±10%, PPM
- Multi-Layer Films, Silicon Re-cycle
- Bulk, PV, Trace element, Unknowns
- Profile Speed: up to 10 micron/min
- 50 elements per profil
- Element versus Depth infoe
- Monolayer resolution
- Excellent Quantitative Results
- Etch Depth Resolution 2-10 Å
- Final etch depth ~200 µ
- No molecular fragments

Surface Info

FE-Auger — Li - U, 1-5 nm, UHV, ±30%, 0.1 atom%
- Particles, Defects, FA
- Contamination, Unknowns
- Conductors, Semicon (Insulator)
- Chemical States (Si vs SiO2)
- XY Map, Depth/Line Profiling
- Angle Resolve AES: 1-5 nm
- Ar+ Ion Cleaning inside
- Final etch depth ~1 µ
- Insulators need charge neutralizer and high tilt angle

XPS — Li - U, 1-12 nm, UHV, ±5%, 0.1 atom%
- Surface Contamination, Thin Films
- Powders, Greases, Glove Contam.
- QC, QA, FA, Unknowns
- Conductors, Semi, Insulators
- Chemical States (Si vs SiO2)
- XY Map, Depth/Line Profiling
- Angle Resolve XPS: 1-10 nm
- Ar+ Ion Cleaning inside
- Final etch depth ~1 µ
- Insulators need charge neutralizer

ToF-SIMS — H - U, 2-6 Å, UHV, ±50%, PPB
- Monolayer Contamination
- Conductors, Semi, Insulators
- Molecular Fragments
- XY Map, full spectrum each pixel
- Ga+ Ion Cleaning inside
- Final etch depth ~100 nm
- Insulators need charge neutralizer

Sub-Surface Info

µ FT-IR — Molecular Bonding, 0.2-2.0 µ, in air, ±10%, 0.5 wgt%
- Contamination (>0.2 µ)
- Organics, Silicon
- No Metals or Inorganics
- Molecular Bonding
- Fingerprint Identification
- XY Map, Confocal Profiling
- Not for metals or alloys

EDX - SEM — Be - U, 0.3-3.0 µ, UHV, 10%, 1 atom%
- Sub-Surface Elements, Particles
- >300 nm Thick Contamination
- Unknowns
- No Chemical States
- XY Sub-Surface Map
- UHR-SEM Imaging
- Insulators need Au coating

Raman — Molecular Bonding, 0.5 - 5.0 µ, in air, ±10%, 0.1 wgt%
- Particles, Contamination, Films
- Organics, Inorganic
- Molecular Bonding
- Carbon Phases (diamond)
- Stress, Orientation
- Film Thicknesses
- Confocal Profiling
- Not for metals or alloys

Ion Milling Info

FIB/Dual-Beam — Etch Depth: 0.1-100 µ, UHV
- Prep for STEM, TEM, UHR-SEM
- Used to mill a trench by using Ga+ ions to expose multiple layers or to cut a defect in half exposing the inside for EDS, TEM or Auger analysis.

Buried Layer Info

XRR — ~1% of thickness, 3-10 nm, in air
- Crystalline Materials, Semicon
- Film Thicknesses
- Thickness of layers must be >3 nm
- Density of buried layers
- Roughness of interfaces
- Need 10-20 mm length (1 mm width)

XRD — ~5%, 10 nm-1 µ, in air
- Crystalline Materials, Semicon
- Stress, Identify Phase
- Texture orientation
- Degree of crystallinity
- Size of crystallites
- % of amorphous nature
- Solid materials only

Atomic Scale Info

TEM-EDX — Al - U, 2-100 nm, UHV, ±20%, 0.5 atom%
- Defects, Atomic layers (>2nm)
- Particles, Unknowns
- Element Maps, Line Profiles
- TEM Imaging
- No Chemical States

STEM/TEM-EELS — Li - Mg, 0.8-100 nm, UHV, ±20%, 0.5 atom%
- Defects, Atomic layers (>0.8 nm)
- Particles, Unknowns
- Element Maps, Line Profiles
- STEM/TEM Imaging
- No Chemical States

Central diagram labels
- >50 microns
- <10 nm
- <1 micron
- <4 Å
- >500 nm (0.5µ)
- <5 nm
- >5 microns
- <1 micron
- >500 nm
- ~500 microns
- ~1000 microns
- Pt
- Pt
- SiNOx
- SiO2
- W
- TiN
- B-doped Si
- 10 nm
- 300 nm
- 15 nm
- 400 nm
- 500 nm
- Depth of Sample Measured
- LA-ICP-MS
- XRF
- FT-IR
- D-SIMS
- GD-OES
- 0.5-20 µ
- 1-5 µ
- 1-10 µ
- 1-20 µ
- 1-200 µ

Analysis Modes that Measure in X-Y and Z
- Point Mode Spectra
- Angle Resolve Profile
- Line Profile
- Depth Profiles
- XY Mapping

Instruction on Use
Locate the SIZE and DEPTH of a feature-problem and follow the arrow to the tool suggested for the 1st chemical analysis

* This guide helps the user to select the first chemical analysis tool to analyze or measure the feature-problem. Additional analysis tools are often used to confirm or further understand the feature-problem.

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- Optical transmittance- FTIR (???)

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Film topograpby and thickness

- Film thickness
  - direct measurement by definition
    - profilometer by using masked surface
    - cross section profile + microscopy
    - spectroscopy
- Contact profilometer
  - diamond tip with 1 – 50 mN load
  - tip radius 20 nm – 25 µm (12µm)
  - depth sensitivity/range 0.5 nm/60 µm

Lift-off mask lithography and contact profilometry
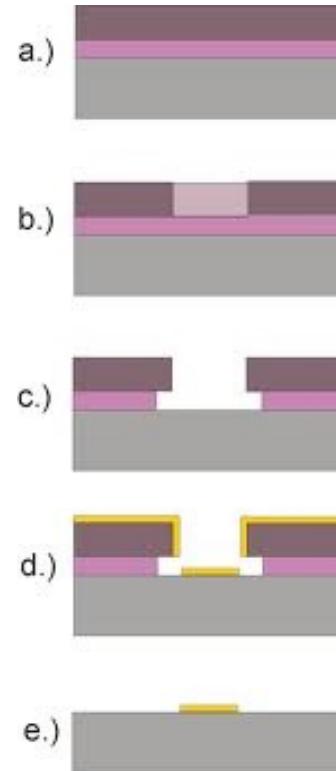
- Simple and reliable step height
- Reflecting surfaces problematic

Optical profilometer
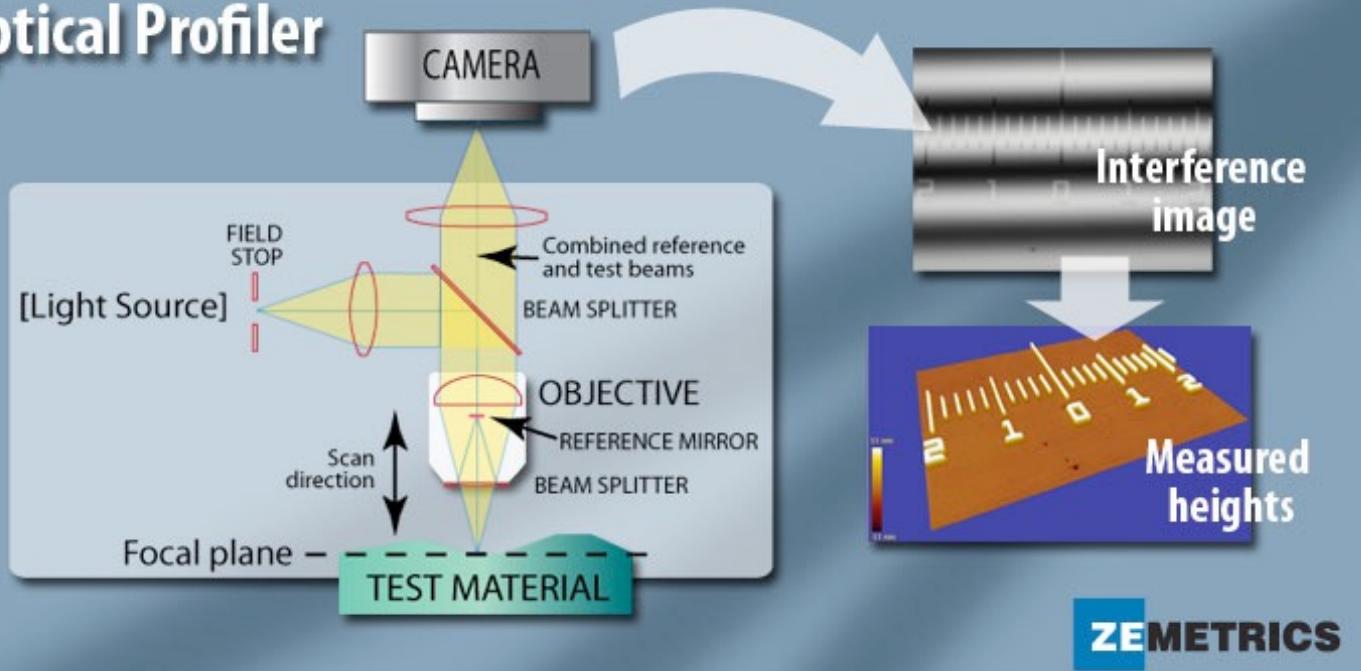
- Non contact 2D (3D surface map)
- Fast
- Reflecting surfaces problematic

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Internal stress of thin film-substrate curvature by profilometer
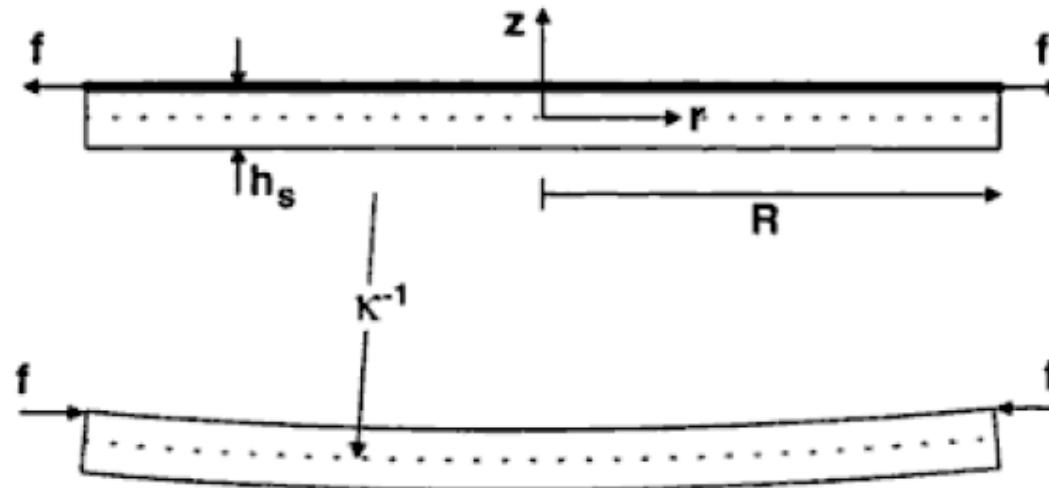
Stoney equation substrate modulus

$$\sigma_{\mathrm{m}} = \frac{M_s\, h_s^2}{6\, h_f} \left\{ \frac{1}{\rho_2} - \frac{1}{\rho_1} \right\}$$

radius of curvature after and intially
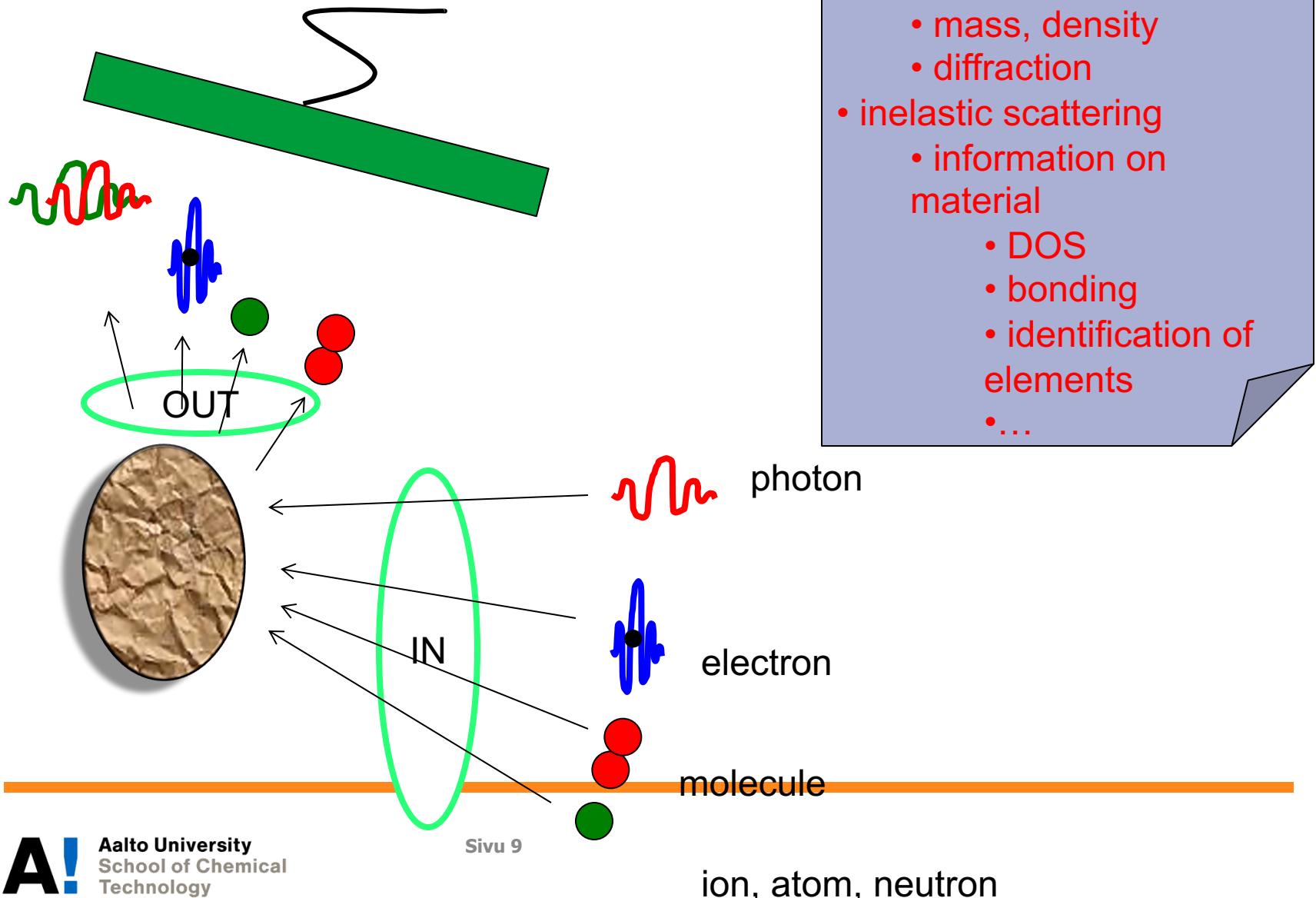
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Scattering experiment

- particles ➜ in vacuum !!
- elastic scattering
    - mass, density
    - diffraction
- inelastic scattering
    - information on material
        - DOS
        - bonding
        - identification of elements
        - …

OUT

IN

photon

electron

molecule

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ion, atom, neutron

Contents

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Composition

- What elements present in the film
- Depth distribution
- Interface
- Often a direct feedback for deposition parameters
  - gas ratio, target composition etc.

SEM EDS and WDS

- Microanalysis EDS and WDS (material of an other course)

Excerpts from lectures in X-ray microanalysis

Thin surface layer analysis by SEM + x-ray microanalysis (EDS or WDS)

https://www.youtube.com/watch?v=KfQ4VNpWN4M

E. Heikinheimo

Aalto - Dept. of MS & E - 2011

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SEM EDS
Interaction volume

https://whatiscl.info/how/spatial-mapping/optimizing-maps
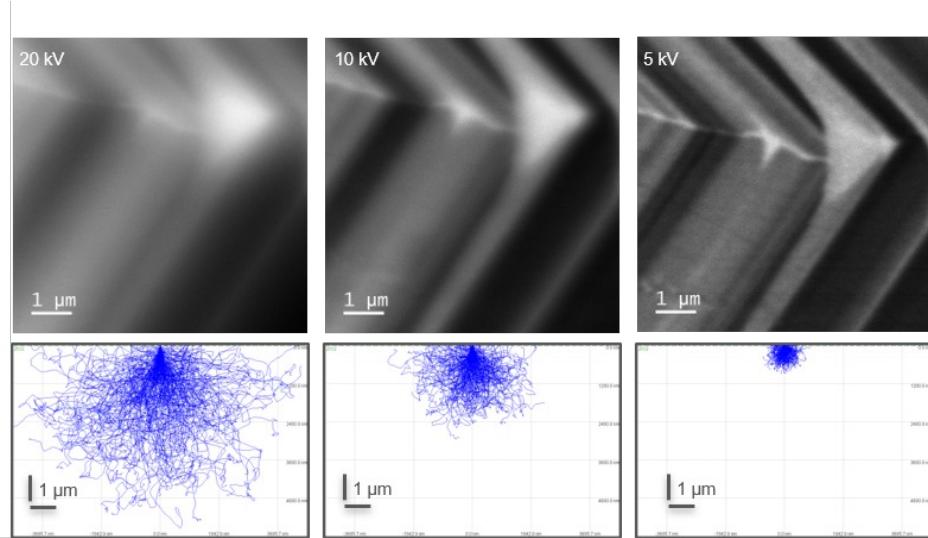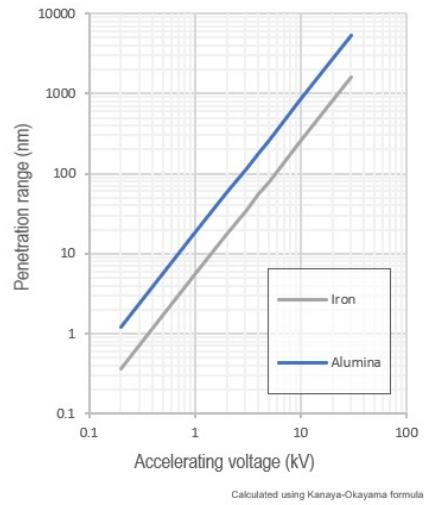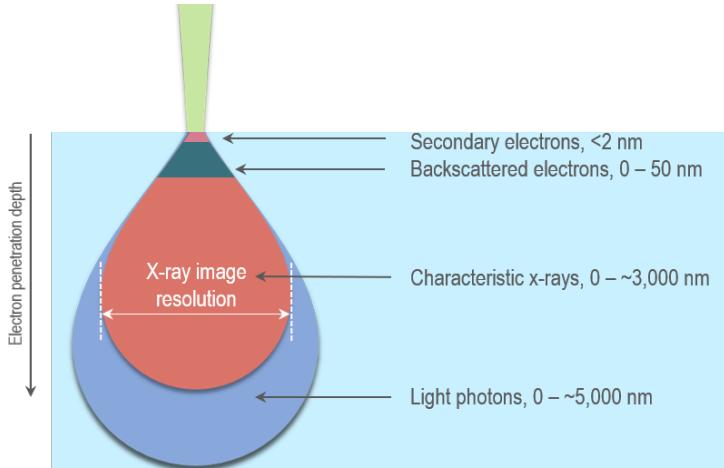
Thin-film analysis (I)
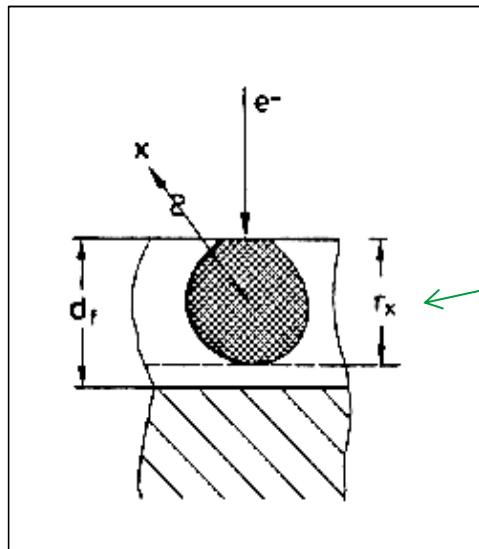
Excitation volume

* Thickness of surface film $d_f > r_x$, substrate does not influence

* Film can be processed as bulk, with normal matrix correction program

* $d_f = 0.2…2$ μm (e.g. by adjusting beam energy)

Thin film analysis (II)

- $d_f << r_x$, $d_f > 1$ nm

- Substrate signal is decisive

- There can be several films on top of each other: "sandwich structure"

- Thin-film software is needed, which is based on calculating $\Phi(\rho z)$- function (amount of generated radiation) as function of depth; a hypothesis of studied film structure is needed

- In principle thickness and composition of film is obtained from both film and substrate signal (checking possibility).

- Non-destructive method, same sample can be analysed by other methods, e.g. RBS.

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FIB focused ion beam

FIB-3D imaging

3D EDX

3D cross sections

FEI Nova NanoLab

FEI COMPANY

3D EBSD

Orientation contrast

5 um

TEM foil preparation
Ultra-thin foils (< 30 nm)

20 um

Micromachining

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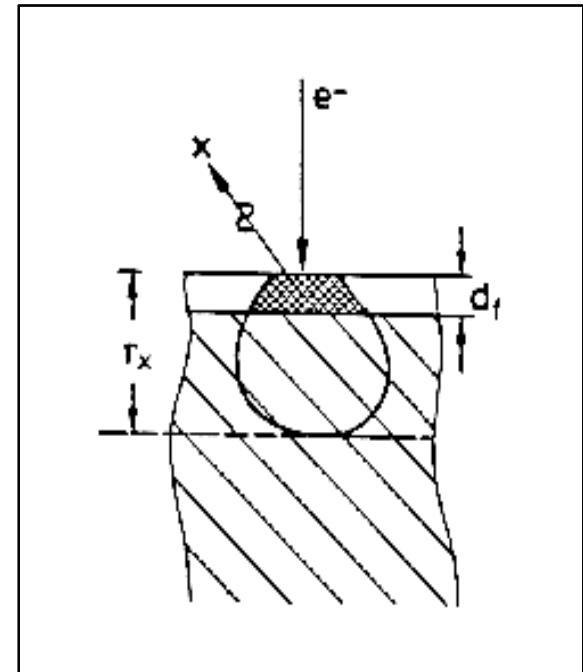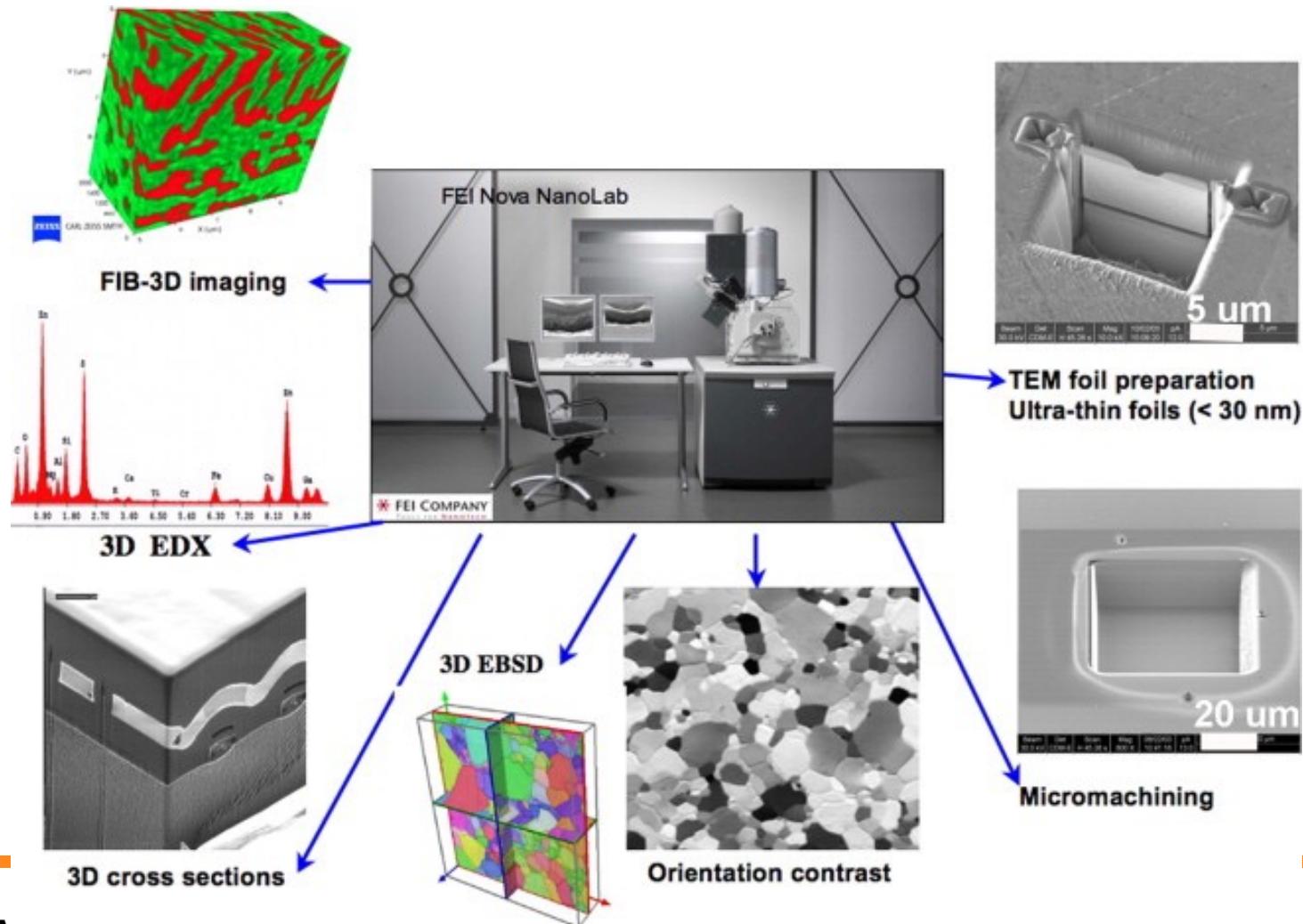
FIB
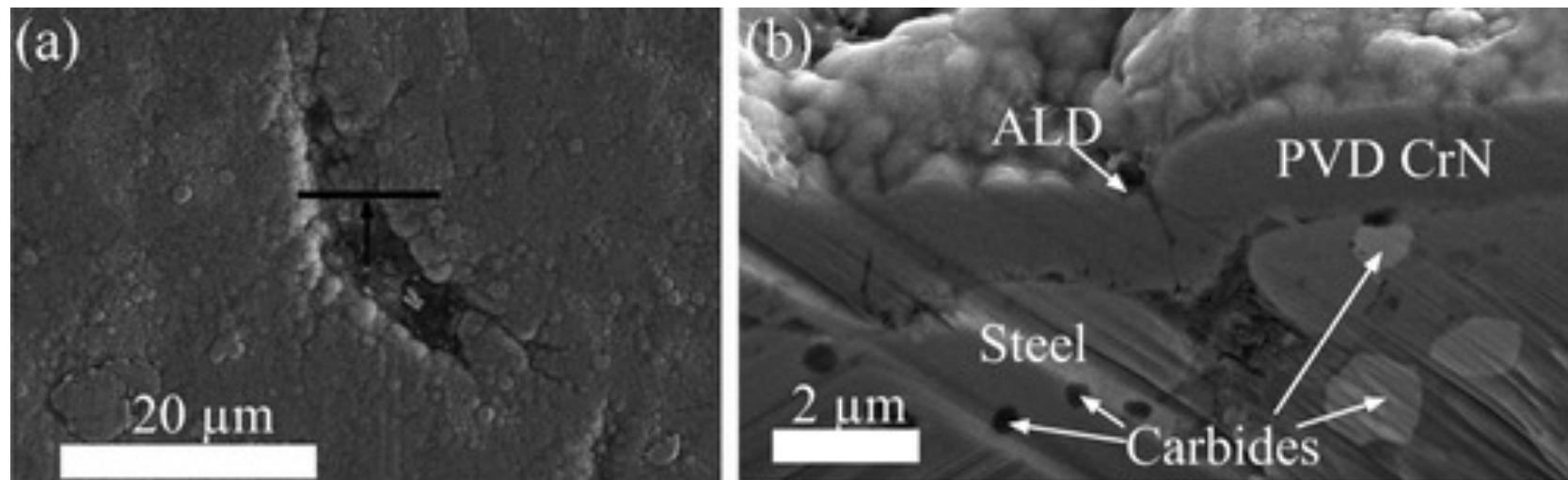
Figure 9. FIB/SEM analysis done on the hybrid PVD/ALD-coated steel after the LSV5-Wear4. Top view (a) of a major defect on a wear track. The black arrow denotes the location of the cross-sectional image (b) prepared by FIB milling

Scattering experiment – Ion in Ion out

OUT

IN

photon

electron

molecule

ion, atom, neutron

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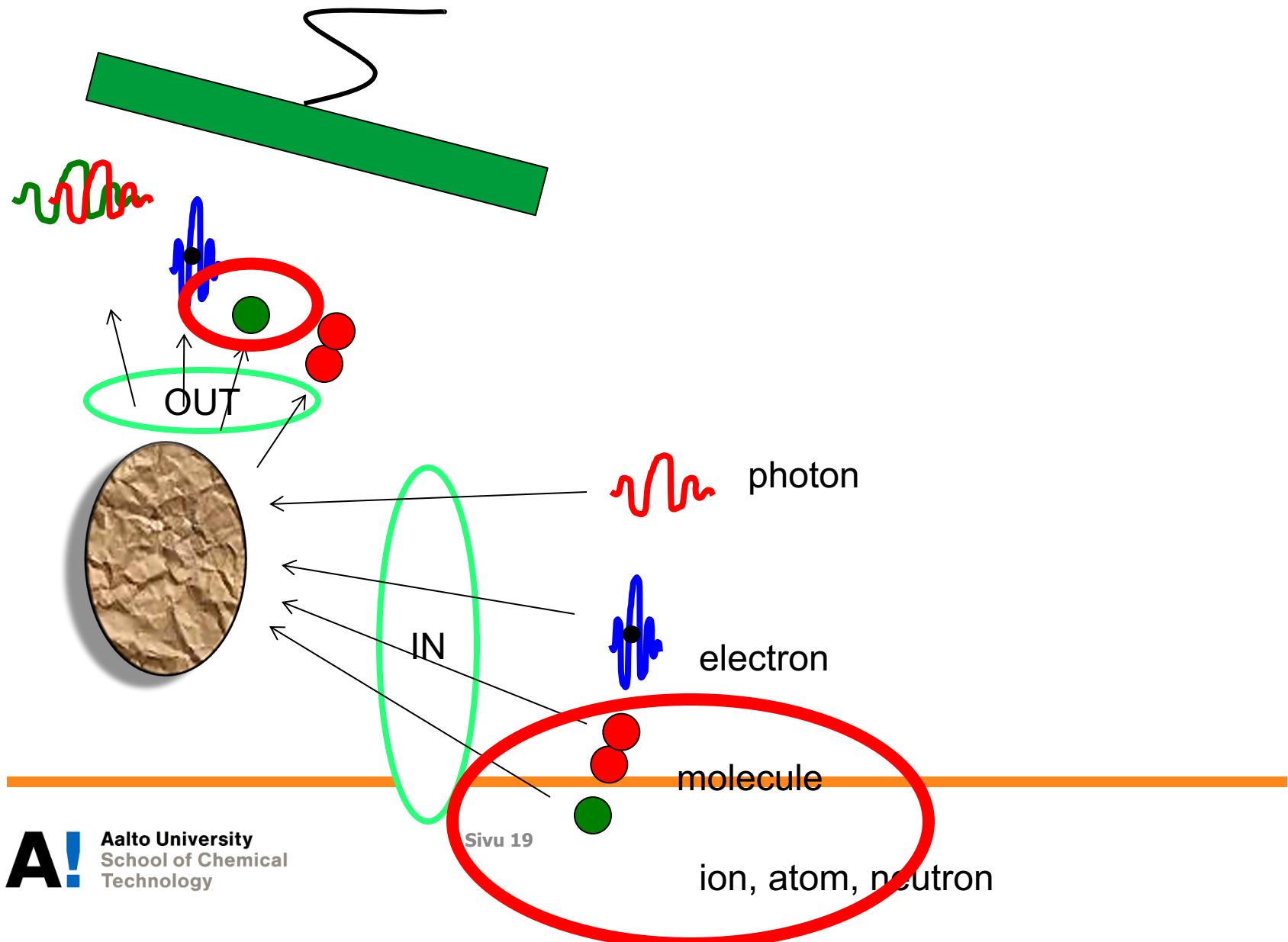
Secondary Ion Mass Spectrometry - SIMS

1. Cesium ion source
2. Duoplasmatron
3. Electrostatic lens
4. Sample
5. Electrostatic sector - ion energy analyser
6. Electromagnet - mass analyser
7. Electron multiplier / Faraday cup
8. Channel-plate / Fluorescent screen - ion image detector

SIMS by Leena-Sisko Johansson

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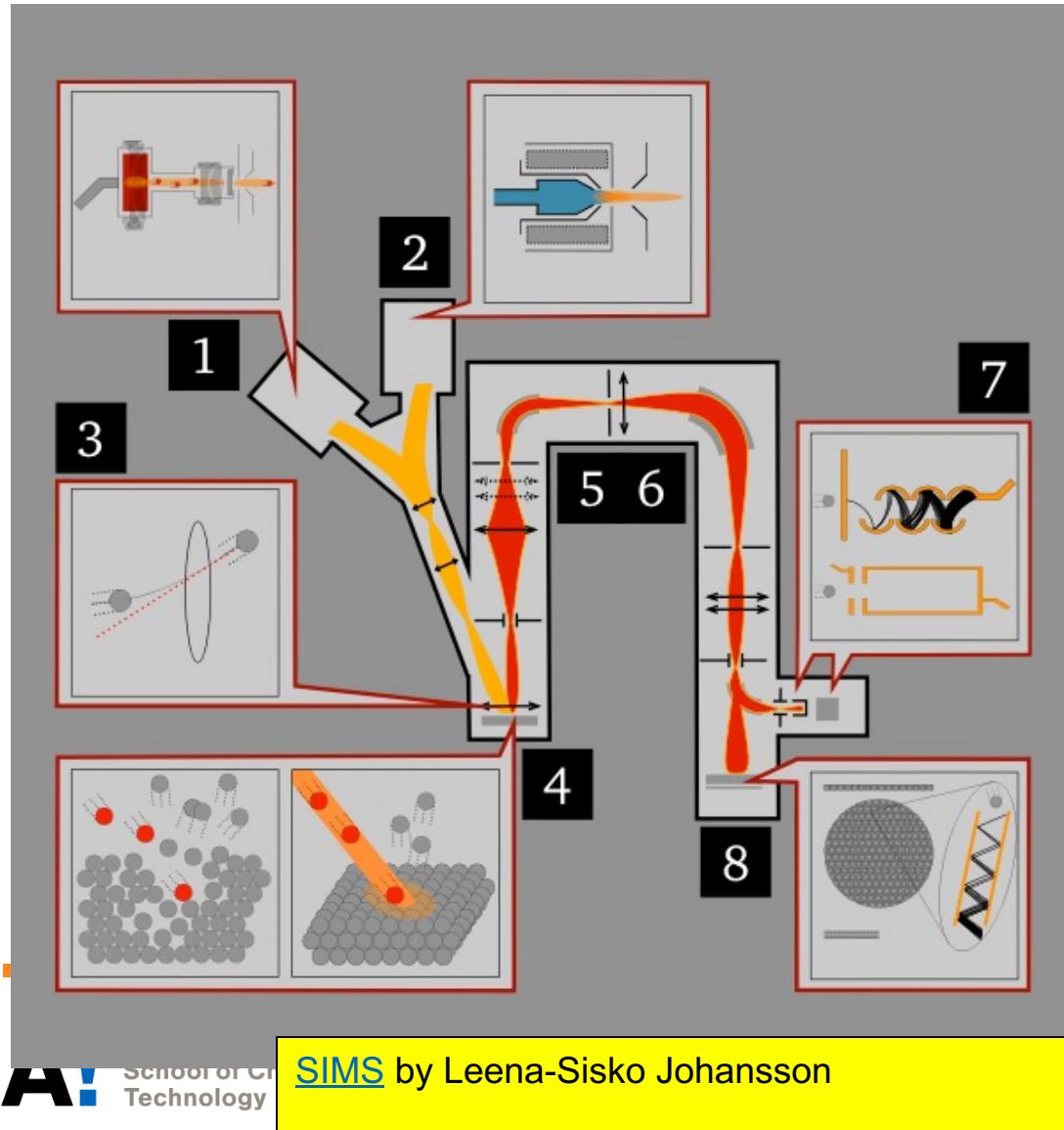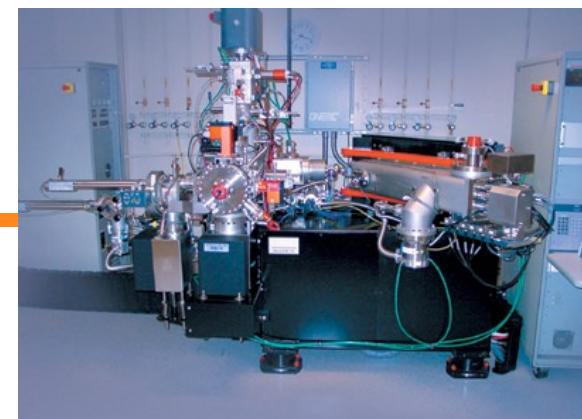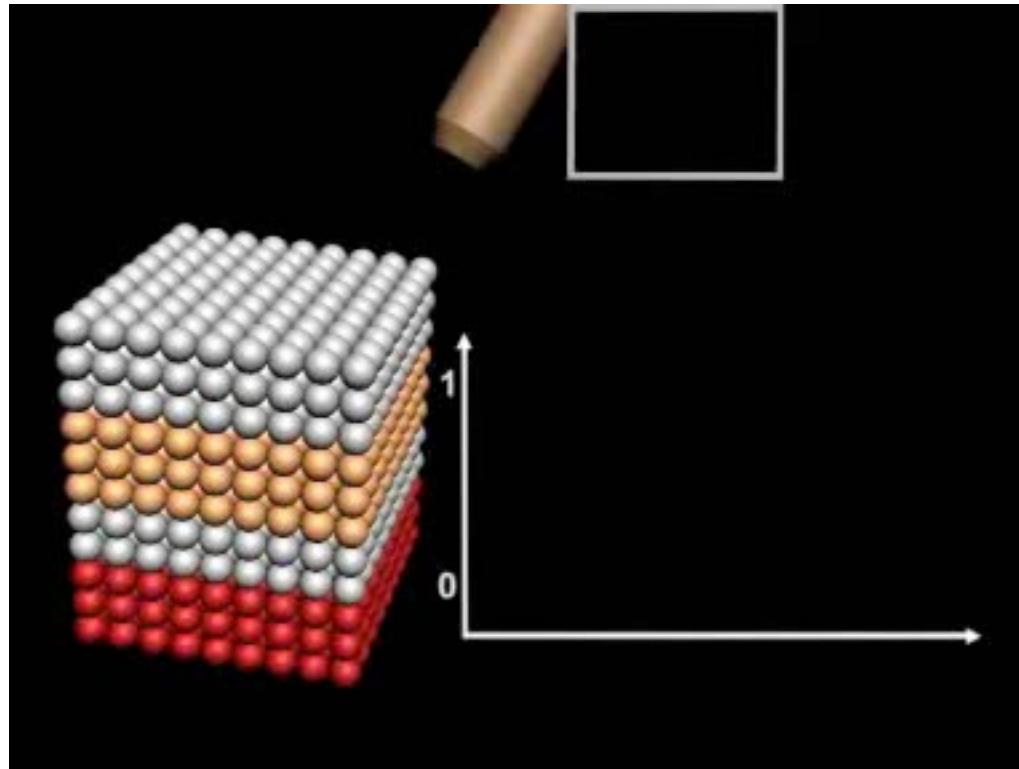
SIMS

SIMS - also molecular ions
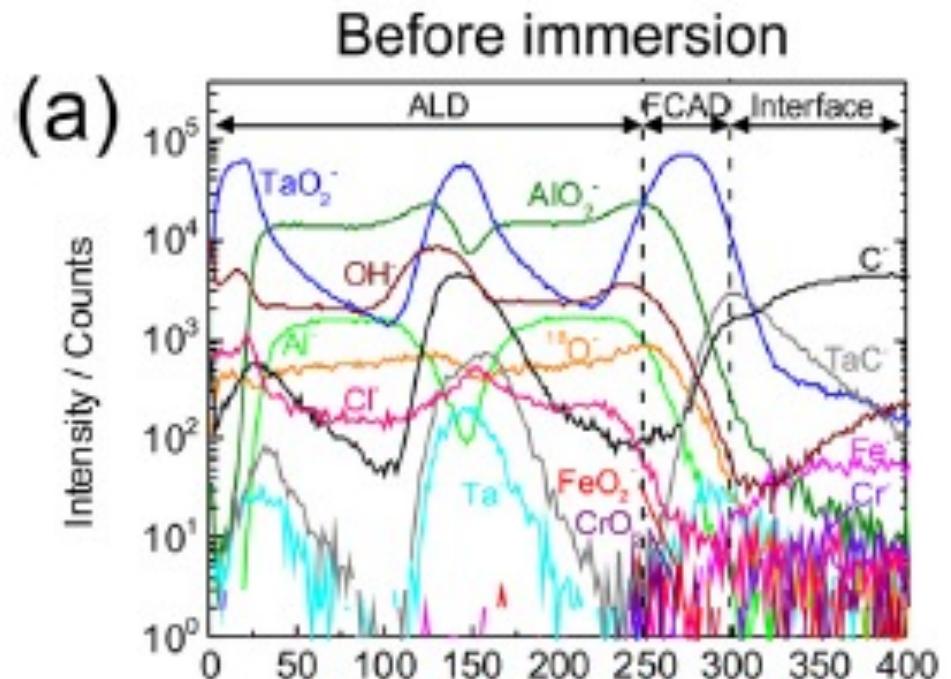
Ion Beam Analysis Techniques

For a detail discussion on Ion Beam Analysis and the various techniques, please see **IBA lecture** by K. M. Yu.

Inelastic

Elastic

Incident Ions

Rutherford backscattering (RBS), resonant scattering, channeling

Nuclear Reaction Analysis (NRA) p, α, n, γ

Particle induced x-ray emission (PIXE)

Elastic recoil detection

Defects generation

Absorber foil

Ion Beam Modification

Ion beam analysis

- Backscattering spectroscopy

Ion beam accelerator
with several beam lines
and ion sources

Ion beam analysis

- Backscattering spectroscopy

$E_0 =$ 2 MeV ^{4}He

recoil energy -> what element

atomic mass of element

Probability of recoil -> amount of element

Kinetic energy loss inside material – stopping -> depth scale

$E_1 = k * E_0$

$$k = \left(\frac{m_1 \cos \theta_1 \pm \sqrt{m_2^2 - m_1^2 (\sin \theta_1)^2}}{m_1 + m_2} \right)^2$$

$$\frac{d\omega}{d\Omega} = \left(\frac{Z_1 Z_2 e^2}{4 E_0} \right)^2 \frac{1}{(\sin \theta / 2)^4}$$

$$S(E) = -\frac{dE}{dx}$$

Detector

E_1

Sample
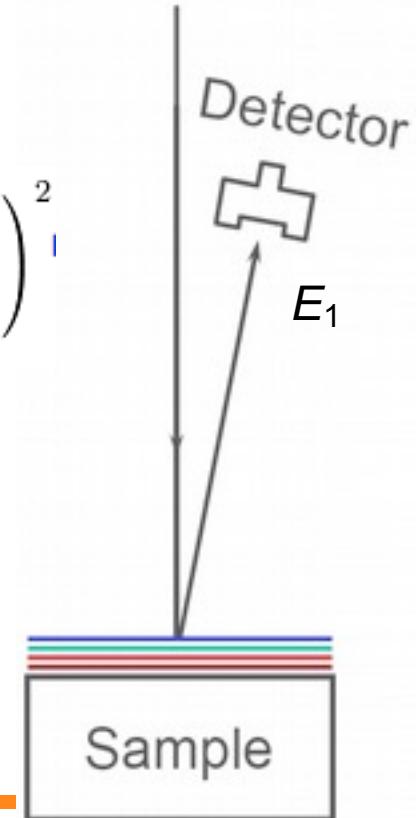
Ion beam analysis

- Backscattering spectroscopy
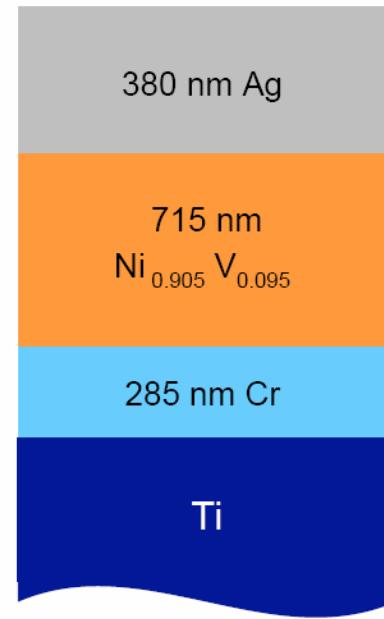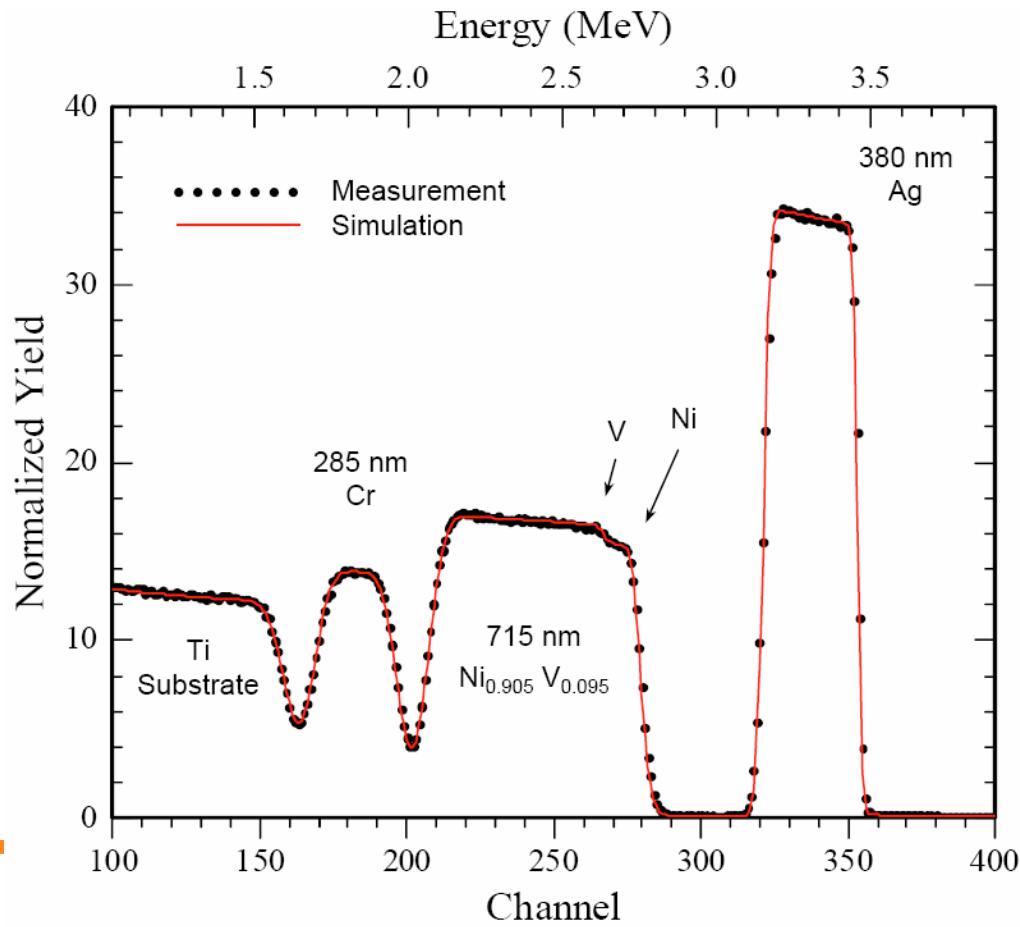
Ion beam analysis
^{4}He$^+$ ion

Elastic Recoil Detection Analysis (ERDA)

Detector

Surface
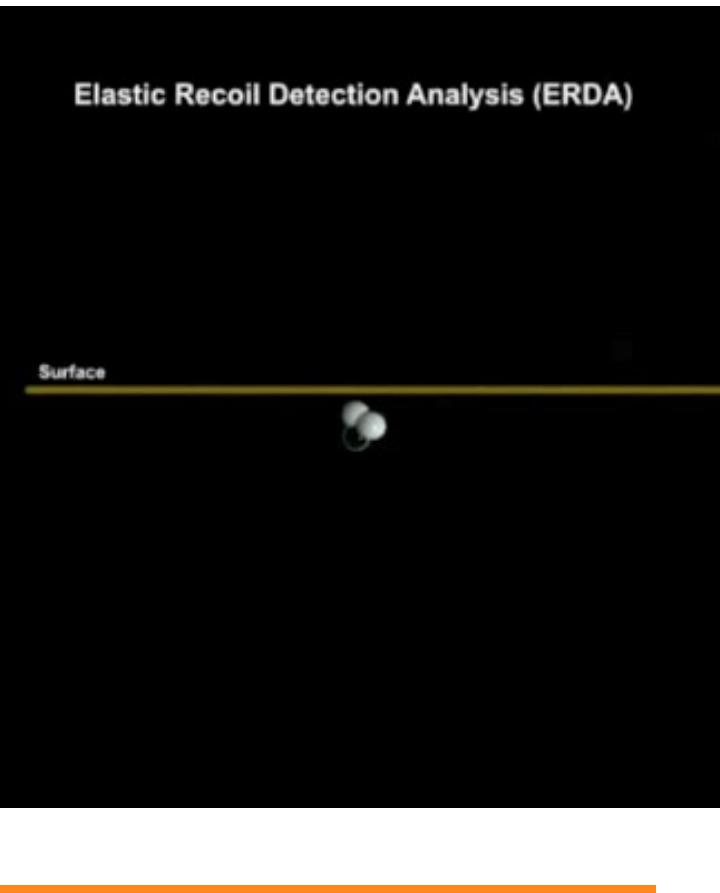
^{4}He^{++} Ion Beam

Recoiled ^{1}H and ^{2}D

Energy Detector

dPS-PVP~15nm

hPS-PVP~1μm

Anneal

Si substrate

...strate

...easures Depth-Concentration Profile of ^{2}D

Energy (MeV)

Bottom

H surface

D surface

Channel

A!
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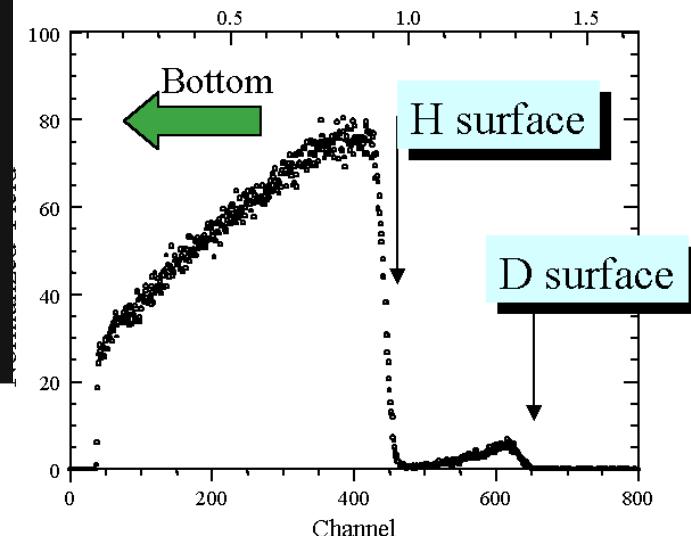
^{63} Cu$^+$ ion
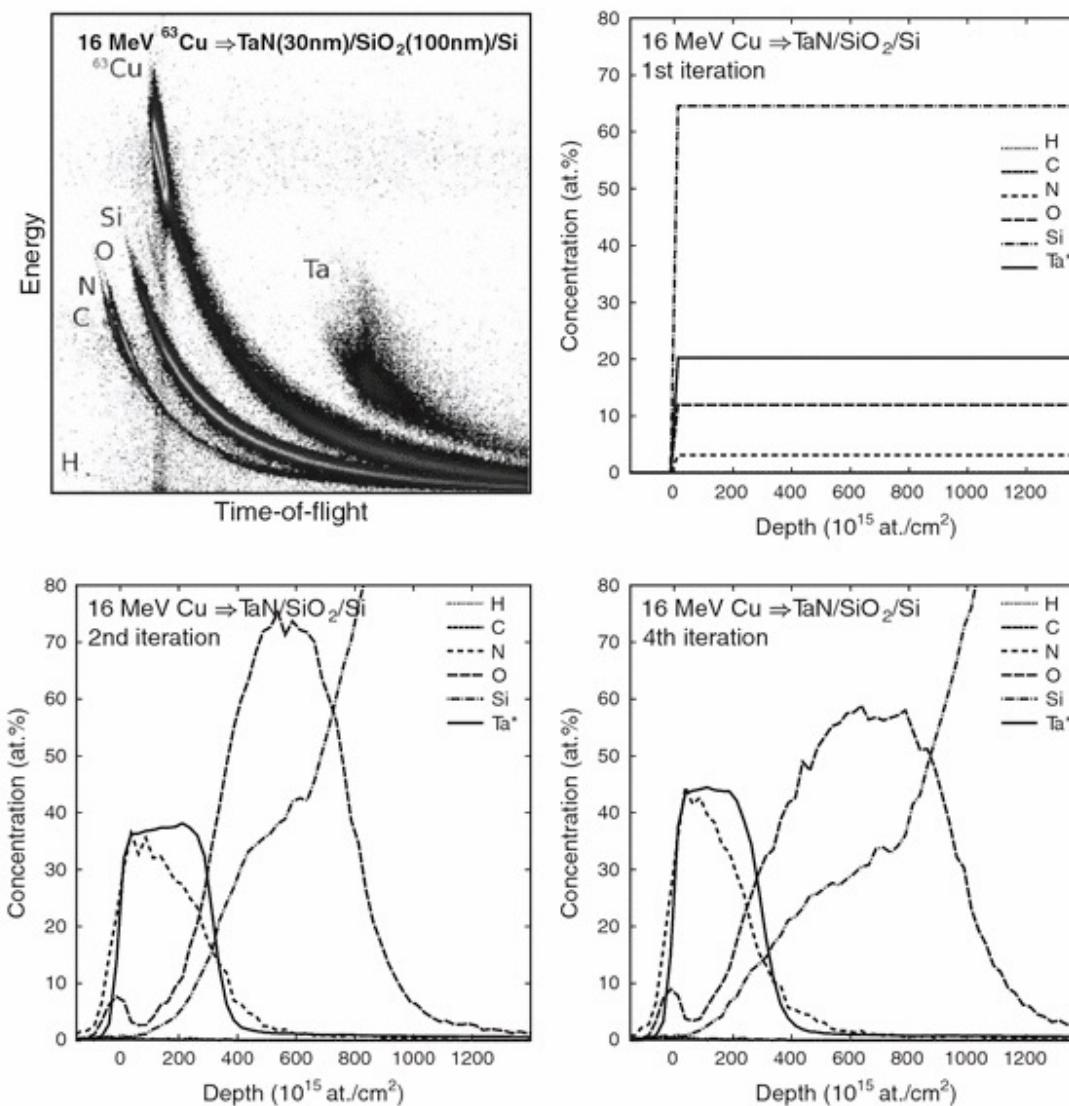
Fig. 5 Iterative procedure for analysis of a HI-ERDA measurement without prior knowledge of the sample structure. See the text for a detailed description of the analysis
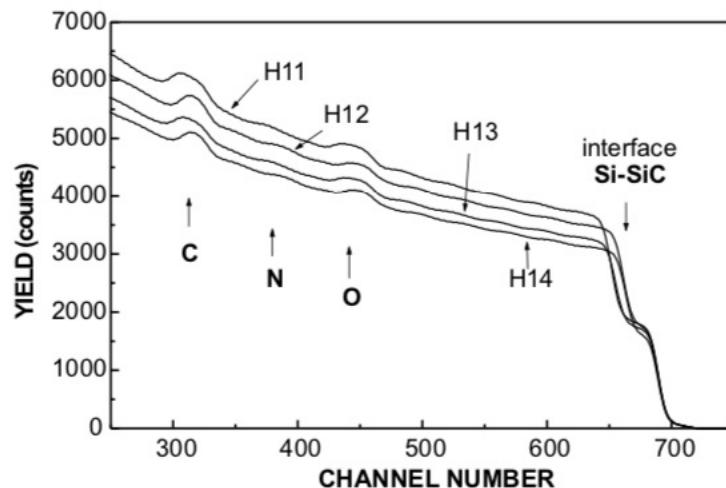
Fig. 1. RBS spectra of SiC films deposited onto a silicon substrate for 2 MeV alpha particles detected at scattering angle of 170°. The spectra are for samples H11 (thickness of film 120 nm), H12 (90 nm), H13 (110 nm) and H14 (80 nm).
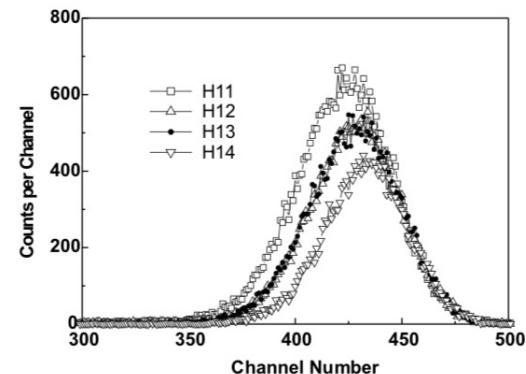
Fig. 2. The ERD spectra of recoiled hydrogen obtained with 2.4 MeV ^{4}He$^+$. The concentration of hydrogen for samples H11, H12, H13 and H14 are 22, 20, 19 and 18 at. %, respectively.

J. Huran, I. Hotovy, A. P. Kobzev, N. I. Balalykin

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Scattering experiment – ION SPECTORSCOPY

OUT

photon

electron

IN

molecule

ion, atom, neutron

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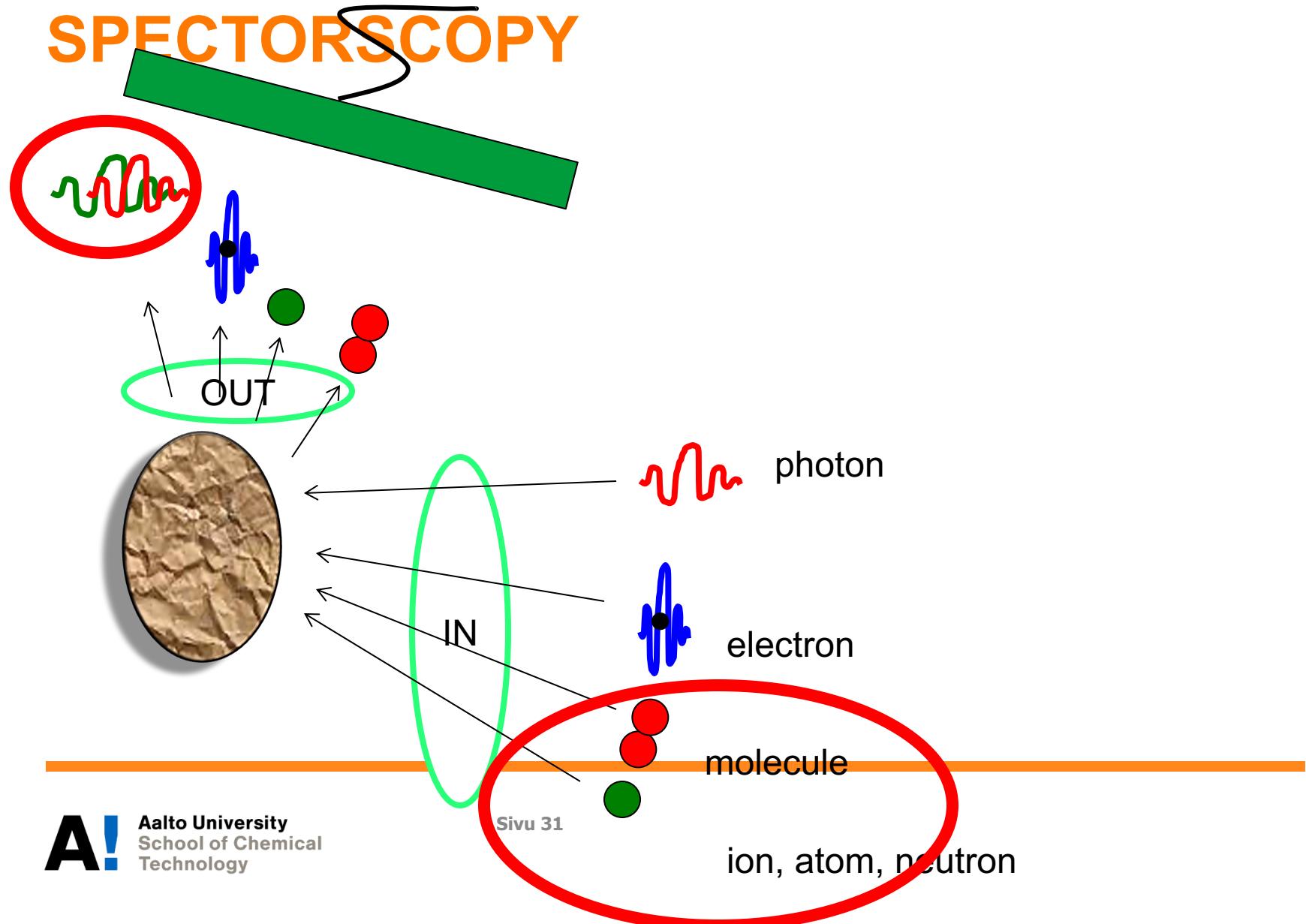
Ion beam analysis

- Nuclear Reaction Analysis NRA
  Detection of **hydrogen** – depth distribution in surface

$$^1H(^{15}N,\alpha\gamma)^{12}C$$

$$E_{res} = 6.385 \text{ MeV}$$

GDOES

Principle of GD-OES

- The light intensity emitted by the plasma is a function of the element concentration in the plasma

- The element concentration in the plasma is a proportional to the product of the element concentration in the sample and the sputtering rate or transfer rate

Grounded Anode

Sample

Cathode

Technology

GDOES

Principle of GD-OES

To Vacuum Pump

To Spectrometer

Sample (Cathode)

- Ground Energy Ar atom
- Argon Ion
- Sample atom
- Excited Sample atom
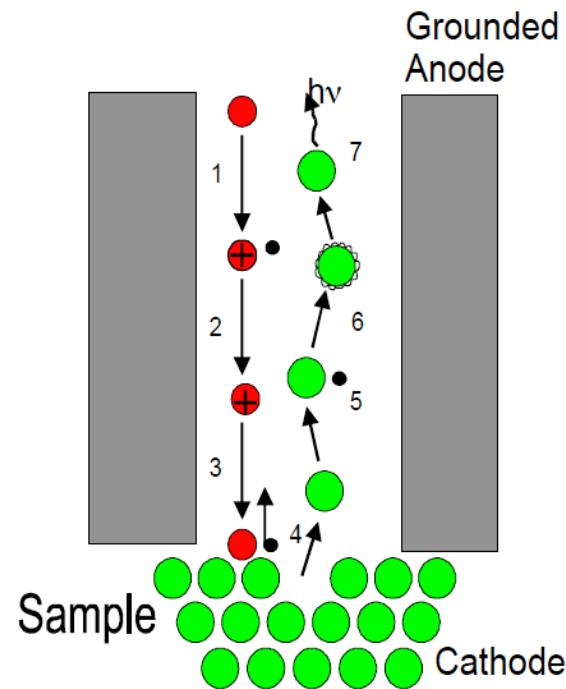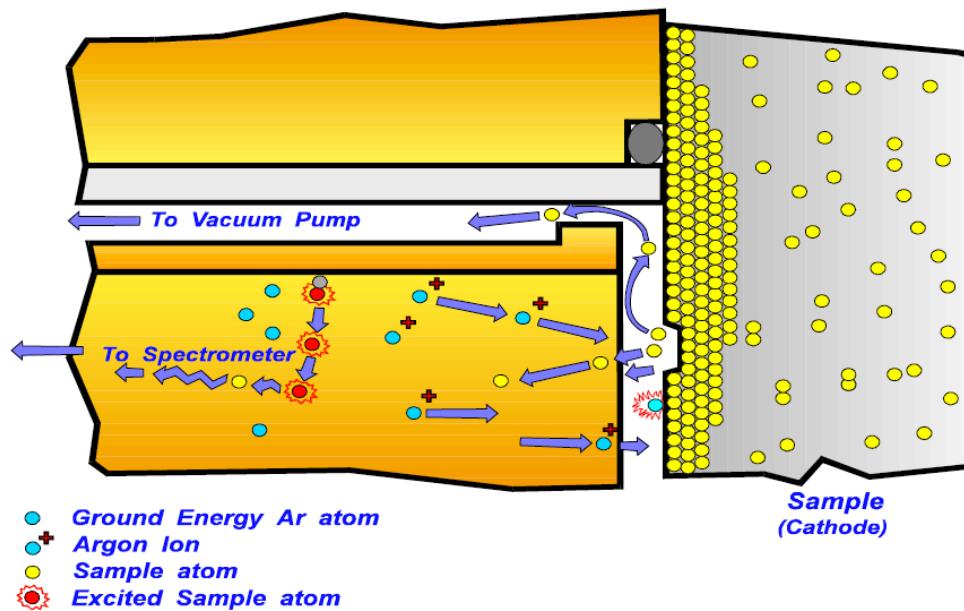
GDOES
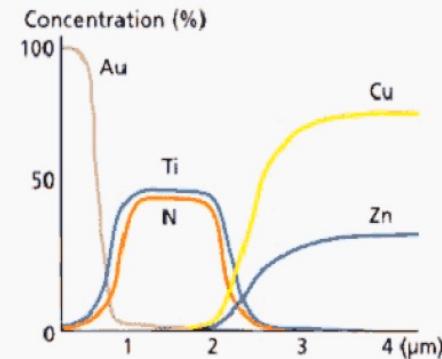
Coated sheets
Complete characterization of the coating layer with respect to chemical composition, thickness and element distribution.
Analyze non-conductive coatings such as varnishes and paints with the optional RF source.
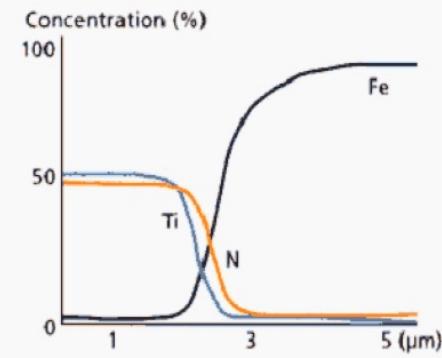
Hardphase coatings
Compound layer development can be determined by rapid analysis of the chemical composition. Other important material aspects such as depth penetration of the treatment process are possible.
Ceramics
Precise and accurate determination of the chemical composition is possible with the optional Radio Frequency source.

Interesting also: https://wcnt.wisc.edu/wp-content/uploads/sites/882/2018/11/GD_Profiler_2_GDOES_Brochure.pdf

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- Optical transmittance- FTIR (???)

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Microstructure

- Crystallinity

- crystal size

- orientation – texture

- Defects

Transmission electron microscopy TEM

Atomic level
resolution
0.7 Å

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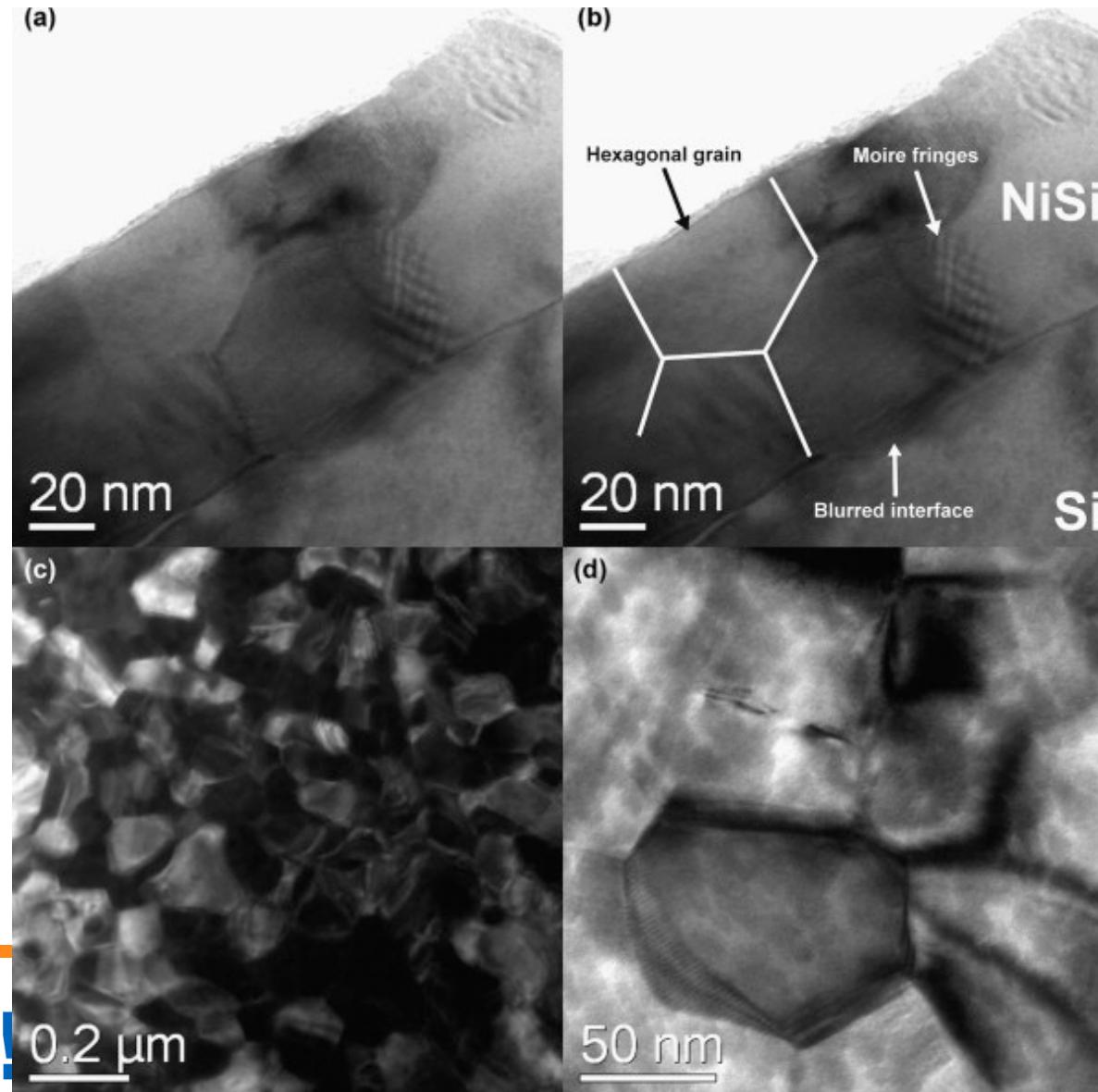
NiSi thin film

Results from TEM analysis of NiSi thin films: (a) XTEM highlighting equiaxed grains in the NiSi film in which Moiré (interference) fringes due to orientation differences between grains can be observed; (b) notable features in the as-obtained image (a) are indicated; (c) plan view, elastic hollow cone dark field image of the film, highlighting individual grains with diameters of 60–200 nm; and (d) plan view TEM image showing polygon al NiSi grains.

Electron diffraction
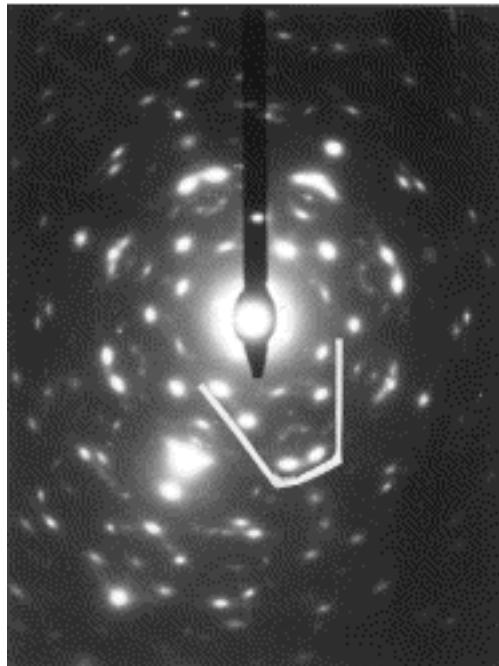
a
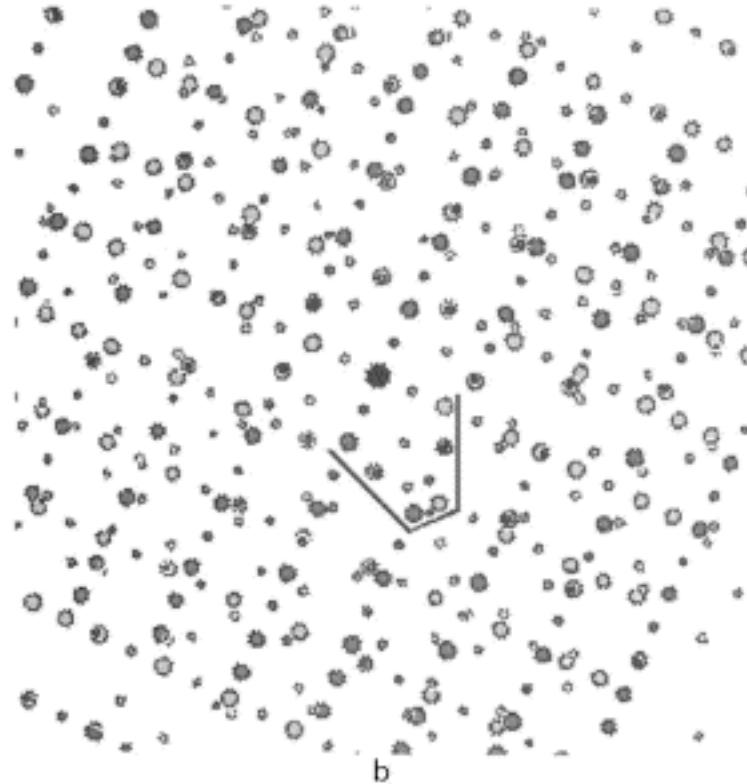
b

Measured diffraction pattern of a plan-view prepared ReSi1.75
film on Si (100) (——— guiding line for orientation); (b)
theoretical diffraction diagram of ReSi1.75 with zone axis [0 1
0] and four superposed patterns, each turned around 45°.

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Electron energy loss spectroscopy EELS

energy filtered

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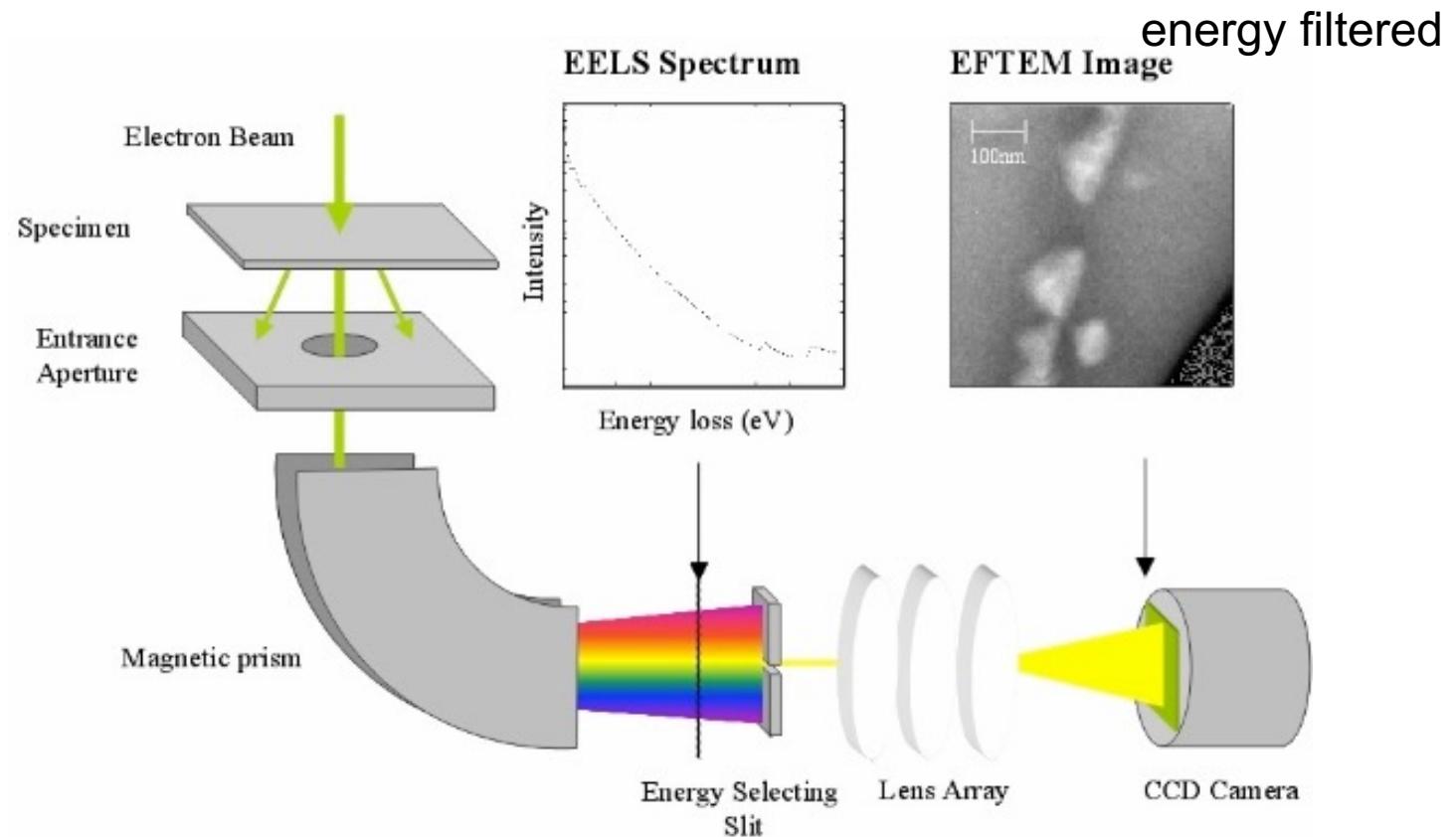
Electron energy loss spectroscopy EELS

- Elemental analysis
  - light elements C
    - ➔ 3d transition metals Sc, Zn
- chemical bonding e.g carbon sp^2/sp^3
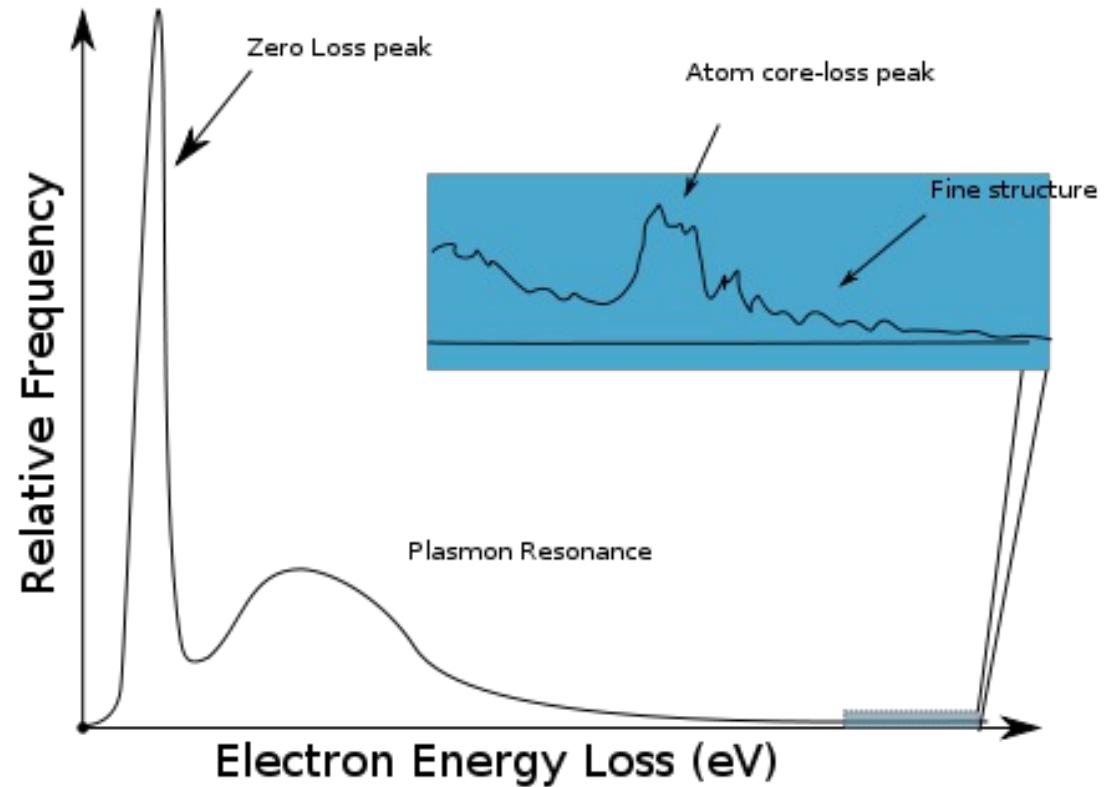
Electron energy loss spectroscopy EELS
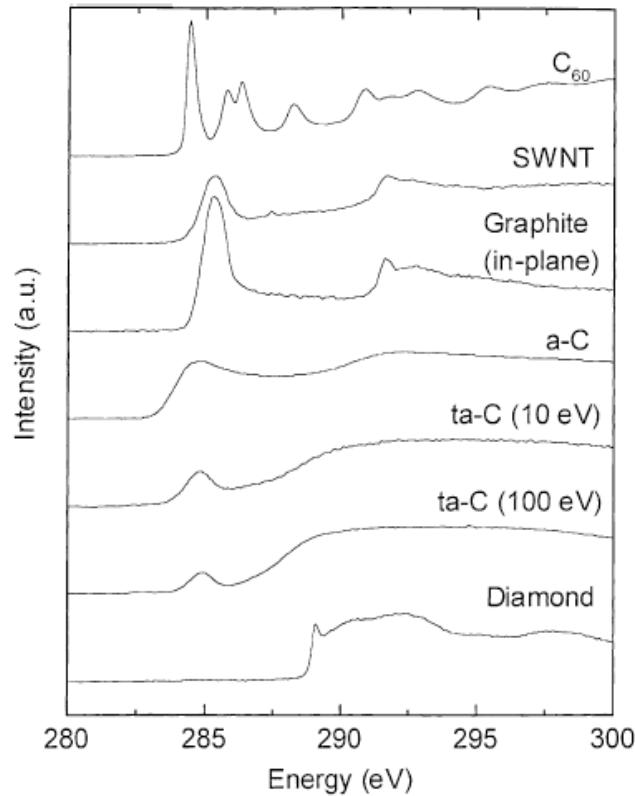
Fig. 29. Carbon K edge electron energy loss spectra of various carbon phases, after Waidmann et al. [196].

S. Waidmann, M. Knupfer, J. Fink, B. Kleinsorge, J. Robertson, J. Appl. Phys. 89 (2001) 3783.

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Scattering experiment – X-ray SPECTORSCOPY

photon

electron

molecule

OUT

IN

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ion, atom, neutron
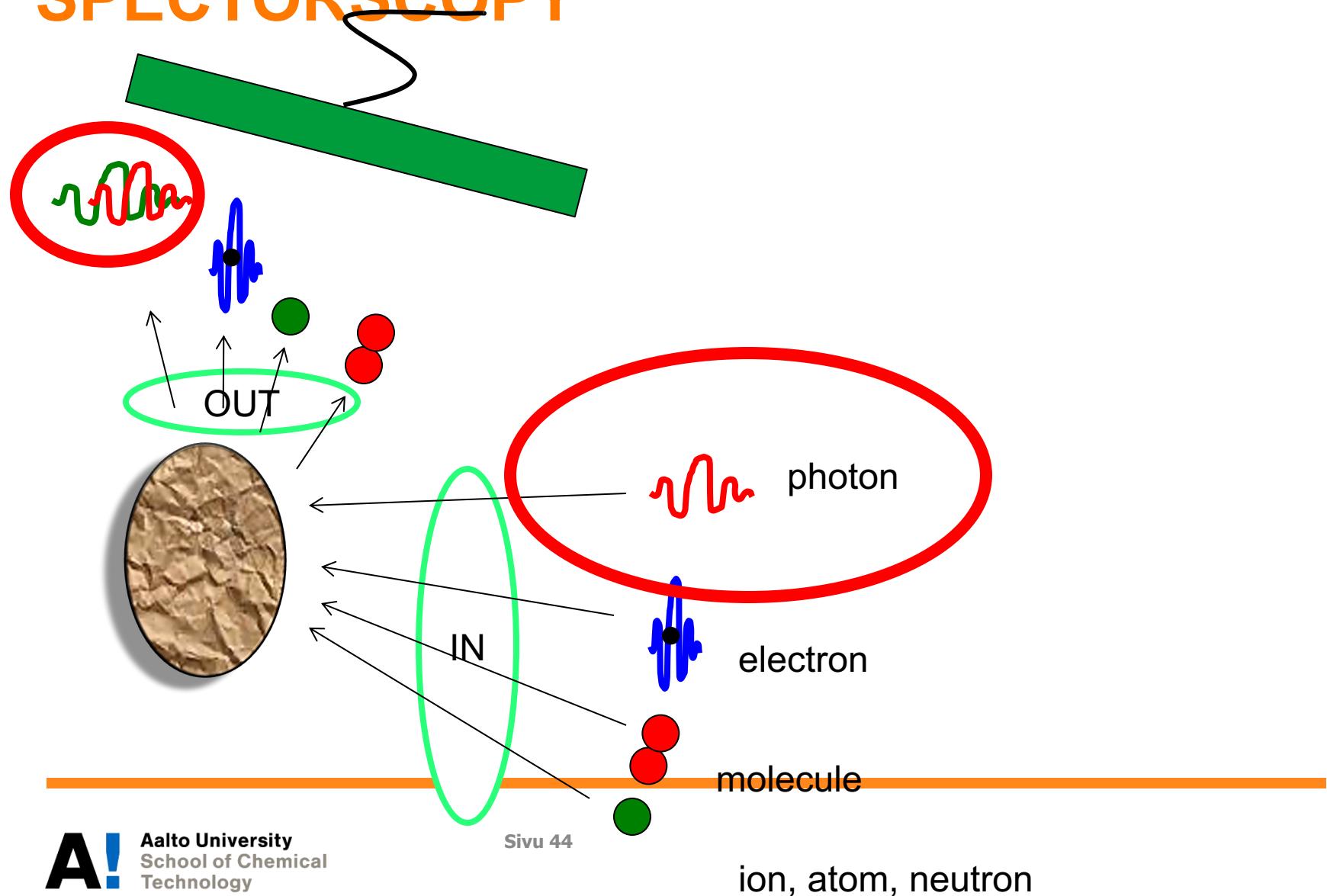
Glancing Angle X-ray Diffraction (GAXRD)

- In the x-ray diffraction pattern of thin films deposited on a substrate, contribution from substrate to the diffraction can sometimes overshadow the contributions from thin film.

- *GAXRD is used to record the diffraction pattern of thin films, with minimum contribution from substrate.*

- Non-destructive surface sensitive technique

www1.chm.colostate.edu/Files/GAXRD.pdf

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Technique

- Parallel, monochromatic X-ray beam falls on a sample surface at a fixed angle of incidence (α_I) and diffraction profile is recorded by detector only scan.

X-ray Tube with
Göbel mirror

Soller Slits

Detector

α

2θ

Film

Substrate
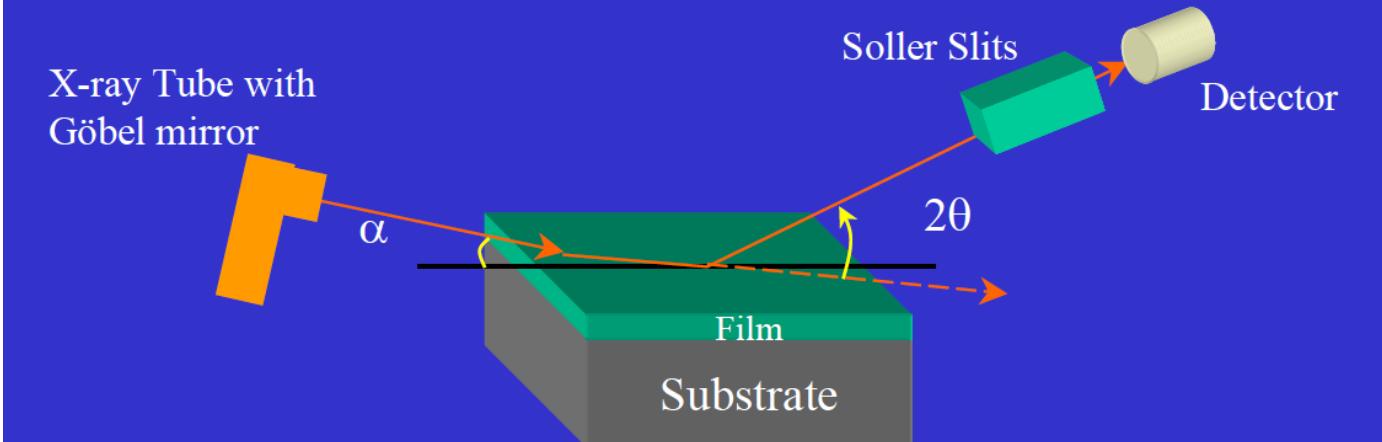
www1.chm.colostate.edu/Files/GAXRD.pdf

Penetration Depth Vs Angle of Incidence
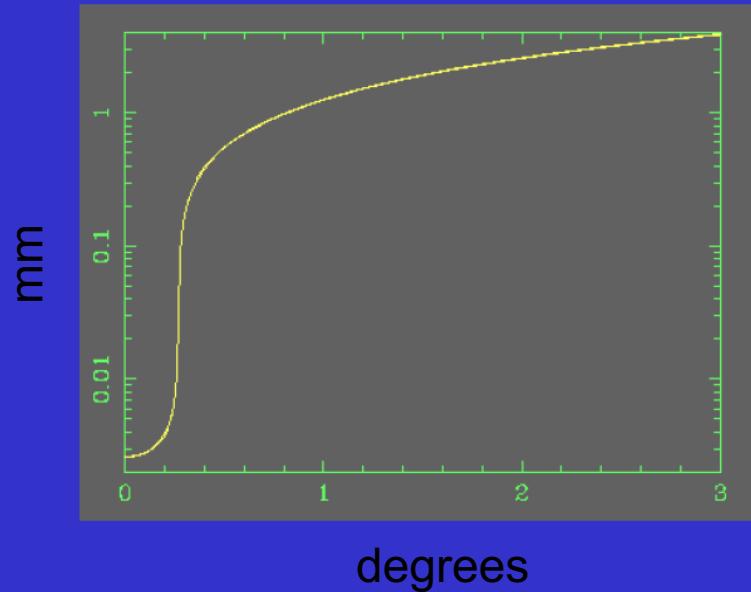
This figure shows penetration depth as a function of incident angle for Si_3N_4 for CuK_α ($\lambda=0.154$ nm) radiation

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GAXRD: Example

- (a) As deposited 20 nm Ir metal film deposited on Si wafer. XRD curve for **α=0.5° and 1.0°** shows the peaks for cubic iridium metal phase represented by (+)

- (b) Ir film annealed at 873K for 1hr. XRD curve for **α=0.5°** shows the presence of the dominating IrO$_2$ phase (*). As **α** was increased to **1.0°**, the contribution from the underlying layer of Ir metal increased and the Ir peaks dominated the XRD curve. The results indicate the presence of an overlying oxidized layer of Ir metal
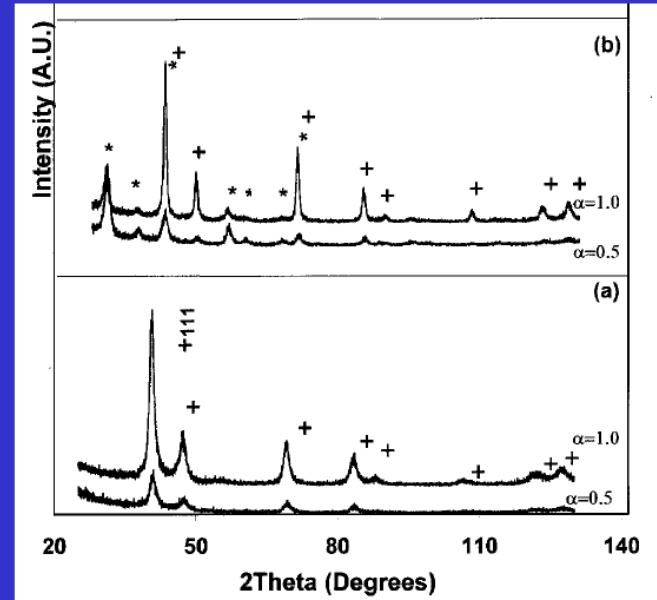
X-Ray Reflectivity XRR

• Thin Film
  • thickness
  • density
  • roughness
  • rougness of interface

Diffused reflections specularly reflected

θ θ

θ'

Refracted wave
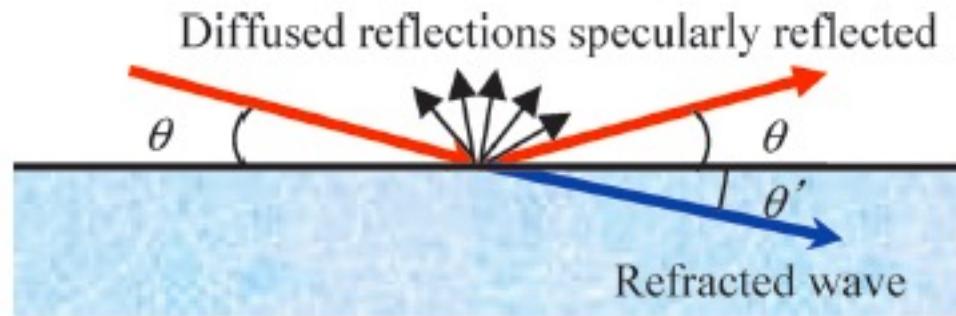
Fig. 1. Reflection and refraction of X-rays on material surface.

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X-Ray Reflectivity XRR

$\theta < \theta c$

A) Incident angle < Total reflection critical angle
All incident X-rays are reflected.

$\theta = \theta c$
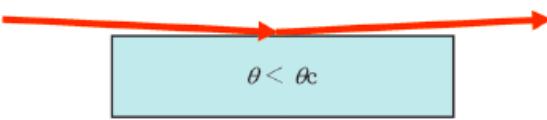
B) Incident angle = Total reflection critical angle
Incident X-rays propagate along the sample surface.

θ θ θ

$\theta > \theta c$
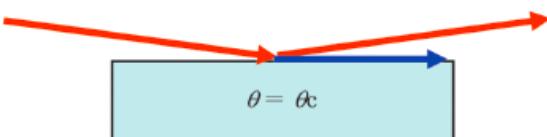
C) Incident angle > Total reflection critical angle
Incident X-rays penetrate into the material by refraction
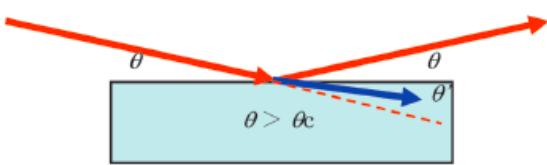
Fig. 3. Reflection and refraction of X-rays at material surface with the changes in the grazing angle.

— : Film thickness 5 nm
— : Film thickness 20 nm

Reflectivity (I/I₀)

0   2   4   6   8   10
2θ (deg.)
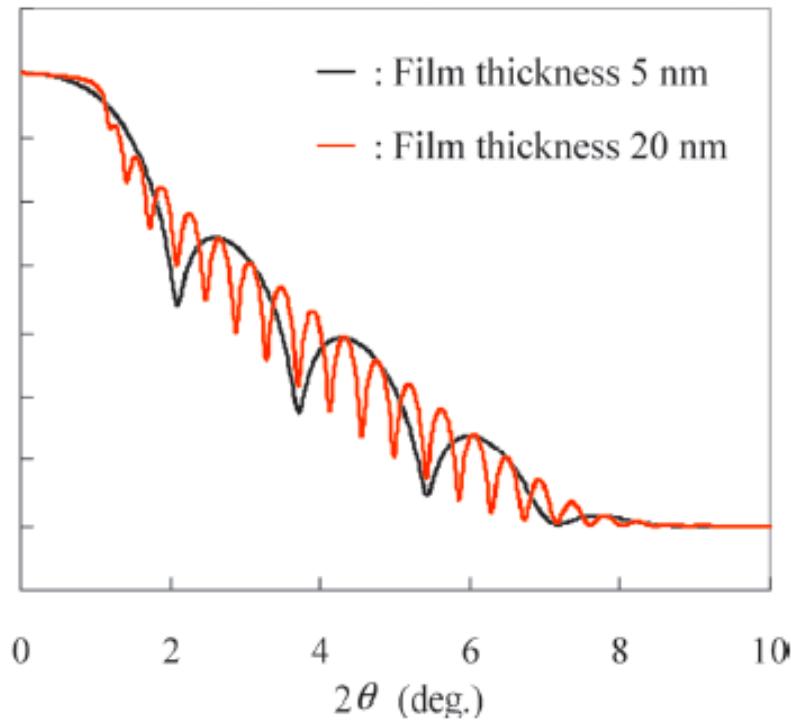
Fig. 4. Reflectivity of Au film on Si substrate.

X-Ray Reflectivity XRR
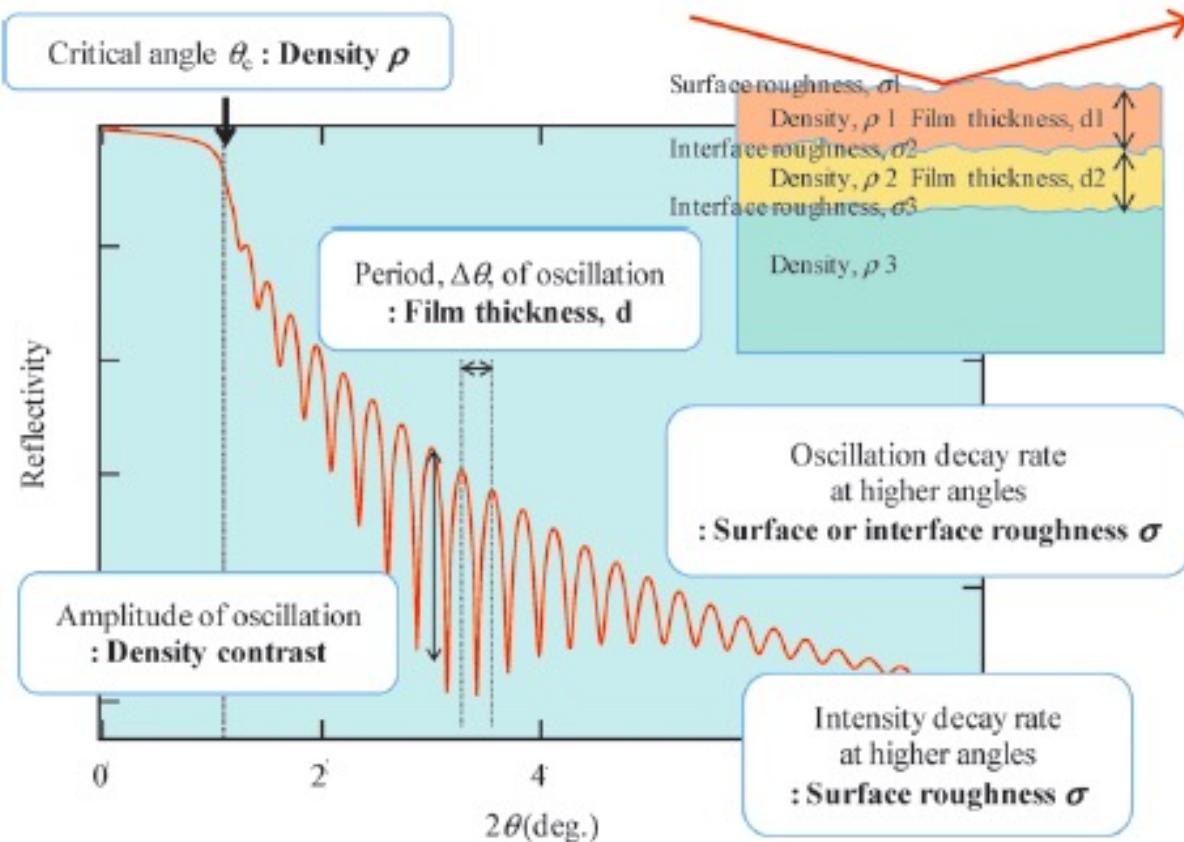
Fig. 8. Information provided by X-ray reflectivity profile.

Miho Yasaka, The Rigaku Journal, 26(2), 2010

X-Ray Reflectivity XRR
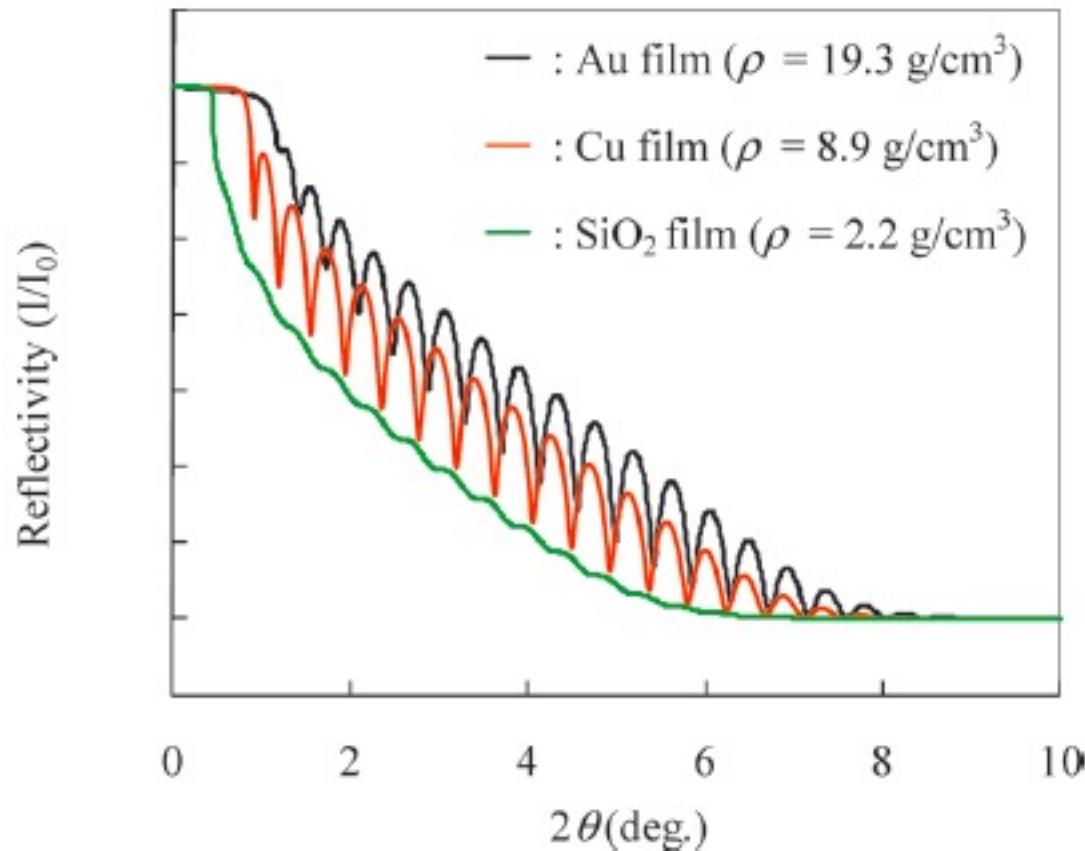
Fig. 5. X-ray reflectivity curves of Au, Cu and SiO$_2$ film on Si substrates (film thickness is 20 nm).

X-ray Reflectivity (XRR)

Fe-doped carbon films
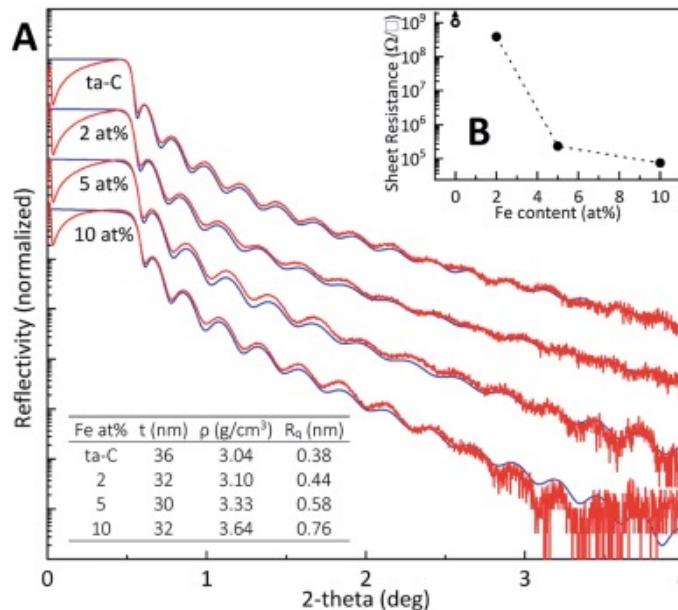
Fig. 1 (A) X-ray reflectivity scans showing experimental and simulation data in red and blue, respectively. Fitted parameters thickness (t), density (ρ), and roughness (R_q) presented in the inset table were calculated from the simulated curve. (B) Four-point probe average sheet resistances and standard deviations ($N = 10$) plotted as a function of Fe at%. Error bars are smaller than their respective dots. The reference ta-C, represented with an open circle, was too resistive to be measured.

J. Etula, N. Wester, S. Sainio, T. Laurila and J. Koskinen, , DOI:10.1039/c8ra04719g.

Platinum/ta-C/Ti/Si films
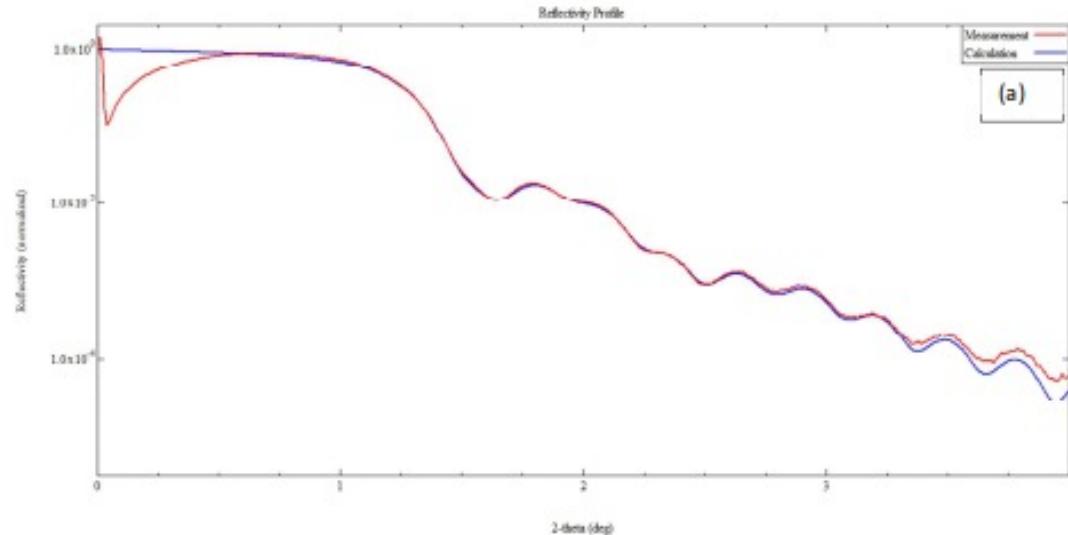
No.	Layer name	Thickness(nm)	Density(g...	Roughne...	Depth dis...
☑ 6	Pt	8.38352	22.0088	0.563942	No distrib...
☑ 5	Pt + aC	0.274786	3.20843	1.19581	No distrib...
☑ 4	taC	4.93845	3	0	No distrib...
☑ 3	TiCx	8.84105e-006	4.93[--]	0.599974	No distrib...
☑ 2	Ti (sputtered)	16.1898	4.13378	3.90669e-...	No distrib...
☑ 1	SiO2	0.0220998	0.352924	0.151561	No distrib...
☑ 0	Si(single)	0.0[--]	2.32919[--]	1.11942e-...	No distrib...

T. Laurila, S. Sainio, H. Jiang, N. Isoaho, J. E. Koehne, J. Etula, J. Koskinen and M. Meyyappan, *ACS Omega*, 2017, **2**, 496–507.
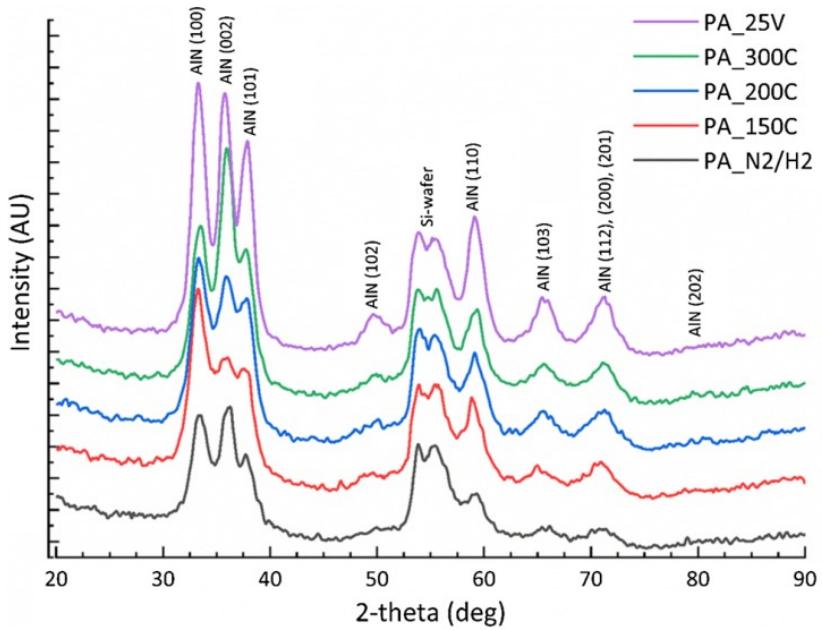
Fig. 3. As-measured GIXRD patterns with constant offset of the PEALD AlN samples at 0.4° incidence angle and with AlN planes indexed.

P. Sippola, A. P. Perros, O. M. E. Ylivaara, H. Ronkainen, J. Julin, X. Liu, T. Sajavaara, J. Etula, H. Lipsanen and R. L. Puurunen, *Cit. J. Vac. Sci. Technol. A*, 2018, **36**, 51508.
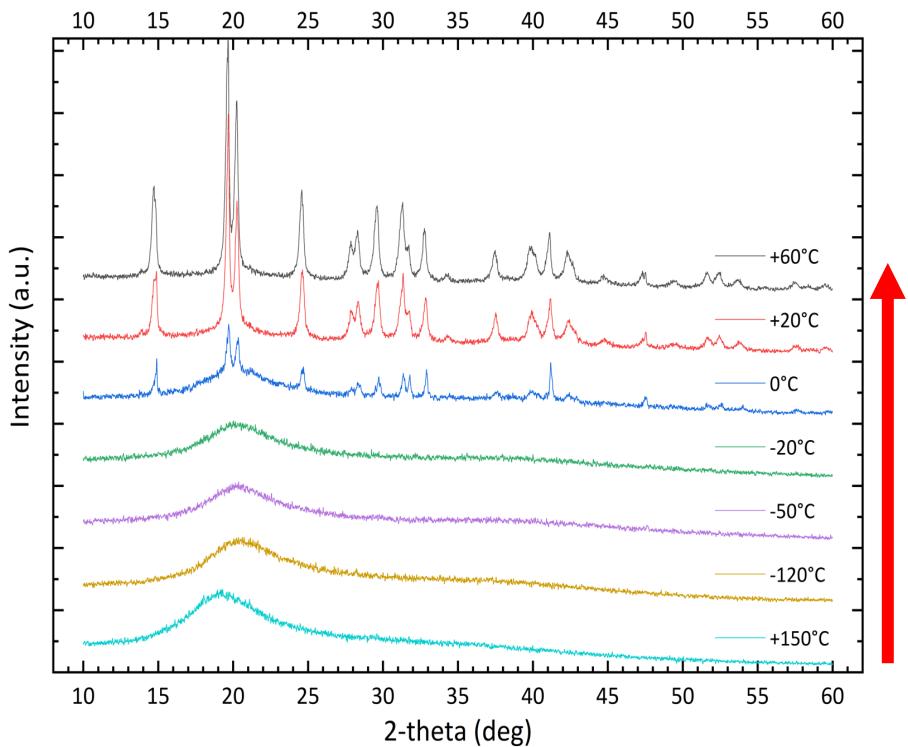
In-situ XRD spectra of heated/LN2-cooled energy storage material: Rapid freezing from +150C to -120C inhibits crystallization. Subsequent warming from -120C to 0C induces crystallization and heat release.

Grazing angle (GIXRD) and normal theta/2theta X-ray Diffraction using Rigaku Smartlab
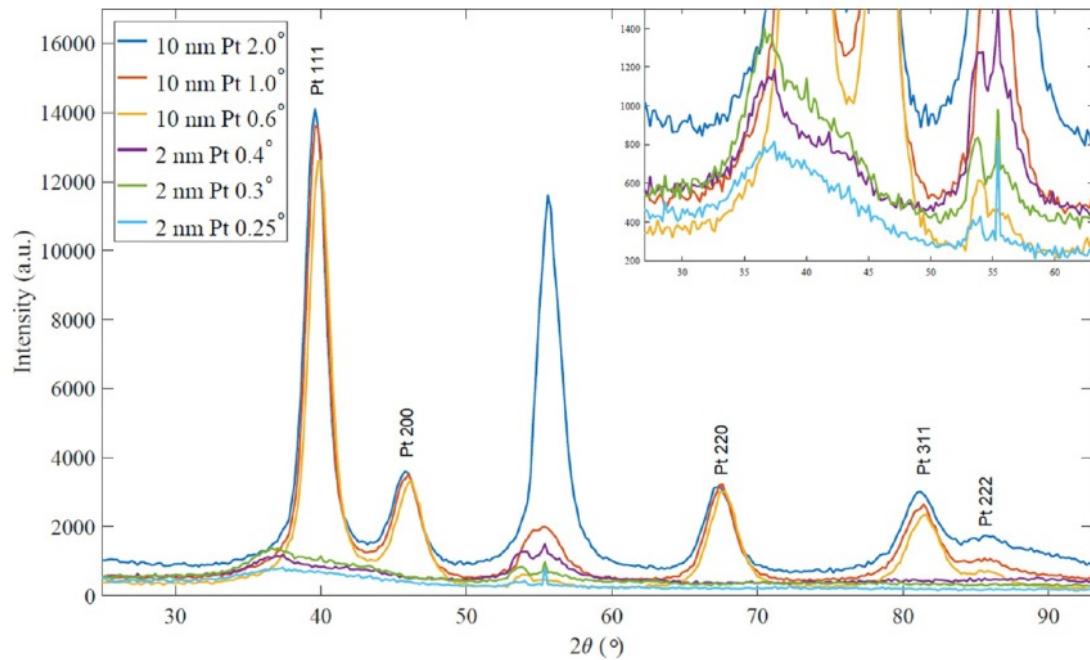
Figure 6. GIXRD spectra from the Si/Ti/ta-C/Pt (10 nm) and Si/Ti/ta-C/Pt (2 nm) samples. The inset shows the magnified view from the region between 30 and 60° (2θ). Note that the peak around 50° could be indexed both to Ti and Si and has therefore been left unindexed. Peaks' locations are based on the data from refs 26−28.

T. Laurila, S. Sainio, H. Jiang, N. Isoaho, J. E. Koehne, J. Etula, J. Koskinen and M. Meyyappan, *ACS Omega*, 2017, **2**, 496–507.

Grazing angle X-ray Diffraction (GIXRD) using Rigaku Smartlab
- Ultra-sensitive detection of 8.4 nm Pt film crystallinity

Pentadecylphenol (PDP) $CH_3(CH_2)_{13}CH_2$

Polydimethylacrylamide (PDMA)

$I-(CF_2)_m-CF_3$

Iodoperfluoroalkane (IPF-)
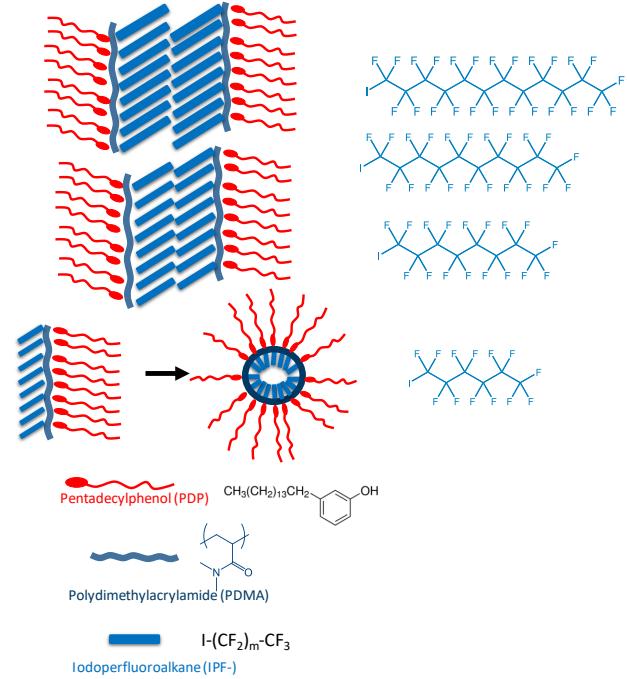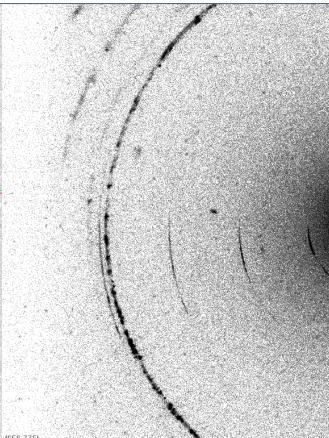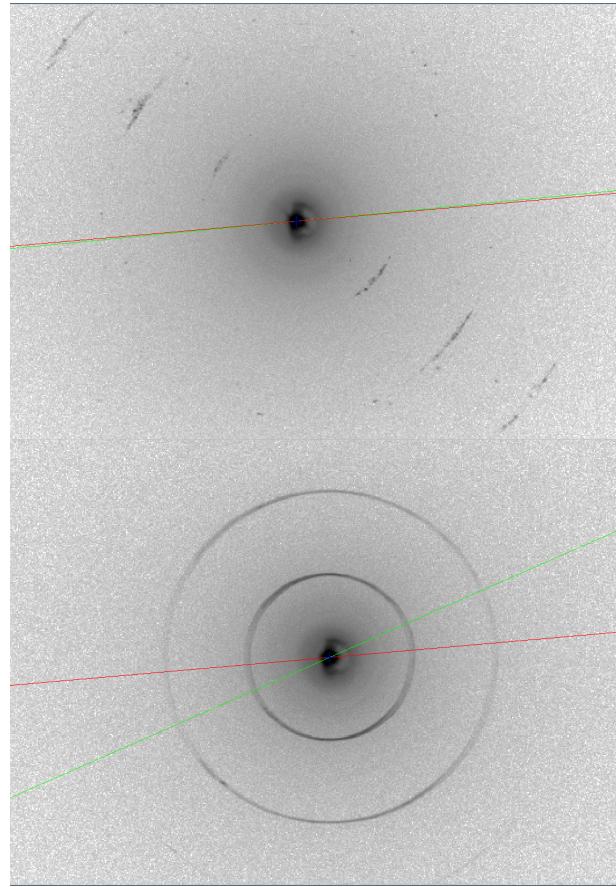
Small/Medium Angle X-ray Scattering (SAXS/MAXS) using 2D-detector (Rigaku Smartlab)

- Formation of **periodic supramolecular lamellar structures** from polymers

Scattering experiment ELECTRON SPECTROSCOPY
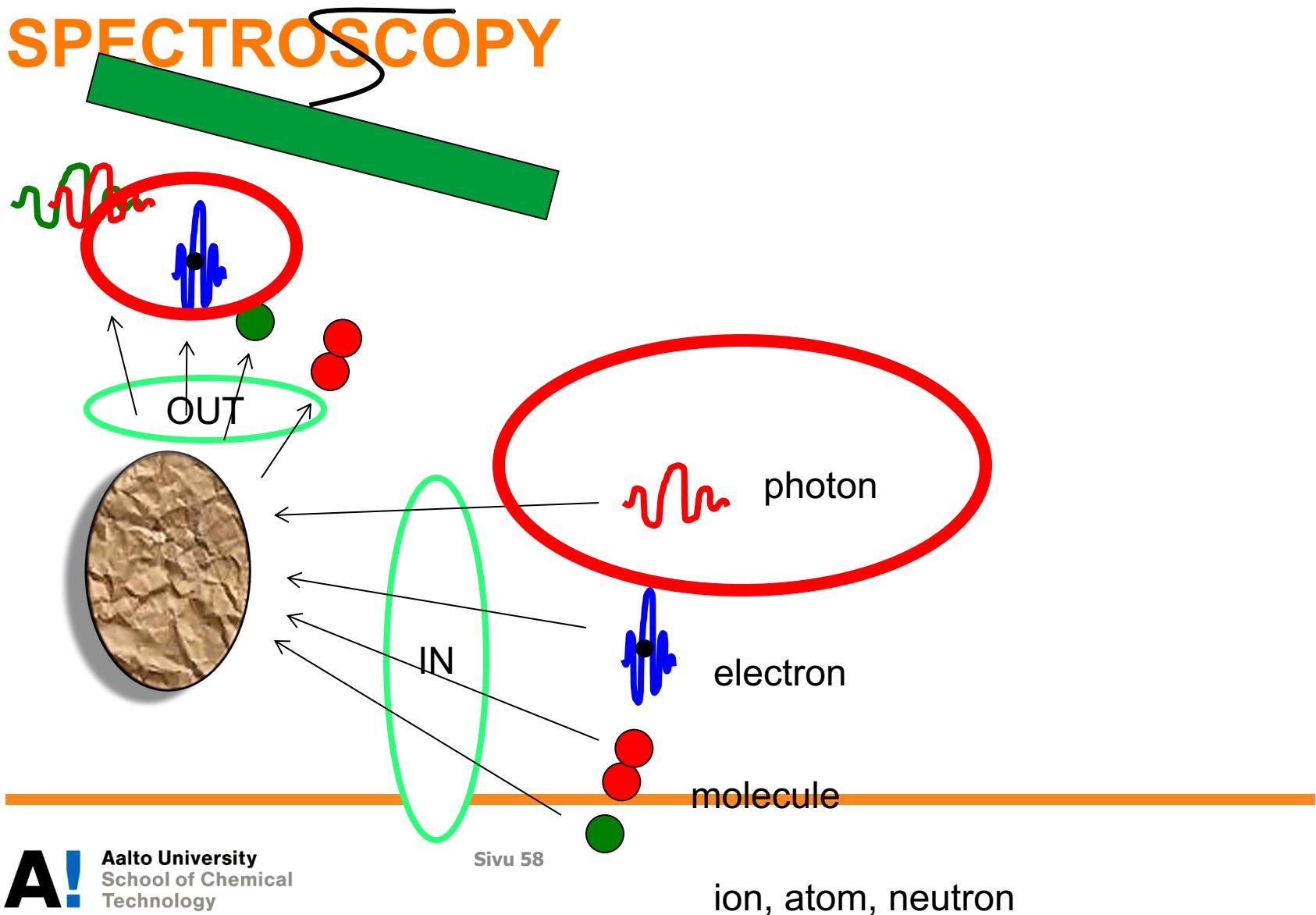
OUT

photon

IN

electron

molecule

ion, atom, neutron

Contents

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Bonding

- Chemical reactions particularly on surface
- Cemical bonding in amorphous thin films (oxides, carbon, some metals)
- Contaminations
- Methods used also to determine composition

Photoelectron spectroscopy techniques
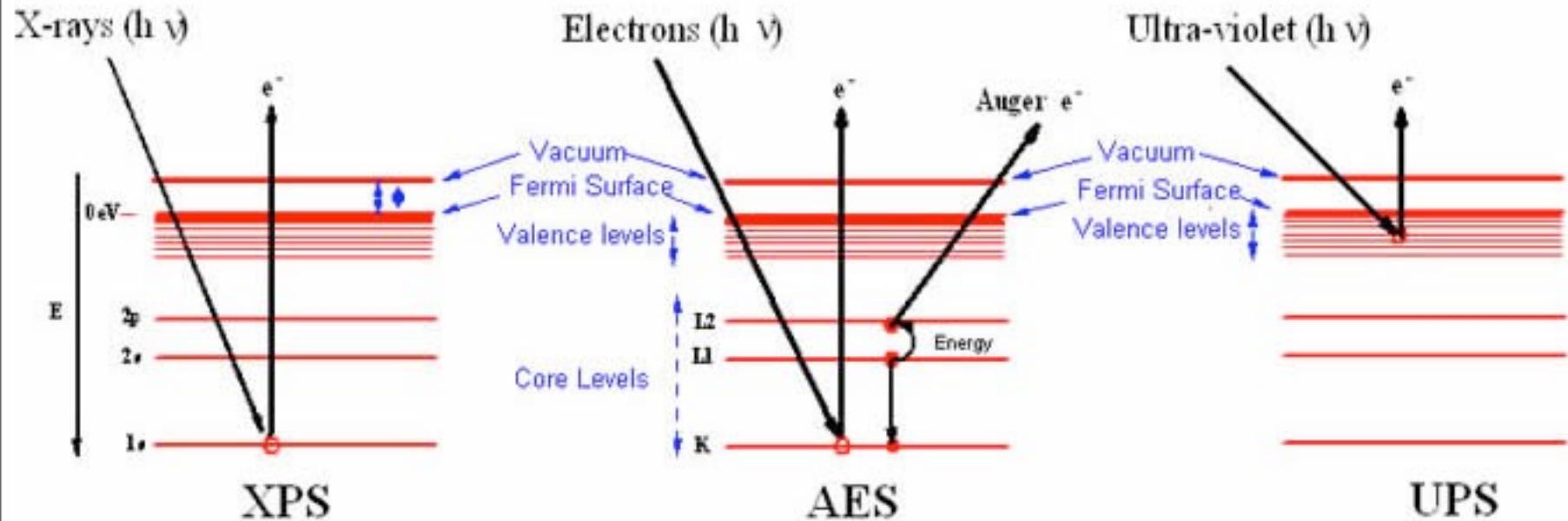
X-ray photoelectron spectroscopy - Electron Spectroscopy for Chemical Analysis ESCA

Auger electron spectroscopy

Ultraviolet phoelectron spectroscopy

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XPS by Leena-Sisko Johansson

XPS

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XPS

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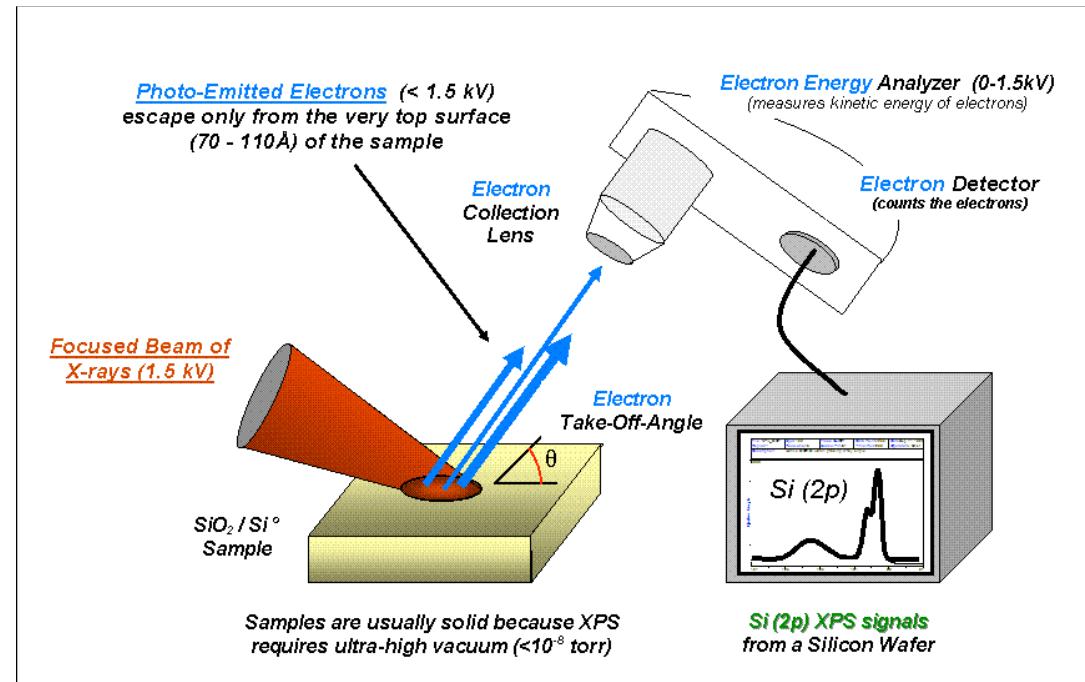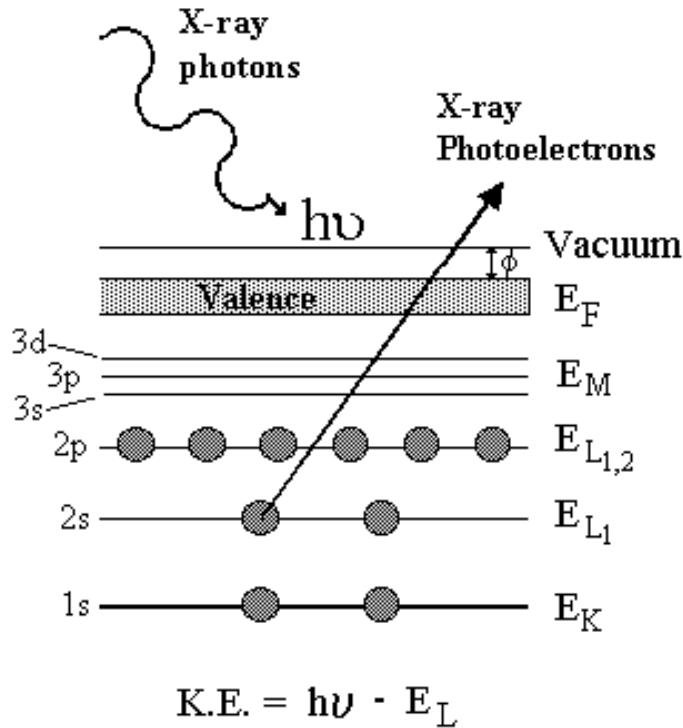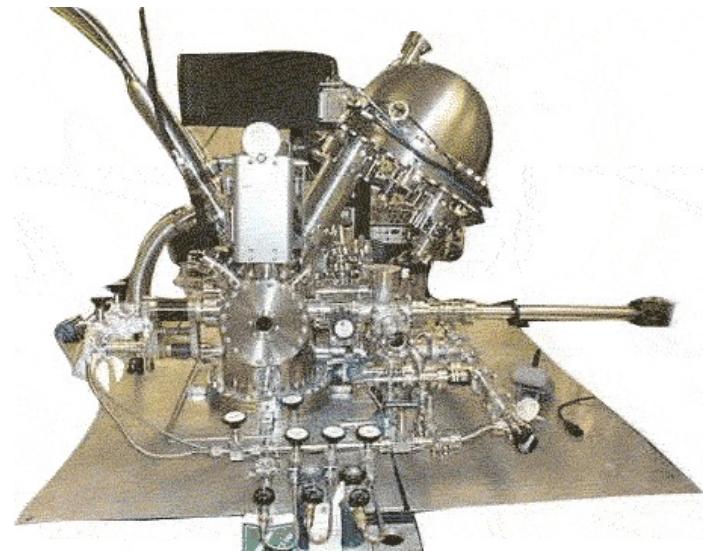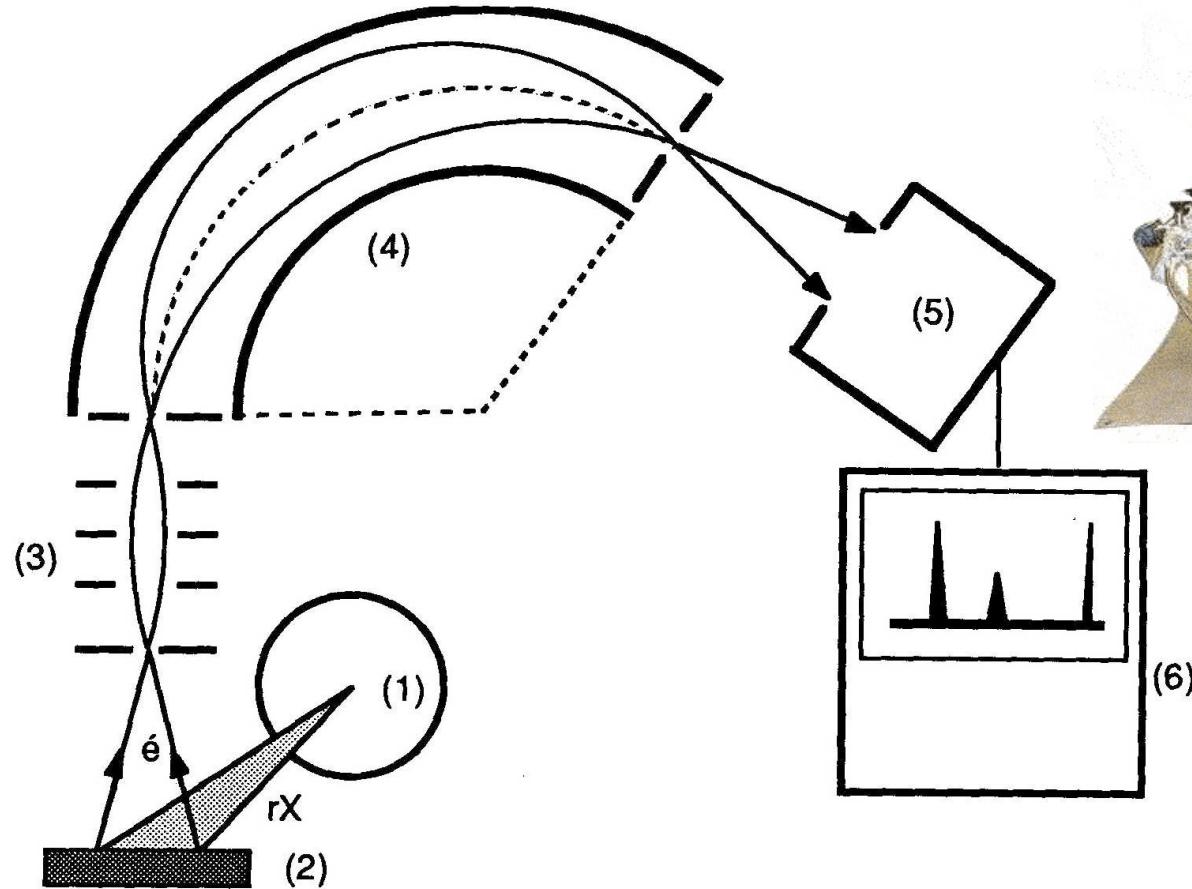
XPS

- used for elemental analysis
- all elements Z > 2
- detection limit 1/1000
- 1 – 10 nm depth
- x-ray beam 20 – 200 μm
- mapping

Peak ID	Atomic %	BE (eV)
F 1s	0.5%	687.19
O 1s	38.9%	533.72
N 1s	1.7%	402.74
C 1s	25.6%	285.43
Si 2p	33.3%	99.71

Counts

Binding Energy, eV
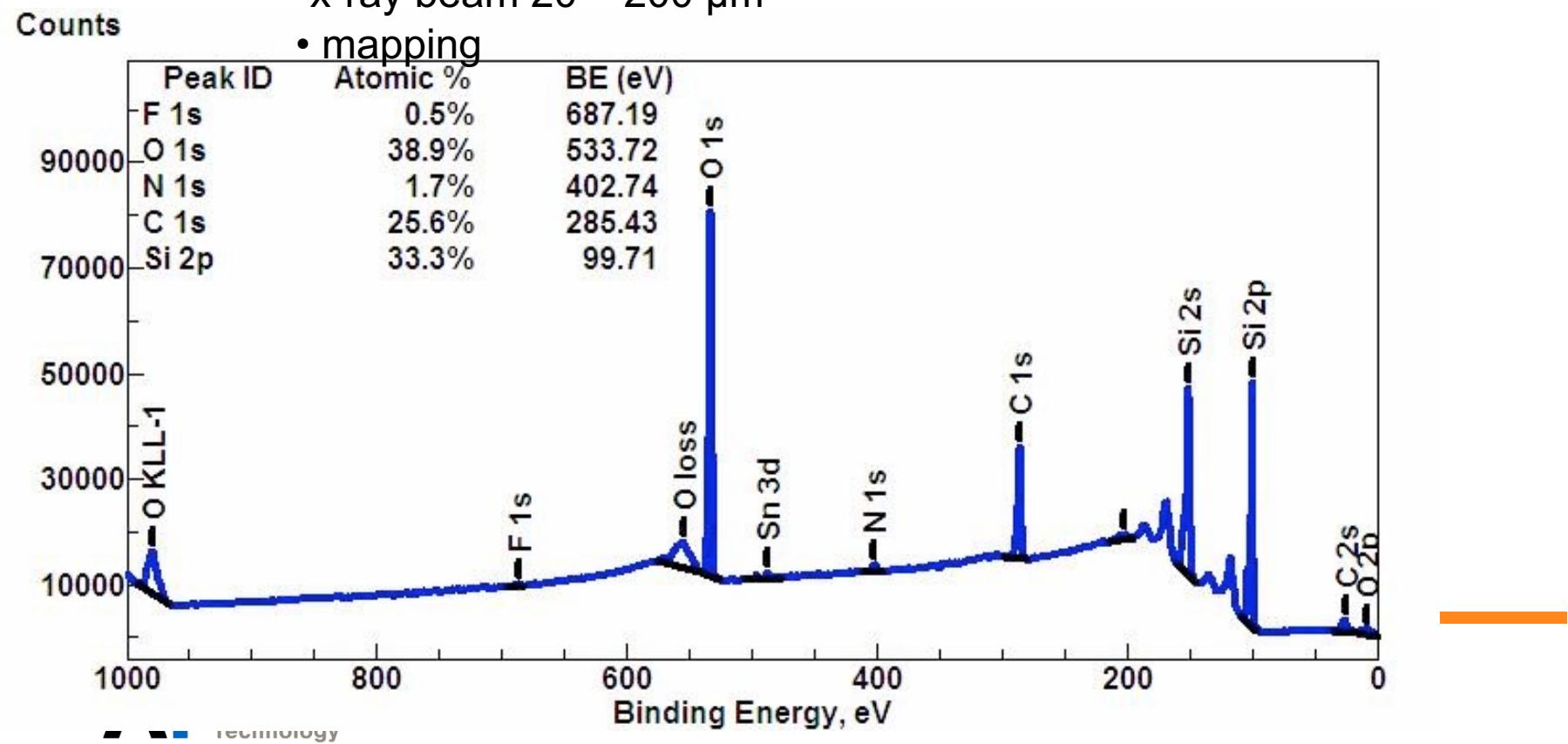
XPS

sensitive to chemical bonding, e.g. type of bonding of carbon
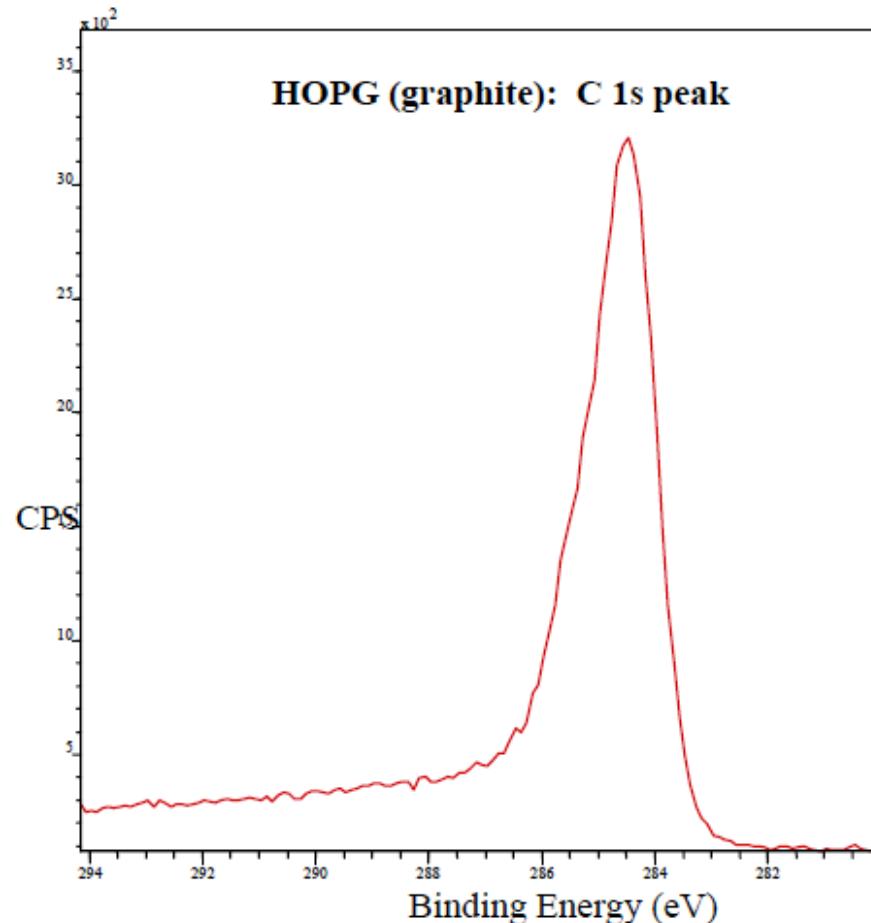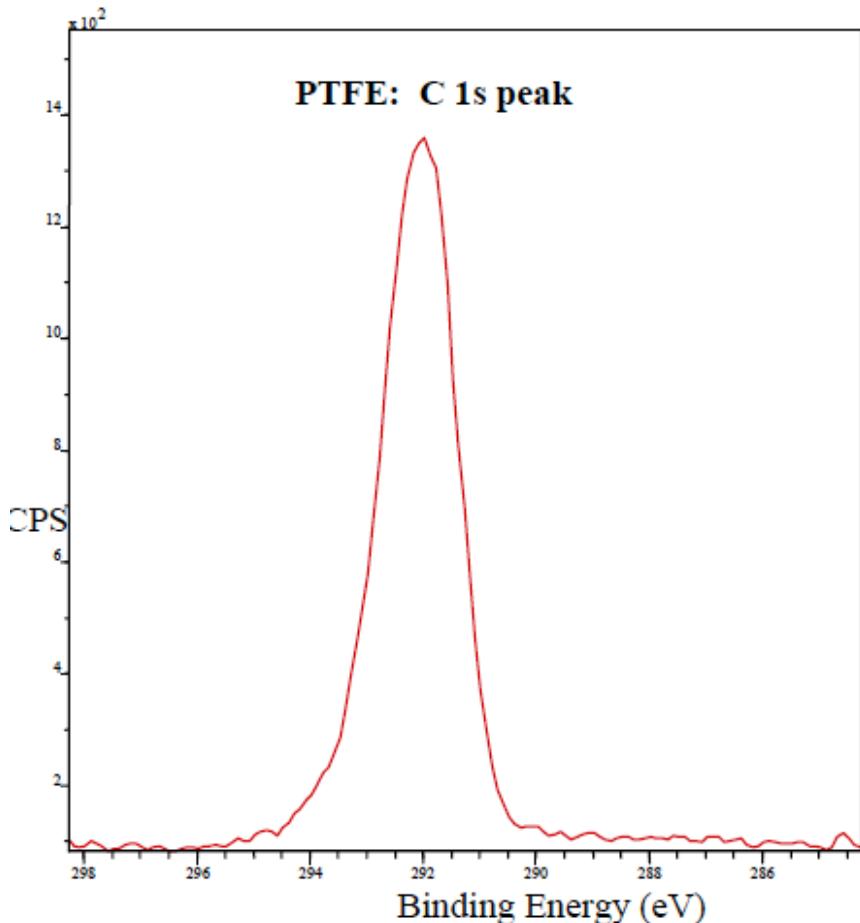
X-ray Absorption Spectroscopy XAS
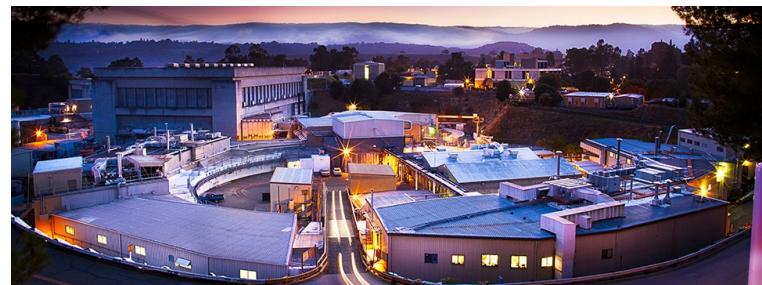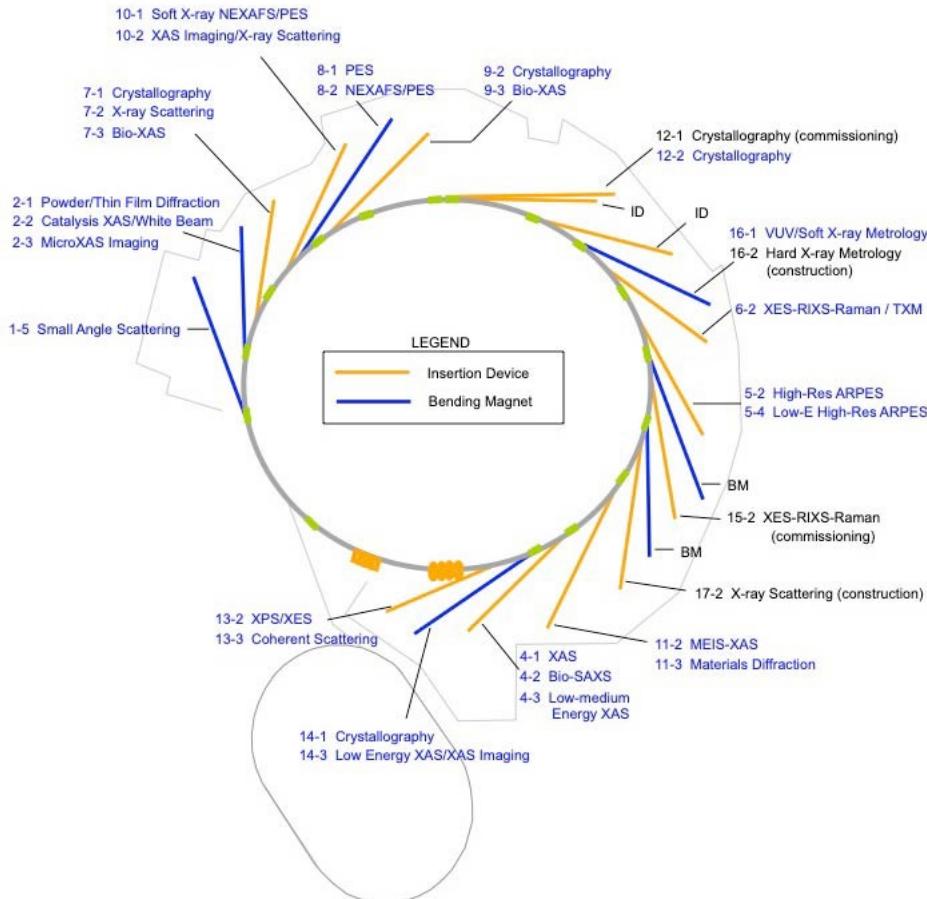
The Stanford Synchrotron Radiation Lightsource (SSRL)

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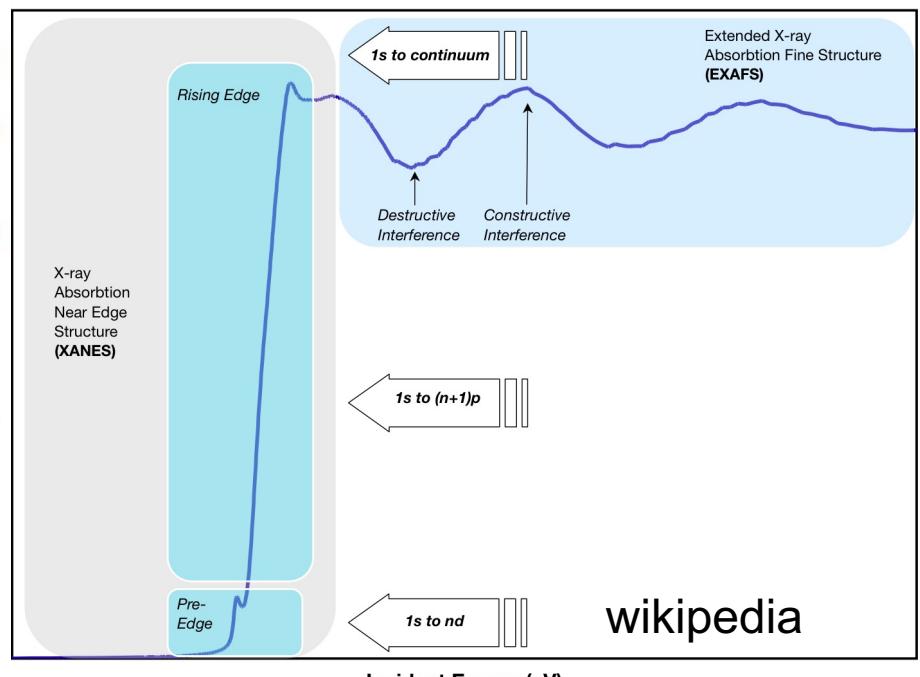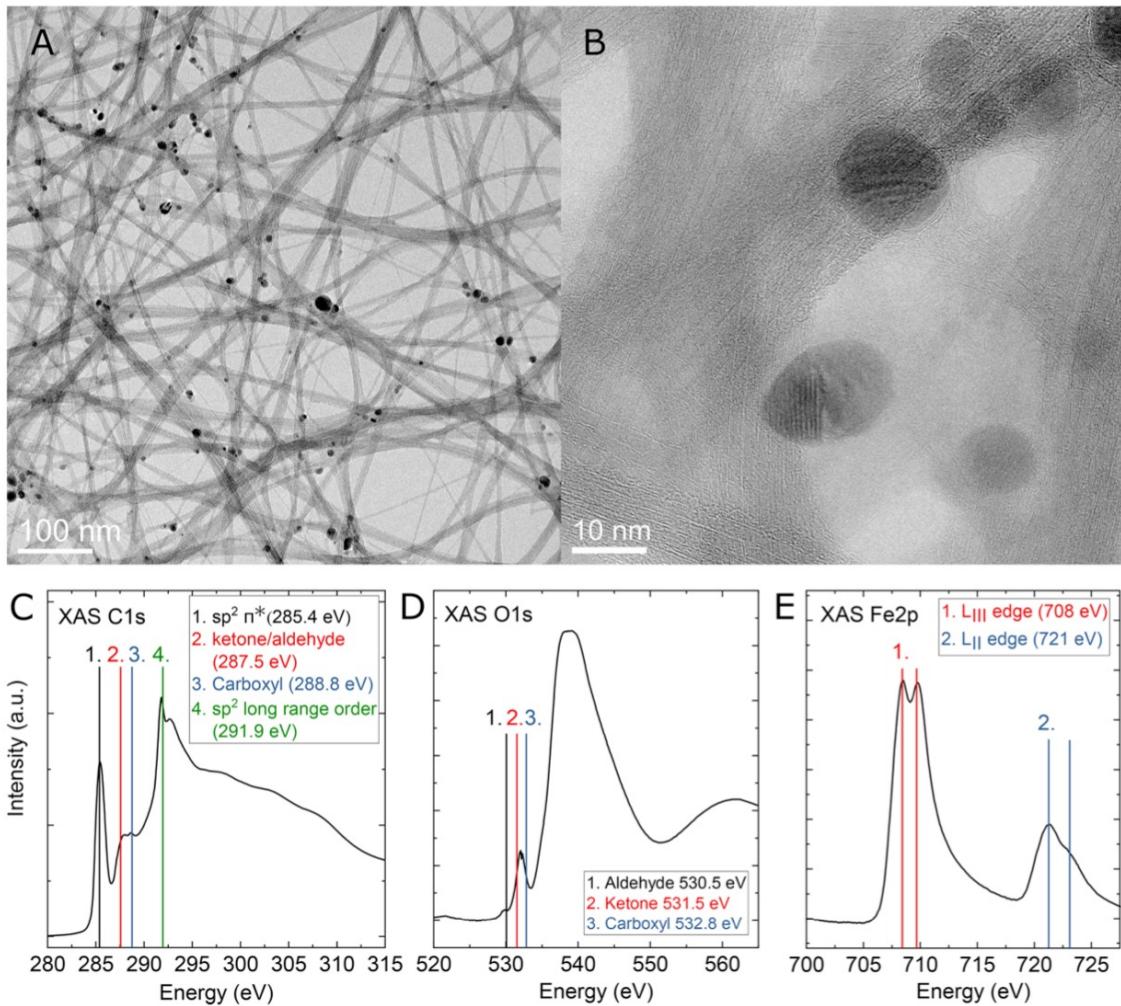
Figure 2. Characterization of the SWCNT network. (A) TEM image and (B) HRTEM image of the SWCNT network. (C) C 1s, (D) O 1s, and (E) Fe 2p XAS spectra of the SWCNT.

N. Wester et al., ACS Appl. Nano Mater. 2020, 3, 1203−1212
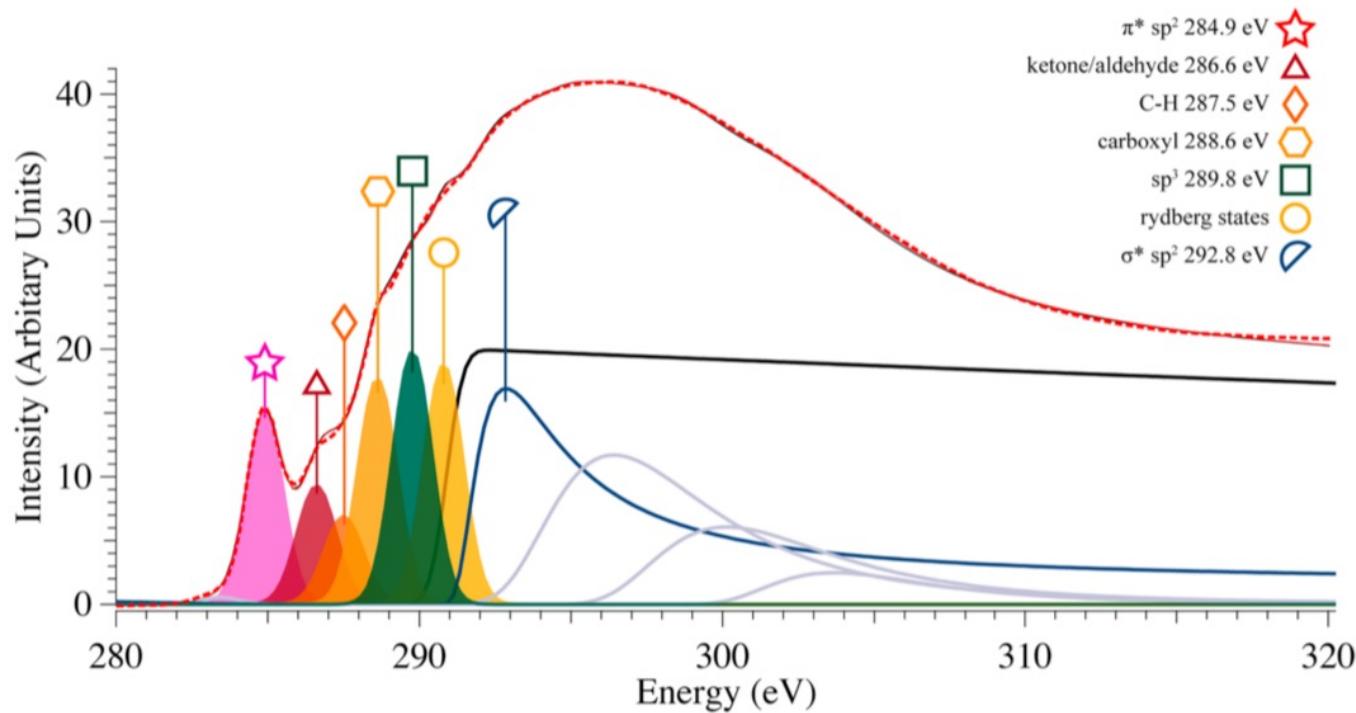
Figure 1. ta-C 1 C 1s TEY spectra. Peaks fitted to the actual XAS-curve (red).

High quality graphene   Carbon nanofibers   Detonation nanodiamonds

sp² carbon

Oxygen functional groups bonded to carbon

sp² carbon long range order

284   288   292   Energy (eV)
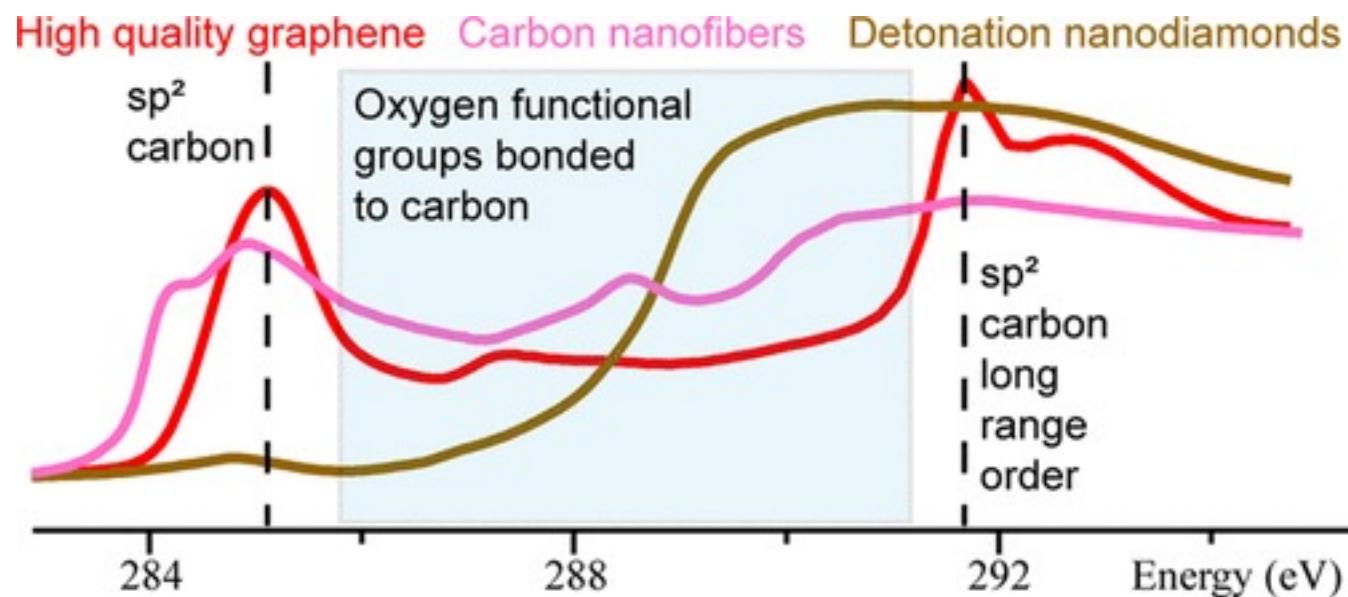
Scattering experiment - OPTICAL

OUT

IN

photon

electron

molecule

ion, atom, neutron
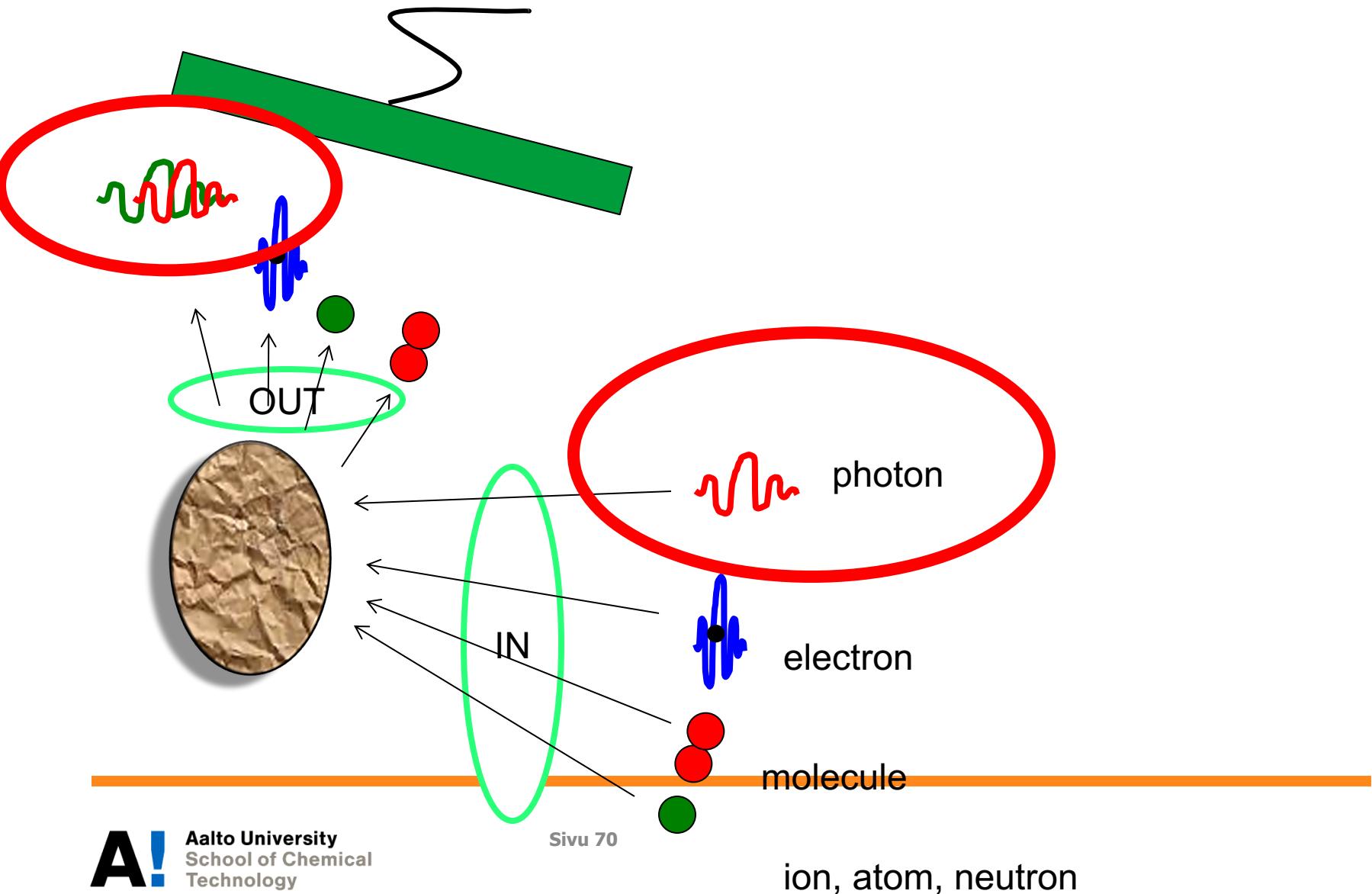
When electromagnetic radiation passes through matter, it interacts with the matter and can be:

- absorbed (1)
- reflected (2)
- scattered (3)
- transmitted (4)

- depending upon:
  - its **frequency**
  - the **structure of molecules** of the matter it encounters.

(3)

(2)

$h\nu$

M*(1)

M

(4)

$h\nu$

(2)

(3)
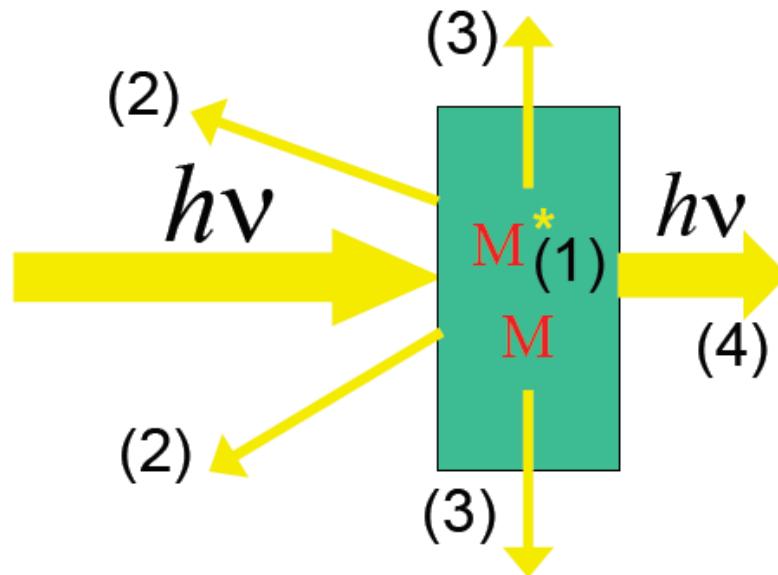
- **Vibrational Spectroscopy**

  Vibrational spectroscopy is a method of chemical analysis where the sample is illuminated with incident radiation in order to excite molecular vibrations. Vibrational excitation is caused by the molecule absorbing, reflecting or scattering a particular discrete amount of energy. There are two major types of vibrational spectroscopy: Infrared (IR) and Raman.

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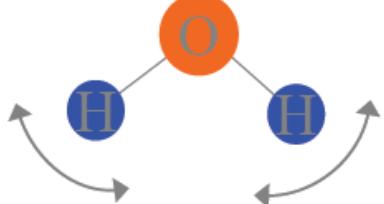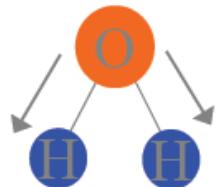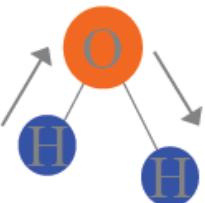
IR Light *Absorption* Measurement.

- Light energy absorbed by increasing vibrations between atoms in a molecule.
- Energy (wavelength) absorbed related to strength of bond.
- Strength of bond related to molecular structure and environment.
- Amount of light absorbed related to concentration and *absorptivity* constant.

I_o I
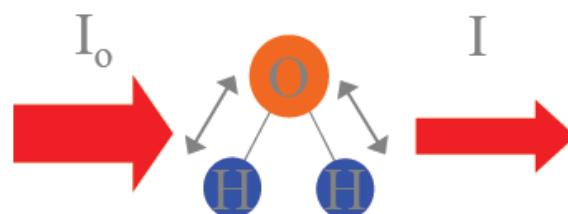
Infrared

- Absorption
- Requires a dipole moment change (O-H, N-H, C=O)
- Sample preparation or accessory usually necessary
- Short optical pathlength required
- Non-aqueous samples

Raman

- Emission of scattered laser light
- Requires polarizability change (C=C, aromatics)
- Little or no sample preparation necessary
- Measure through transparent packaging
- Aqueous samples

RAMAN
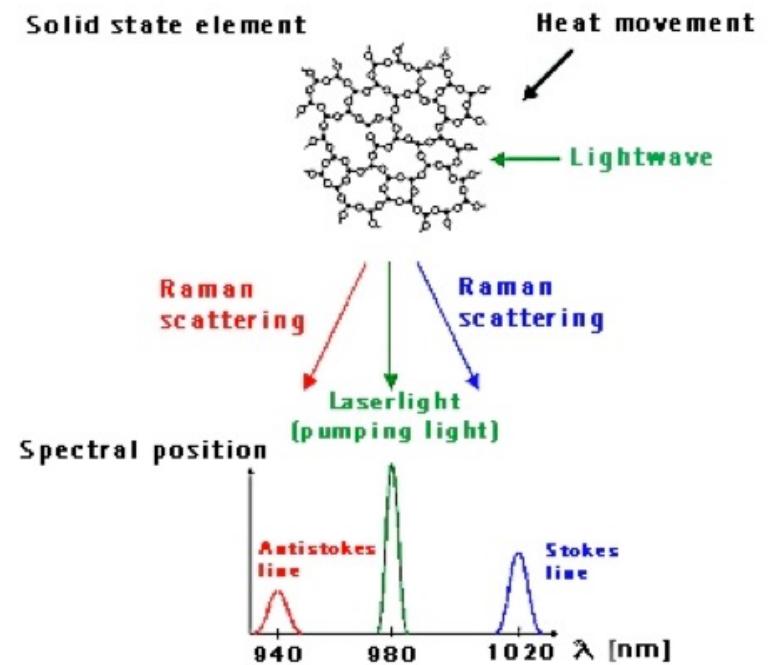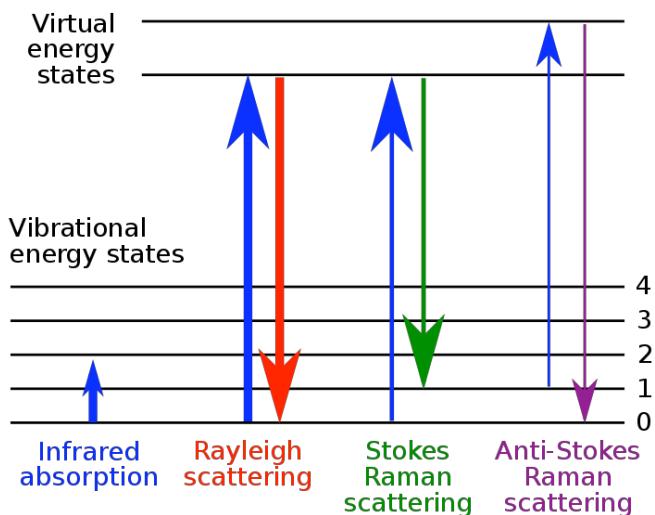
RAMAN
example carbon
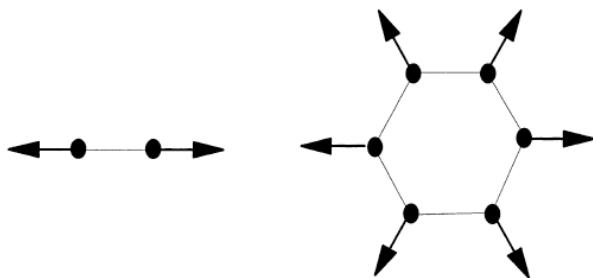
Fig. 34. Eigenvectors of the Raman G and D modes in graphite and amorphous carbons.

diamond

graphite

D   G

µc-graphite

glassy C

sputtered a-C

a-C:H

ta-C

Raman intensity

500   1,000   1,500   2,000

Wavenumber (cm^{-1})
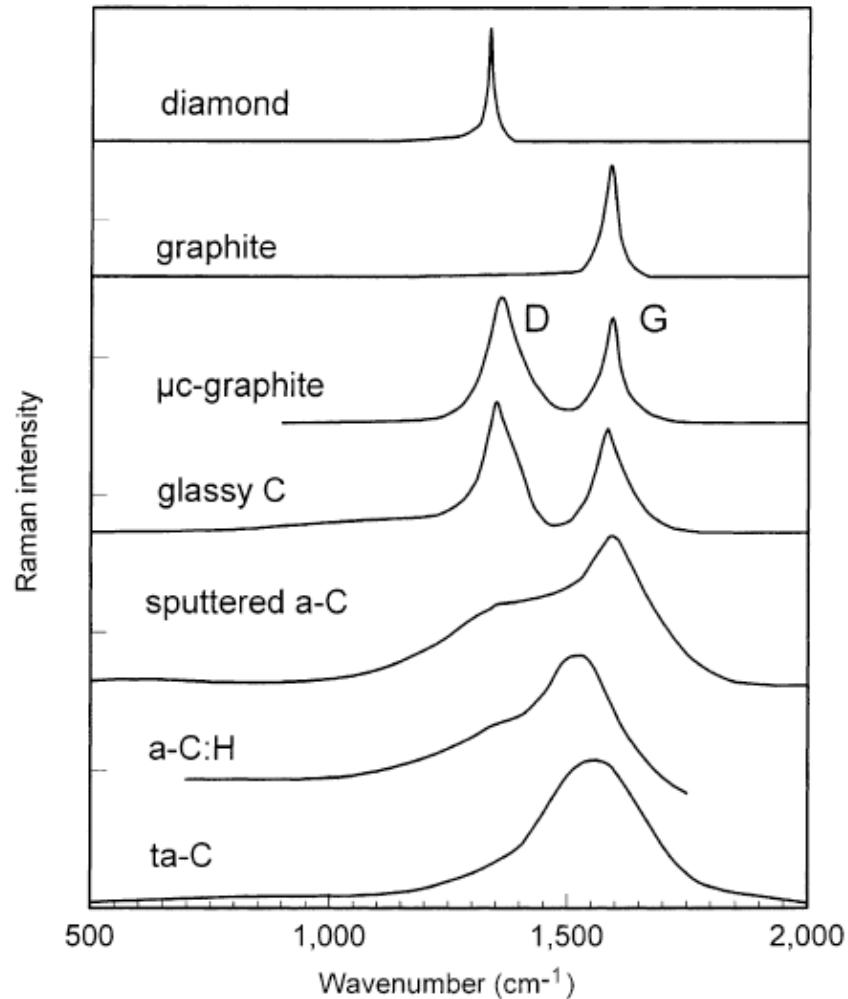
Fig. 33. Comparison of typical Raman spectra of carbons.

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Sivu 76

RAMAN
example carbon

- amorphous materials
- finger print of different bonds (materials)
- mapping
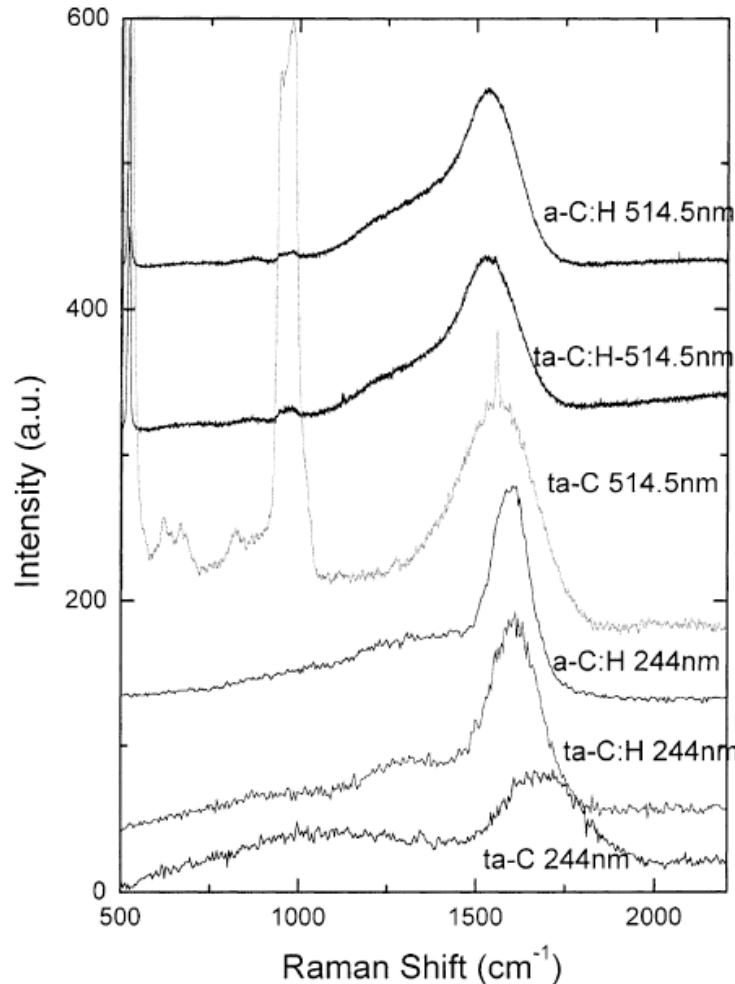
Mapping
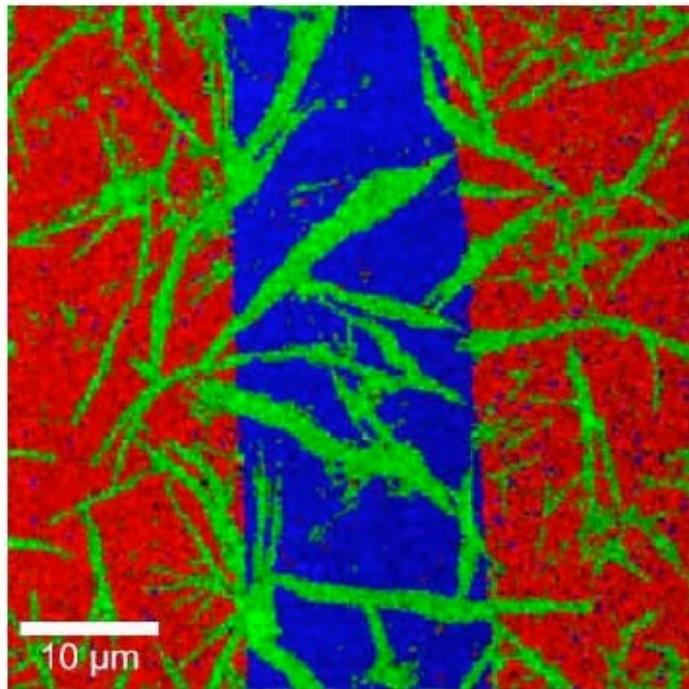
Figure 4. Color-coded confocal Raman image of a 7.1 nm PMMA layer (red) and a 4.2 nm contamination layer (green) on glass (blue). 200 x 200 spectra, 7 ms integration time/spectrum. Total acquisition time 5.4 minutes.
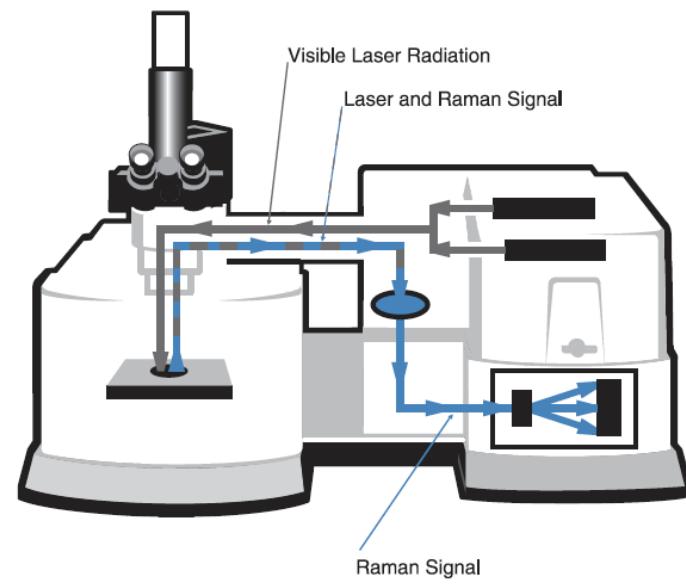
Visible Laser Radiation

Laser and Raman Signal

Raman Signal

Contents

- Thin film properties
- Wealth of methods – MATRIX
- Scattering
- Thickness - profilometry
- Composition – EDS, WDS, SIMS, RBS, ERDA, GDOES
- Microstructure –XRD, TEM
- Bonding – ESCA, RAMAN
- **Topography - ADM**
- Electrical conductivity – four point probe
- Mechanical properties - indentation
- Optical transmittance- FTIR (???)

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Scattering experiment- Mechanical

OUT

photon

electron

molecule

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ion, atom, neutron
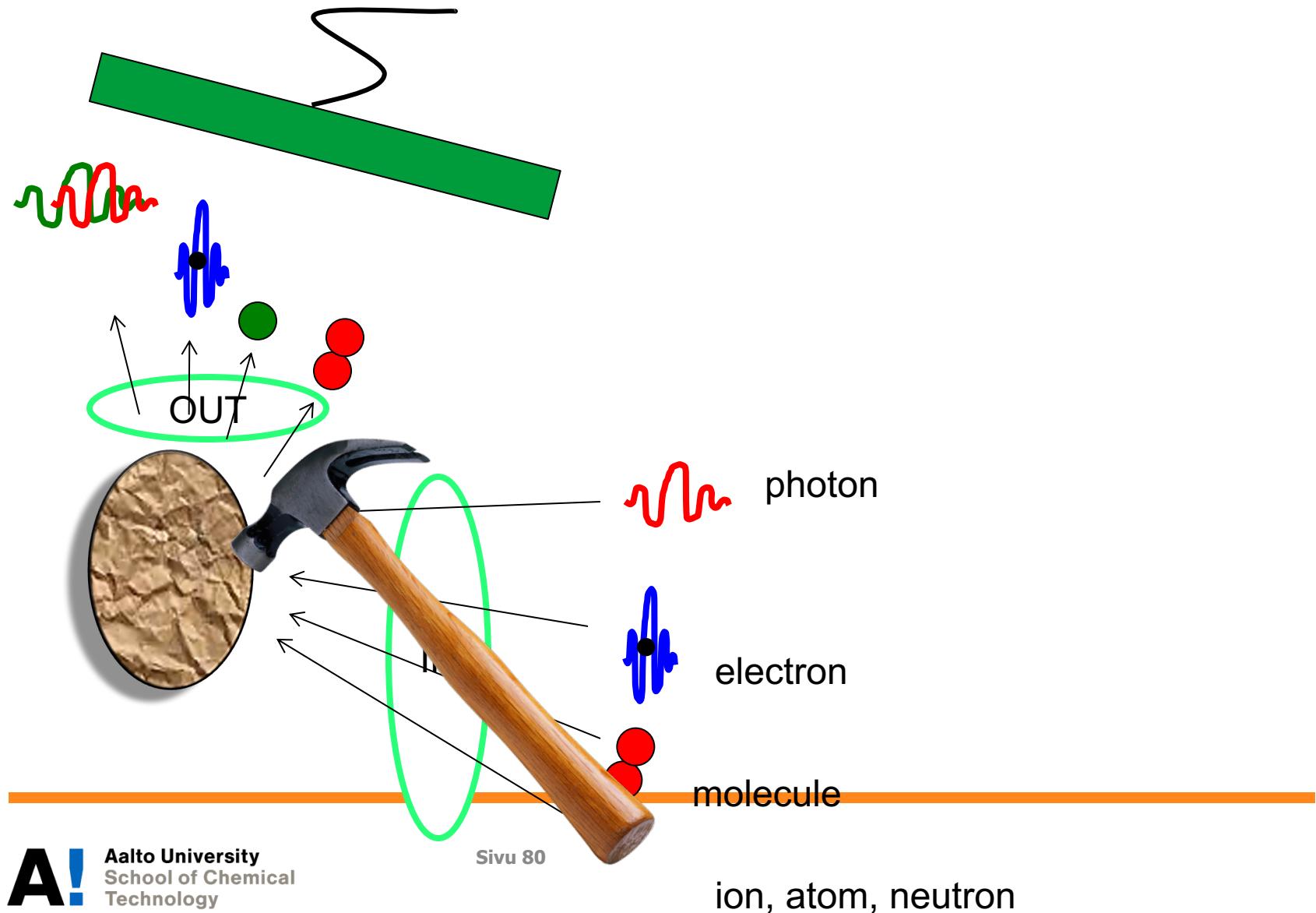
Scanning Probe Microscopy

Basic idea of scanned probe techniques:

Tip is scanned relative to the sample
(or sometimes the sample is scanned)

Tip measures
some property of
the surface

A feedback mechanism
is used to maintain the
tip at a constant height
above the sample

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Sivu 81
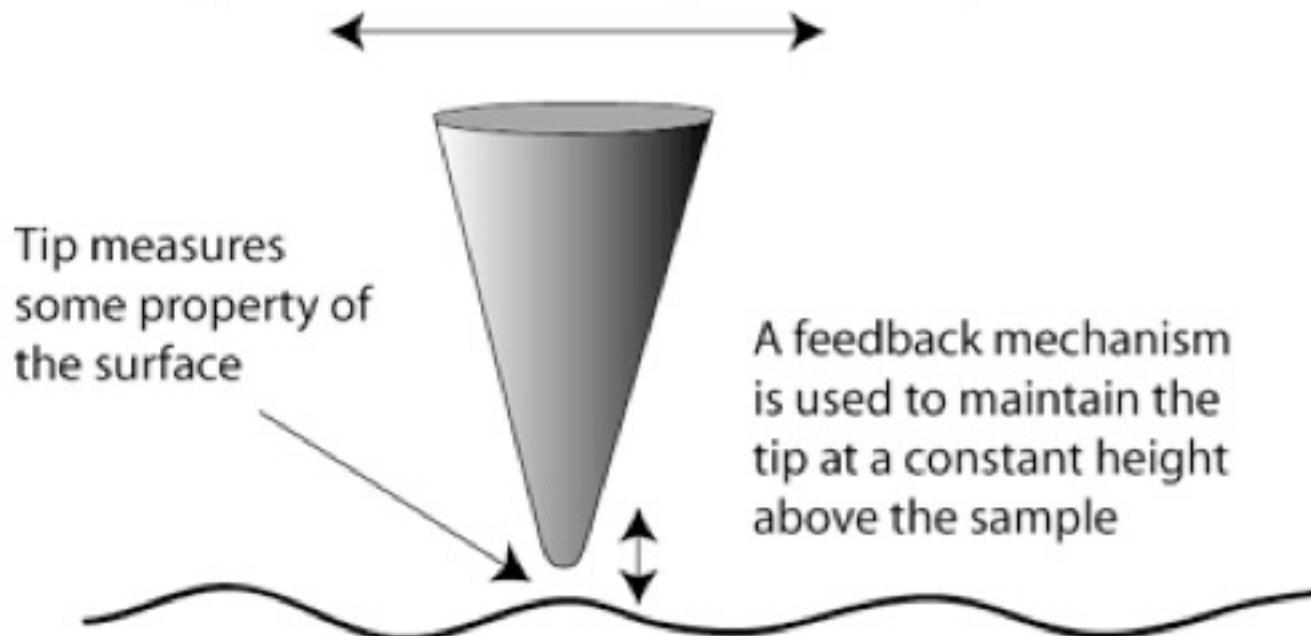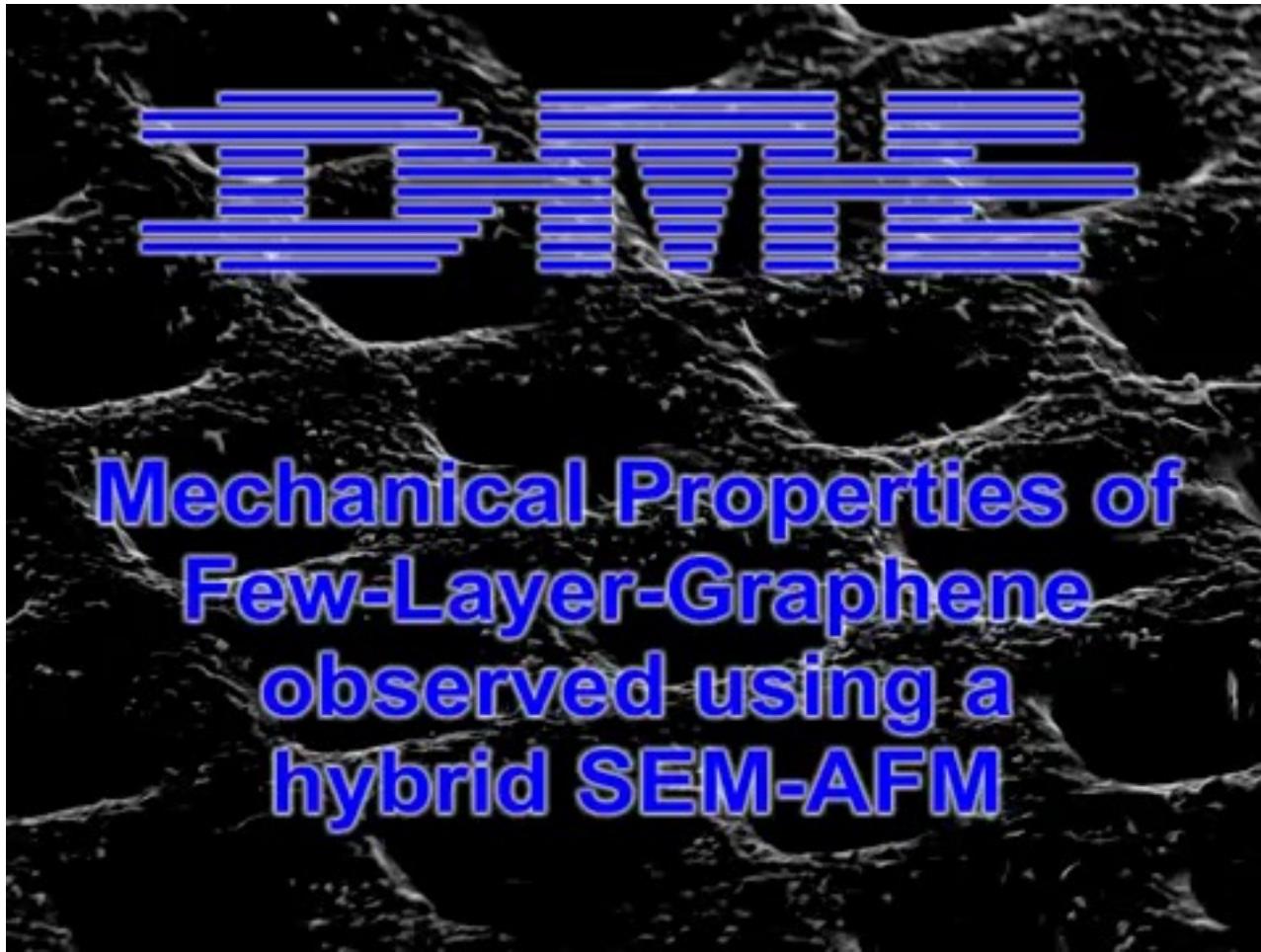
Mechanical Properties of Few-Layer-Graphene observed using a hybrid SEM-AFM

Contents

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Indentation

- H = constant*load/(indentation area)
- Thin film/substrate: composite hardness
- Coating hardness: h< film thickness
- Very thin coatings: hardness by modelling (FEM, MD)
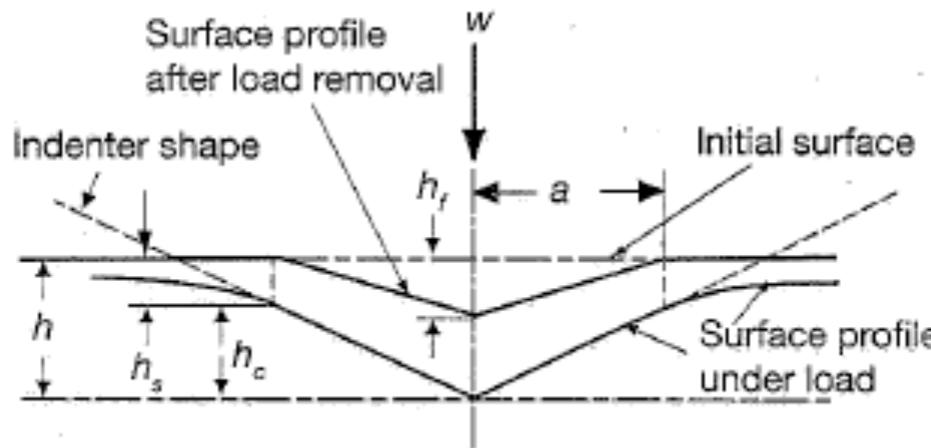
Fig. 5.9. Schematic representation of a section through an indentation using a conical indenter. h_c = contact depth, h_s = sink-in depth and h_f = final depth.

Elastic modulus E from loading - unloading curve
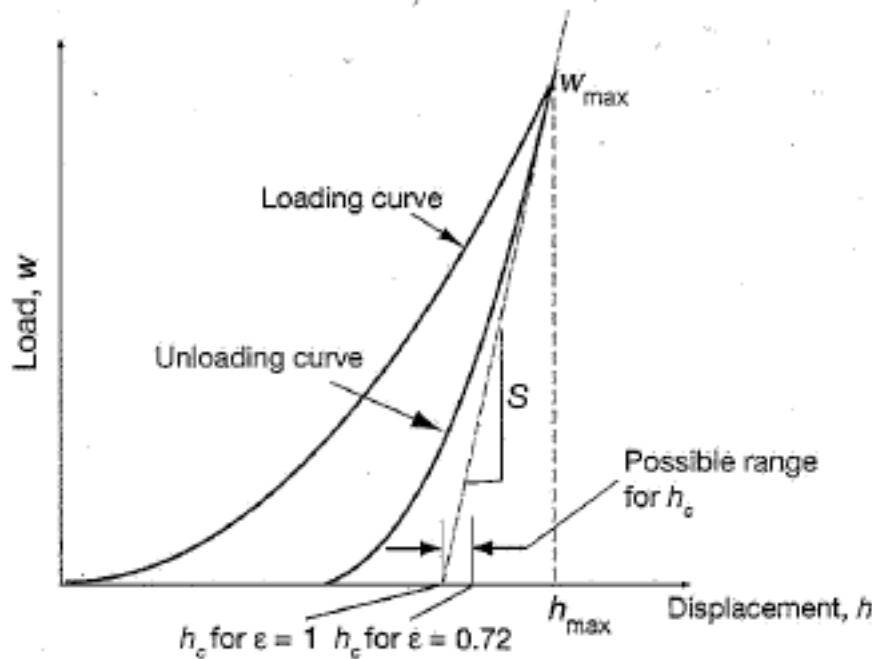
Fig. 5.10. A typical load-displacement indentation curve.

$$E_r = \frac{\sqrt{\pi \cdot S}}{2 \cdot \sqrt{A}}$$

$$h_c = h_{max} - \varepsilon \cdot w_{max}/S$$

$$\frac{1}{E_r} = \frac{1 - v_i^2}{E_i} + \frac{1 - v^2}{E}$$

- h < 1/10 film thickness
- Very thin coatings: E by modelling (FEM, MD)

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Hardness and E as a function of indentation depth

Depth profiles of Er and H data from 200 µN partial-unload nanoindentation tests on 50 nm TiN thin film samples. www.hysitron.com

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Indentation test

Muhannad Abuhaikal
Prof. Franz-Josef Ulm

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Technology
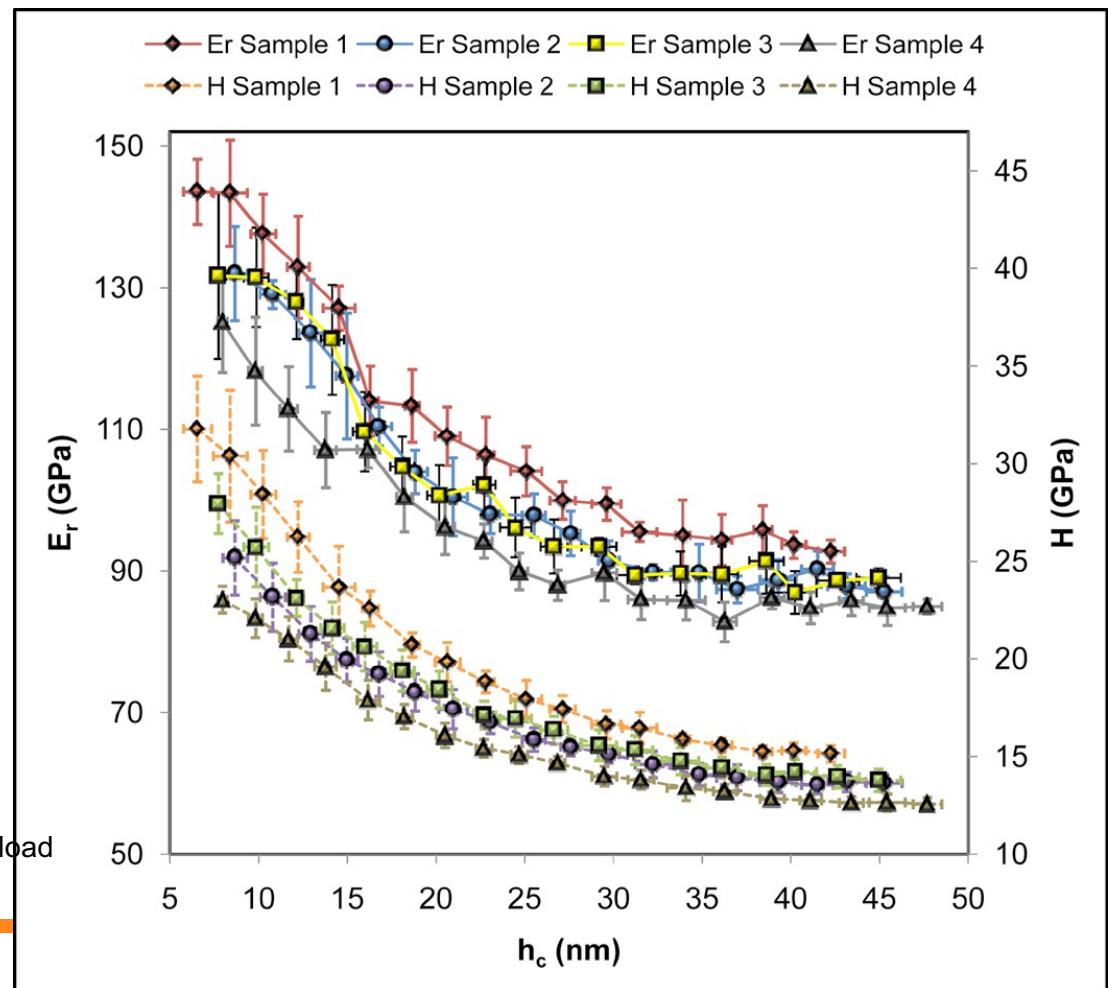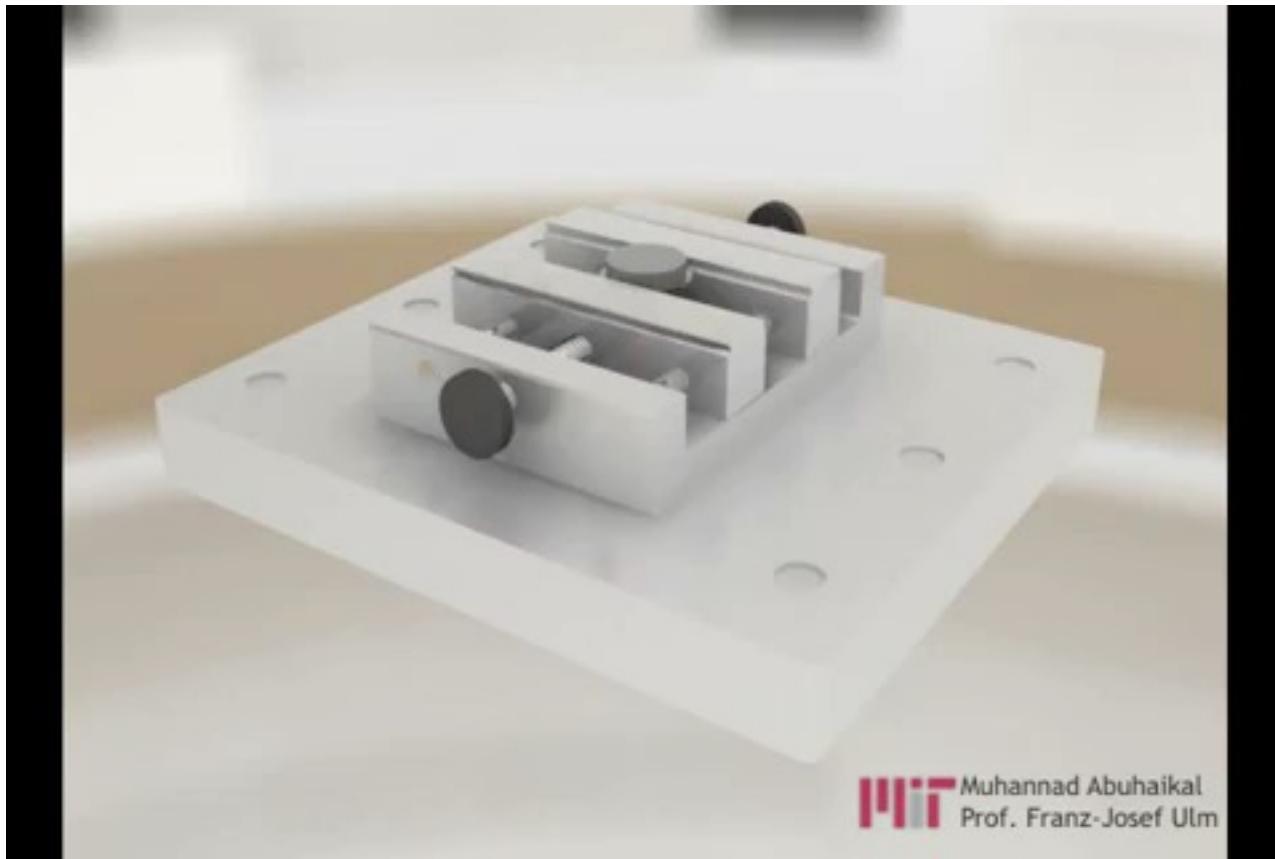
Nano wear
TiO₂ ALD, varying deposition temperature
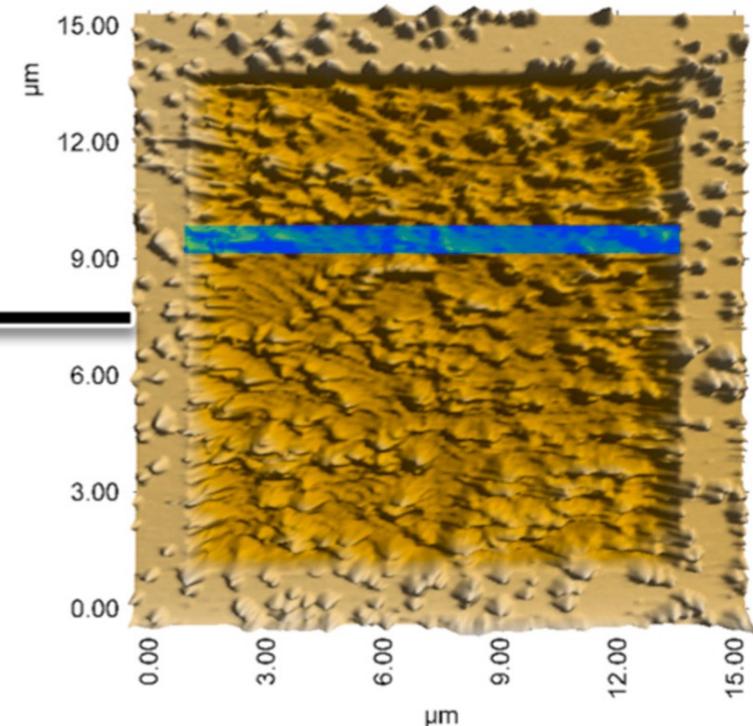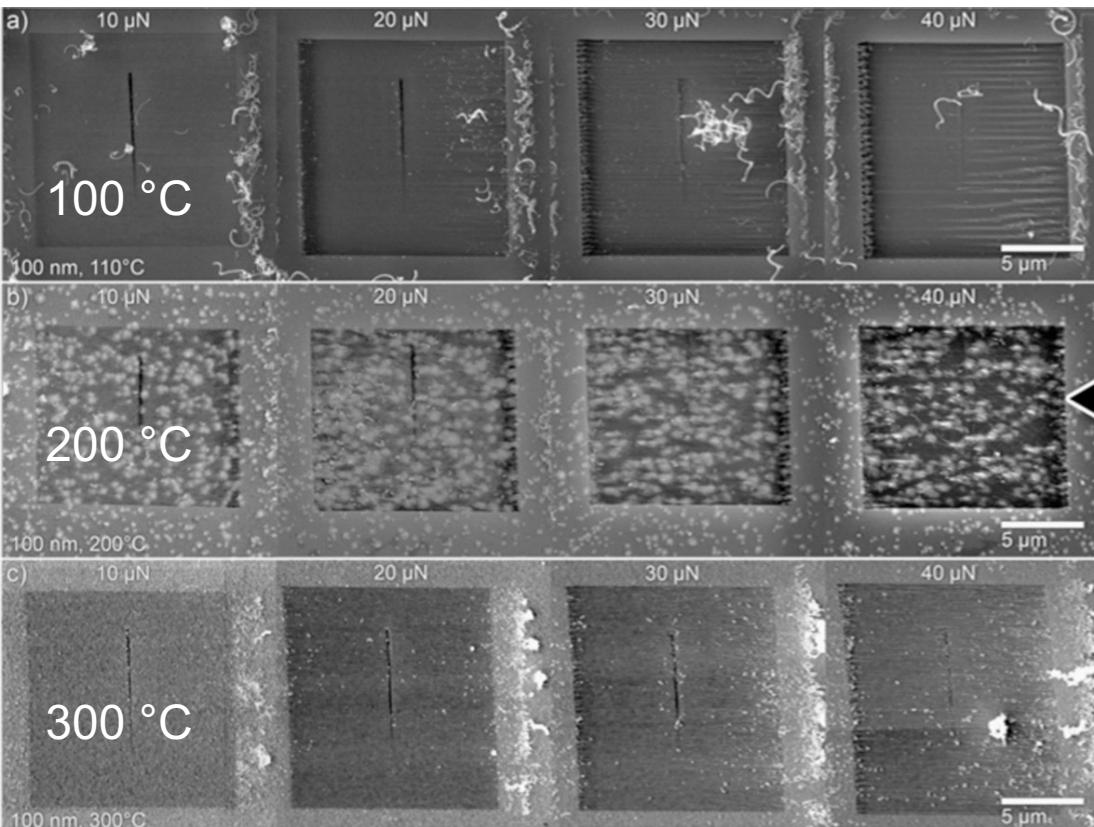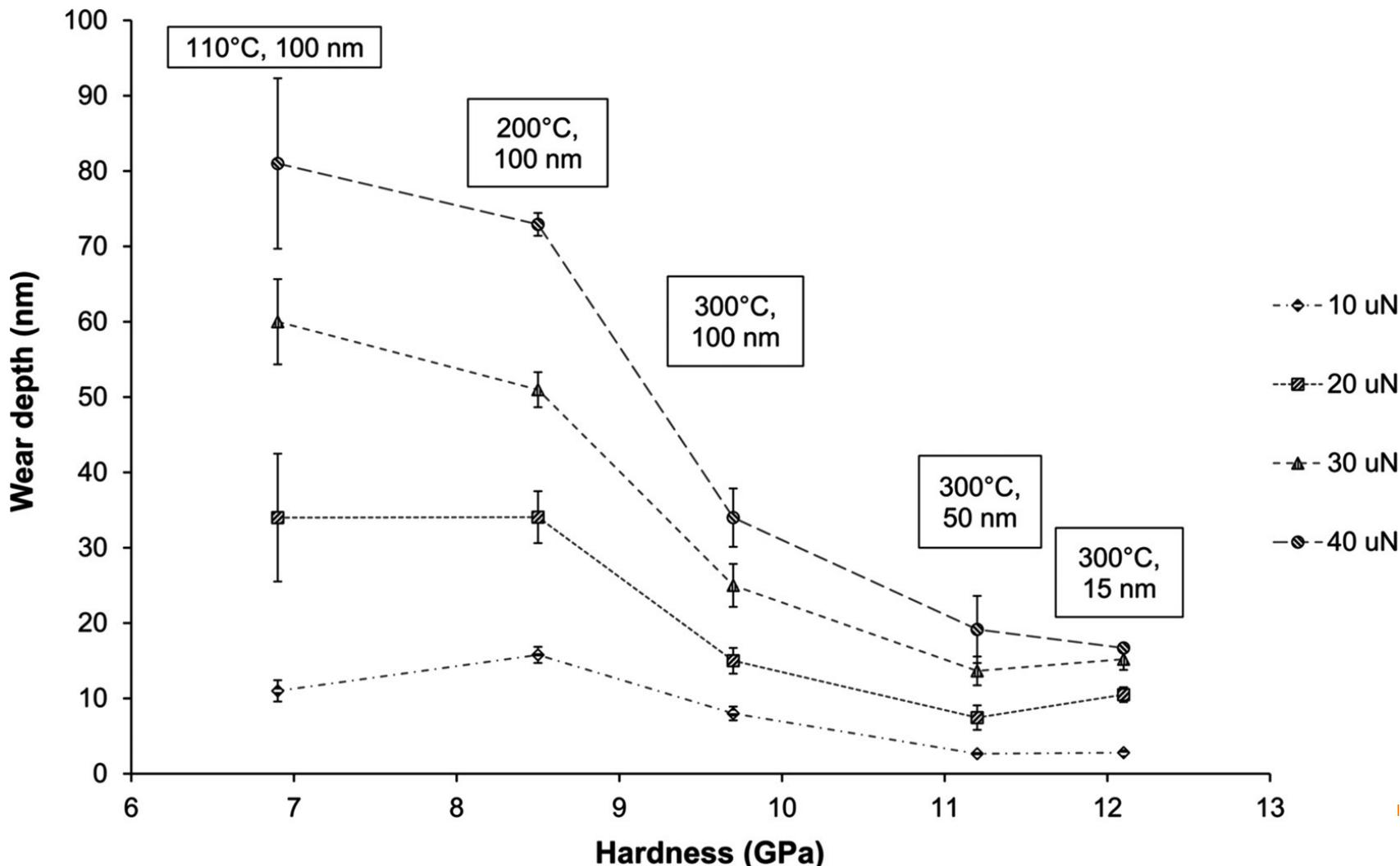
J. Lyytinen et al. / Wear 342-343 (2015) 270–278272

Wear depth

J. Lyytinen et al. / Wear 342-343 (2015) 270–278272

Contents

- Thin film properties
- Wealth of methods – MATRIX
- Scattering
- Thickness - profilometry
- Composition – EDS, WDS, SIMS, RBS, ERDA, GDOES
- Microstructure –XRD, TEM
- Bonding – ESCA, RAMAN
- Topography - ADM
- Electrical conductivity – four point probe
- Mechanical properties - indentation
- Optical properties

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Optical coatings

- Control of reflectance and emission
    - Lenses
    - Photo voltaic
    - Solar thermal
- Protective optical coatings
- Self-cleaning or easy to clean films on optical surfaces
- Measuring thin dielectric film properties

Ellpsometry

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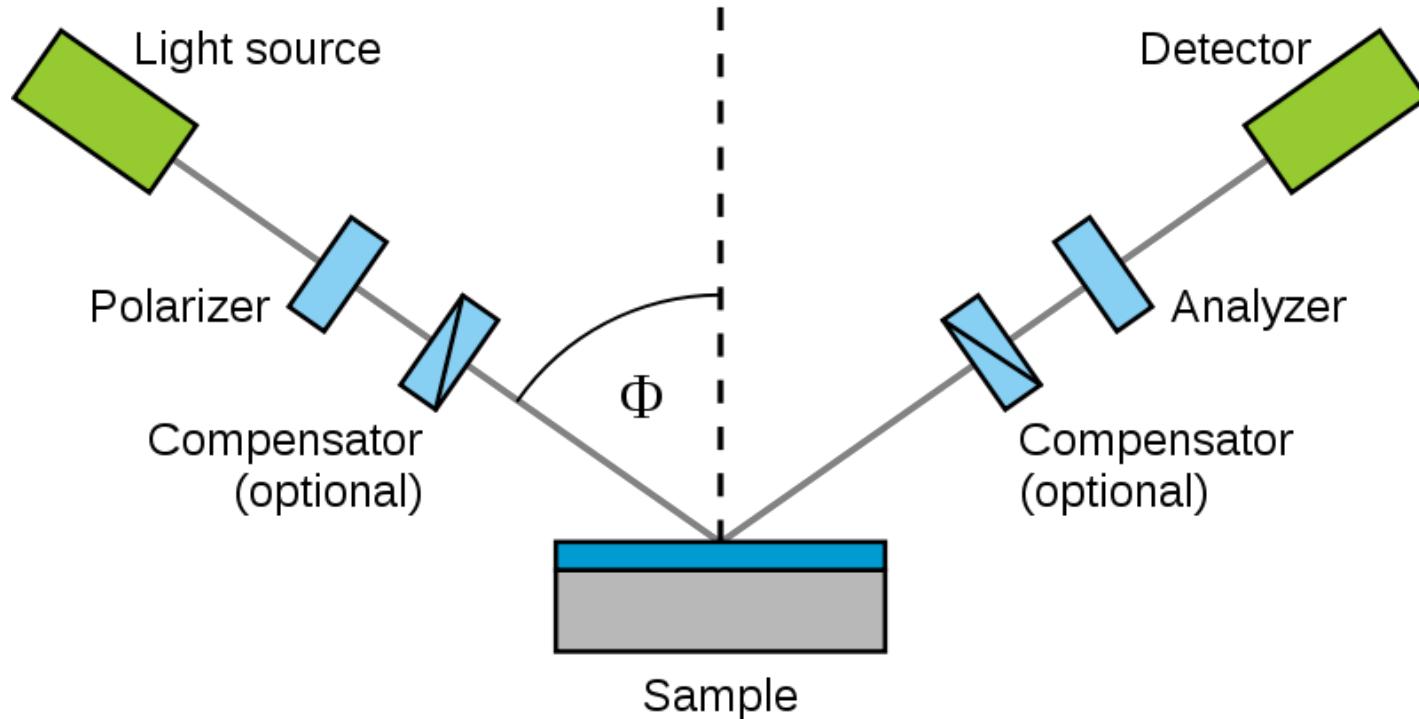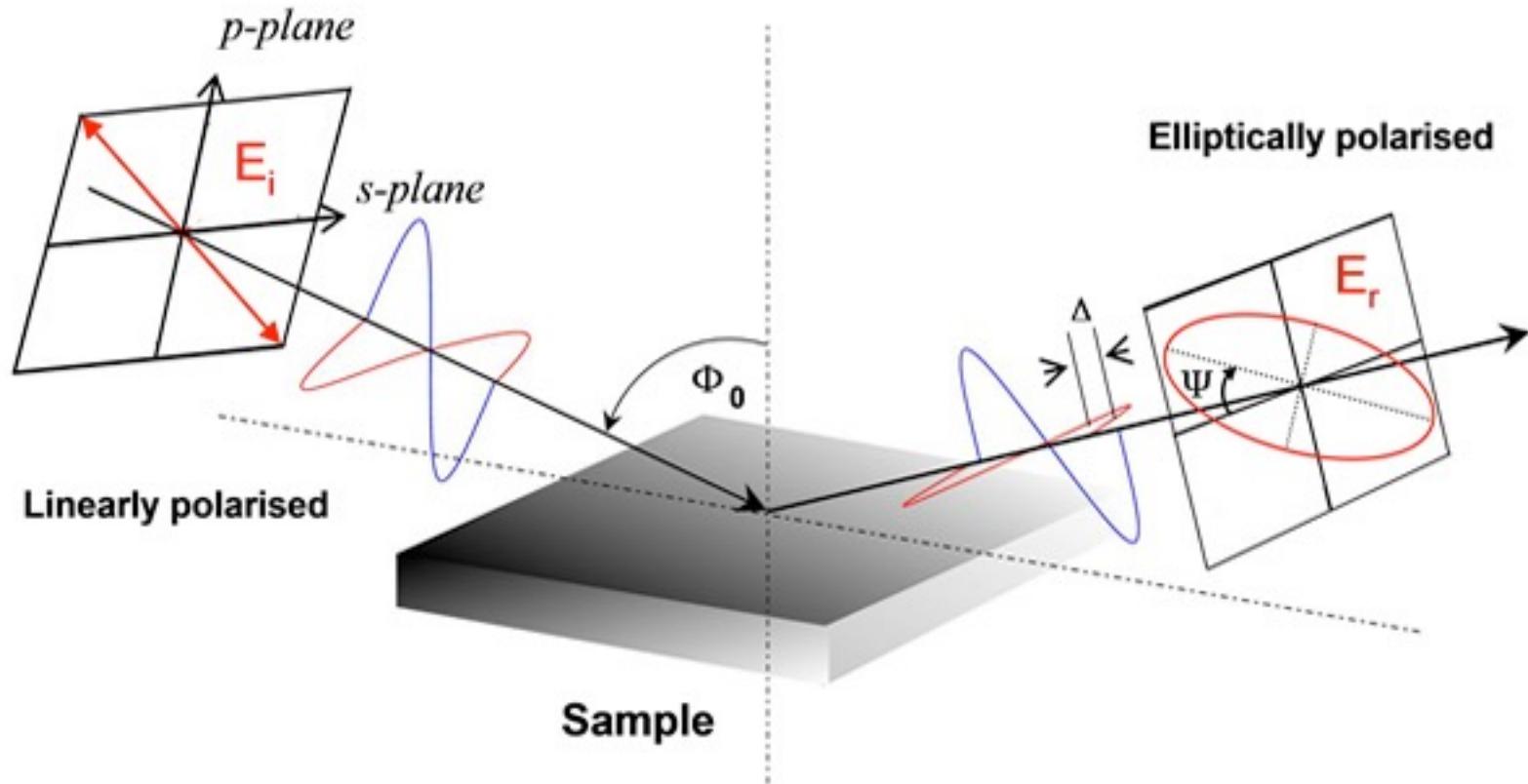
Ellpsometry

Ellipsometry

- real part (refractive index), $n(\lambda)$
- imaginary part (extinction coefficient), $k(\lambda)$
- complex refractive index, of a material, $N(\lambda) = (n(\lambda)+ik(\lambda))$, where λ

- If $N(\lambda)$ known ➔ film thickness
- measure of phase shift ➔ very thin films can be measured < 1nm – several µm
- multilayer films may be measured when using numerical models

Reflectometry

- Film thickness
  - 3 nm -> 200 µm
- n and k values
- multilayers

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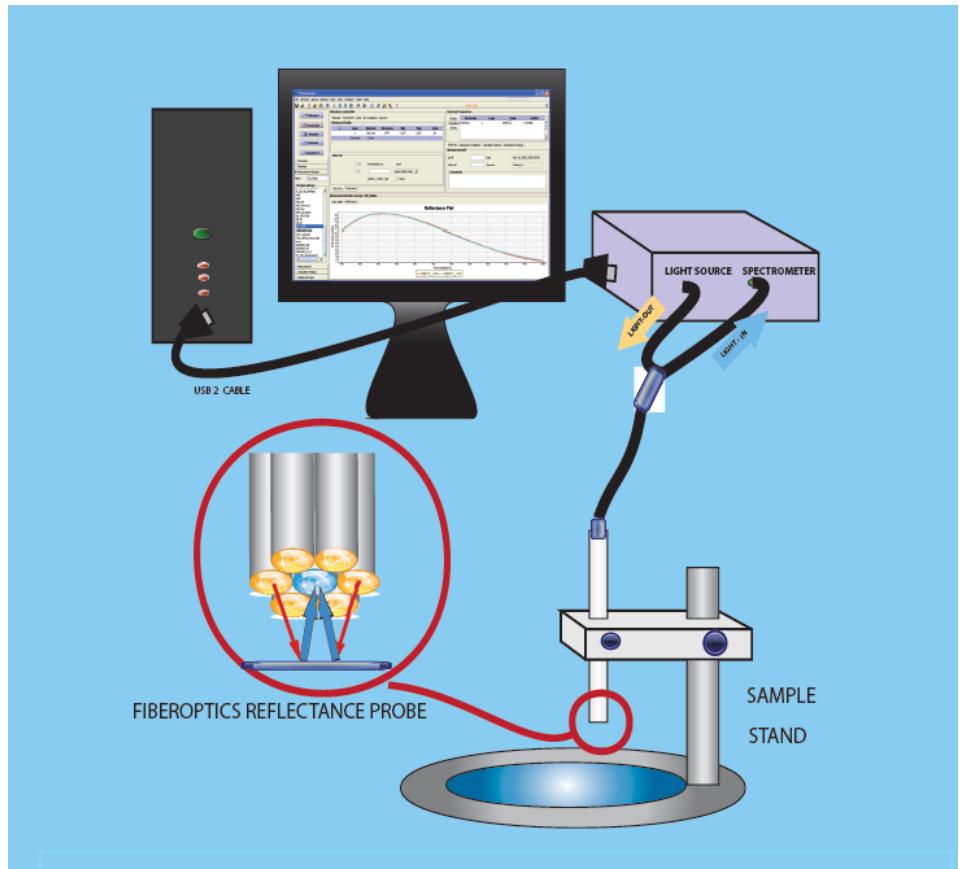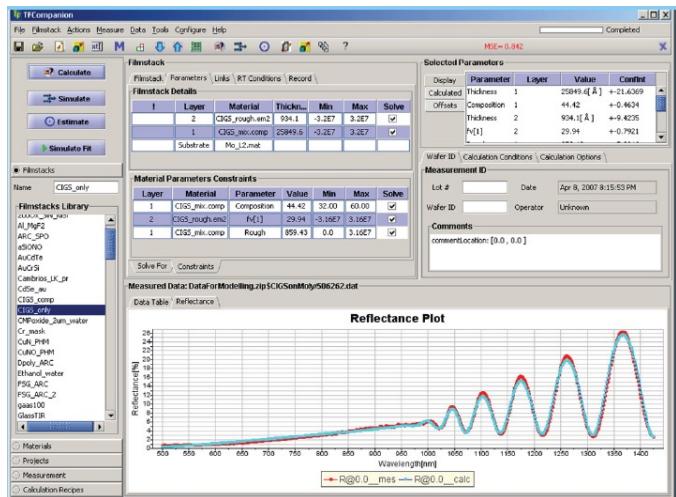
Reflectometry
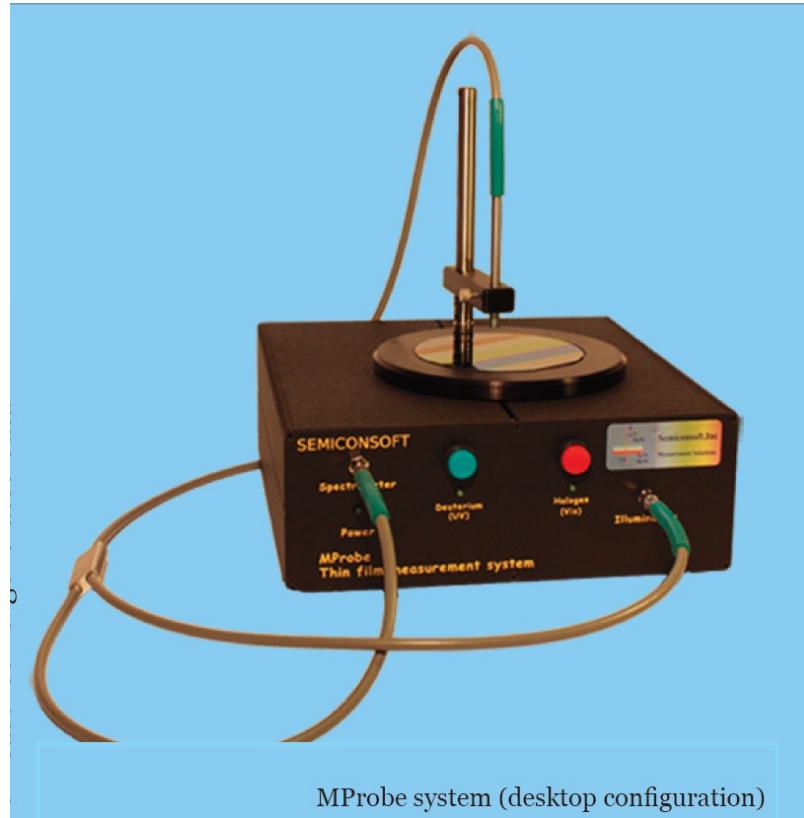
MProbe system (desktop configuration)

And there is whole lot more…But one can get an idea with simple methods:

- interference colors: thickness, absoption

- reflection: metals identification

- Scotts Tape Test: adhesion

- electrical conductivity

- scraching by a tip: hardness, adhesion, friction

- shine light tanget to surface: impurities, particles on film

- breathe moisture (no slime!): surface energy, hydrophilicity, adhesion (try only on your own samples)