Aalto University
School of Chemical Engineering

Characterization

CHEM-E5125 Thin Films Technology

2021

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

- SEM/EDX,WDS, kaikki osaa
- - XPS, Sami varmistaa Jouko Lahtiselta, opiskelija mittaa?
- - RAMAN Joonas Heikkinen
- - XRD/XRR (Jarkko Etula)
- - ellipsometry, Robin group, Micronova
- - reflectometry, Victor Ovchinnikov
- - contact angle (goniometer), Joksa
- - tribometer, Jari ryhmä
- - indentation, Trebala (mahdollisesti mikrokovuus)

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 — Ultimate Detection Limit

Li - U | ±30% | 1-5 nm | Tool | UHV | 0.1 atom%

Legend for Tool

- Major Applications
- Type of Chemistry Info
- XY Map, Profile or Angles
- Other Applications
- Not good for...
- Chemical State (Yes/No)
- Measures thickness

nanolab technologies
www.nanolab1.com
Tel 1-408-433-3320

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

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 | ~1 µ | UHV | ±50% | PPB

Contamination, Unknowns, FA
Conductors, Semicon, Insulators
Measured Elemental Ions
~ 1 micron per laser pulse
No Chemical States

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 — 3-10 nm | in air | ~1% of thickness

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 — 10 nm-1 µ | in air | ~5%

Crystalline Materials, Semicon
Stress, Identify Phase
Texture orientation
Degree of crystallinity
Size of crystallites
% of amorphous nature
Solid materials only

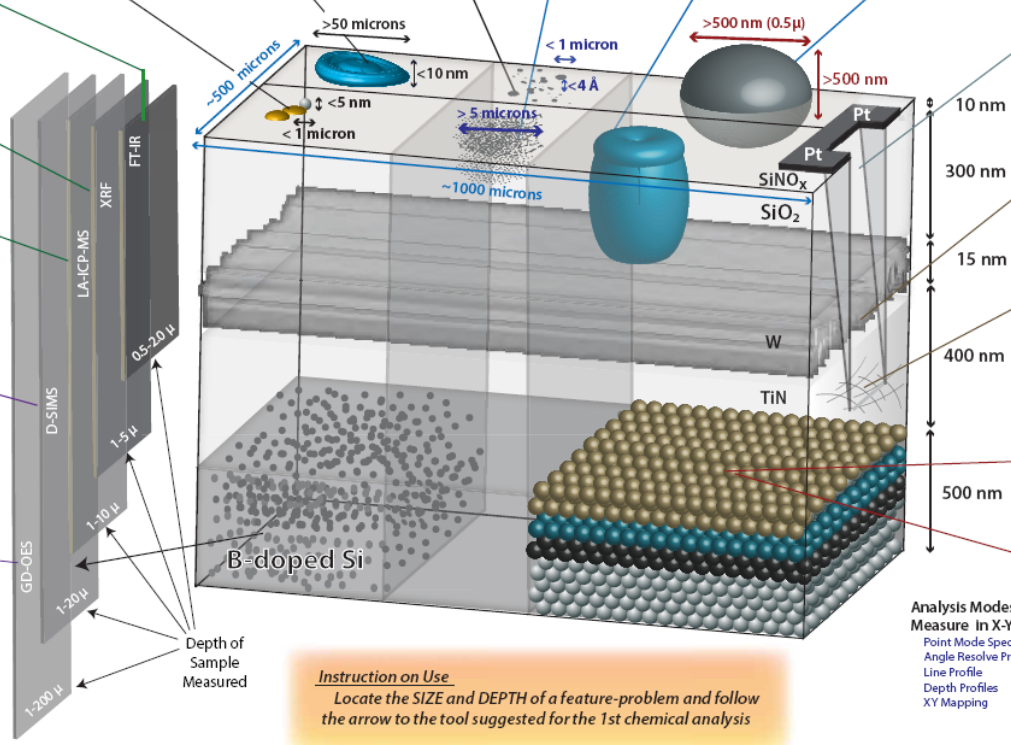
Depth Profiling Info

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



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

Atomic Scale Info

TEM-EDX — Al - U | 2 -100 nm | UHV | ±20% | 0.5 atom%

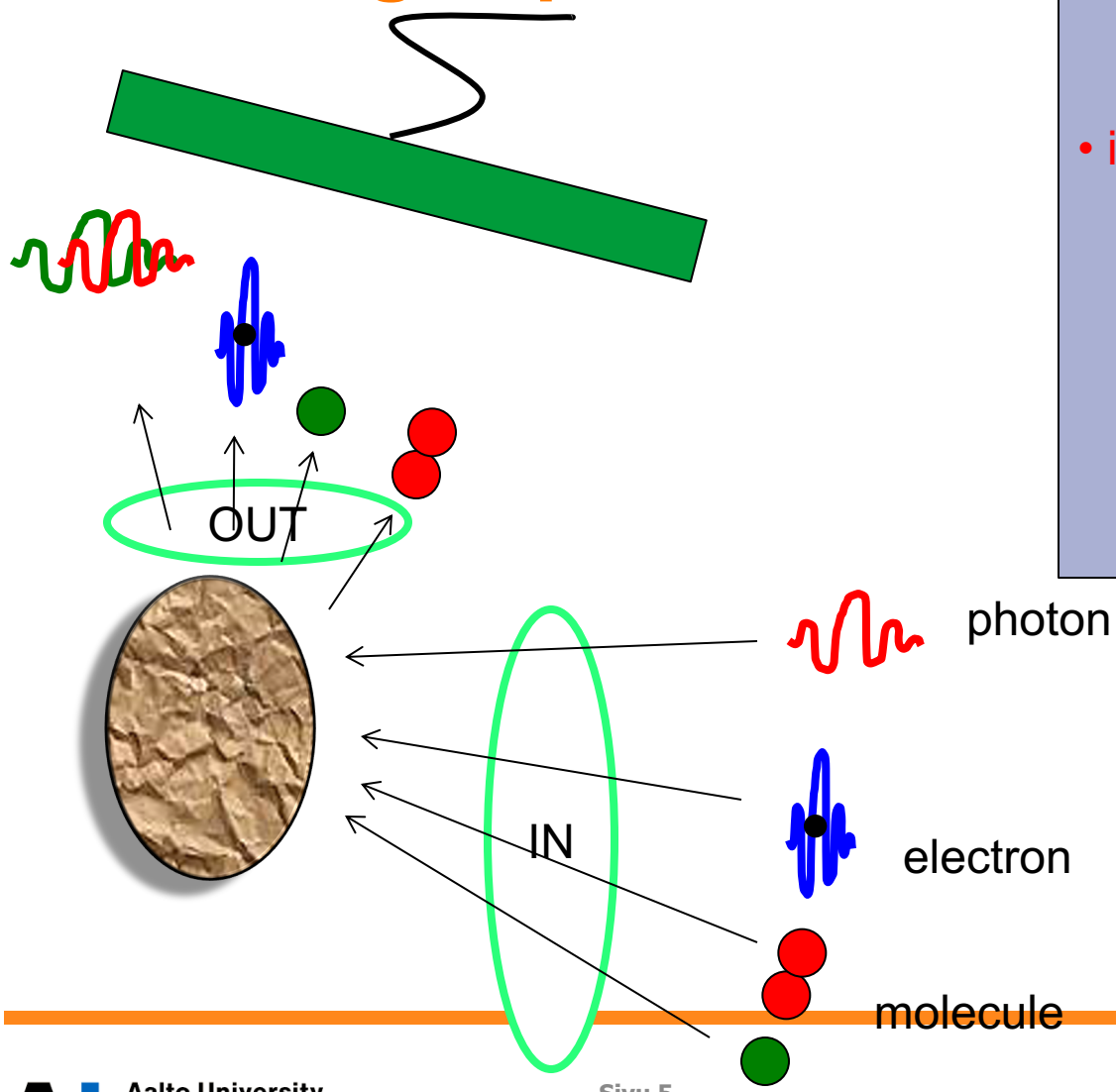
Defects, Atomic layers (>2nm)
Particles, Unknowns
Element Maps, Line Profiles
TEM Imaging
No Chemical States

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

* 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.

Scattering experiment



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

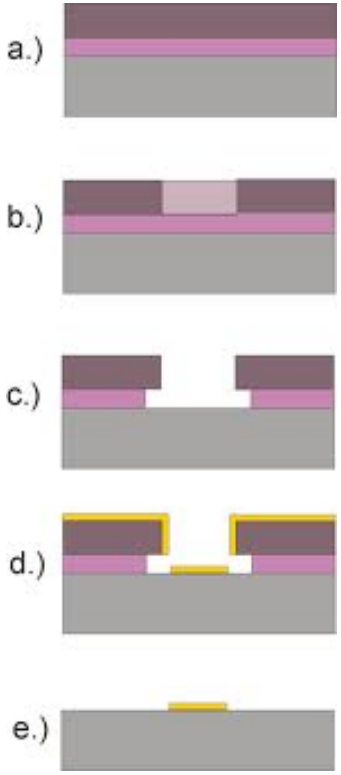
Contents

- 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 (???)

Film topograpby and thickness

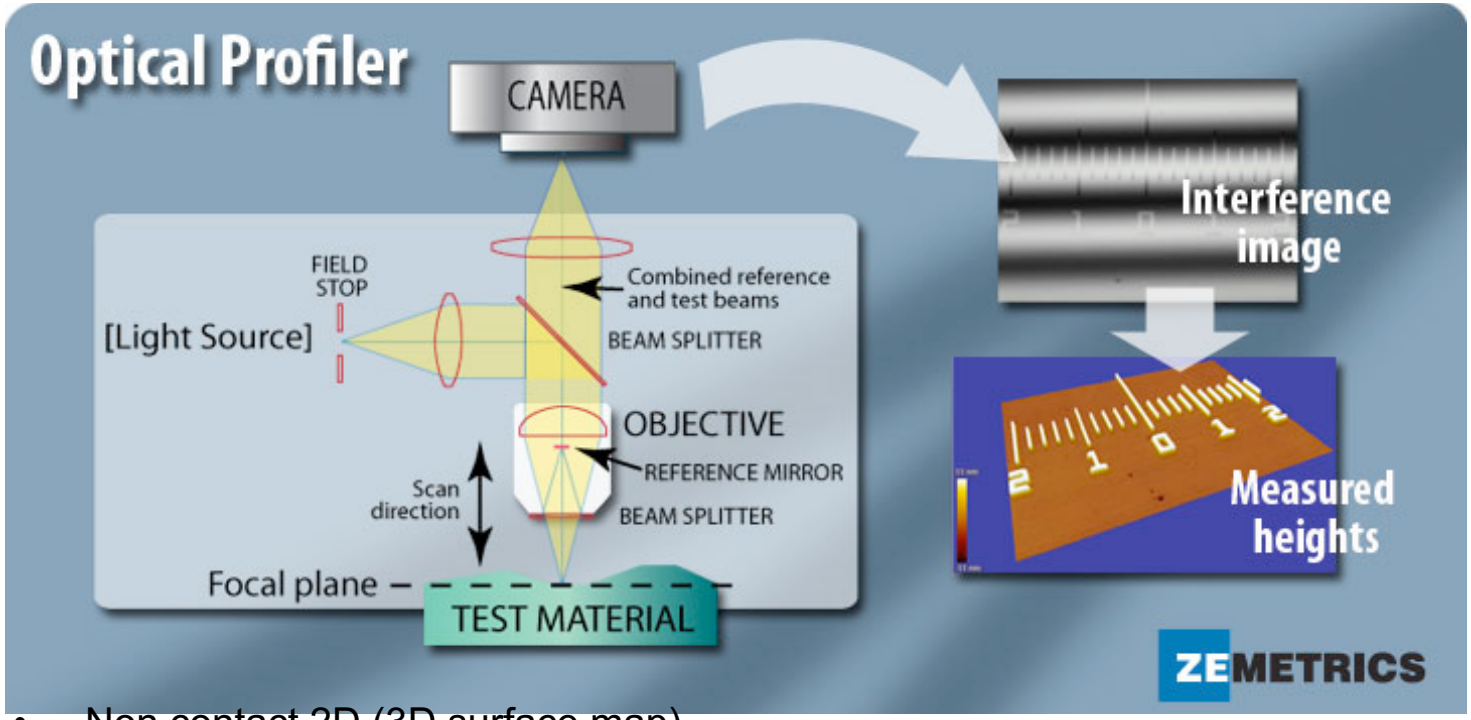
- Film thickness
  - direct measurement by definition
    - profilometer by using masked surface
    - cross section profile + microscopy
    - spectroscopy
- Contact profilometer
  - diamond tip with 1 – 50 mN load
  - tip radius 20 nm – 25 µm (12µm)
  - depth sensitivity/range 0.5 nm/60 µm

Lift-off mask lithography and contact profilometry



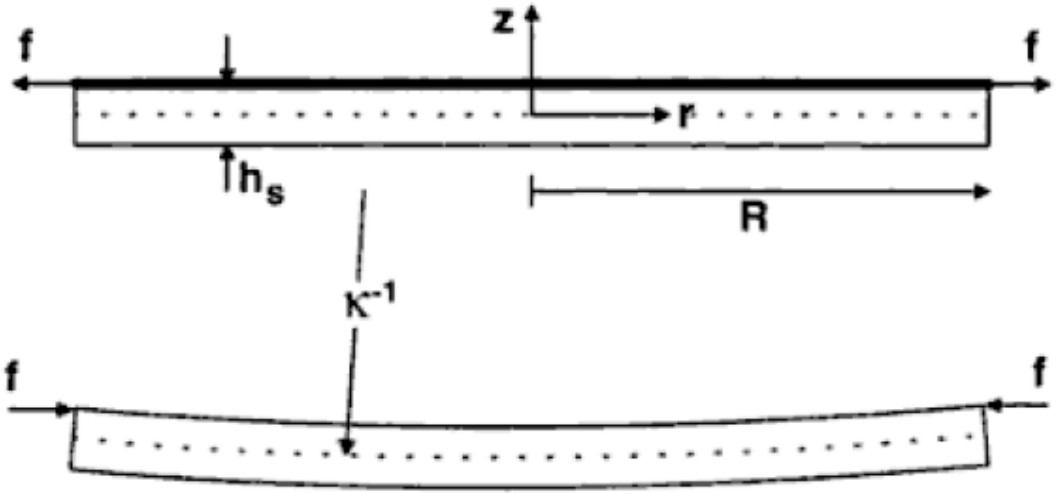
- Simple and reliable step height
- Reflecting surfaces problematic

Optical profilometer



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

Internal stress of thin film-substrate curvature by profilometer



Stoney equation
substrate modulus

$$\sigma_m = \frac{M_s h_s^2}{6 h_f} \left\{ \frac{1}{\rho_2} - \frac{1}{\rho_1} \right\}$$

radius of curvature after and intially

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 (???)

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)

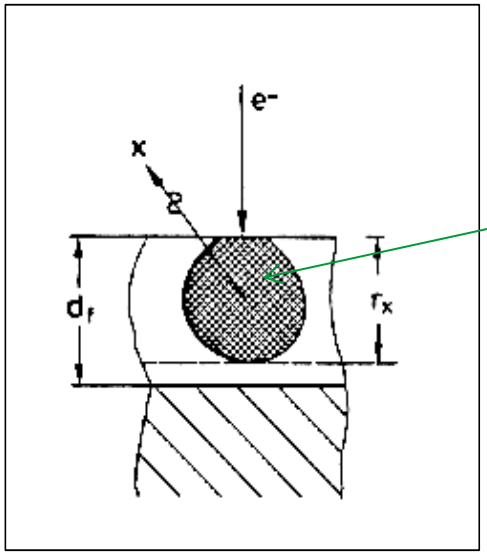
https://www.youtube.com/watch?v=KfQ4VNpWN4M

E. Heikinheimo

Aalto - Dept. of MS & E - 2011

Aalto University
School of Chemical Technology

Thin-film analysis (I)

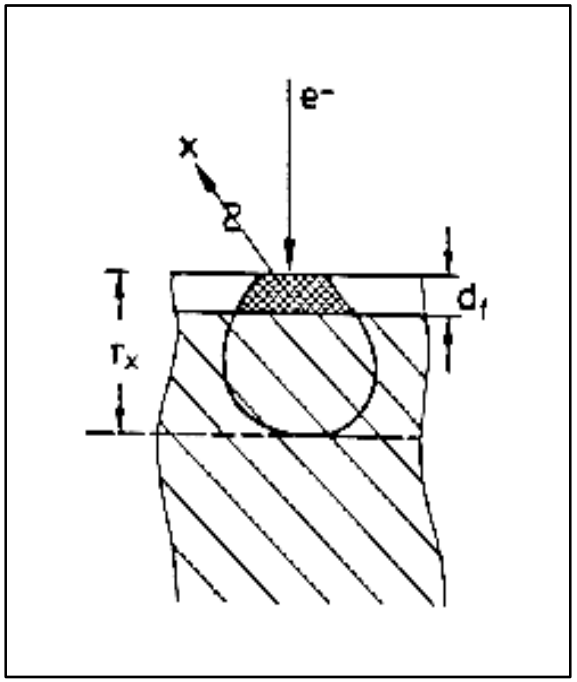


Excitation volume

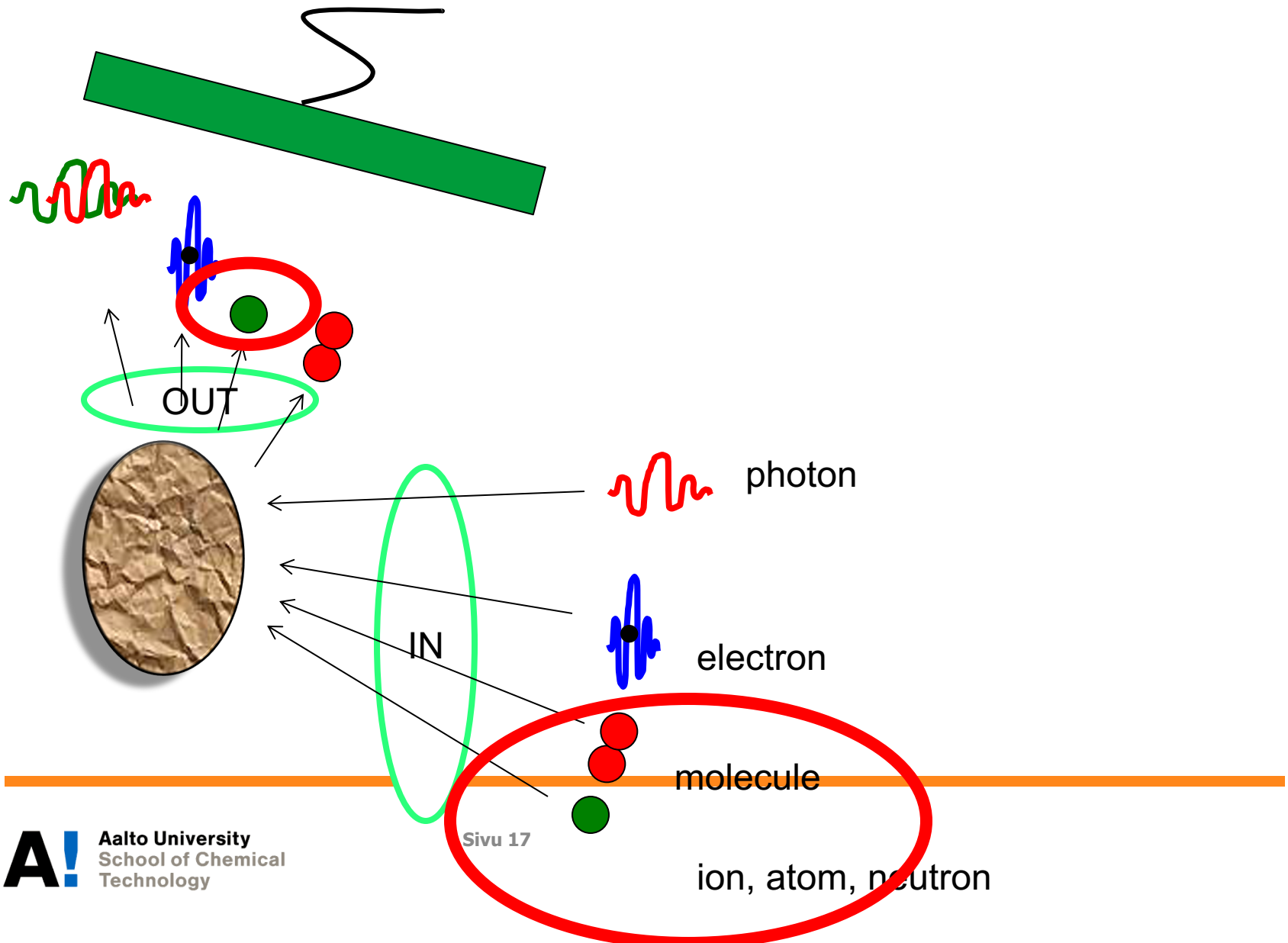
* Thickness of surface film $d_f > r_x$, substrate does not influence
* Film can be processed as bulk, with normal matrix correction program
* d_f = 0.2…2 µm (e.g. by adjusting beam energy)

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.

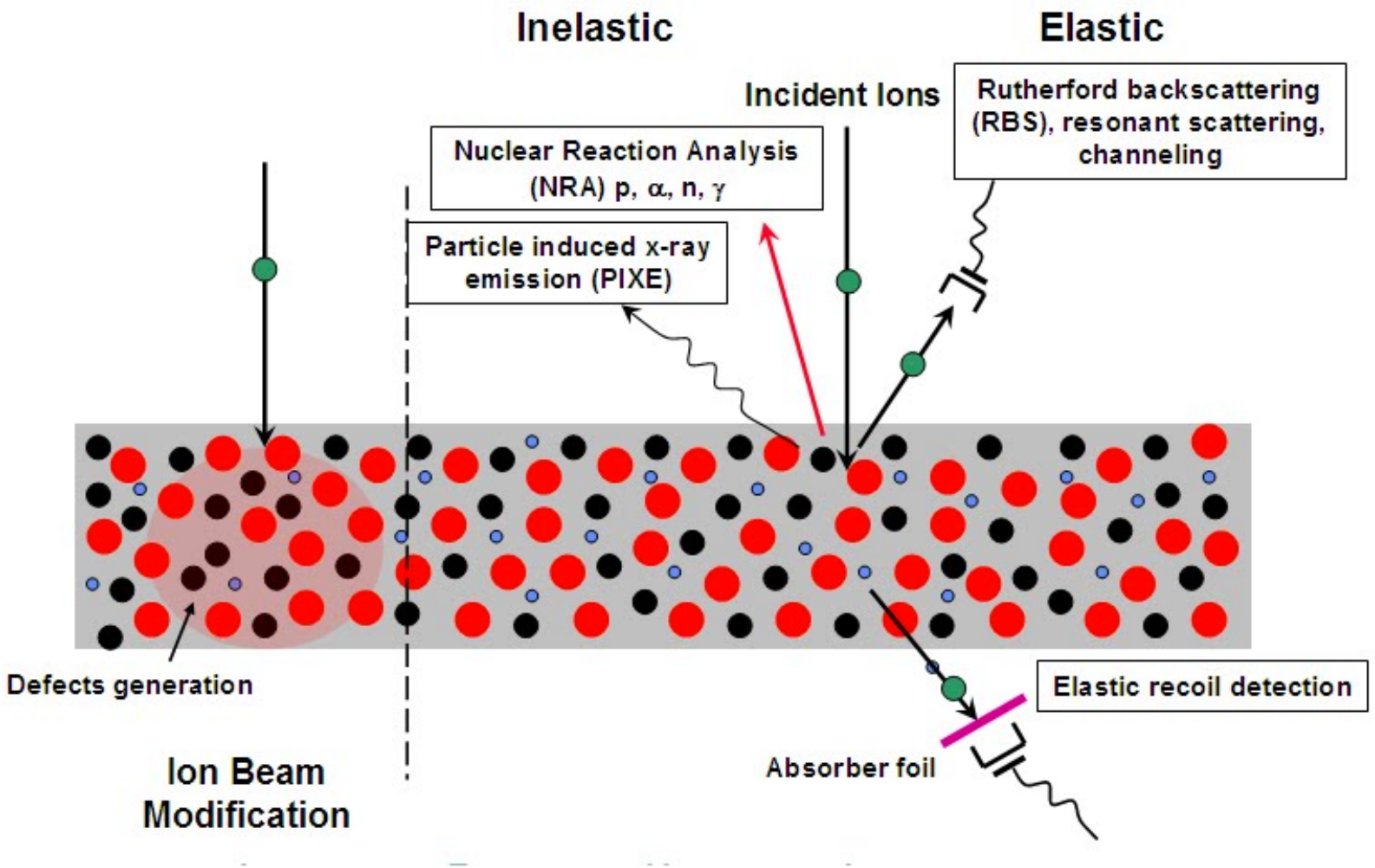


Scattering experiment – Ion in Ion out

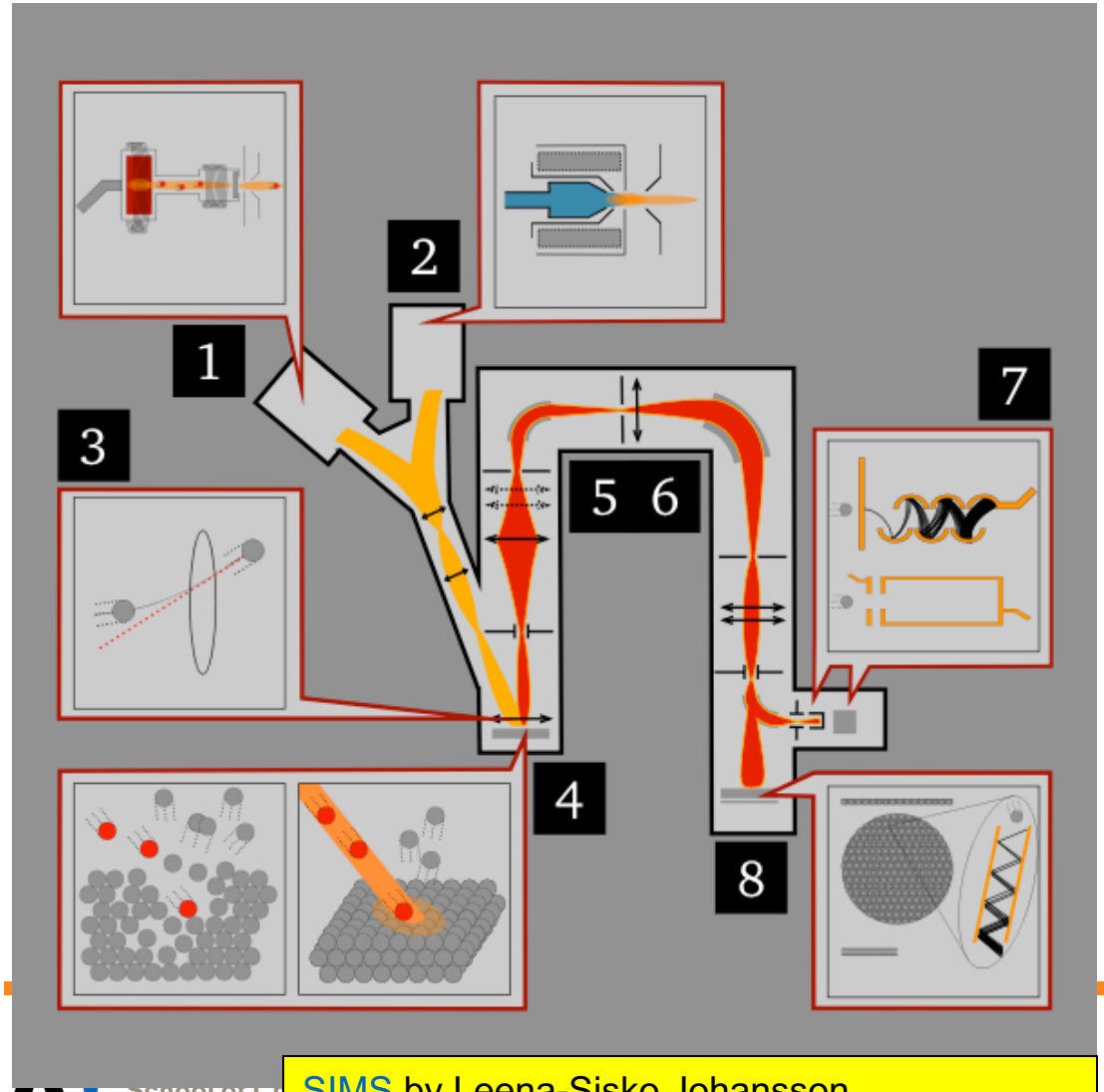


Ion Beam Analysis Techniques

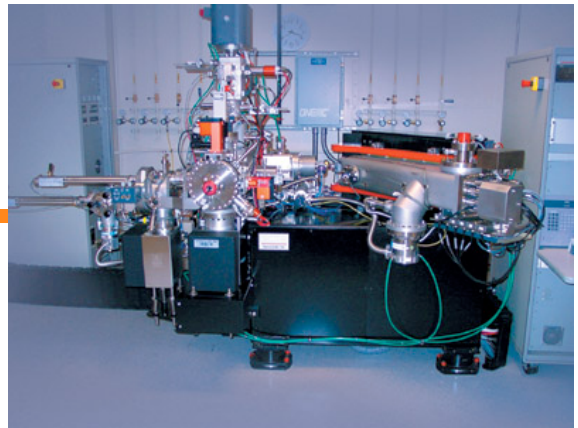
For a detail discussion on Ion Beam Analysis and the various techniques, please see IBA lecture by K. M. Yu.



Secondary Ion Mass Spectrometry - SIMS

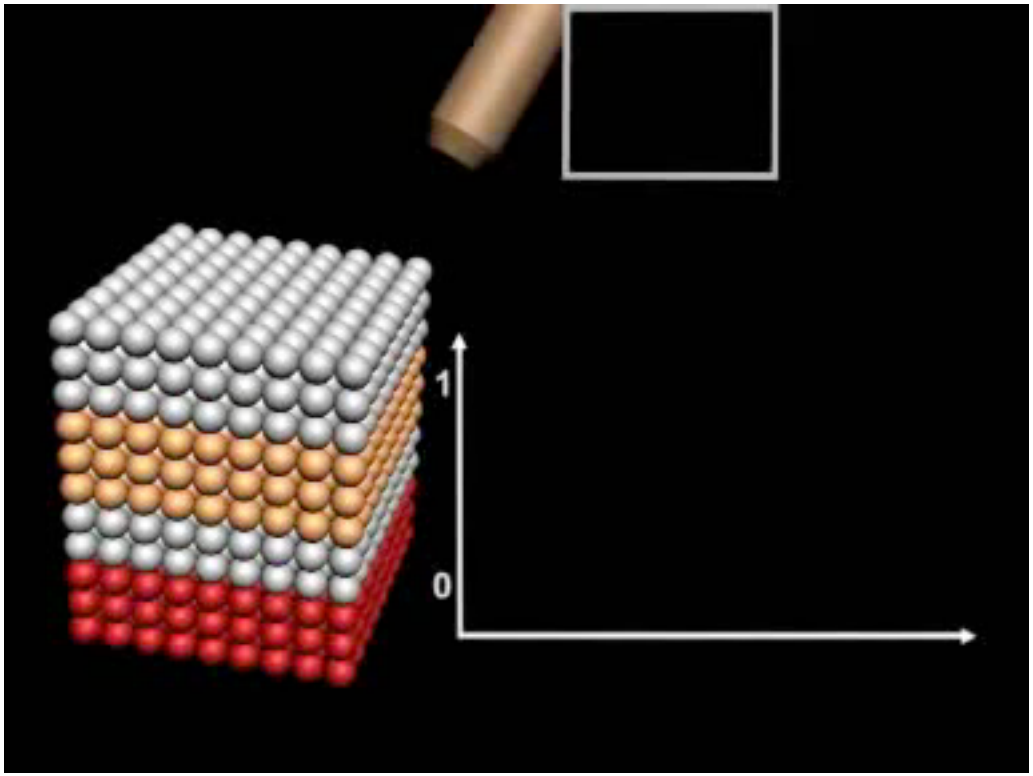


1. Cesium ion source
2. Duoplasmatron
3. Electrostatic lens
4. Sample
5. Electrostatic sector - ion energy analyser
6. Electromagnet - mass analyser
7. Electron multiplier / Faraday cup
8. Channel-plate / Fluorescent screen - ion image detector

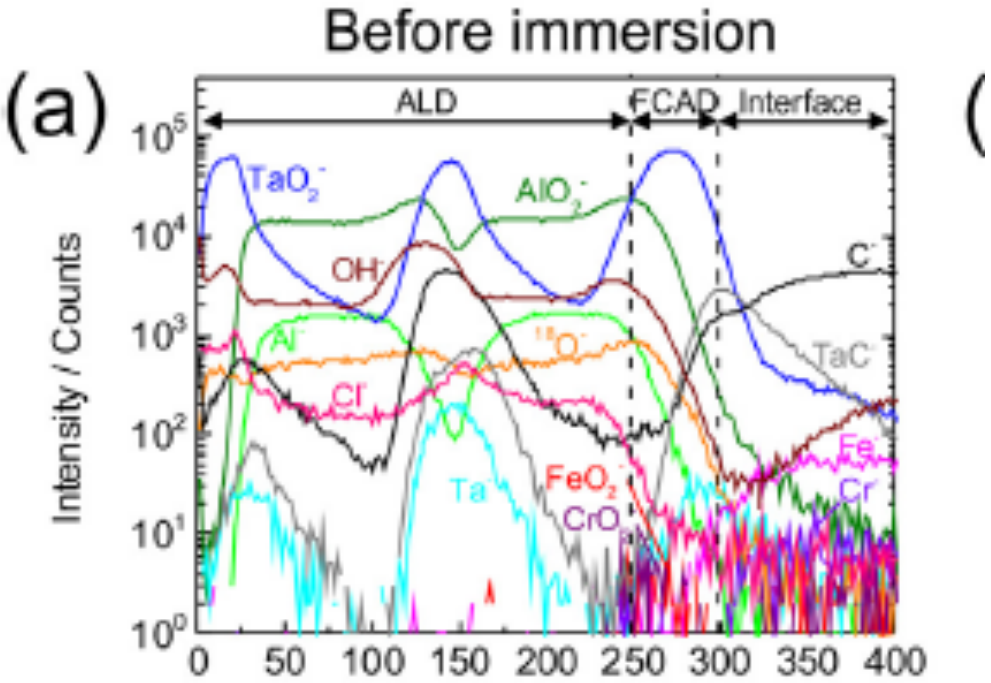


SIMS by Leena-Sisko Johansson

SIMS

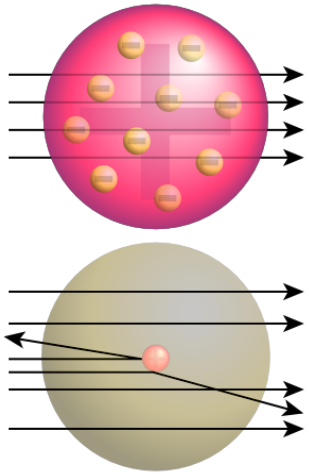


SIMS - also molecular ions

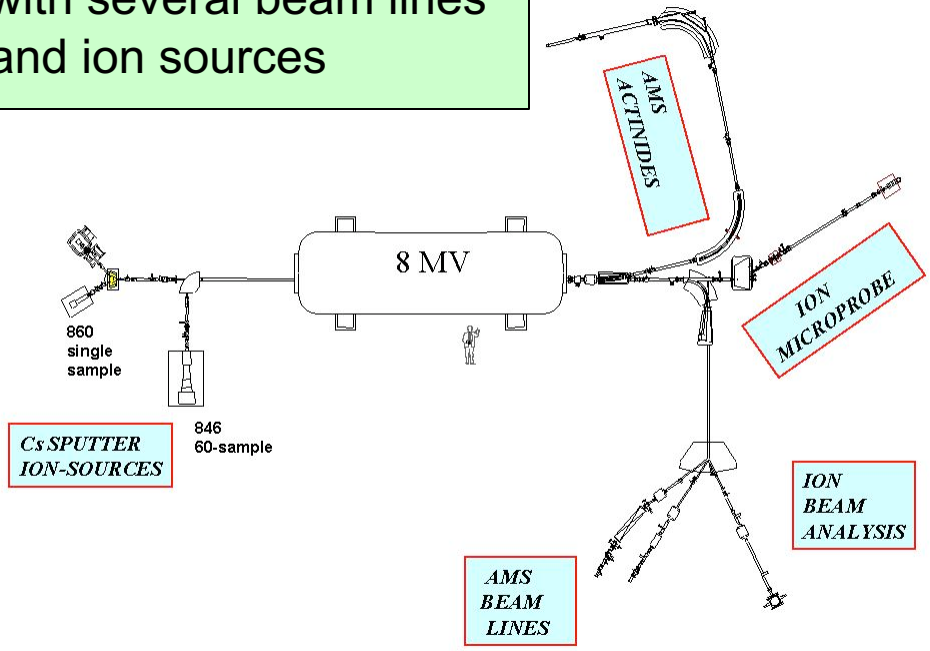


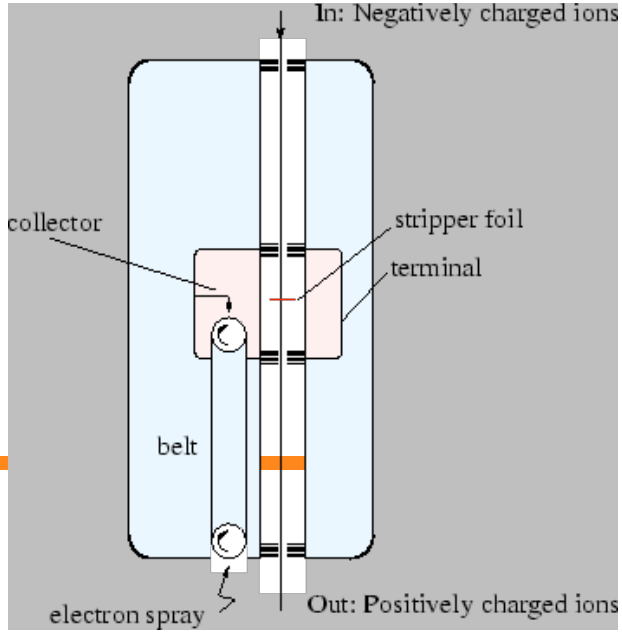
Ion beam analysis

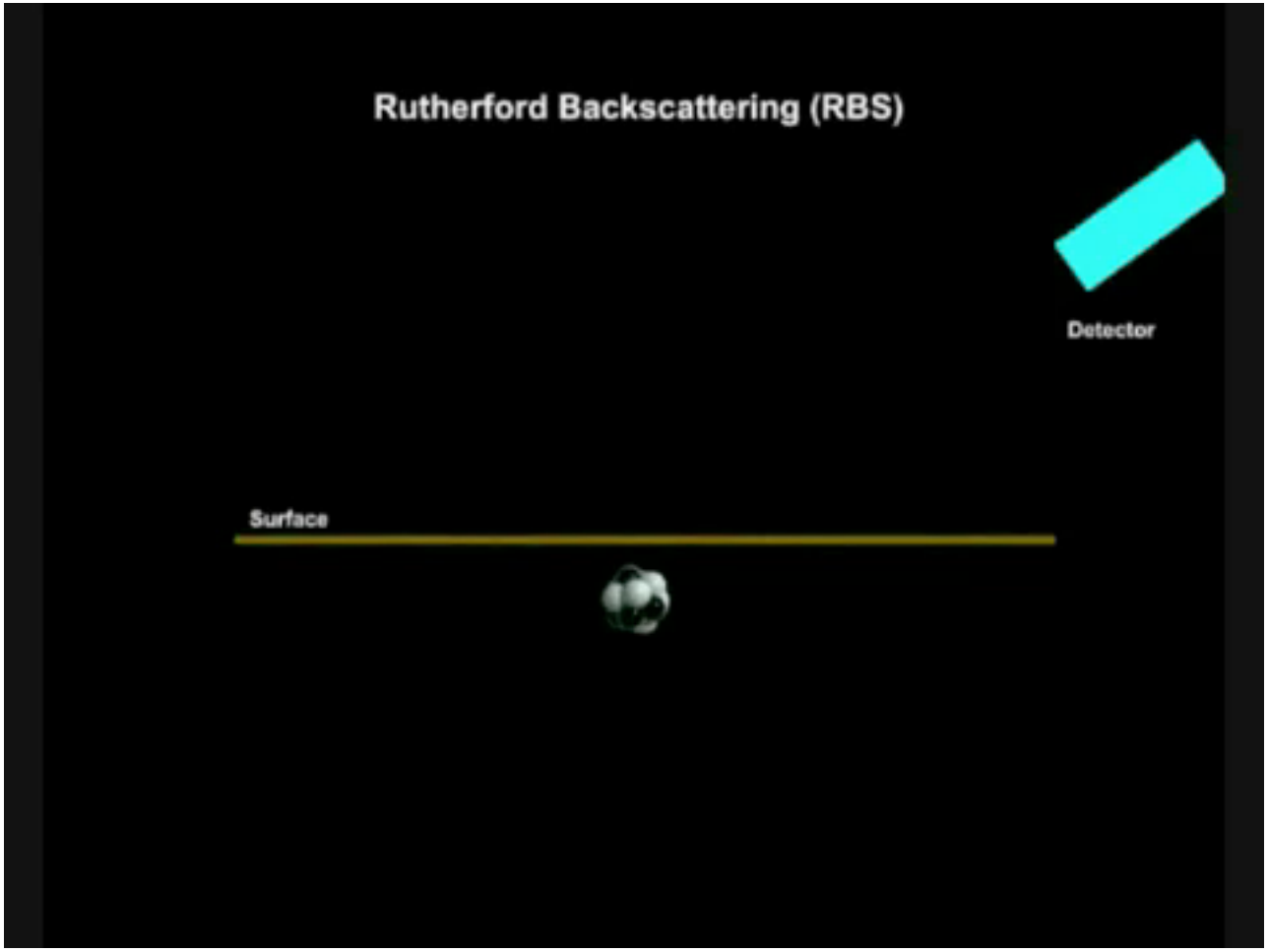
- Backscattering spectroscopy



Ion beam accelerator with several beam lines and ion sources






Rutherford Backscattering (RBS)
Detector
Surface

Ion beam analysis

- Backscattering spectroscopy

recoil energy -> what element

atomic mass of element

Probability of recoil -> amount of element

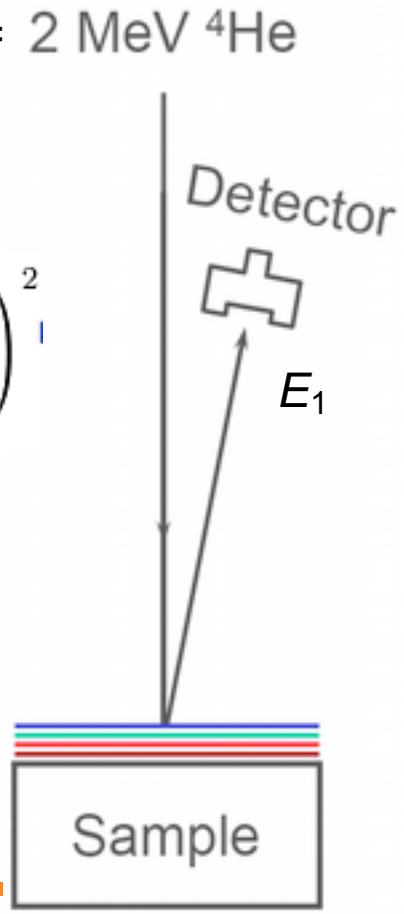
Kinetic energy loss inside material – stopping -> depth scale

$E_1 = k * E_0$

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

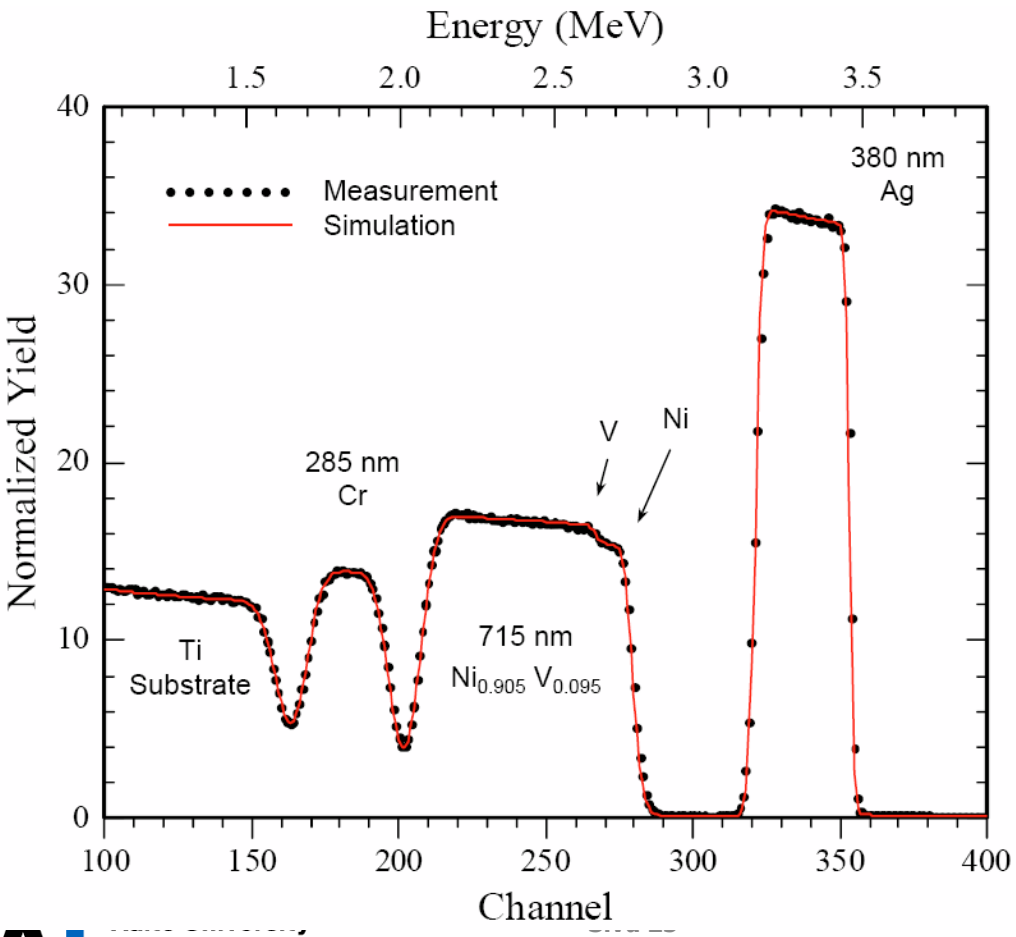
$$\frac{d\omega}{d\Omega} = \left(\frac{Z_1 Z_2 e^2}{4E_0} \right)^2 \frac{1}{(\sin\theta/2)^4}$$

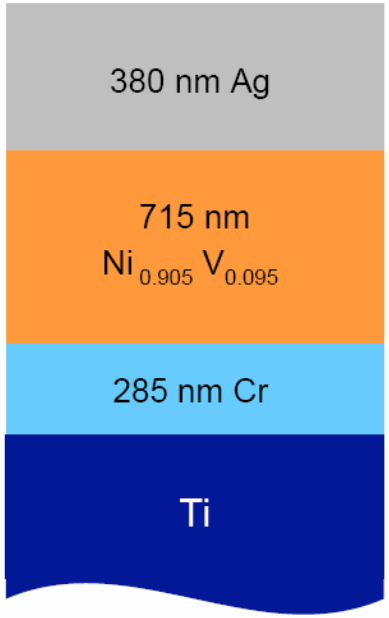
$$S(E) = -\frac{dE}{dx}$$



Ion beam analysis

- Backscattering spectroscopy

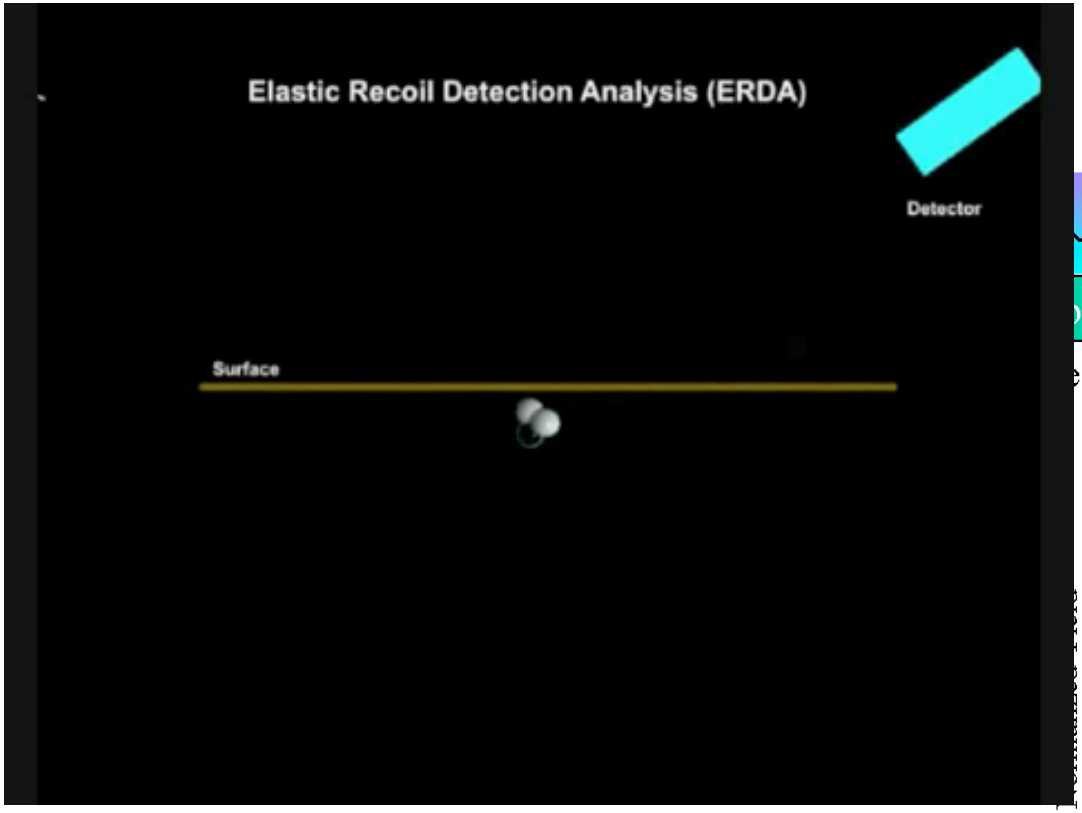


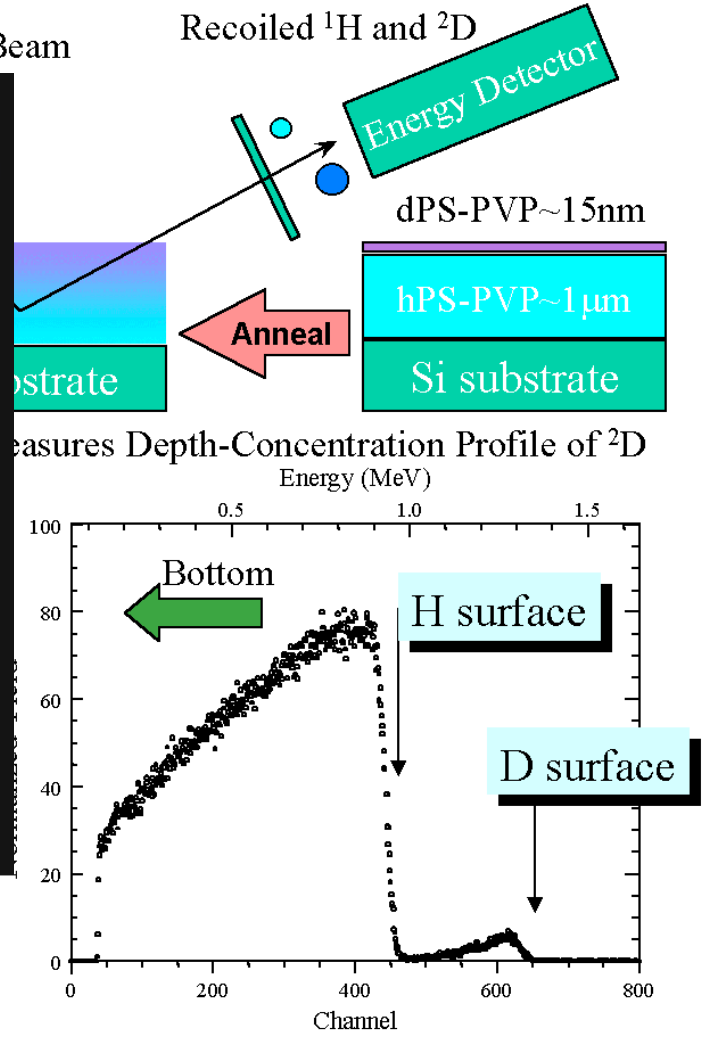


Ion beam analysis

$^4He^+$ ion

Forward Recoil Spectrometry (FRES)





$^{63}Cu^{+}$ ion

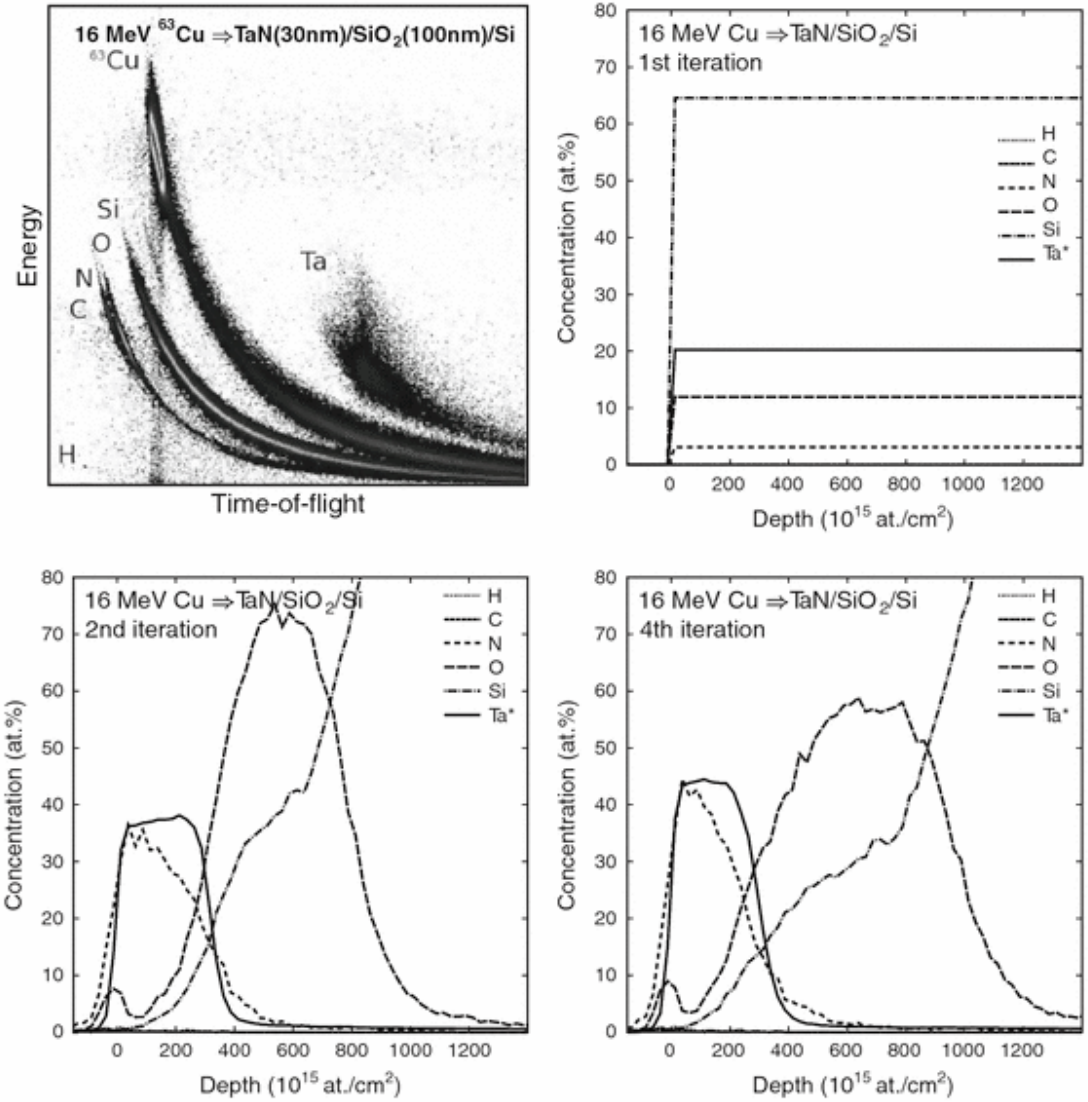
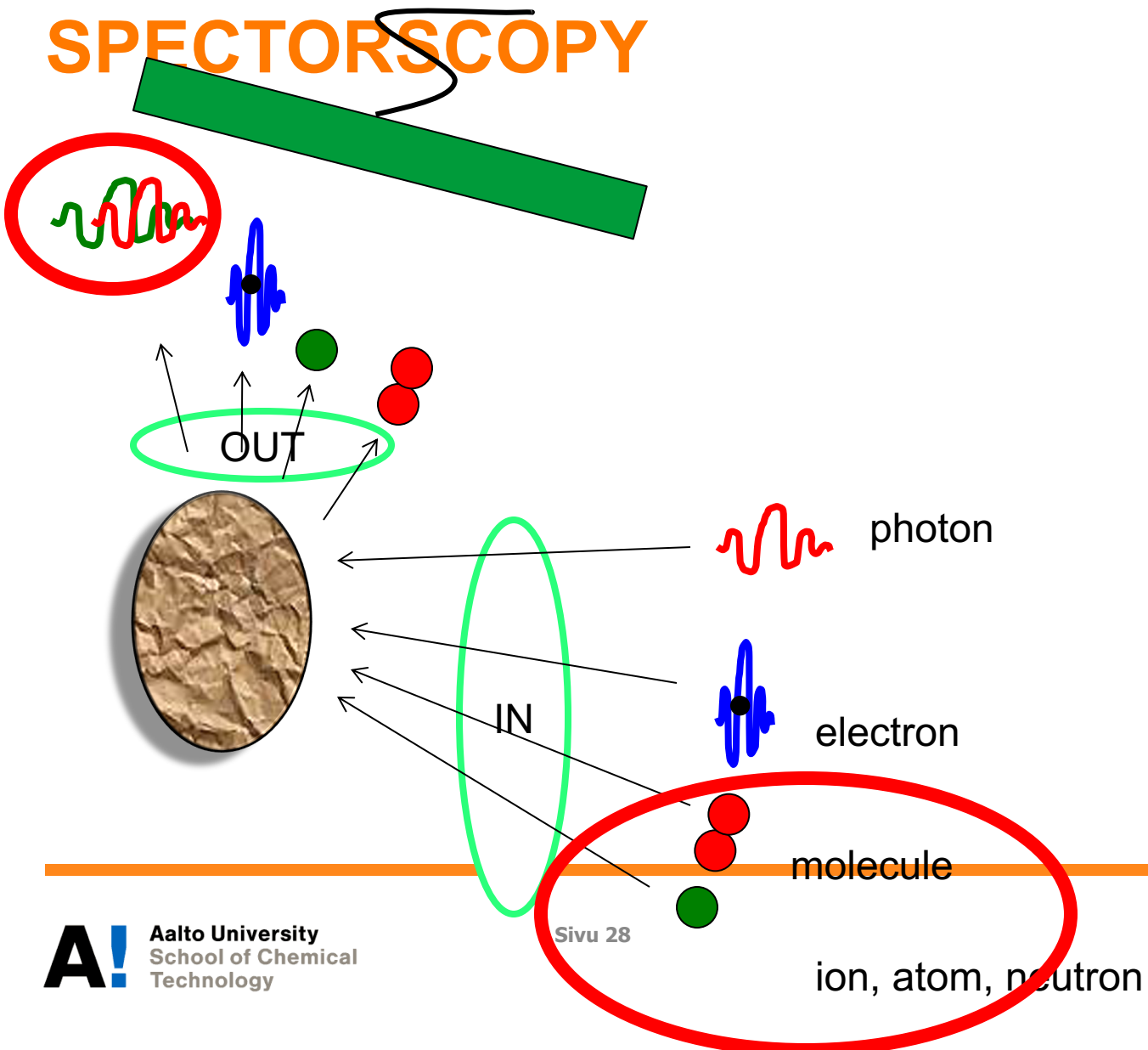


Fig. 5 Iterative procedure for analysis of a HI-ERDA measurement without prior knowledge of the sample structure. See the text for a detailed description of the analysis

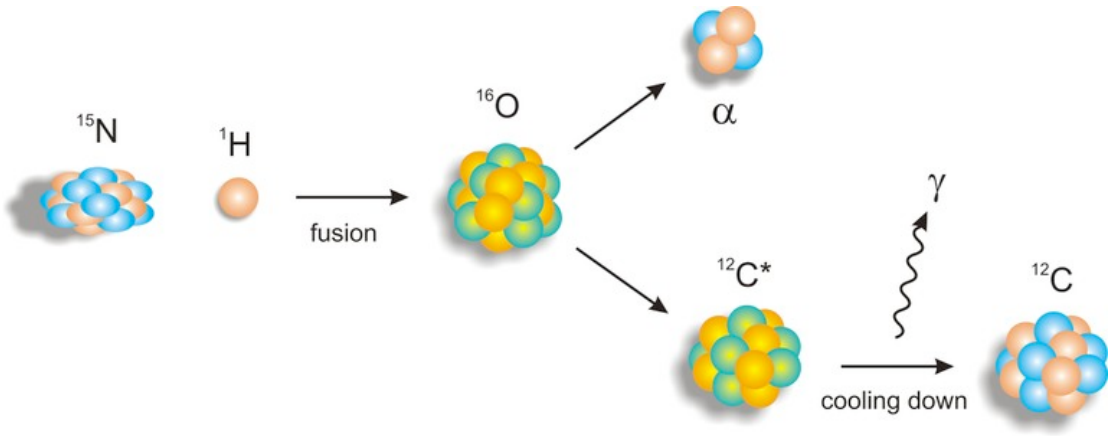
Scattering experiment – ION SPECTORSCOPY



Ion beam analysis

- Nuclear Reaction Analysis NRA

  Detection of **hydrogen** – depth distribution in surface



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

E_{res} = 6.385 MeV

Contents

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

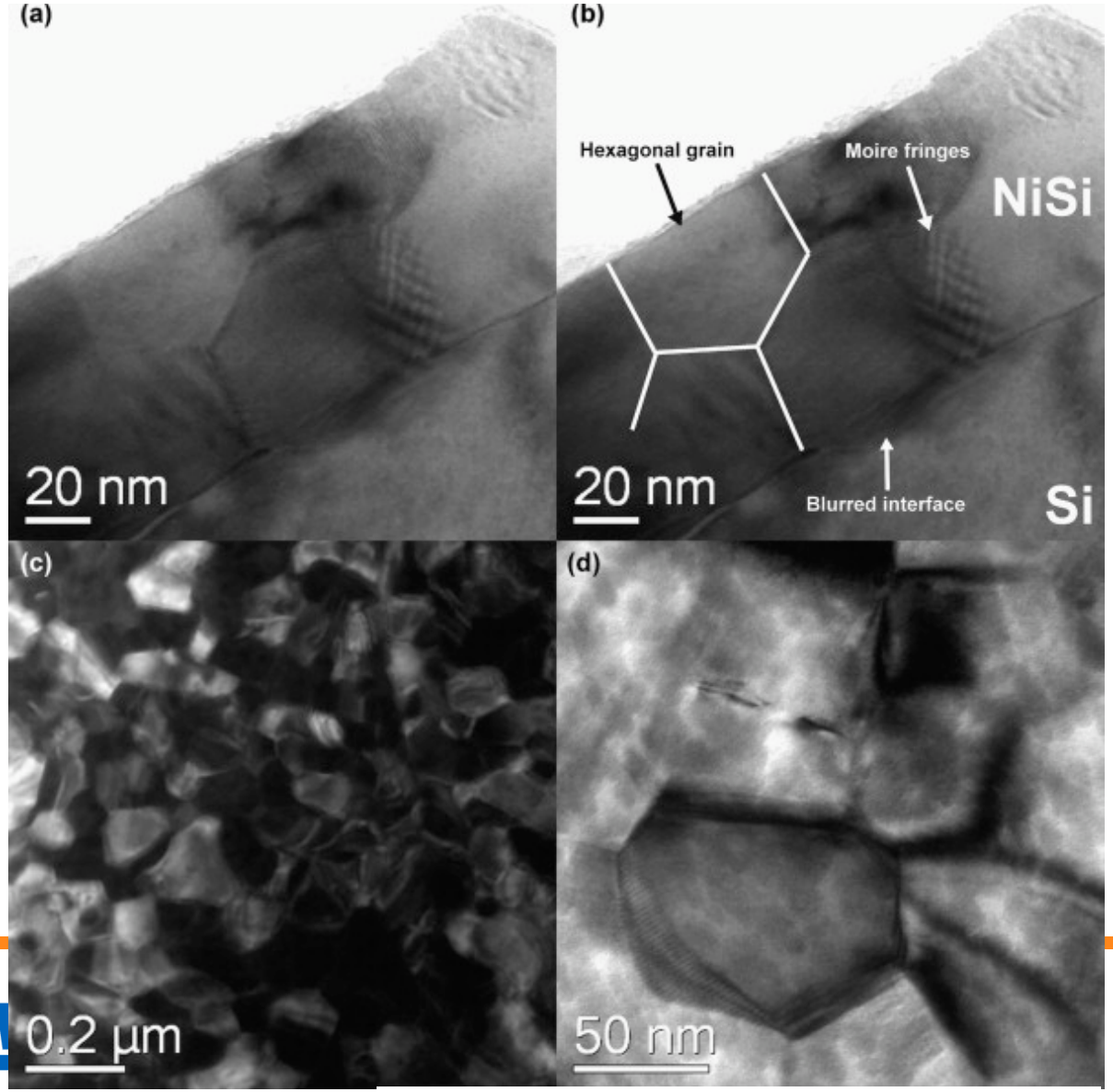
Microstructure

- Crystallinity
- crystal size
- orientation – texture
- Defects

Transmission electron microscopy TEM

Atomic level
resolution
0.7 Å

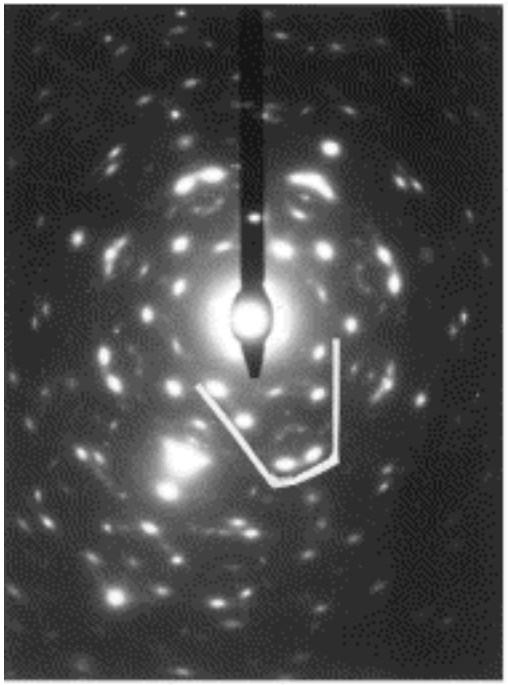
NiSi thin film



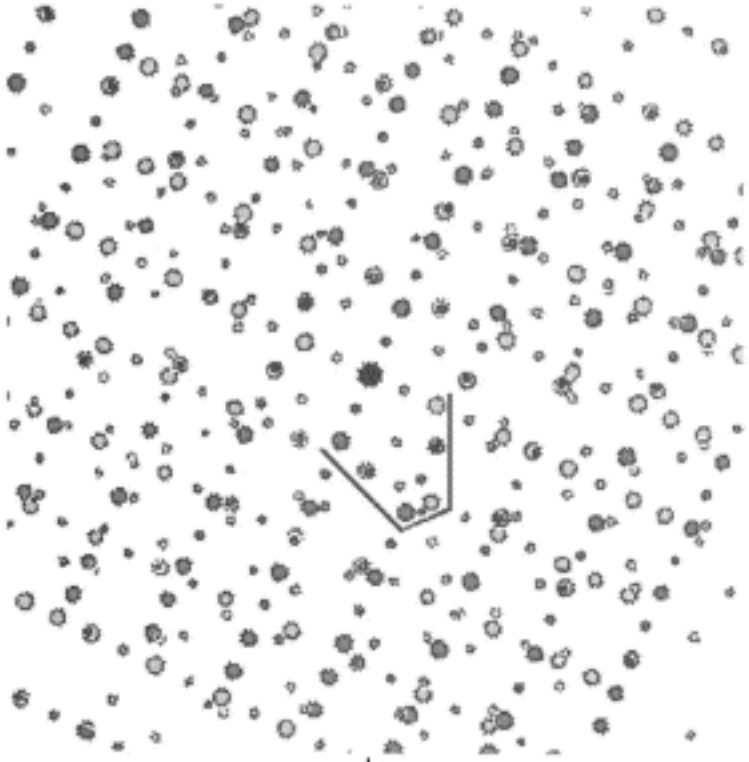
Results from TEM analysis of NiSi thin films: (a) XTEM highlighting equiaxed grains in the NiSi film in which Moiré (interference) fringes due to orientation differences between grains can be observed; (b) notable features in the as-obtained image (a) are indicated; (c) plan view, elastic hollow cone 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.

M. Bhaskaran et al. / Micron 40 (2009) 11–14

Electron diffraction



a



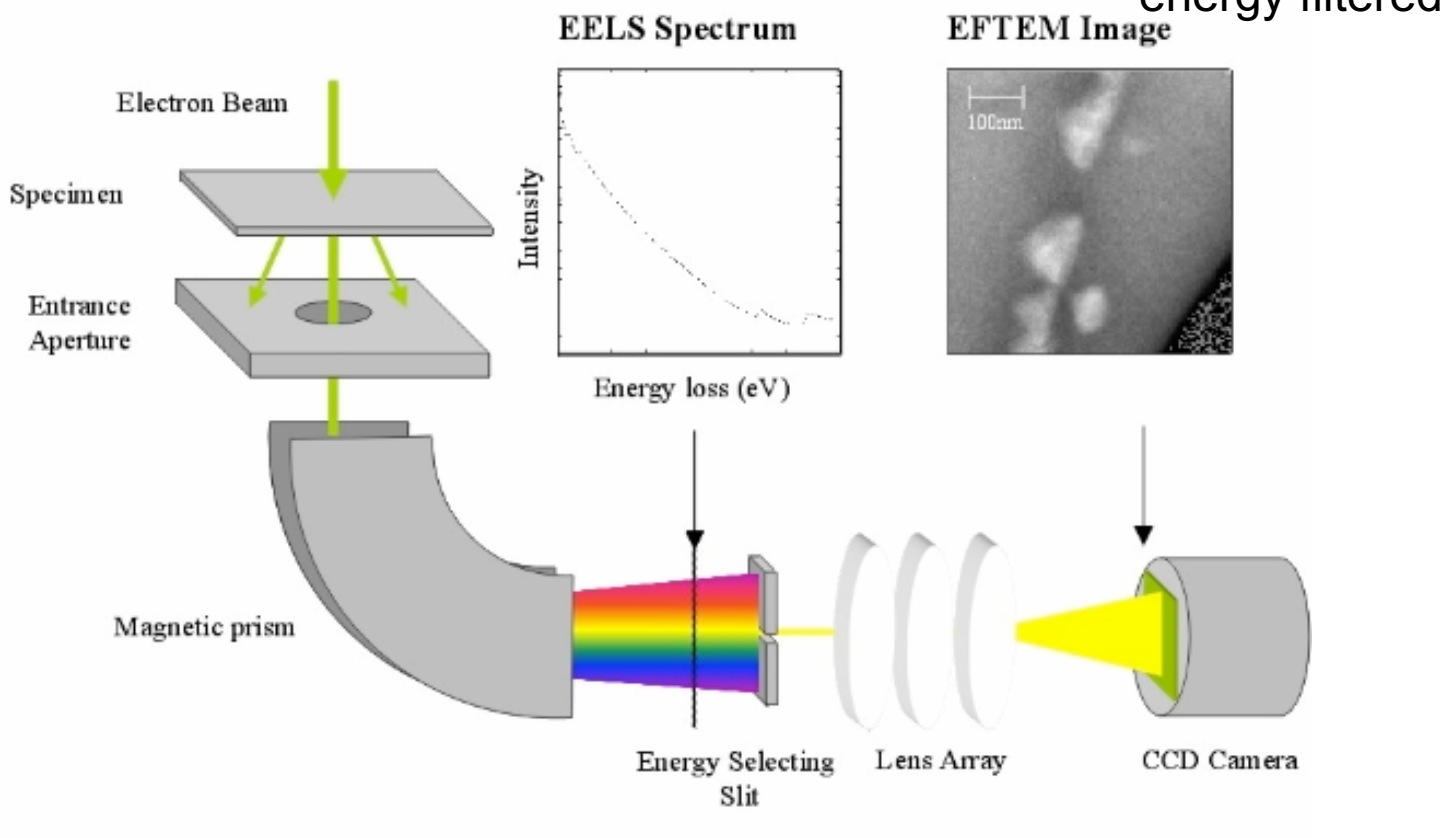
b

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°.

D. Hofman et al. / Ultramicroscopy 81 (2000) 271–277

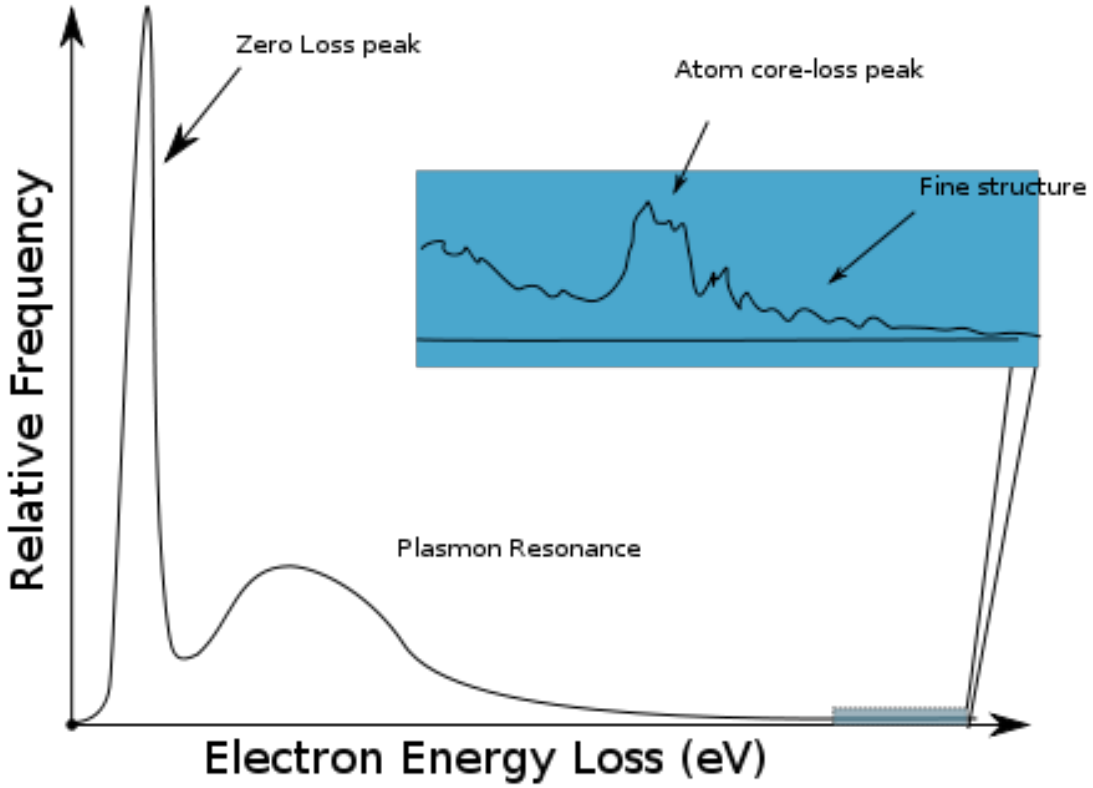
Electron energy loss spectroscopy EELS

energy filtered



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

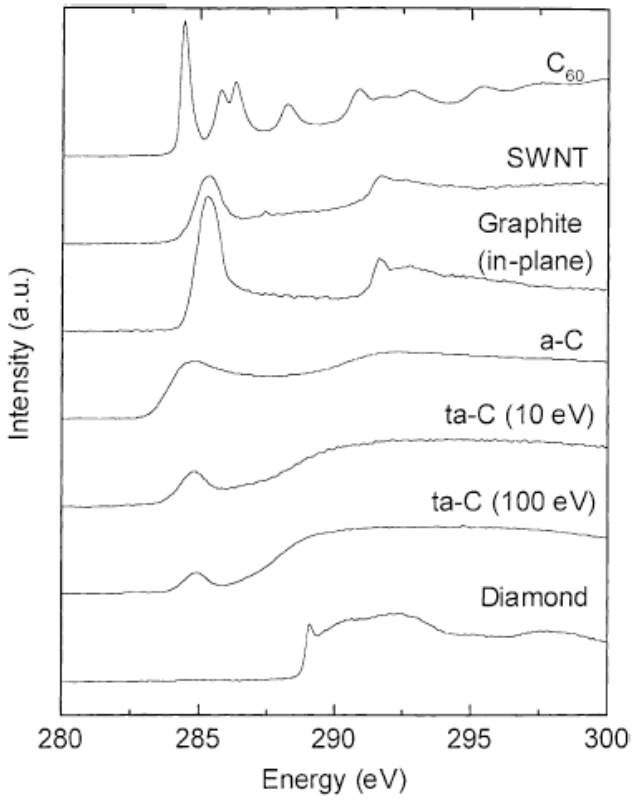


Fig. 29. Carbon K edge electron energy loss spectra of various carbon phases, after Waidmann et al. [196].

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

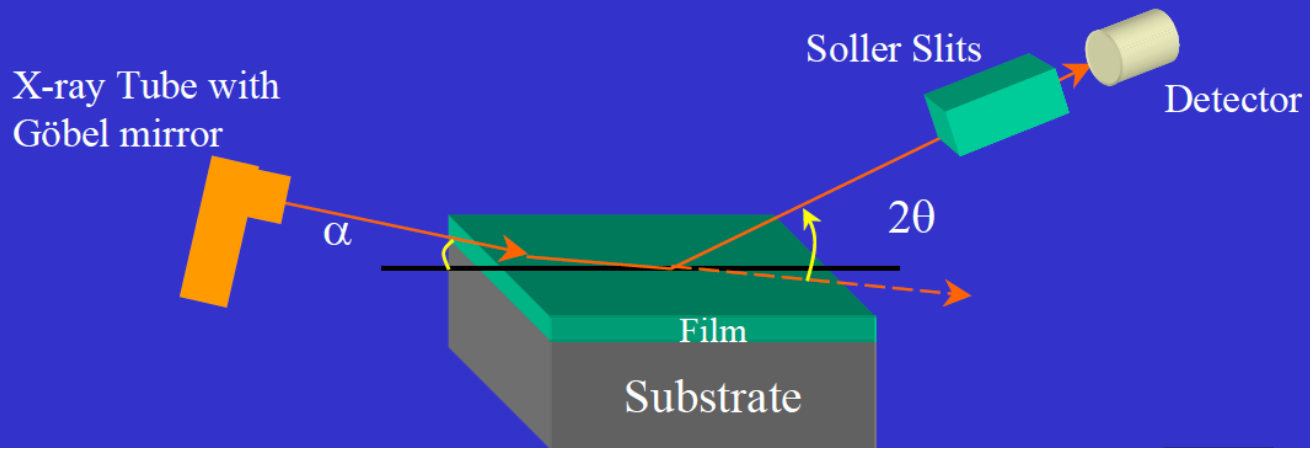
Glancing Angle X-ray Diffraction (GAXRD)

- 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/GA**XRD**.pdf*

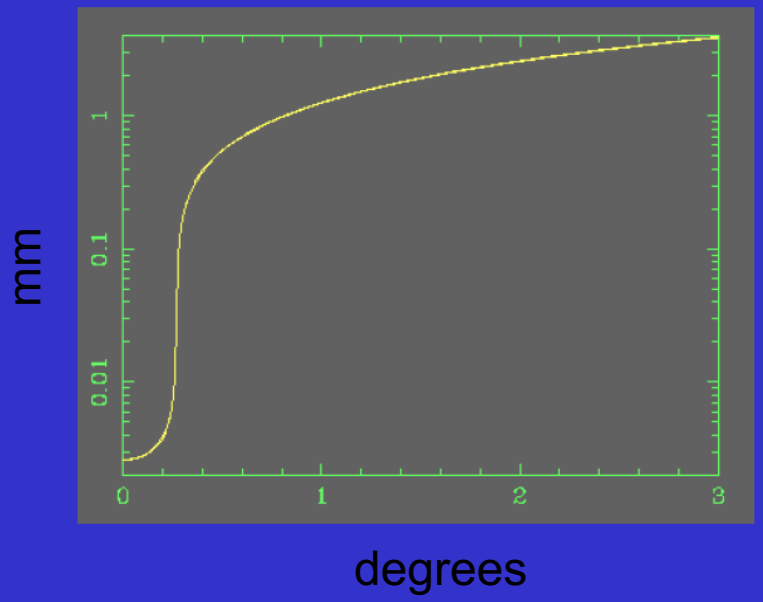
Technique

- 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.



www1.chm.colostate.edu/Files/GA**XRD**.pdf

Penetration Depth Vs Angle of Incidence

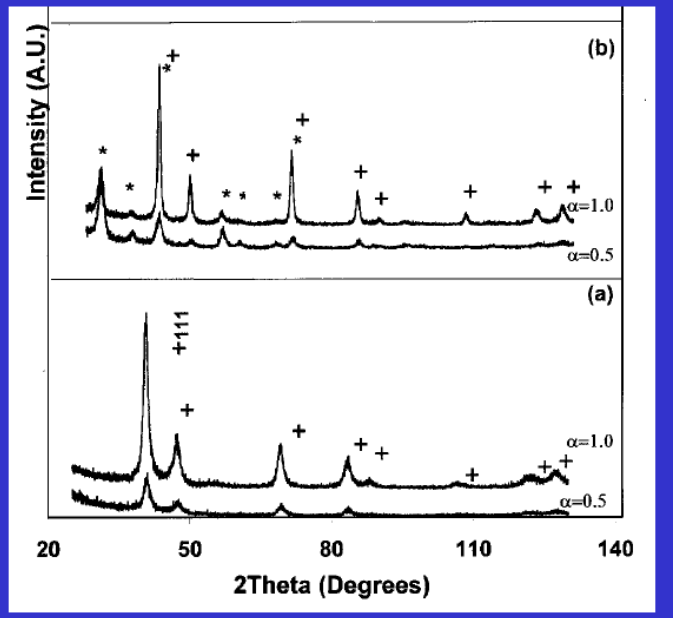


This figure shows penetration depth as a function of incident angle for Si_3N_4 for CuK_α (λ=0.154 nm) radiation

*www1.chm.colostate.edu/Files/GA**XRD**.pdf*

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



*www1.chm.colostate.edu/Files/GA**XRD**.pdf*

X-Ray Reflectivity XRR

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

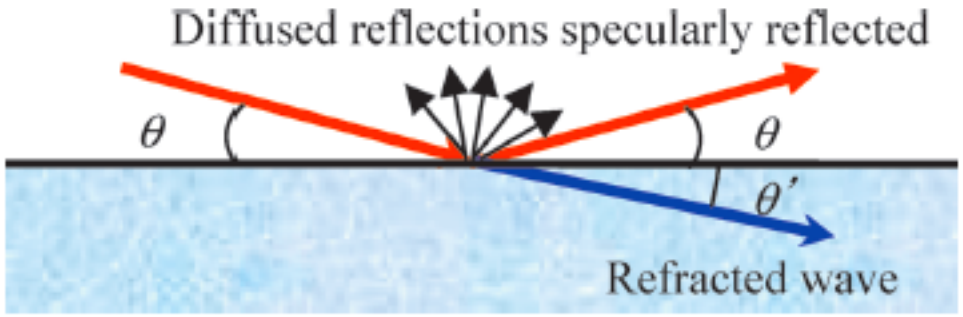
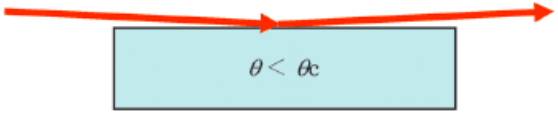


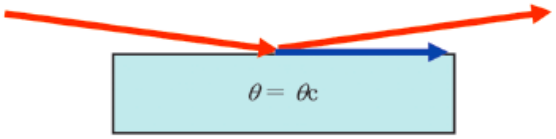
Fig. 1. Reflection and refraction of X-rays on material surface.

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

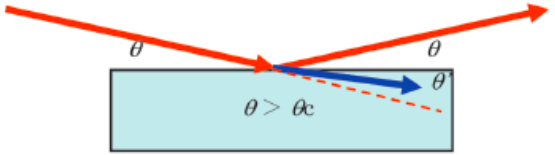
X-Ray Reflectivity XRR



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



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



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.

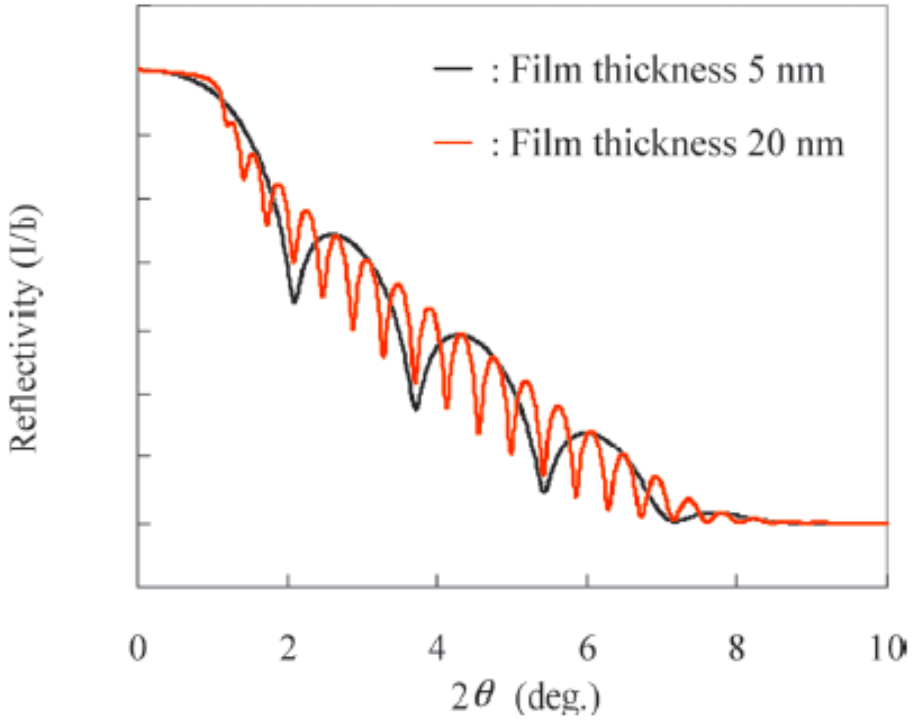


Fig. 4. Reflectivity of Au film on Si substrate.

Aalto University
School of Chemical Technology

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

X-Ray Reflectivity XRR

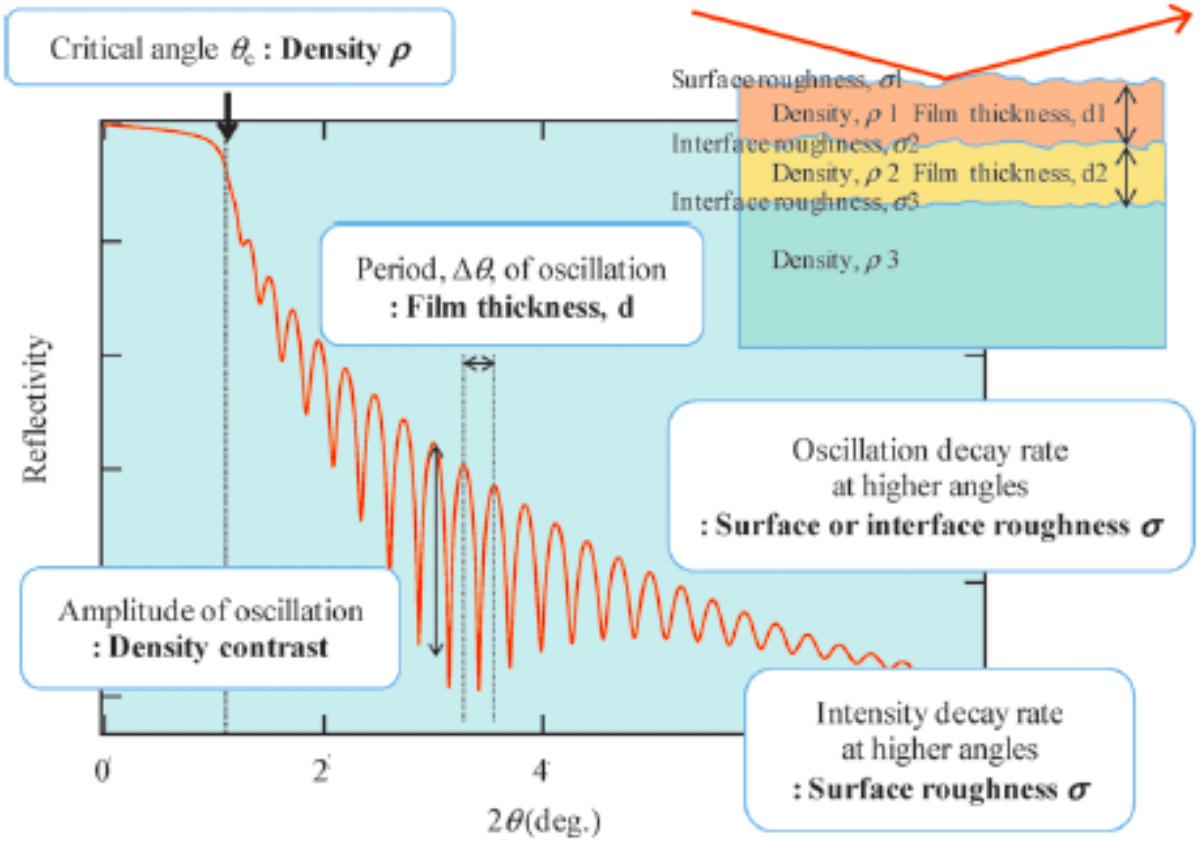


Fig. 8. Information provided by X-ray reflectivity profile.

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

X-Ray Reflectivity XRR

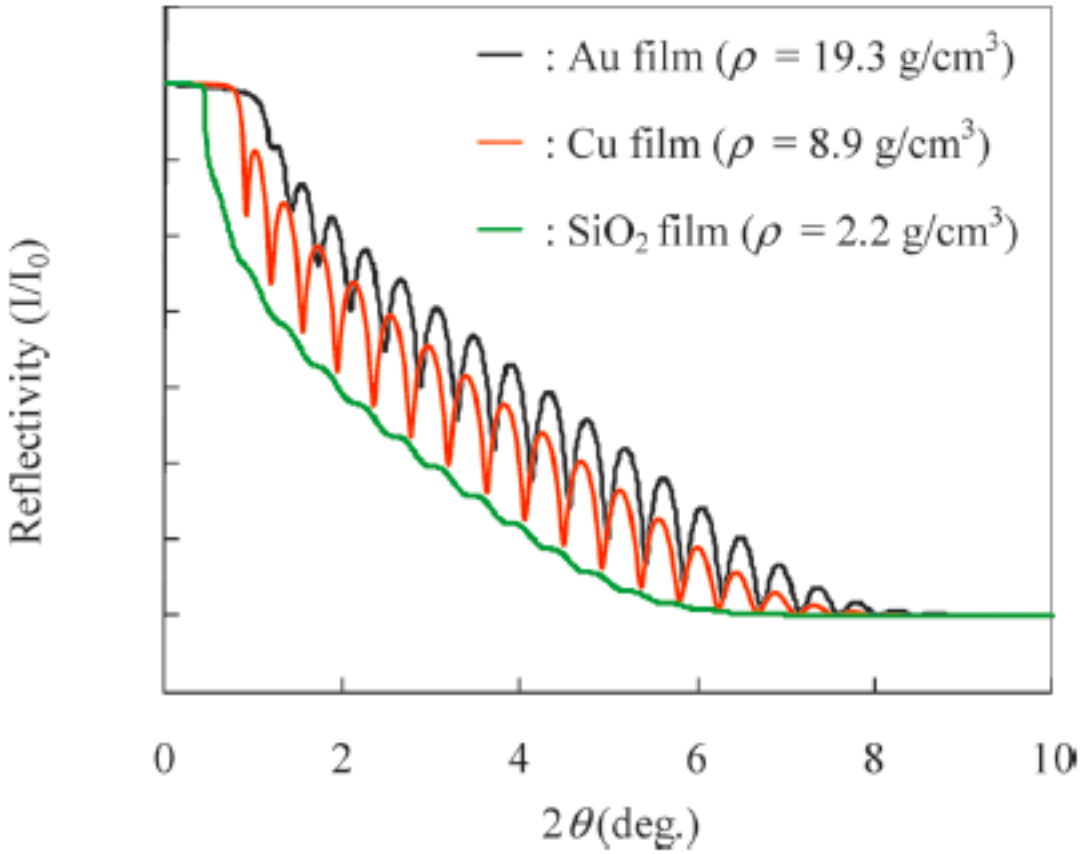


Fig. 5. X-ray reflectivity curves of Au, Cu and SiO_2 film on Si substrates (film thickness is 20 nm).

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

SmartLab

X-RAY DIFFRACTOMETER

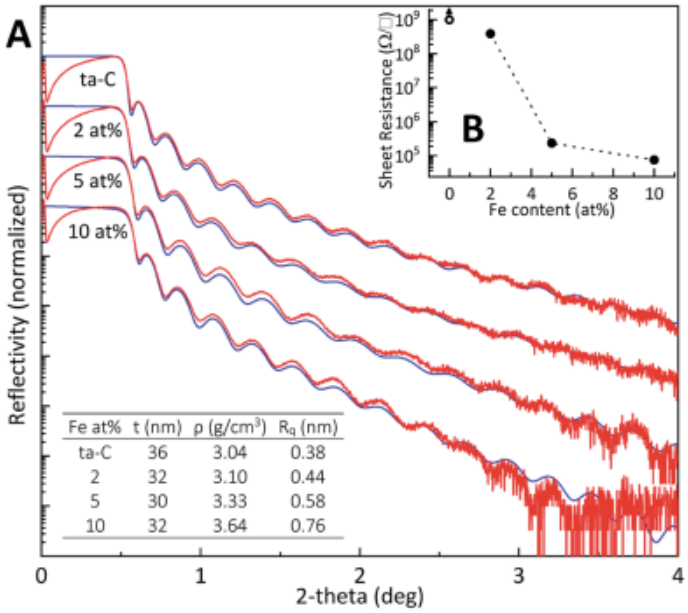
Symmetric "coupled" scanning

Rigaku

Leading With Innovation

X-ray Reflectivity (XRR)

Fe-doped carbon films

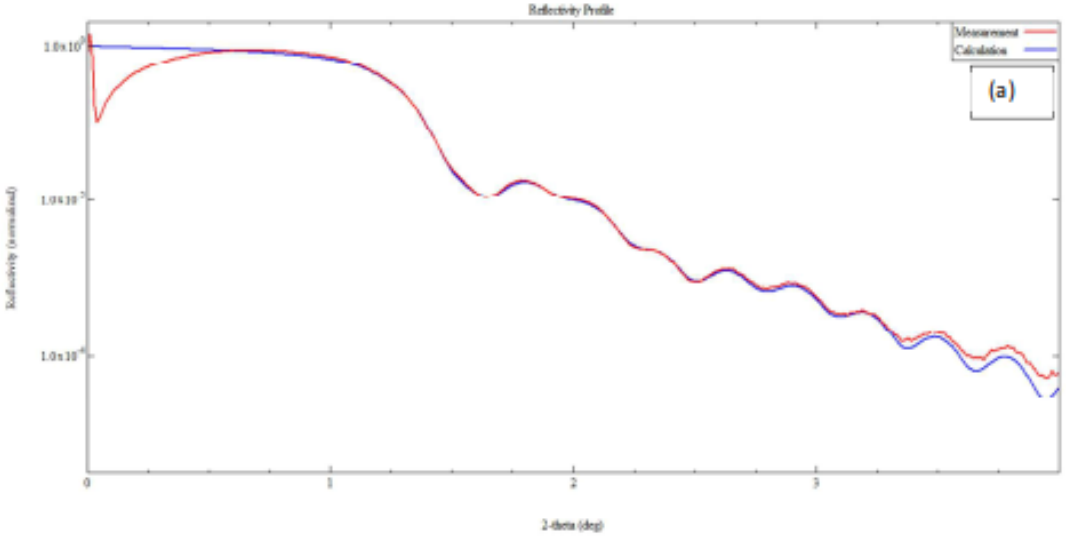


Fe at%	t (nm)	ρ (g/cm³)	R_q (nm)
ta-C	36	3.04	0.38
2	32	3.10	0.44
5	30	3.33	0.58
10	32	3.64	0.76

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.

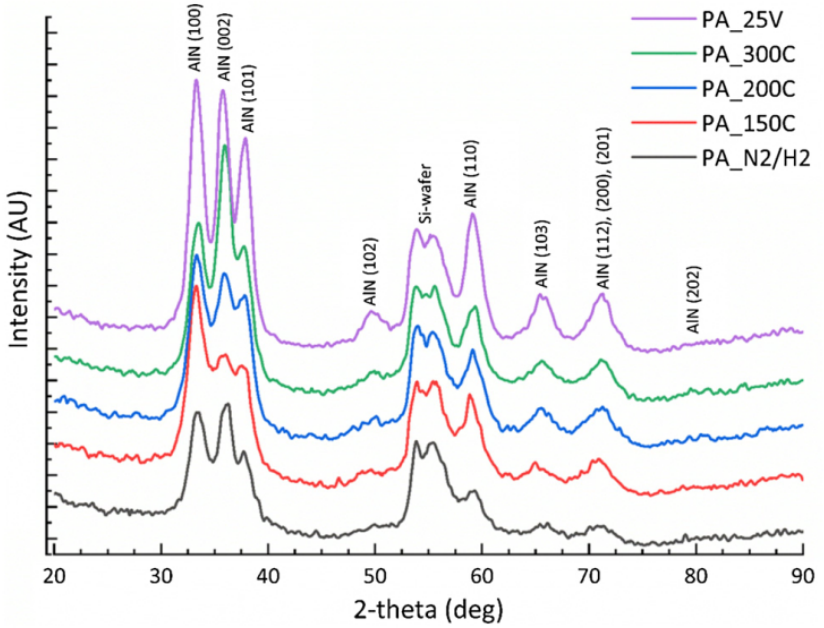
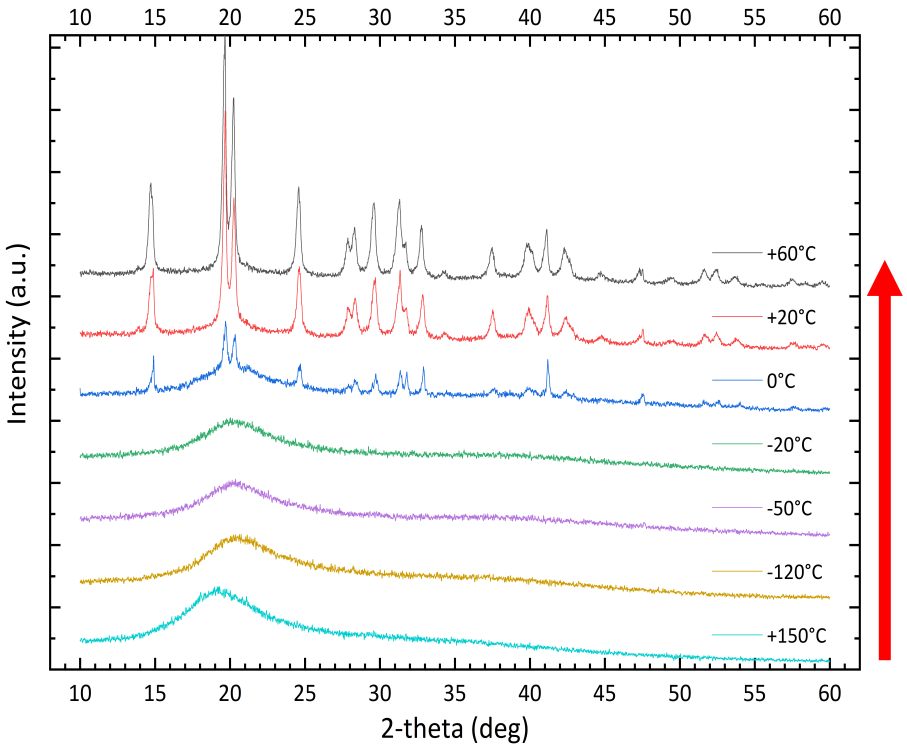


FIG. 3. As-measured GIXRD patterns with constant offset of the PEALD AlN samples at 0.4° incidence angle and with AlN planes indexed.

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

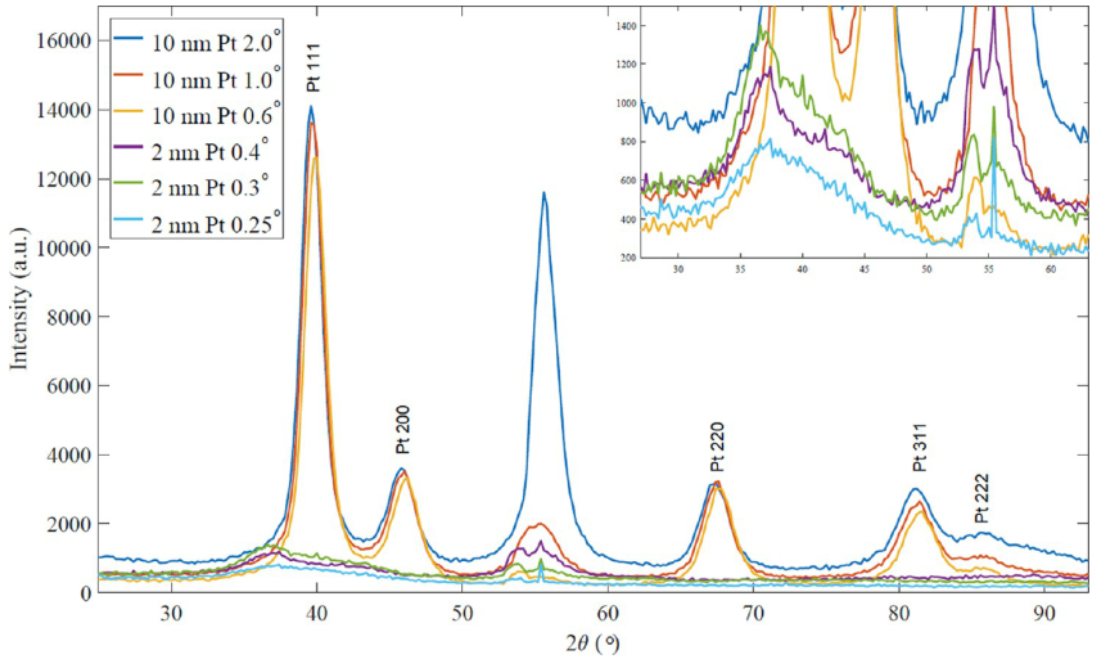
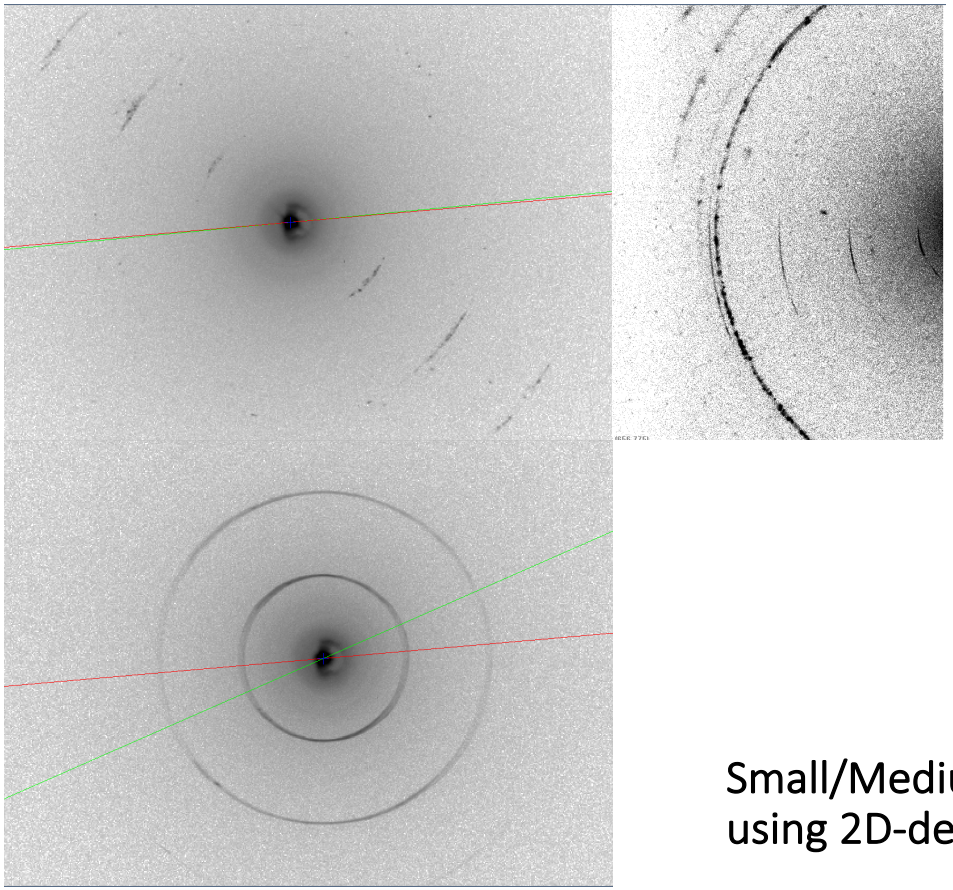
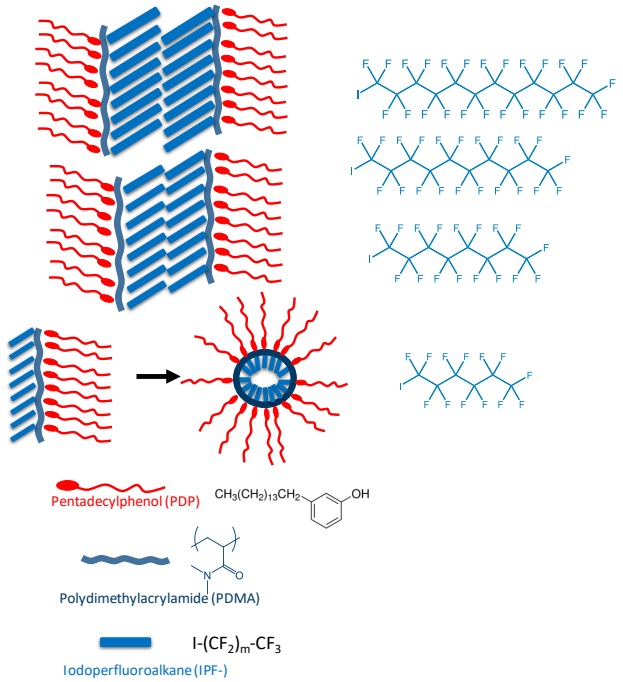


Figure 6. GIXRD spectra from the Si/Ti/ta-C/Pt (10 nm) and Si/Ti/ta-C/Pt (2 nm) samples. The inset shows the magnified view from the region between 30 and 60° (2θ). Note that the peak around 50° could be indexed both to Ti and Si and has therefore been left unindexed. Peaks' locations are based on the 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





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

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

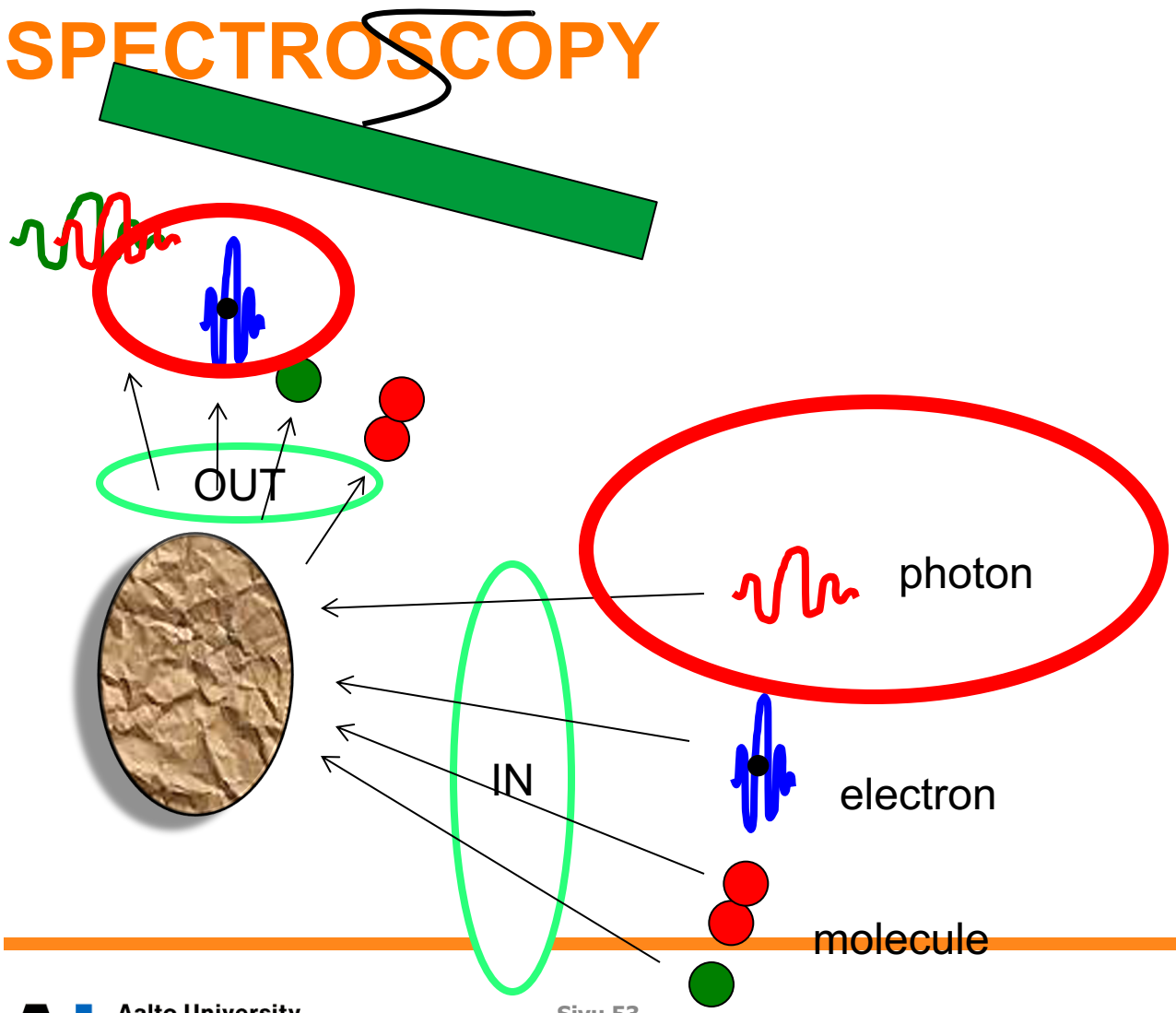
Contents

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

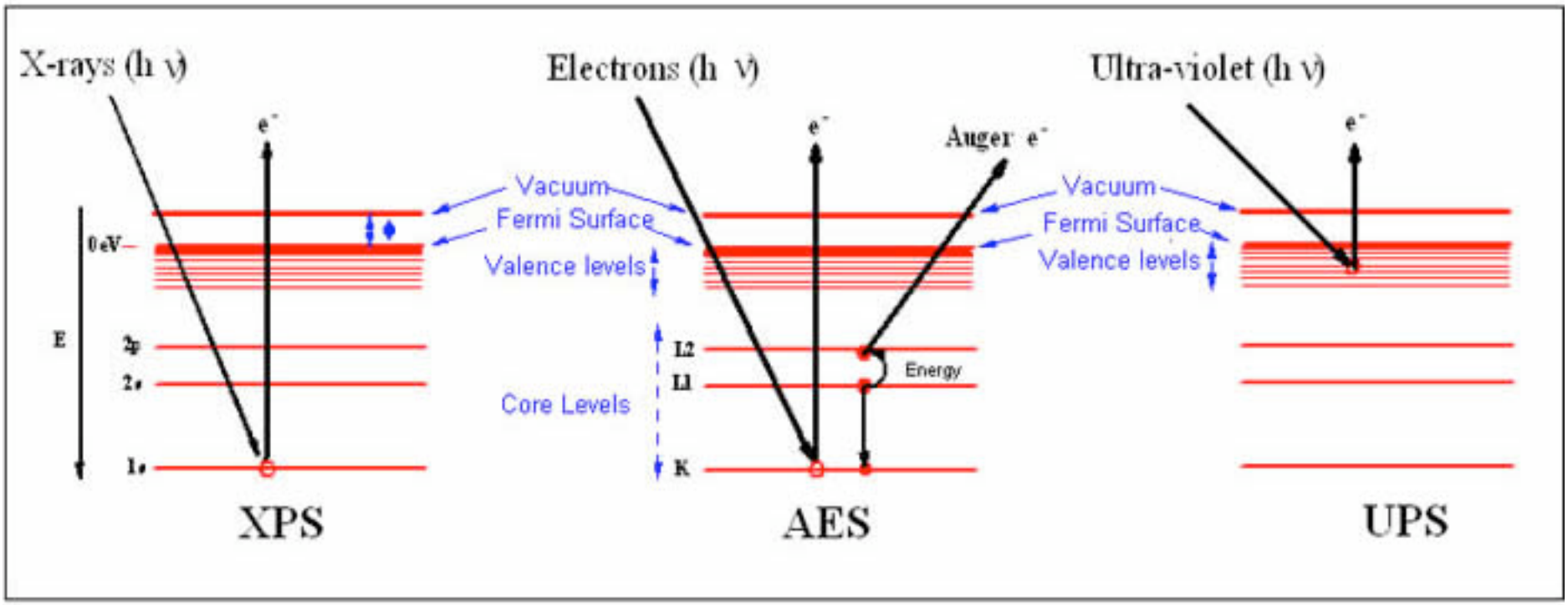
Bonding

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

Scattering experiment ELECTRON SPECTROSCOPY



Photoelectron spectroscopy techniques



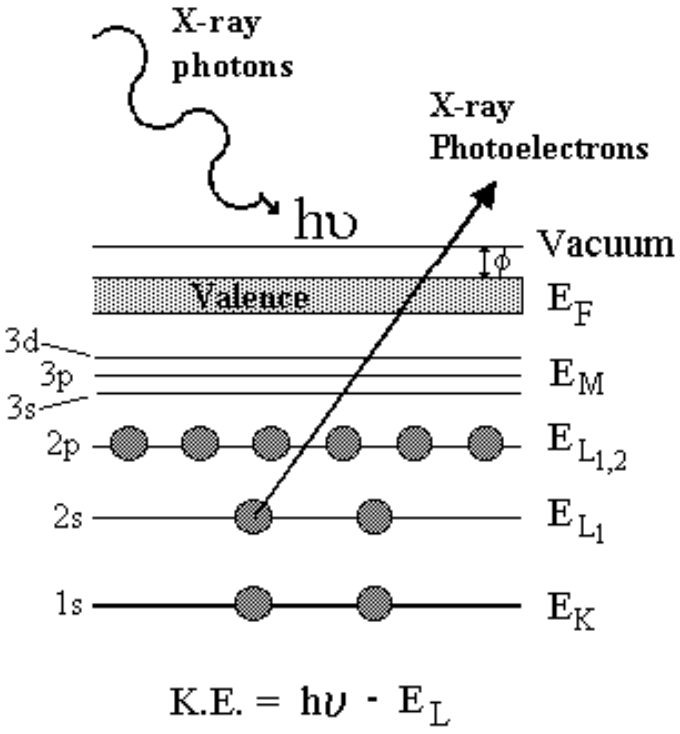
X-ray photoelectron spectroscopy - Electron Spectroscopy for Chemical Analysis ESCA

Auger electron spectroscopy

Ultraviolet phoelectron spectroscopy

XPS by Leena-Sisko Johansson

XPS


X-ray
photons
X-ray
Photoelectrons
hυ
Vacuum
Valence
φ
E_F
3d
3p
3s
E_M
2p
$E_{L_{1,2}}$
2s
E_{L_1}
1s
E_K
K.E. = hυ - E_L

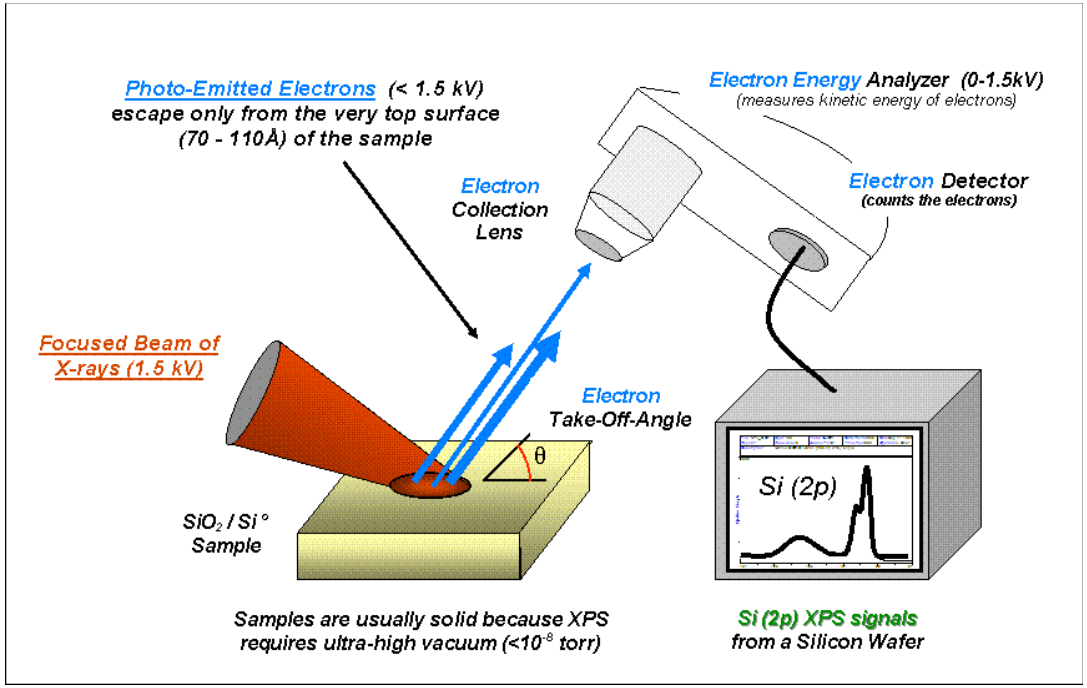
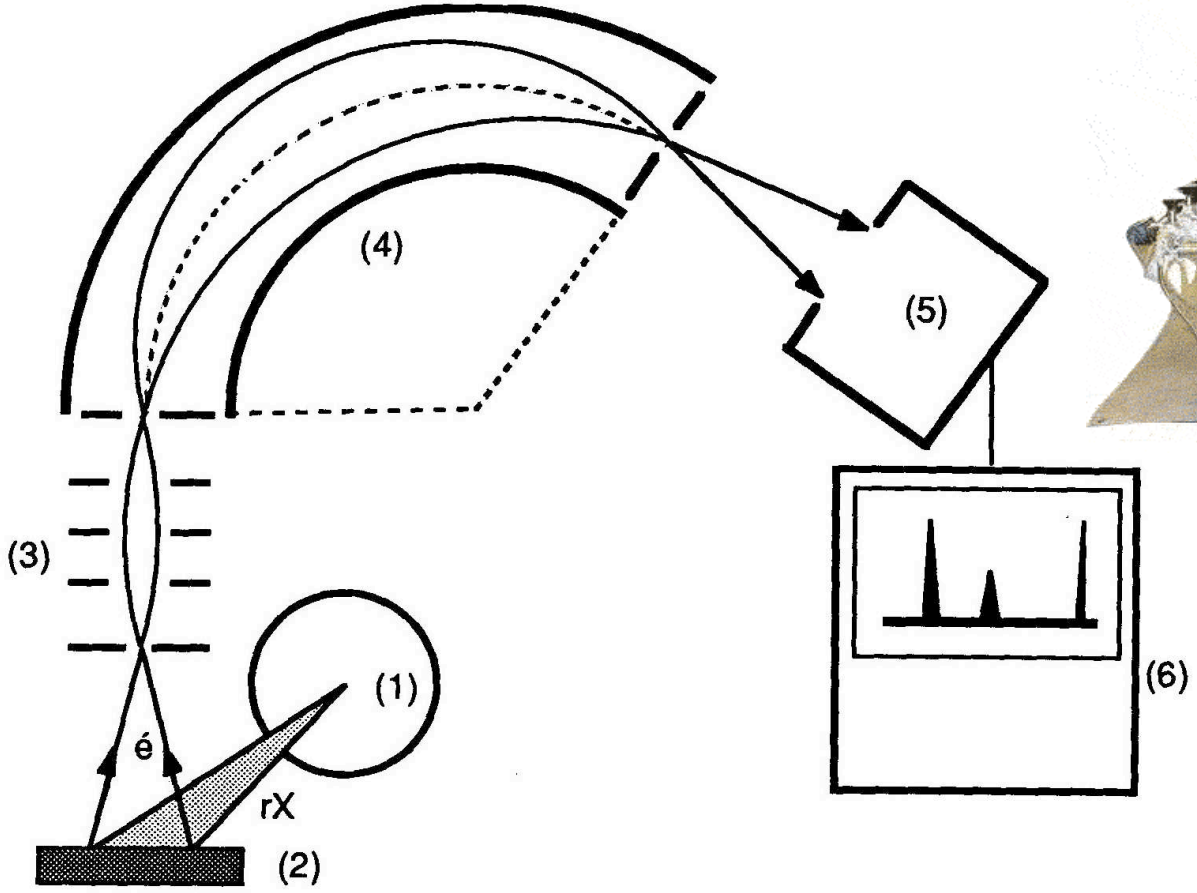
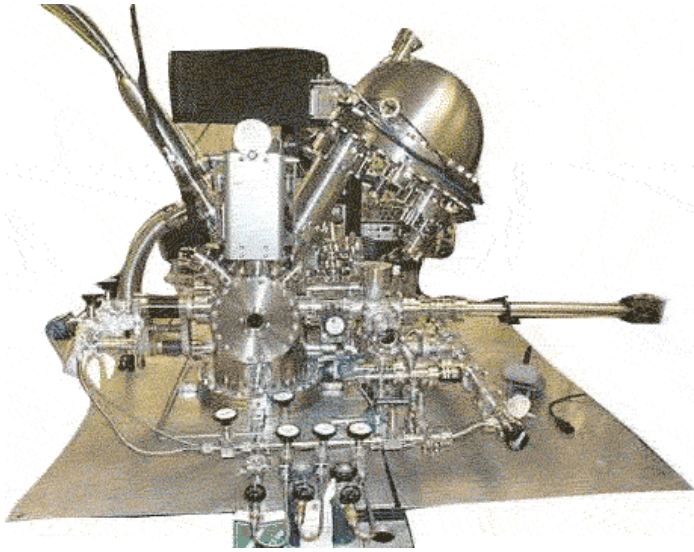


Photo-Emitted Electrons (< 1.5 kV)
escape only from the very top surface
(70 - 110Å) of the sample
Electron Energy Analyzer (0-1.5kV)
(measures kinetic energy of electrons)
Electron Detector
(counts the electrons)
Electron
Collection
Lens
Focused Beam of
X-rays (1.5 kV)
Electron
Take-Off-Angle
θ
SiO_2 / Si °
Sample
Si (2p)
Samples are usually solid because XPS
requires ultra-high vacuum (<10^{-8} torr)
Si (2p) XPS signals
from a Silicon Wafer

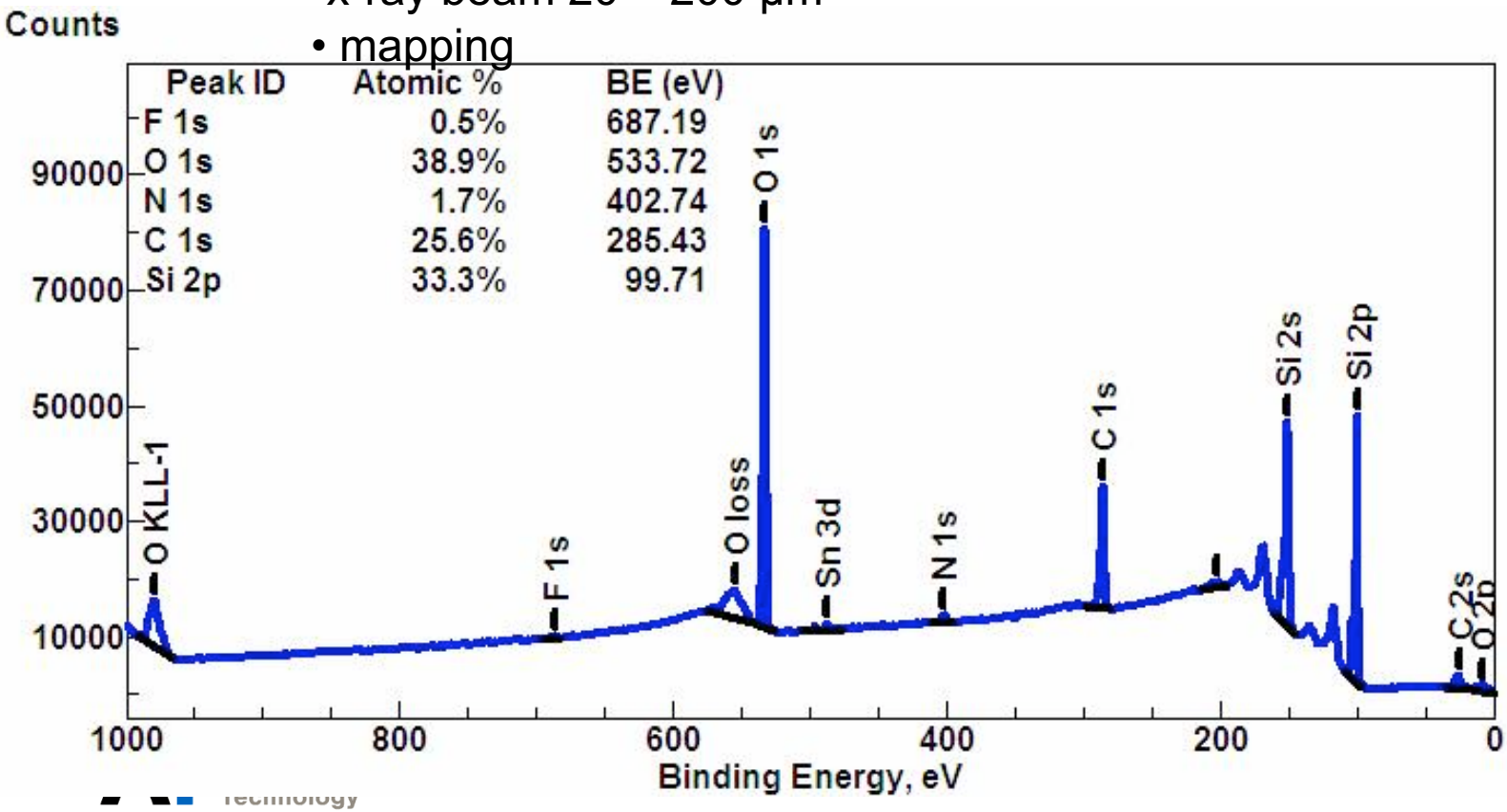
XPS





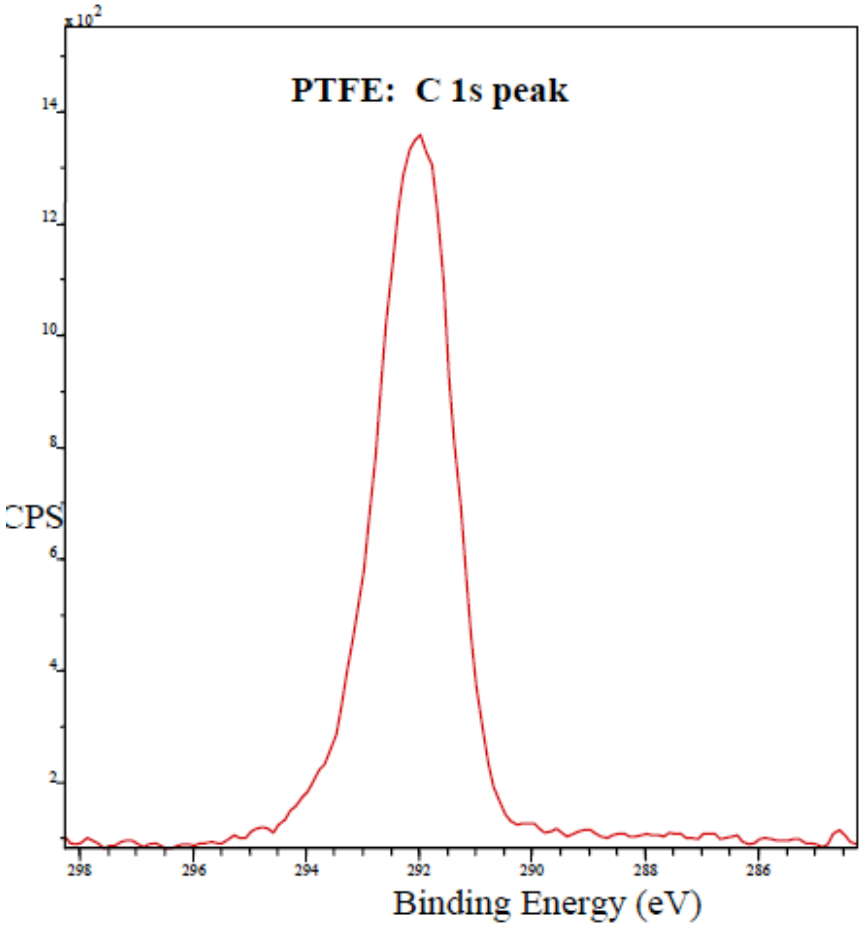
XPS

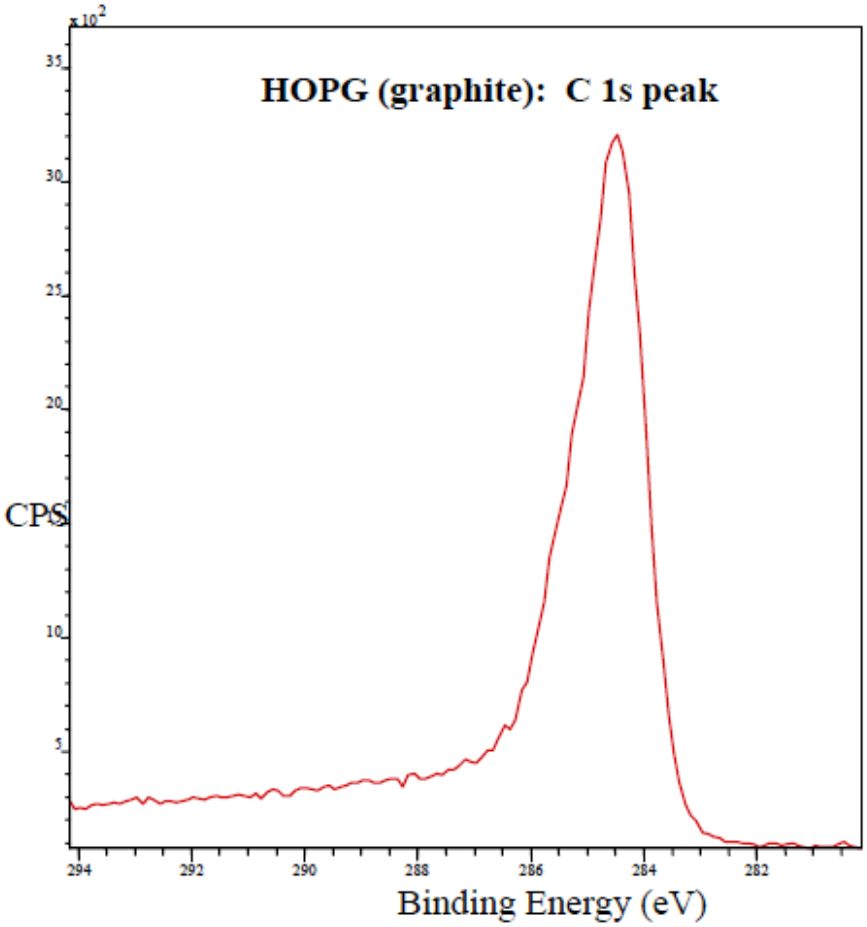
- used for elemental analysis
- all elements Z > 2
- detection limit 1/1000
- 1 – 10 nm depth
- x-ray beam 20 – 200 μm
- mapping



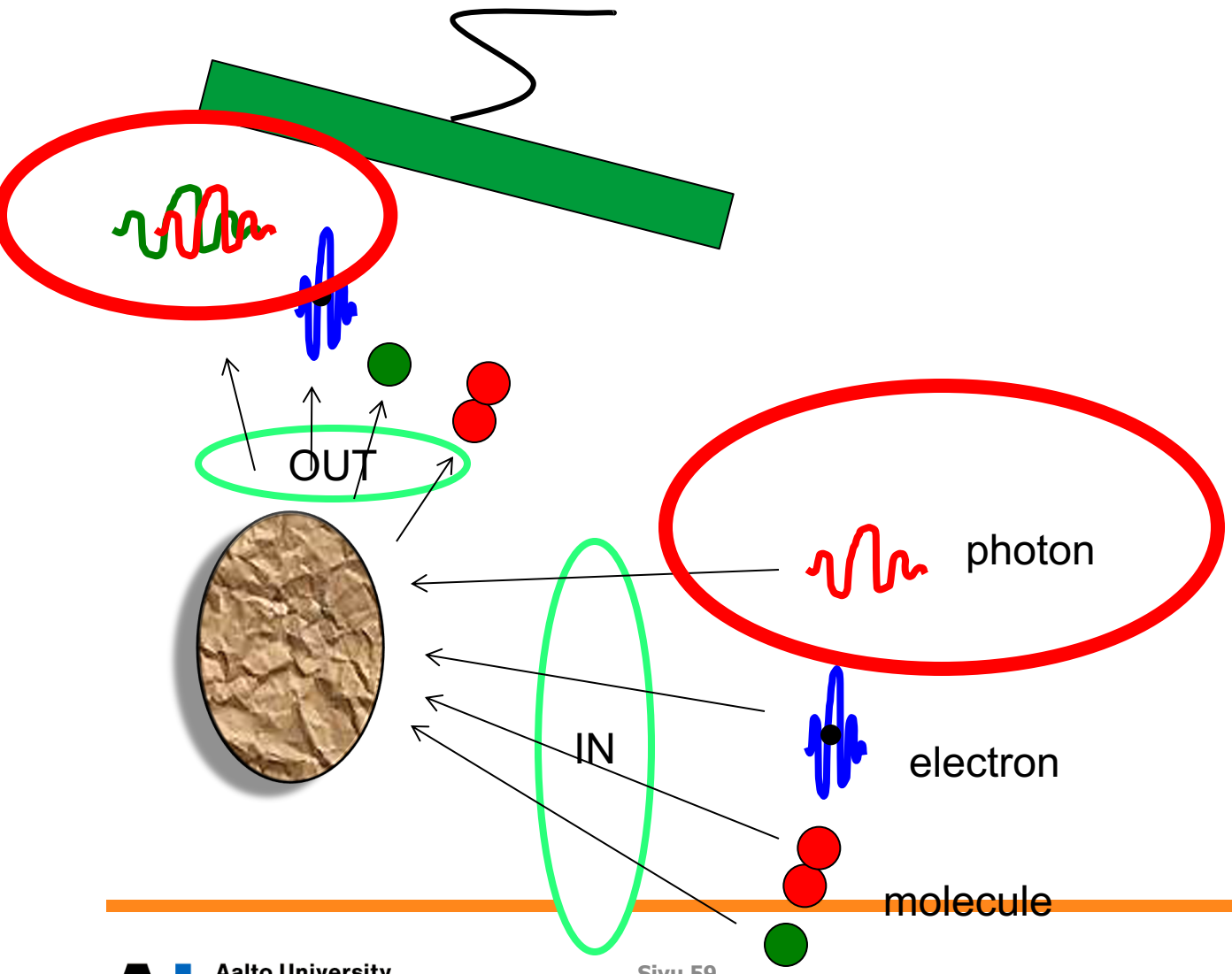
XPS

sensitive to chemical bonding, e.g. type of bonding of carbon



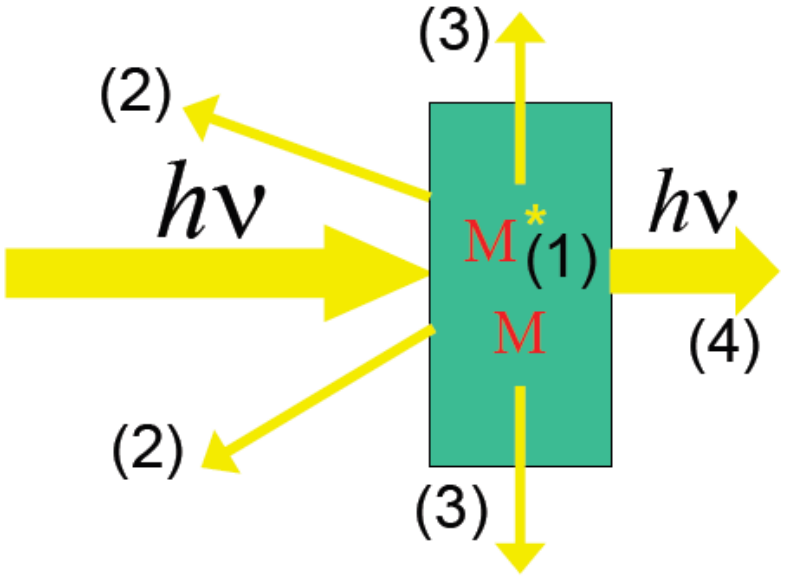


Scattering experiment - OPTICAL



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

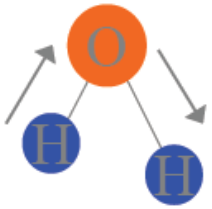
- absorbed (1)
- reflected (2)
- scattered (3)
- transmitted (4)

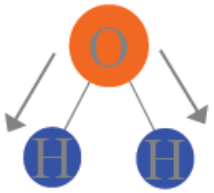


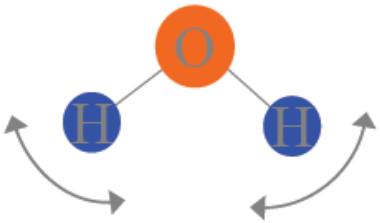
- depending upon:
  - its **frequency**
  - the **structure of molecules** of the matter it encounters.

- **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.

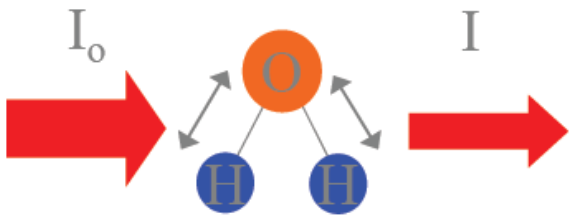






IR Light *Absorption* Measurement.

- 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.



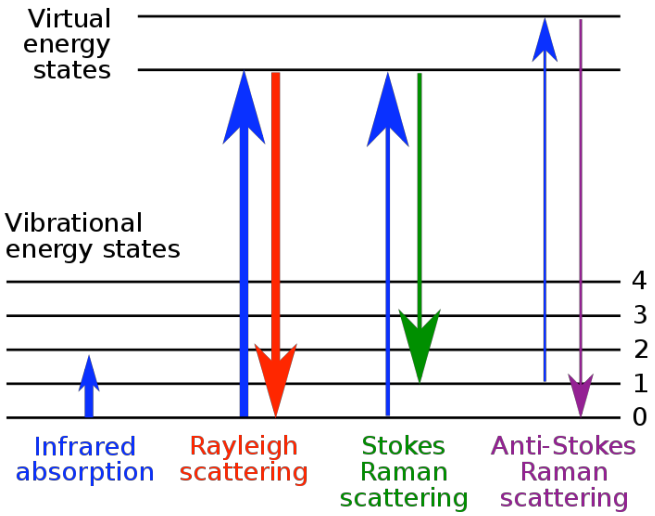
Infrared

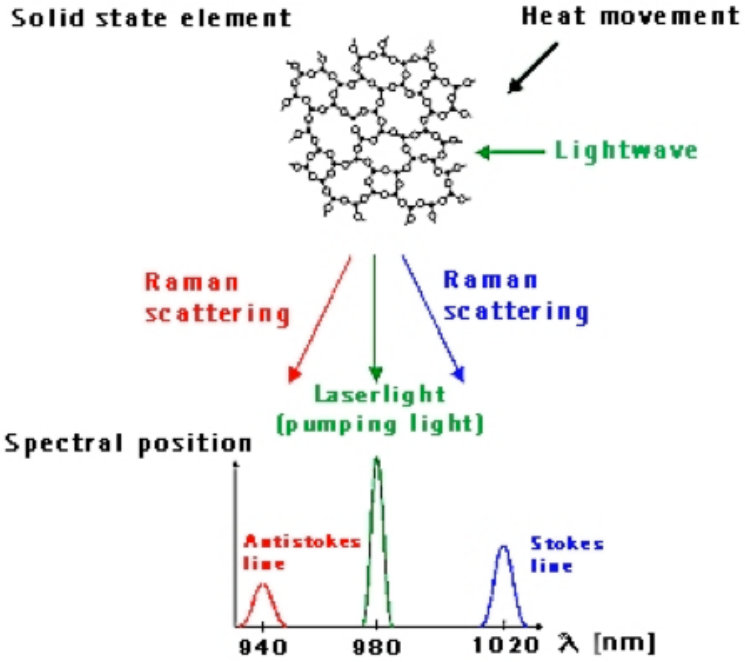
- Absorption
- Requires a dipole moment change (O-H, N-H, C=O)
- Sample preparation or accessory usually necessary
- Short optical pathlength required
- Non-aqueous samples

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


Virtual
energy
states
Vibrational
energy states
4
3
2
1
0
Infrared
absorption
Rayleigh
scattering
Stokes
Raman
scattering
Anti-Stokes
Raman
scattering


Solid state element
Heat movement
Lightwave
Raman
scattering
Raman
scattering
Laserlight
(pumping light)
Spectral position
Antistokes
line
Stokes
line
940
980
1020
λ [nm]

RAMAN
example carbon

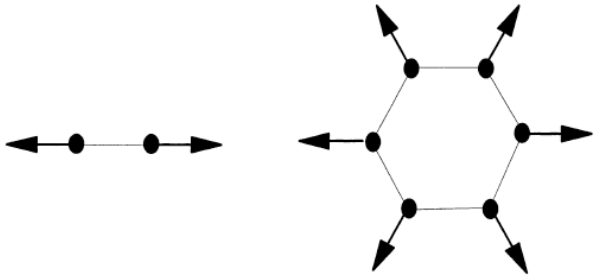


Fig. 34. Eigenvectors of the Raman G and D modes in graphite and amorphous carbons.

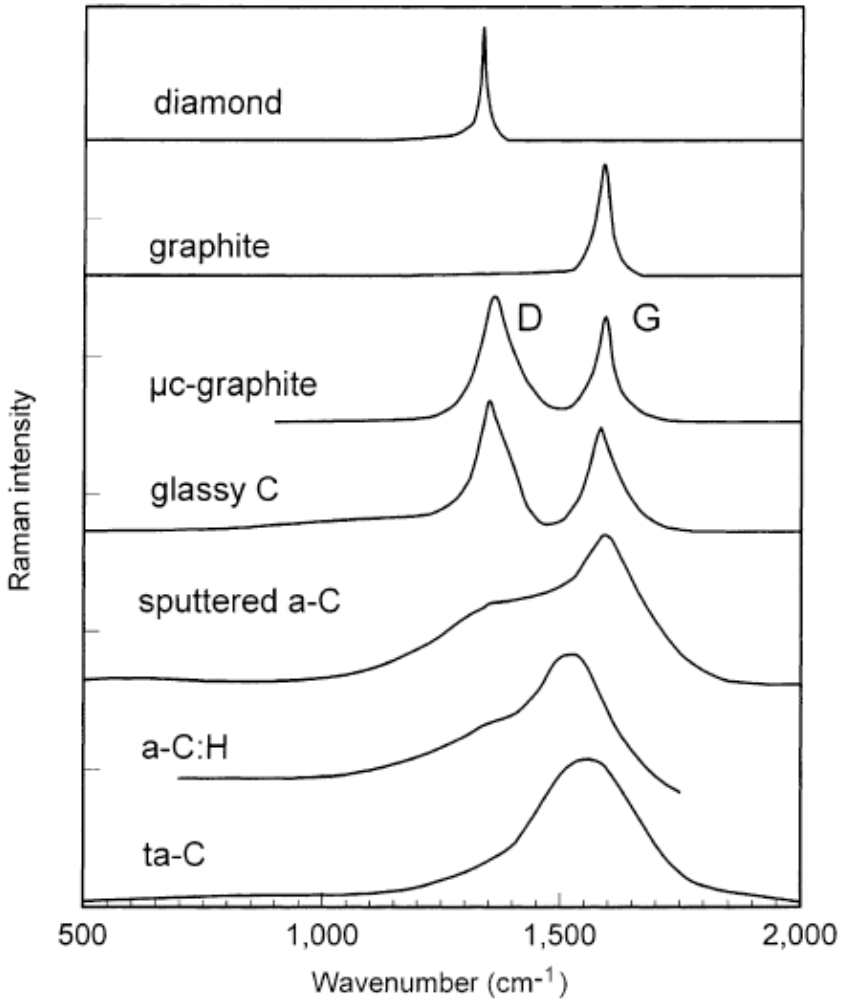
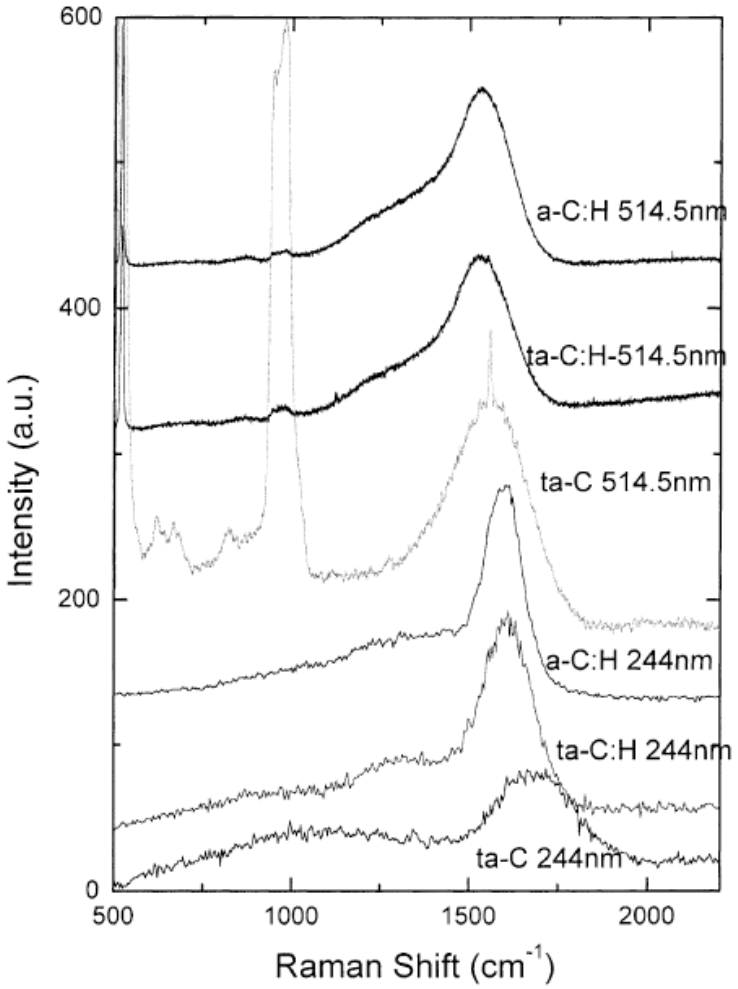


Fig. 33. Comparison of typical Raman spectra of carbons.

RAMAN
example carbon

- amorphous materials
- finger print of different bonds (materials)
- mapping



Mapping

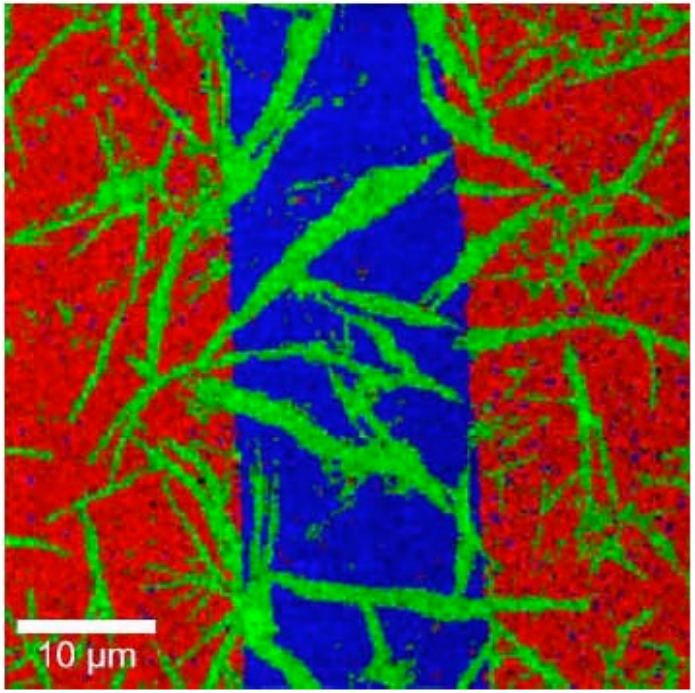
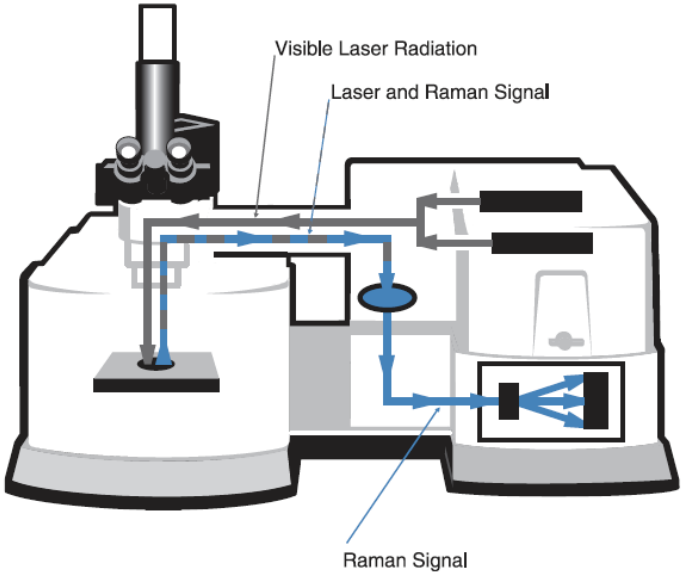


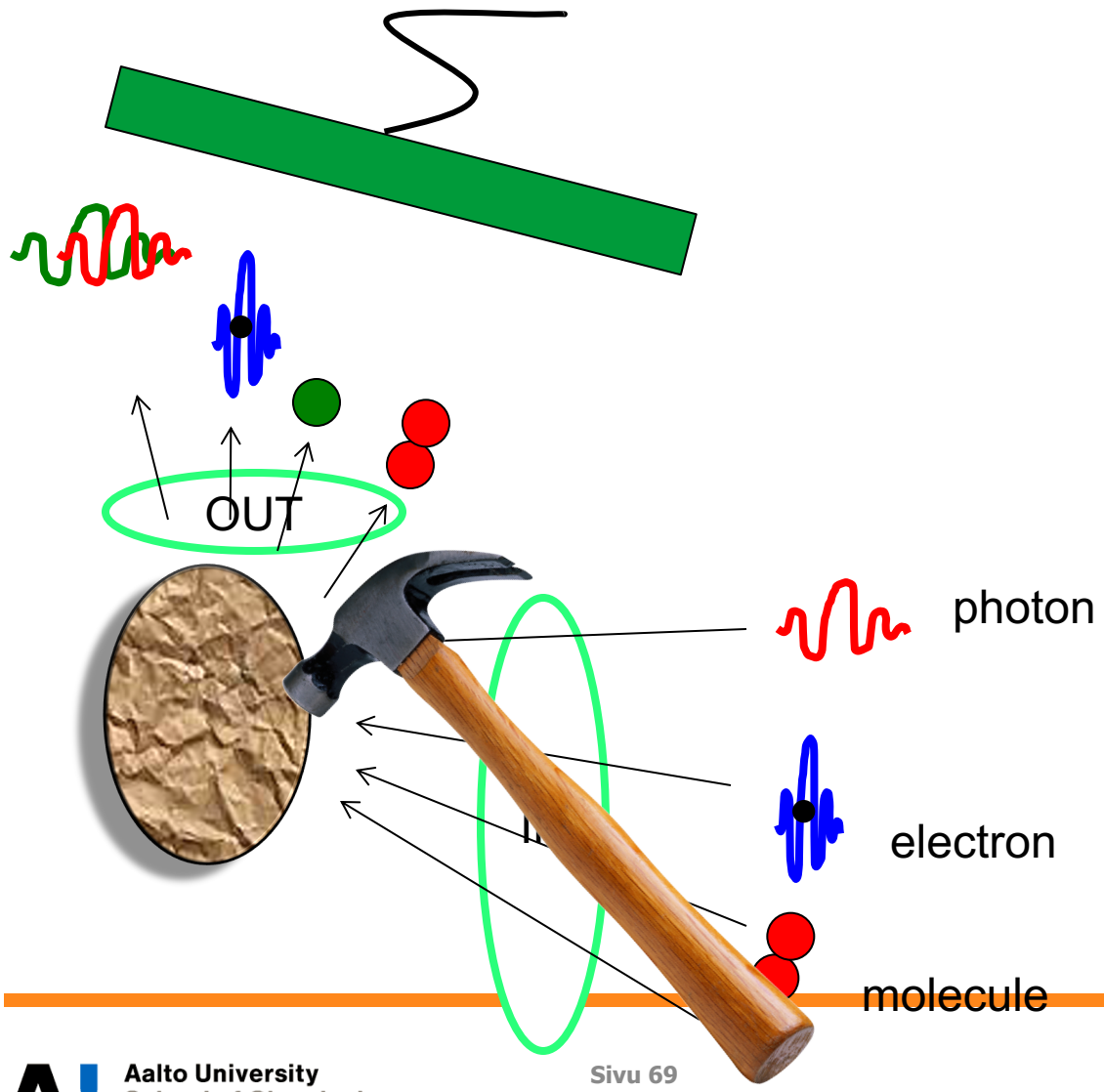
Figure 4. Color-coded confocal Raman image of a 7.1 nm PMMA layer (red) and a 4.2 nm contamination layer (green) on glass (blue). 200 x 200 spectra, 7 ms integration time/spectrum. Total acquisition time 5.4 minutes.



Contents

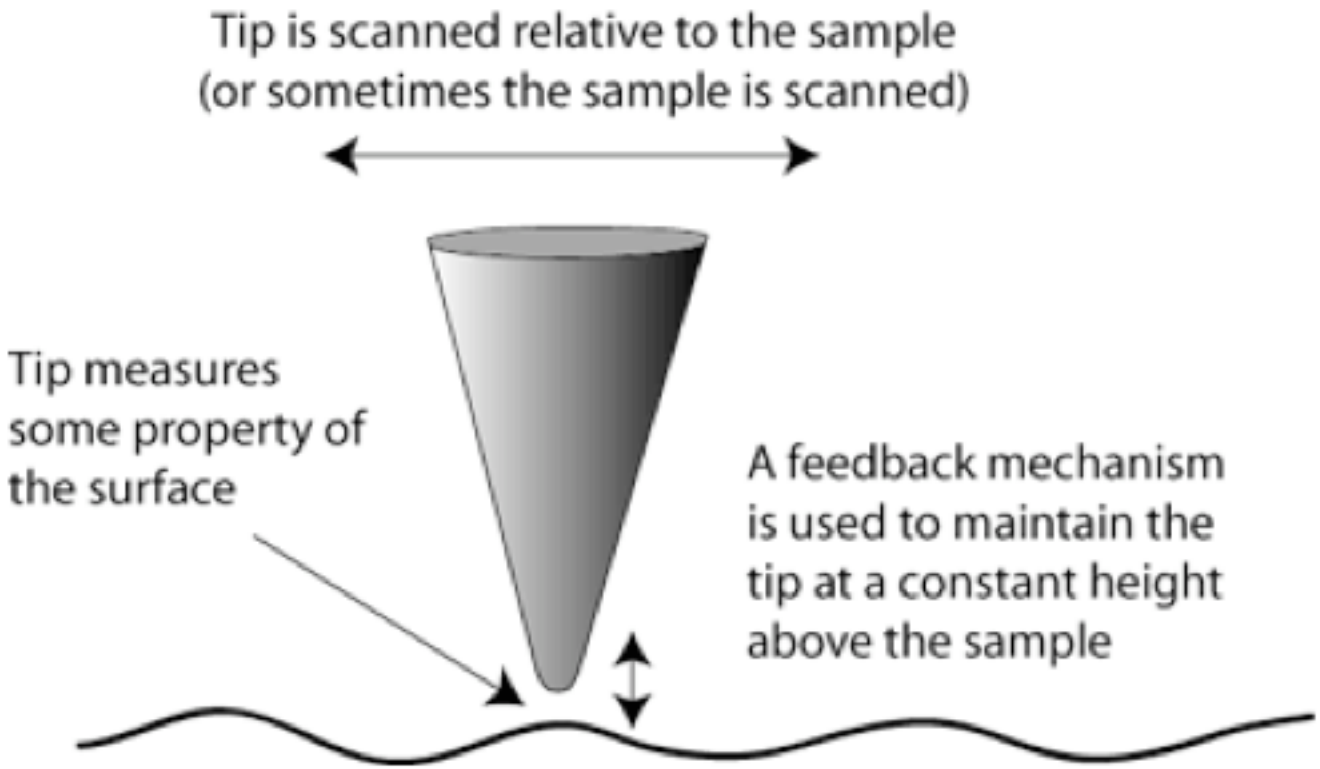
- Thin film properties
- Wealth of methods – MATRIX
- Scattering
- Thickness - profilometry
- Composition – EDS, WDS, SIMS, RBS, ERDA, GDOES
- Microstructure –XRD, TEM
- Bonding – ESCA, RAMAN
- Topography - ADM
- Electrical conductivity – four point probe
- Mechanical properties - indentation
- Optical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

Scattering experiment- Mechanical

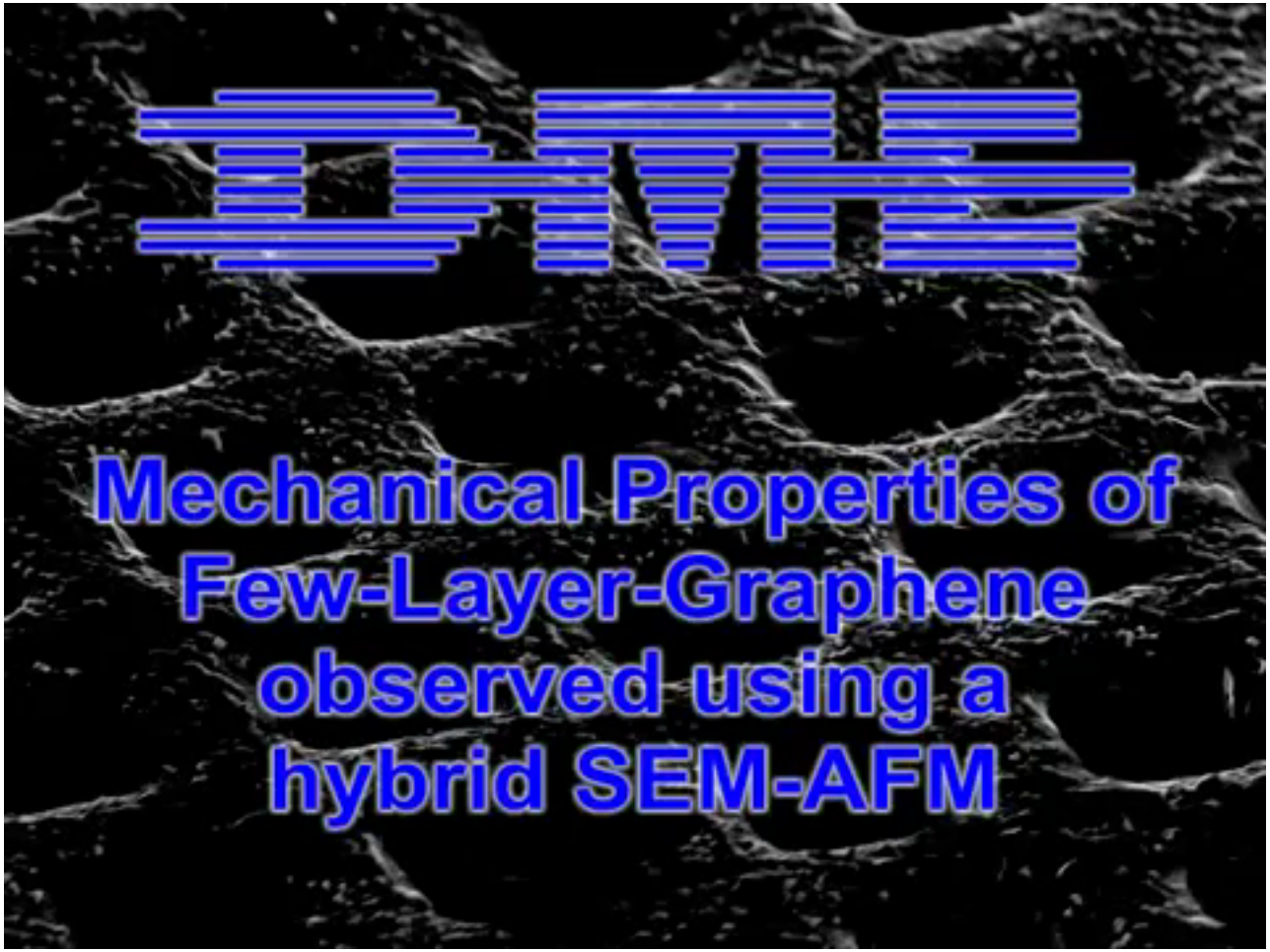


Scanning Probe Microscopy

Basic idea of scanned probe techniques:



nanoScience Inc.



Aalto University
School of Chemical
Technology

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 (???)

Indentation

- H = constant*load/(indentation area)
- Thin film/substrate: composite hardness
- Coating hardness: h< film thickness
- Very thin coatings: hardness by modelling (FEM, MD)

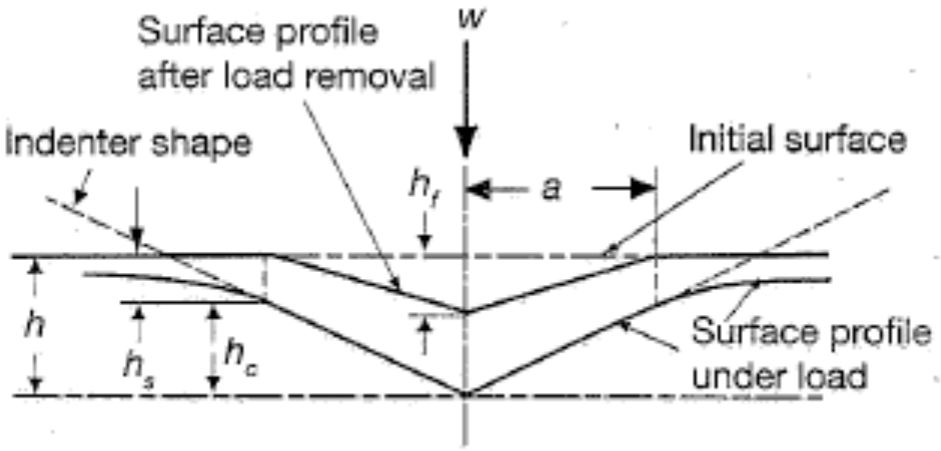


Fig. 5.9. Schematic representation of a section through an indentation using a conical indenter. h_c = contact depth, h_s = sink-in depth and h_f = final depth.

Elastic modulus E from loading - unloading curve

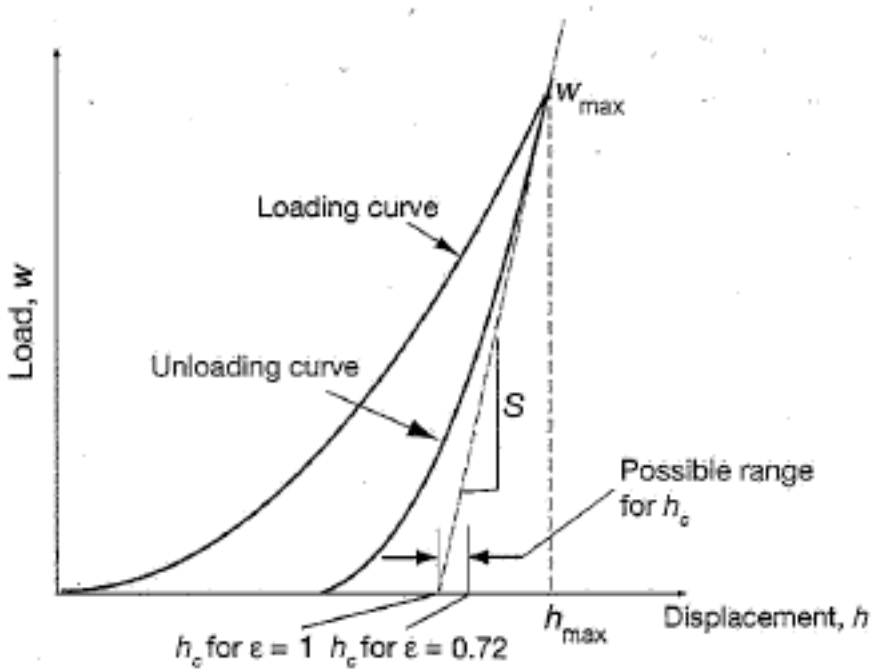


Fig. 5.10. A typical load–displacement indentation curve.

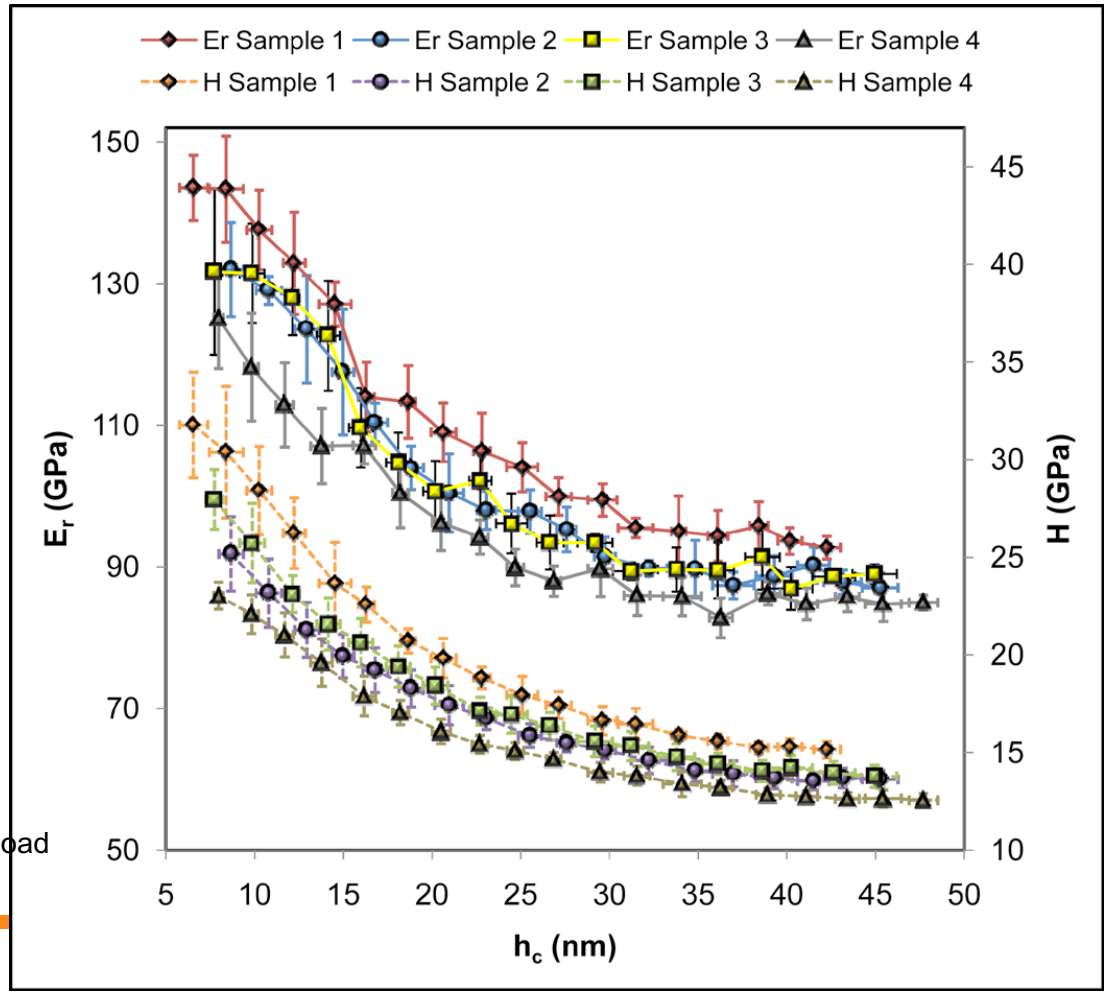
$$E_r = \frac{\sqrt{\pi \cdot S}}{2 \cdot \sqrt{A}}$$

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

$$\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu^2}{E}$$

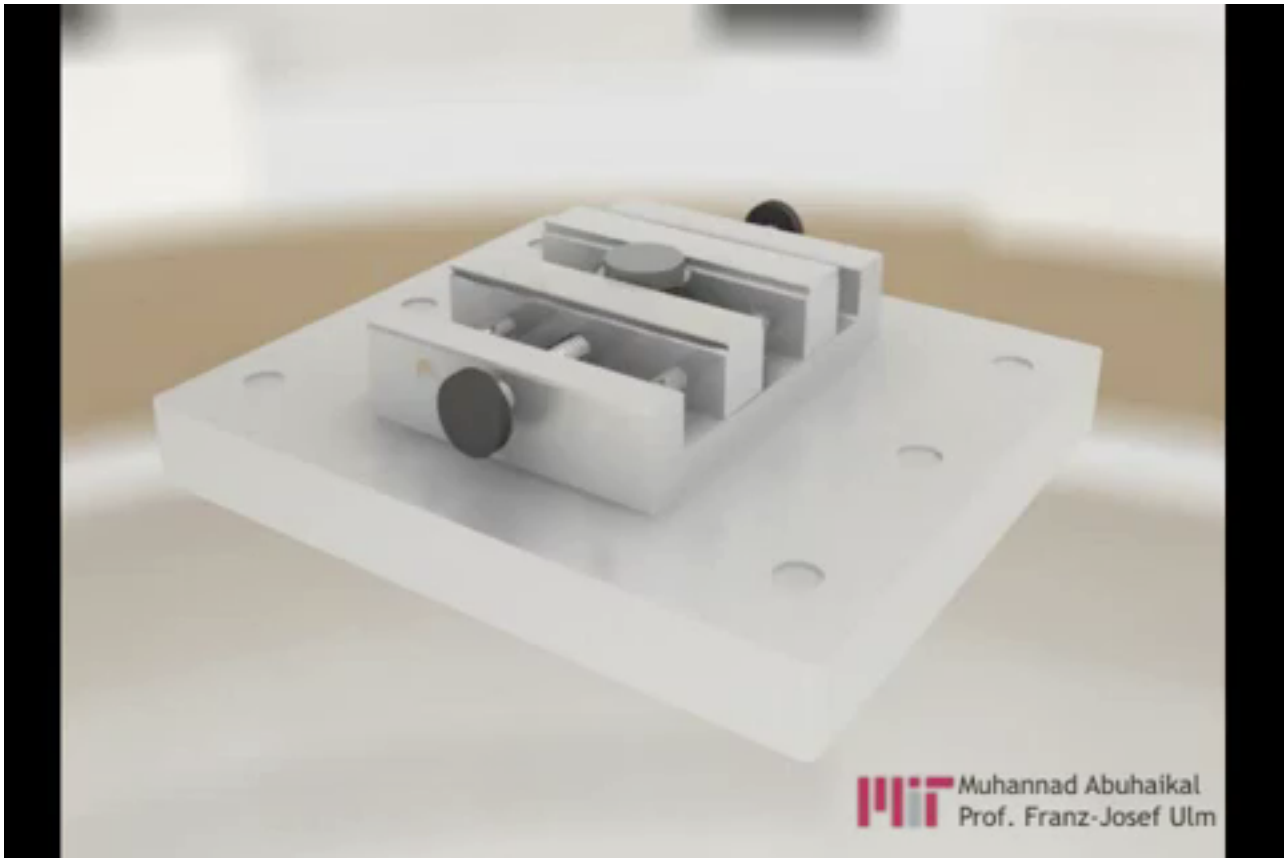
- h < 1/10 film thickness
- Very thin coatings: E by modelling (FEM, MD)

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

Indentation test



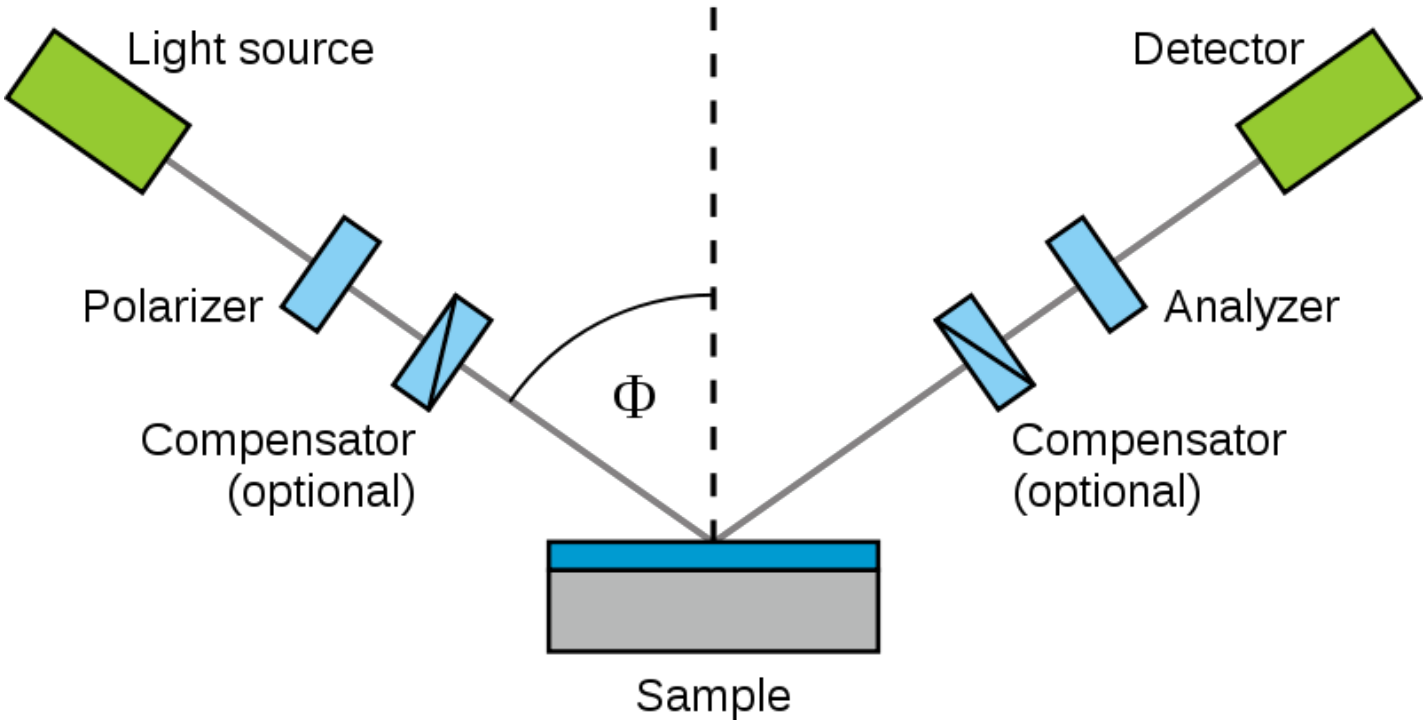
Contents

- 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

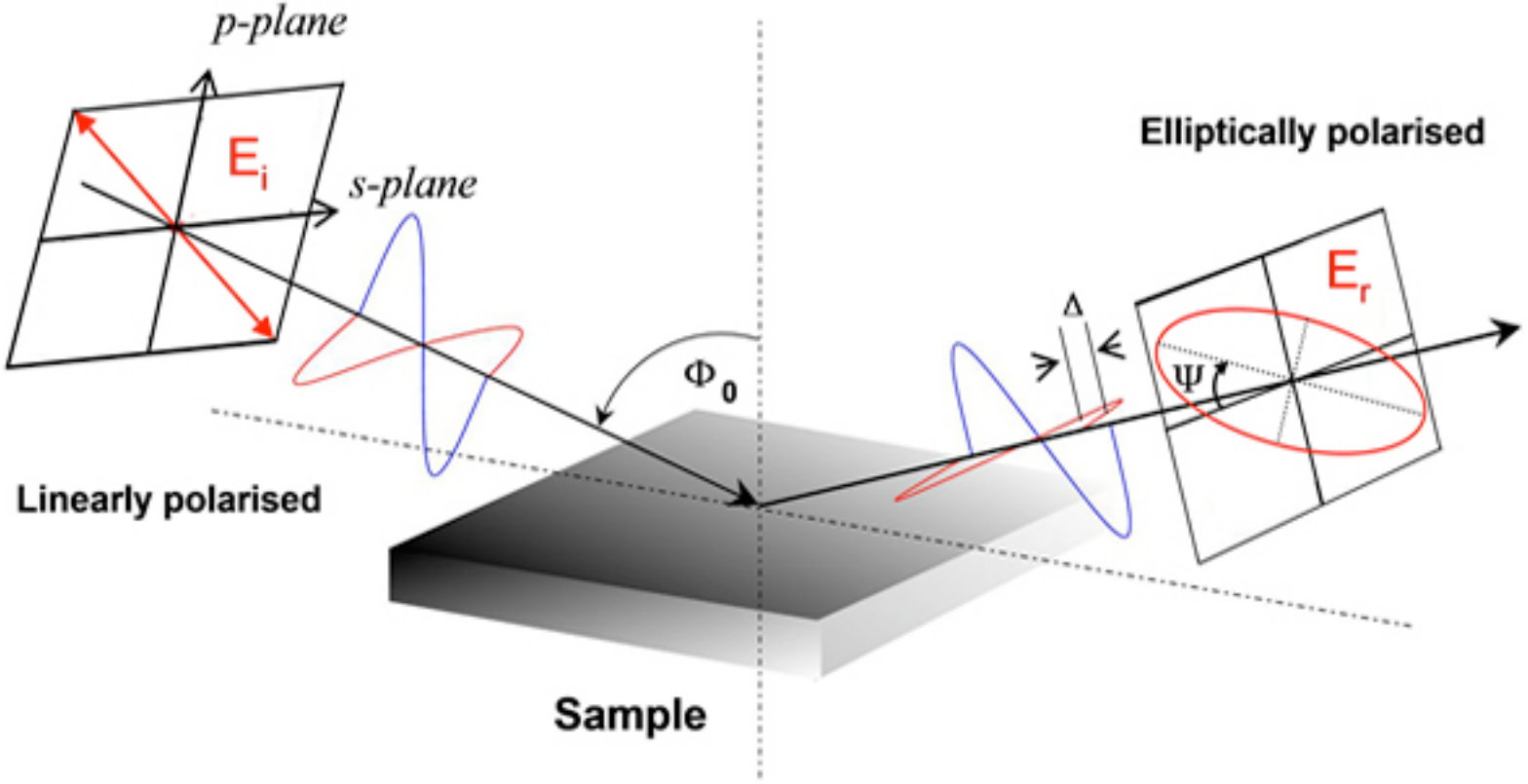
Optical coatings

- 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



Ellpsometry



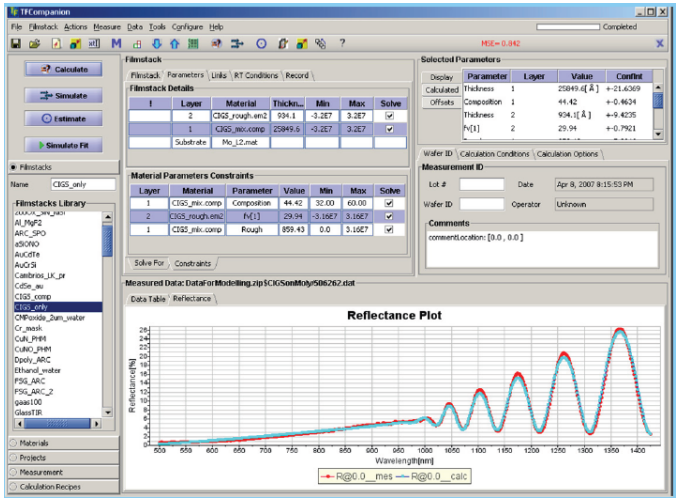
Ellipsometry

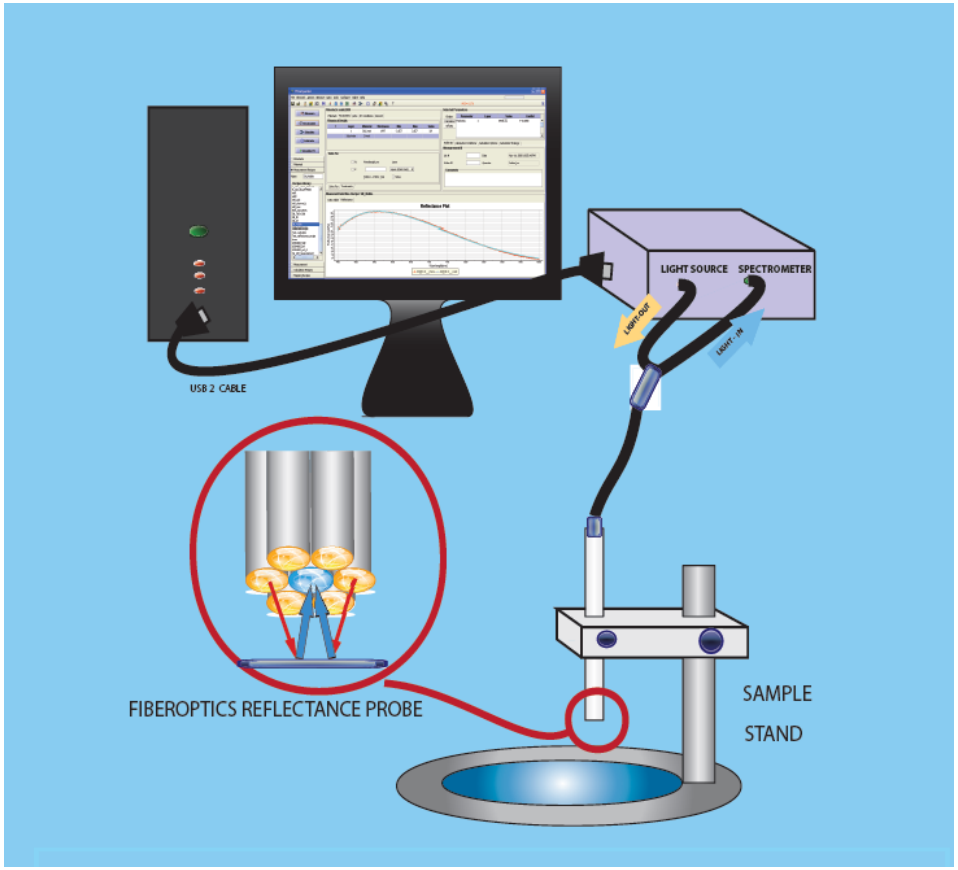
- real part (refractive index), n(λ)
- imaginary part (extinction coefficient), k(λ)
- complex refractive index, of a material, N(λ) = (n(λ)+ik(λ)), where λ

- If N(λ) 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

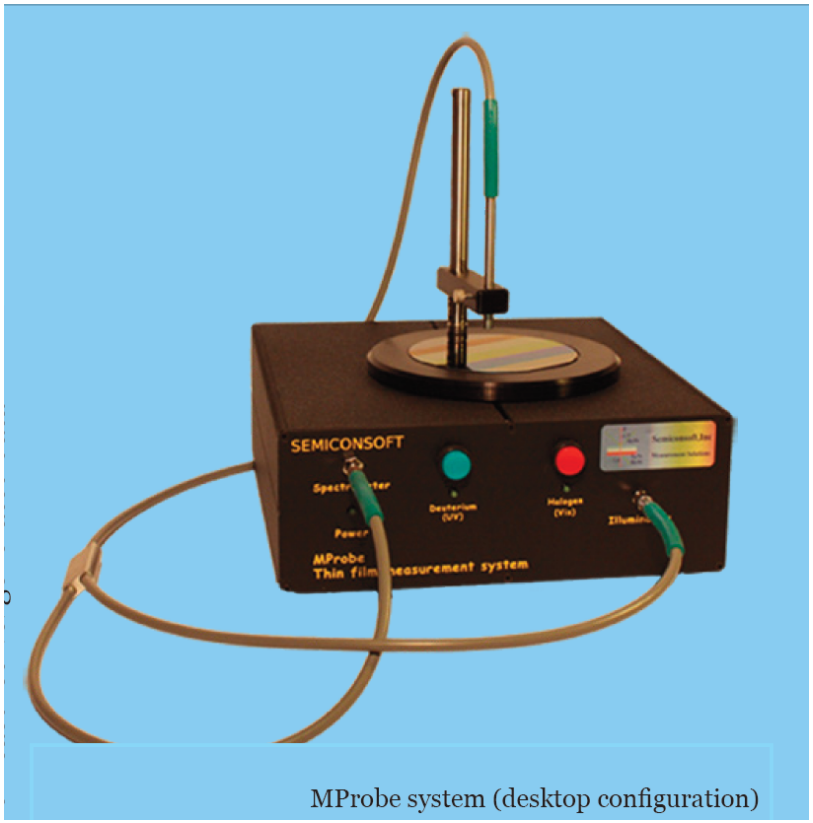
Reflectometry

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





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)