Electron probe microanalysis of thin films and multilayers

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Outlook:

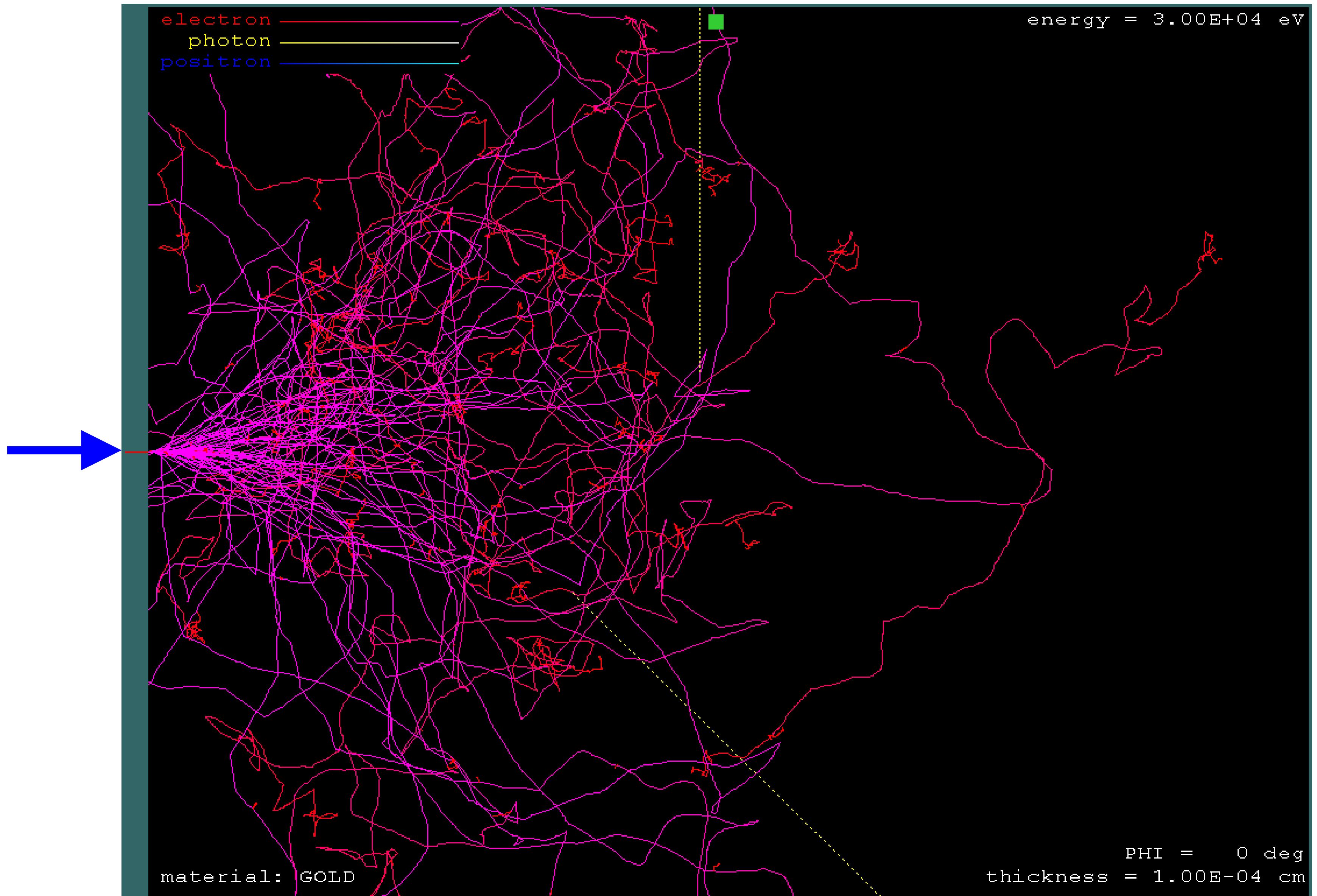
- Introduction
- Electron-specimen interactions. X-ray generation
- Quantitative analysis: bulk samples
- Quantitative analysis: thin films and multilayers
- Practical aspects
- Examples

Electron Probe Microanalysis (EPMA)

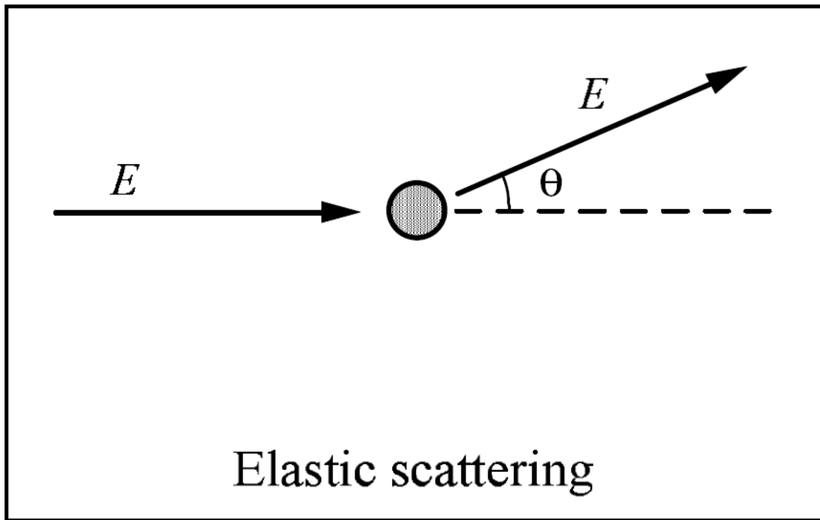
- Non-destructive technique used for determining the “local” composition of solid samples
- The basis of quantitative analysis and the first electron microprobe instrument were developed by Raimond Castaing (1951)
- Composition is obtained from the measurement of characteristic x-ray intensities emitted by the sample when it is bombarded with a focused electron beam.
- Transformation from measured x-ray intensities to concentrations is performed by means of relatively simple, analytical algorithms
- Conventional EPMA is suitable for the analysis of samples that are homogeneous at the micrometer scale.
- Thin films and multilayers can also be analyzed by EPMA.

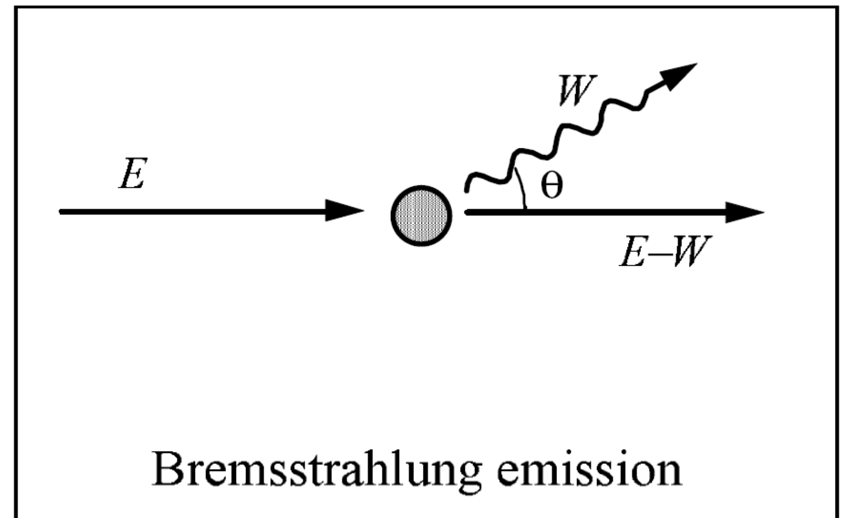
- **Analysis of thin films and multilayers by EPMA**
  - First attempts: empirical methods, based on calibration curves and thin-film standards (Cockett & Davies, 1963; Marshall & Hall, 1968..)
  - Monte Carlo simulations: pioneering work of Kyser & Murata (1974)
  - Systematic extension of EPMA algorithms (1980-1990's):
    - Pouchou & Pichoir (1984)
    - Packwood *et al* (1985-86)
    - Willich & Obertop (1988)
    - Bastin *et al* (1990-91)
    - Merlet (1995)
- **Available today:**
  - Commercial programs:
    - LAYERF, STRATAgem (Pouchou & Pichoir)
    - TFA, MTFA (Bastin *et al.*)
    - XFILM (Merlet)
  - Free software: GMRFilm (Waldo)
  - Monte Carlo simulation codes: CASINO, WinXRay, PENELOPE...

Electron-specimen interactions



Electron scattering and bremsstrahlung emission





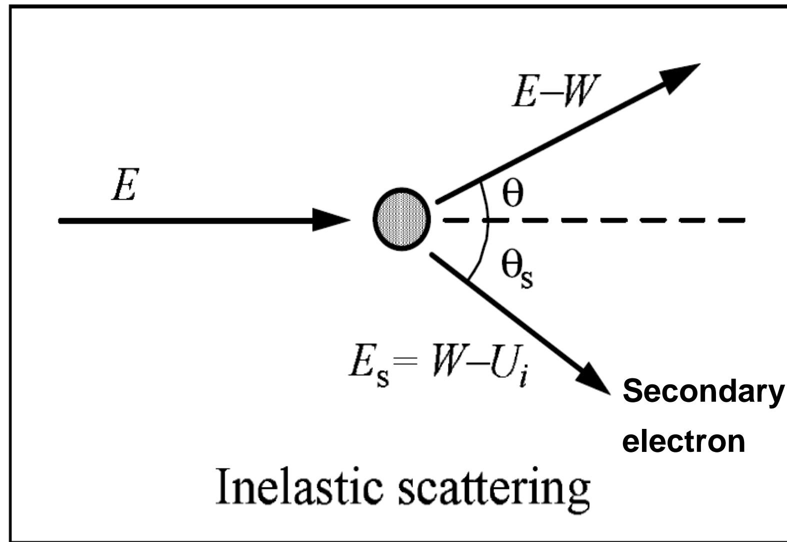
- Collisions without electronic excitation of the target.
- Deflection of the direction of movement of incident electron

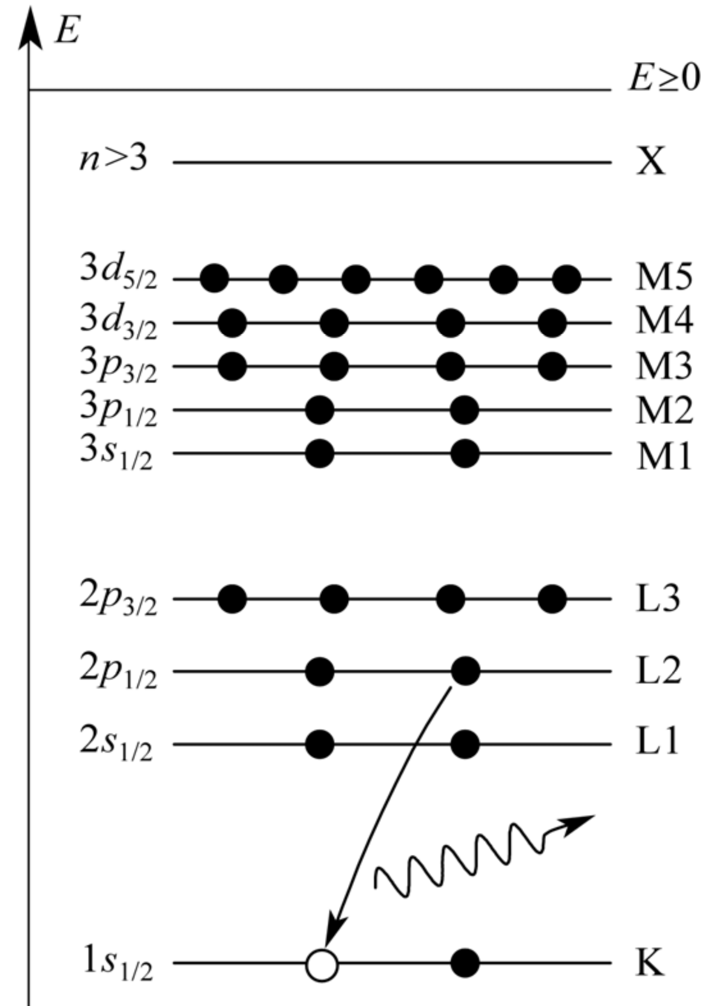
θ = scattering angle

- Electrons are accelerated by the electrostatic field of the target atom and emit electromagnetic radiation

W = energy of the emitted photon
θ = polar angle of the photon direction relative to the electron direction

• Inelastic scattering and atomic relaxation

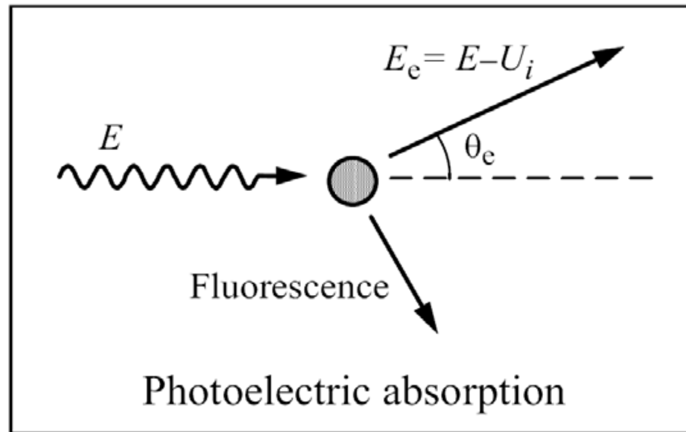


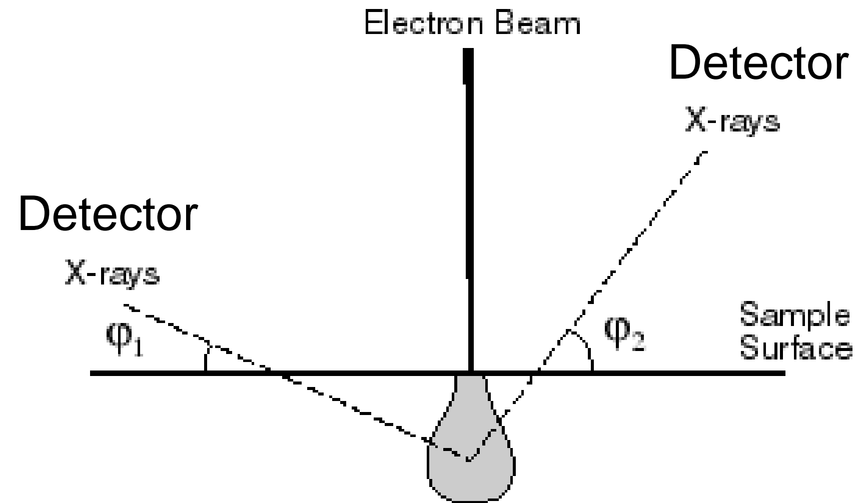


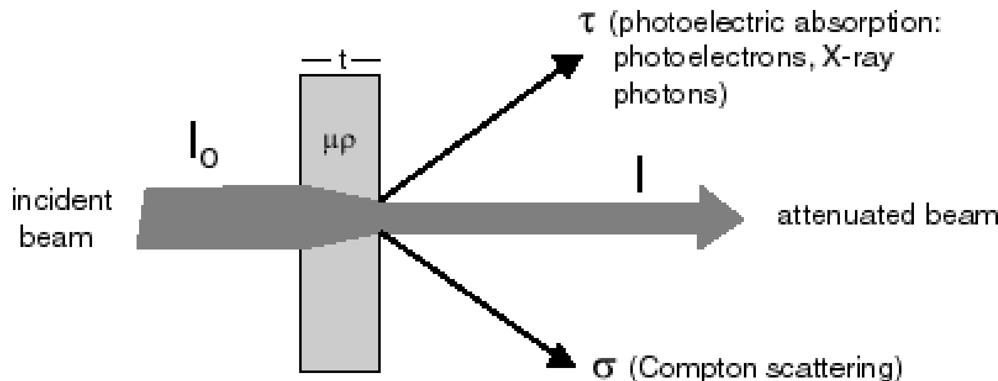
- Collisions that cause electronic excitation of the target:
  - plasmon excitation
  - outer-shell ionization
  - inner-shell ionization

- After inner-shell ionization atomic relaxation causes the emission of x-rays or Auger electrons

• Photon interactions



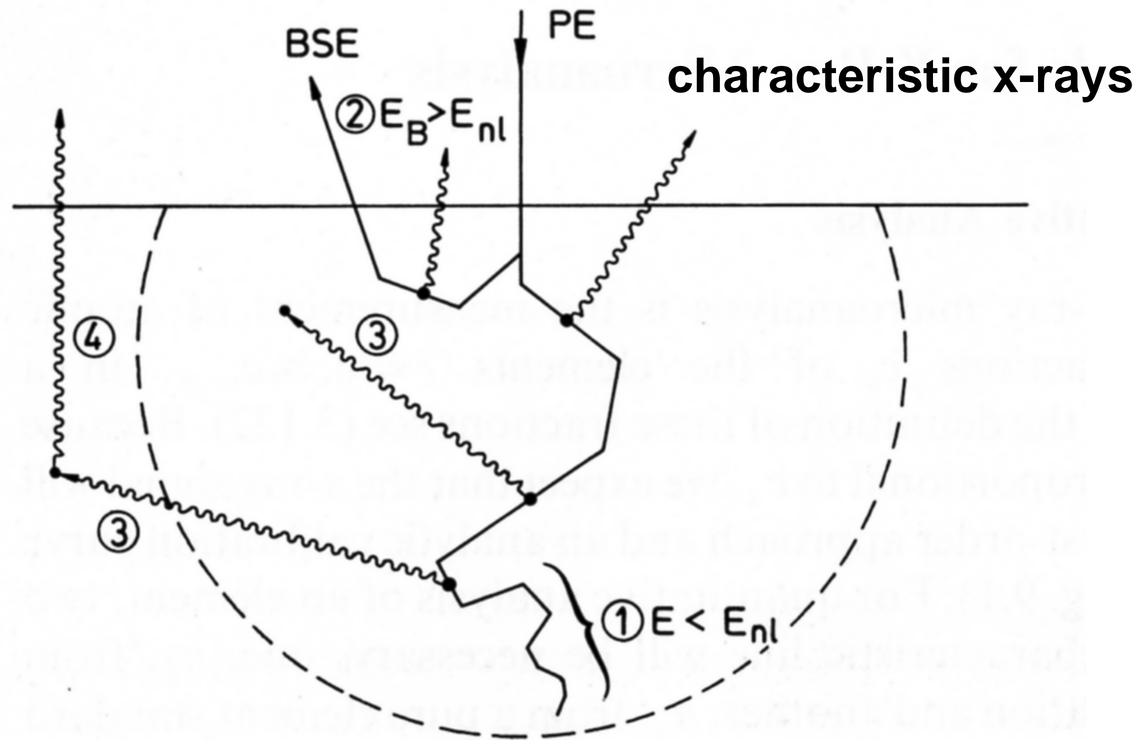




Take-off angle: direction of the detector with respect to the sample surface. It is typically in the range 35°-45°.

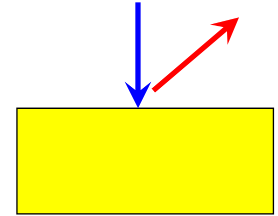
- Emitted x-rays can interact within the sample via photoelectric absorption and Compton scattering. The global global effect is x-ray attenuation

- **Effects influencing the x-ray emission:**



1) Electron with energy below the ionization threshold
2) Decrease of x-ray emission when backscattered electrons have energy above the ionization threshold
3) Photoelectric absorption
4) Fluorescence emission after photoelectric absorption

● *Depth-distribution of ionizations*



Au, Si Kα

E = 10 keV

8

6

$\Phi(\rho z)$

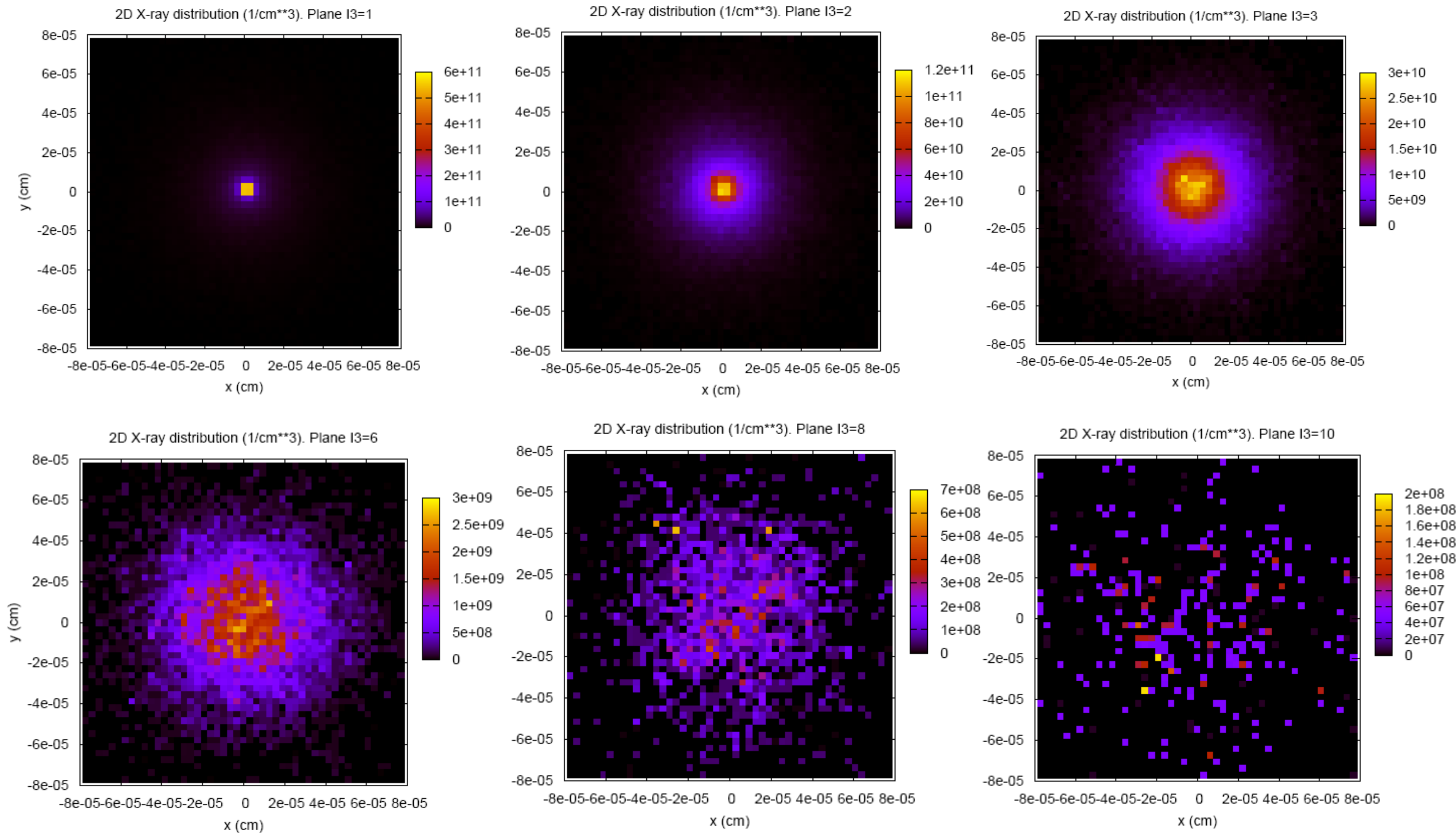
ρz ($\mu g/cm^2$)

0 200 400

0 1 2 3

Depth distribution of ionizations for Si Kα x-rays in Au at different energies
Comparison of Monte Carlo simulation using PENELOPE with experiments

● 2D depth-distribution of x-ray production



2-D depth distribution of x-ray emission for Pu Mα x-rays from Pu at 25 keV. Simulation results using PENELOPE

• Quantitative analysis. Bulk samples

Relation between the measured intensity and the concentration (element *i*):

$$I_i = \mathcal{A}\, c_i \left[\int_0^\infty \Phi_i(\rho z)\; \exp\left(-\chi_i\, \rho z\right)\; \mathrm{d}(\rho z) \right] \mathcal{F}$$

- I_i: characteristic x-ray intensity
- c_i: concentration
- $\exp(-\chi_i \rho z)$: attenuation
- $\Phi_i(\rho z)$: depth-distribution of ionizations
- $\mathcal{F}$: fluorescence correction

i = 1,..,N
N = number of elements

$$\mathcal{A} = n_{\mathrm{el}}\, (N_{\mathrm{A}}/A_i)\, \epsilon\, \Omega/(4\pi)\, \omega_i\, p_i\, \sigma_i(E)\, (1 + T_{CK})$$

Instrumental and atomic factors

n_{el} = Number of electrons
ε = Detector efficiency
Ω = Solid angle
ω = Fluorescence yield
p = X-ray line emission rate
σ = Inner-shell ionization cross section
T = Coster-Kronig correction

$$\chi_i = (\mu/\rho)_i \csc\theta$$

Attenuation factor

μ = mass attenuation coefficient
ρ = density
θ = take-off angle

• Quantitative analysis. Bulk samples

K-ratio: measurements on reference standards

$$K_i = \frac{I_i}{I_i^*} = \frac{c_i}{c_i^*} \frac{\int_0^\infty \Phi_i(\rho z)\ \exp(-\chi_i\ \rho z)\ \mathrm{d}(\rho z)}{\int_0^\infty \Phi_i^*(\rho z)\ \exp(-\chi_i^*\ \rho z)\ \mathrm{d}(\rho z)} \frac{\mathcal{F}}{\mathcal{F}^*}$$

← standard

- Different parameterizations of $\phi(\rho z)$:
  - Quadrilateral model (Love & Scott)
  - Surface-centered Gaussian (Packwood & Brown, Bastin *et al.*)
  - Parabolic model (Pouchou & Pichoir)
  - Double-Gaussian model (Merlet, Bastin *et al.*)
- MACs': Heinrich, Henke, XCOM, FFAST, etc..

1) K-ratios are obtained for each element (except for those estimated by stoichiometry or other means)
2) The system of equations is solved by using an iterative procedure [$\phi(\rho z)$ and χ also depend on c_i]

→ Relative accuracies better than 2% can be achieved

- **The X-PHI model**
  - Merlet (1992)
  - Double Gaussian model: 2 branches

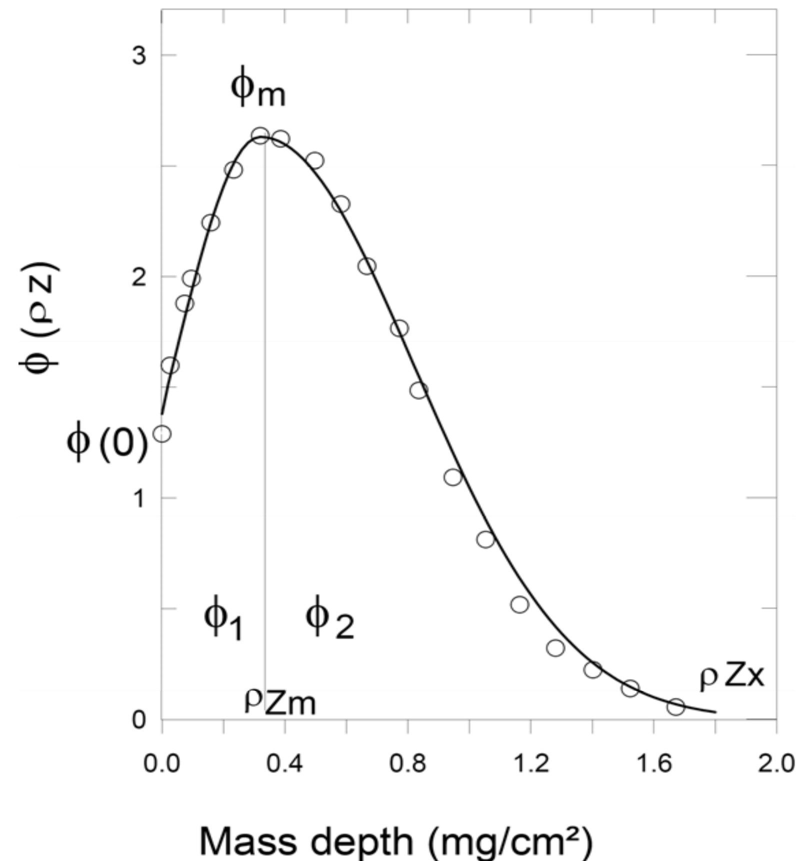
ϕ_1 and ϕ_2 joined at the maximum

  - Characterized by 4 parameters:
    - $\phi(0)$: surface ionization
    - ϕ_m: maximum
    - ρz_m: depth of the maximum
    - ρz_x: x-ray range
  - X-ray intensity: obtained analytically

$$\Phi_1 = \Phi_m \exp\left[-\left(\rho z - \rho z_m\right)^2/\beta^2\right] \quad \text{for } 0 < \rho z < \rho z_m$$

$$\Phi_2 = \Phi_m \exp\left[-\left(\rho z - \rho z_m\right)^2/\alpha^2\right] \quad \text{for } \rho z_m < \rho z < \rho z_x$$

$$\alpha = 0.46598\,(\rho z_x - \rho z_m) \qquad \beta = \rho z_m \frac{\ln(\Phi_m)}{\sqrt{\Phi(0)}}$$



Depth-distribution of ionizations for Al Kα in Cu. Comparison of the predictions of X-PHI with the experimental data of Castaing & Henoc (1965)

• Quantitative analysis. Thin films & multilayers

- Thin films on substrates:

$$I_{\mathrm{F}i} = \mathcal{A}\; c_i \left[\int_0^t \Phi_{\mathrm{F}i}(\rho z)\; \exp\left(-\chi_{\mathrm{F}i}\; \rho z\right)\; \mathrm{d}(\rho z)\right] \mathcal{F}_{\mathrm{F}}$$

film

$$I_{\mathrm{S}j} = \mathcal{A}\; c_j\; \exp\left[(\chi_{\mathrm{S}j} - \chi_{\mathrm{F}j})\; t\right] \left[\int_t^\infty \Phi_{\mathrm{S}i}(\rho z)\; \exp\left(-\chi_{\mathrm{S}j}\; \rho z\right)\; \mathrm{d}(\rho z)\right] \mathcal{F}_{\mathrm{S}}$$

substrate

t = mass thickness of the layer

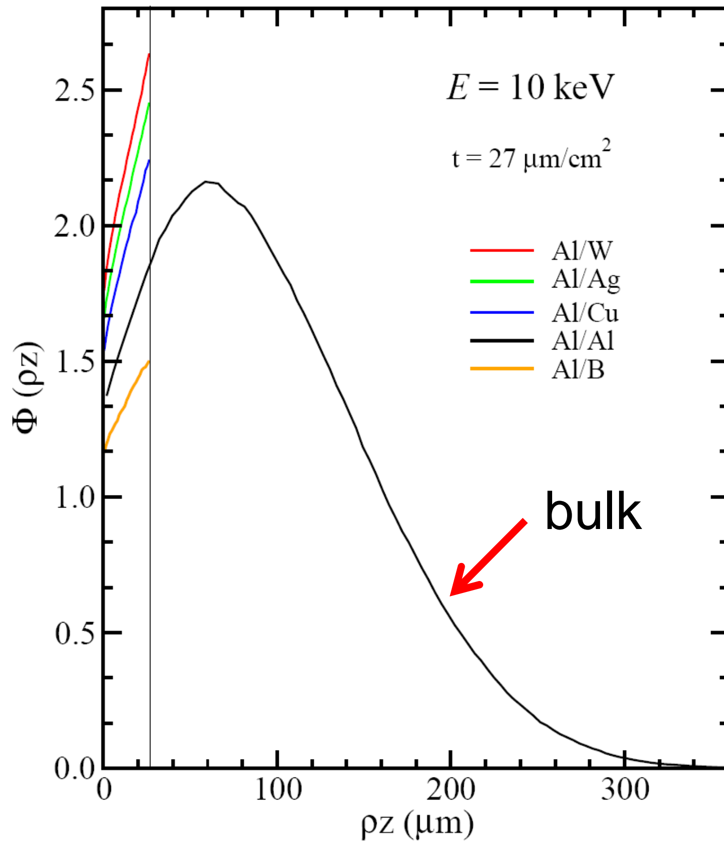
- Multilayer films:

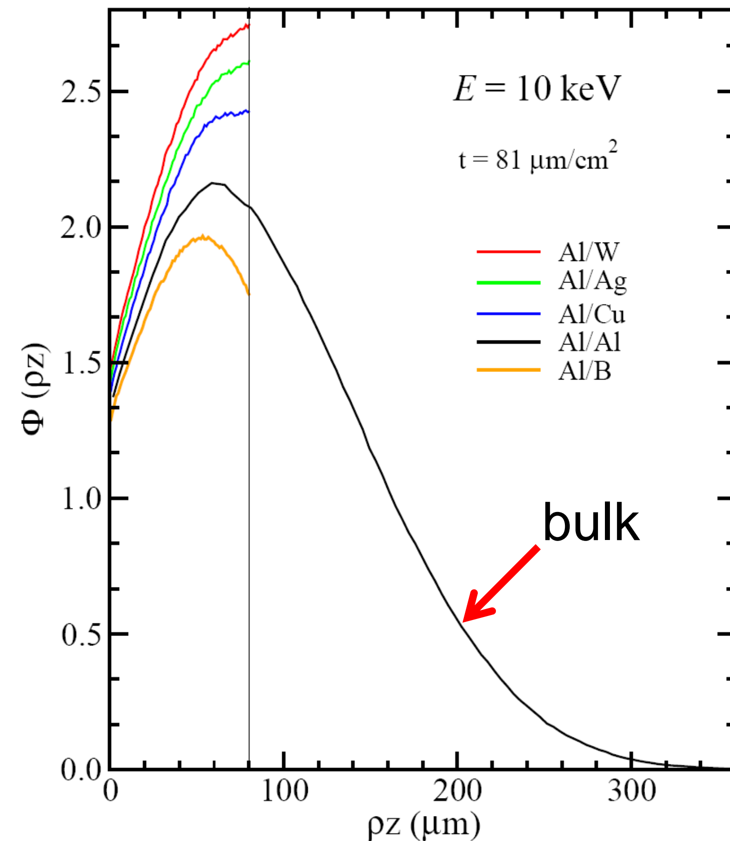
$$I_{ki} = \mathcal{A}\; c_i\; \prod_{j=1}^{k-1} \exp\left[-(\chi_{ki} - \chi_{ji})\; T_j\right] \left[\int_{t_k}^{t_{k+1}} \Phi_{ki}(\rho z)\; \exp\left(-\chi_{ki}\; \rho z\right)\; \mathrm{d}(\rho z)\right] \mathcal{F}_k$$

k = 1,..,number layers

- *K*-ratio measurements performed at varying incident electron energy (variable-voltage EPMA)
- Systems of equations solved by using iterative procedure: values of composition and thickness that best match the experimental data are obtained

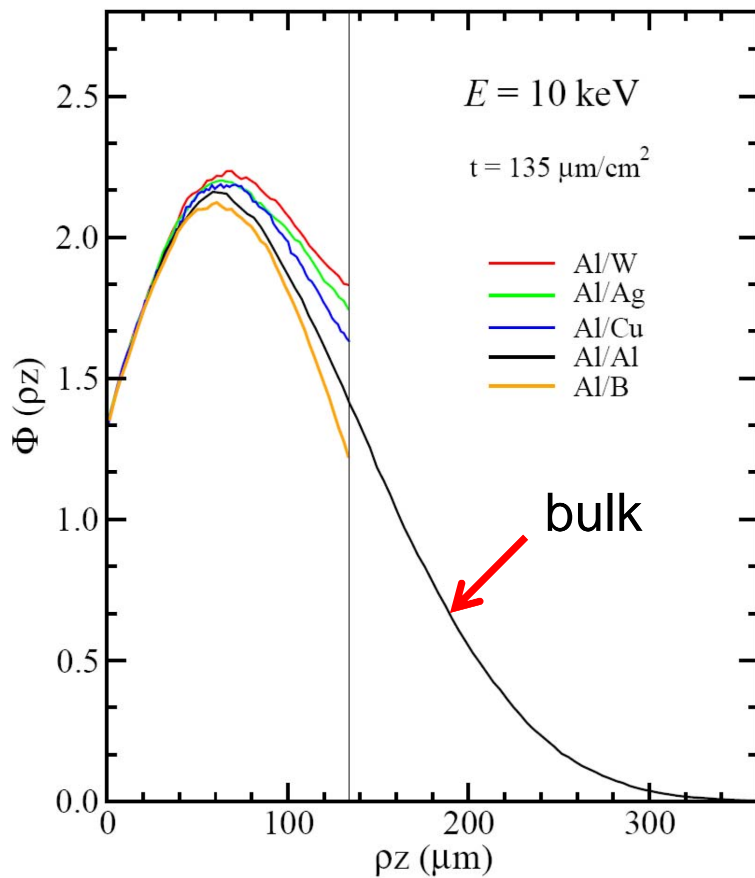
- **Depth-distribution of ionizations for thin films**

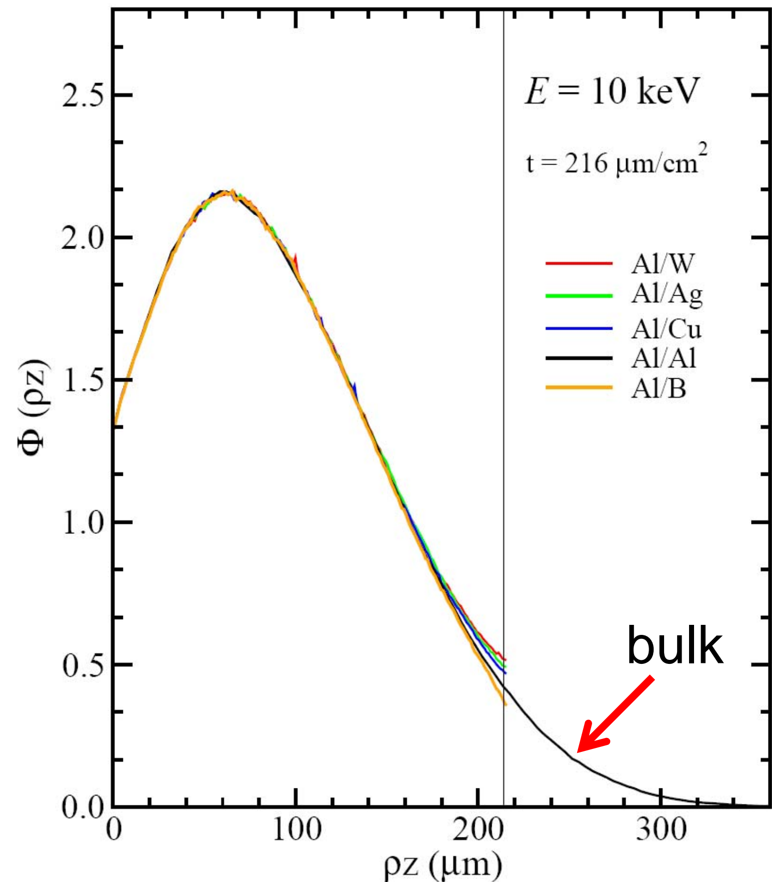




- Number of ionizations increases for increasing *Z* of substrate
- Differences between film-bulk are larger at the interface
- For relatively thin films, the surface ionization increases for increasing *Z* of substrate

• Depth-distribution of ionizations for thin films





- For intermediate thicknesses: shift of the maximum to larger depths
- For relatively thick films, backscattered electrons are absorbed in the film (surface ionization not affected)

- **Some difficulties:**
  - System of equations more difficult to solve than for bulk samples:
    - Additional variables (thickness)
    - Elements can be present simultaneously in different layers
  - Convergence to a unique solution is not guaranteed, especially if:
    - The structure of the layers is not known
    - X-rays from buried layers do not emerge due to strong absorption

  ✓ Large number of voltage measurements (to check consistency)
  ✓ Use of different x-ray lines for the same element
  ✓ Accurate initial values of estimations (concentration, thickness)
  ✓ Data processing by trial-error procedure (simulation mode)

  - Analytical predictions not firmly established for multilayer films with adjacent layers with large differences in *Z*
    - ✓Suitable selection of electron incident energies

Nevertheless, in extreme situations, the composition and thickness may not be obtainable only by EPMA

• The X-FILM model

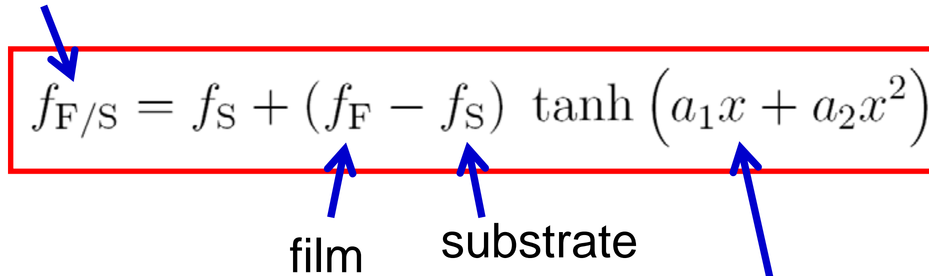
Merlet (1994): extension of X-PHI for thin-film analysis

Assumptions:

- $\phi_{F/S}(\rho z)$ described by a "weighted" combination of $\phi_F(\rho z)$ and $\phi_S(\rho z)$
- $\phi_{F/S}(\rho z)$: corresponds to a ficticious bulk sample with parameters calculated using an empirical "weighting" rule

Weighting rule (Hunger & Rogaschewski, 1984)

film-substrate



Applied to all parameters:

f = $\Phi(0)$, Φ_m, ρz_m and ρz_x

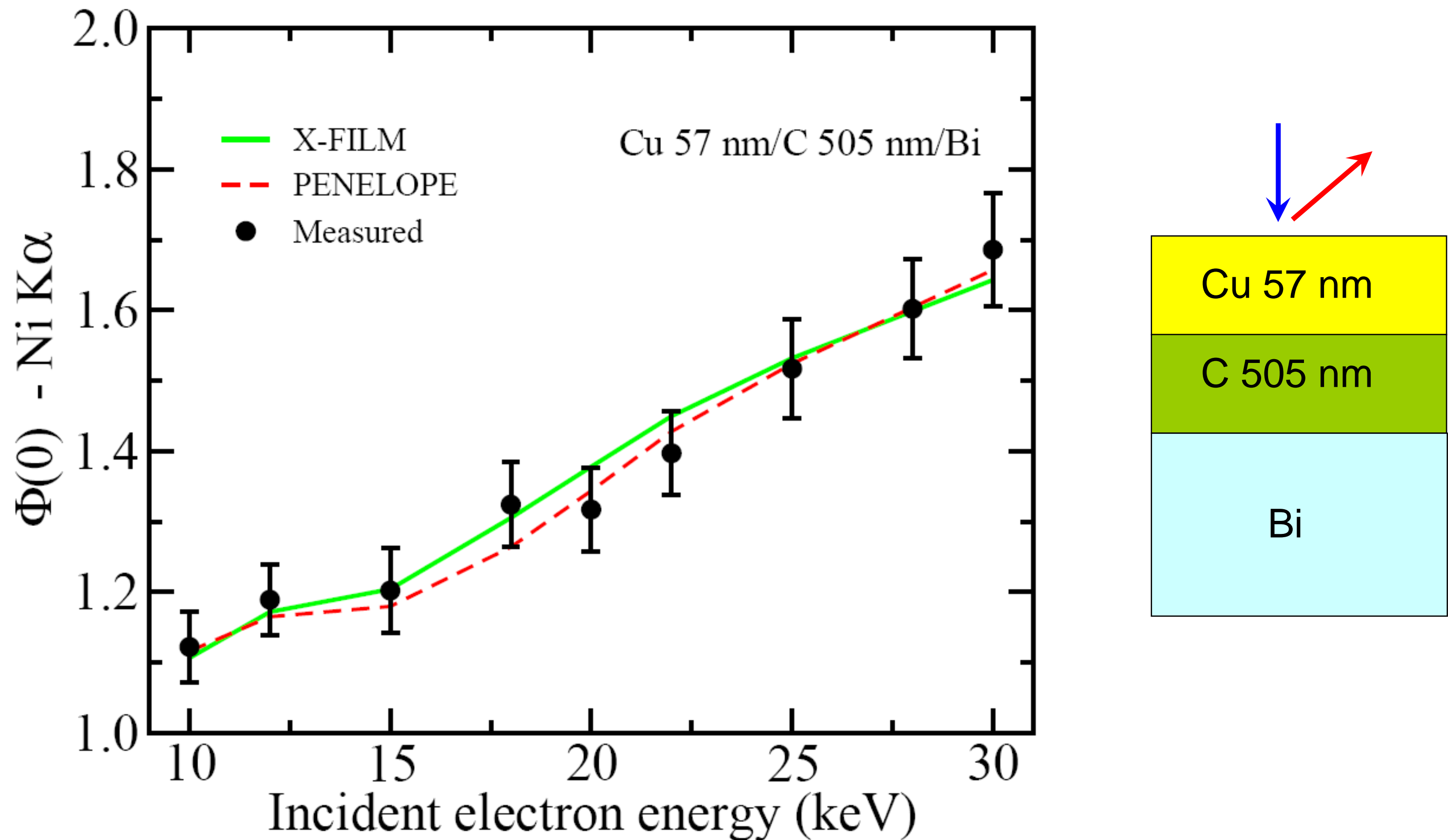
a_1,a_2: parameters

reduced thickness $x = 4t/\rho z_x$

Other thin-film programs: similar assumptions, with different weighting rules

Difficulties: experimental measurements of $\phi_{F/S}(\rho z)$ scarce

• The X-FILM model: surface ionization from multilayers



• The "weigthing" rule of Hunger & Rogachewsky describes satisfactorily the surface ionization from multilayer films, even for adjacent layers with very different *Z*

● The X-FILM model: emitted x-ray intensity

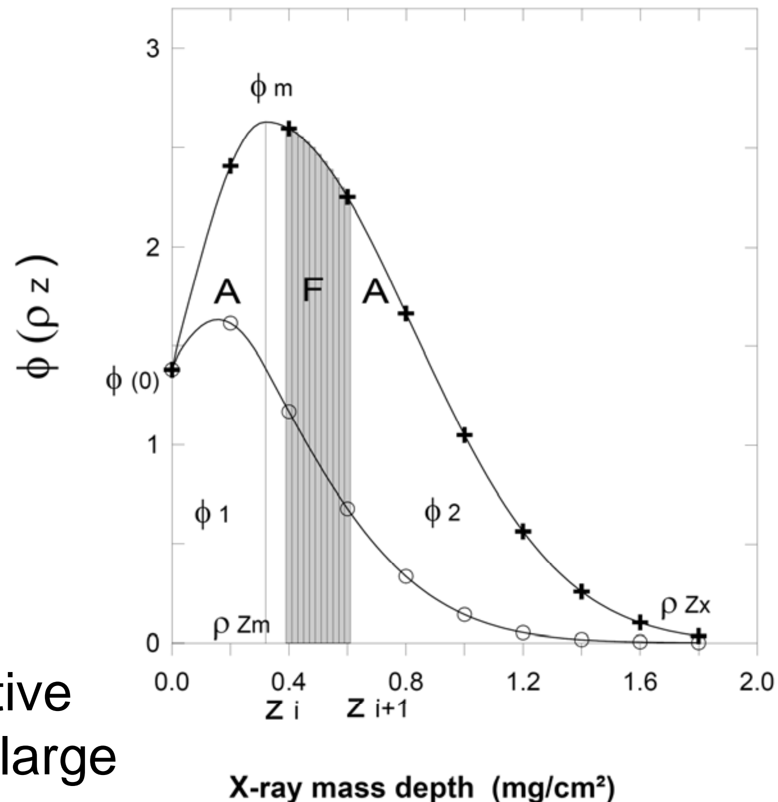
X-ray intensity can be computed analytically:

$$I_{ki} = \frac{\mathcal{A}\, c_i \Phi_m \zeta \sqrt{\pi}}{2} \exp(b) \prod_{j=1}^{k-1} \exp\left[-(\chi_{ki} - \chi_{ji})\, T_j\right] \left[\operatorname{erf}\left(\frac{t_{k+1} - \delta}{\zeta}\right) - \operatorname{erf}\left(\frac{t_k - \delta}{\zeta}\right)\right]$$

with: $\zeta = \begin{cases} \alpha & \text{for } 0 < \rho z < \rho z_{\mathrm{m}} \\ \beta & \text{for } \rho z_{\mathrm{m}} < \rho z < \rho z_{\mathrm{x}} \end{cases}$

$$b = \left[(\zeta\ \chi_{ki})/2\right]^2 - \rho z_{\mathrm{m}} \chi_{ki}$$

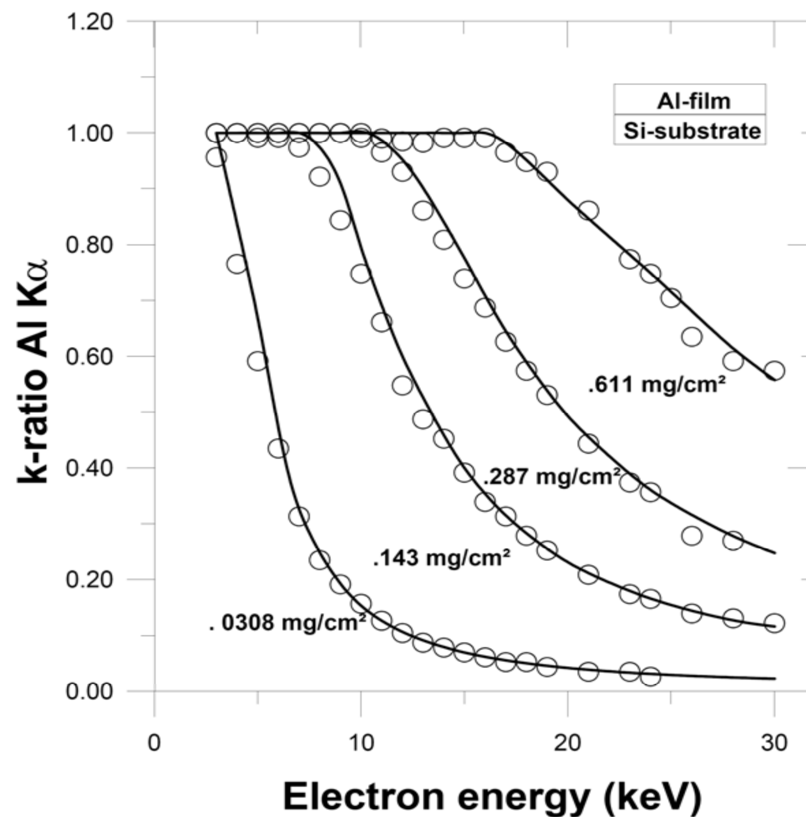
$$\delta = \rho z_{\mathrm{m}} - (\zeta\ \chi_{ki})/2$$

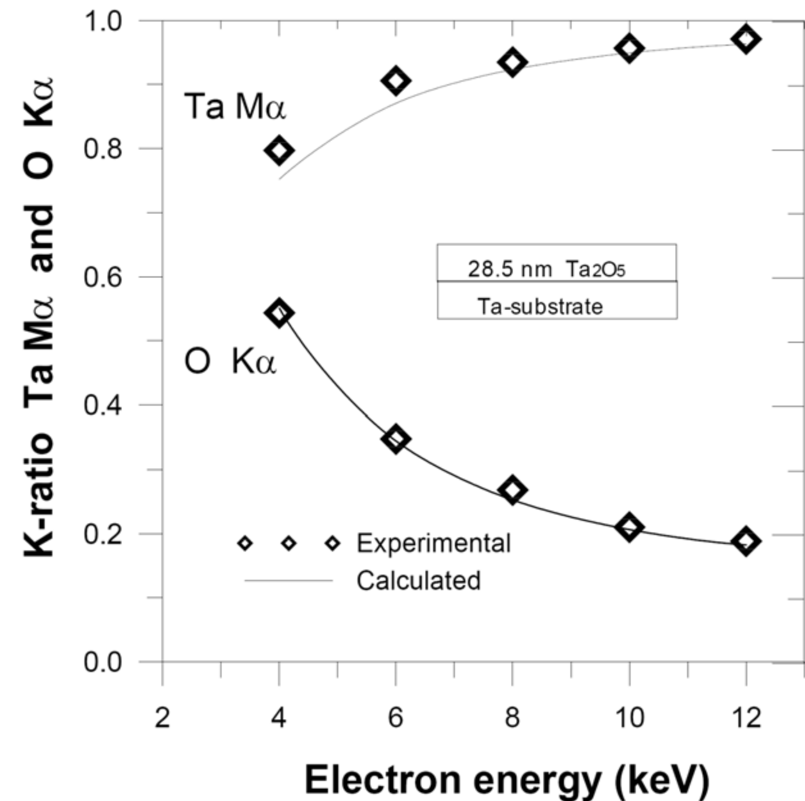


Fast calculations, useful for iterative procedures involving a relatively large number of iterations.

• Assessment of thin-film algorithms

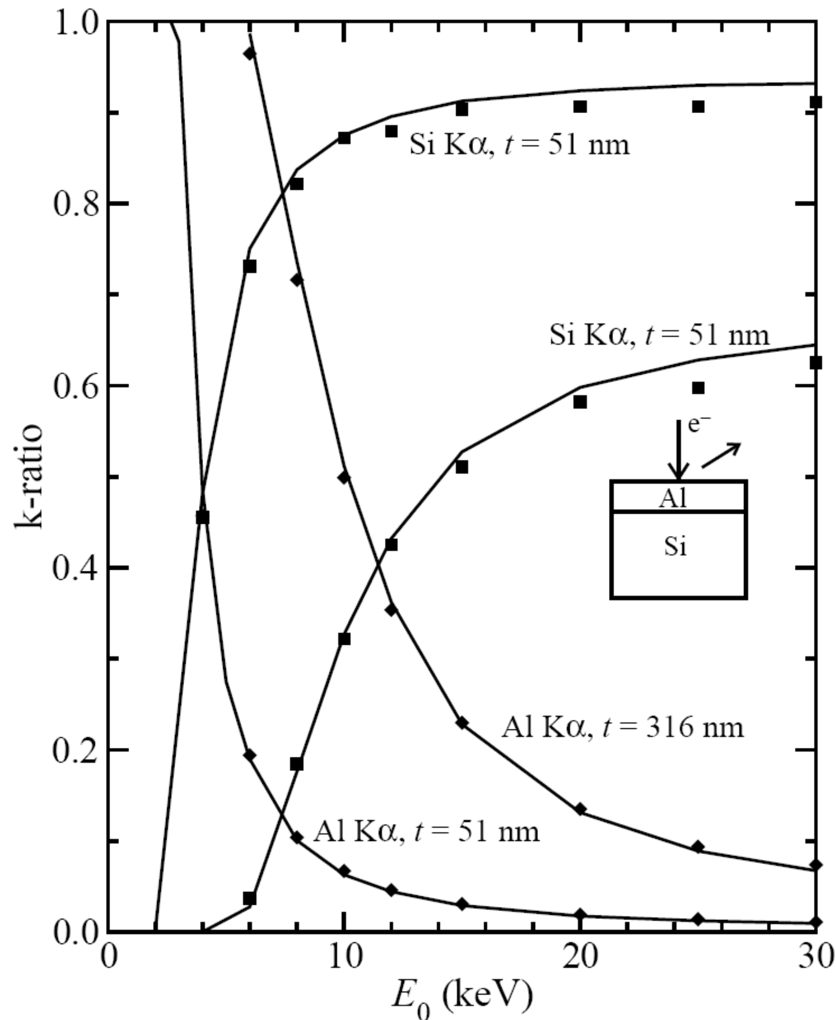
● Large number of *k*-ratio measurements on well characterized samples available in the literature: Reuter (1978), Bastin (2000), etc..

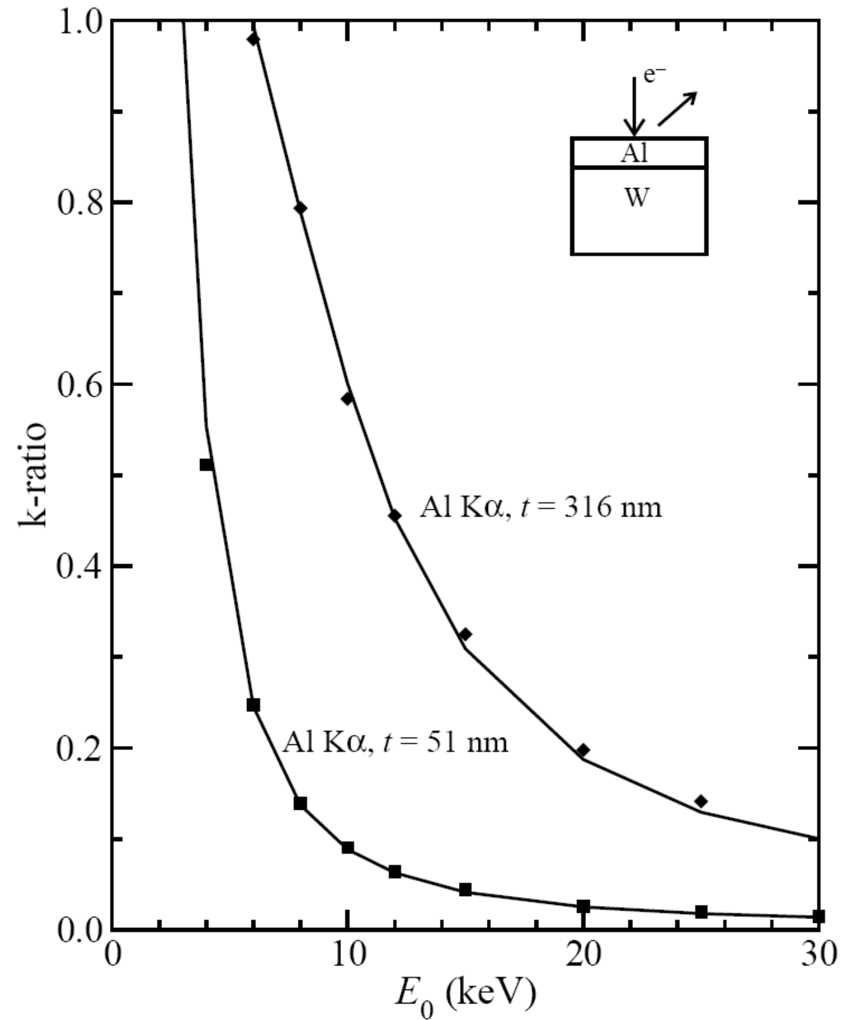




Experimental data: Reuter *et al* (1978) and Willich & Schiffmann (1992).
Continuous line: predictions of XFILM

• Assessment of thin-film programs

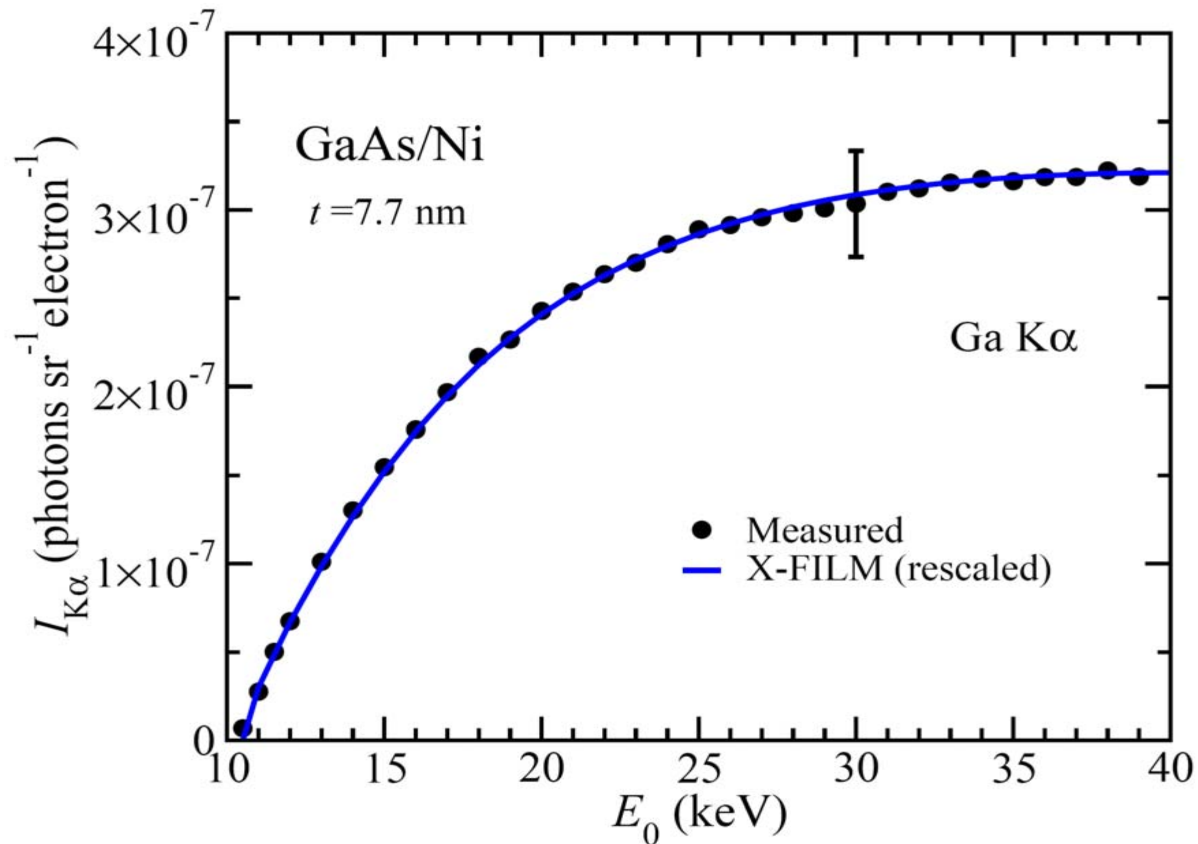




Experimental data: Bastin & Heijligers (2000)
Continuous line: Monte Carlo simulation results using PENELOPE

• Assessment of thin-film algorithms

Comparison of absolute x-ray intensities: stringent test of algorithms



Continuous line: predictions of XFILM

Stratagem - [M133.tff] - Parabolic, Fluo : L+C

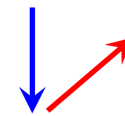
File Setup Computation Absorption Window Help

Sample Description

Layer	Element		Weight	# atoms		Mass Thick. (µg/cm²)	Thickness (nm)	Density
1	Bi	u	0.6609	0.2095	u	26.4	264.7	1.00
	Mn	u	0.2090	0.2520				
	O	u	0.1301	0.5385				
Substrate	Sr	k	0.4774	1.0000				
	Ti	k	0.2610	1.0000				
	O	k	0.2615	3.0000				

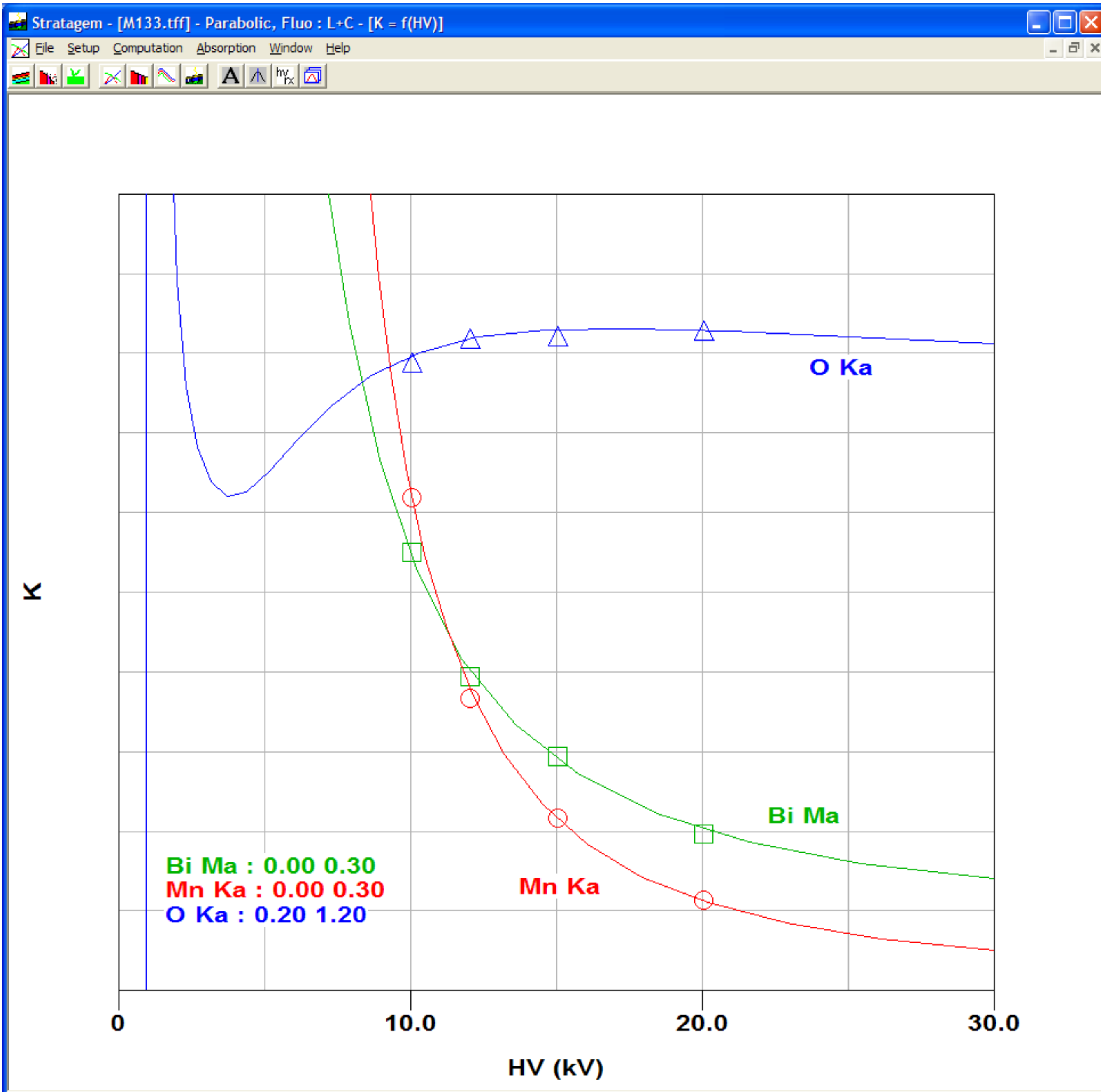
Experimental Data

anal.	Element	Line	Standard	HVstd	HVx	Ix/Istd	Kratio	Iter	Show
☑	Bi	Ma	Bi_BiSe_	10.06	10.06	0.1650	0.0903	☑	☑
				12.06	12.06	0.1181	0.0644	☑	☑
				15.06	15.06	0.0881	0.0472	☑	☑
				20.05	20.05	0.0588	0.0304	☑	☑
☑	Mn	Ka	Mn_Rhod	10.06	10.06	0.1858	0.0537	☑	☑
				12.06	12.06	0.1101	0.0328	☑	☑
				15.06	15.06	0.0648	0.0198	☑	☑
				20.05	20.05	0.0339	0.0105	☑	☑
☑	O	Ka	Sr_SrTiO	10.06	10.06	0.9895	0.0871	☑	☑
				12.06	12.06	1.0186	0.0705	☑	☑
				15.06	15.06	1.0228	0.0524	☑	☑
				20.05	20.05	1.0500	0.0379	☑	☑
☐	Sr	La	Sr_SrTiO	10.06	10.06	0.4637	0.1849	☐	☑
				12.06	12.06	0.8384	0.3370	☑	☑
				15.06	15.06	0.8672	0.3495	☑	☑
				20.05	20.05	0.8591	0.3431	☑	☑
☐	Ti	Ka	Sr_SrTiO	10.06	10.06	0.7849	0.2001	☑	☑
				12.06	12.06	0.8354	0.2132	☑	☑
				15.06	15.06	0.8852	0.2237	☑	☑
				20.05	20.05	0.9237	0.2267	☑	☑



Example: determination of thickness and composition of $BiMnO_3$ films on $SrTiO_3$ obtained by CVD

Results from STRATAgem



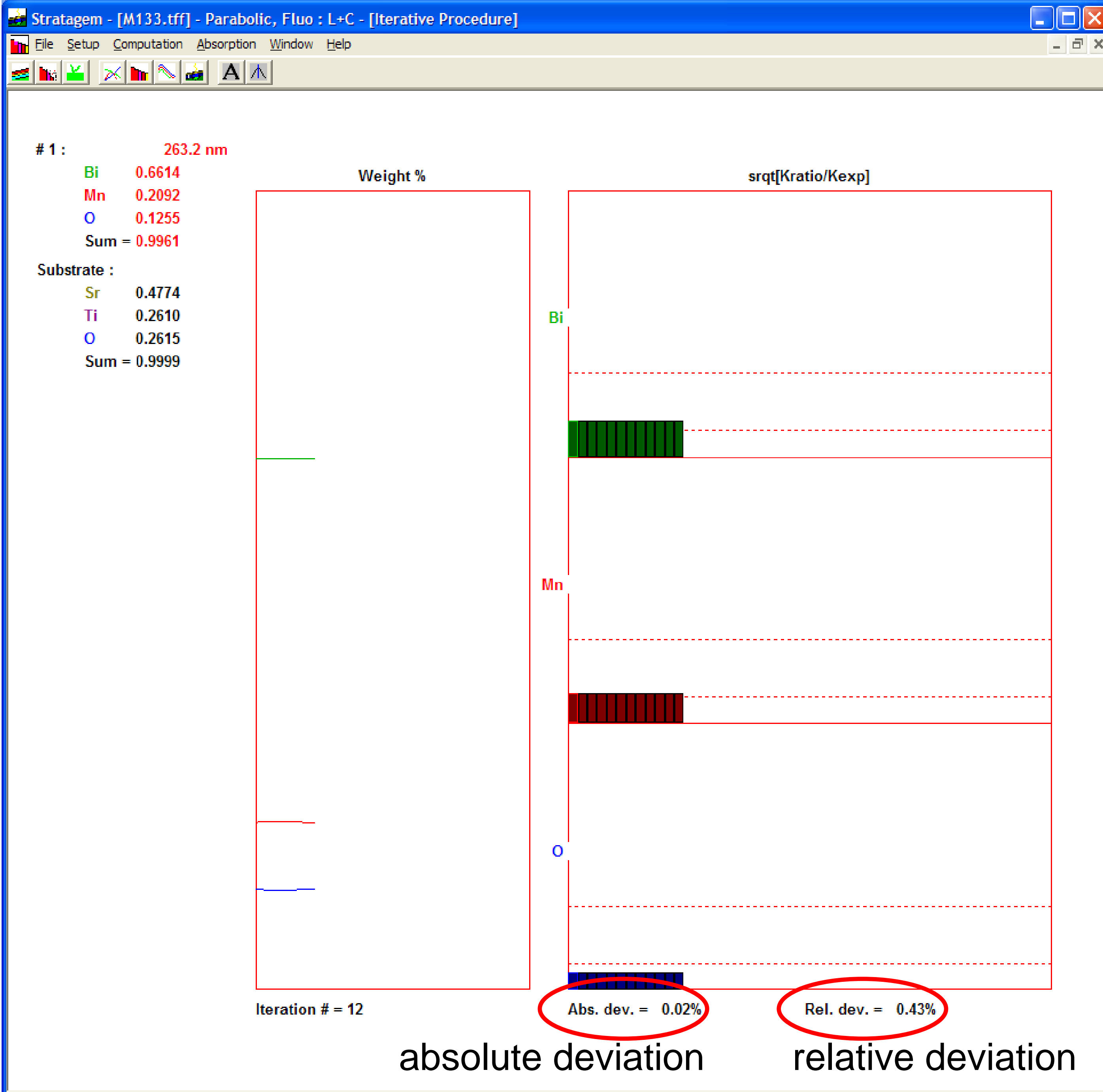
Bi = 66.1 wt.%

Mn = 20.9 wt.%

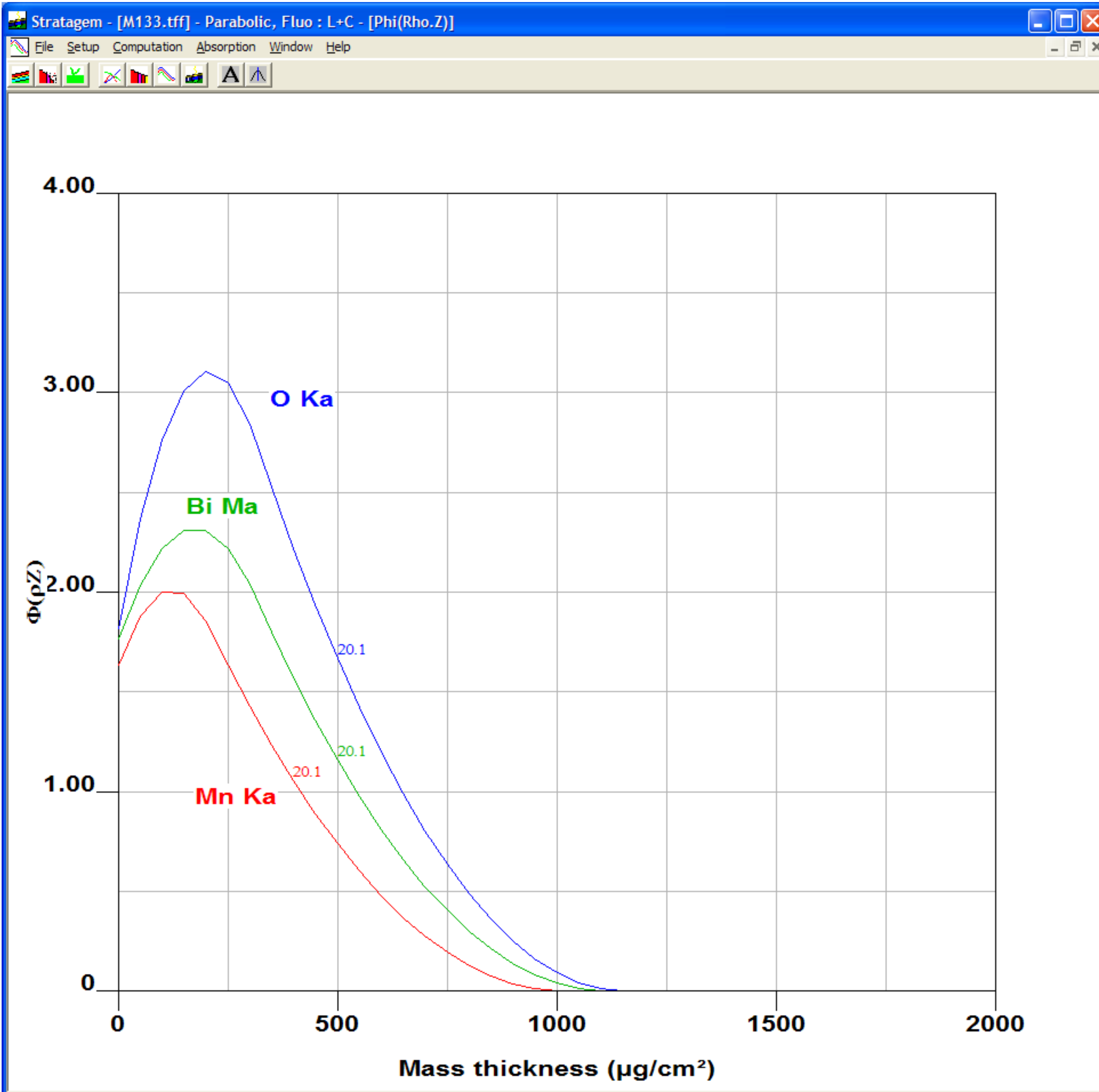
O = 12.55 wt.%

t = 26.4 $\mu g/cm^2$

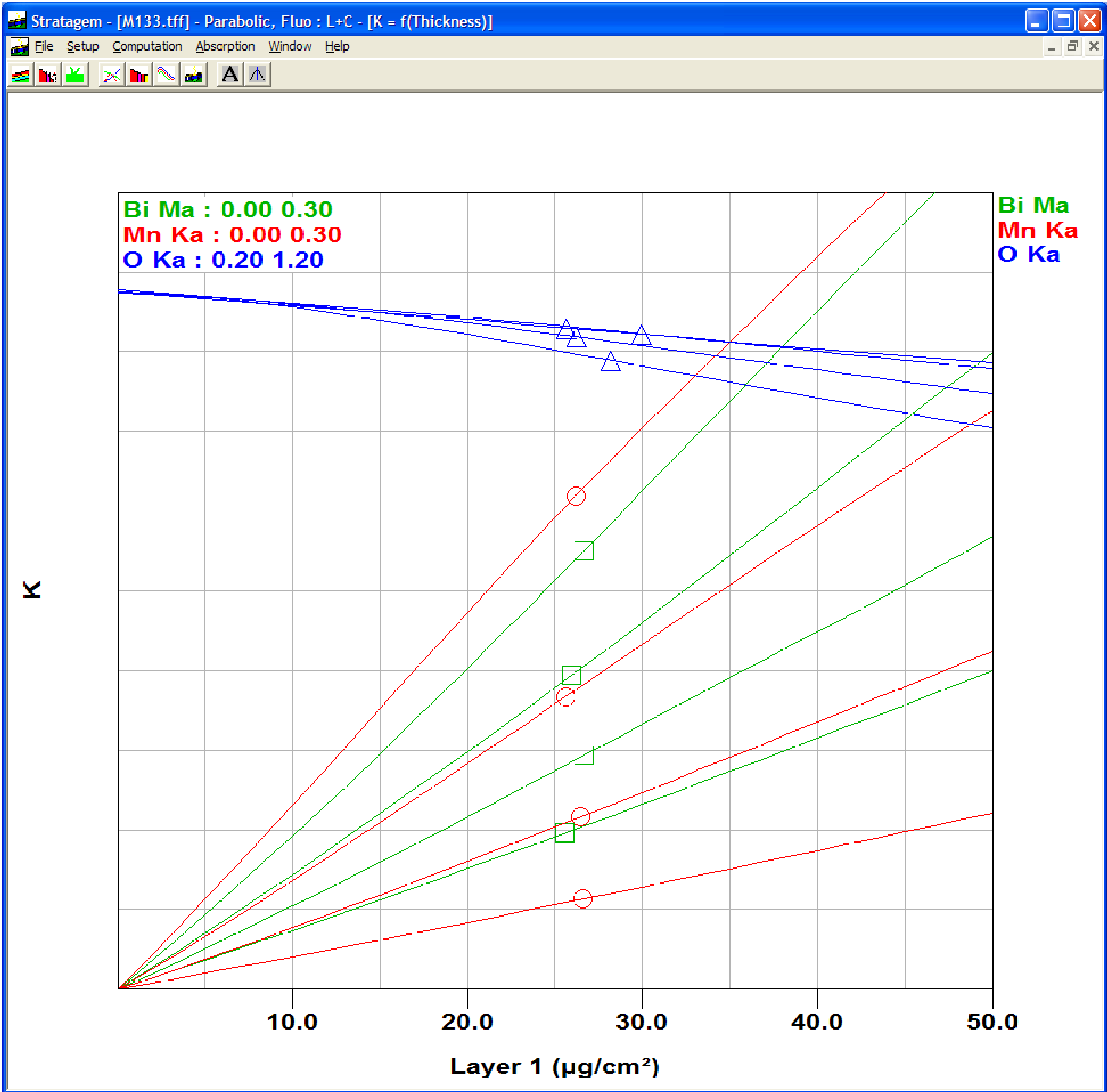
Comparison of the experimental *k*-ratios as functions of the incident electron energy with the predictions of the thin-film program for the estimated thickness and composition



Iterative process with the estimated concentrations and thickness and errors



Depth-distribution of ionizations for the measured elements at 20 keV



Bi = 66.1 wt.%

Mn = 20.9 wt.%

O = 12.55 wt.%

t = 26.4 $\mu g/cm^2$

Comparison of the k-ratio as a function of the estimated mass thickness for each energy

• Au/Ta

Ta Mα

Au/Ta

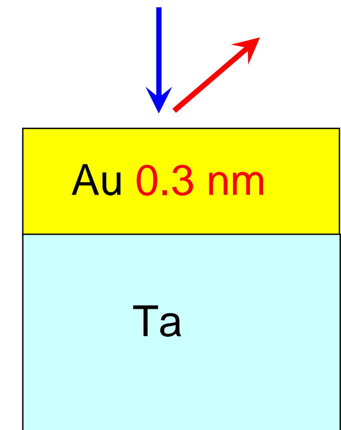
t = 0.5 μg/cm^2

Calculated XFILM
Measured
Calculated XFILM
Measured

Au Mα

K-ratio

Energy (keV)



Unknown:
film thickness

- Accuracy depends on number of measurements and x-ray lines used
- Similar difficulties to those found in trace element analysis
- Excellent sensitivity to surface layers

• Ge/Fe

Ge 7.0 nm / Fe

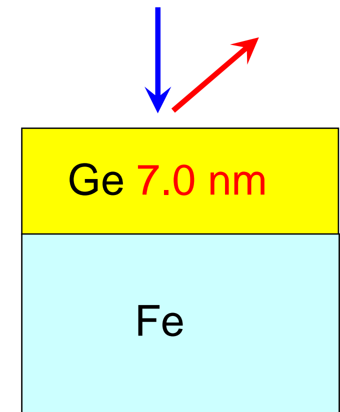
Fe Lα (x 0.2)

Ge Lα

- Calculated XFILM
- Measured
- Calculated XFILM
- Measured

K-ratio: 0.00, 0.05, 0.10, 0.15, 0.20, 0.25

Energy (keV): 0, 10, 20, 30



Unknown:
film thickness

- Optimal choice of accelerating conditions depends on thickness
- Good accuracy achieved in part due to similar *Z*

• Ni/GaAs

Ga $L\alpha$

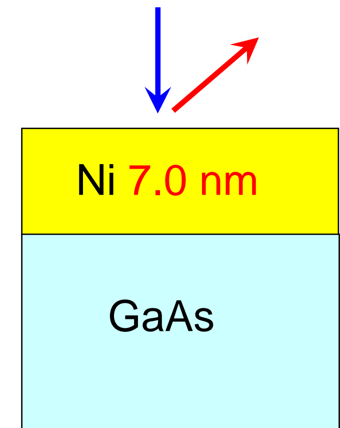
As $L\alpha$ (x 0.8)

Ni (6.6 μg/cm^2)/GaAs

Ni $L\alpha$

K-ratio

Energy (keV)

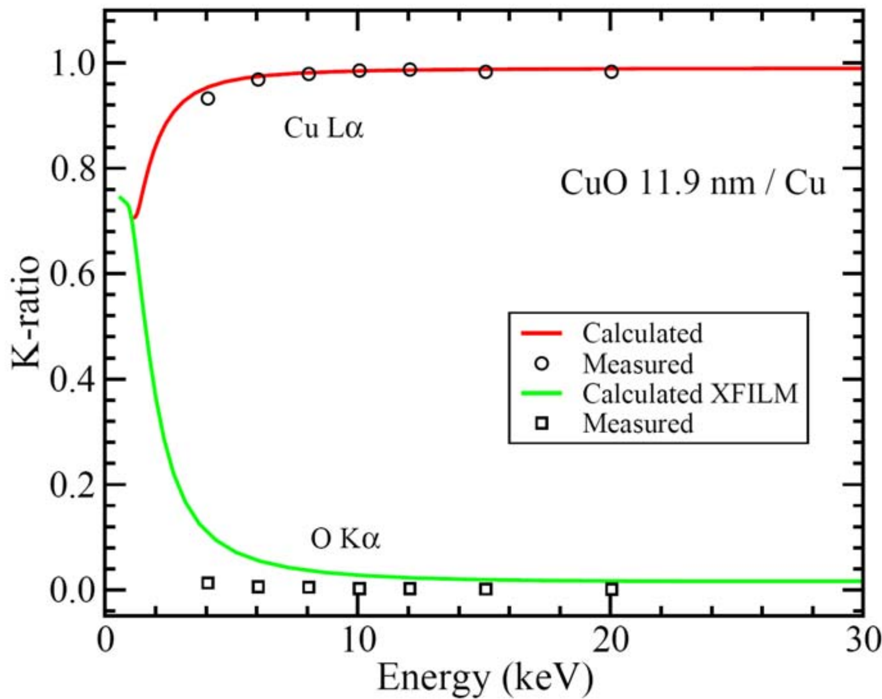


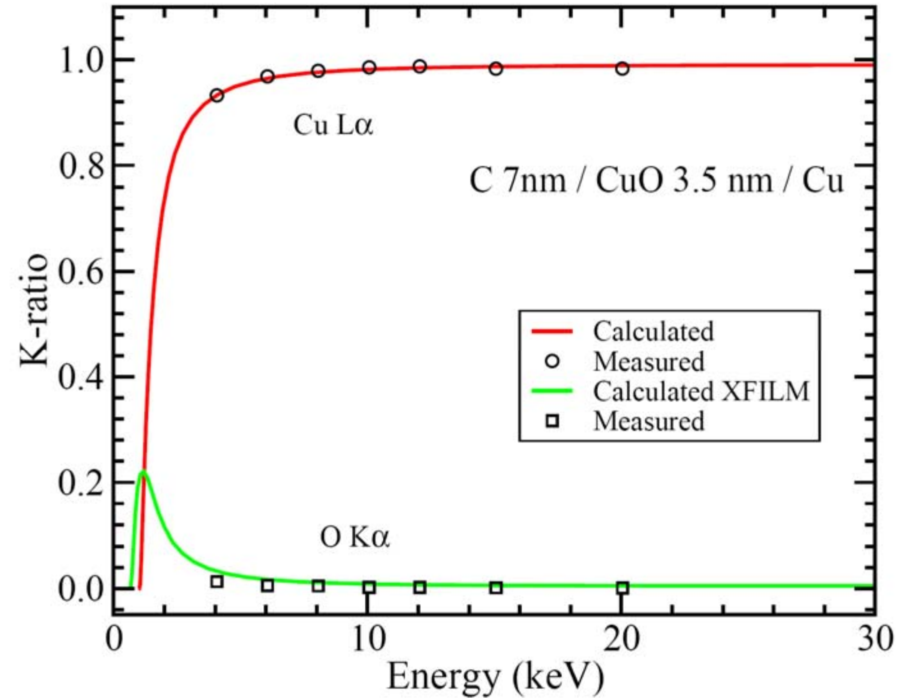
Unknown: film thickness

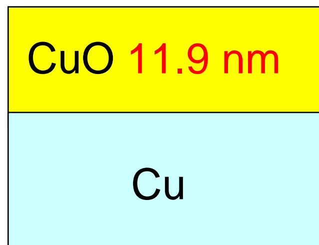
- Influence of surface contamination: native oxide layer, carbon, Si, etc..
- Accuracy may also depend on conditions of the standards

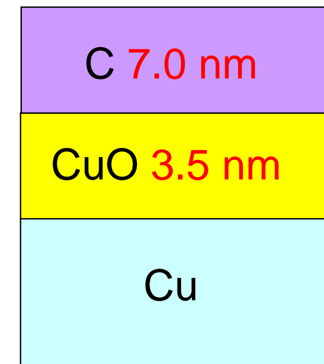
• Cu oxide films

- Measurements from substrate elements useful to check consistency
- Agreement improves by assuming a C layer on top

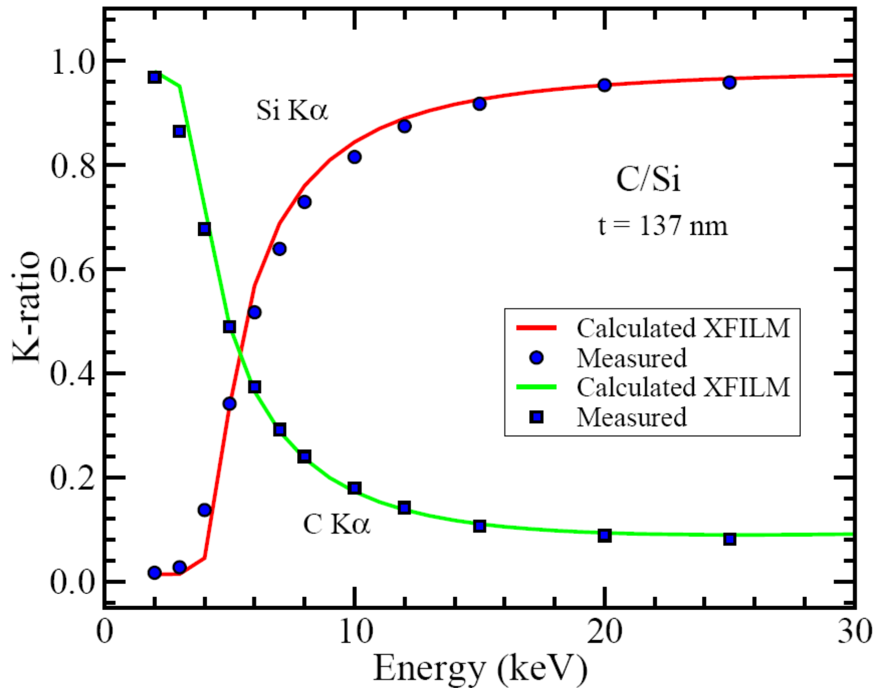


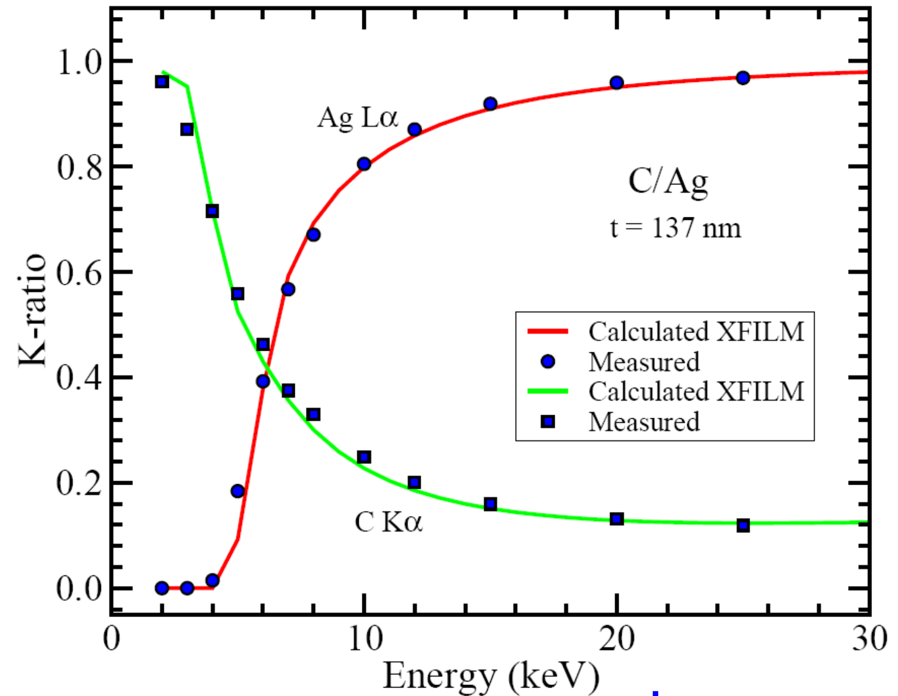




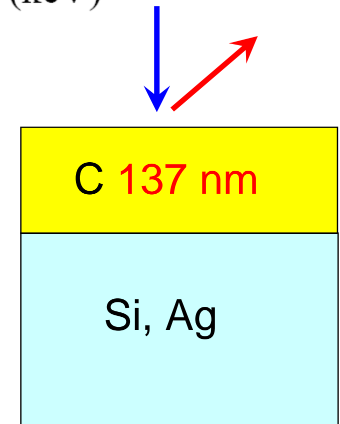


• Carbon films on several substrates





- Films obtained simultaneously (same thickness) by evaporation
- Good agreement even for large differences in *Z*



• Ga-As/Ni

$Ga_{0.62}As_{0.38}$ (5.6 nm)/Ni

Ni $L\alpha$ (x 0.015)

As $L\alpha$

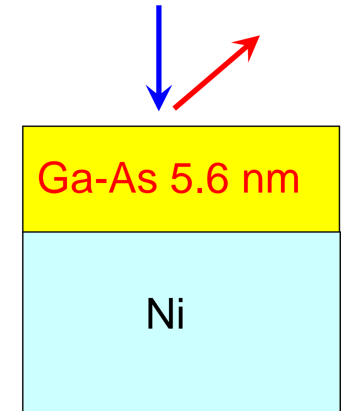
Ga $L\alpha$

As $K\alpha$

Ga $K\alpha$

K-ratio

Energy (keV)



Unknown: film thickness and composition

- Measurements using different x-ray lines (film and substrates elements) not required but useful to check consistency.

• In-Ga-As/GaAs

Continuous line: STRATAgem

K-ratio

1.0
0.8
0.6
0.4
0.2
0.0

As $L\alpha$

Ga $L\alpha$

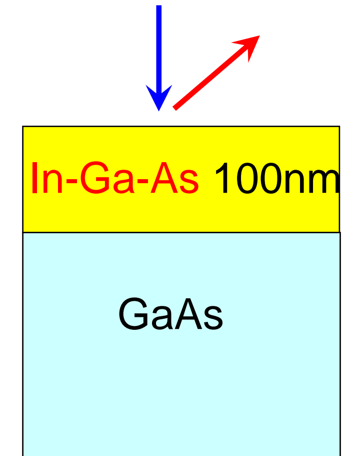
In $L\alpha$

$In_{0.13}Ga_{0.39}As_{0.49}$/GaAs

t = 53.5 $\mu g/cm^2$

0 5 10 15 20 25 30

Energy (keV)

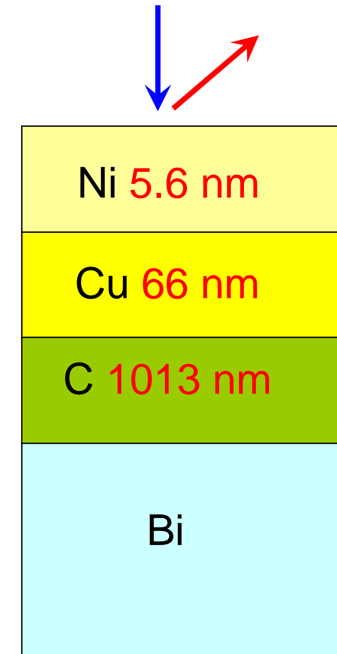


Unknown:
film composition

- Elements present simultaneously in both film and substrate
- Thickness obtained by other techniques

• Ni/Cu/C/Ag

Cu $L\alpha$
Cu $K\alpha$
Ag Lα
Ni $L\alpha$
C $K\alpha$
X-ray intensity ratio
0.00 0.20 0.40 0.60 0.80
10 20 30
Energy (keV)



Unknown: thicknesses

- Accuracy may vary depending on the particular case

Continuous line: X-FILM

• Au-Pd/Al_2O_3/Al/SiO_2/Si

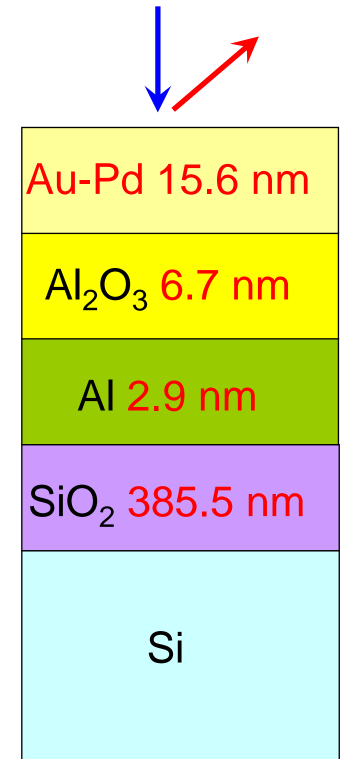
Experimental measurements: E. Heikinheimo
Continuous line: STRATAgem

Au Mα
Pd La
Si Ka
O Kα
Al Kα

$Au_{0.68}Pd_{0.32}/Al_2O_3/Al/SiO_2/Si$

K-ratio: 0.0, 0.2, 0.4

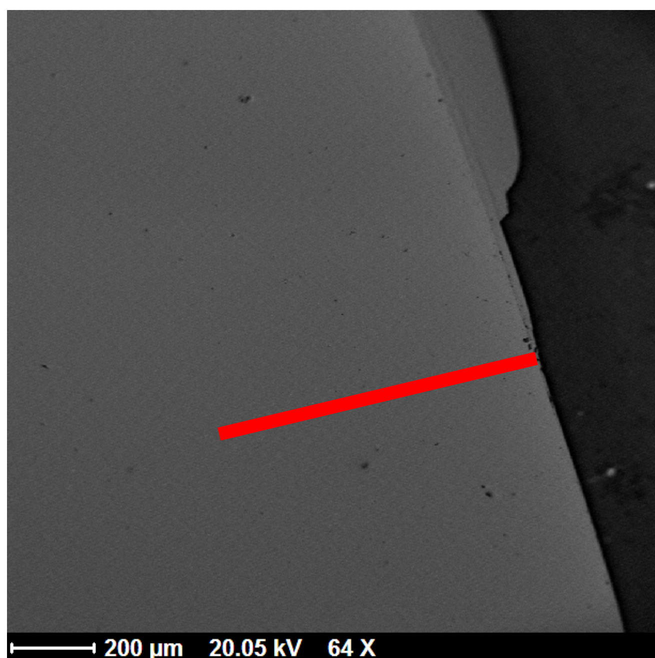
Energy (keV): 5, 10, 15

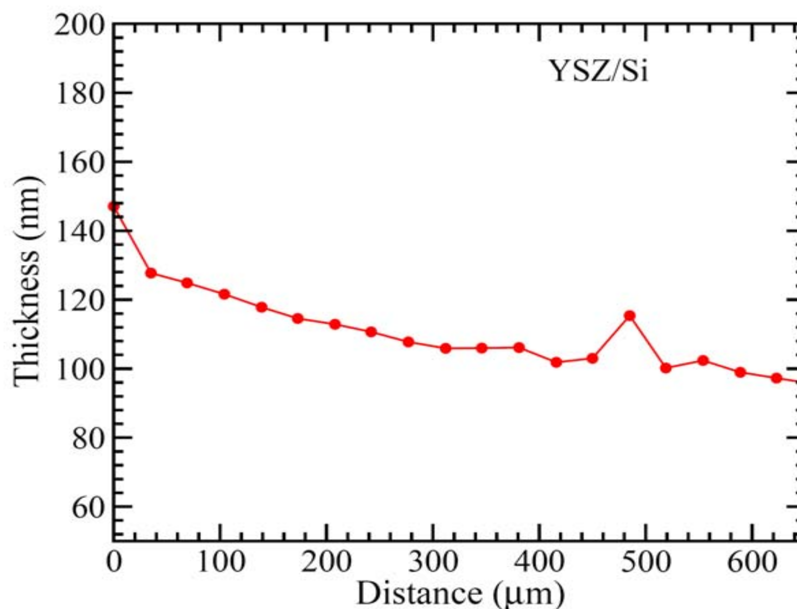


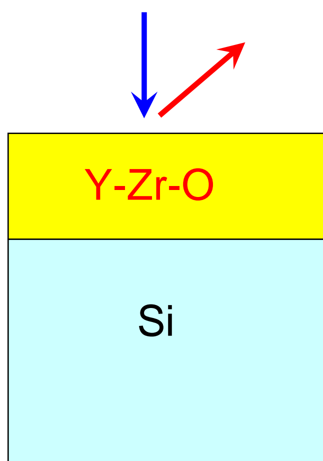
Unknown:
Au-Pd composition
& layers thickness

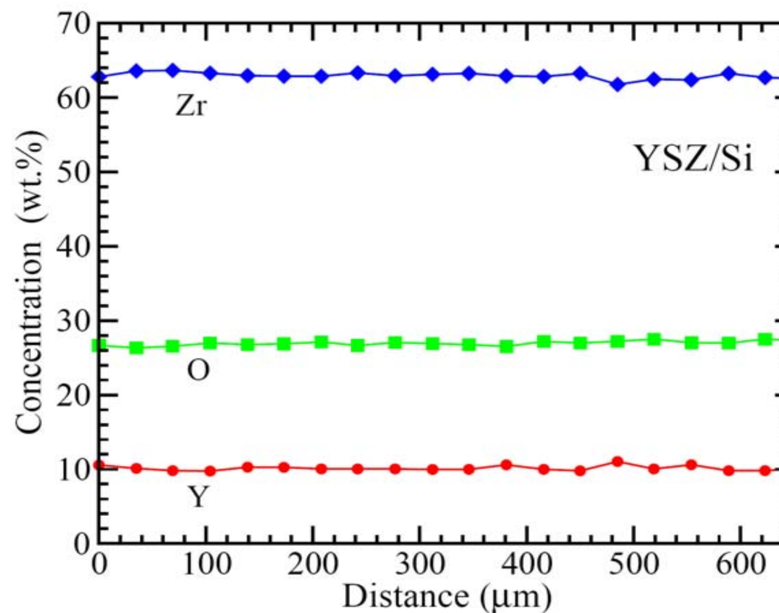
- Sample structure required if elements present in different layers
- Alternatively, solution by trial-error mode (graphical interface)

• Lateral resolution of thickness & composition



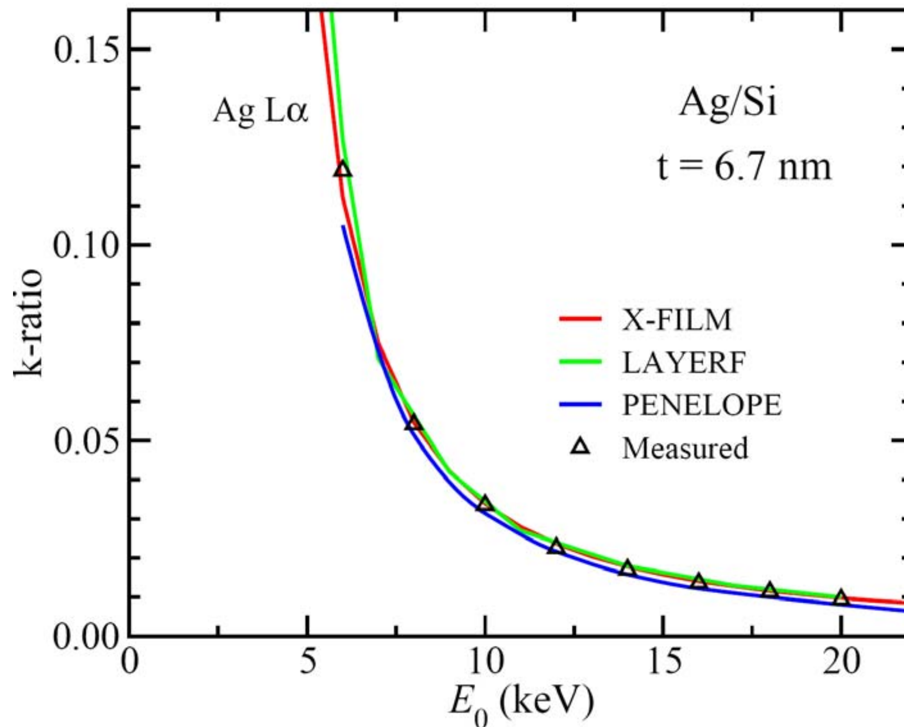






Results obtained by using STRATAline

• Comparison with other thin-film programs & techniques



- Campos *et al.* (1999): thickness difference < 5% for very thin films on Si from different approaches (quartz crystal, LAYERF, X-FILM, PENELOPE)

Layer element	Quartz crystal	LAYERF Lα	LAYERF Mα	X-FILM Lα	X-FILM Mα	PENELOPE
	Thickness (nm)					
Ge	6.8 (0.2)	6.9 (0.3)	-	6.6 (0.3)	-	6.6 (0.4)
Ag	6.7 (0.3)	6.8 (0.3)	-	6.7 (0.1)	-	6.9 (0.3)
Sn	6.4 (0.4)	6.3 (0.1)	-	6.2 (0.1)	-	6.1 (0.2)
Au	7.1 (0.2)	7.0 (0.2)	7.0 (0.2)	7.0 (0.1)	7.2 (0.1)	6.9 (0.7)

• Conclusions

- It is possible to determine the composition and thickness of thin films and multilayers non-destructively by EPMA
- The technique requires measurements at varying incident electron energies and analysis of measured *k*-ratios by means of a thin-film program
- High sensitivity for detecting surface layers (thickness of 0.1 μg/cm^2)
- Thin films on substrates. Thicknesses and compositions with accuracy better than 5% can be routinely obtained
- Difficulties for complex multilayers if elements are present in different layers and/or x-rays from buried layers are strongly attenuated. Accuracy depend on each particular case.
- Lateral resolution of the order of 1 micron

EPMA is a versatile tool for thin-film analysis, supplementing the information obtained from conventianal surface-analytical techniques (SIMS, AES, XPS..)