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Surface Characterization

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Outline

- Surface and surface Characterisation
- X-ray Photoelectron Spectroscopy (XPS)
- Rutherford Backscattering (RBS)
- Secondary Ion Mass Spectroscopy (SIMS)

Surface

What is surface in vacuum?

- A special interface between solid and vacuum Interface: a small number of atomic layers that interact with residual gas and charged particle in the vacuum.

Why surface is important?

- Many properties determined by the surface/interface
  - ✓ SEY and PEY,
  - ✓ ESD and PSD
- Many processes happens mainly at surface
  - ✓ Chemical reaction
  - ✓ Gettering,
  - ✓ Field emission
  - ✓ Corrosion
  - ✓ Adhesion
- Surface/interface may differ significantly from the bulk
  - ✓ Phase Density,
  - ✓ Composition,
  - ✓ Mechanical,
  - ✓ Electronic

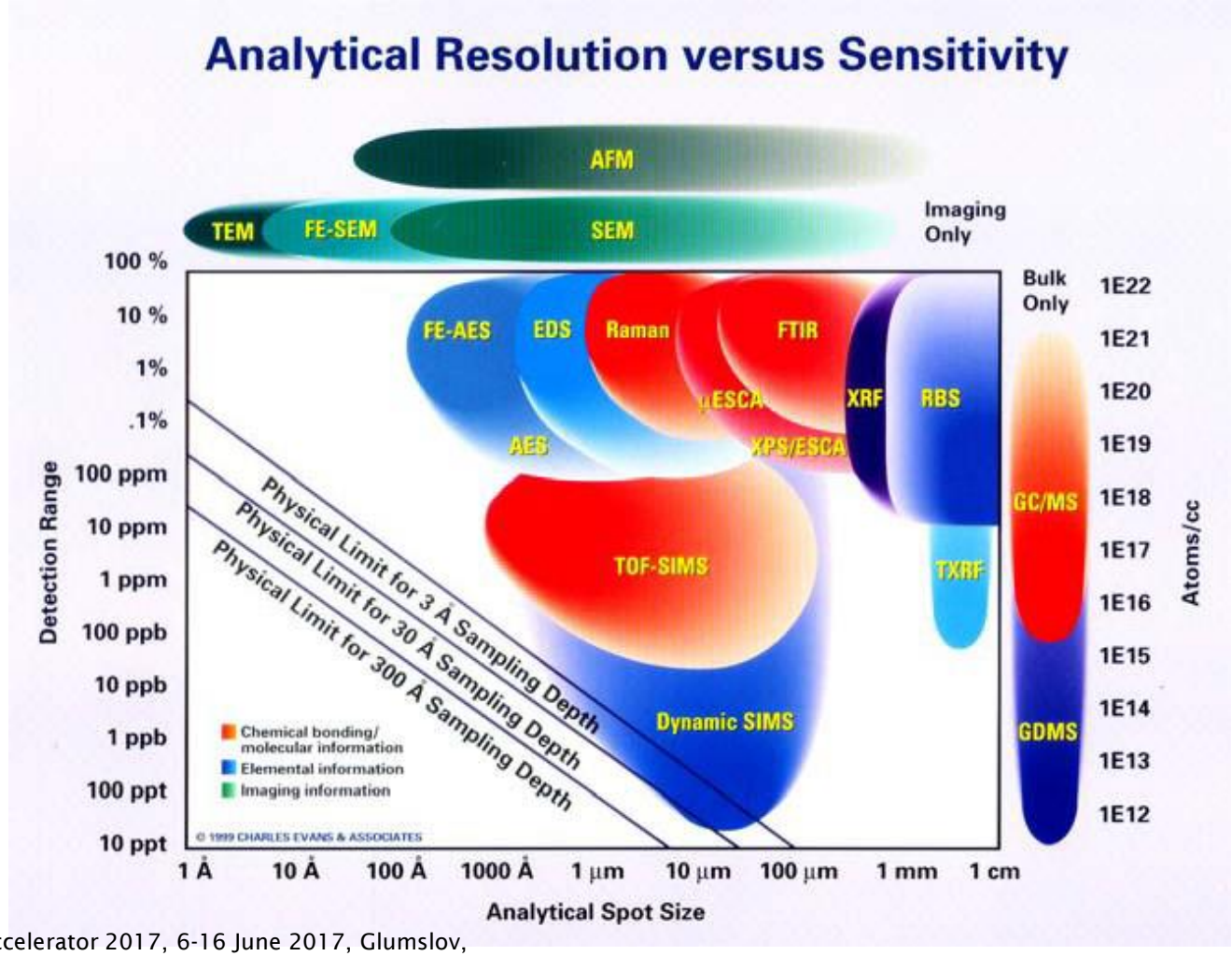
How to achieve desired surface

- **Surface preparation:**
  - ✓ Using solvent to wash away any organic contaminants
  - ✓ Polishing
  - ✓ Chemical etching
  - ✓ Plasma cleaning
  - ✓ Surface coating
  - ✓ Nanotechnology structuring
  - ✓ Surface passivation

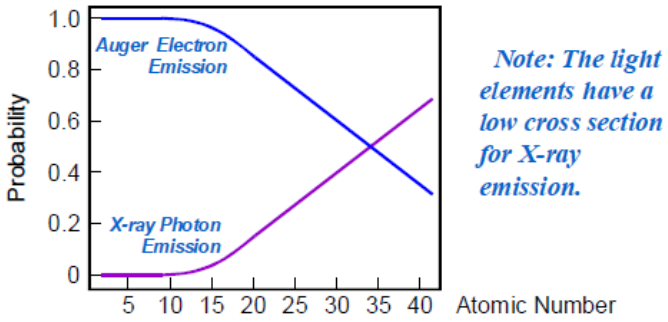
- **Determining the surface properties:**
  - ✓ Composition
  - ✓ Chemical states
  - ✓ Surface roughness
  - ✓ Surface morphology
  - ✓ Surface electronic properties
  - ✓ Surface area

Surface Characterisation

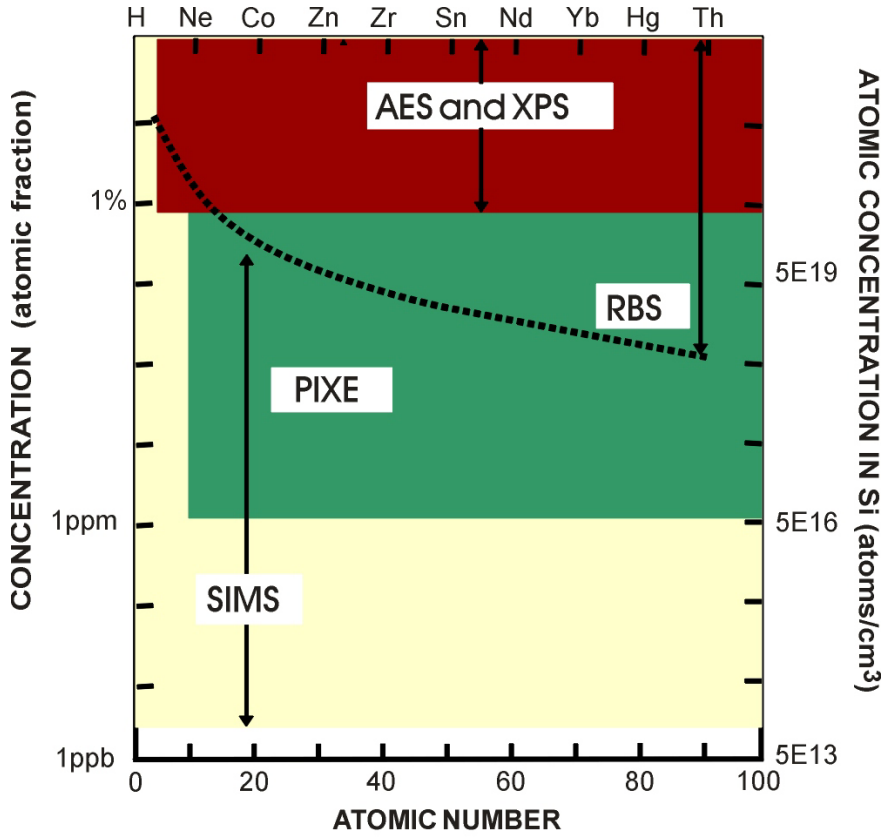
What surface characterisation is available?



Comparison of Sensitivities.



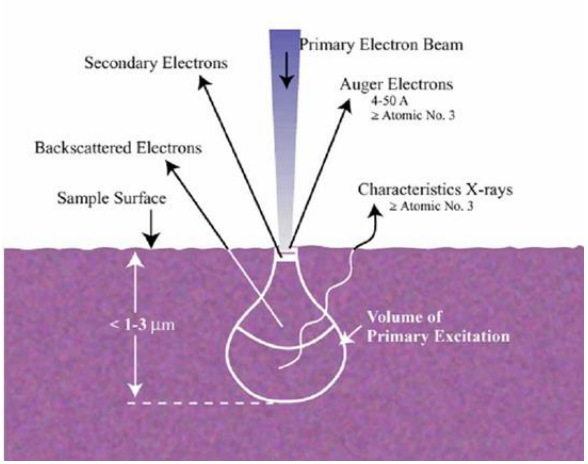
Note: The light elements have a low cross section for X-ray emission.



XPS X-ray Photoelectron Spectroscopy
AES Auger Electron Spectroscopy
RBS Rutherford Backscattering
SNMS Plasma-based Sputtered Neutral Mass Spectrometry
SIMS Secondary Ion Mass Spectrometry

Electron solid interaction

Secondary electrons (SEs): are produced by the interactions between energetic e's and weakly bonded valence e's of the sample



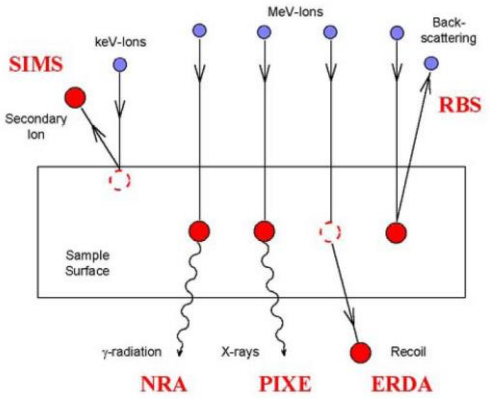
Backscattered electrons (BSEs): are primary e's leaving the specimen after a few large angle elastic scattering events

Auger electron: incident e- kicks out an inner shell e-, a vacant e- state is formed; this inner shell vacant state is then filled by another e- from a higher shell, and simultaneously the energy is transferred to another e- that leaves the sample

Characteristic X-rays: emitted when a hole is created in the inner shell of an atom in the specimen due to inelastic e- scattering, as it can recombine with an outer shell e- (EDX)

Cathodoluminescene (CL): light emission arising from the recombination of e-h pairs induced by excitation of e's in the valence band during inelastic scattering in a semiconducting sample

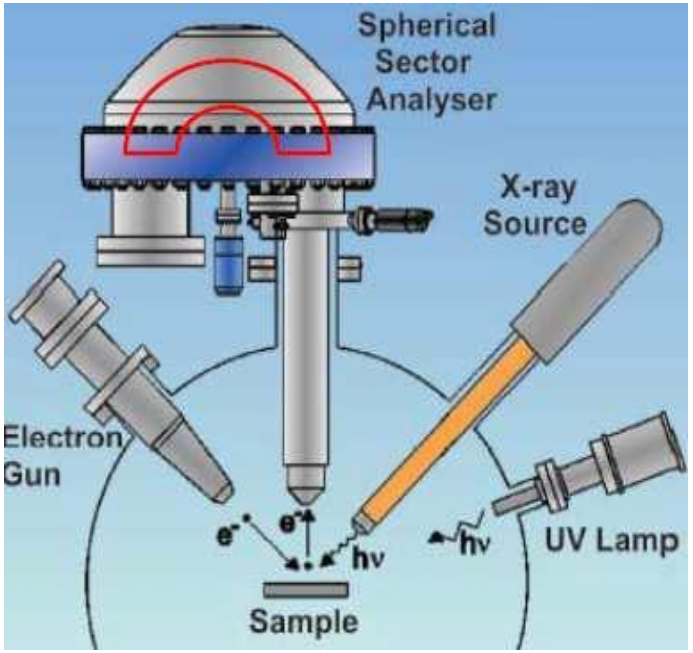
Ion-solid interaction

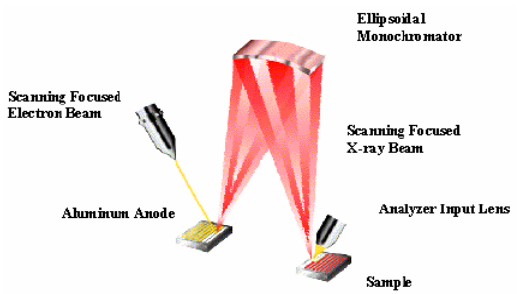


1) elastic scattering
2) fast recoils arising from elastic scattering
3) steering effects due to the crystalline structure of target atoms
4) inelastic processes: energy loss as a function of depth
5) nuclear reactions
6) X-Ray production

XPS , Auger and UPS Instrumentation

- Essential components:
- Sample: usually 1 cm2
- X-ray source: Al 1486.6 eV;
  Mg 1256.6 eV
- Electron Energy Analyzer:
  100 mm radius concentric hemispherical analyzer (CHA); vary voltages to vary pass energy.
- Detector: electron multiplier (channeltron)
  Electronics, Computer
- Note: All in ultrahigh vacuum (<10-8 Torr) (<10-11 atm)
- State-of-the-art small spot ESCA: 5 μm spot size Sputtering gun for profiling





Strength and limitation of XPS

Strength:

- Surface sensitive technique (top 10 nm)
- Identifies the surface chemical states
- Identifies the surface composition
- Quantitative analysis, including chemical differences
- A wide variety of material can be analysed, including non conducting samples
- Oxide thickness measurements
- Depth profiling

Limitations:

- Detection limit typically 0.1%
- Limited organic information,
- Long acquisition time
- Samples must be in XHV vacuum

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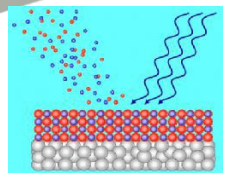
X-ray Photoelectron spectroscopy

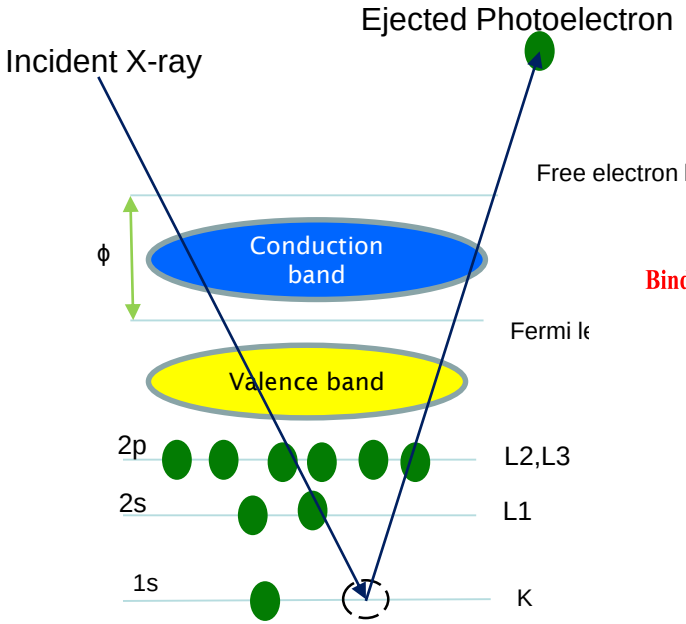


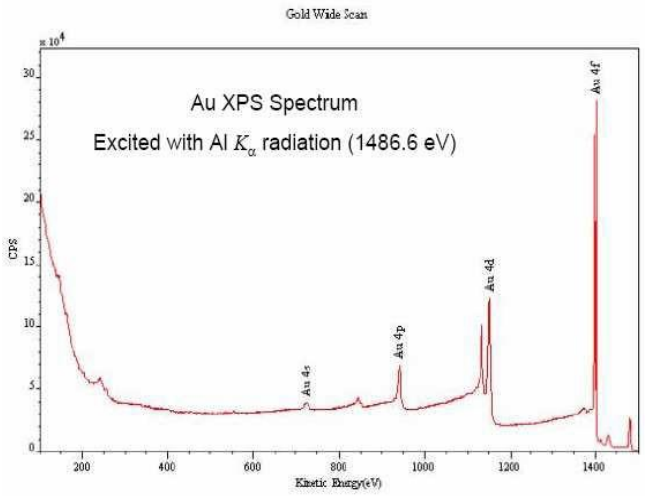
Conservation of that :

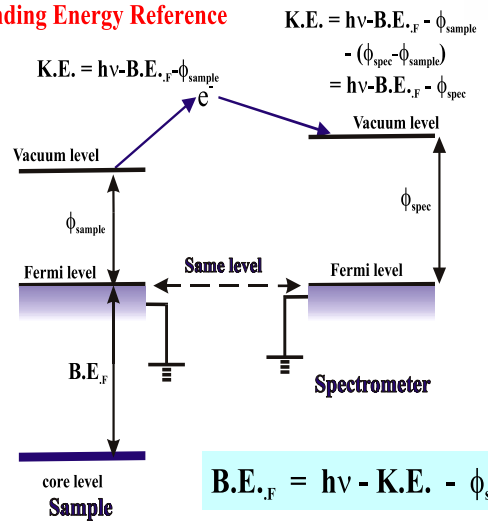
KE = hν - (E(A⁺) - E(A)) – Φ

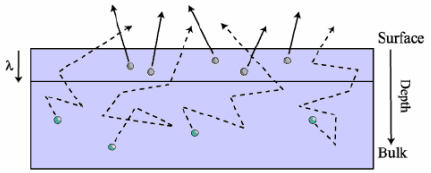
Where

(E(A⁺) - E(A)) is the binding energy (BE) of the electron.









B.E.$_{.F}$ = hν - K.E. - ϕ$_{spec}$

atoms have valence and core electrons: Core-level Binding energies provide unique signature of elements.

Sampling depth

Beer-Lambert relationship

$$I_d = I_0 \exp(-d/\Lambda \sin\theta)$$

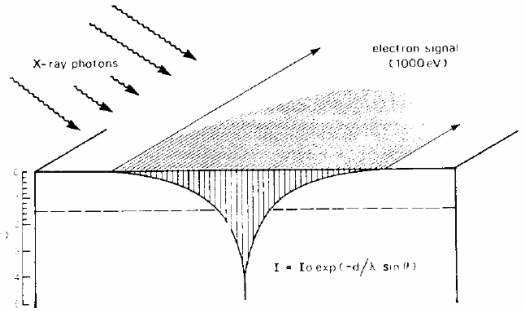
Where

I_d= intensity of emitted photoelectron as a function of depth (d)

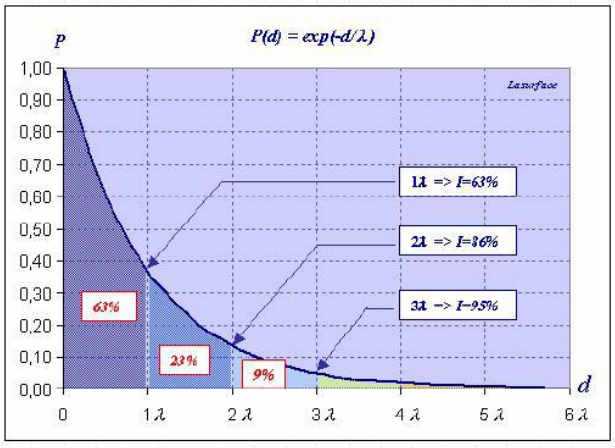
I_0 = intensity of emitted photoelectron from an infinity thick substrate

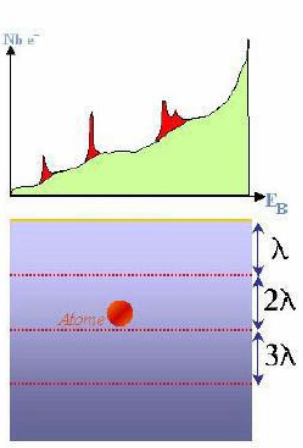
Λ = inelastic mean free path of electron **(1-3.5 nm)**

θ = electron take-off angle relative to the surface



P = probability of emitted electron reaches the surface and being analysed.



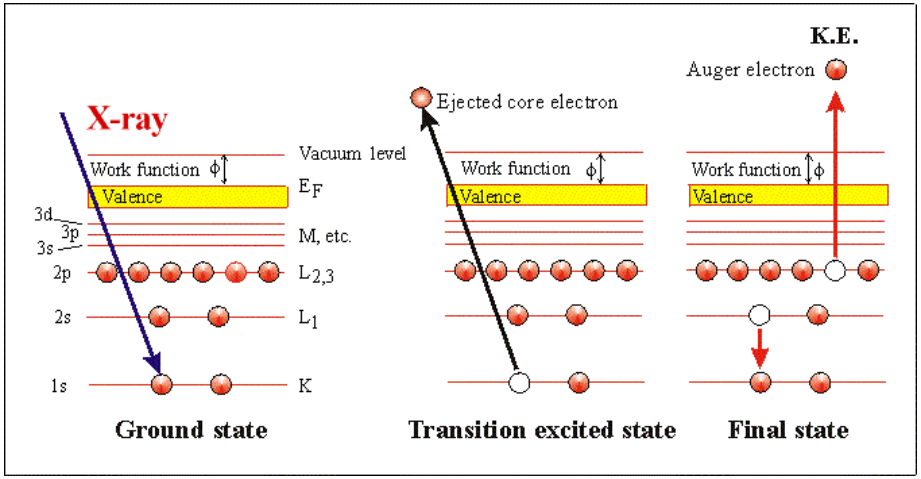


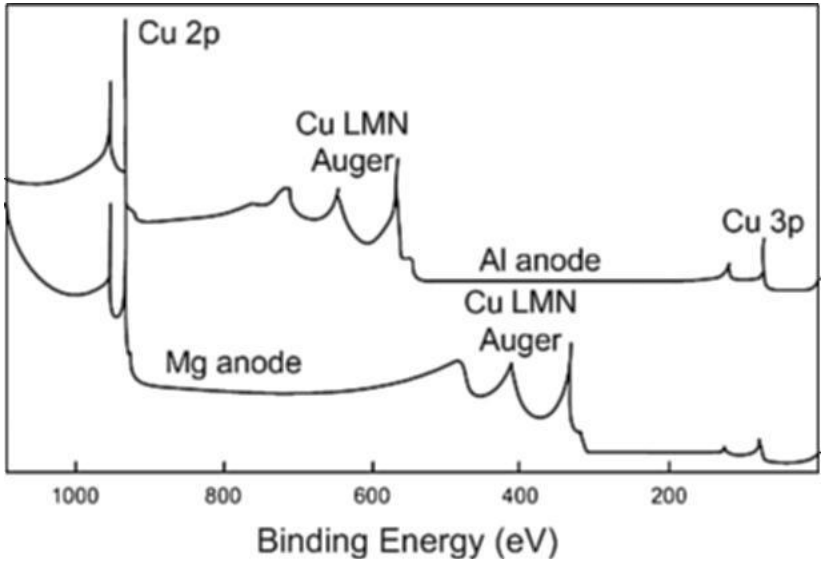
If $\theta = 90^o$

$$P = I_d/I_0 = \exp(-d/\lambda)$$

Sampling Depth is defined as the depth from
which 95% of all photoelectrons are scattered
by the time they reach the surface (3λ)
for XPS this is (1-10nm)

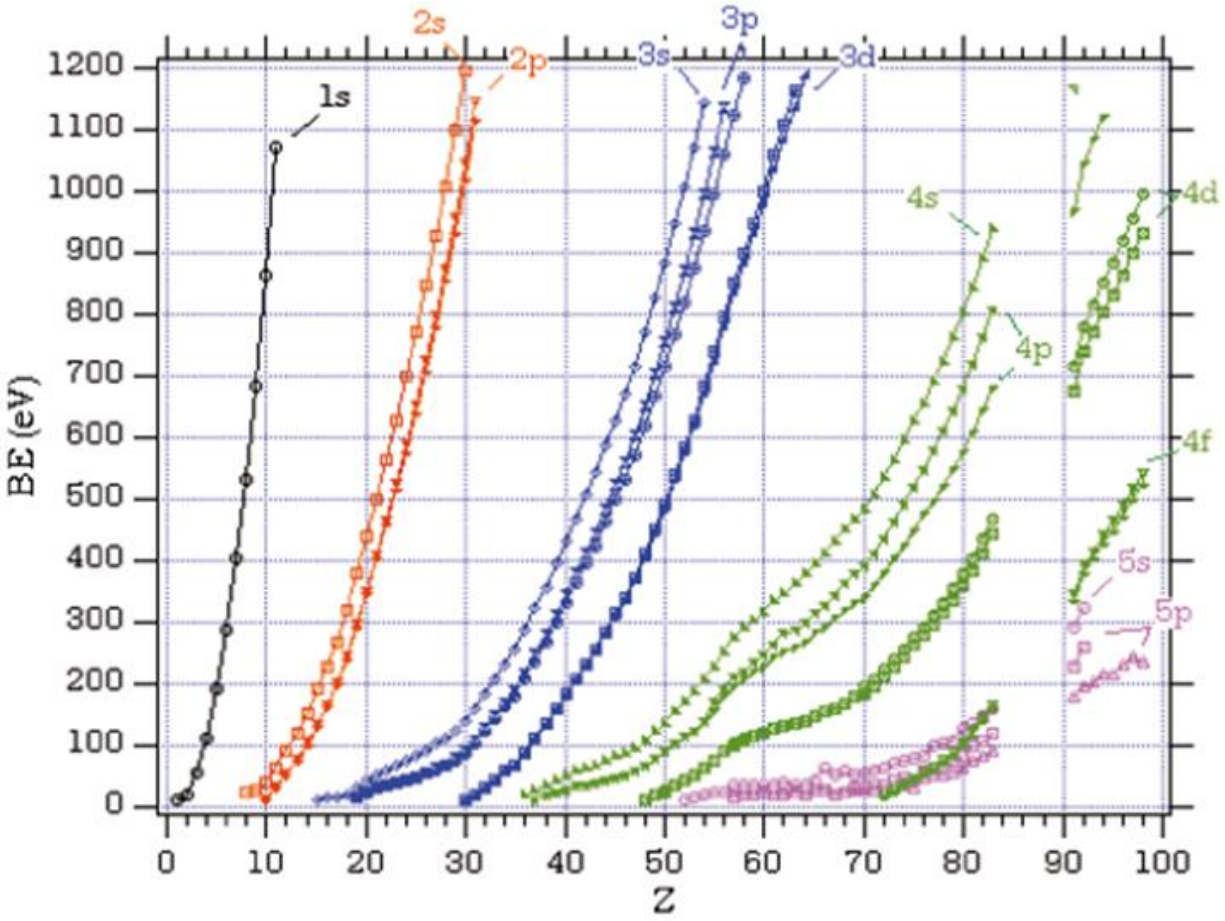
X-ray induced Auger electron





Cu XP spectra illustrating the shift in Auger peak positions with change from Mg to Al anodes in the x-ray source (Auger is dependent on the photon energy)

Z dependence of BE(eV)

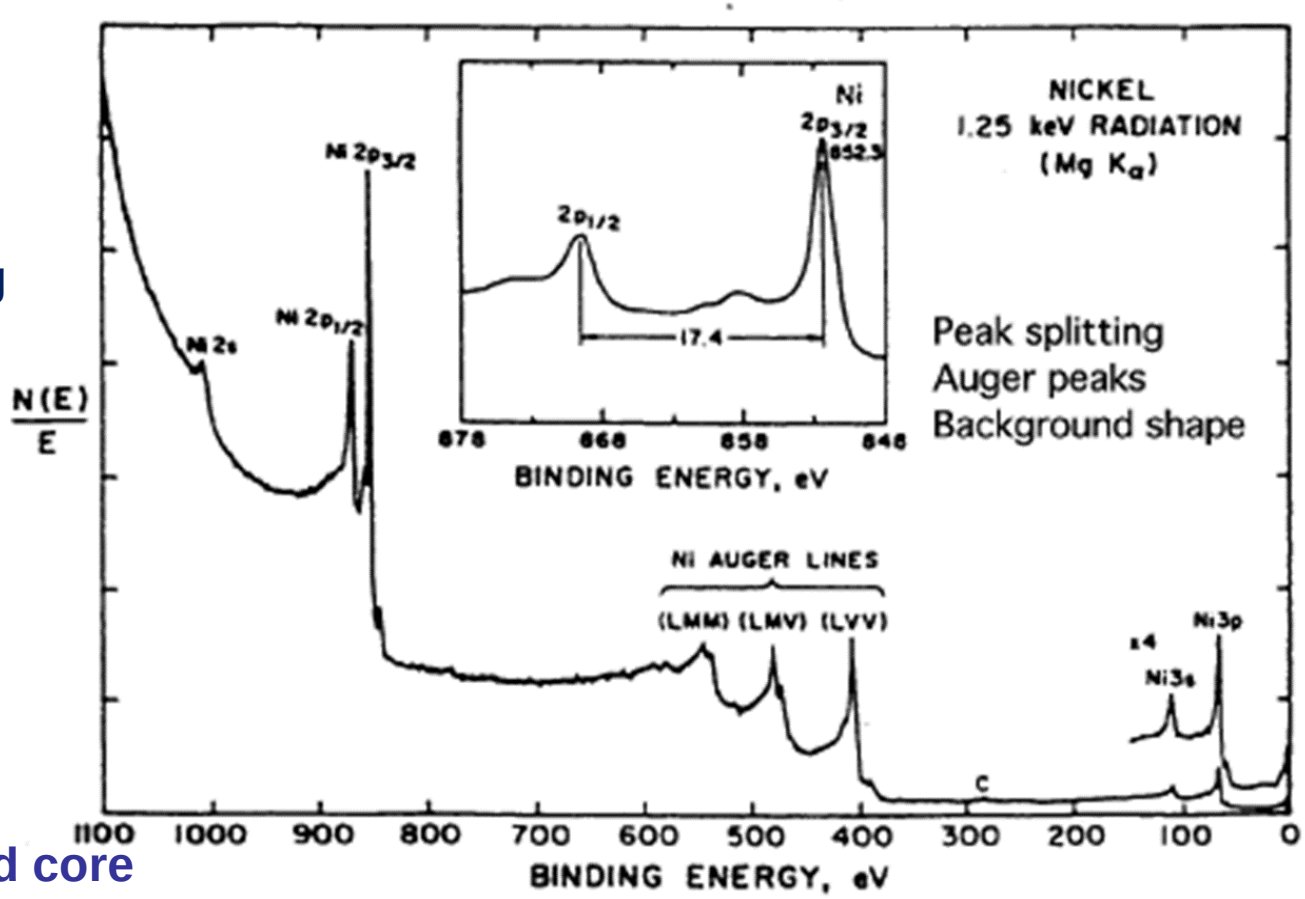


BE follows the energy levels: BE(1s)>BE(2s)>BE(2p)

BE with same orbital increase with Z: BE(Mg1s)>BE(Na1s)

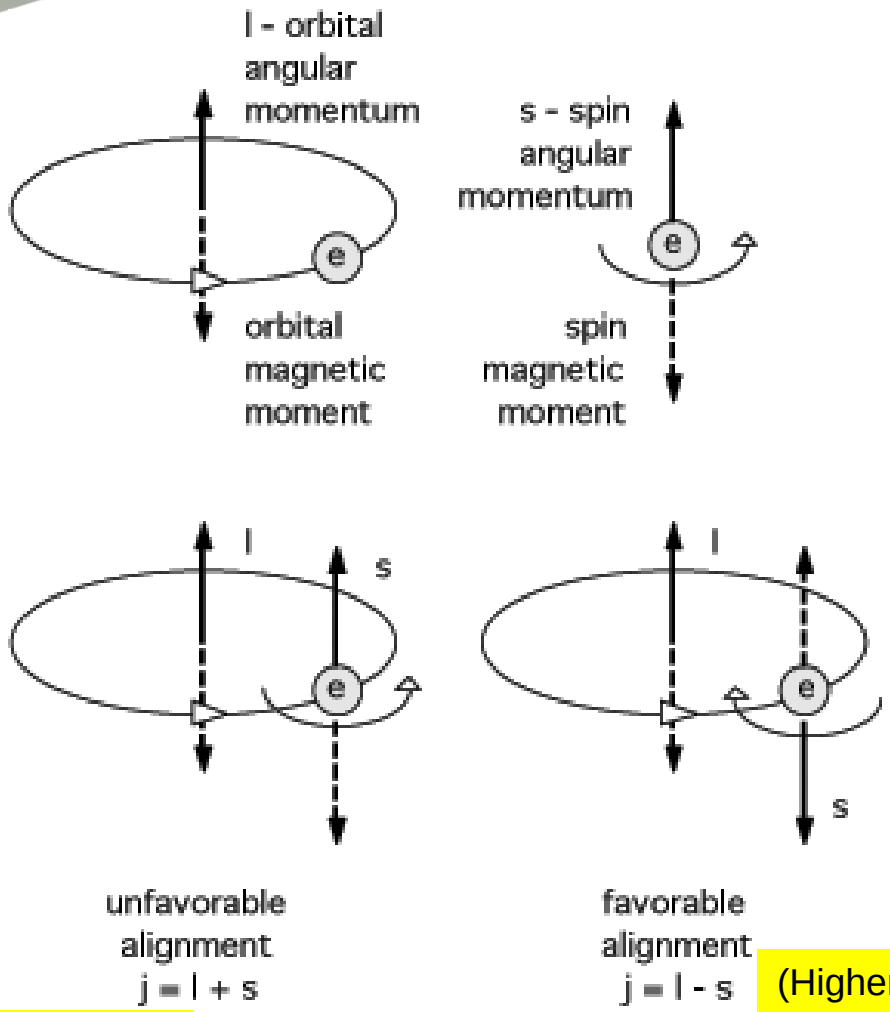
Main features of XPS wide spectra

- Photoelectron lines:
  - ✓ Core-levels
  - ✓ Valence bands
  - ✓ Spin-orbit splitting
- Auger lines
- Chemical shifts
- X-ray satellites
- X-ray "Ghost"
- Shake-up satellite
- Multiplet satellite
- Energy loss lines



Atoms have valence and core electrons: Core-level Binding energies provide unique signature of elements.

Spin-orbit splitting



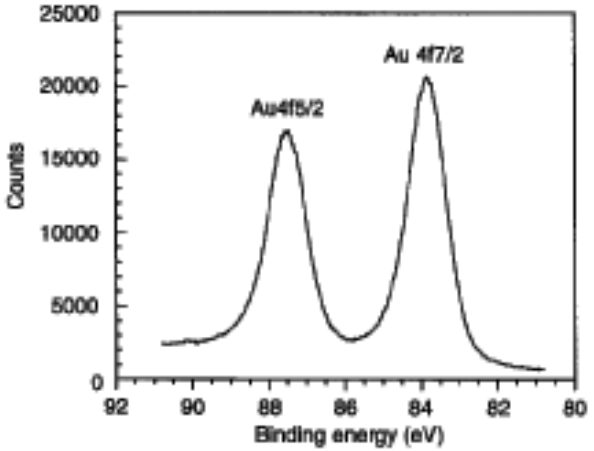
Spin-orbit splitting is an initial state effect.
For any electron in orbital angular momentum, coupling between magnetic fields of spin (s) and angular momentum (l) occurs

(Higher binding energy)

Lower binding energy

Spin-orbit splitting

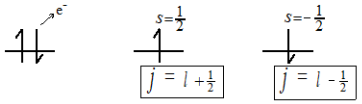
- S orbitals are not spin-orbit split – singlet in XPS
- P, d, f, … orbitals are spin-orbit split – doublets in XPS
- BE of lower j value in doublet is higher (BE2p1/2>BE2p3/2)
- Magnitude of spin-orbit splitting increases with Z

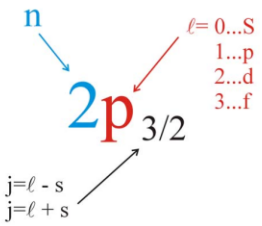


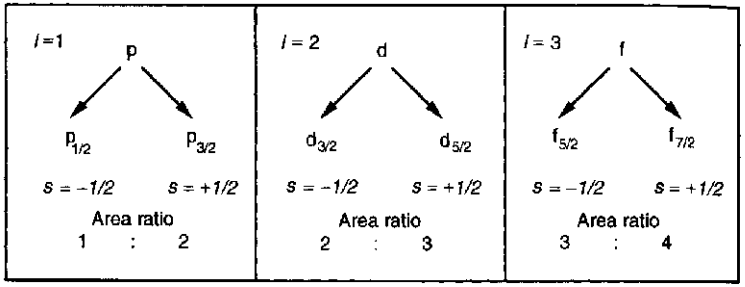
Spin-orbital splitting

Peak Notations

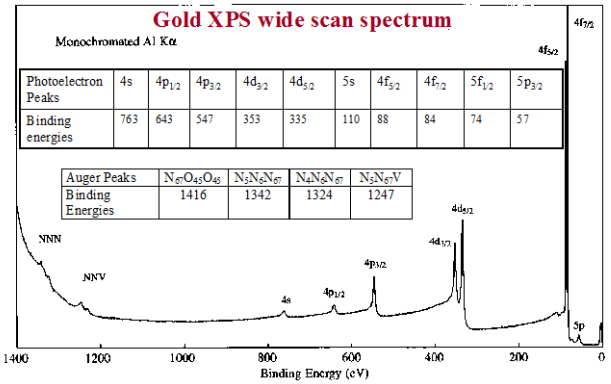
L-S Coupling ($J = l \pm s$)



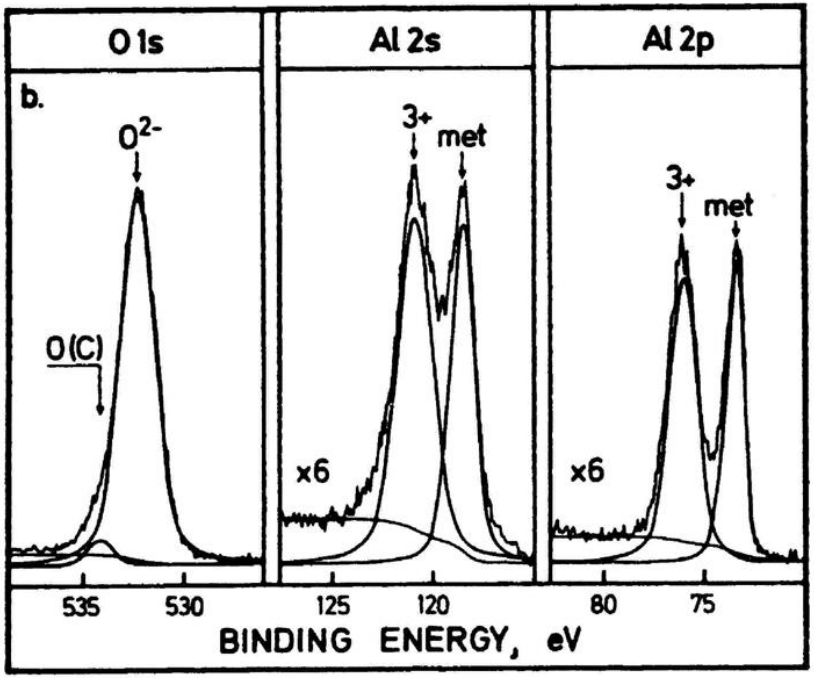




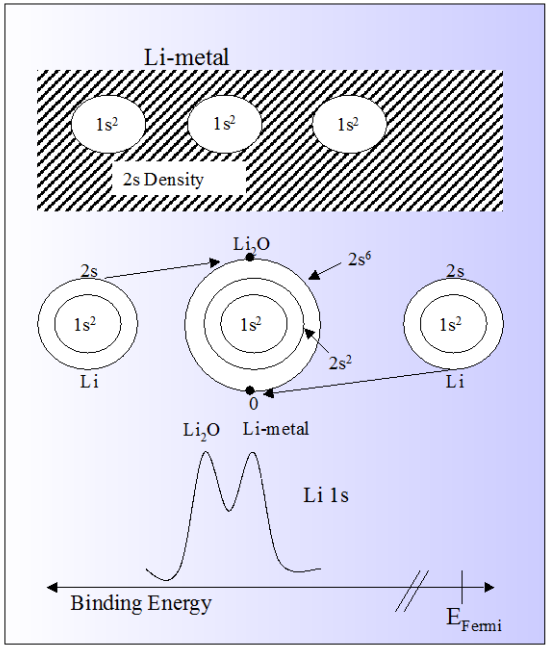
Qualitative analysis



Core level chemical shift



Chemical Shifts: Oxide Compared to Metal



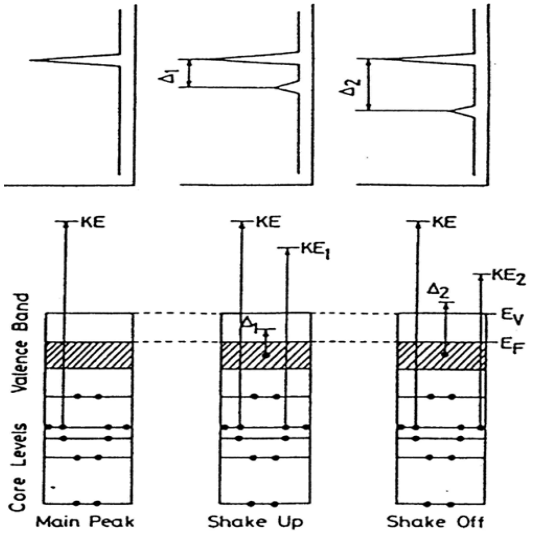
Binding Energy is lower due to increased screening of the nucleus by 2s conduction by 2s electrons

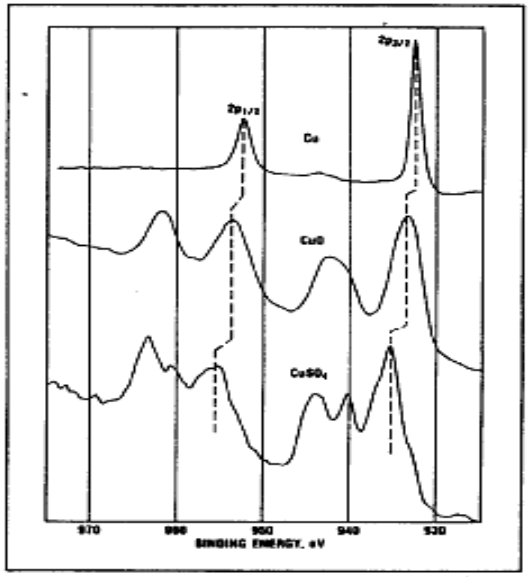
Binding Energy is higher because Li 2s electron density is lost to oxygen

PE spectrum

Note : the binding energy of Al2s and Al2p in metallic state is at lower energy than the AL^{3+}, while the biding energy of the O atoms (more positive charge) is higher than the O^{2-}.

Satellites

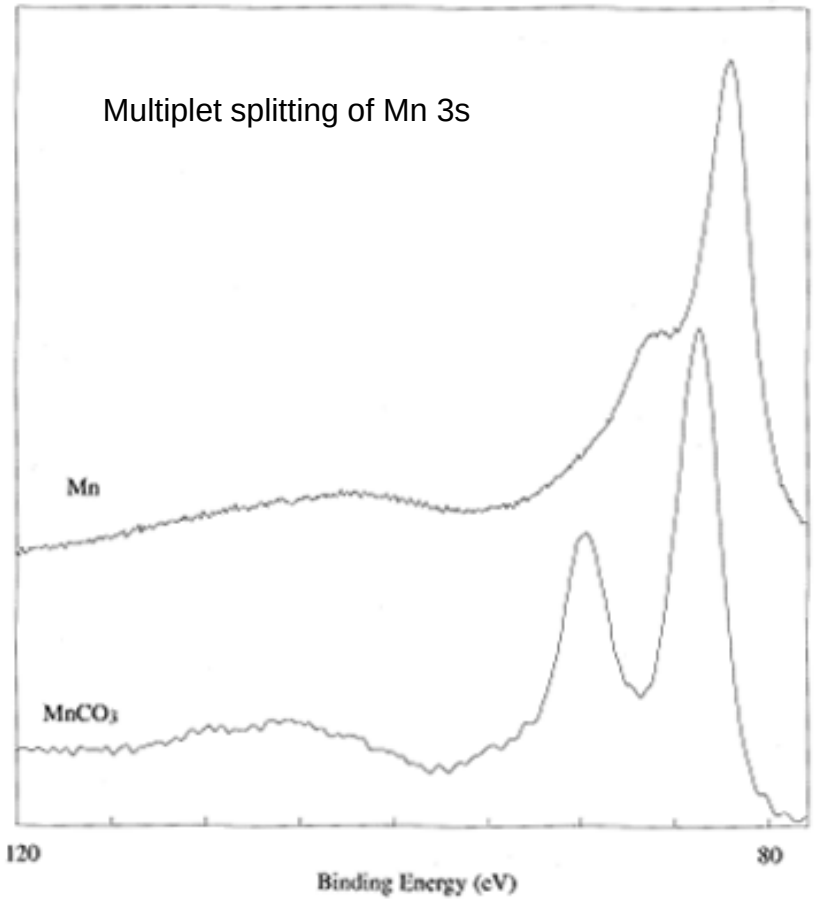




- Shake-up: the outgoing electron interact with the valence electron and excites it (shakes it up) to a higher energy level. Therefore the energy core electron is reduced and a satellite structure appears a few EV below (KE scale)the core level position
- Shake-off: the valence electron is ejected from the ion completely (to the continuum). Appears a broadening of the core level or contribute to the inelastic background.

Arises when a core electron is removed by photoionization. There is a sudden change in the effective charge due to loss of shielding electrons.
The perturbation induces a transition in which an electron from a bonding orbital can be transferred to an anti-bonding orbital simultaneously with core ionisation.

Multiplet satellite

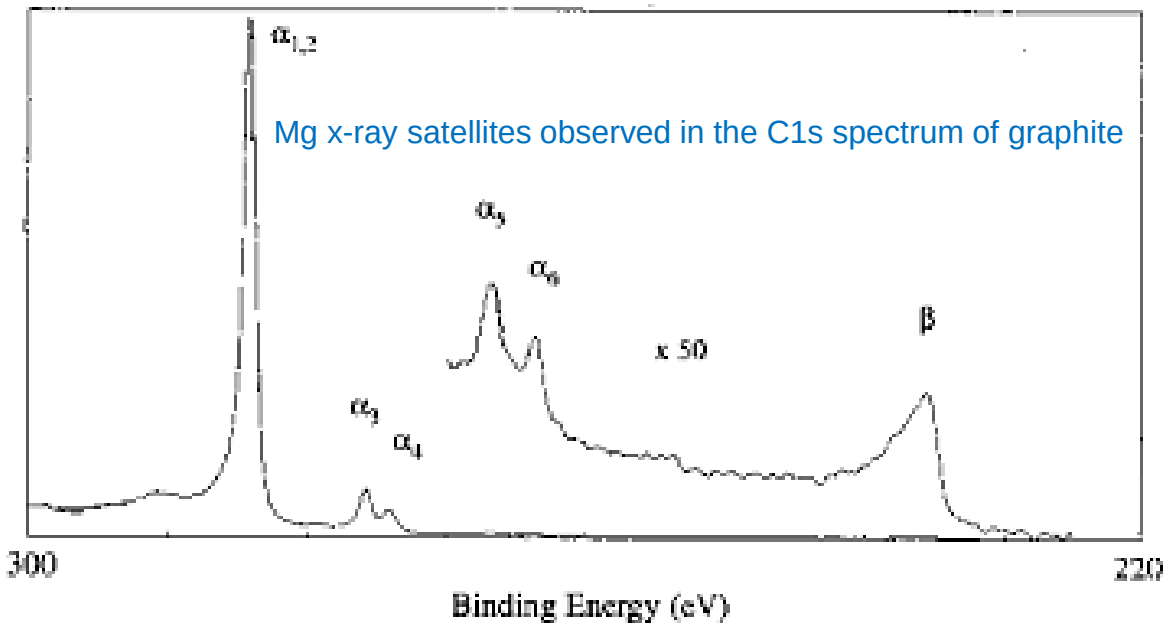


After photoelectron emission, the remaining unpaired electrons may couple with other unpaired electrons with several possible final state configuration with as many different.
This produces a line which is split asymmetrically into several component.
For S-type orbital with other unpaired electrons in the atoms there are split lines like in the shown figures.
For P-type is more complex and subtle.

X-Ray Satellite

	$\alpha_{1,2}$	α_3	α_4	α_5	α_6	β
Mg displacement eV	0	8.4	10.1	17.6	20.6	48.7
Relative Height	100	8.0	4.1	0.6	0.5	0.5
Al displacement eV	0	9.8	11.8	20.1	23.4	69.7
Relative height	100	6.4	3.2	0.4	0.3	0.6

Emission from non monochromatic x-ray sources produces satellite peaks in XPS spectrum at lower BE

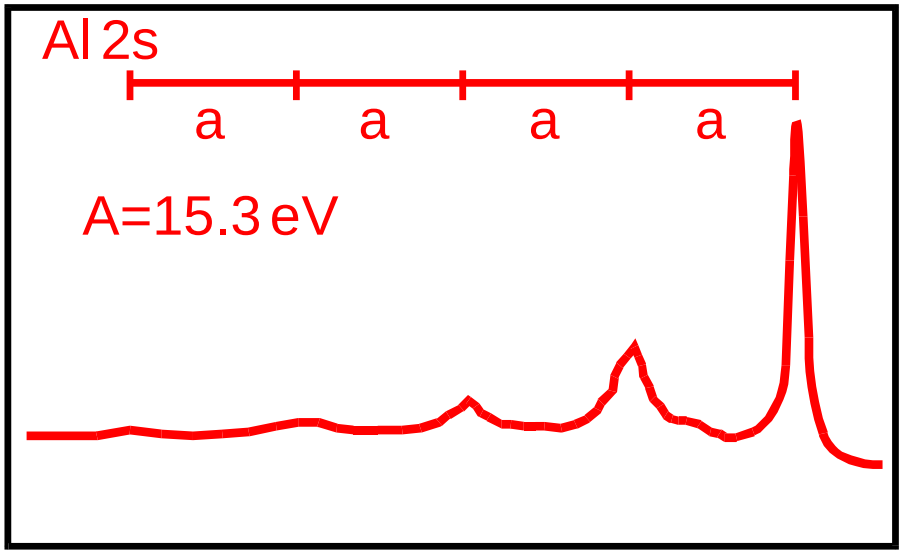


Electron scattering effects

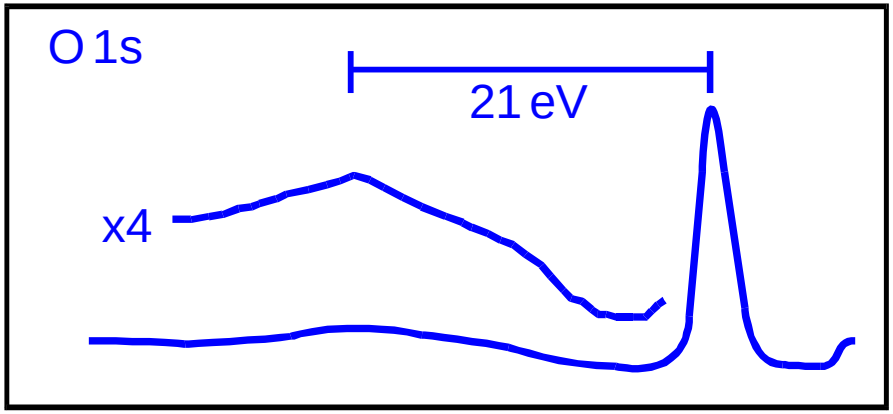
$e_{ph} + e_{solid} \rightarrow e^*_{ph} + e^{**}_{solid}$

Photoelectrons travelling through the solid can interact with other electrons in the material. These interactions can result in the photoelectron exciting an electronic transition, thus losing some of its energy (inelastic scattering).

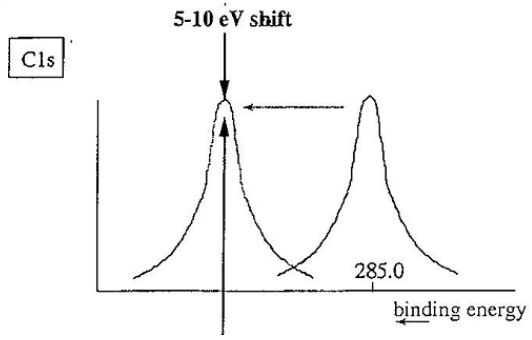
Metal



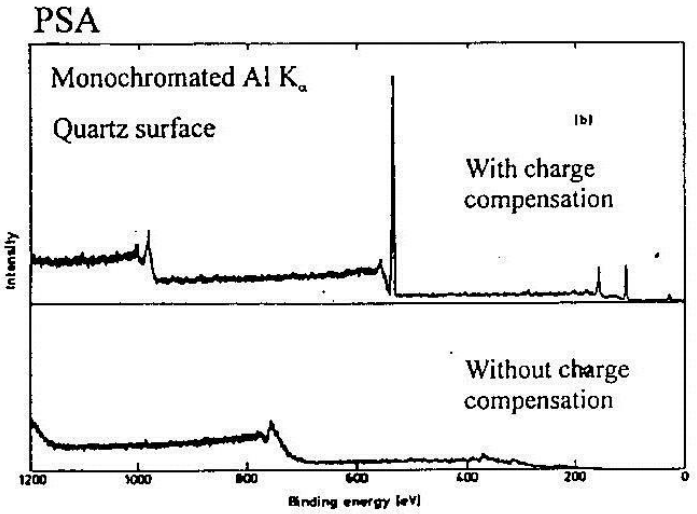
Insulating Material



Sample Charging effects



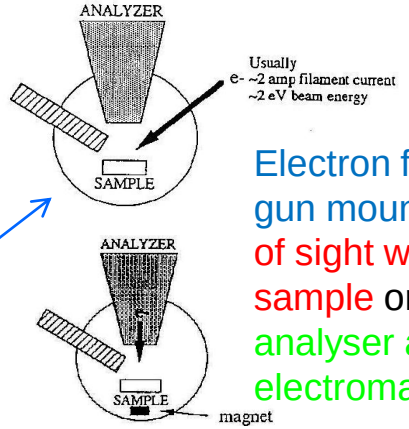
C 1s shifts due to the charging



Charging can even change the line shape due to Inhomogeneous Surface Charging, which have different positive voltage on the surface

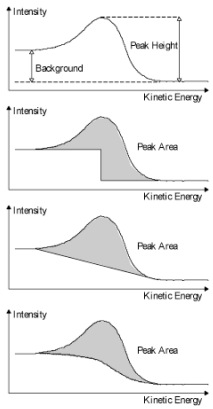
In a lot of cases, there is only spectral shift due to charging, which can be determined by comparison with known elemental XPS lines, for example C 1s.

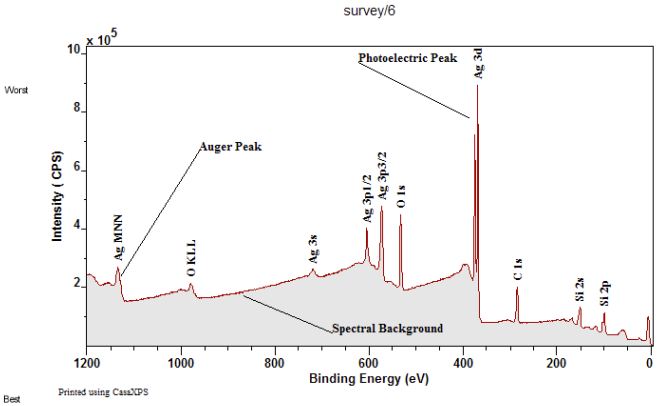
XPS always charges surface positively (shifting of spectrum to higher binding energy) and leads to general instability (spectral noise). For the metal sample, which can be grounded and the charges can be quickly gone. However, for insulator, this effects are serious and need to be treated.



Electron flood gun mounted line of sight with sample or in analyser axis + electromagnet

Quantitative analysis





- Identify the peak position and relative peak intensity of 2 or more peaks (photoemission lines and Auger) of an elements.
- Check for any charging effect
- Check for any chemical shift
- Check spin orbital splitting and area ratio of the p, d, f peaks
- Subtract the back ground and find the area under the curve.

Total intensity detected

$$I_i = J\, C_i\, \sigma_i\, D\, T_i \int_0^{\infty} e^{-x/\lambda_i} dx \quad \text{when polar angle is } 0^o$$

$$I_i = J\, C_i\, \sigma_i\, D\, T_i \int_0^{\infty} e^{-x/\lambda_i \cos\theta} dx \quad \text{when polar angle is } \theta$$

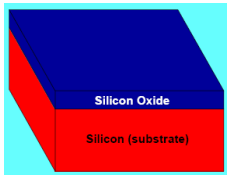
$$I_i = J\, C_i\, D\, T_i\, \lambda_i \quad (\cos\theta)$$

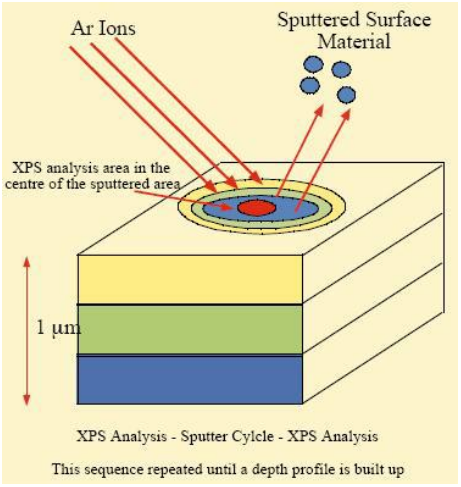
For a sample with different elements

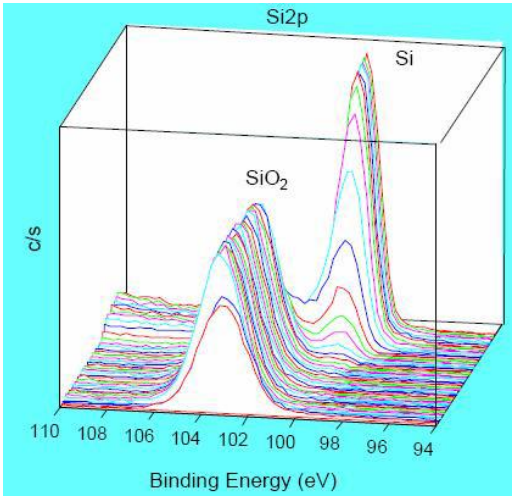
$$C_i = \frac{I_i / (\sigma_i\, T\, \lambda_i)}{\sum_{j=1}^{n} I_j / (\sigma_j\, T_j\, \lambda_j)} = \frac{I_i / S_i}{\sum_{j=1}^{n} I_j / S_j}$$

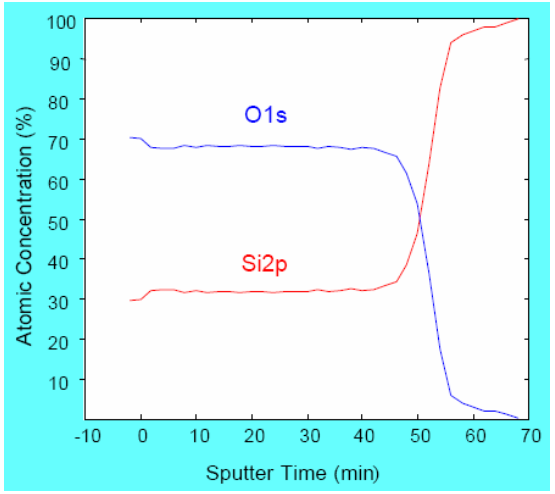
Value from the handbook

J: X-ray flux
C_i: Fraction of atomic concentration of element "i"
D: Geometrical factor
T_i: Transmission factor/element "i"
σ_i: Cross-section/element "i"
S_i: Sensitivity/element "i"
λ_i: Inelastic mean free path/element "i"









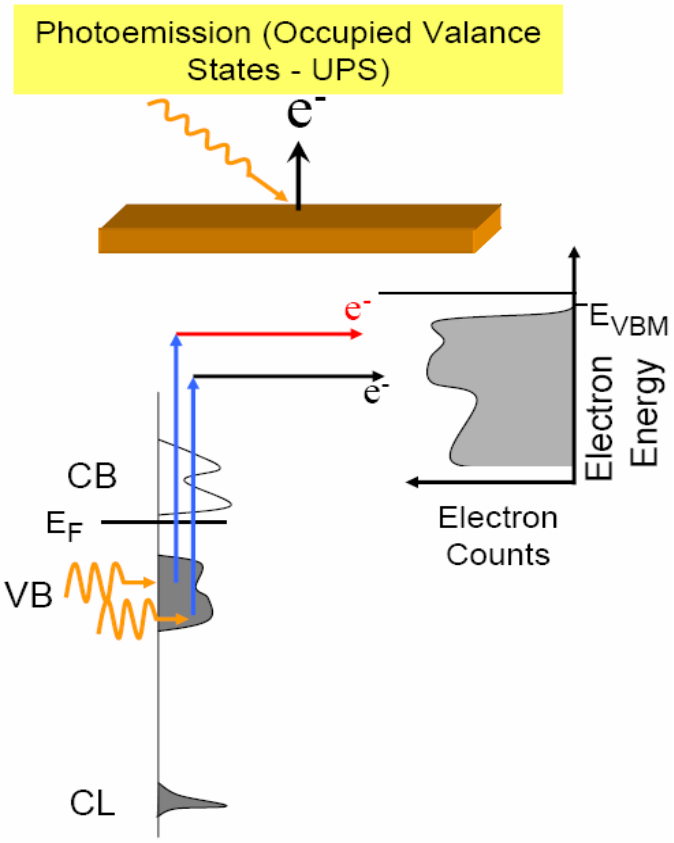
If sputter rate is known, thickness of the surface layers can be calculated.

Si = 99.3 eV
SiO_2 = 103.3 eV

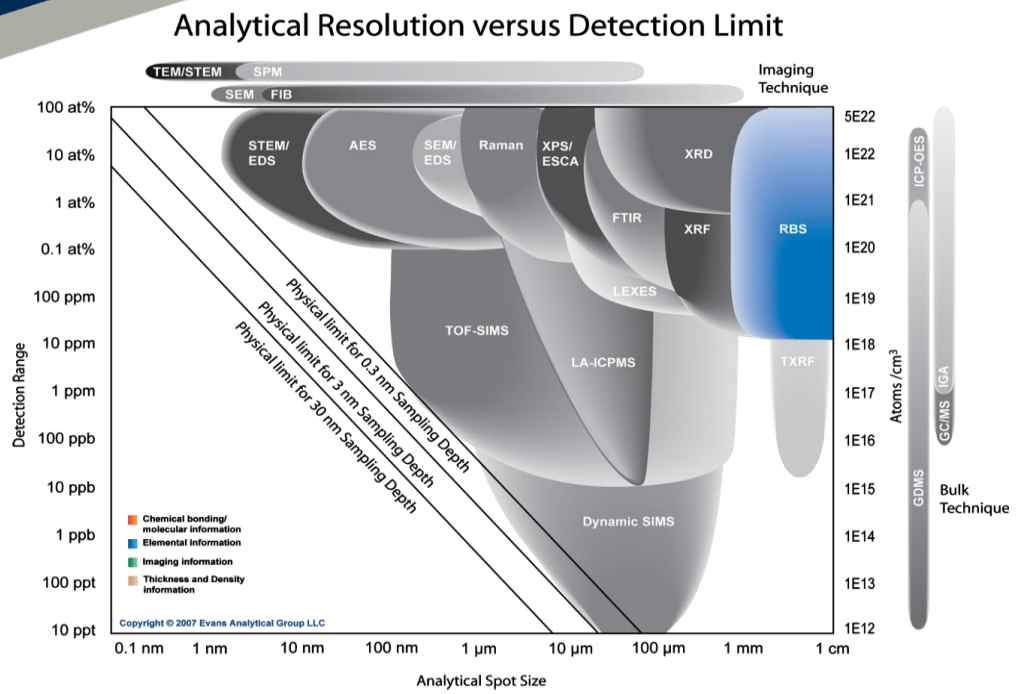
Wide scan – quantitative analysis

UV photo electron spectroscopy

- XPS:
  photon energy hν=200-4000 eV to probe core-levels (to identify elements and their chemical states).
- UPS:
  photon energy hν=10-45 eV to probe filled electron states in **valence band** or adsorbed molecules on metal.
- UPS source of irradiation:
  He discharging lamp (two strong lines at 21.2 eV and 42.4 eV, termed He I and He II) with narrow line width and high flux
- Synchrotron radiation source:
  continuously variable photon energy, can be made very narrow, very intense, now widely available, require a mono-chromator



RBS: Rutherford Backscattering Spectroscopy

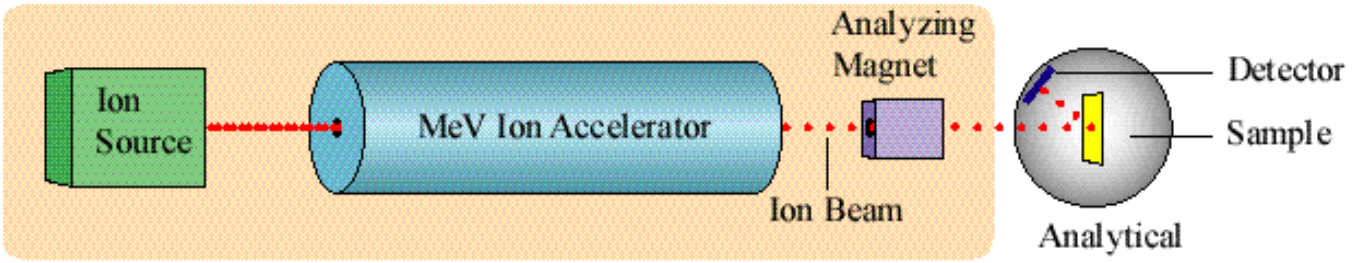


RBS accurately measures the composition and depth profile of thin films, including hydrogen

Quantitative?	**Yes**	**Destructive?**	**No**
Detection limits?	0.001 – 10 at%	Lateral resolution (Probe size)?	≥ 1 mm
Chemical bonding?	No	Depth resolution?	5– 20 nm

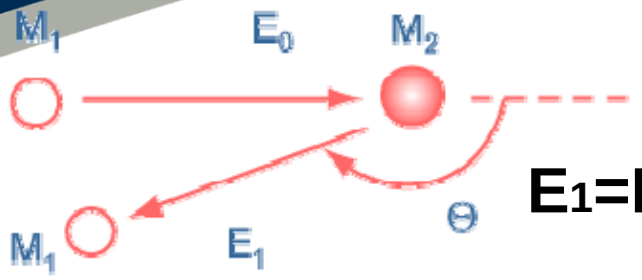
Application and Instrumentation

- Determine thickness and composition of thin films
- Determine film density from a film of known thickness
- Assess damage to crystal structure as a result of processing
- Quantification of films on whole wafers (up to 300 mm)
- Qualify & monitor deposition systems (also fab-to-fab comparisons)

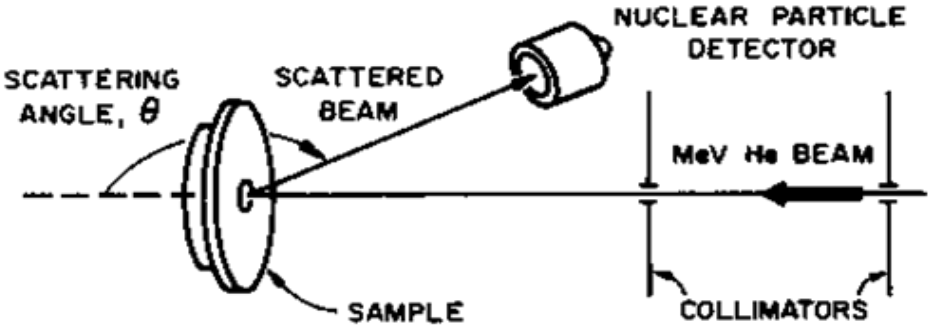


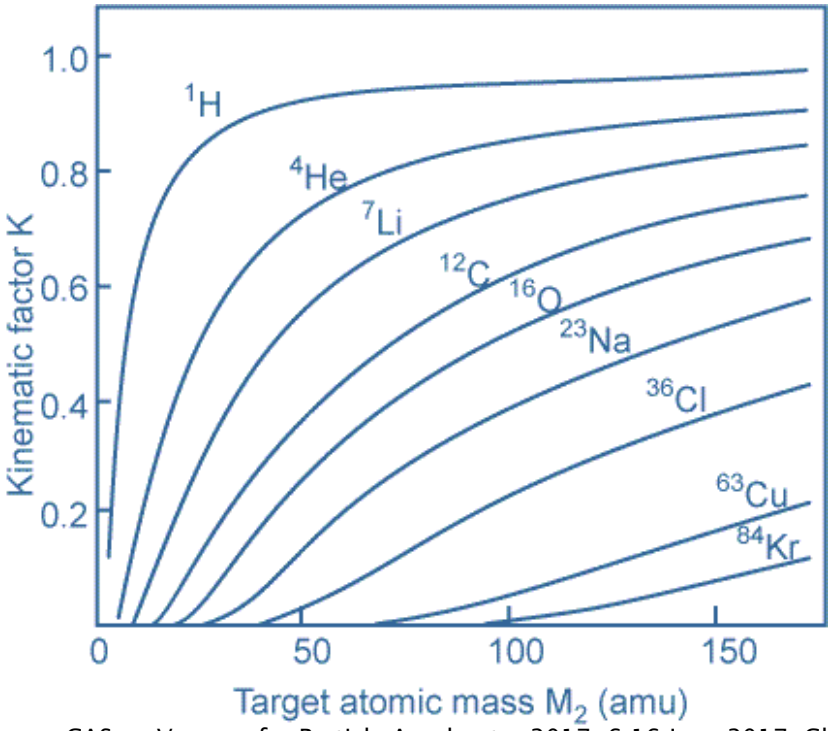
- MeV ions from an electrostatic accelerator are focused on a sample in a vacuum chamber for analysis.
- Typically, 2 MeV He^{++} ions are used.

Kinematic factor



$E_1 = KE_0$



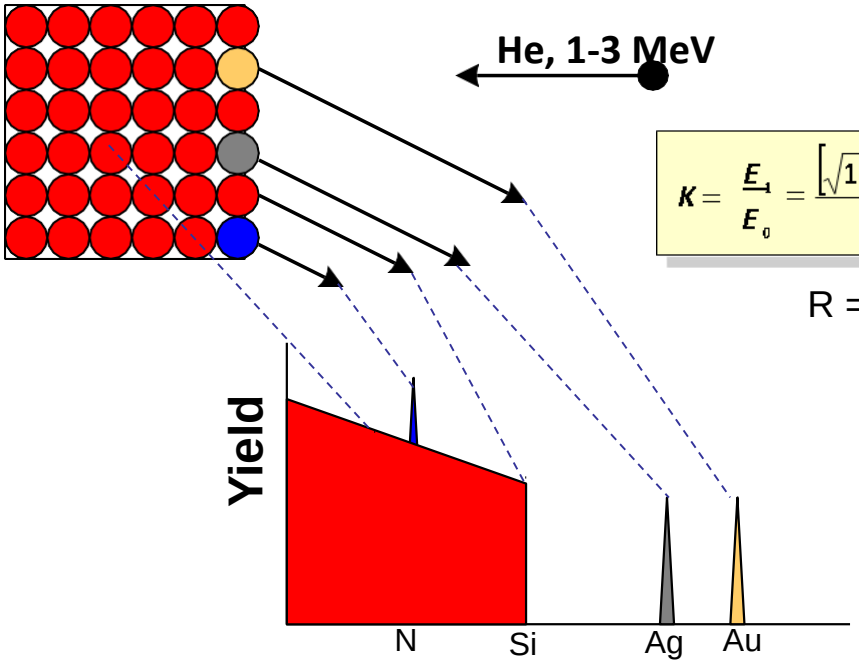


$$K = \frac{E_{scattered}}{E_{incident}} = \left[\frac{\left(1 - \left(\frac{M_1 \sin\theta}{M_2}\right)^2\right)^{1/2} + \frac{M_1 \cos\theta}{M_2}}{1 + \frac{M_1}{M_2}} \right]^2$$

E *Ion energy*
M_1 *Mass of incident ion*
M_2 *Mass of t arget atom*
θ *Scattering angle*

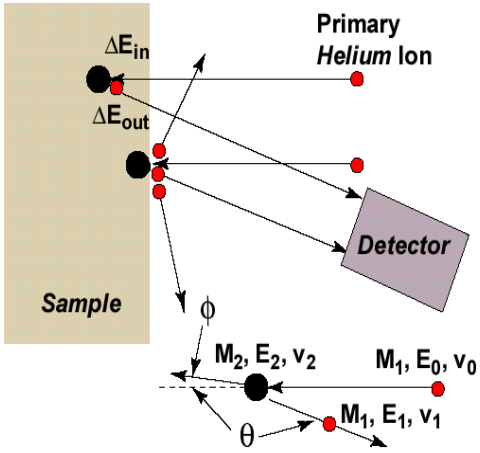
Surface doping

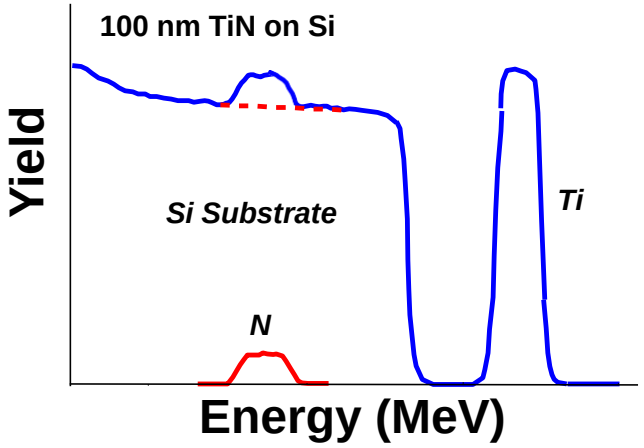
- **Works best for heavy elements on light substrates**



$$K = \frac{E_1}{E_0} = \frac{\left[\sqrt{1-(R\sin(\theta))^2} + R\cos(\theta)\right]^2}{(1+R)^2}$$

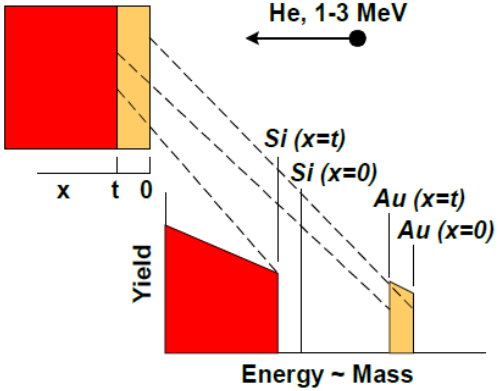
$R = M_1/M_2$





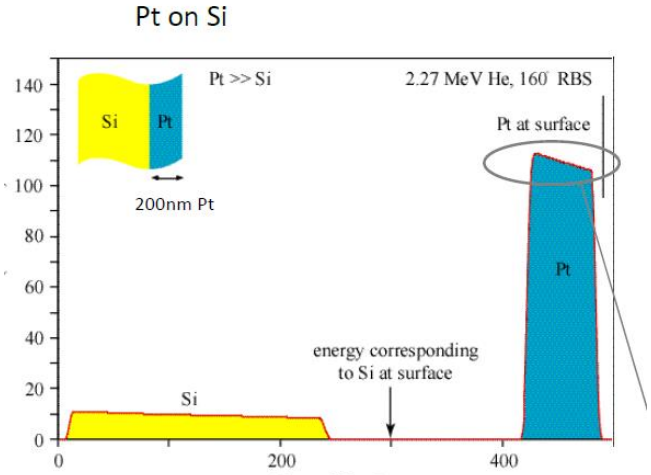
Thin film deposited on substrate

$$Yield = \sigma \Omega Q N t$$



$$\sigma = \frac{q^2 Z_1 Z_2}{4E} \frac{4}{\sin^4 \theta} \frac{\left(\sqrt{1-(R\sin\theta)^2} + \cos\theta\right)^2}{\sqrt{1-(R\sin\theta)^2}}$$

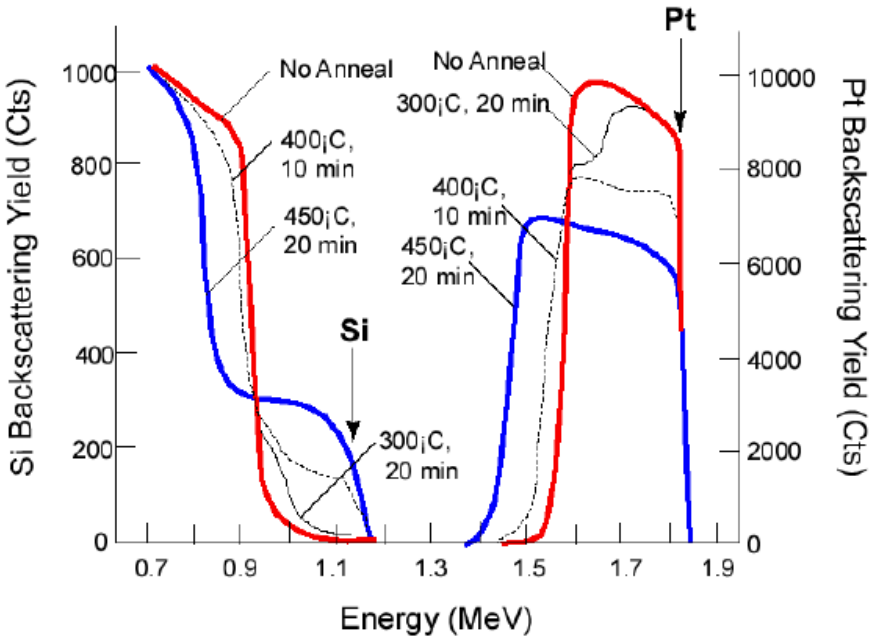
σ: scattering cross section
Ω: solid detector angle
Q: no. of incident ions
N: target atom density
t: thickness



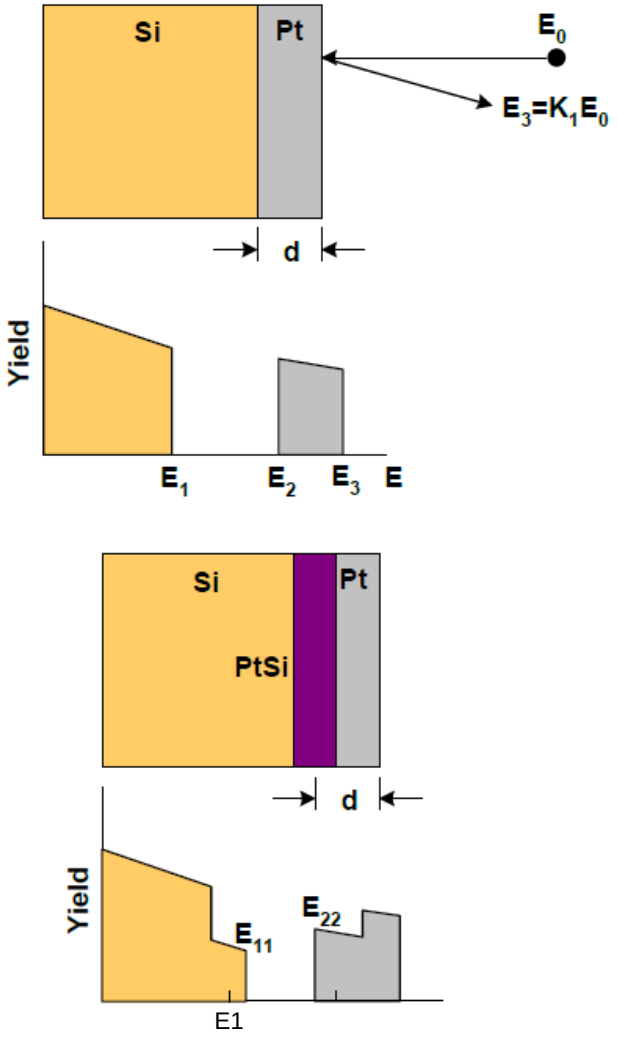
- Channel number = Backscattering energy
- Surface is on the right (high energy) greater depths to the left (lower energy) à DE ~ t
- Heavier elements produce higher energy backscattering.
- Heavier elements produce larger peaks per unit concentration.

Interface mixing

- **RBS is ideal for measuring the formation of silicides**

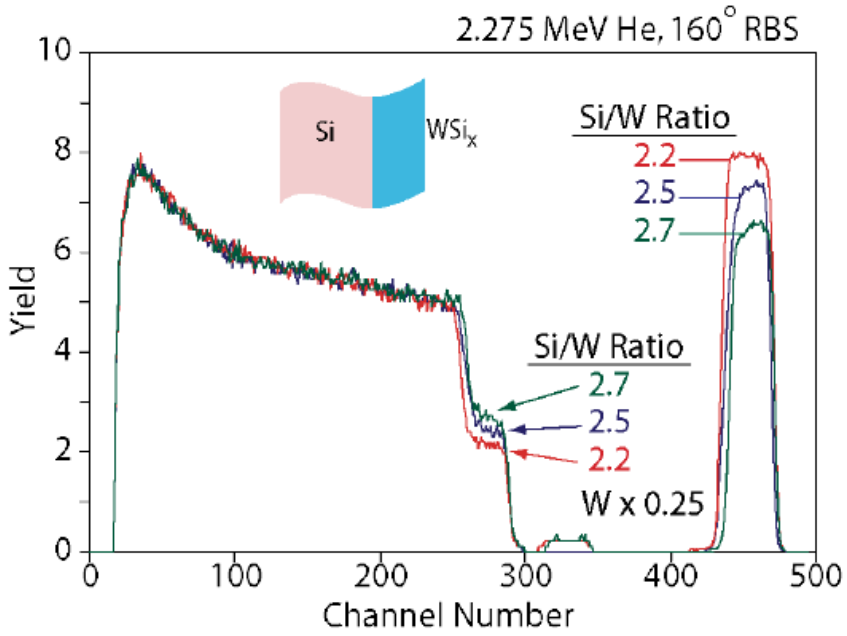


M.A. Nicolet et al. *Science*, **177**, 841 (1972)

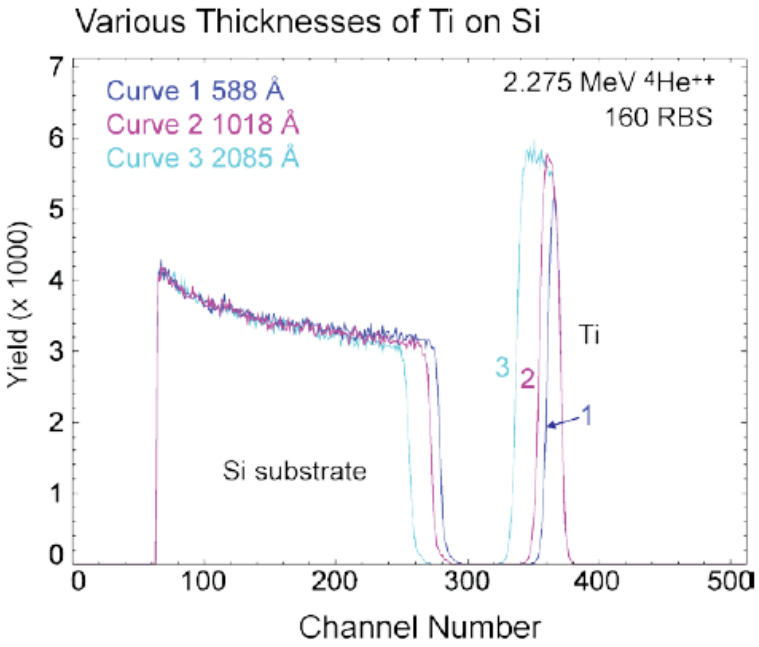


Measuring Concentration and thickness

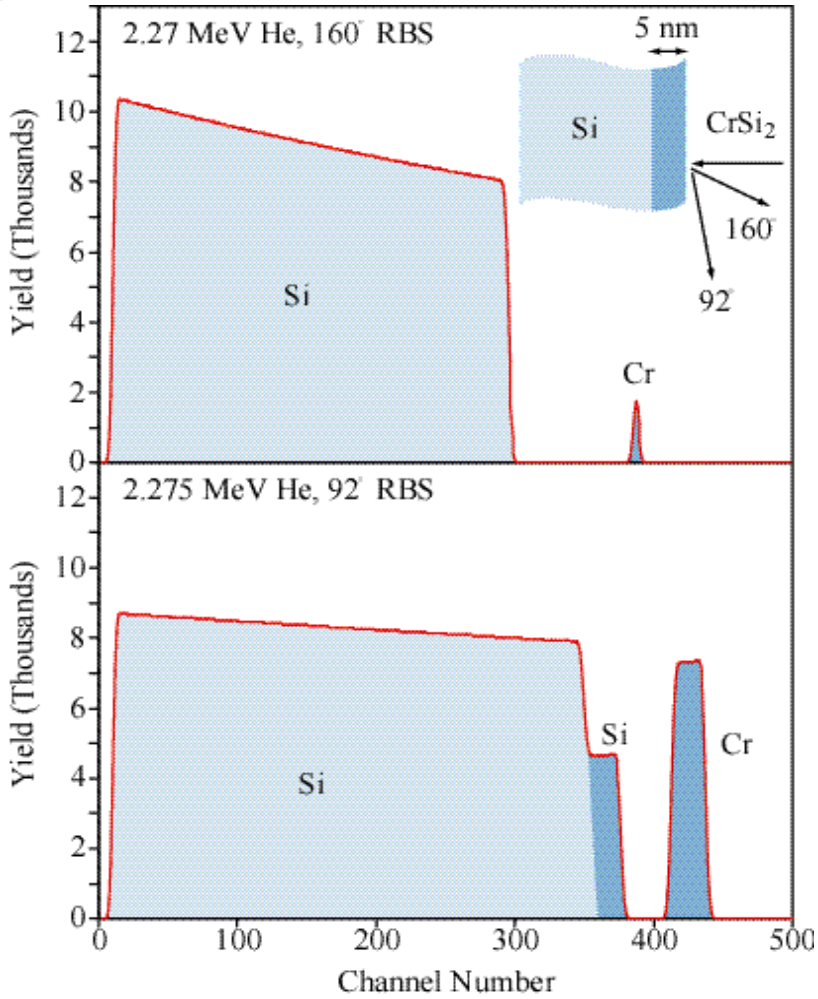
Comparison of Three WSi_x Films with varying W concentrations

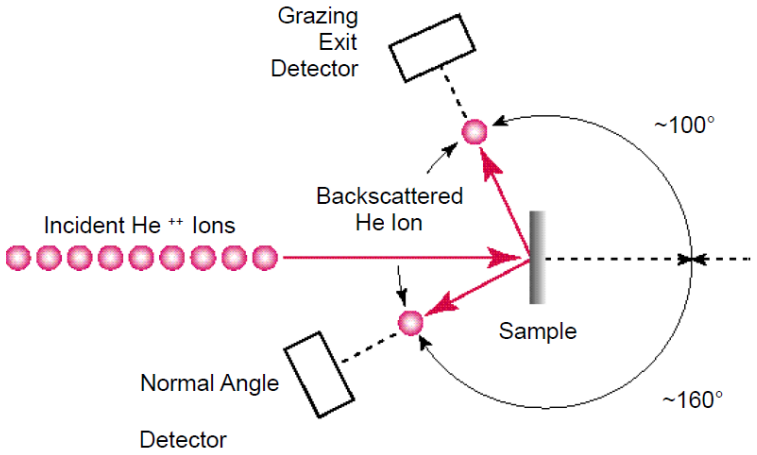


Comparison of Three Ti Films with varying thickness



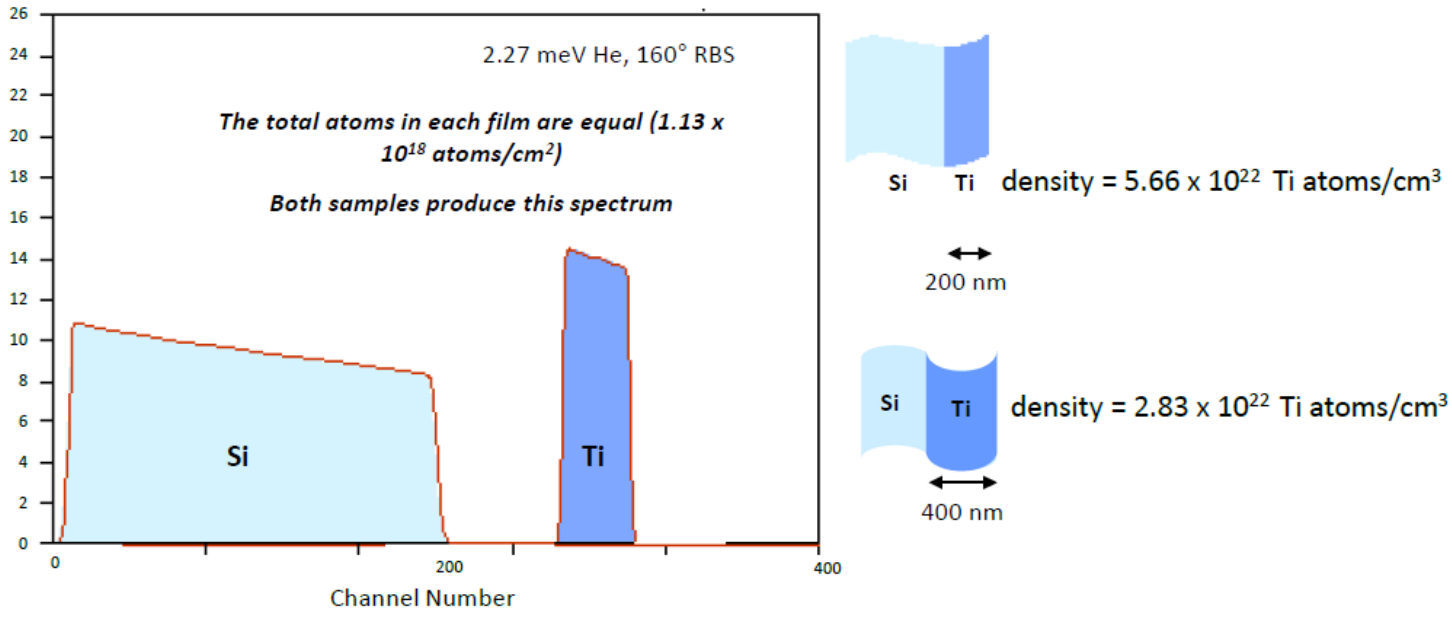
Scattering geometry affects depth resolution





Grazing angle detector improves depth resolution for thin film layer

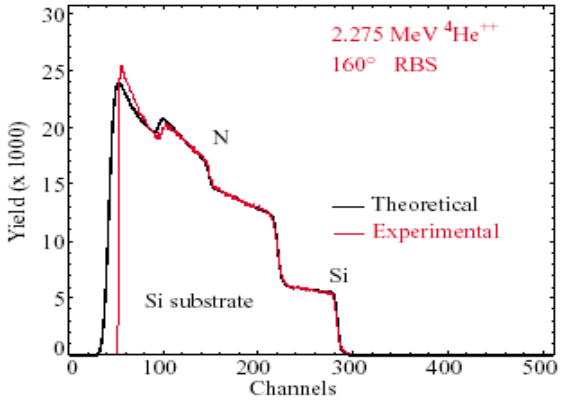
Effect of film density on thickness



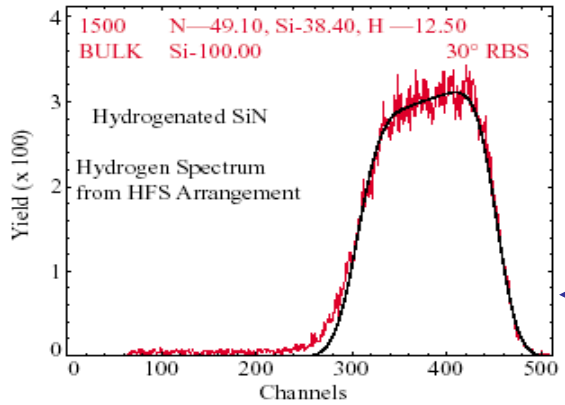
- Fundamental unit of measurement for RBS is atoms/cm2
- Density × thickness = atoms/cm2
- To calculate a film thickness using RBS alone one must assume a film density
- If the film thickness is known (by TEM, SEM, profilometry, etc.), then the film density can be calculated

Hydrogen forward scattering spectroscopy

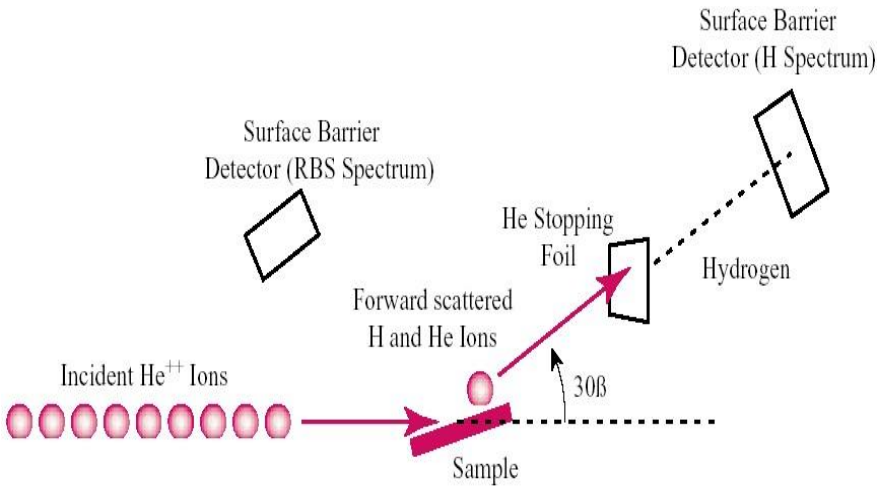
- **Also called Forward Recoil Spectrometry**
- He is heavier than H, so no He backscatters from H (or D)
- He does forward scatter H at significant energy
- Energy of recoiling H is measured



RBS spectrum

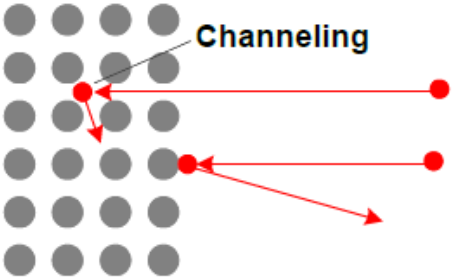


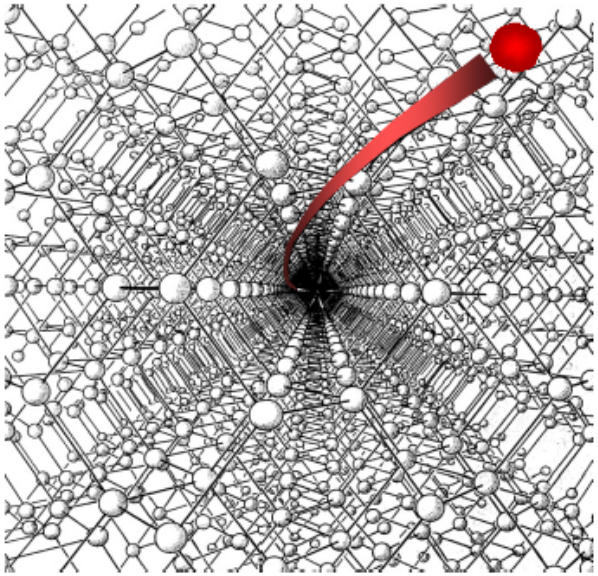
HFS spectrum



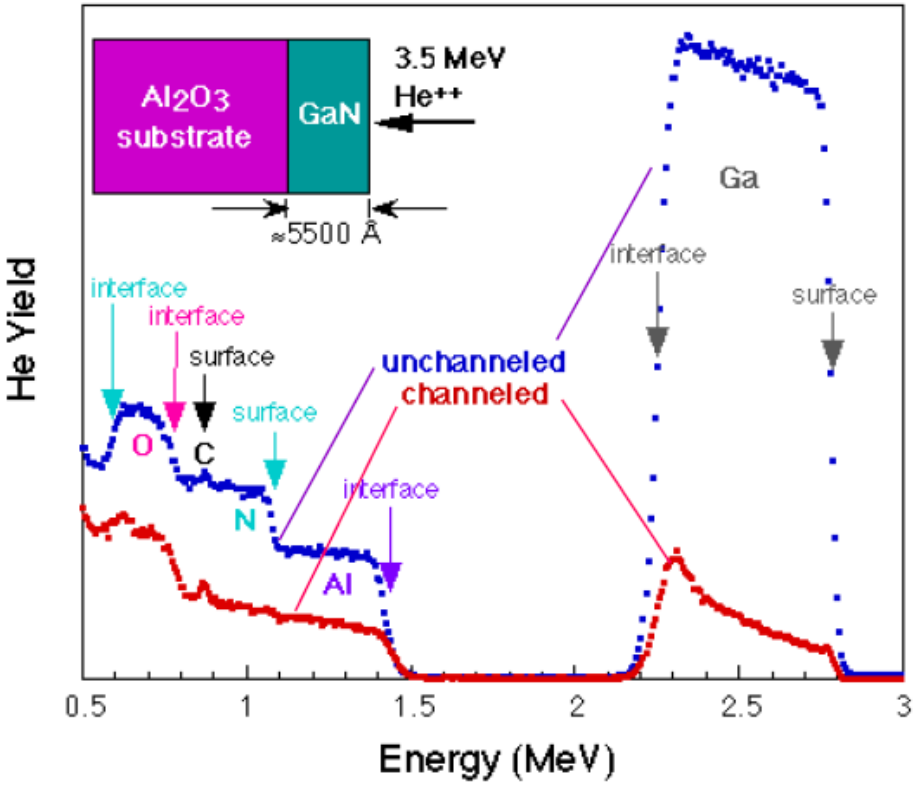
Channeling

- He Ions are scattered more when they are not channeled

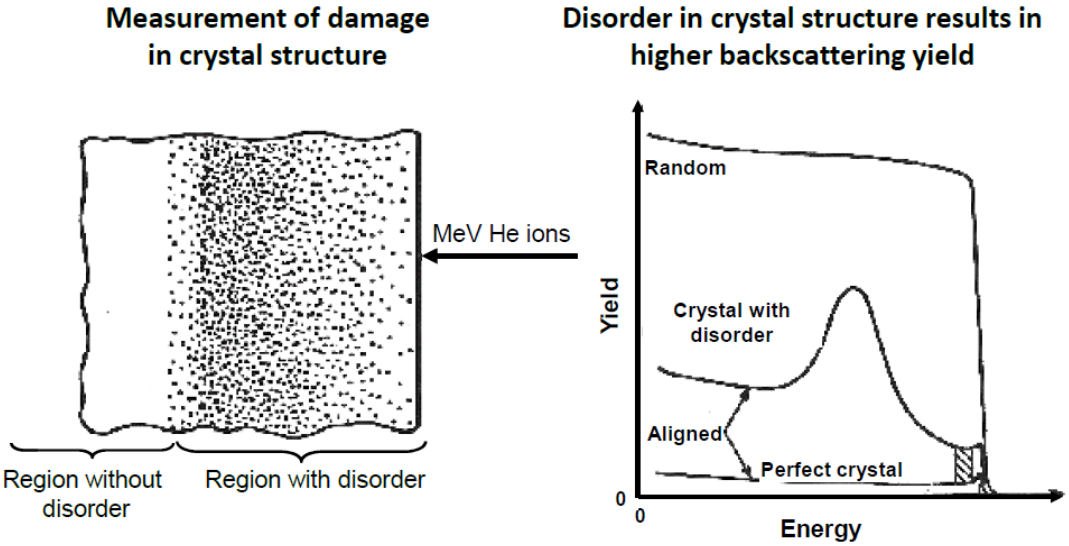




Scient. Am. **218**, 90 (March 1968)



Channeling: Crystal damage



- Quantitative crystal damage profiling
  - ✓ Ion Implants
  - ✓ Regrowth of damaged crystals
  - ✓ Polishing damage
  - ✓ Ion etching
  - ✓ Epitaxial layers
  - ✓ Thickness of amorphous layers

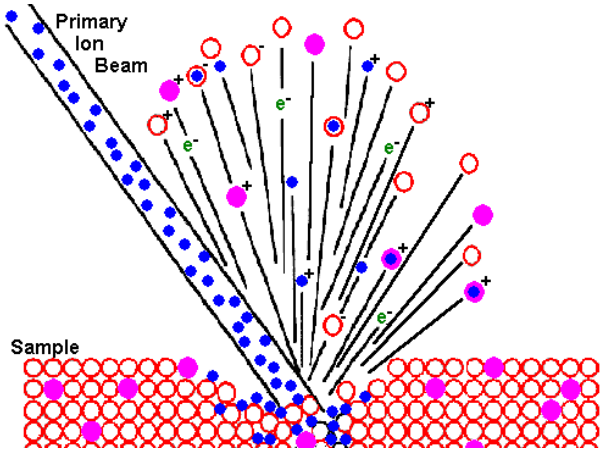
- Damage detection limit:
  1×10^{15} to 1×10^{17} displaced at/cm^2
- Substitutionality of dopants / impurities

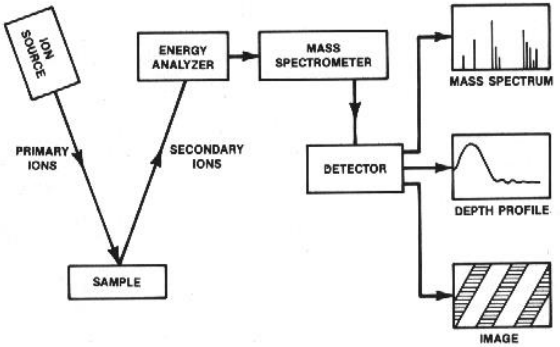
Strength and weaknesses

- Strengths
  - ✓ Non-destructive depth profiling
  - ✓ Quantitative without standards
  - ✓ Analysis of whole wafers (150, 200, 300 mm), irregular and large samples
  - ✓ Can analyse conductors and insulators
  - ✓ Can measure hydrogen
- Weaknesses
  - ✓ Large analysis area (1 mm)
  - ✓ Poor sensitivity for low Z elements
  - ✓ In many cases, useful information limited to thin films (<0.5 μm)
  - ✓ Generally not good for bulk samples

Principle of SIMS Analysis

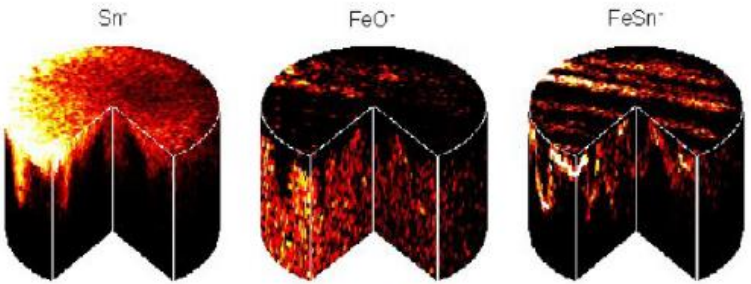
- Bombardment of a sample surface with a primary ion beam (Ip) followed by mass spectrometry of the emitted secondary ions (Is) constitutes secondary ion mass spectrometry.
- SIMS is a surface analysis technique used to characterize the surface and sub-surface region of materials and based on m/e ratio measurement of ejected particles under ion bombardment.





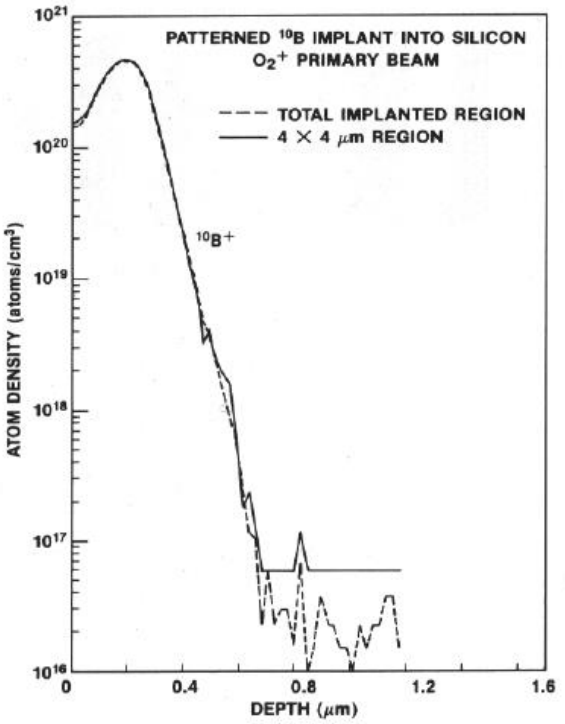
Application 1

- Depth profiling of elements (Dynamic SIMS)
  - Sputter rate ~ 10 μm/hr
  - Typical depth resolution : 10 ~ 20 nm
  - Optimal depth resolution : 2 ~ 5 nm
  - Detectable elements >= H
  - Detection limit : ppm-ppb
  - Typical beam diameter : 1 ~ 100 μm
  - Extreme beam diameter ~ 100 nm
- Image depth profile



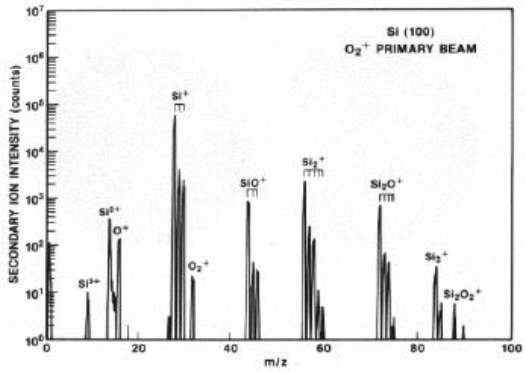
Source: R2

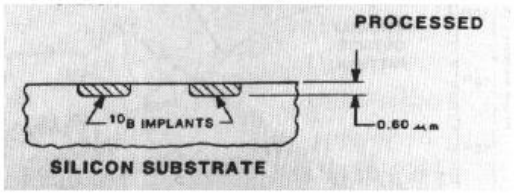
Source: R1

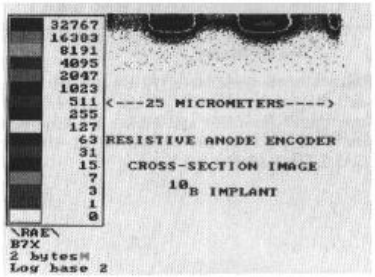


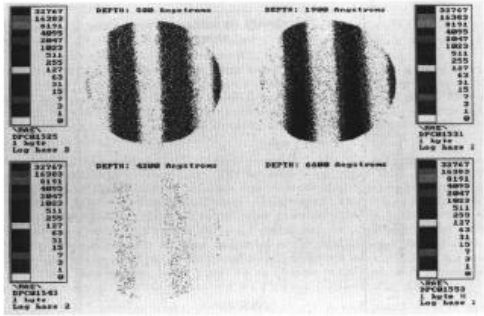
Application2

- Surface analysis (Static SIMS)
  - Low sputtering rate ~ 1 A/hr
  - Depth ~ 0.5 nm
  - Typical spatial resolution ~100 μm
  - Optimal spatial resolution ~ 10 nm ~ 1 μm
  - Element >= H
  - Detection limit ~ $1x10^{10}$ ~ $1x10^{11}$ cm^{-2}
- Ion mapping









Instrumentation

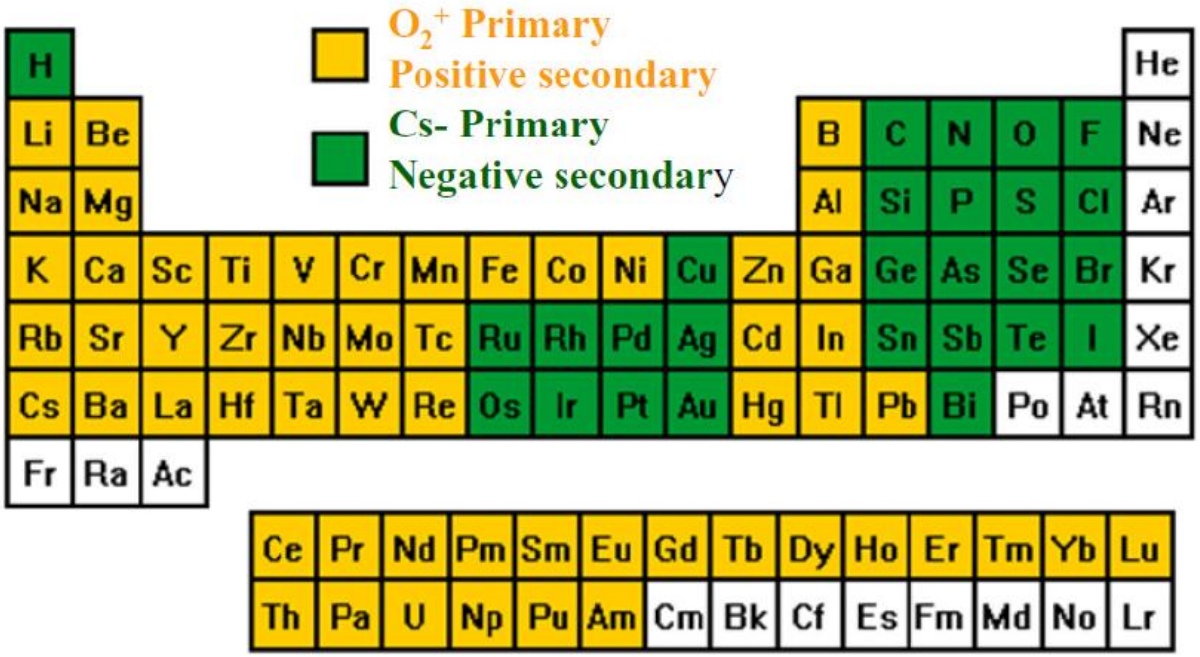
- Primary beam
  - O_2^+, O^-, Cs^+, Ar^+, Xe^+, Ga^+, etc.
    - O_2^+ for electropositive species (B, Al, etc)
    - Cs^+ for electronegative species (N, P, As, etc)
    - Ga^+ for improved lateral resolution
  - Primary beam angle : 0 - 60 deg. (high sputter rate => low secondary ion yield)
  - Beam energy : 0.5 - 20 keV
  - Beam diameter : typical 10 ~ 100 μm, extreme 0.1 μm
  - Mass analyzers : magnetic sector (precision mass analysis), quadrupole (depth profiling), time of flight (TOF, organic materials)
    - Magnetic sector : mass/charge ratio, good transmission, very high mass resolution (^{28}Si and $^{12}C^{16}O$, ie. 27.976 and 27.995). High extraction energy results in surface roughness and charging.
    - Quadrupole : low transmission, low mass resolution, very fast peak switching
    - TOF : time taken to travel a drift space, high mass resolution, very high mass range

Advantages and Disadvantages

- Advantages
  - All elements detectable and isotopes can be distinguished.
  - Detection limits of ppm for most elements and ppb for favorable elements.
  - Good depth resolution (2~5 nm) and lateral resolution (20 nm ~ 1 μm)
  - Insulator analyzable
  - Chemical information obtained from relative molecular ion abundances.
- Disadvantages
  - Mass interferences.
  - Secondary ion yield vary by more than six orders of magnitude over the periodic table.
  - Secondary ion yields are often matrix dependent.
  - Numerous secondary standards are required to quantify data.
  - Flat surface required for best depth resolution and for ion microscopy.
  - Destructive analysis.

Secondary ion Yield

- The variability in ionization efficiency leads to different analysis conditions for elements as indicated on the periodic table.

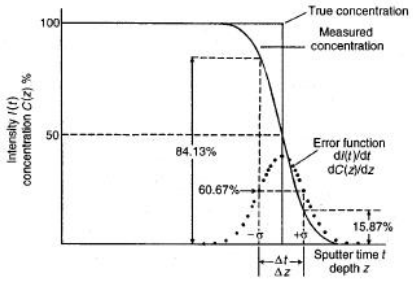


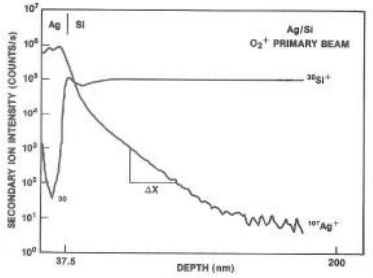
Profiling Issues

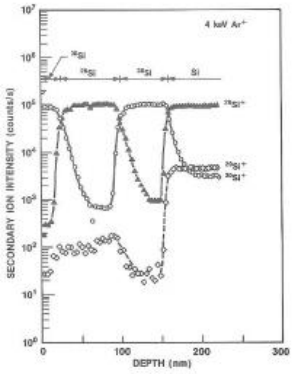
- **Profiling Issues**
  - ✓ Ion beam mixing
  - ✓ Depth resolution
  - ✓ Segregation
  - ✓ Charge driven diffusion
  - ✓ Matrix Effects
  - ✓ Surface Effects
  - ✓ Crater shape
  - ✓ Microtopography
  - ✓ Memory Effects
  - ✓ Mass Interference
  - ✓ Count Rate Saturation

Ion Beam Mixing

- Three different ion beam mixing processes can be identified: recoil mixing, cascade mixing, and radiation enhanced diffusion(RED).
  - ✓ Recoil mixing arises from direct collisions of the primary ions with sample atoms that are driven into sample. Anisotropic movement.
  - ✓ Cascade mixing results from the motion and collisions of sample atoms with each other in the collision cascade. Isotropic movement.
  - ✓ RED is thermally-activated diffusion, enhanced by the vacancies and defects produced by the bombardment.
- Interface width is defined as the depth interval over which the intensity drops from 84% to 16% of the maximum.

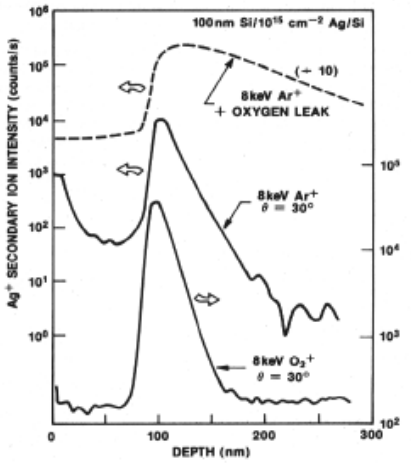


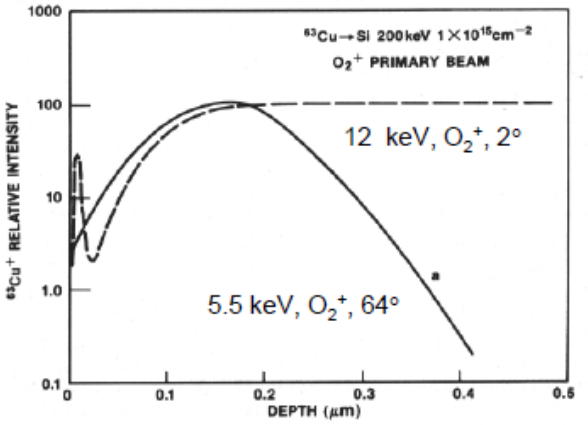




Segregation and charge diffusion

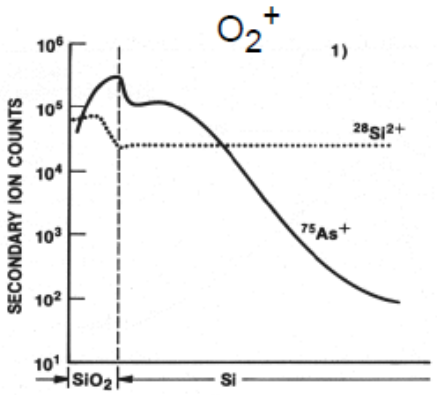
- **Segregation**
  - ✓ Gibbsian segregation is the tendency of one species in a multi-element solid to increase its concentration at the surface because this constitutes a site of lower chemical potential than the bulk.
  - ✓ Movement of an analyzed species, such as As in SiO2, can occur during ion bombardment because of chemical gradients.
- **Charge driven diffusion**
  - ✓ Using oxygen primary ion beam at low incident angle, the sputtering rate is low so that a microscopic SiO2 layer is formed.
  - ✓ Charge-driven diffusion of some species, such as Na and Cu, may occur due to the charges accumulated on the oxide.

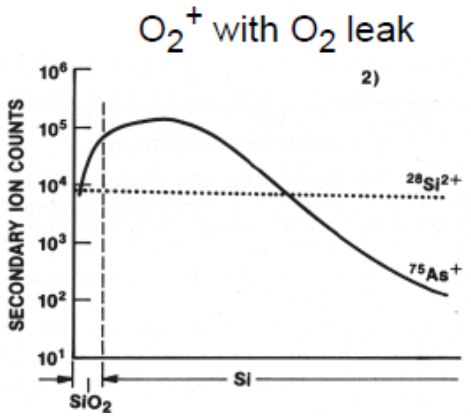


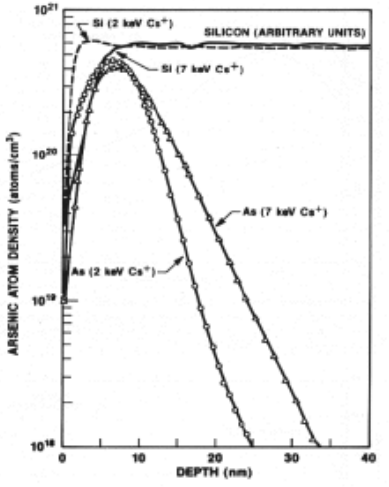


Matrix and surface effect

- **Matrix effects**
  - ✓ Secondary ion yields can vary with sample composition.
  - ✓ The change of primary ion density at surface and interface of multilayer sample affect the secondary ion intensity.
- **Surface effect**
  - ✓ The native oxide, the equilibrium depth, and surface defects produce depth profile aberrations.
  - ✓ Low energy and oxygen flooding can reduce equilibrium depth.

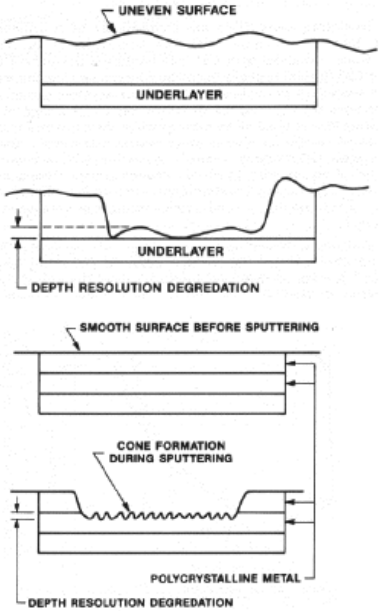


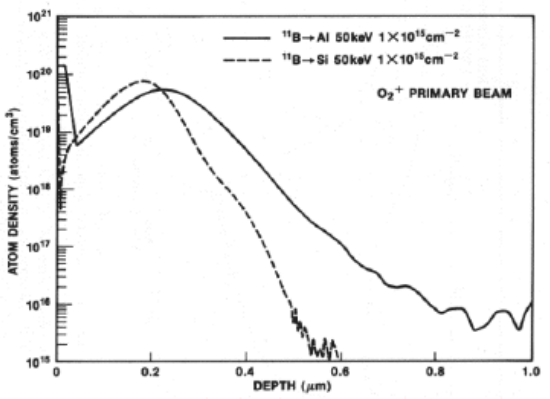


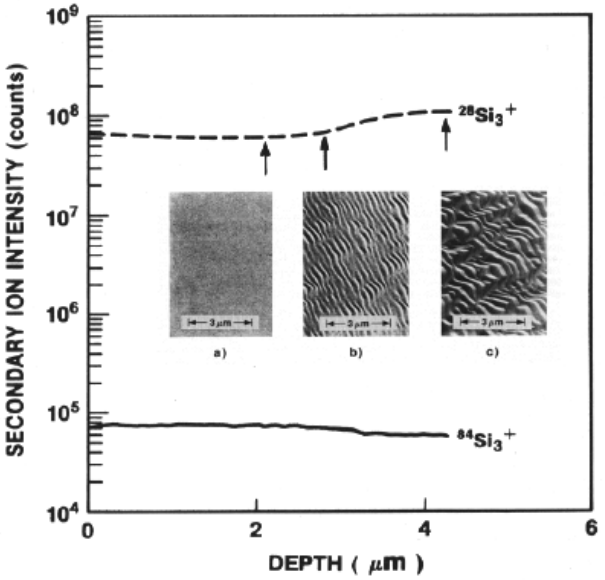


Micro-topography

- **Surface topography may be the property of the original sample surface or changed by ion bombardment.**
  - ✓ Grains with different orientation have different sputtering rate.
  - ✓ Ripple topography is an instability of a plane surface to periodic disturbance.
  - ✓ Signal from various plane are mixed.

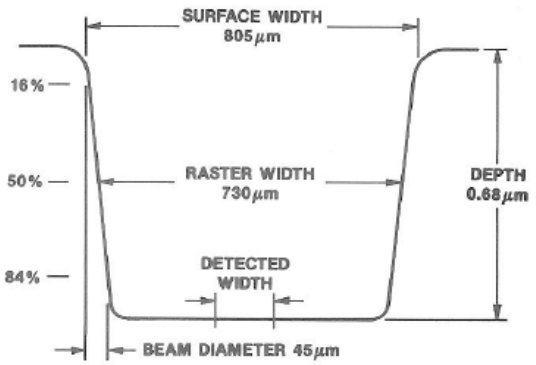


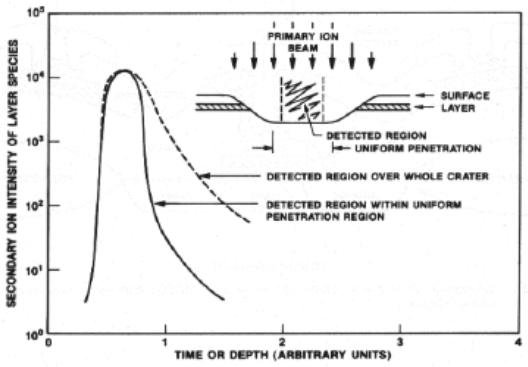


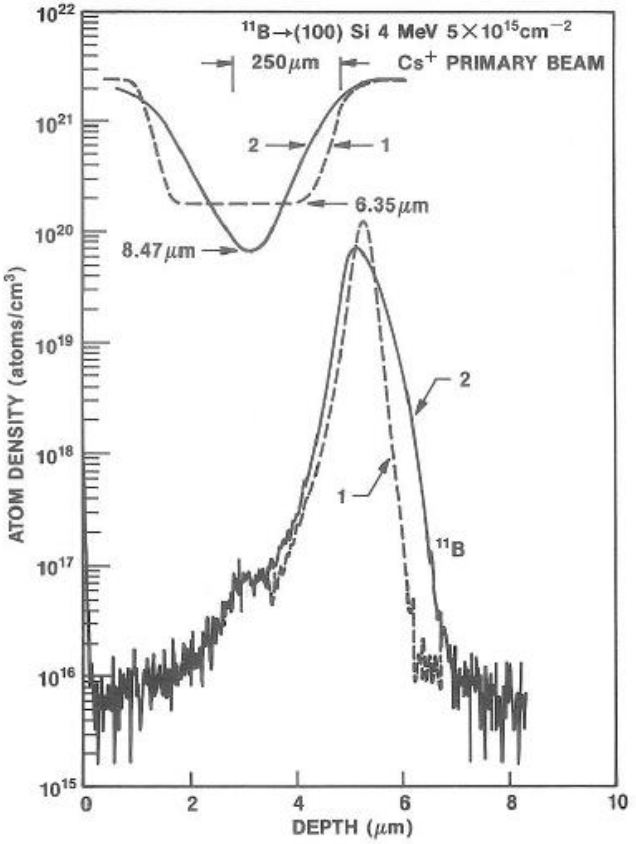


Crater shape

- **Crater shape issue comes from nonuniform raster or asymmetric beam shape.**
  - ✓ Sputtered front is not at the same plane.
  - ✓ Signal from various plane are mixed.







SIMS Summary

SIMS can be used to analyse the composition of organic and inorganic solids.

- SIMS can generate spatial or depth profiles of elemental or molecular concentrations.
- To detect impurities or trace elements, especially in semiconductors and thin filaments.
- Secondary ion images have spatial resolution on the order of 0.5 to 5 μm. The depth resolution is around 2 to 5 nm.
- Detection limits for trace elements range between 10^{12} to 10^{16} atoms/cm^3. That is around ppb ~ ppm.
- SIMS is the most sensitive elemental and isotopic surface microanalysis technique. However, very expensive.