

Auger Electron Spectroscopy (AES)

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CH17D410

Auger Electron Spectroscopy

- **Introduction**
- **Principles**
- **Instrumentation**
- **Qualitative analysis**
- **Quantitative analysis**
- **Depth profiling**
- **Examples**



The **Auger Effect** is named after its discoverer, **Pierre Auger** in 1920.

The idea of using electron-stimulated Auger signals for surface analysis was first suggested in 1953 by **J. J. Lander**.

The technique became practical for surface analysis after **Larry Harris** in 1967 demonstrated the use of differentiation to enhance the Auger signals.

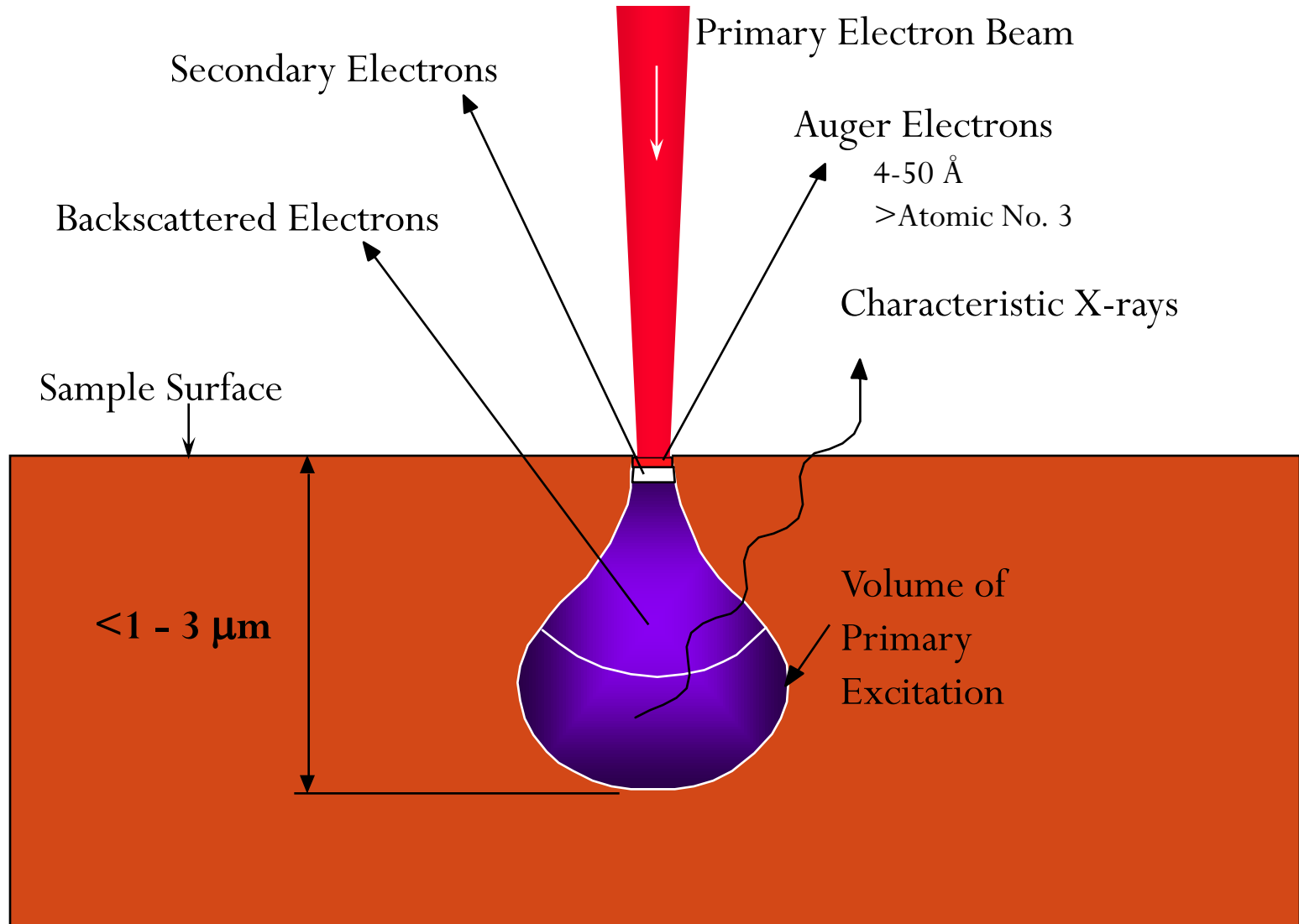
Today Auger electron spectroscopy is a powerful surface analytical tool to probe surfaces, thin films, and interfaces.

This utility arises from the combination of surface specificity (0.5 to 10 nm), good spatial surface resolution (as good as 10 nm), periodic table coverage (except hydrogen and helium), and reasonable sensitivity (100 ppm for most elements).

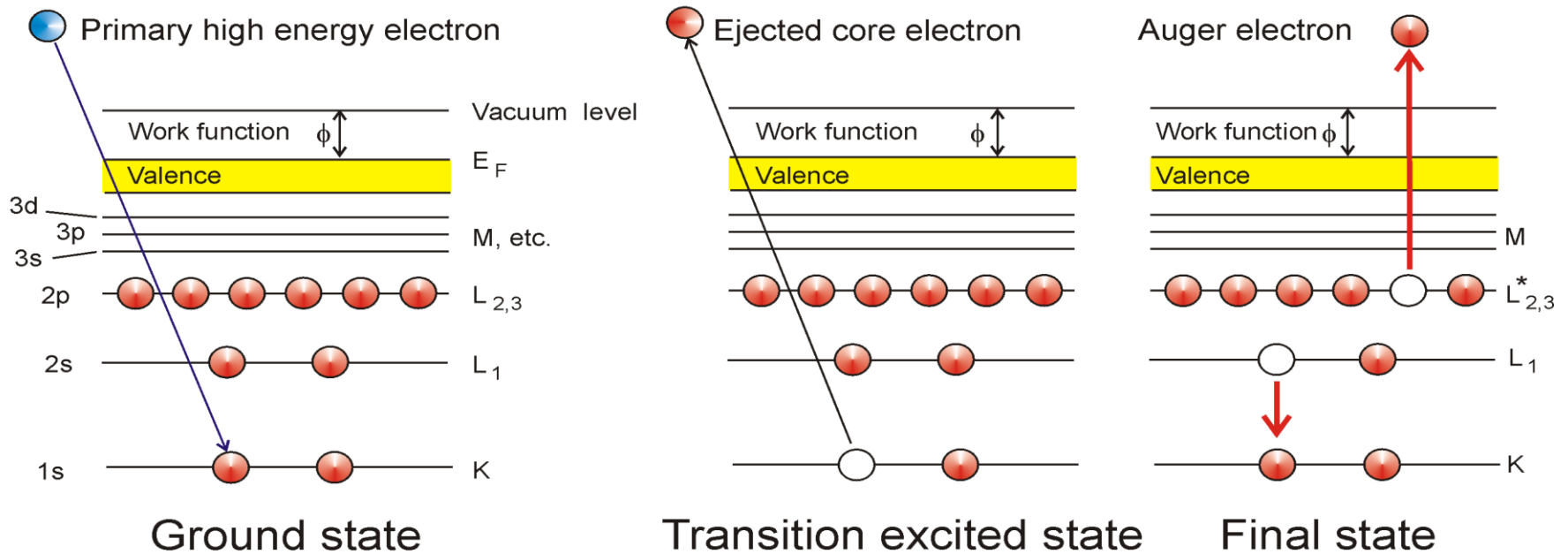


Pierre Auger

Electron Beam - Sample Interaction



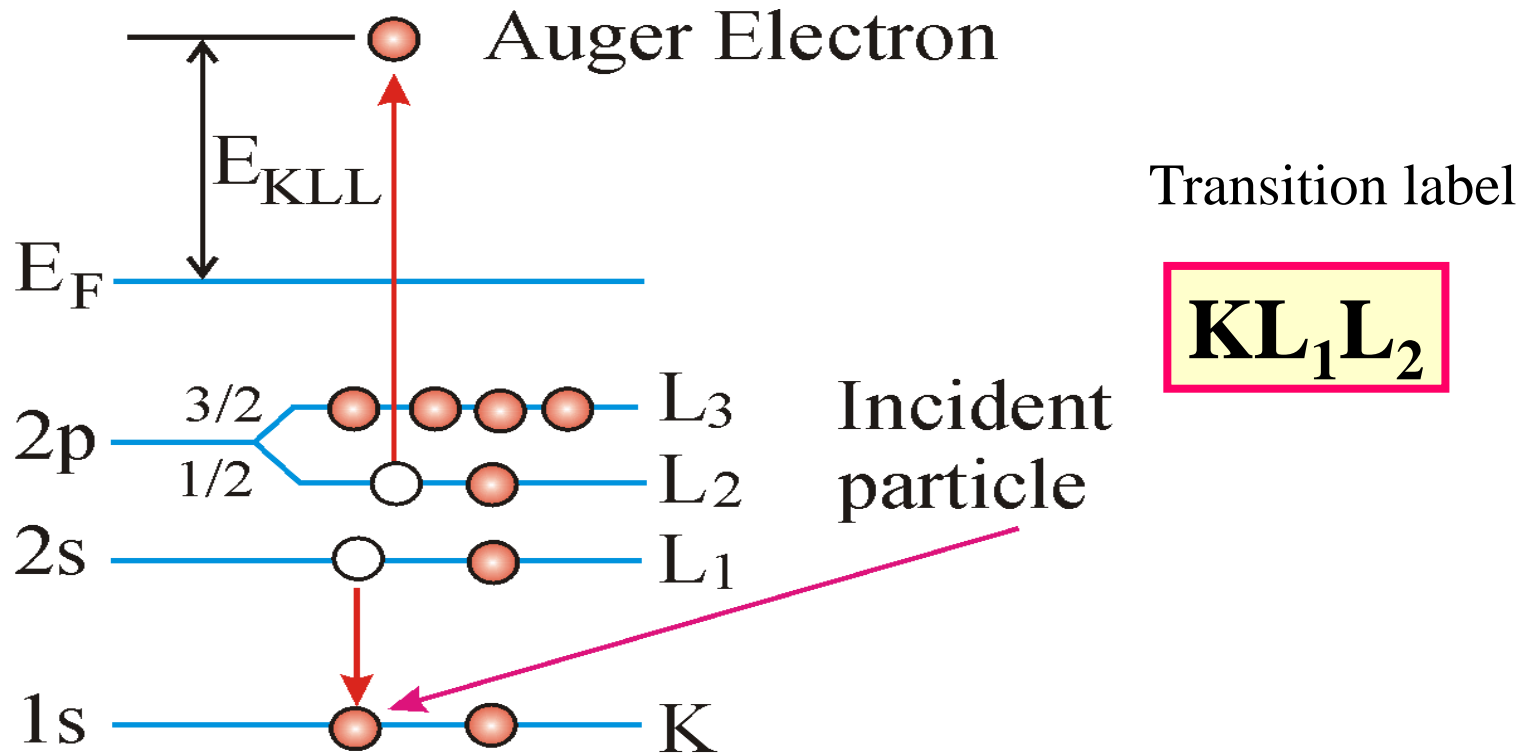
Auger Process



The Auger process starts with the removal of an inner shell atomic electron to form a vacancy. Several processes are capable of producing the vacancy, but bombardment with an electron beam is the most common. The inner shell vacancy is filled by a second electron from an outer shell. The energy released kicks a third electron, the Auger electron, out of the atom.

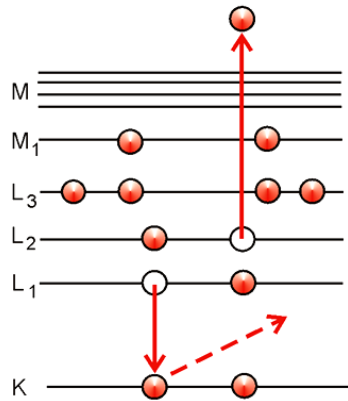
The process of an excited ion decaying into a doubly charged ion by ejection of an electron is called the Auger process.

Nomenclature for Auger Transitions

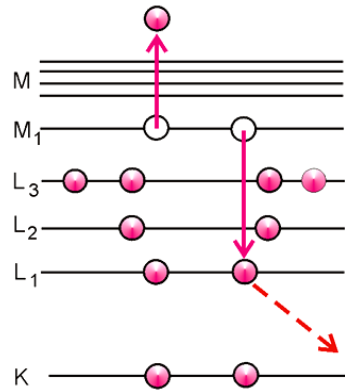


The three symbols in the transition label correspond to the three energy levels involved in the transition.

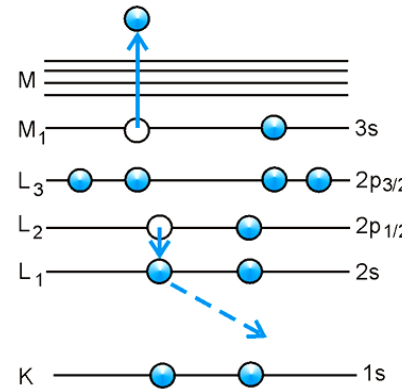
Examples of Auger Processes



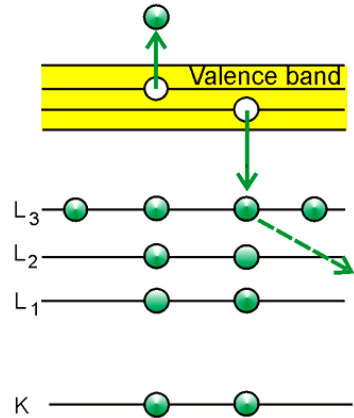
Auger
KL₁L₂
(a)



Auger
L₁M₁M₁
(b)



Coster-Kronig
L₁L₂M₁
(c)



Auger (Solid)
L₃VV
(d)

KL₁L₁
KL₁L₂₃ {
KL₁L₂
KL₁L₃

e. g. Cu LMM
L₃M₂₃M₂₃ (768 eV)
L₂M₂₃M₂₃ (775 eV)
L₃M₂₃M₄₅ (839 eV)
L₃M₂₃M₄₅ (847 eV)
L₃M₄₅M₄₅ (919 eV)
L₂M₄₅M₄₅ (939 eV)

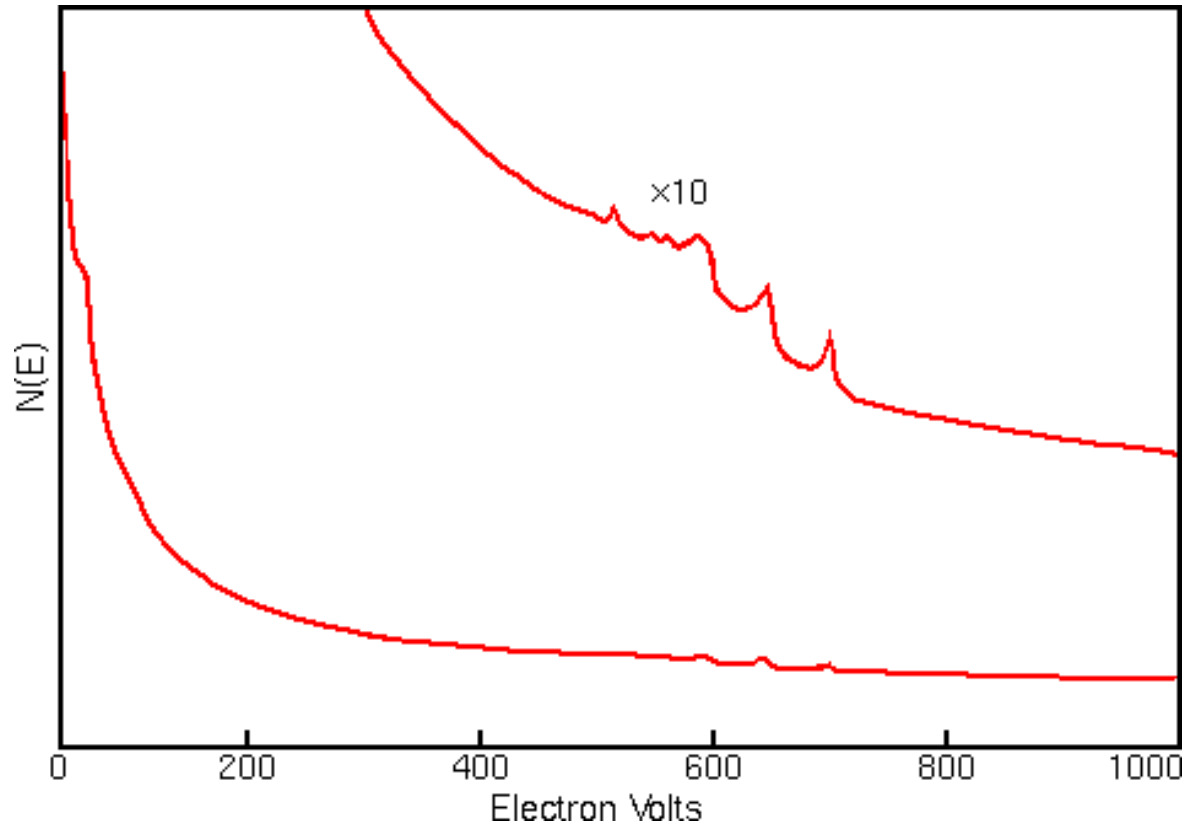
Also MNN Auger

AES Characteristics

- **Range of elements:** All except H and He
- **Destructive:** No, except to electron beam sensitive materials and during depth profiling
- **Elemental analysis:** Yes, semi-quantitative without standards; quantitative with standards
- **Absolute sensitivity:** 100 ppm for most elements
- **Chemical states:** Yes, in many materials.
- **Depth probed:** 0.5- 10 nm (typically 0.5- 3.0 nm).
- **Depth profiling:** Yes, in concert with ion beam sputtering
- **Lateral resolution:** 30 nm for AES; even less for SAM imaging
- **Imaging/mapping:** Yes, Scanning Auger Microscopy (SAM)
- **Sample requirements:** Vacuum (UHV) compatible materials
- **Main use:** Elemental composition of inorganic materials
- **Instrument cost:** US\$ 300,000 – 1,000,000 (2 Cr -6 Cr)

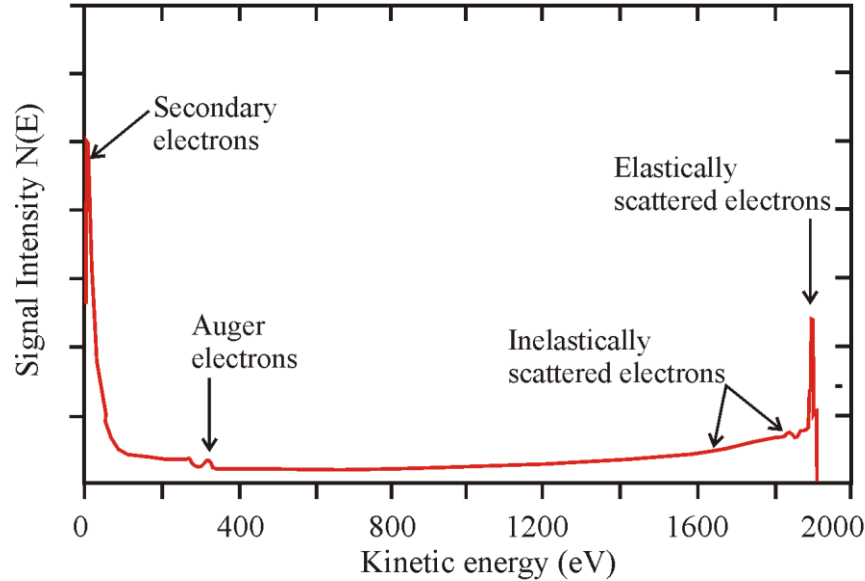
Auger Electron Spectrum

The Auger peaks are obscure even using an expanded vertical scale.

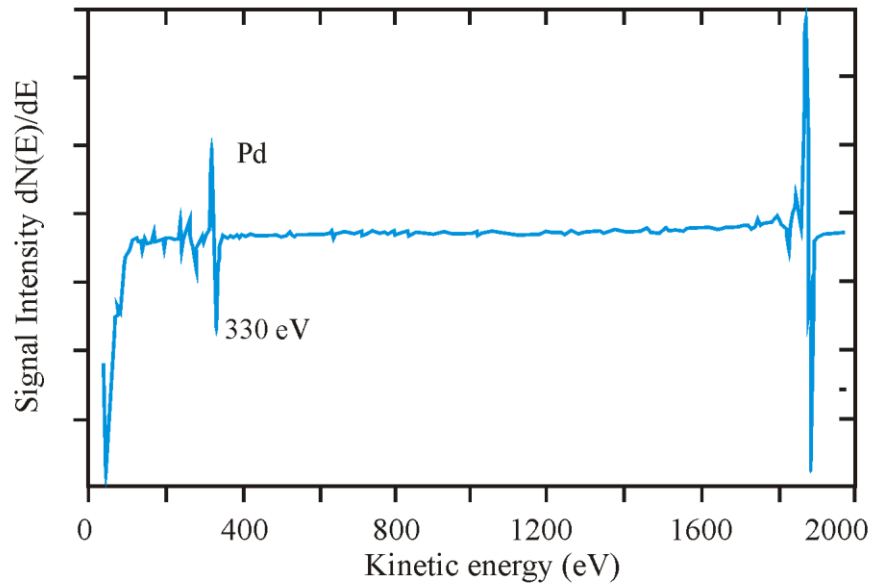


→
Electron signal Vs. electron energy

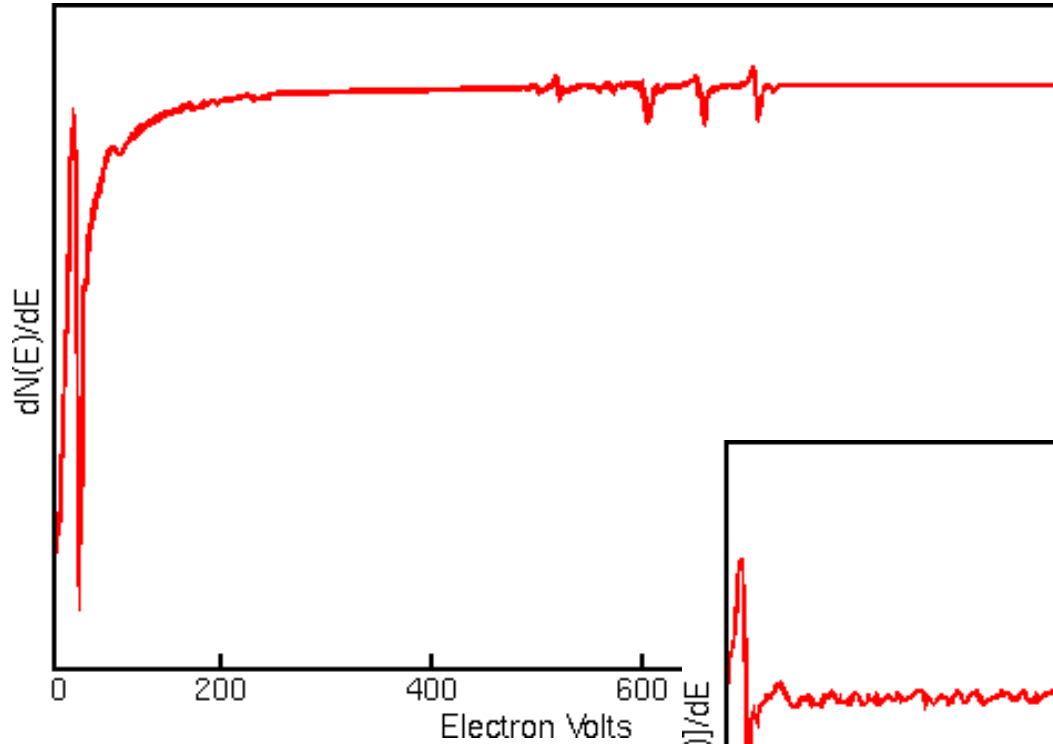
Electron Energy Spectrum of Pd metal



Direct spectrum

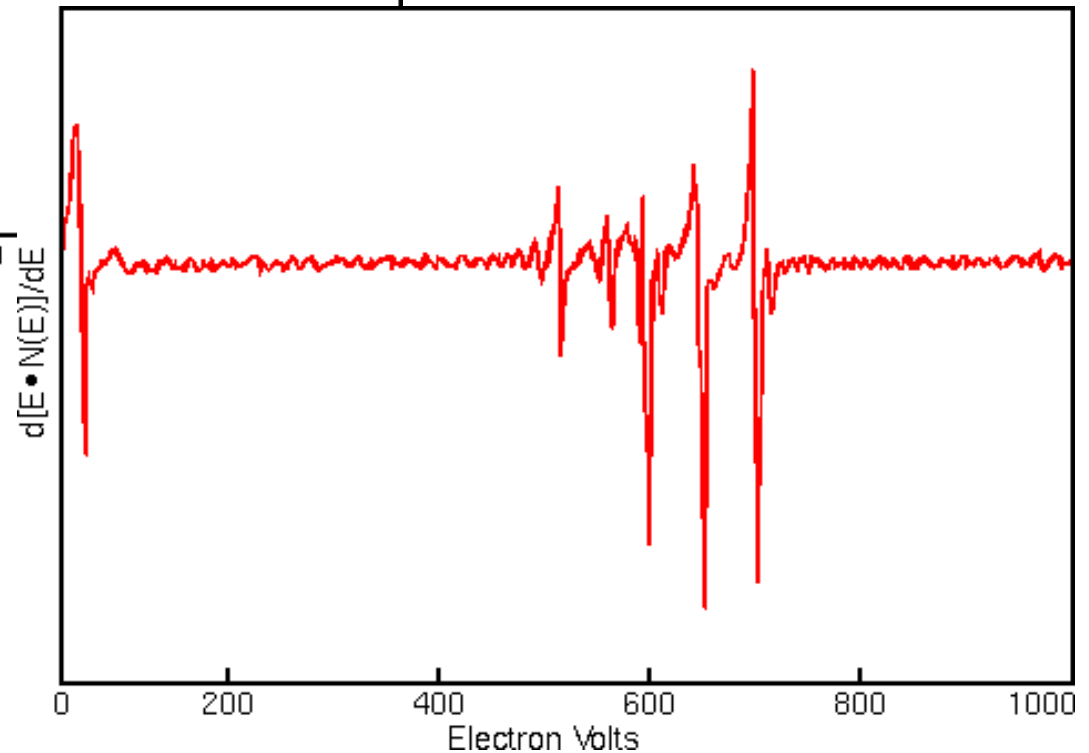


Differential spectrum
- enhances AES features
/ removes background



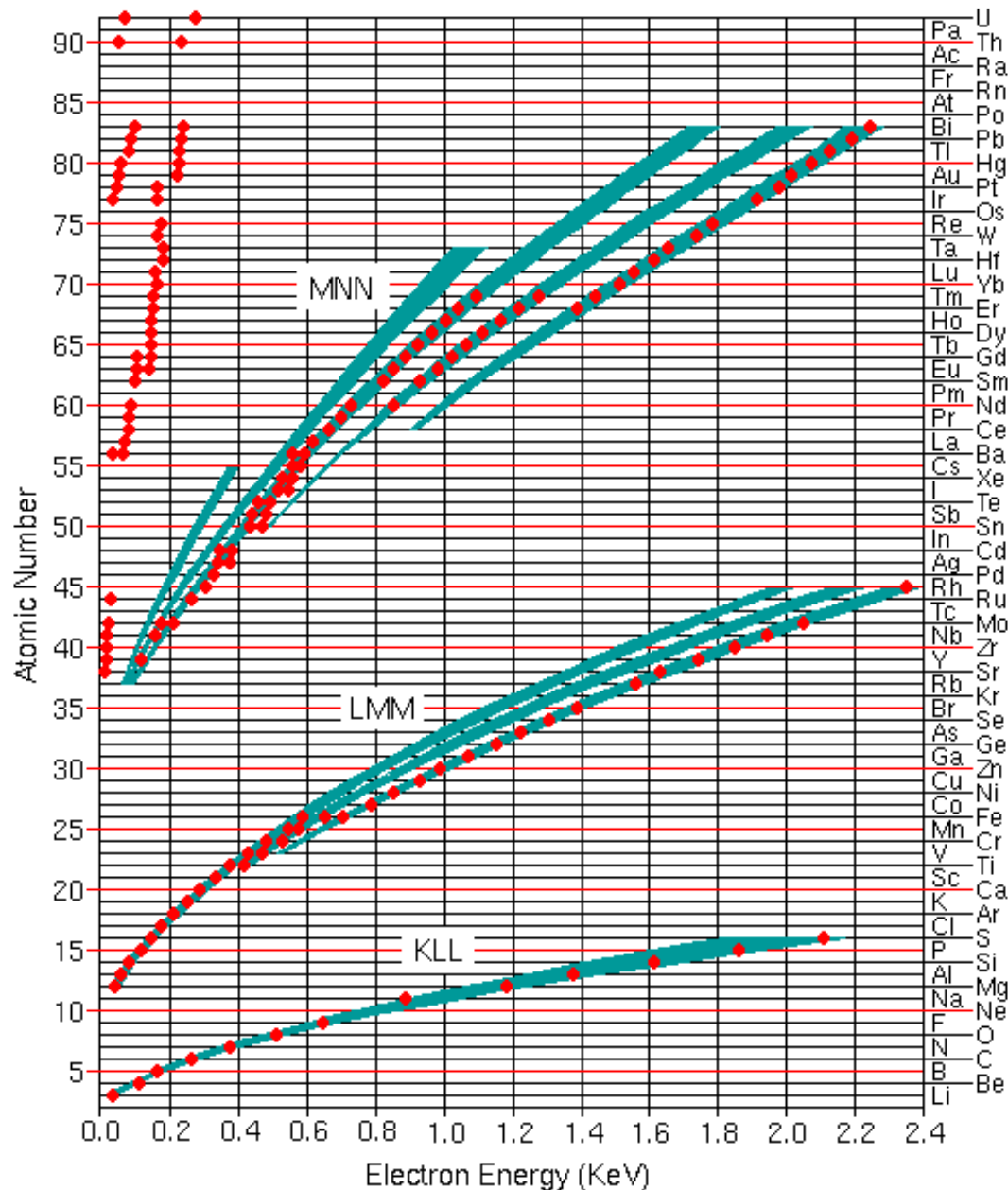
Plotting the spectrum as the differential of the electron signal, $dN(E)/dE$, clarifies some of the spectral details.

Plotting $d[E \times N(E)]/dE$, of the above function provides for clear display of the features in an Auger electron spectrum. This $d[E \times N(E)]/dE$ format is the most common mode for presenting Auger data.



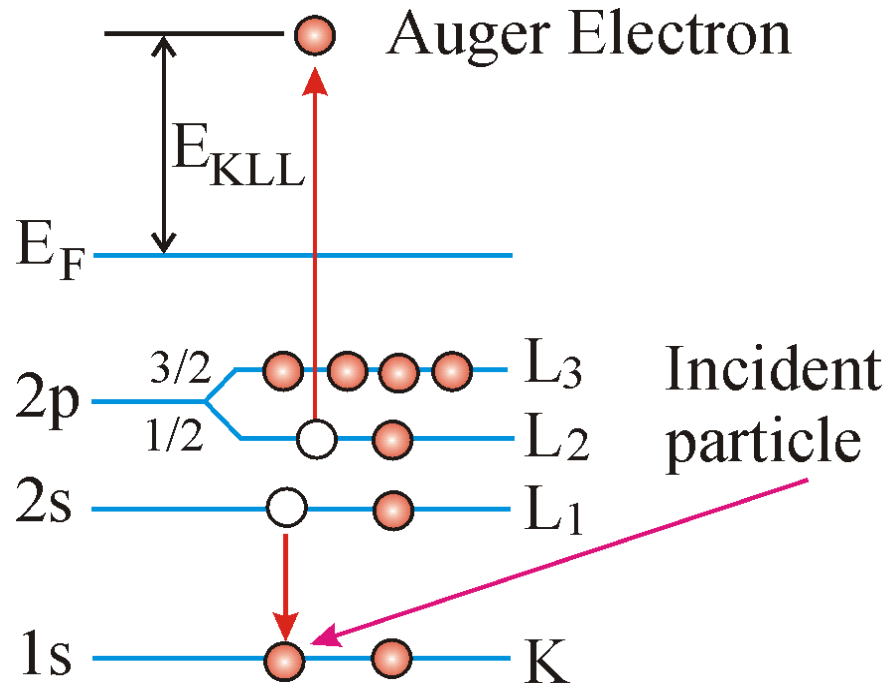
Kinetic Energies

Qualitative analysis depends on the identification of the elements responsible for the peaks in the spectrum. The right figure shows the most useful Auger peaks in the KLL, LMM, and MNN parts of the spectrum as well as higher transitions for elements above cesium. The red dots indicate the strongest and most characteristic peaks.

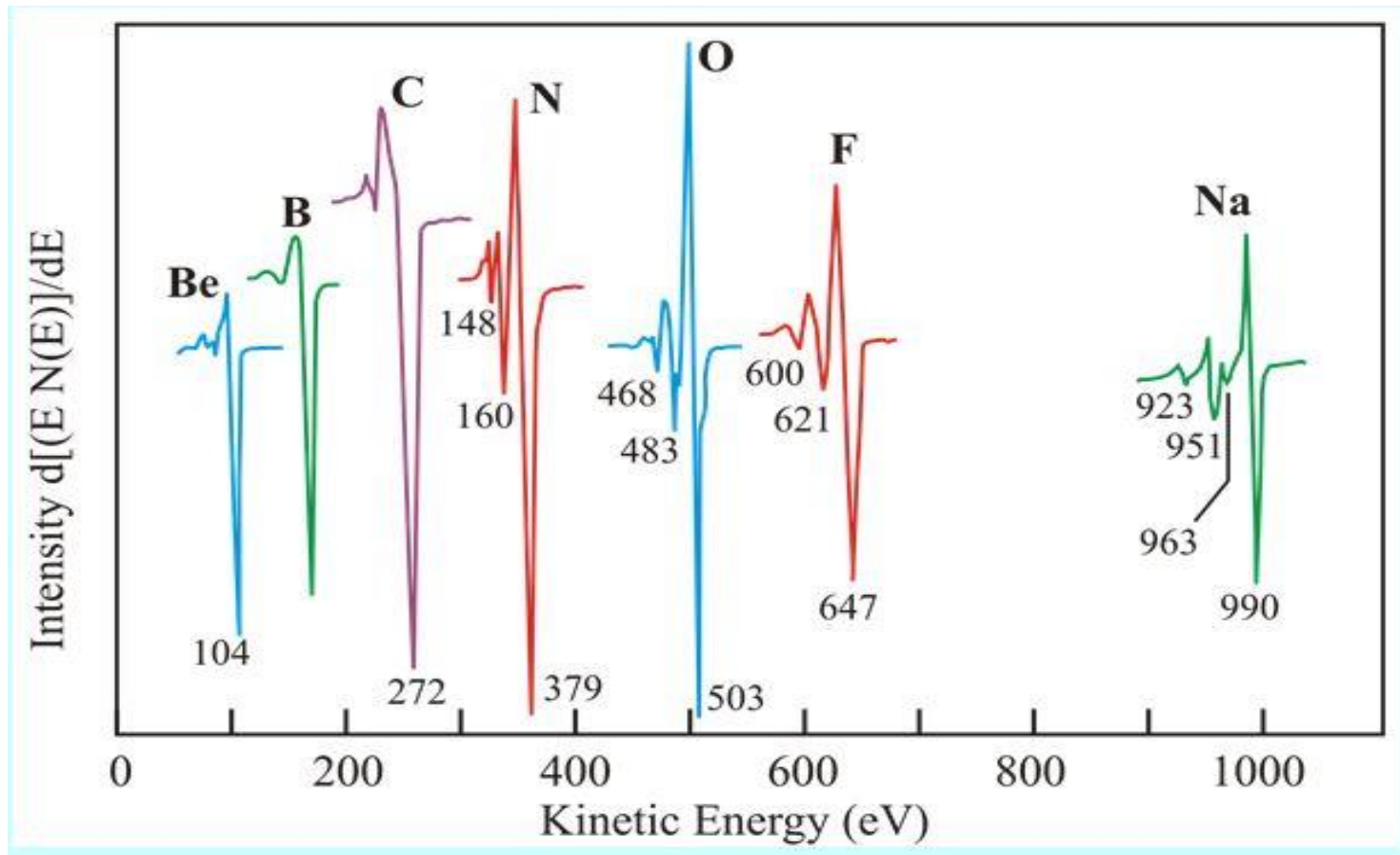


Estimation of Kinetic Energy

For an Auger transition ABC, the kinetic energy of the Auger electron is equal to $E_A - E_B - E_C$, where E_A , E_B , and E_C are the binding energies of electrons in the three levels.

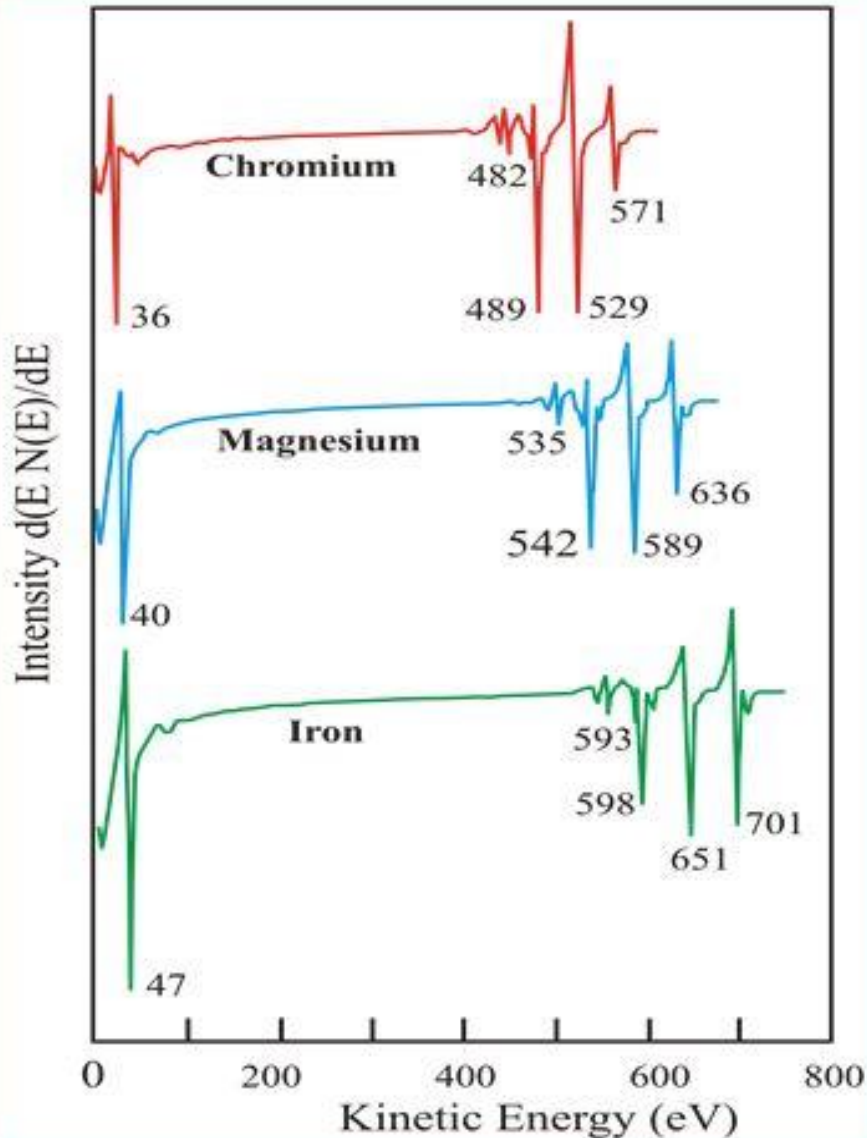


Auger Peaks



Auger spectra in the differential distribution characteristic of the lightest elements (The principal peak is $KL_{2,3}L_{2,3}$ and the relative intensities are not plotted to scale)

Auger Peaks

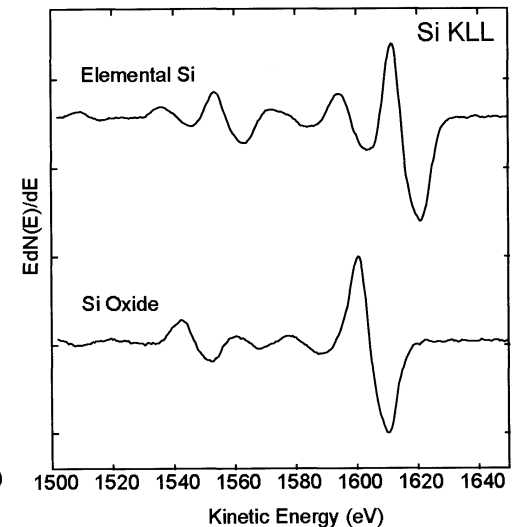
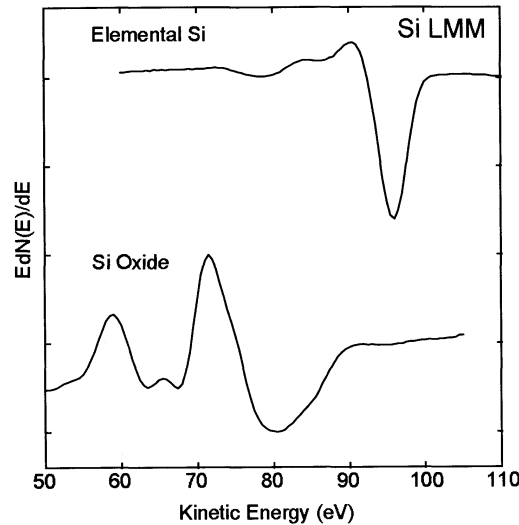
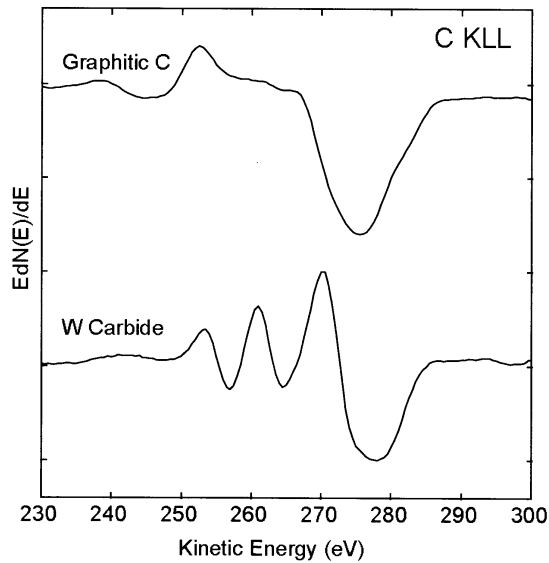
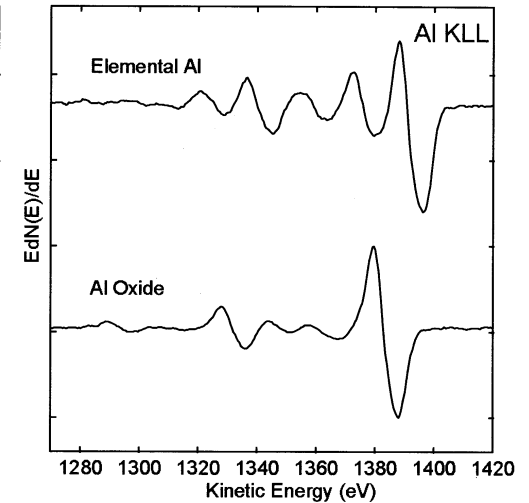
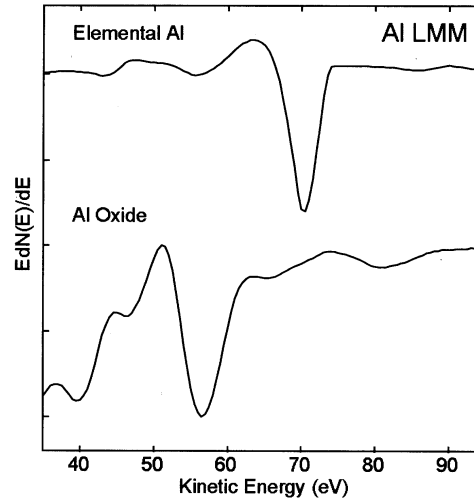


Differentiated Auger spectra of chromium, manganese, and iron

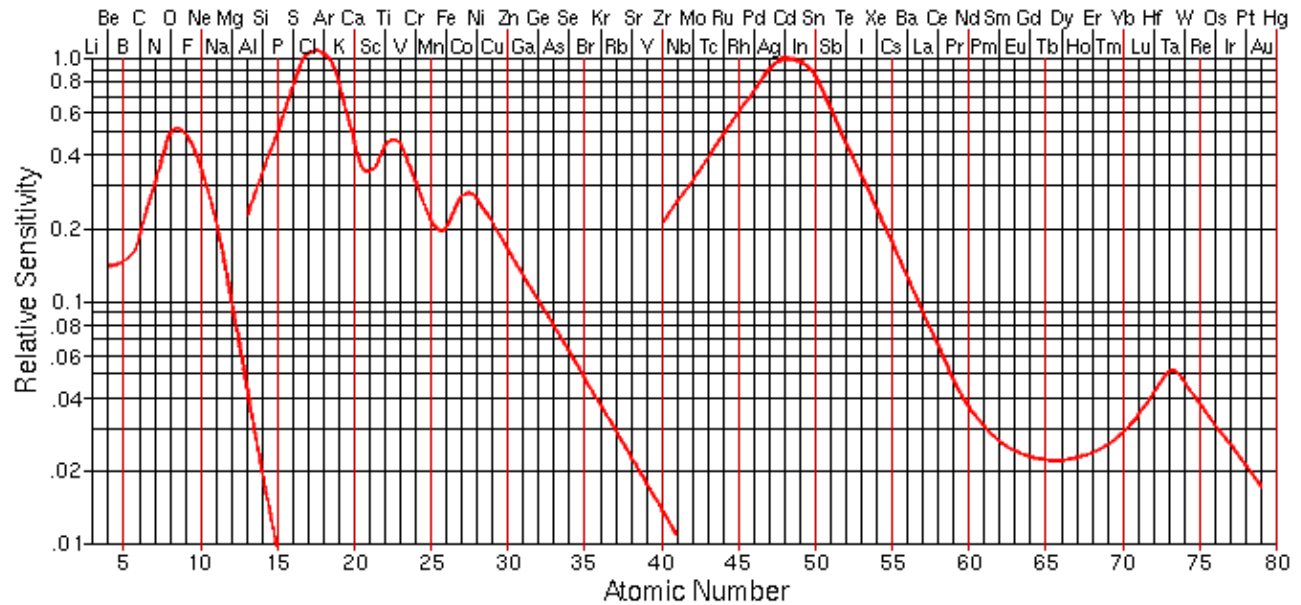
Chemical Information

The energy and shape of an Auger peak contains information about the chemical environment.

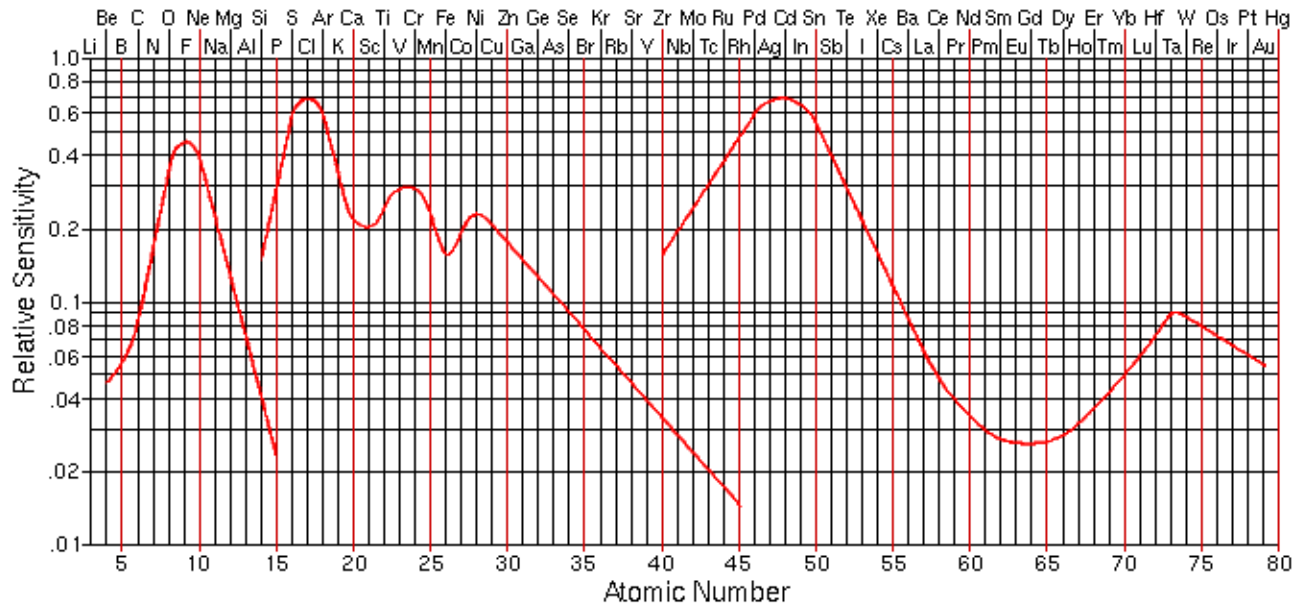
Different electron energies.



The relative intensities of the Auger electrons also depend on the primary excitation energy. (3 KV and 10 KV primary beam)

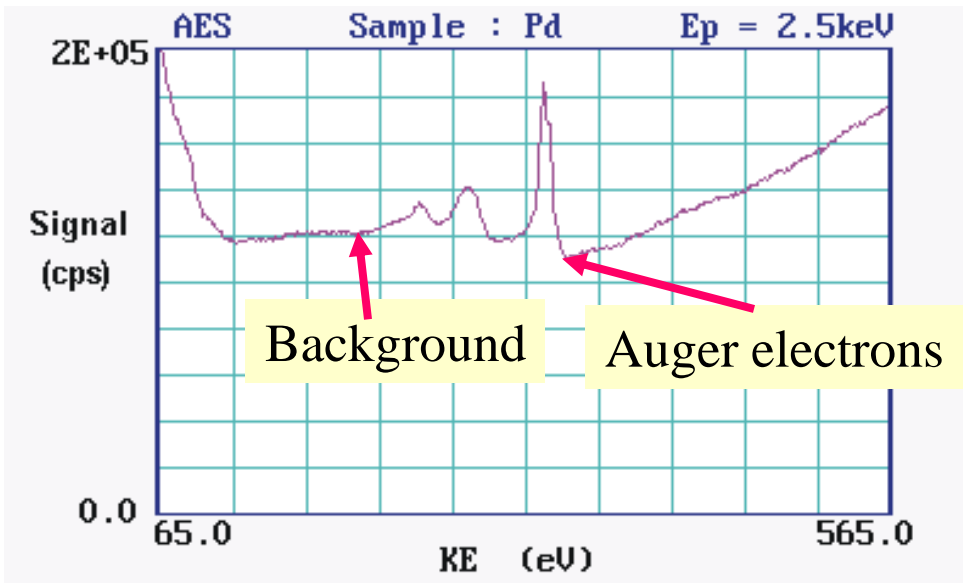


The relative intensities can be used for quantitative analysis



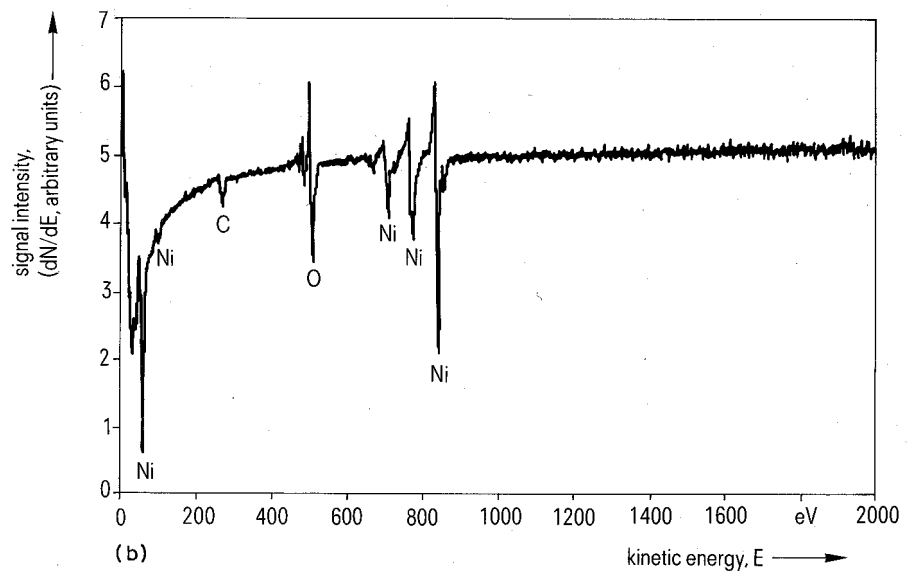
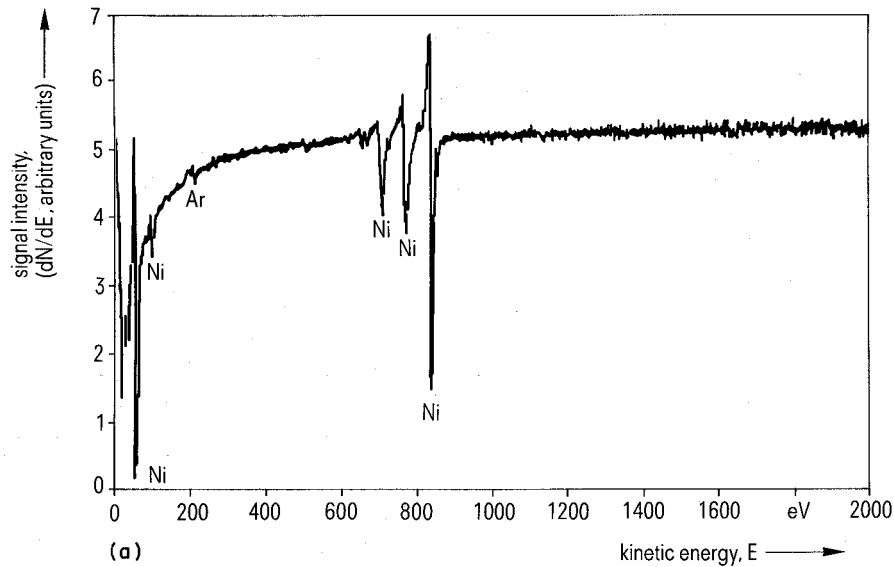
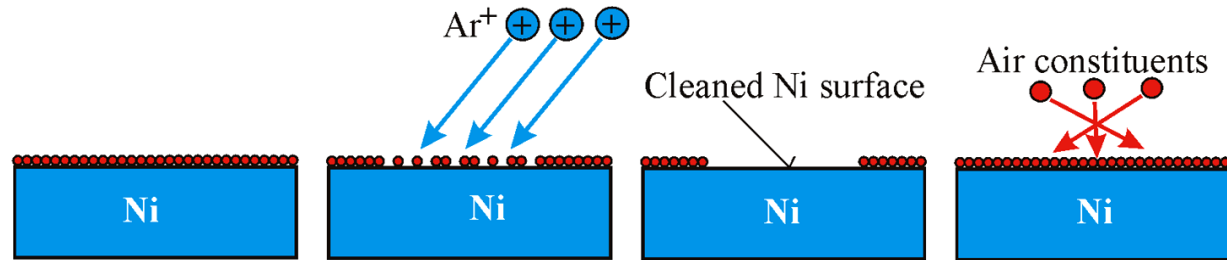
Surface Sensitivity of Auger Electron Spectroscopy

Electrons emitted from the solid must be transported to the surface in order to escape and be analyzed. If electrons undergo inelastic scattering (i.e. collision processes with energy loss), the kinetic energies of the electrons will be less than that of the expected Auger electrons. Such electrons will become the background in the low kinetic energy side of the Auger peaks. Some electrons may nearly lose all the kinetic energies and cannot leave the sample surface. Only the Auger electrons originating from the top surface can escape the sample surface without energy loss.



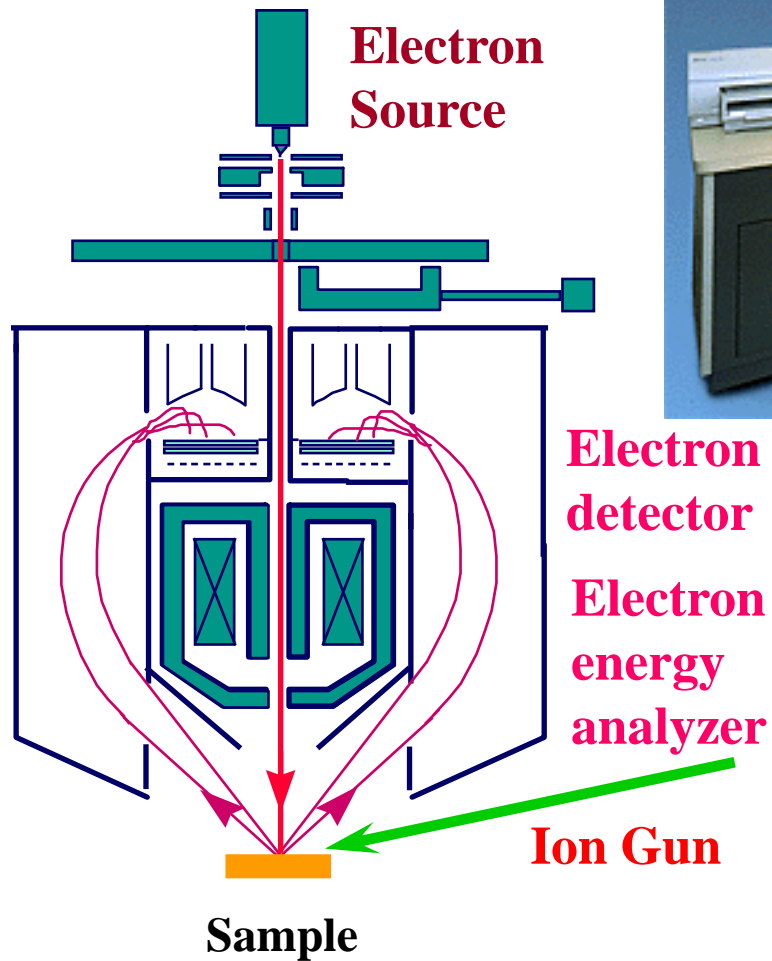
The term “inelastic mean free path” is usually used to describe the surface sensitivity of Auger electrons

Surface Sensitivity of AES



AES spectra of Ni surface: (a) after Ar sputter-cleaning; (b) after exposure to air for 1 min. showing adsorbed carbon and oxygen.

Instrumentation



Vacuum system

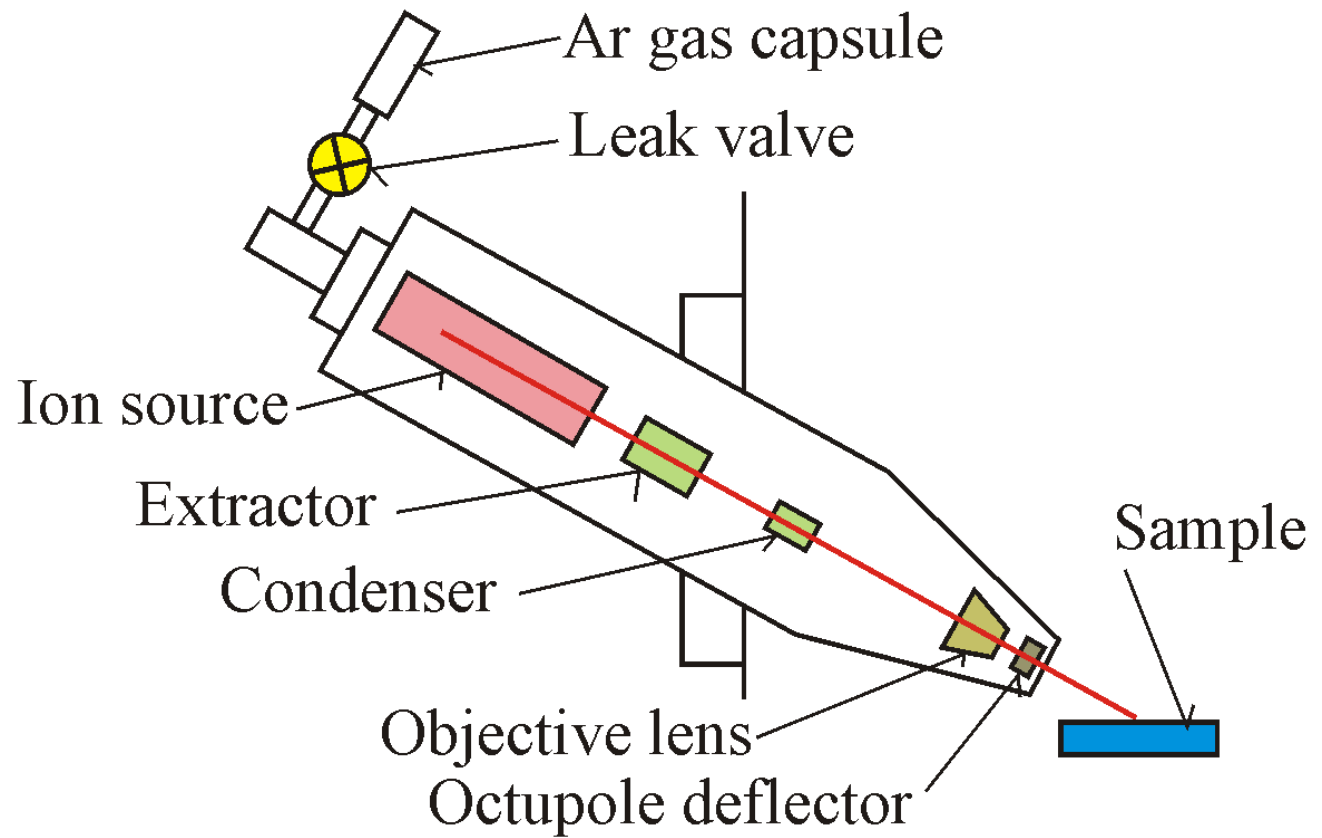
Sample stage

Electronic controls

Computer

Software

Ion Gun



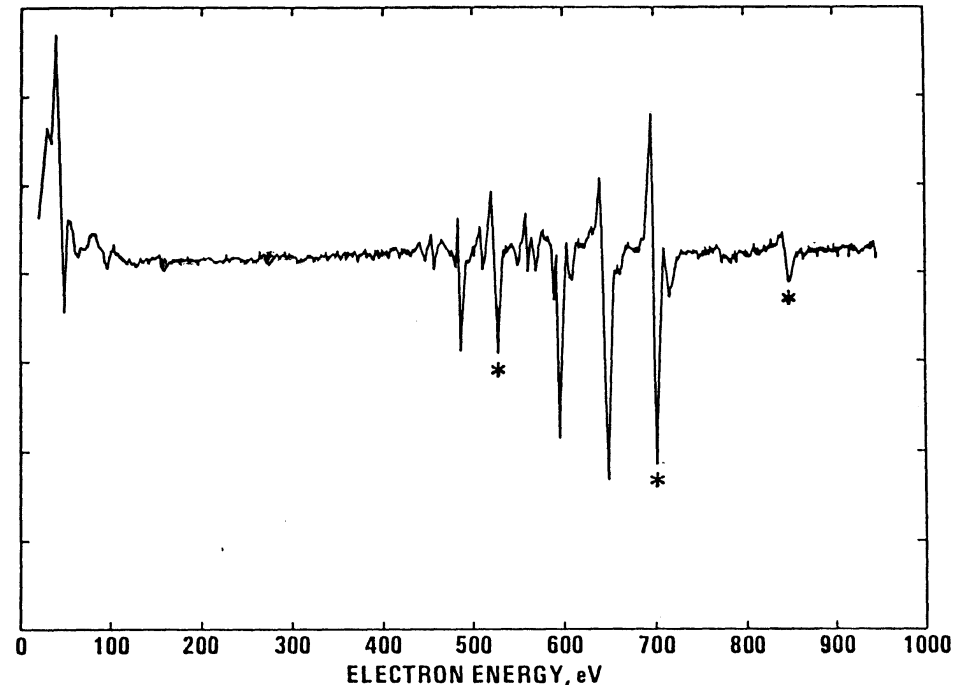
An Ar^+ ion beam at kinetic energy 0.5-5 keV is used to bombard the sample surface to remove surface materials for: (1) surface cleaning, (2) depth profiling

Qualitative Analysis

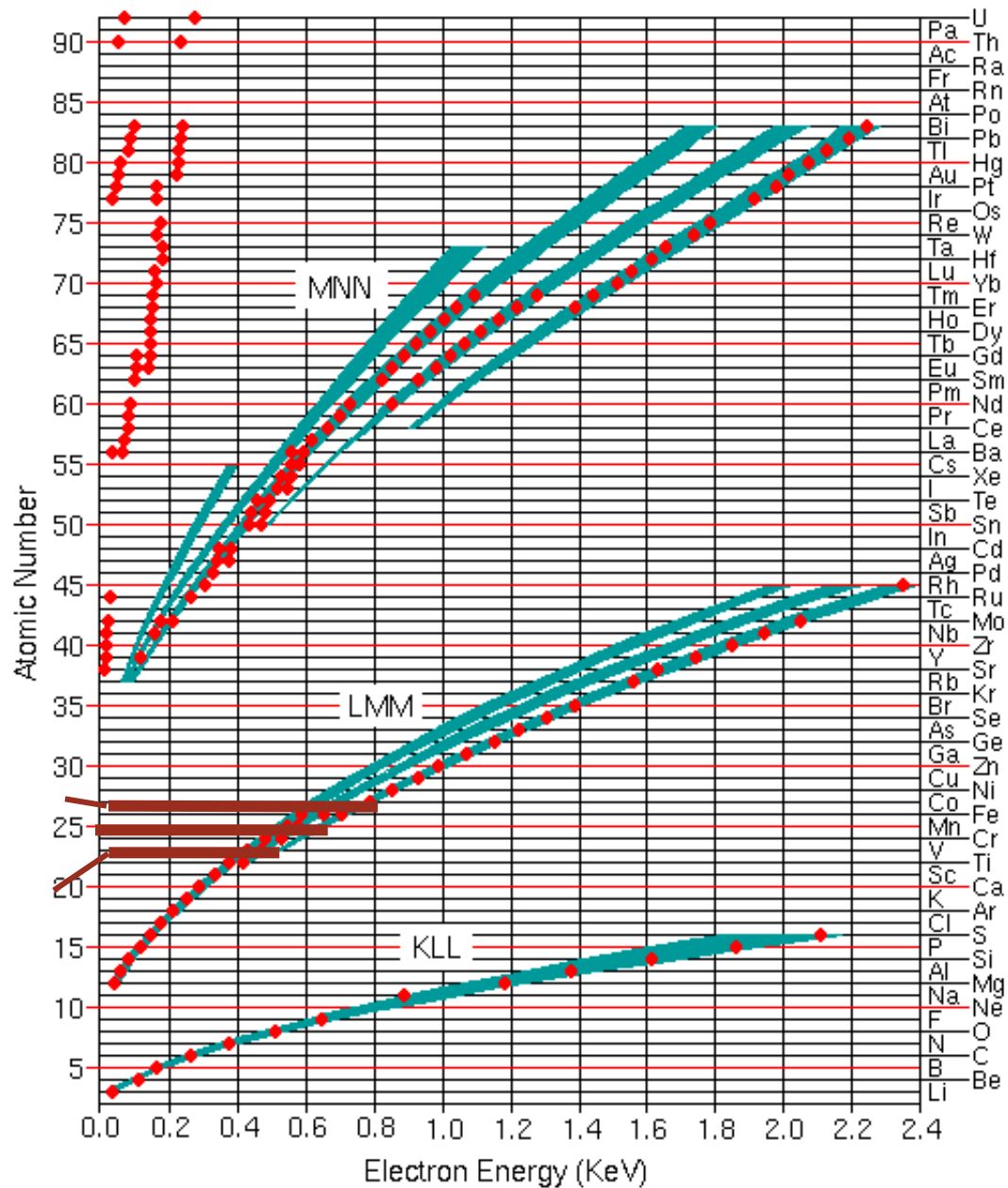
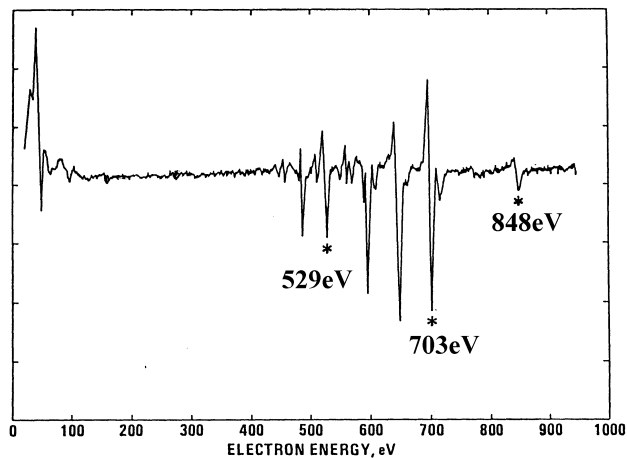
Procedures for Elemental Identification

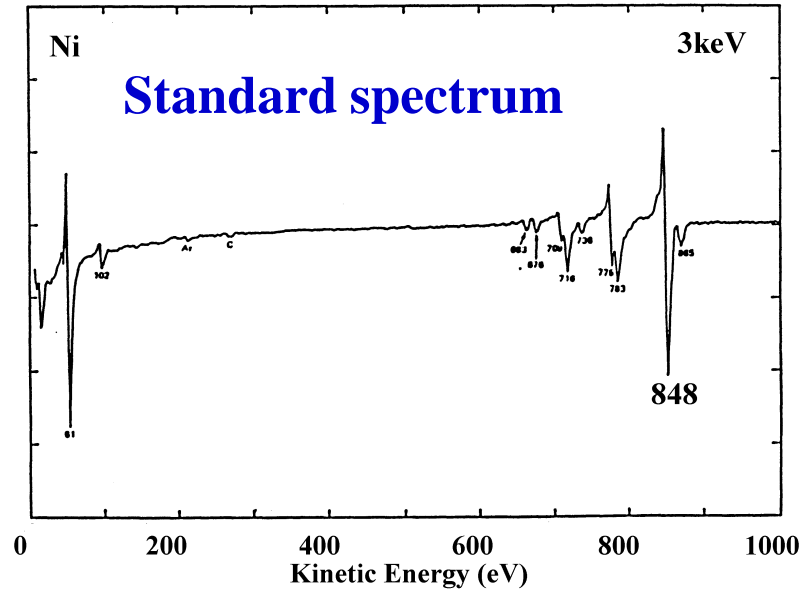
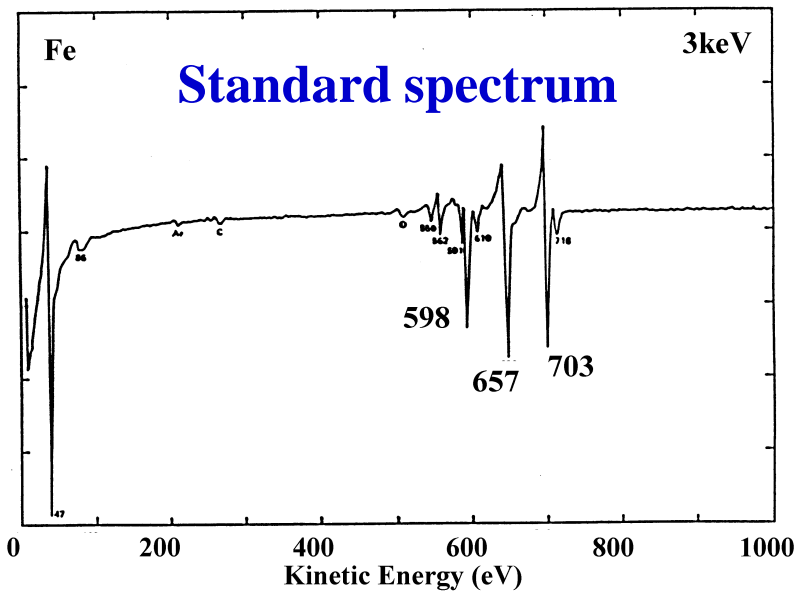
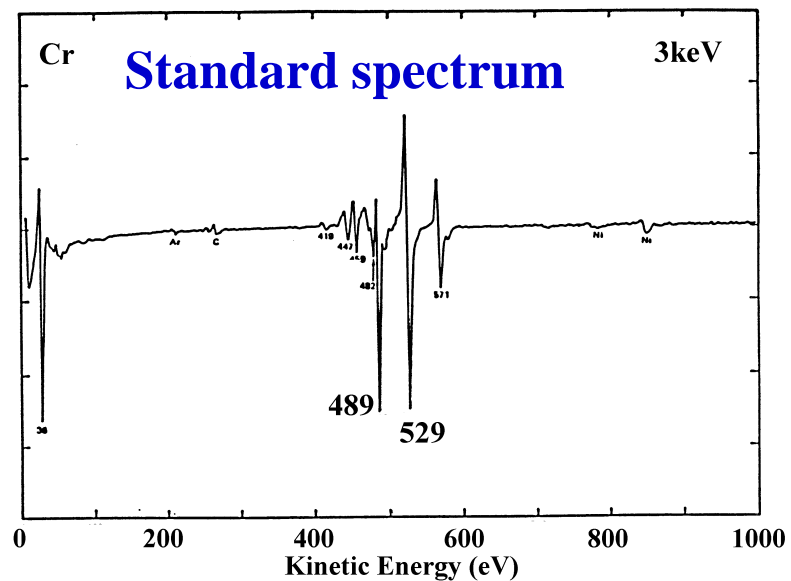
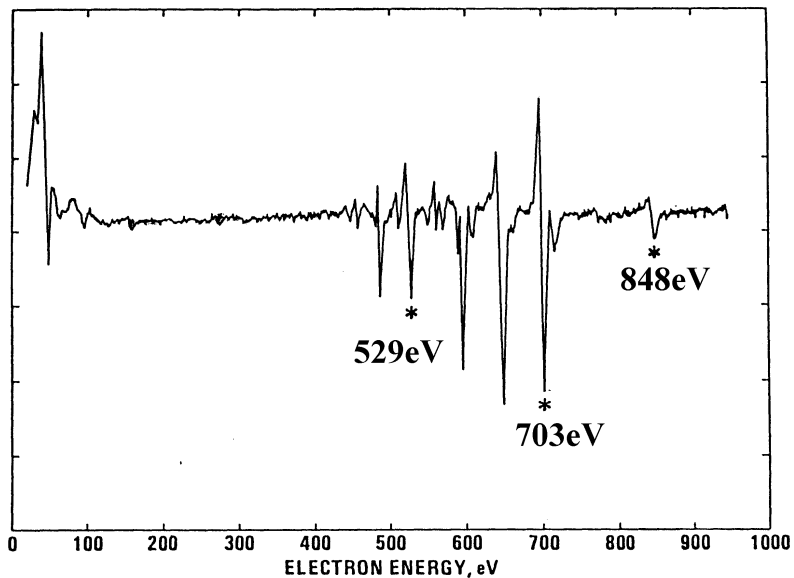
1. Concentrating on the major peaks and comparing the peak positions with Auger electron energy chart or table.
2. Referring to the standard spectra of the elements and making positive identification of major constituents.
3. Labeling all peaks related to the identified major constituents.
4. Repeat 1-3 for other unlabelled peaks.

Auger spectrum of a unknown sample

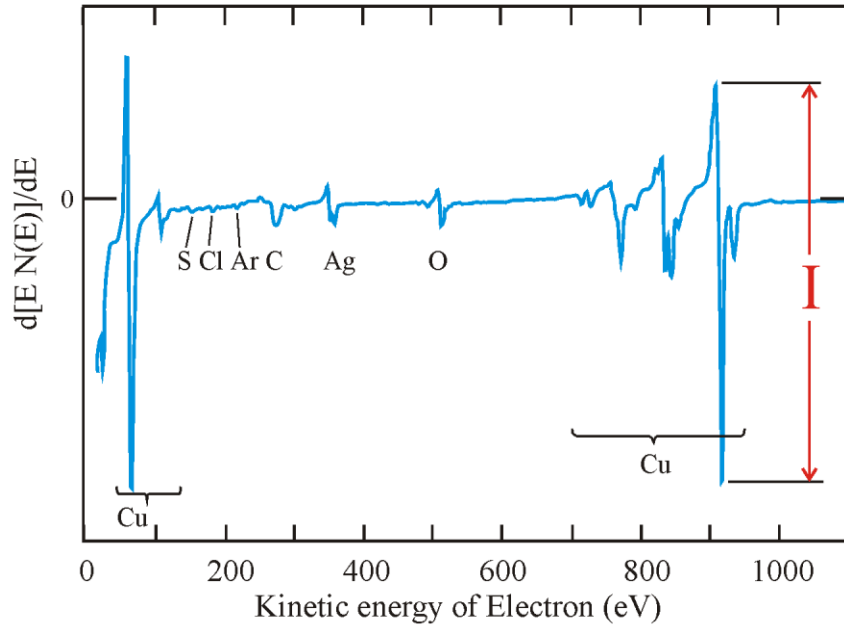


Ni, Fe and Cr are
preliminarily
identified





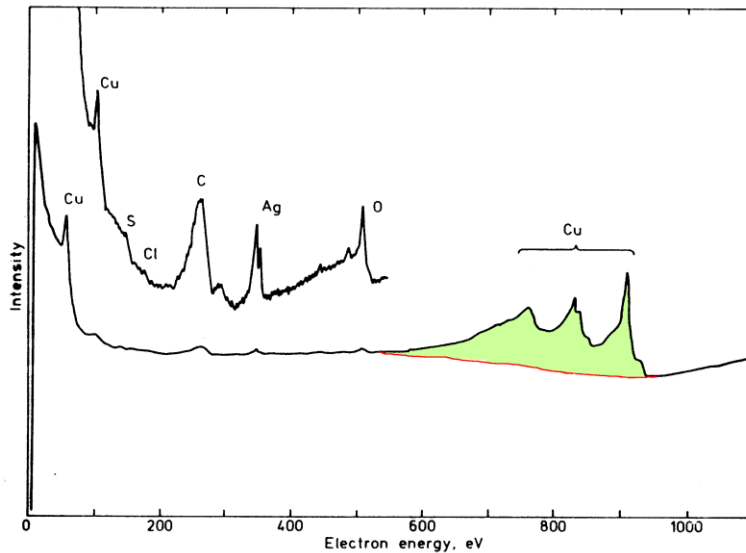
Quantitative Analysis



Peak-to-peak height

Commonly use peak to peak height of differentiated Auger peak. For high resolution, use peak area of the original Auger peak, but this needs background subtraction.

Note: Sensitivities for these two methods are different



Peak area

Need background subtraction

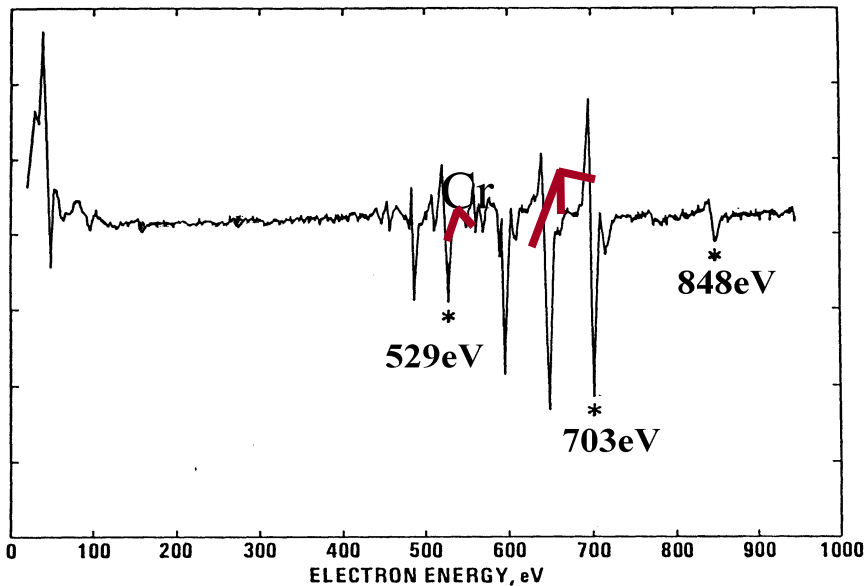
Empirical Approach

The atomic concentration of an element on a sample with N elements can be determined as:

$$X_a = \frac{N_a}{\sum_{i=1 \text{ to } N} N_i} = \frac{I_a / S_a}{\sum_{i=1 \text{ to } N} I_i / S_i}$$

Percentage atomic concentration = $X_a \times 100\%$

The empirical method does not include the matrix effects of the sample, which includes the inelastic mean free path (λ), the backscattering factor (r), and chemical effects on peak shape and surface roughness. General, an error of 15% is expected using the empirical method.



Example

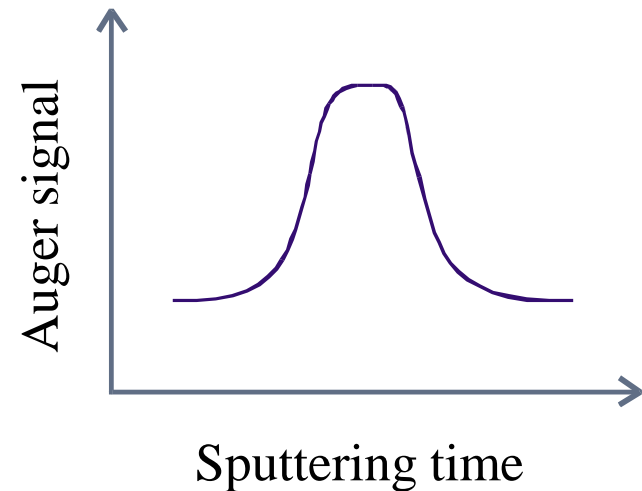
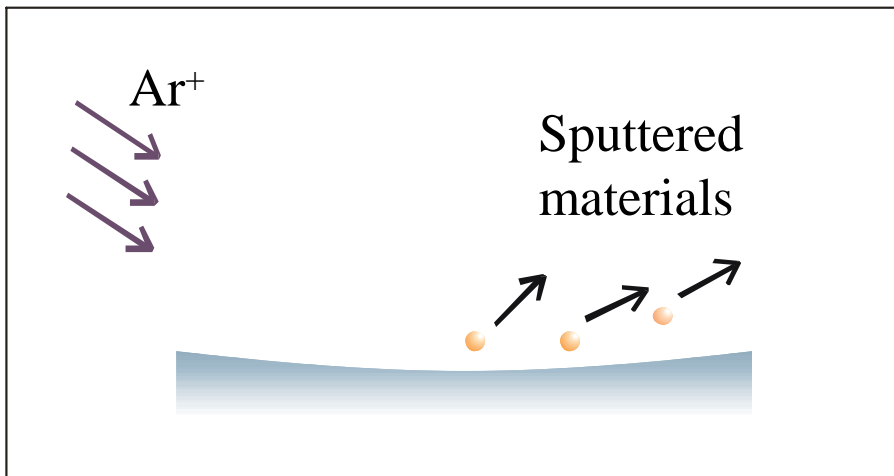
Peak-to-peak height:	S_i
Cr peak at 529eV: 4.7	0.32
Fe peak at 703eV: 10.1	0.20
Ni peak at 848eV: 1.5	0.27

$$\%Cr = \frac{4.7/0.32}{4.7/0.32 + 10.1/0.20 + 1.5/0.27} \times 100\% = 21\%$$

Similarly: %Fe = 71%; %Ni = 8%

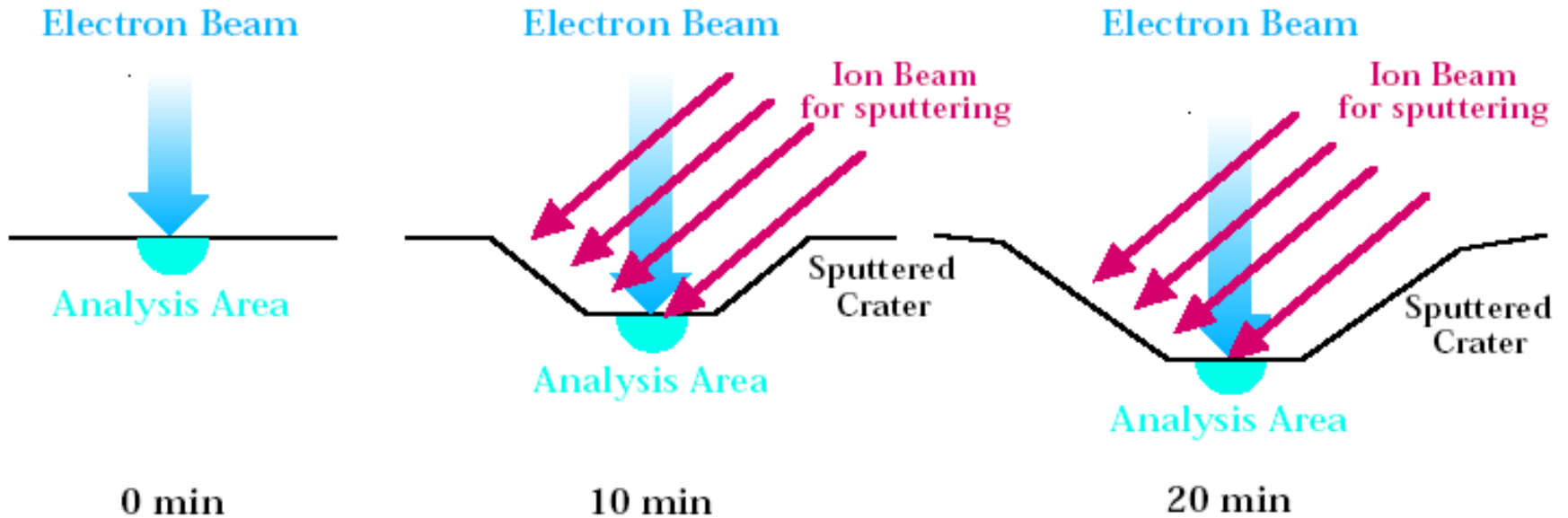
Depth Profiling

To analyze samples in depth, Auger instruments incorporate ion beam sputtering to remove materials from the sample surface sequentially. One cycle of a typical depth profile consists of sputtering a small increment into the sample, stopping, measuring relevant portions of the Auger spectrum, and performing elemental quantification.



Auger signal can be Auger peak area or peak-to-peak height.

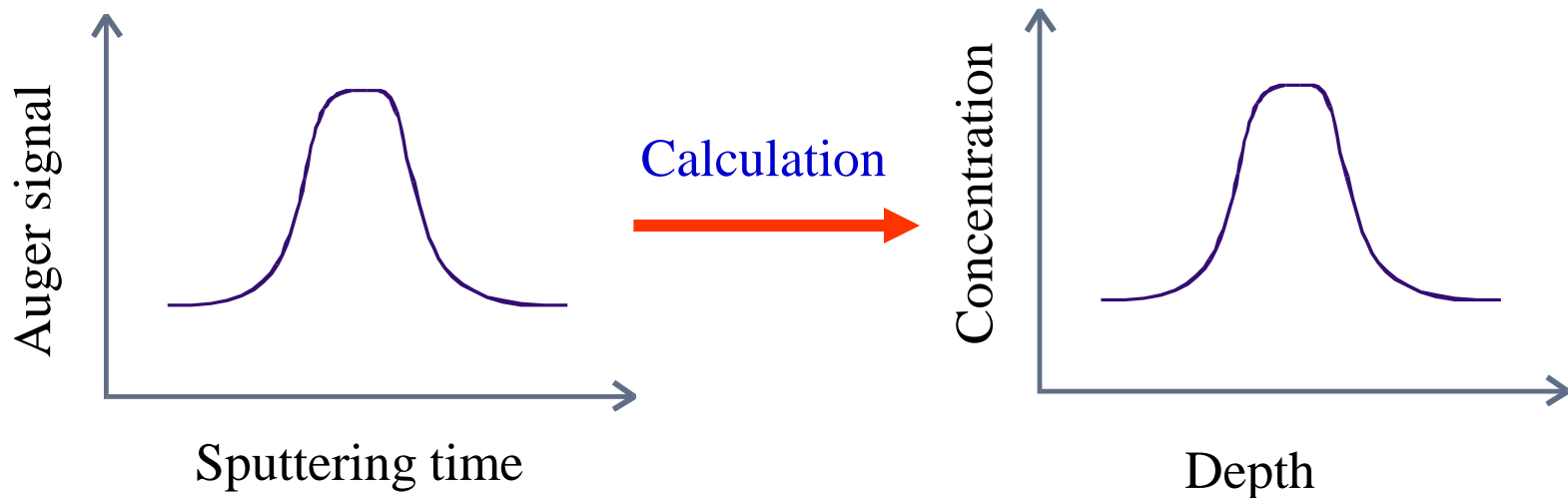
Auger Depth Profiling



Ion sputtering removes the materials systematically

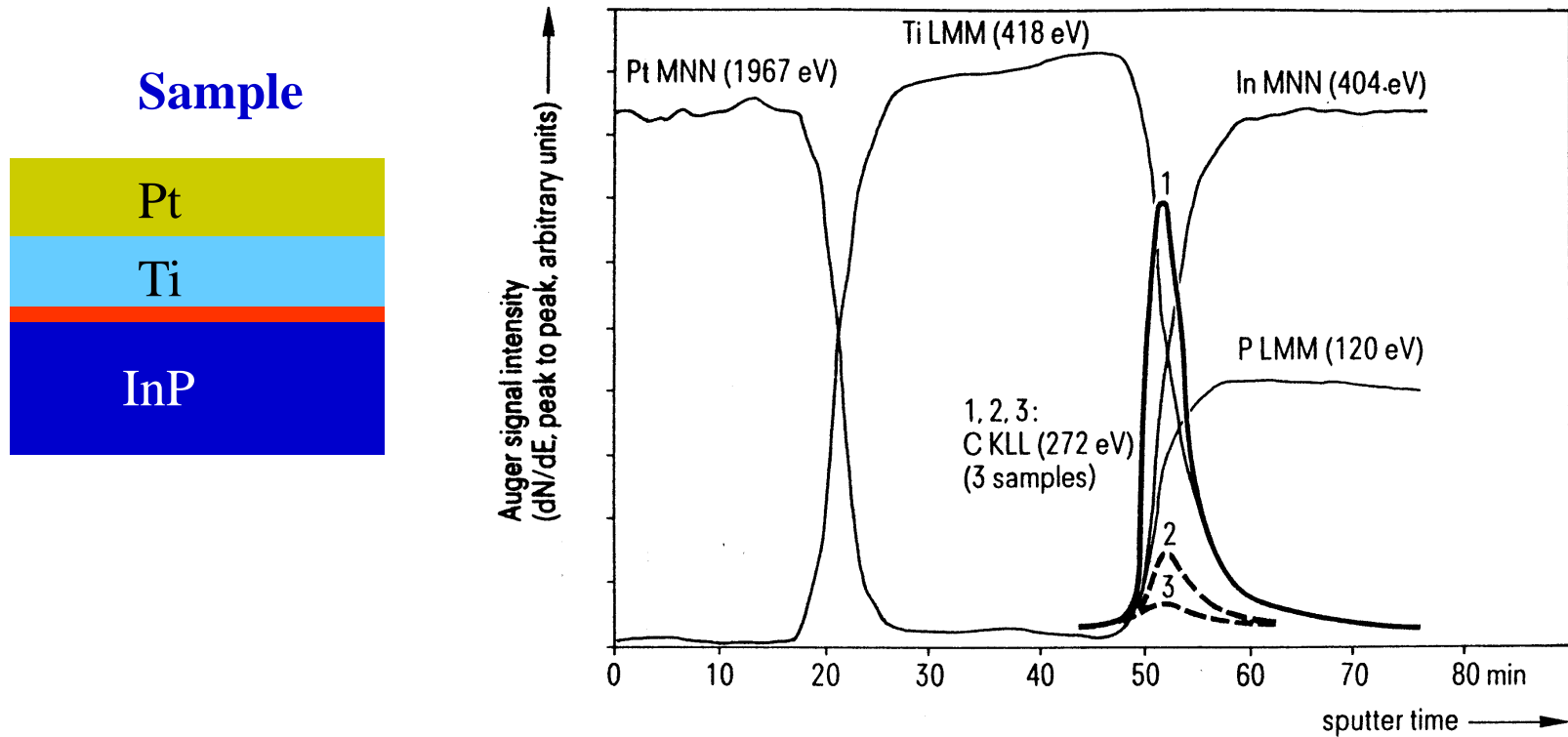
Auger analysis is performed on the newly exposed crater bottom and independent of the sputtering process

Calibration of Depth Scale



1. Sputtering rate determined from the time required to sputter through a layer of the same material of known thickness.
2. After the sputtering analysis, the crater depth is measured using depth profilometry. A constant sputtering rate is assumed.

Semiconductor / Metallization Interface



For each element, an Auger peak is selected at each depth.

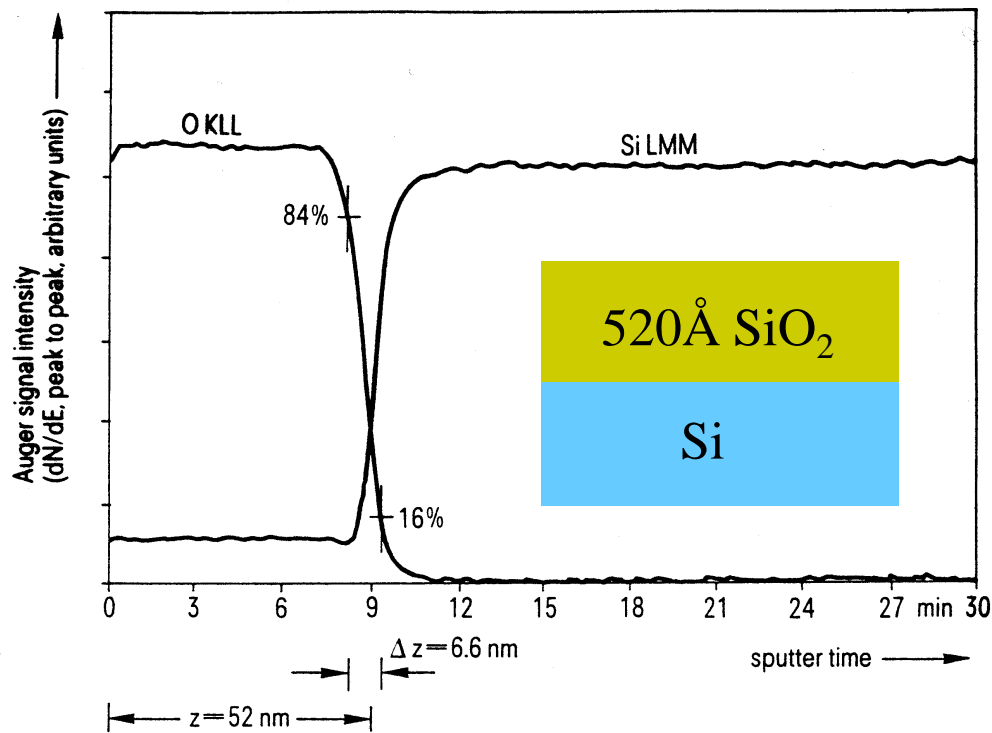
Pt: MNN at 1697 eV

Ti: LMM at 418 eV

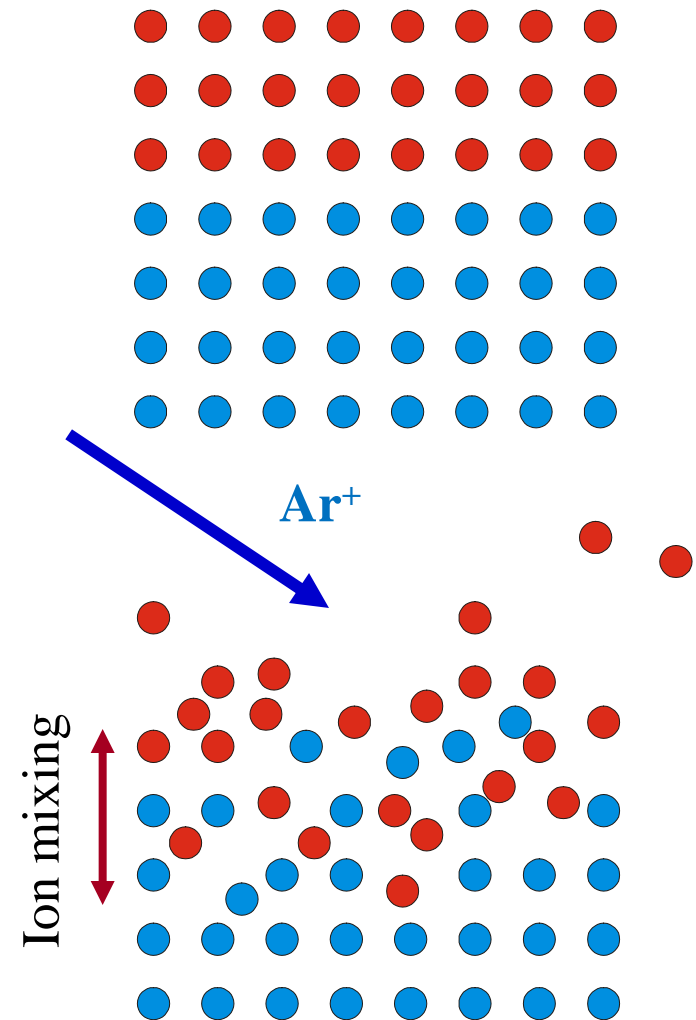
C: KLL at 272 eV

In: MNN at 404 eV

P: LMM at 120 eV



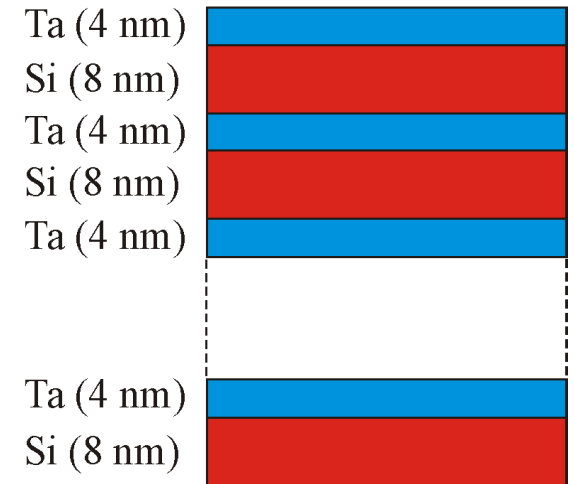
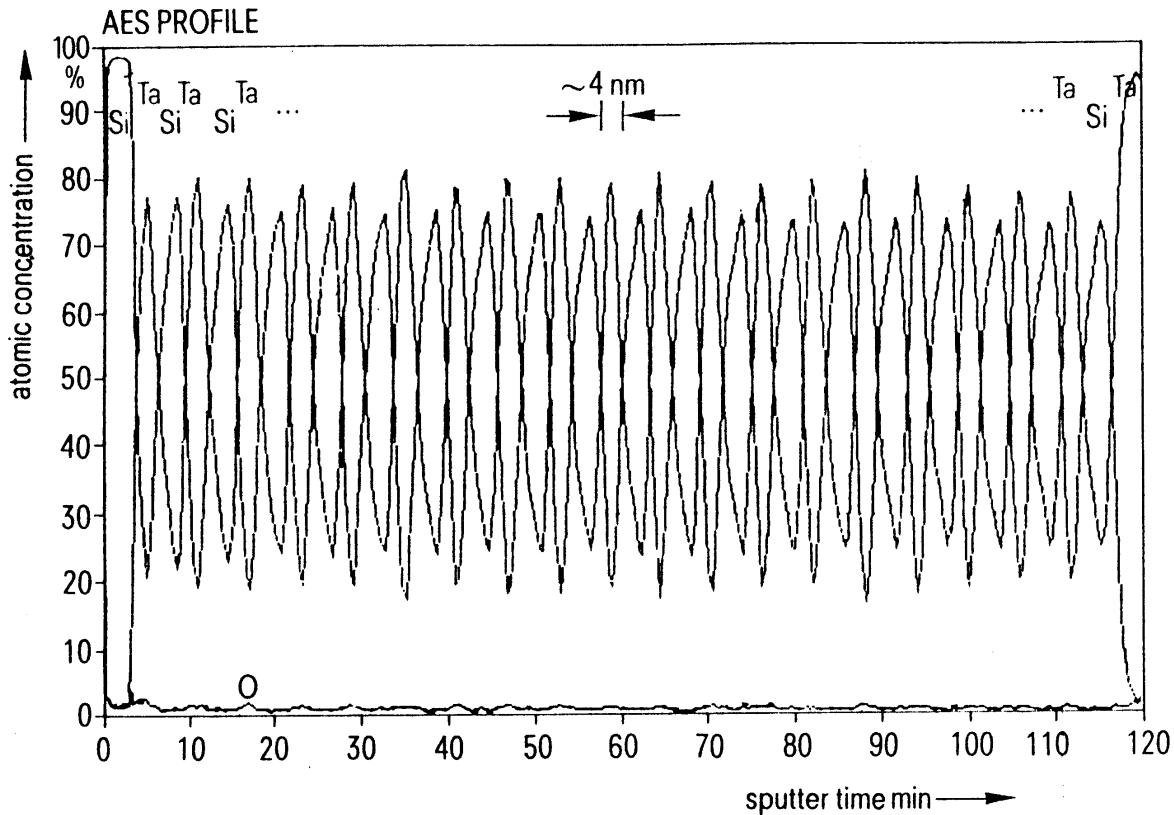
Ion Mixing



Depth Resolution Depends on

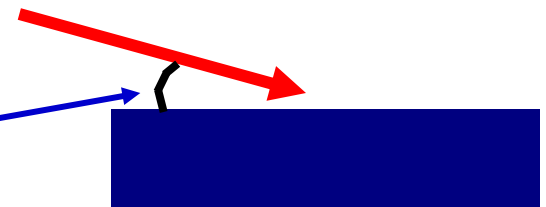
- Ion beam energy and incident angle
- Surface roughness of sample
- Type of materials

Depth Profile of a Ta/Si Multilayer Sample



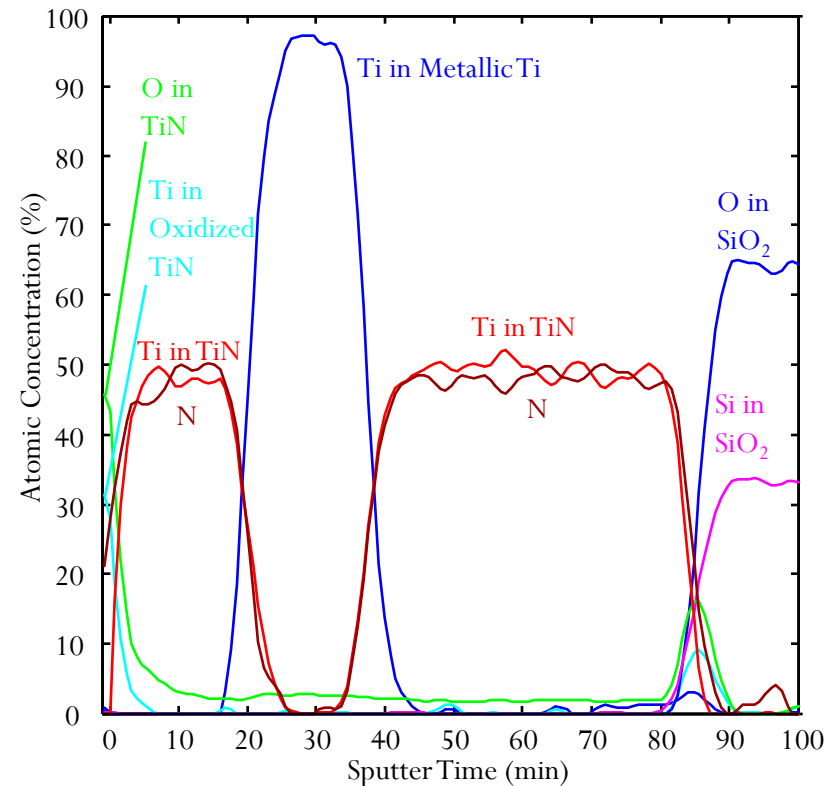
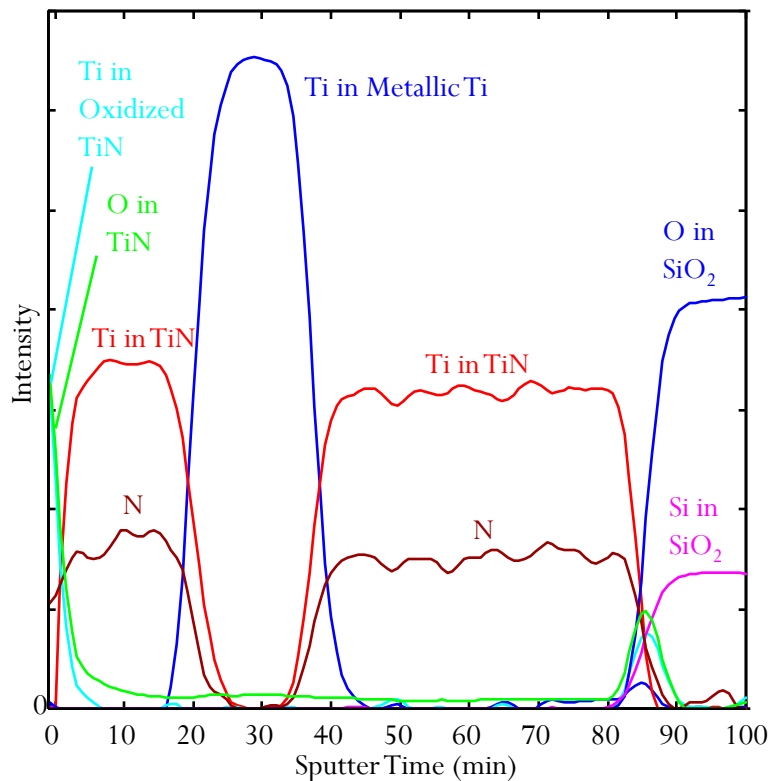
Improve depth resolution:

- Sample rotation during Ar^+ sputtering
- Low Ar^+ energy (less than 1 keV)
- Low incident angle



Depth Profiling of TiN/Ti/TiN on SiO₂

Two TiN(250Å)/Ti(375Å)/TiN(600Å) on SiO₂ samples are analyzed by Auger depth profiling to determine the film composition and thickness.



References

1. C. Richard Brundle, Charles A. Evans, Jr. and Shaun Wilson
“Encyclopedia of materials characterization”.
2. Yang Leng, **“Materials characterization Introduction to Microscopic and Spectroscopic Methods”**
3. D. Briggs and M.P. Seah, **‘Practical Surface Analysis. Volume 1 – Auger and X-ray Photoelectron Spectroscopy’**, Second Edition, John Wiley and Sons, Chichester, 1990

References

1. T.A. Carlson, '**Photoelectron and Auger Spectroscopy**', Plenum Press, New York, 1975
2. J.F. Watts, '**An Introduction to Surface Analysis by Electron Spectroscopy**', Oxford University Press, Oxford, 1990
3. Wikipedia, <https://en.wikipedia.org>
4. NPTEL web course, <http://nptel.ac.in/course.php>

Thank you