Auger Electron Spectroscopy (AES)

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Auger Electron Spectroscopy

Introduction

Principles

Instrumentation

Qualitative analysis

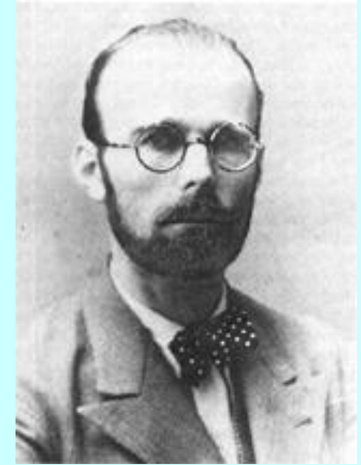
Quantitative analysis

Depth profiling

Mapping

Examples

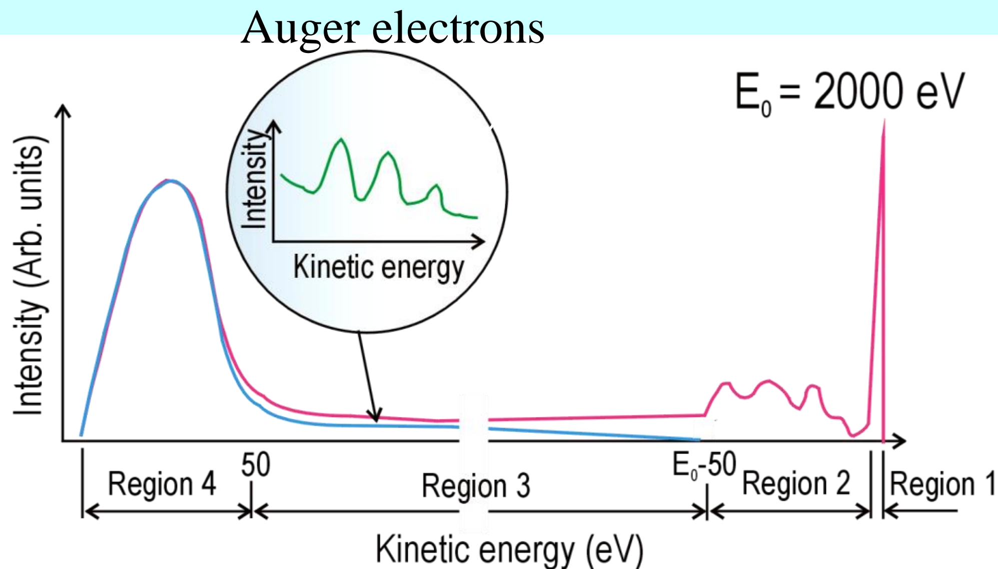
The **Auger Effect** is named after its discoverer, Pierre Auger, who observed a tertiary effect while studying photoemission processes in the 1920s. Auger electrons are emitted at discrete energies that allow the atom of origin to be identified. The idea of using electron-stimulated Auger signals for 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.



Pierre Auger

Distribution of Energies of Emitted Electrons

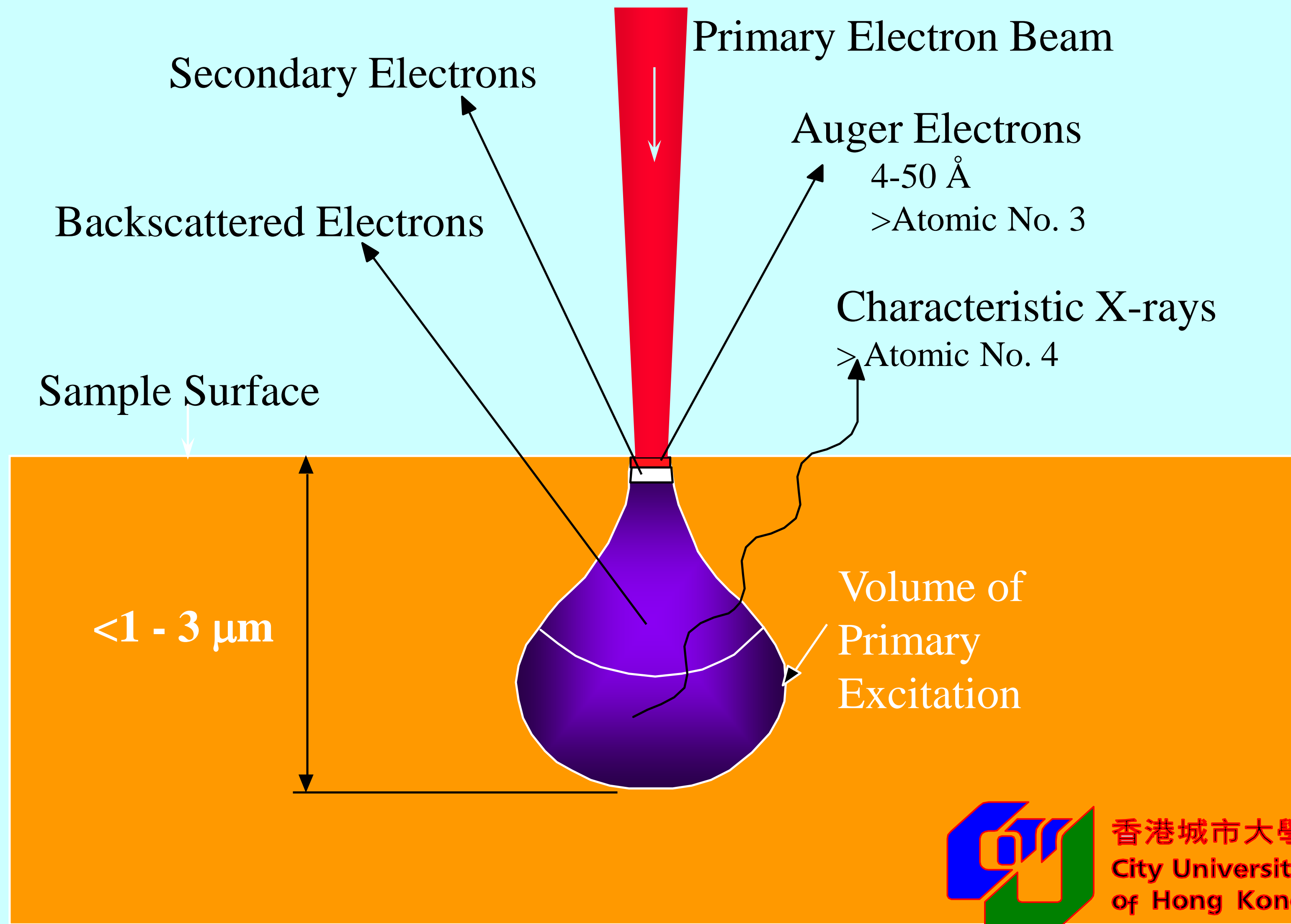
Auger electrons



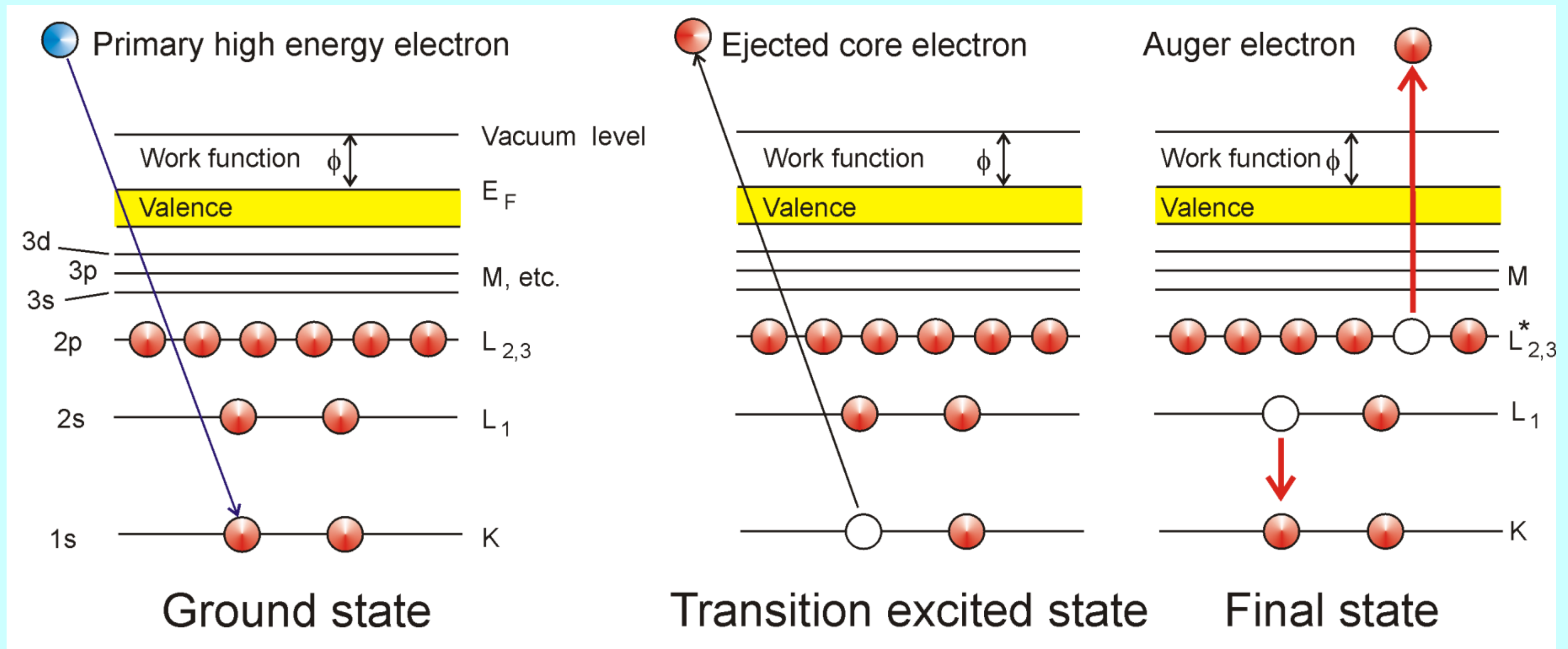
Electron intensity plotted against their kinetic energy

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).

Electron Beam - Sample Interaction



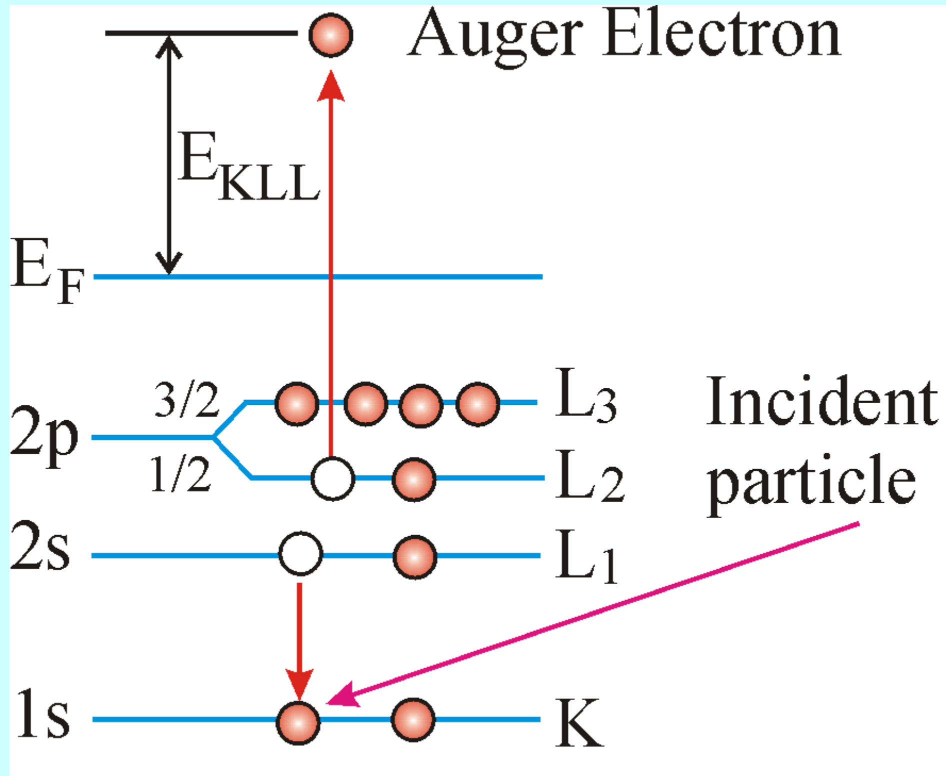
Auger Process



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.

Auger is a radiationless process. 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



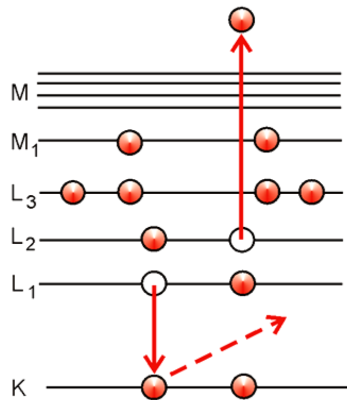
Transition label

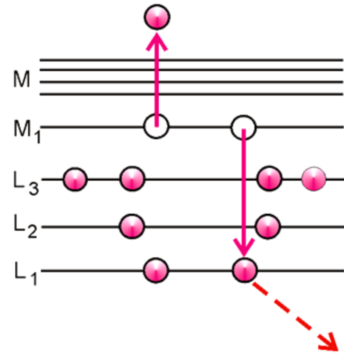
KL_1L_2

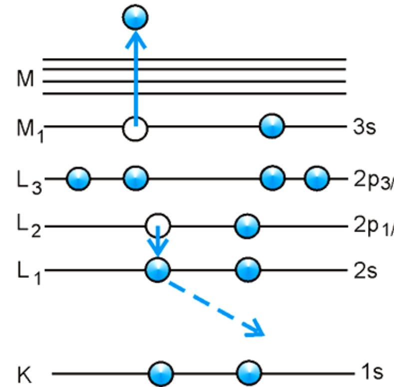
The three symbols in the transition label correspond to the three energy levels involved in the transition.

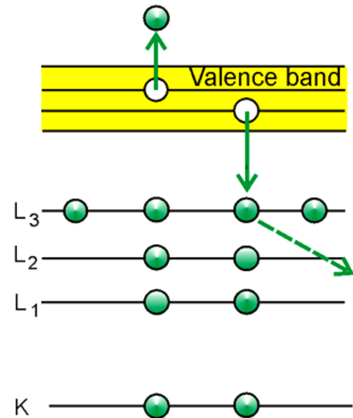
N_{10}	$4f_{7/2}$
N_9	$4f_{5/2}$
N_8	$4f_{3/2}$
N_7	$4f_{1/2}$
N_6	$4d_{5/2}$
N_5	$4d_{3/2}$
N_4	$4d_{1/2}$
N_3	$4p_{3/2}$
N_2	$4p_{1/2}$
N_1	4s
M_6	$3d_{5/2}$
M_5	$3d_{3/2}$
M_4	$3d_{1/2}$
M_3	$3p_{3/2}$
M_2	$3p_{1/2}$
M_1	3s
L_3	$2p_{3/2}$
L_2	$2p_{1/2}$
L_1	2s
K	1s

Examples of Auger Processes









Auger KL_1L_2 (a)

Auger $L_1M_1M_1$ (b)

Coster-Kroning $L_1L_2M_1$ (c)

Auger (Solid) L_3VV (d)

KL_1L_1

KL_1L_{23} { KL_1L_2, KL_1L_3 }

e. g. Cu LMM

$L_3M_{23}M_{23}$ (768 eV)

$L_2M_{23}M_{23}$ (775 eV)

$L_3M_{23}M_{45}$ (839 eV)

$L_3M_{23}M_{45}$ (847 eV)

$L_3M_{45}M_{45}$ (919 eV)

$L_2M_{45}M_{45}$ (939 eV)

Also MNN Auger

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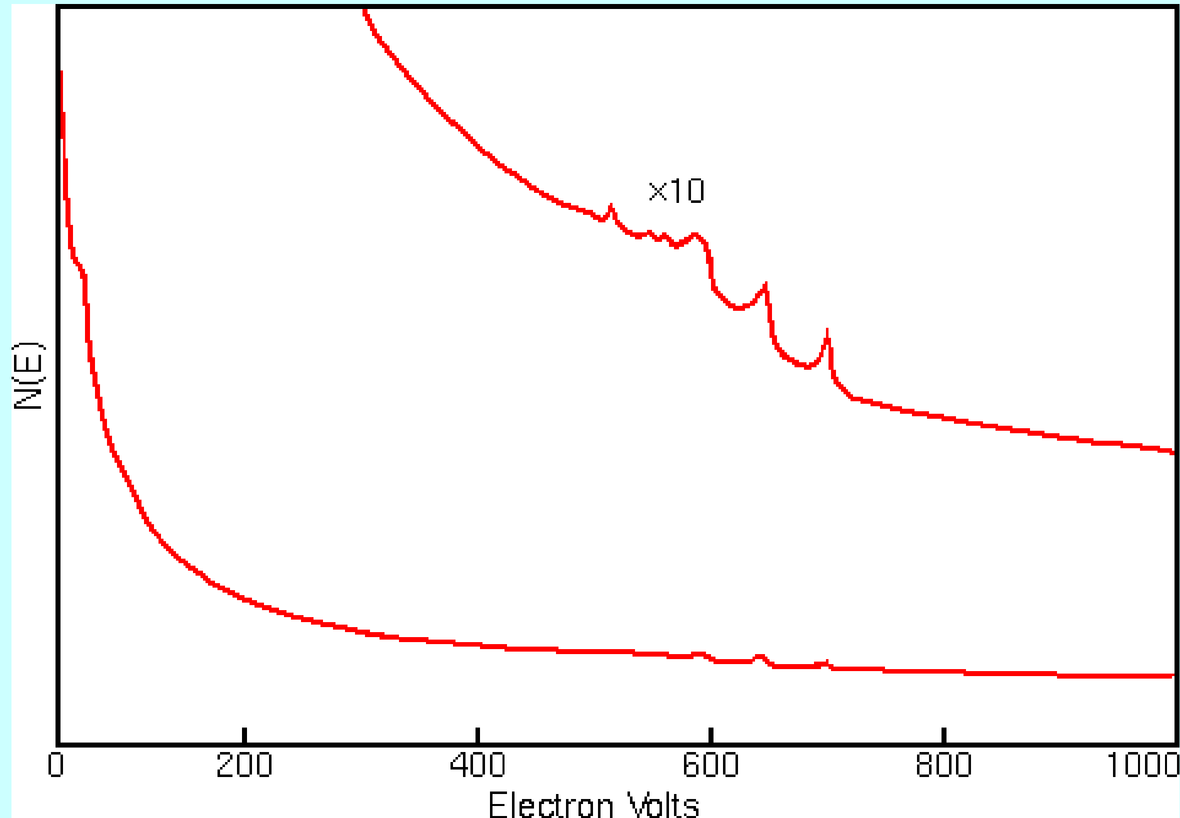
Auger Electron Spectrum

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



Electron signal *vs* electron energy

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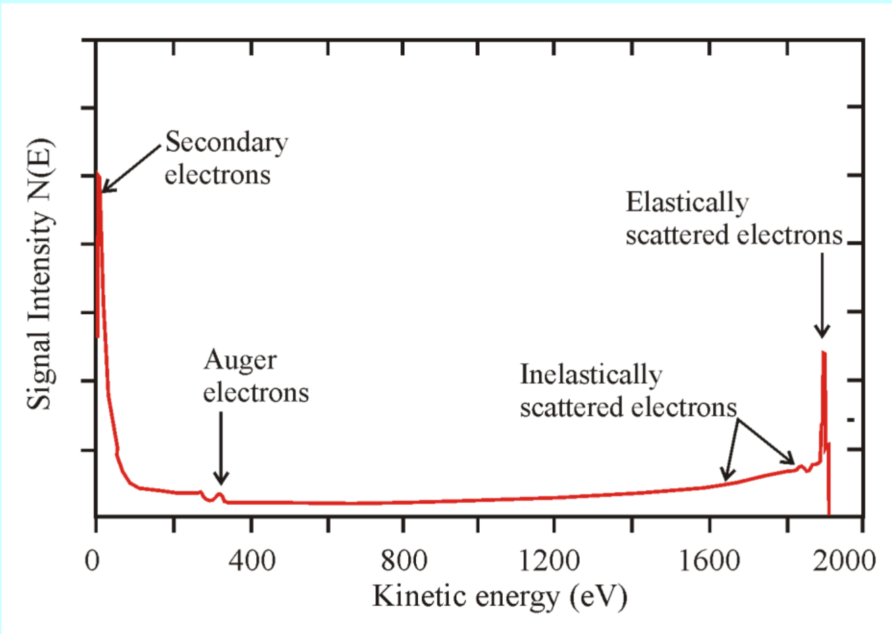
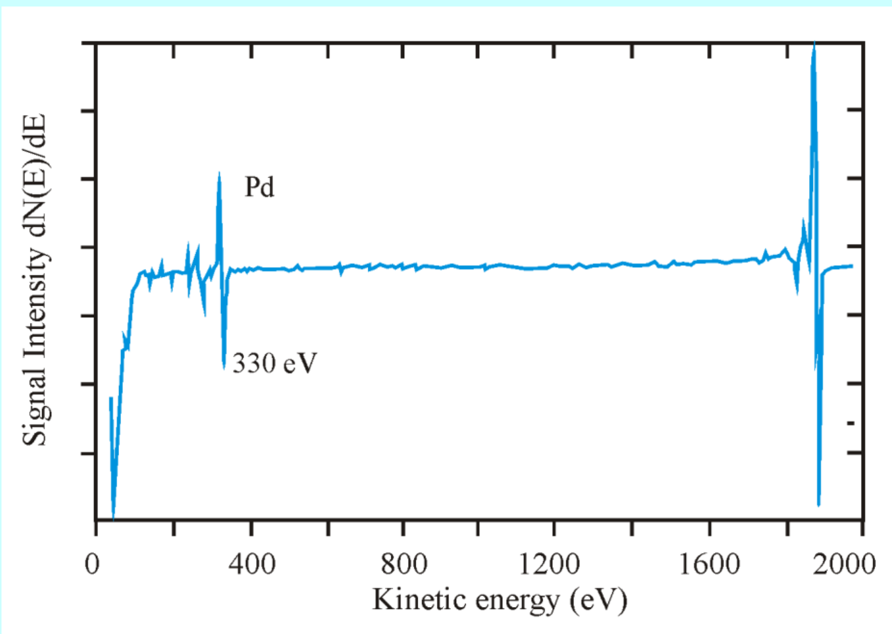
Electron Energy Spectrum of Pd metal



Direct spectrum



Differential spectrum

- enhances AES features

/ removes background

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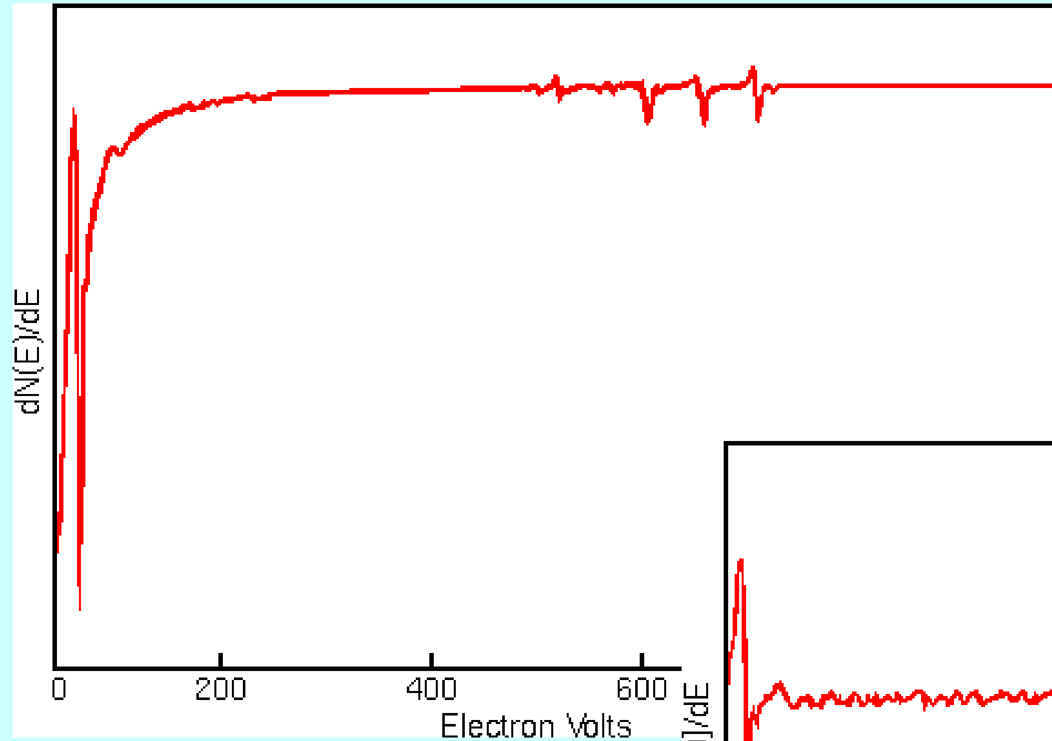
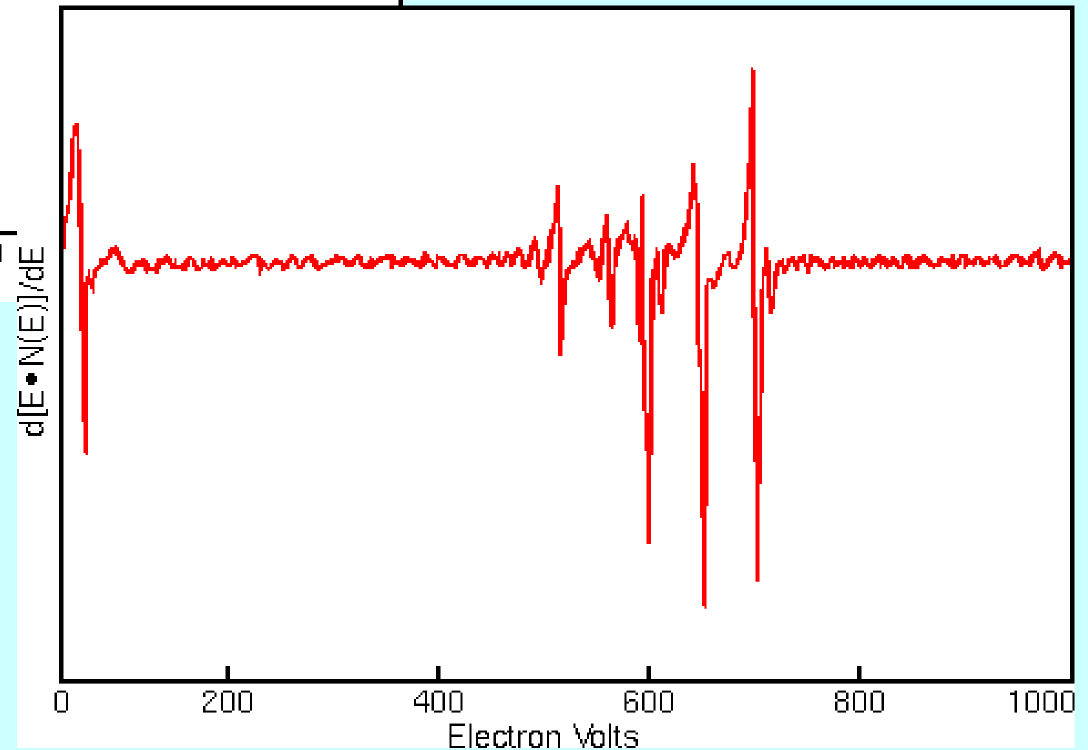


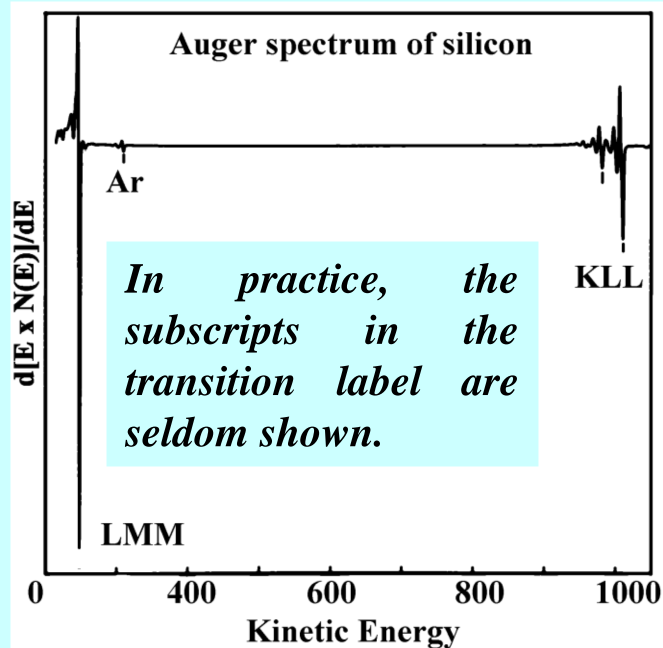
Plotting the spectrum as the differential of the electron signal, dN(E)/dE, clarifies some of the spectral details.

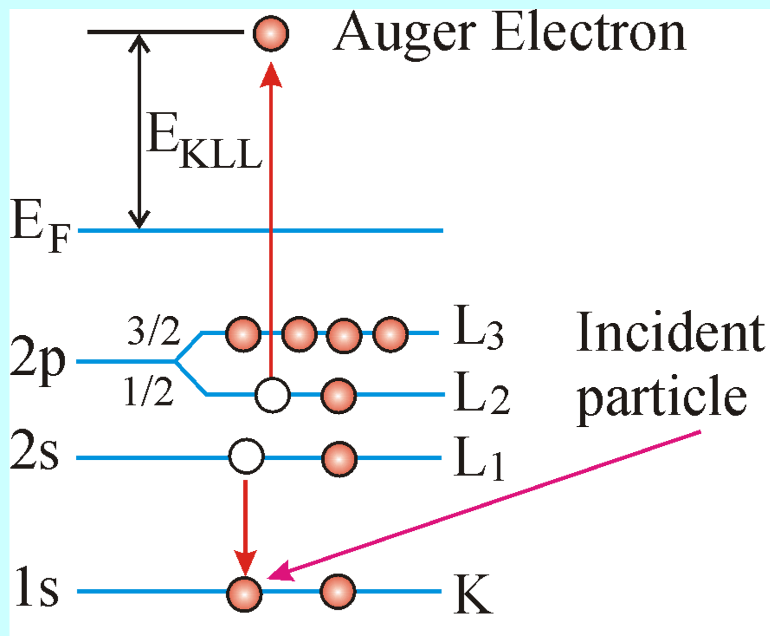


Plotting d[E × N(E)]/dE, of the above function provides for clear display of the features in an Auger electron spectrum. This d[E × N(E)]/dE format is the most common mode for presenting Auger data.

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. The binding energy of a level in the presence of a core hole is greater than the binding energy of the same level in a neutral atom.

For approximation, the following equation is used to calculate the kinetic energy of Auger electrons (z: atomic number of the atom).

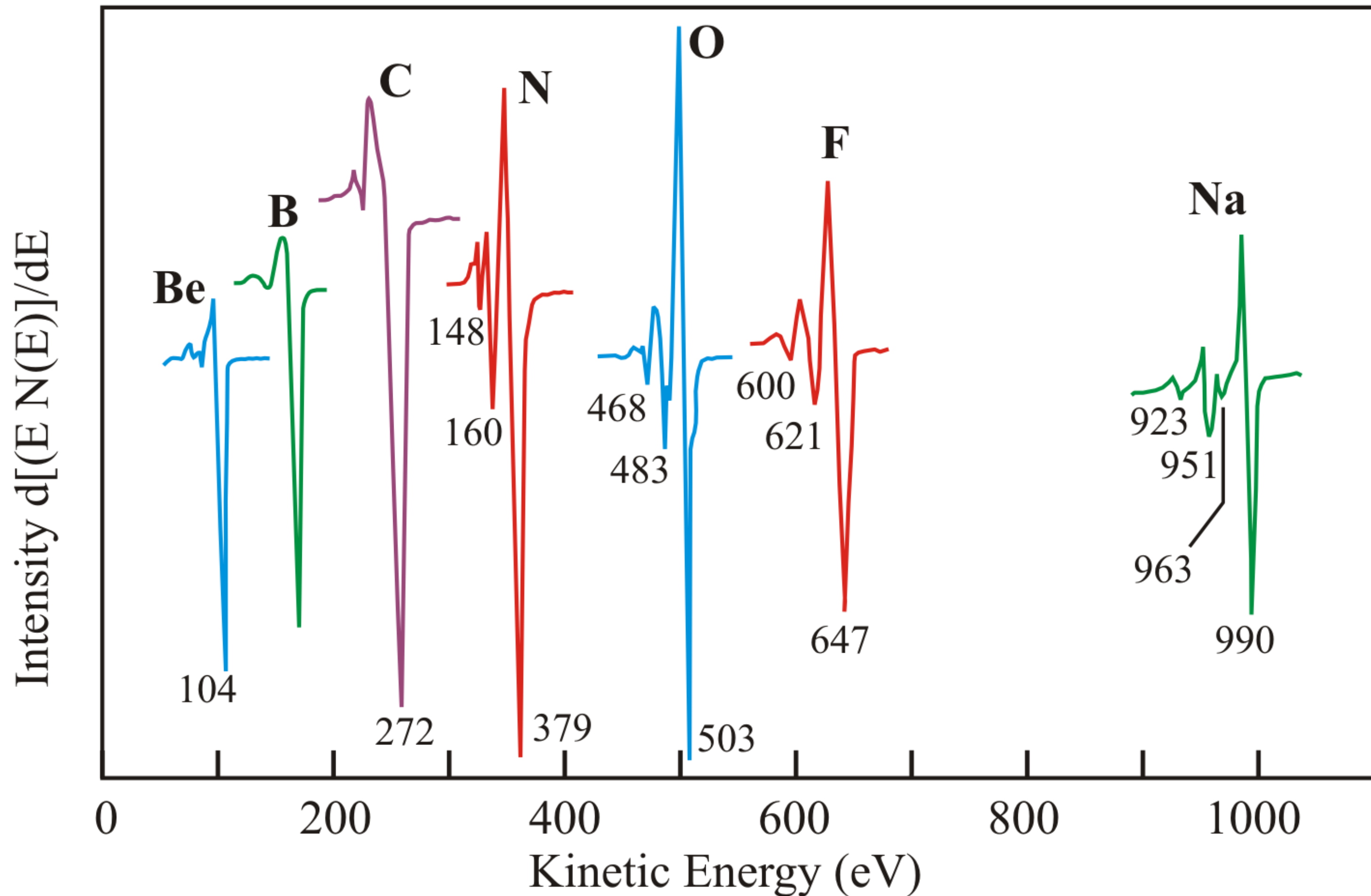
$$E_{ABC} = E_A(z) - \frac{1}{2}\left[E_B(z) + E_B(z+1)\right] - \frac{1}{2}\left[E_C(z) + E_C(z+1)\right]$$

For exact calculation, other effects should be taken into account, such as the Coulombic repulsion energy between two holes as well as the intra-atom and extra atom relaxation energies.

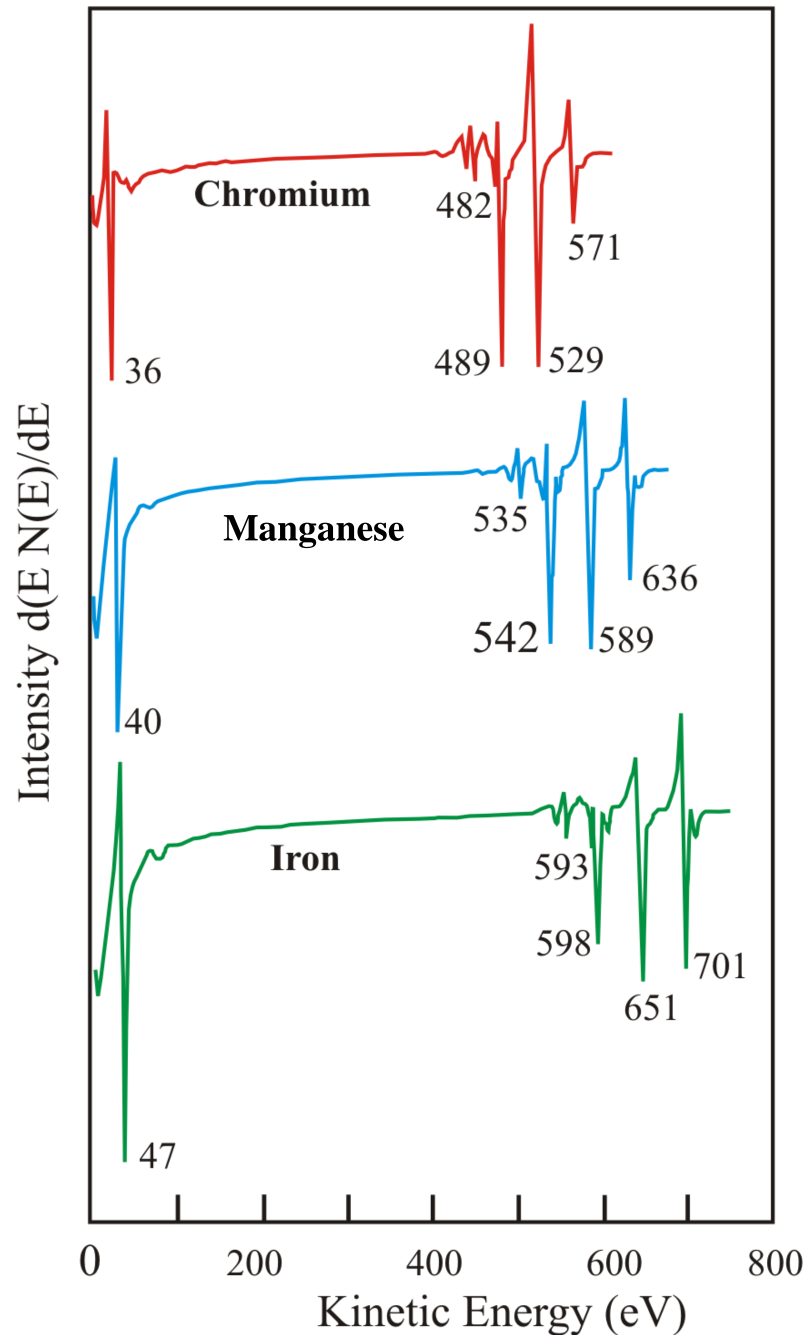
$$E_{ABC} = E_{Final} - E_{Initial}$$

In practice, experimental data are used for peak identification.

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

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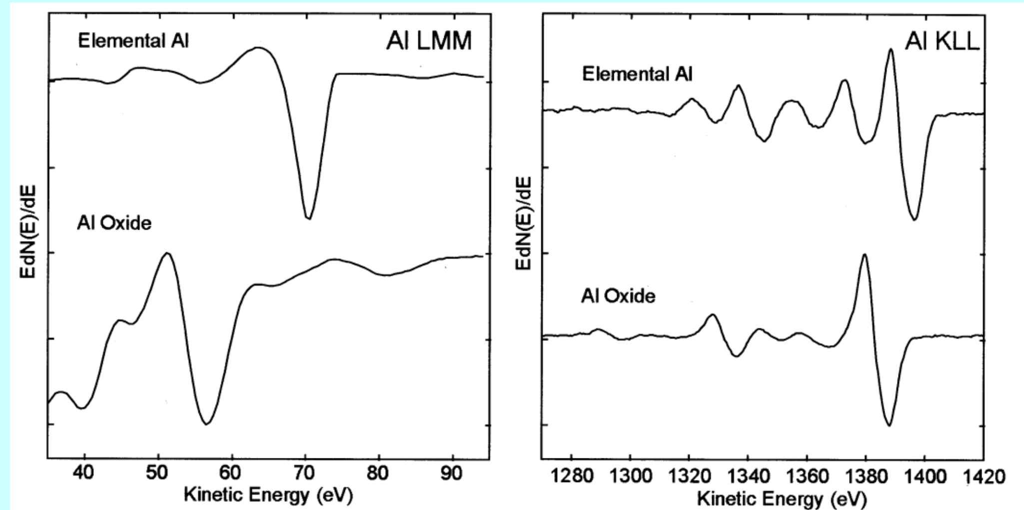
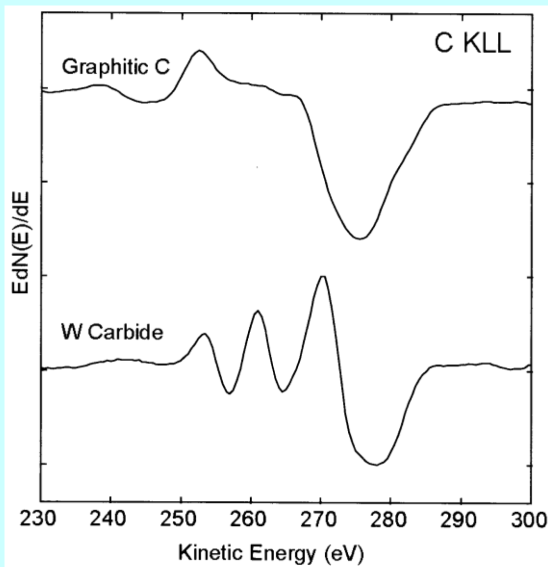
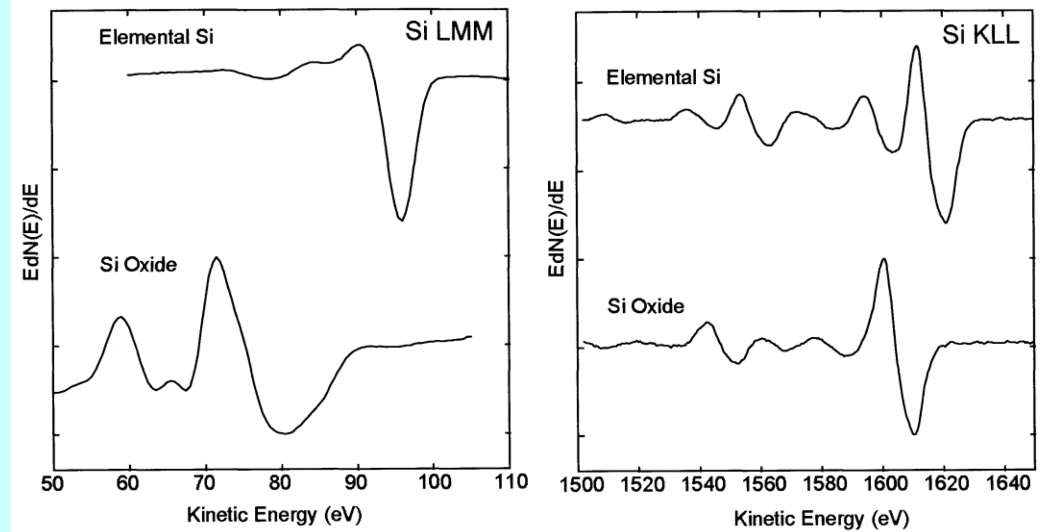
Chemical Information

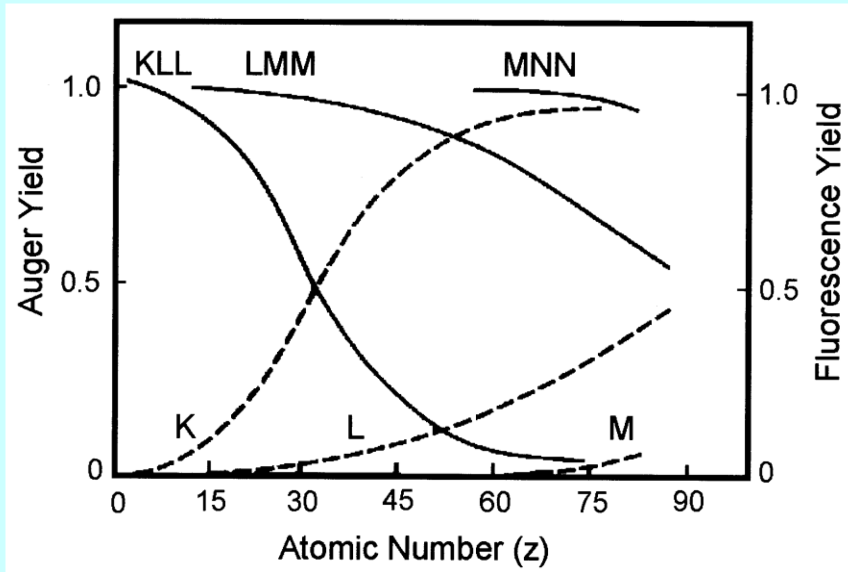
The energy and shape of an Auger peak contains information about the chemical environment. Theoretical predictions are difficult and reference spectra are often used for comparison.

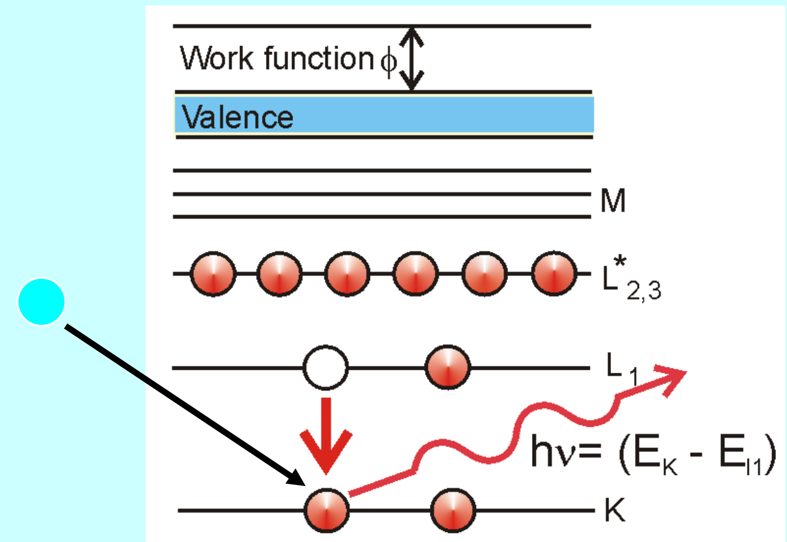






Auger Electron Intensity X-ray Fluorescence





Auger electron emission is the more probable decay mechanism for low energy transitions, i.e., for low atomic number elements with an initial vacancy in the K shell and for high atomic number elements with initial vacancy in the L or M shell. By choosing an appropriate Auger transition, all elements (except H and He) can be detected.

The Auger process competes with x-ray fluorescence in an excited ion.

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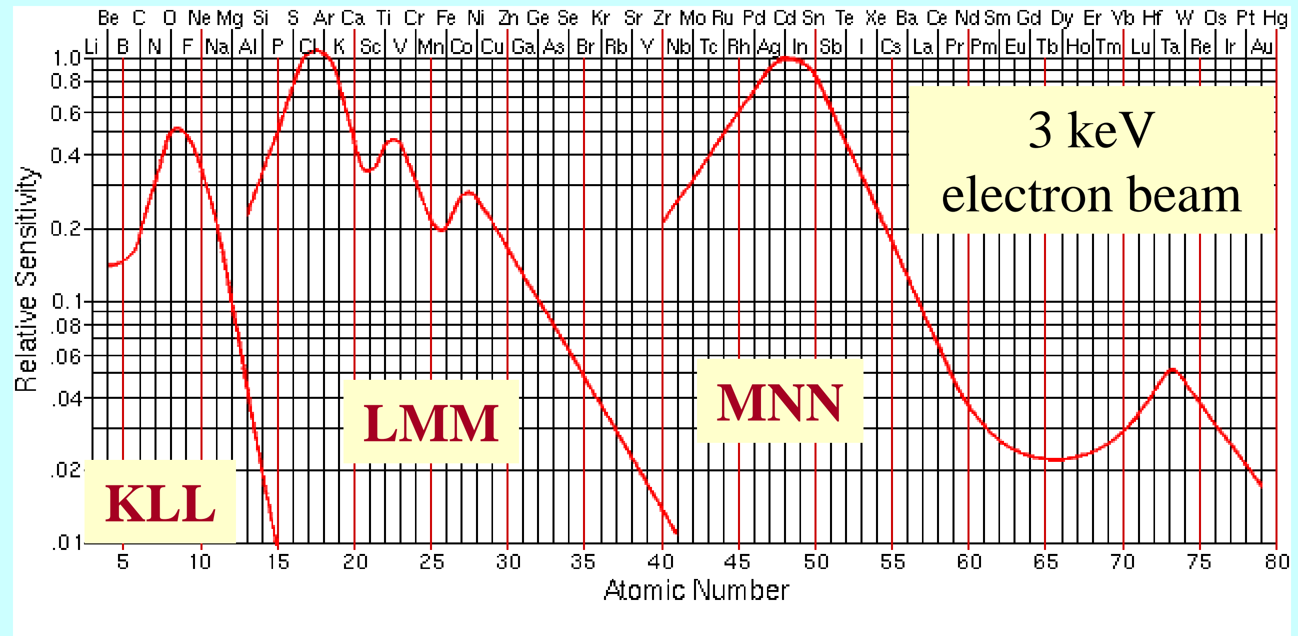
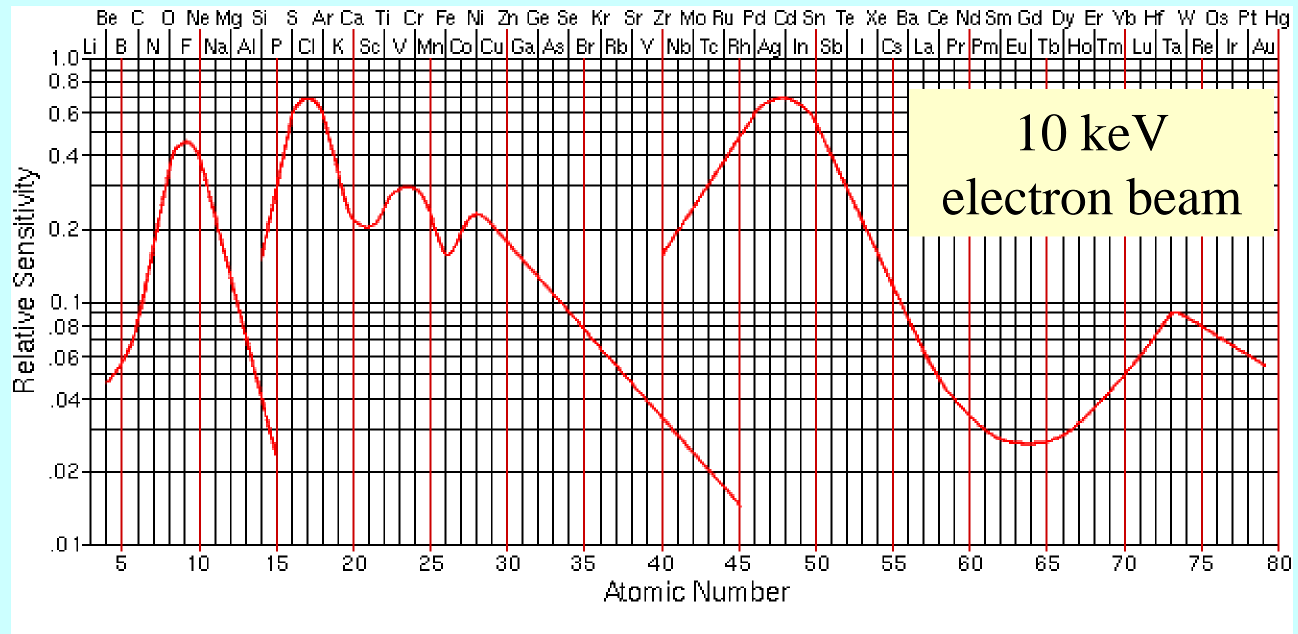
The relative intensities of the Auger electrons also depend on the primary excitation energy.

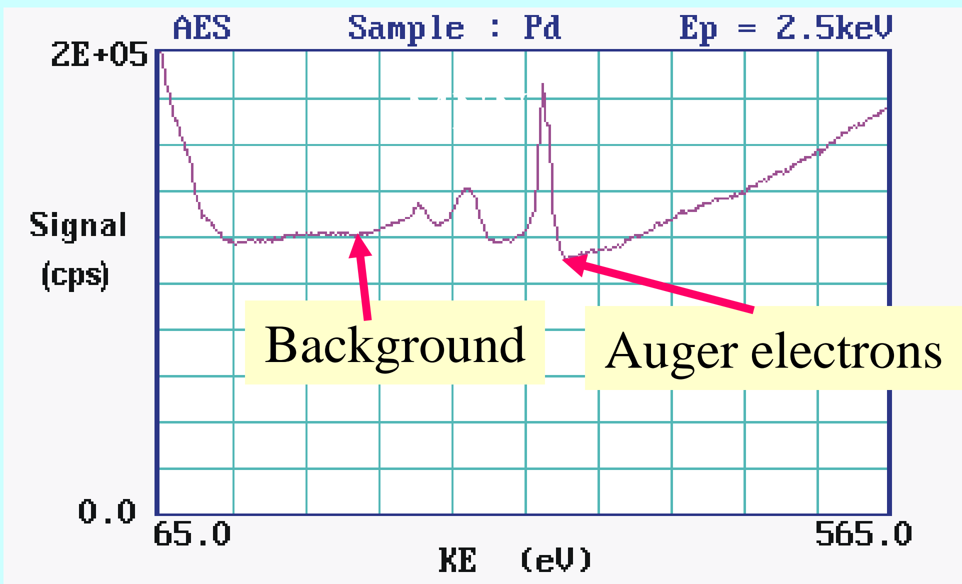


The relative intensities can be used for quantitative analysis



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 loss 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

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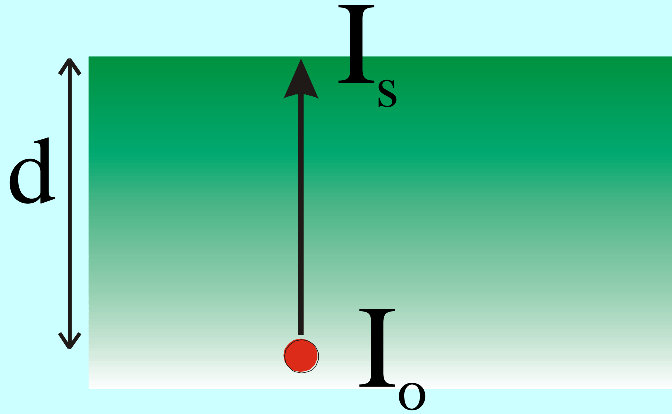
Inelastic Mean Free Path λ



Mean distance that an electron travels without energy loss

$$I_s = I_o e^{-\frac{d}{\lambda}}$$

I_o: number of electrons originating at a depth d

I_s: number of electrons that can escape the surface without energy loss

$$\frac{\int_0^{3\lambda} e^{-\frac{x}{\lambda}} dx}{\int_0^{\infty\lambda} e^{-\frac{x}{\lambda}} dx} = \frac{1-e^{-3}}{1} = 0.95$$

95% of the measured Auger electrons originate from the depth region of 3λ

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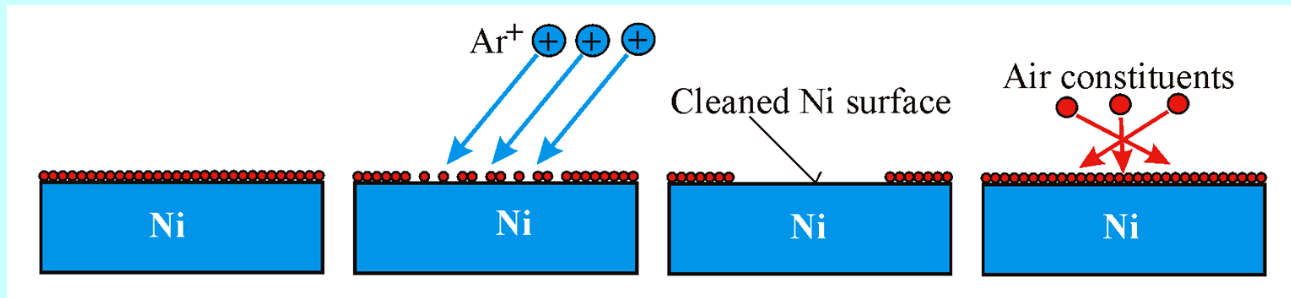
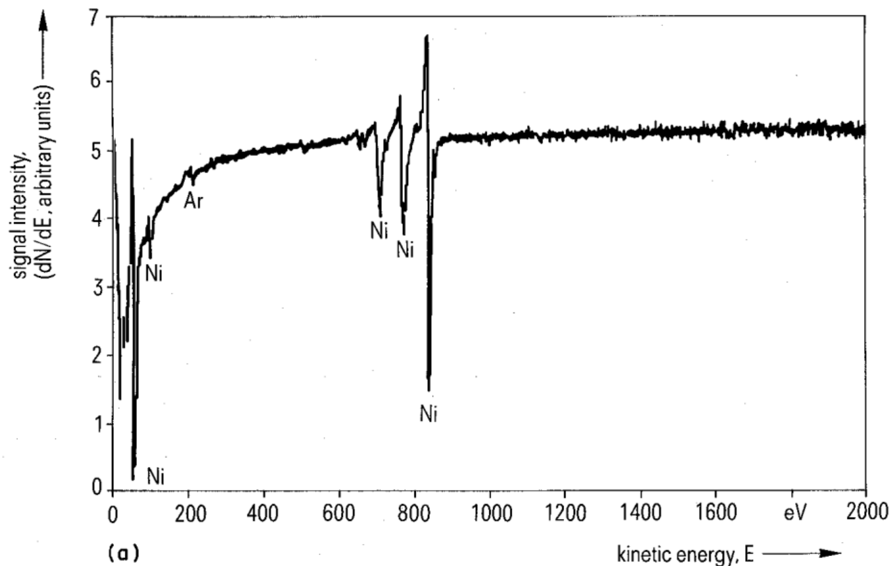
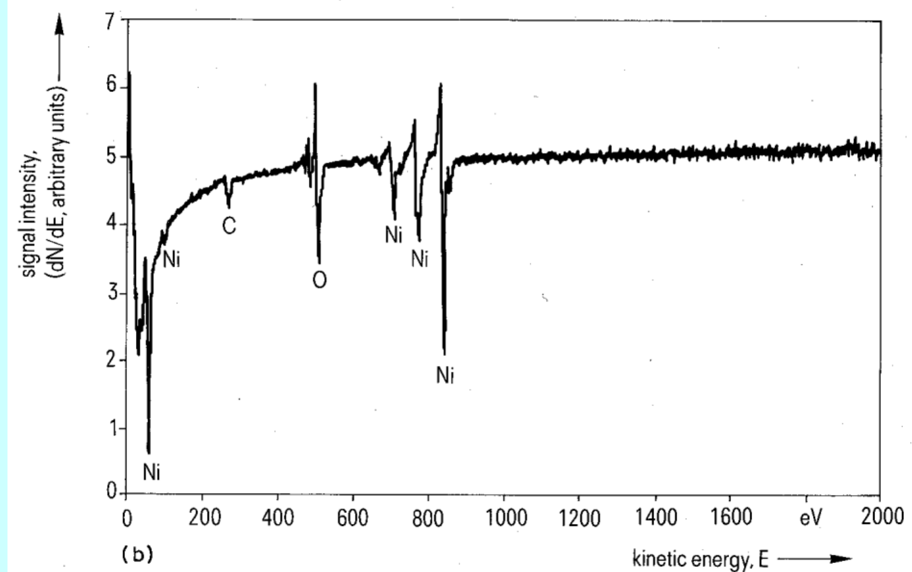
Surface Sensitivity of AES







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

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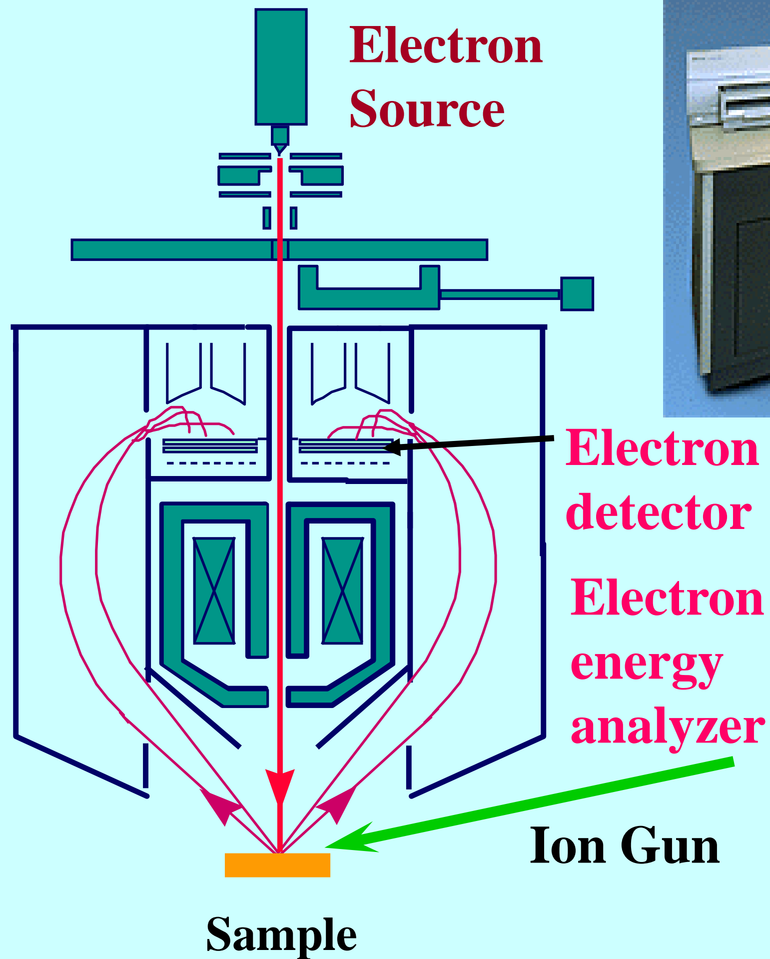
Instrumentation



Vacuum system

Sample stage

Electronic controls

Computer

Software

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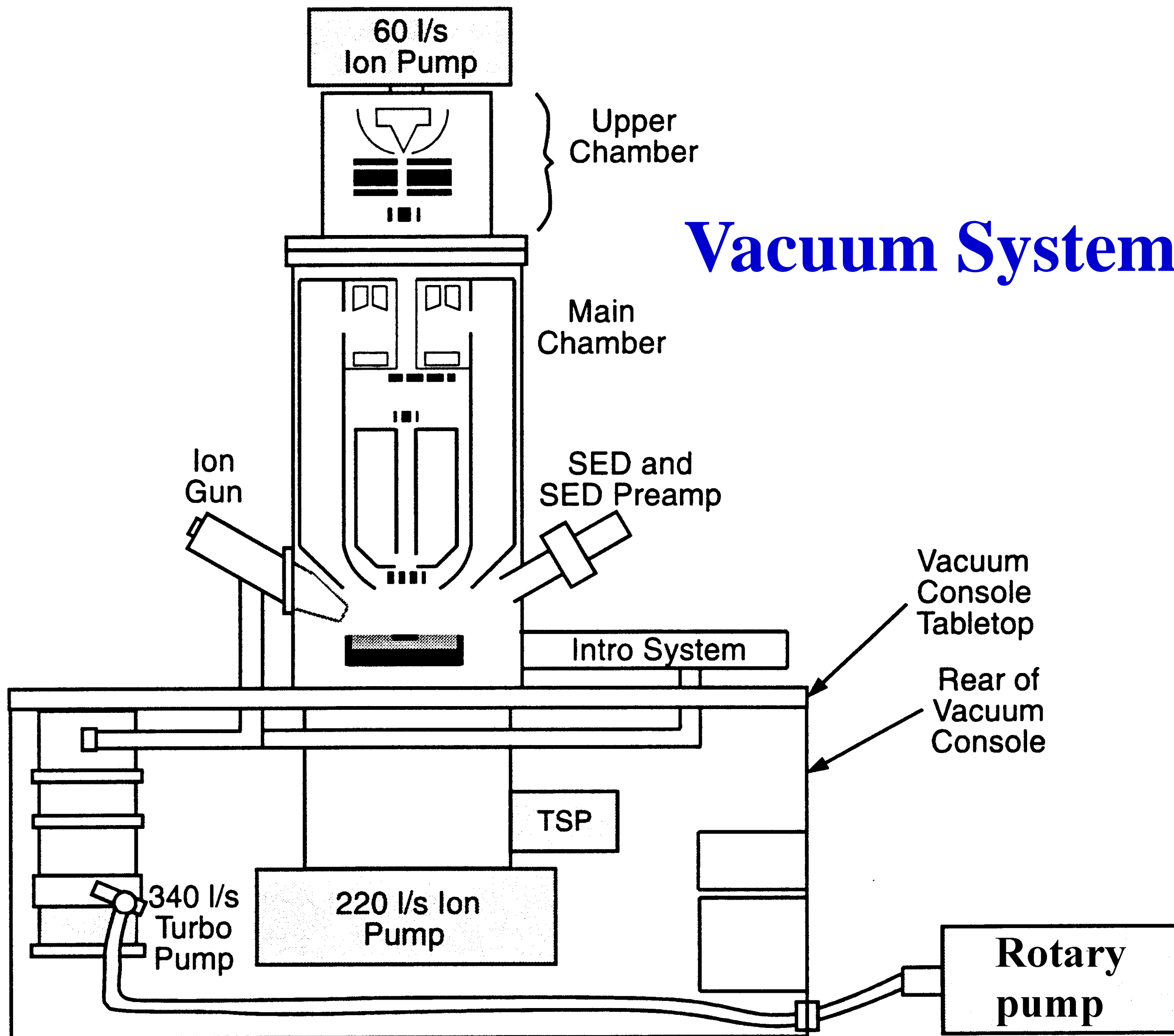
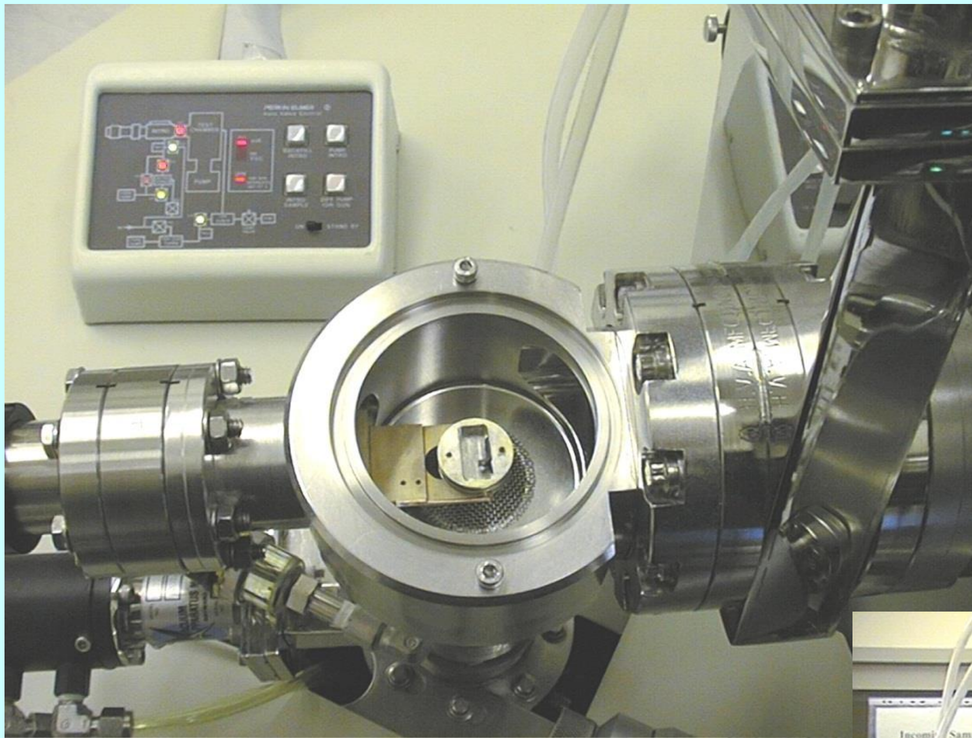
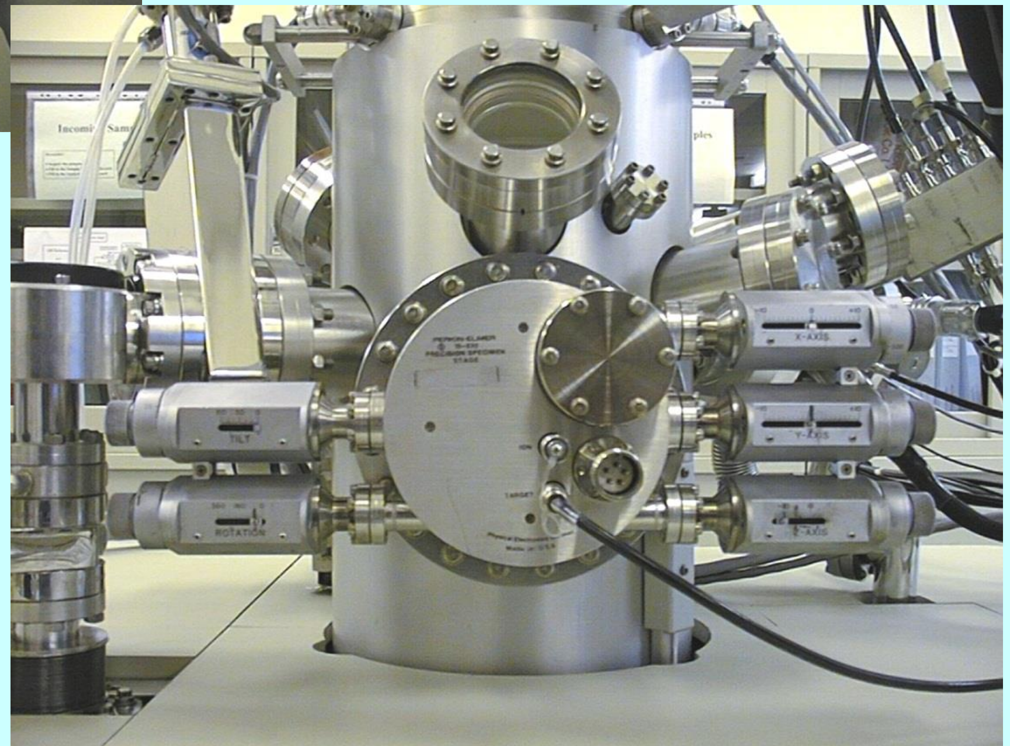
Vacuum System



Sample Handling



Sample introduction



Sample stage with x, y, z, rotation, and tilt

Primary Electron Sources

Tungsten cathode source consists of a wire filament bent in the shape of a hairpin. The filament operates at ~2700 K by resistive heating. The tungsten cathodes are widely used because they are both reliable and inexpensive. The lateral resolution is limited because the tungsten cathode current densities are only about 1.75 A/cm^2.

Lanthanum hexaboride (LaB_6) cathodes provide higher current densities because LaB_6 has a lower work function and greater emissivity than tungsten. At 2000 K, current densities of ~100 A/cm^2 are available. Higher current densities make smaller electron beams possible for analyzing smaller features.

Field Emission electron sources consist of very sharp tungsten points with electrical fields >10^7 V/cm. At these fields, electrons tunnel directly through the barrier and leave the emitter. Field emission guns provide the brightest beams (10^3 to 10^6 A/cm^2) and electron beams as small as 10 nm enable analysis of small features.

Auger instruments have primary electron beam columns similar to electron microscopes.

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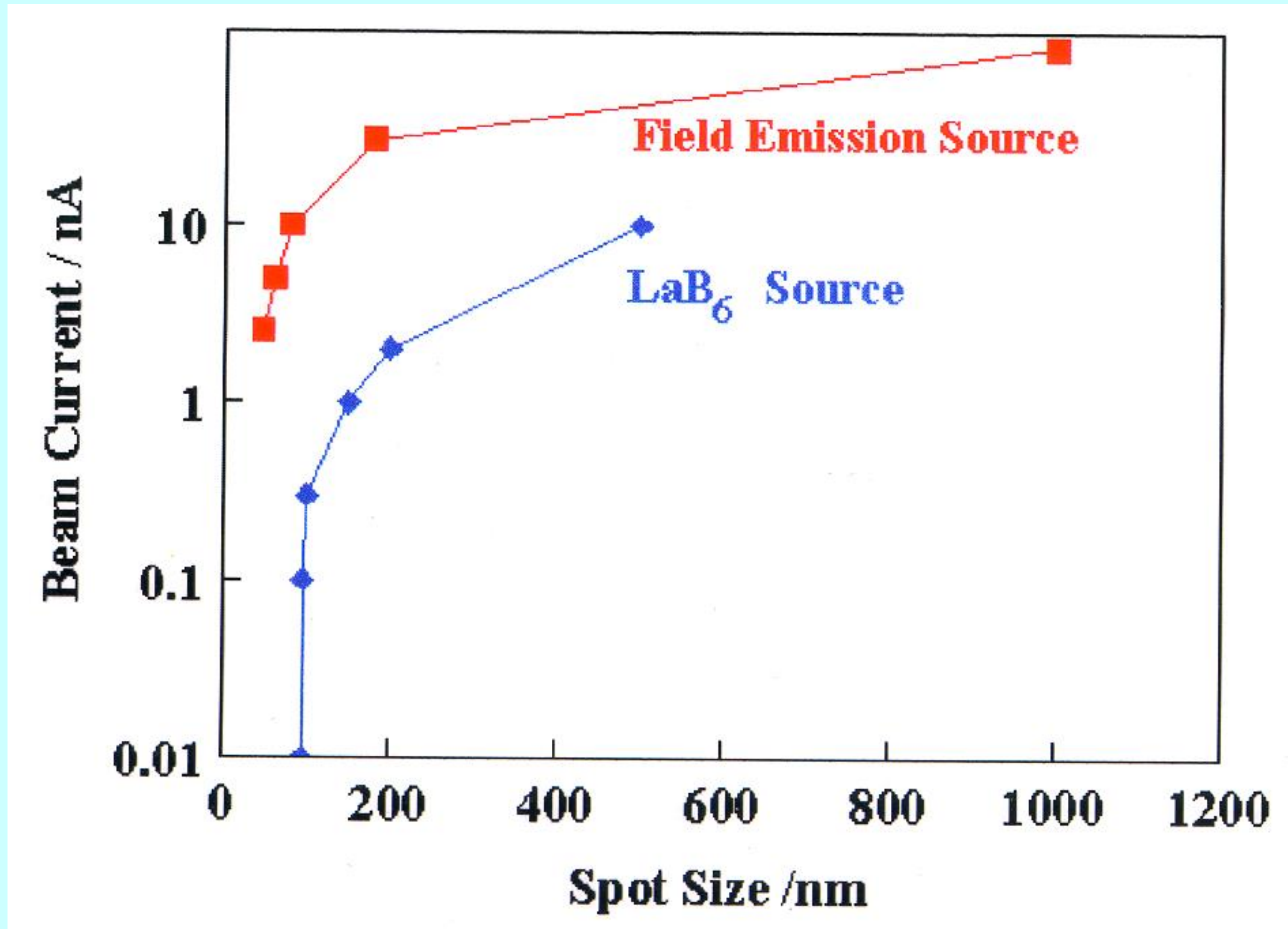
Performance of Field Emission Gun



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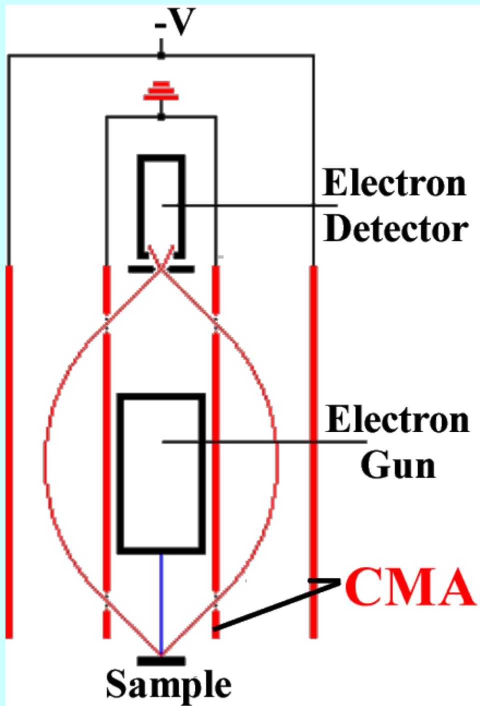
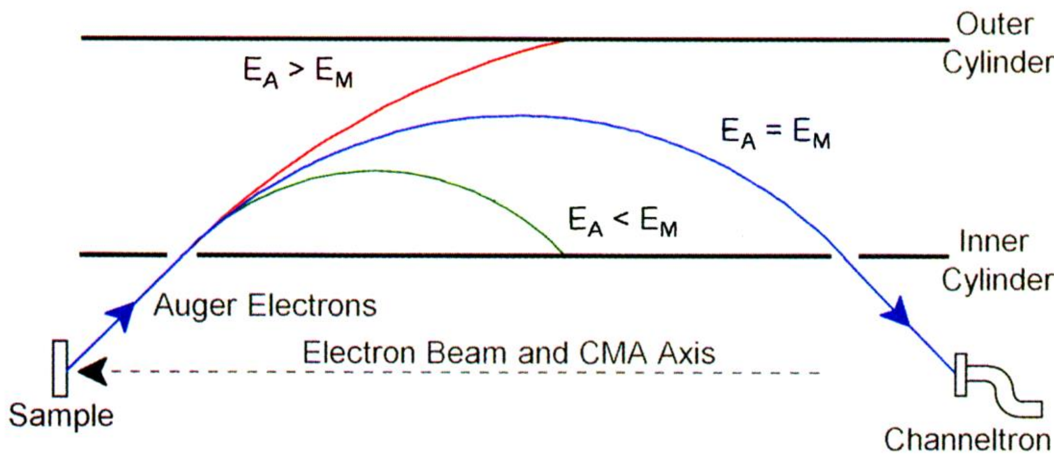
Auger Electron Spectrometer



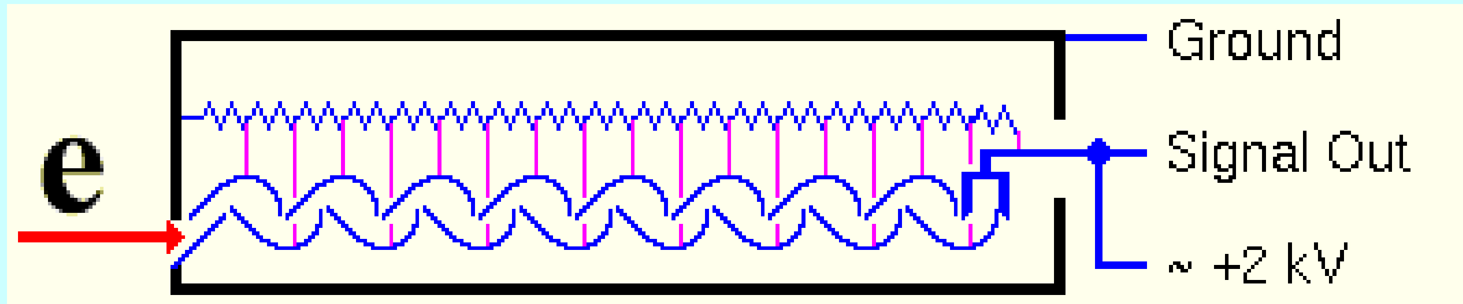
Electron energy analyzers measure the number of ejected electrons as a function of the electron energies.

Cylindrical mirror analyzers are most commonly used because their high transmission efficiency leads to better signal-to-noise ratios. The primary electron beam hits the sample surface at the source point of the analyzer. Auger electrons move outward in all directions and some pass through the aperture in the inner cylinder. A variable negative potential on the outer cylinder bends the Auger electrons back through the second aperture on the inner cylinder and then through an exit aperture on the analyzer axis.



The energy of the transmitted electrons is proportional to the voltage (-V) on the outer cylinder.

Electron Detector – Electron Multiplier



An electron multiplier consists of a series of electrodes called dynodes connected along a resistor string. The output end of the resistor string is attached to a positive high voltage. The other end of the string goes to the electron multiplier case and ground. The dynode potentials differ in equal steps along the chain. When a particle (electron, ion, high energy neutral, or high energy photon) strikes the first dynode, it produces secondary electrons. The secondary electrons are accelerated into the next dynode where more secondary electrons are produced. A cascade of secondary electrons ensues. The dynode acceleration potential controls the electron gain.

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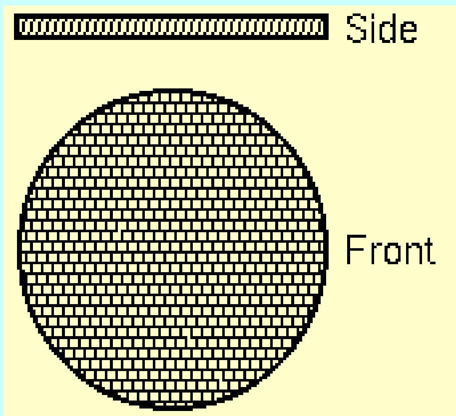
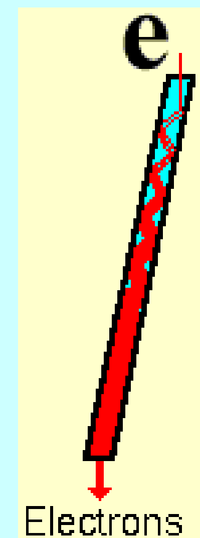
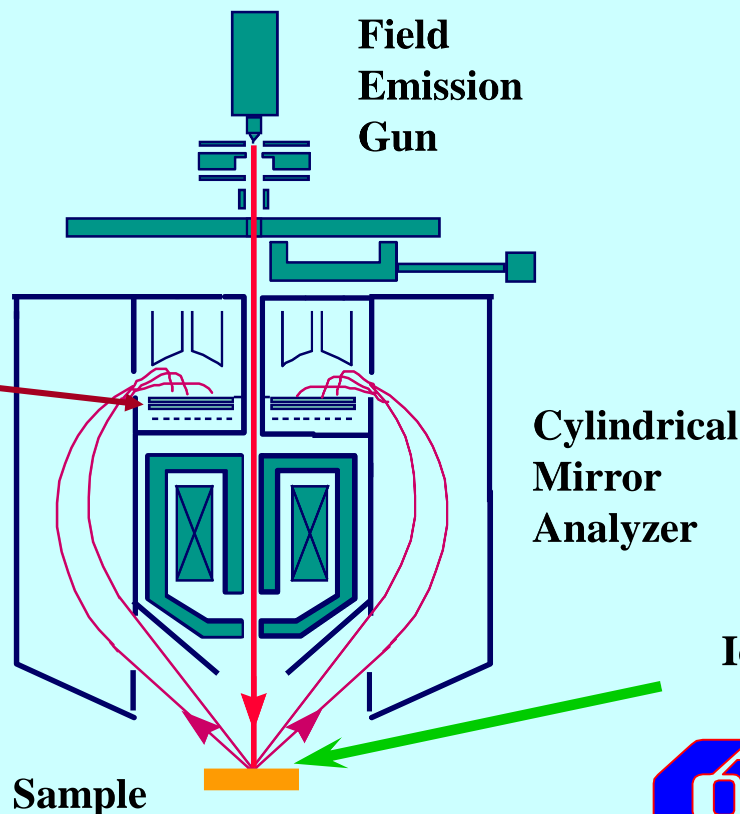
Microchannel Plate Electron Multiplier Arrays



These plates consist of large arrays of small channel electron multipliers





Microchannel Plate Detector

Electrons at different energies can be detected at the same time.

Ion beam for sputtering

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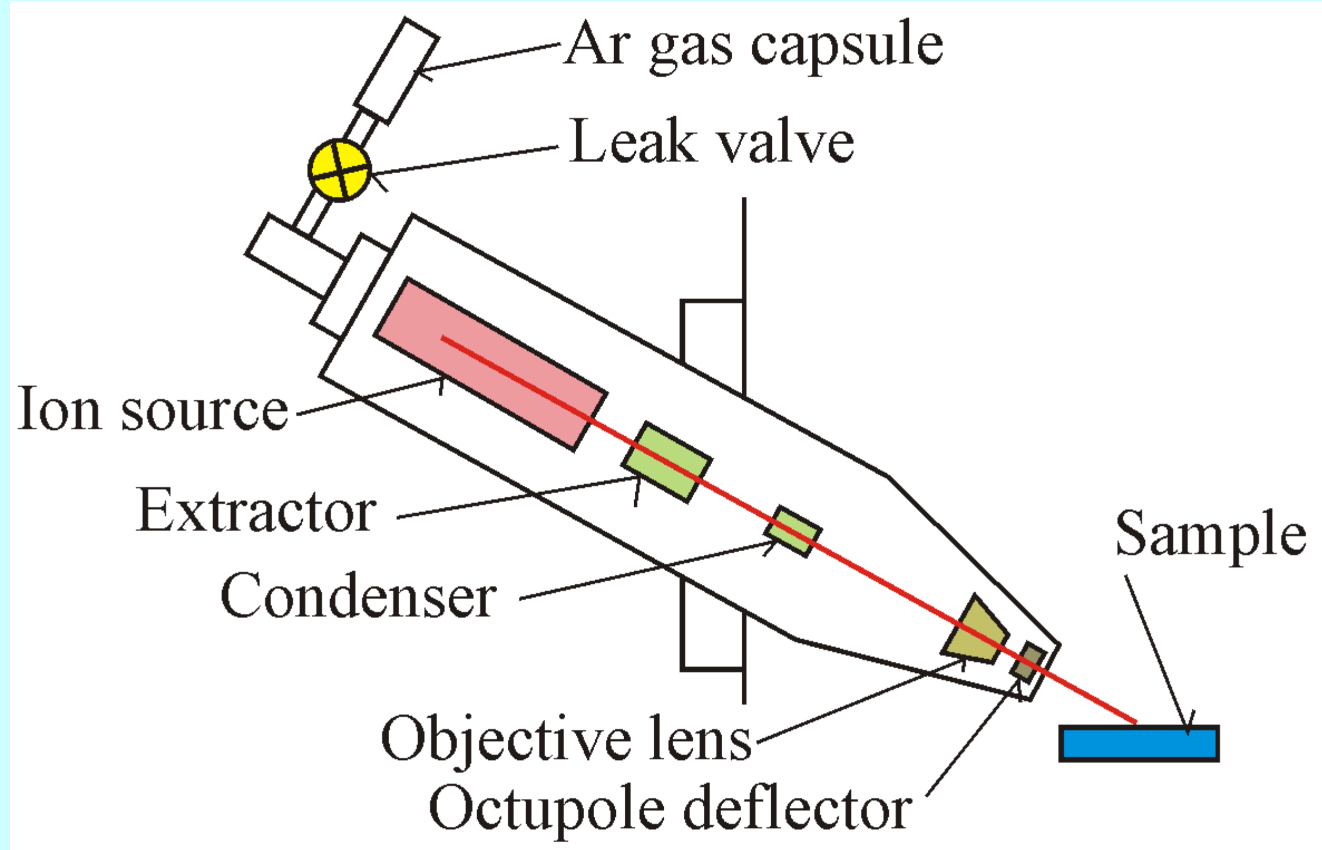
Ion Gun



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

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Parameters Calibration

Energy scale is calibrated using a flat, fine-grained Cu that has been sputtered to remove surface oxide and contamination. The Cu LMM and MNN peaks are measured and the peak positions are compared to the standard values at 917.8eV and 63.3eV. The software of most modern AES instruments allows for the adjustments of the linearity and shifting of the energy scale.

Intensity scale must be calibrated so that the sensitivity factors measured previously can be used. The instrumental factors (transmission function and detector efficiency) are measured on the instrument that gives the sensitivity factors. The instrumental factors are also measured periodically on the instrument for adjustment of the sensitivity factors.

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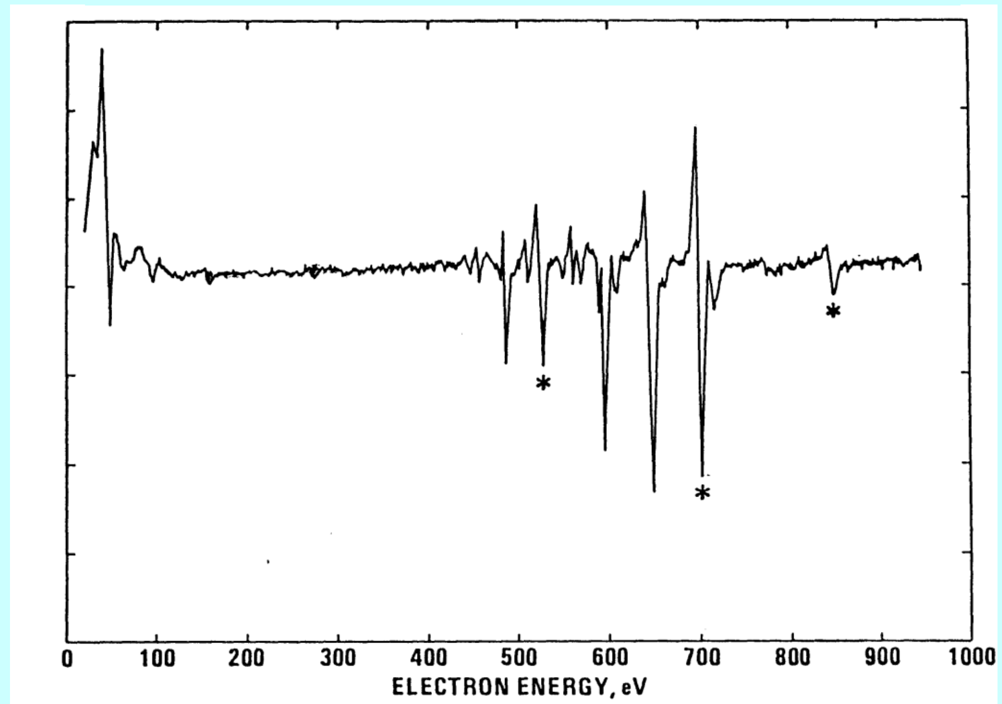
Qualitative Analysis

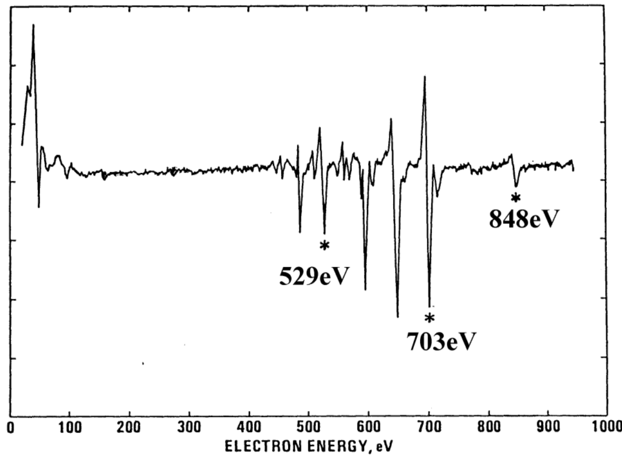
Procedures for Elemental Identification

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 in question 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



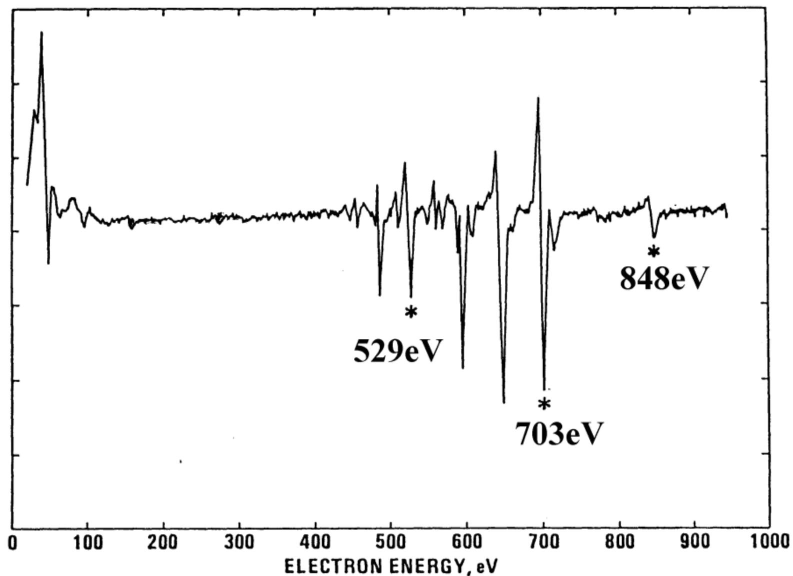
MNN

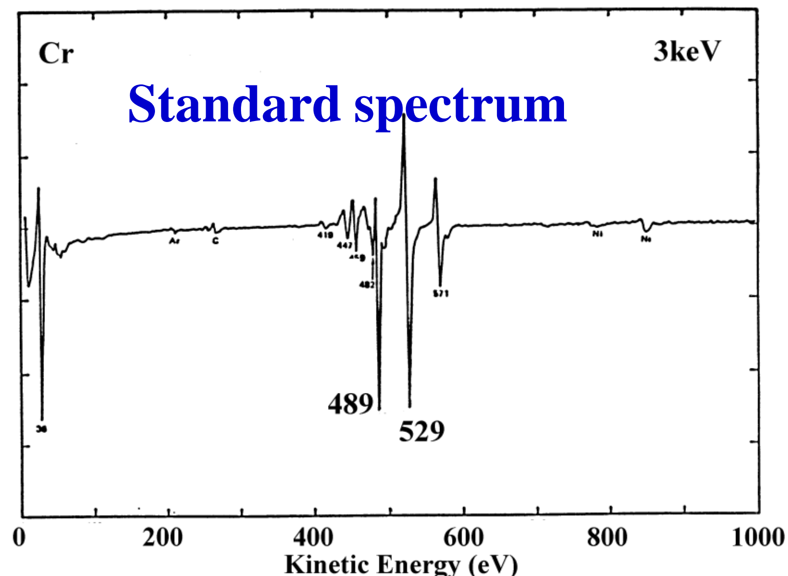
LMM

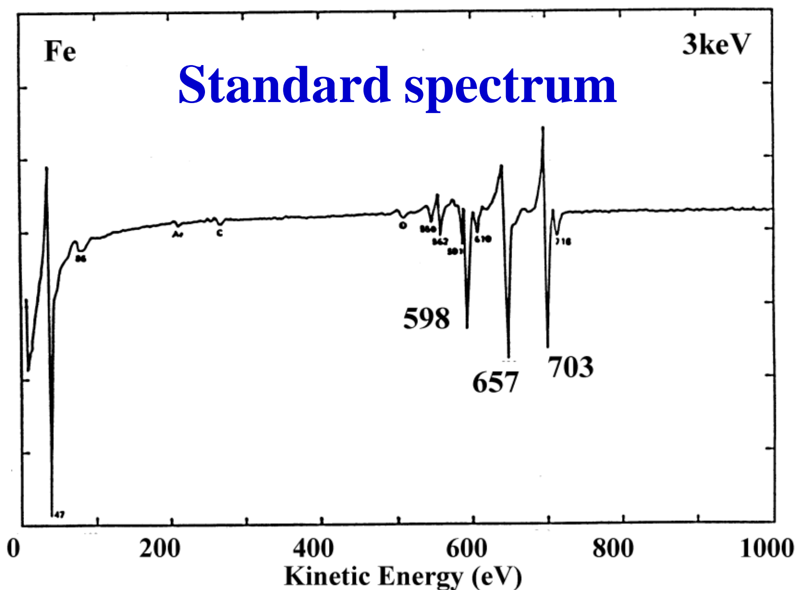
KLL

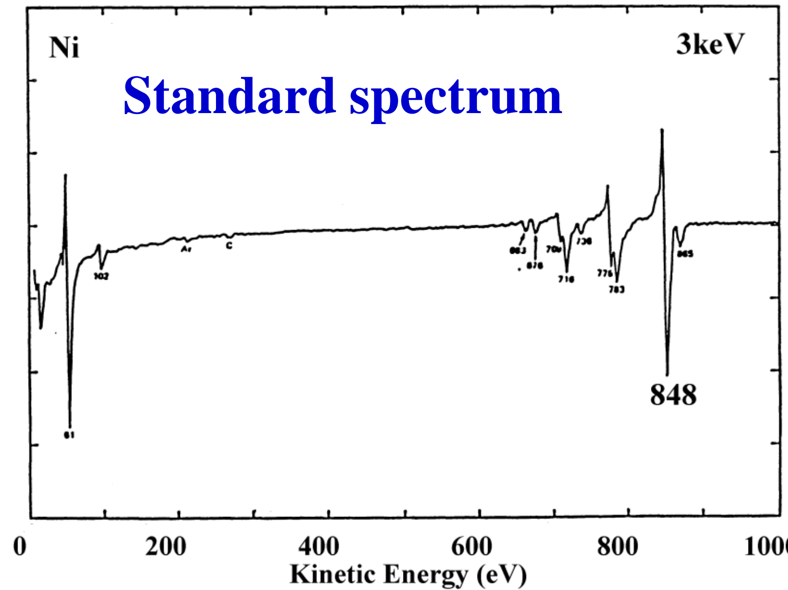
Atomic Number

Electron Energy (KeV)

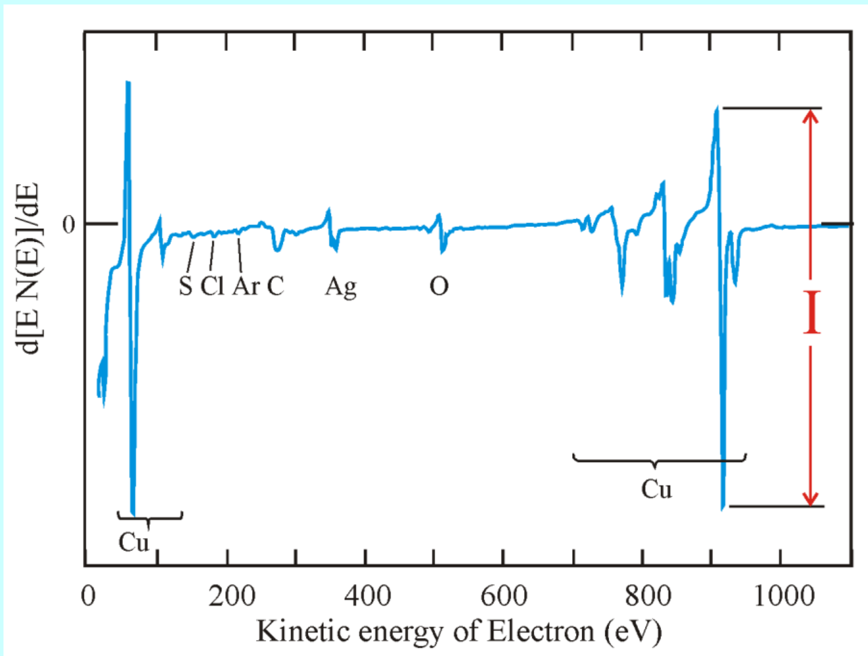

529eV
703eV
848eV
0
100
200
300
400
500
600
700
800
900
1000
ELECTRON ENERGY, eV


Cr
3keV
Standard spectrum
489
529
0
200
400
600
800
1000
Kinetic Energy (eV)


Fe
3keV
Standard spectrum
598
657
703
0
200
400
600
800
1000
Kinetic Energy (eV)


Ni
3keV
Standard spectrum
848
0
200
400
600
800
1000
Kinetic Energy (eV)

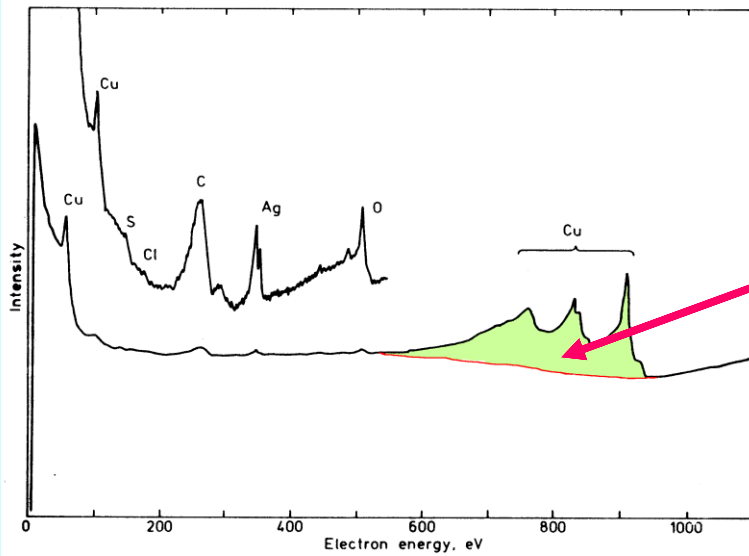
Quantitative Analysis



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

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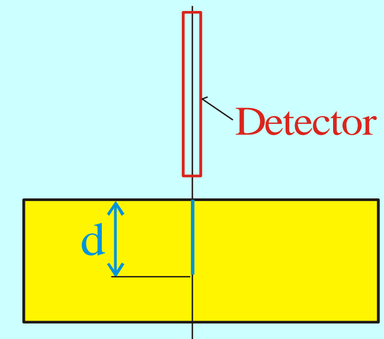
Auger Electron Intensity

For a homogeneous sample, the measured Auger intensity is given by

$$I_i = I_P \cdot N_i \cdot \sigma_i \cdot \gamma_i \cdot (1+r) \cdot \lambda \cdot \cos\theta \cdot F \cdot T \cdot D \cdot R$$



I_i: Auger intensity for the ABC transition of element i

I_P: Primary electron beam current

N_i: Number of atoms of element i per unit volume

σ_i: Ionization cross section for A level of element i

γ_i: Auger transition probability for the ABC transition of element i

r: Secondary ionization for the A level of element i by scattered electrons

λ: Inelastic mean free path

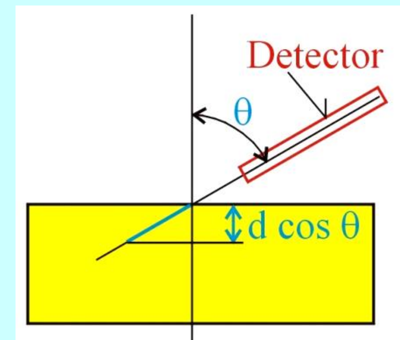
θ: Anger between the direction of Auger electron and the sample normal

F: Factor for analyzer solid angle of acceptance

T: Analyzer transmission function

D: Detector efficiency

R: Surface roughness factor



Empirical Approach

Use of relative sensitivity factors (S_i)

For two pure elements

$$\frac{I_1}{N_1 \cdot S_1} = \frac{I_2}{N_2 \cdot S_2}$$

The relative sensitivity factors were measured for all elements under a certain excitation electron beam energy

Then, the atomic concentration of element a on a sample with N elements can be determined as

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

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

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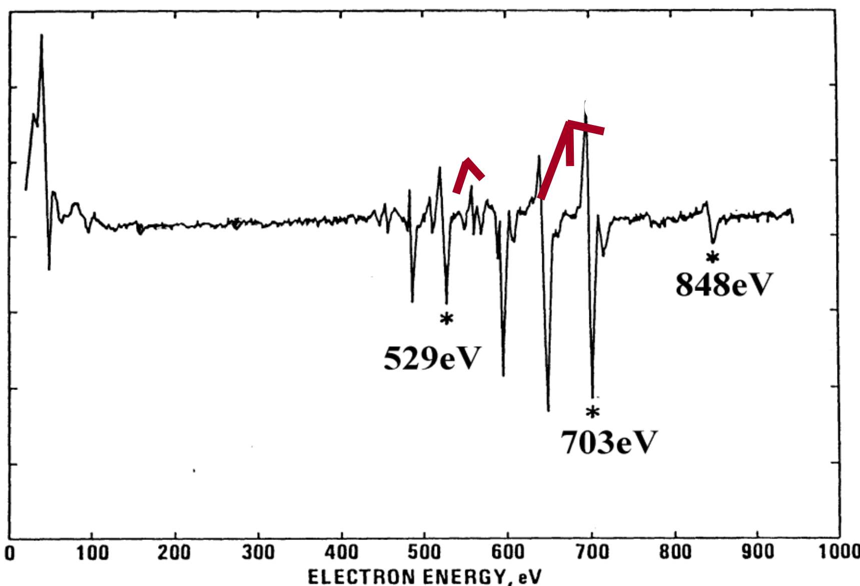
The empirical method does not include the matrix effects of the sample, which includes the inelastic mean free path (λ), the backscattering factor (r), and chemical effects on peak shape and surface roughness. General, an error of 15% is expected using the empirical method.

For example, a sample reported with 80% Fe and 20% Ni. The error for Fe could be in the range of ±12%.

If standard samples with the same matrix is used for the determination of the sensitivity factors, the error can be as small as 1%.



Example

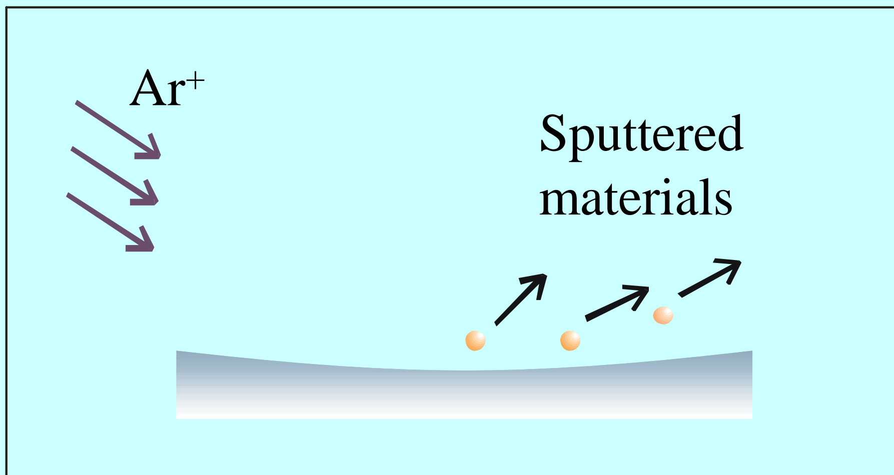
Peak-to-peak height:	S_i
Cr peak at 529eV: 4.7	0.32
Fe peak at 703eV: 10.1	0.20
Ni peak at 848eV: 1.5	0.27

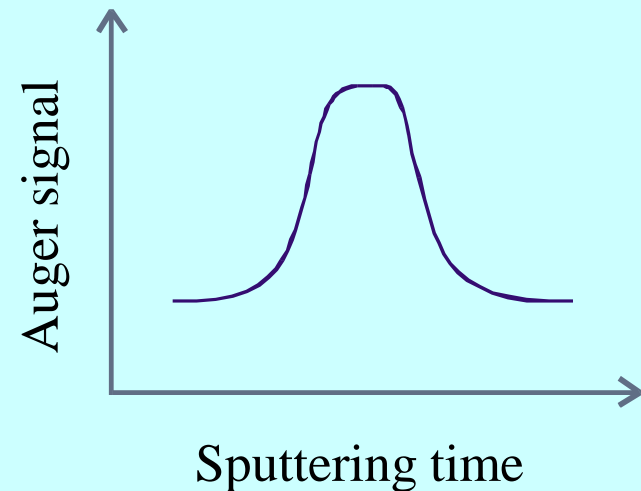
$$\% Cr = \frac{4.7/0.32}{4.7/0.32 + 10.1/0.20 + 1.5/0.27} x100\% = 21\%$$

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

Depth Profiling

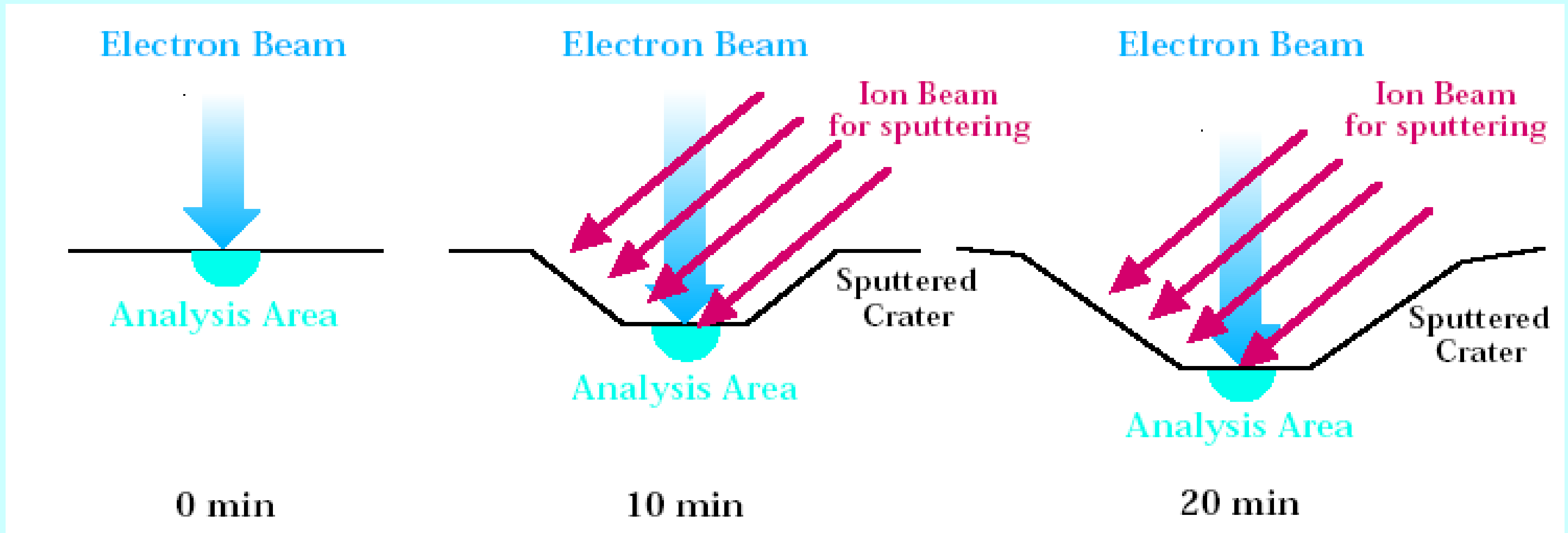
To analyze samples in depth, Auger instruments incorporate ion beam sputtering to remove materials from the sample surface sequentially. One cycle of a typical depth profile consists of sputtering a small increment into the sample, stopping, measuring relevant portions of the Auger spectrum, and performing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

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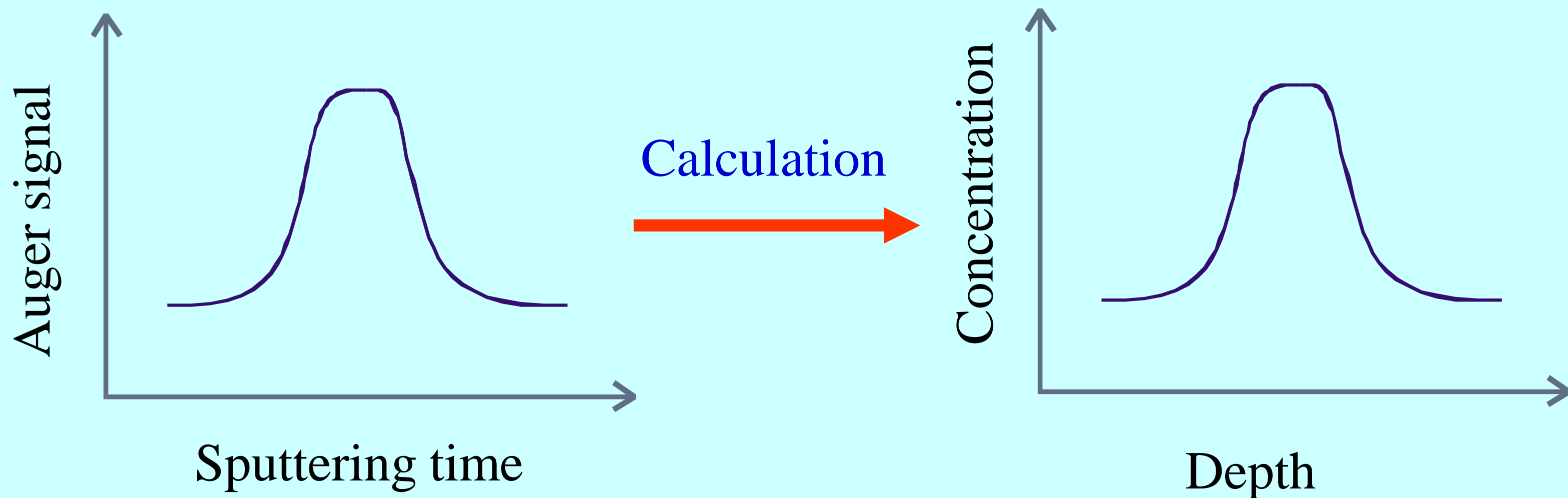
Calibration of Depth Scale

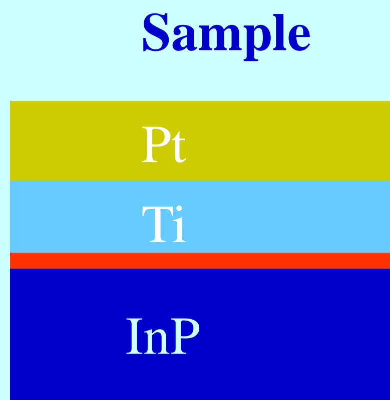


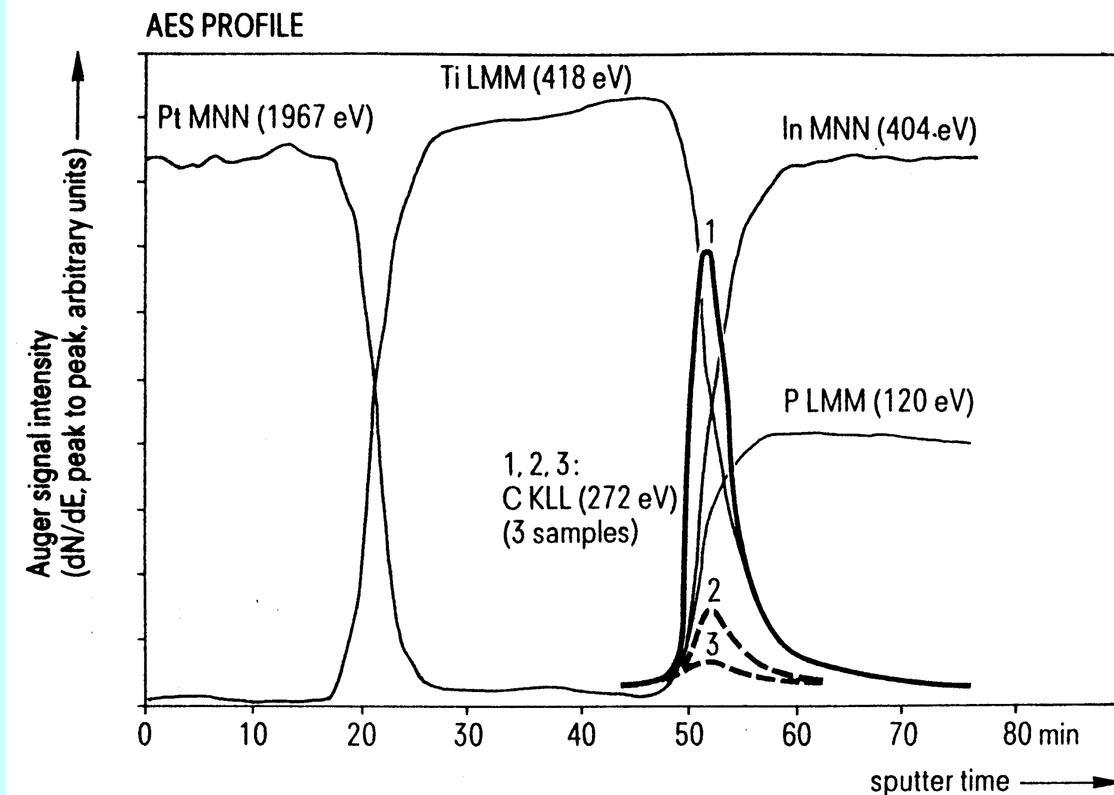
1. Sputtering rate determined from the time required to sputter through a layer of the same material of known thickness.

2. After the sputtering analysis, the crater depth is measured using depth profilometry. A constant sputtering rate is assumed.

Contamination at Semiconductor / Metallization Interface

Sample





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

O: LMM at 120 eV

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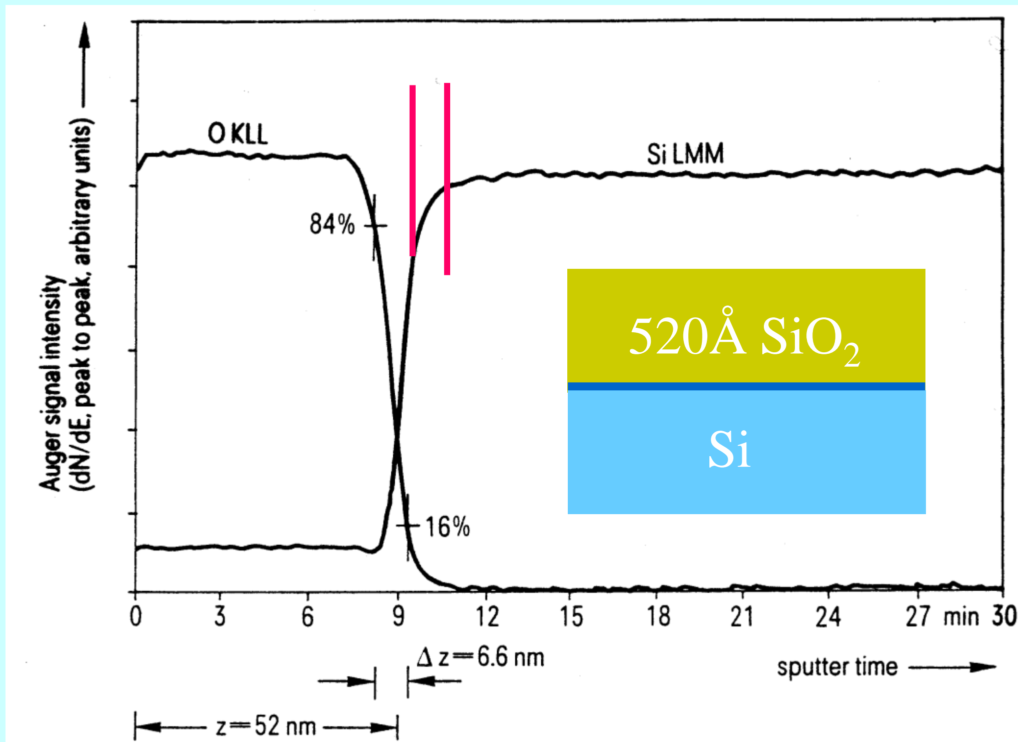
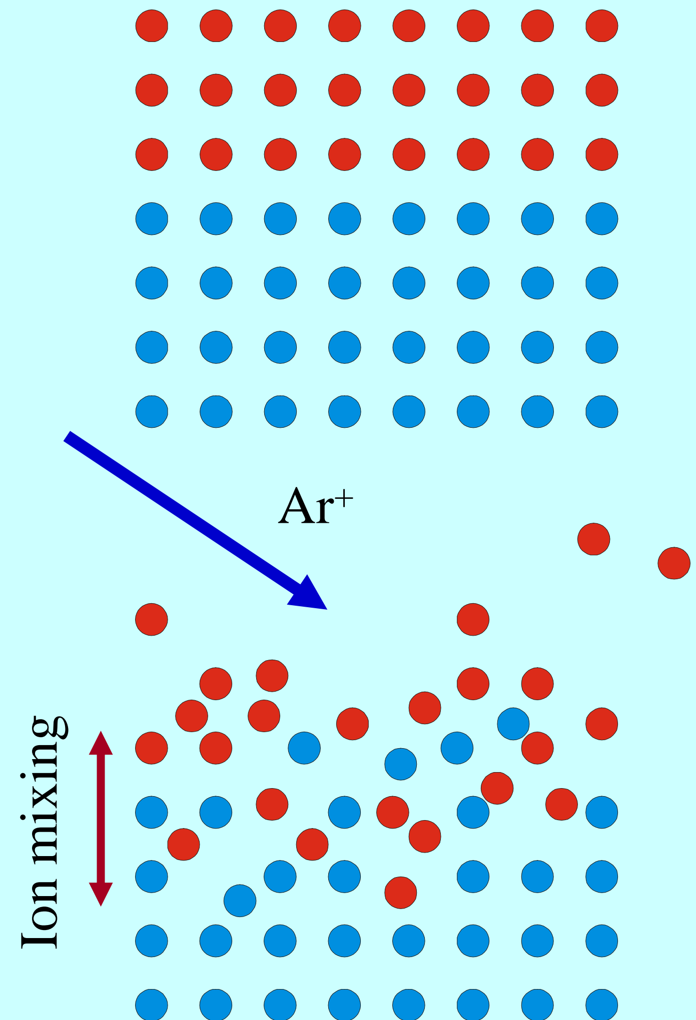
Ion Mixing

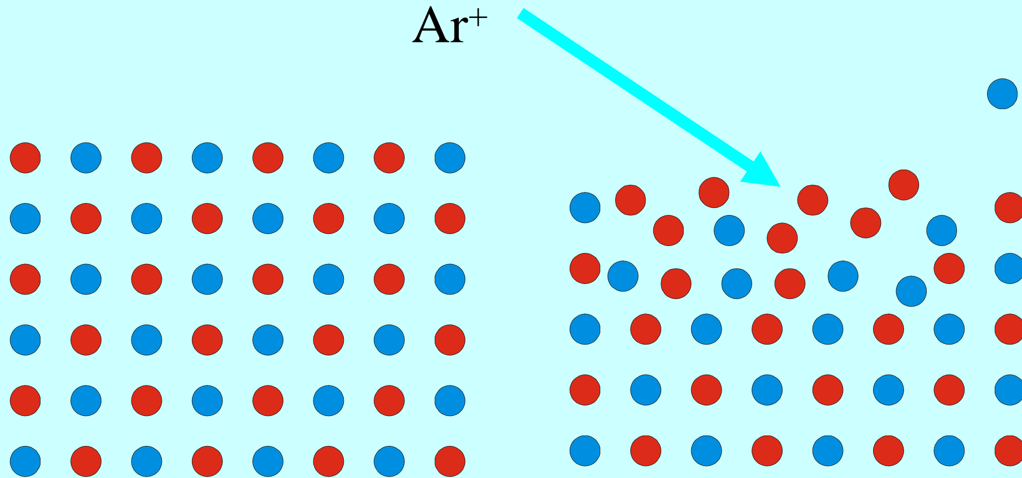


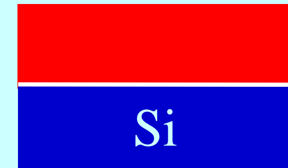


Depth Resolution Depends on

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

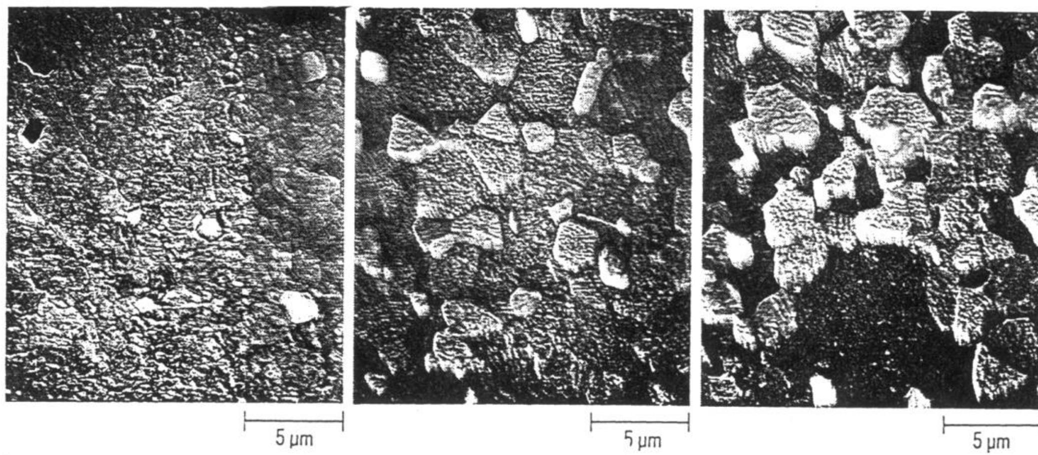
Preferential Sputtering



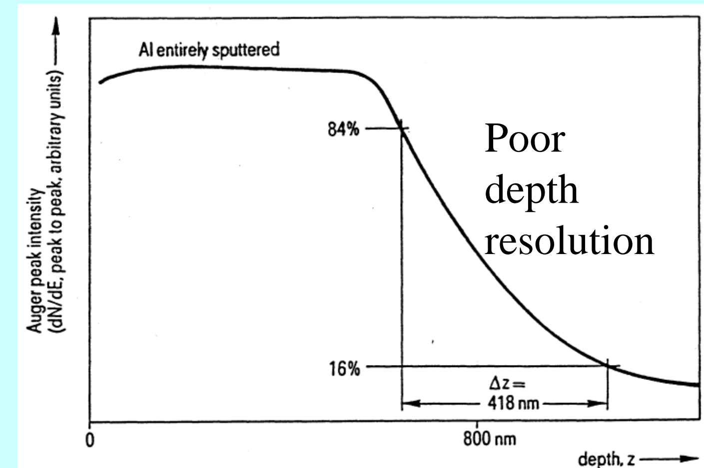


Difference in

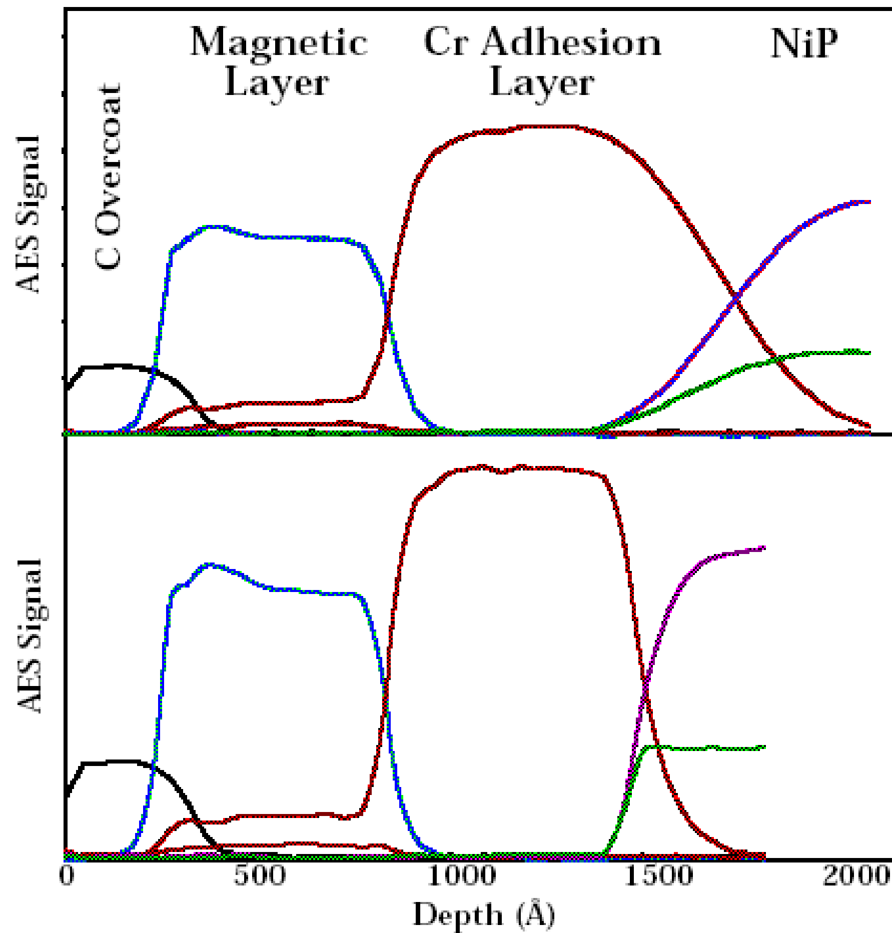
- Chemical composition
- Crystal orientation



SEM Images



Sample Rotation



No sample rotation

With sample rotation

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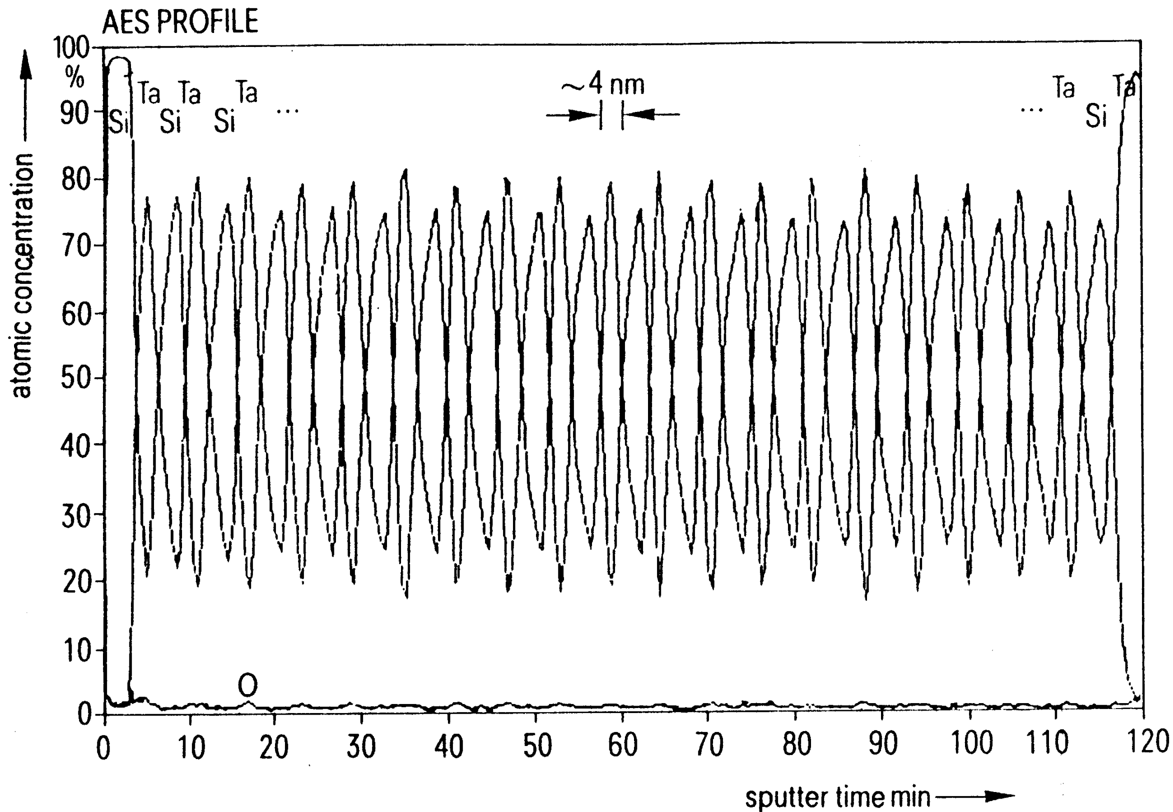
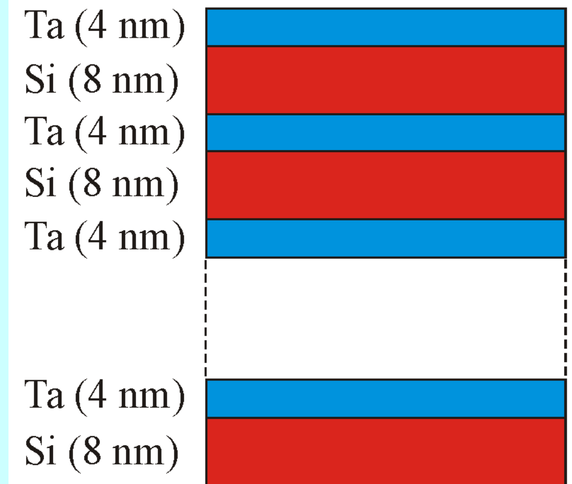
Depth Profile of a Ta/Si Multilayer Sample

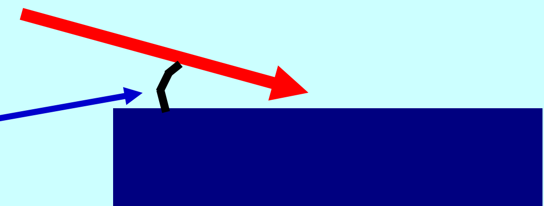


Depth resolution usually degrades with depth



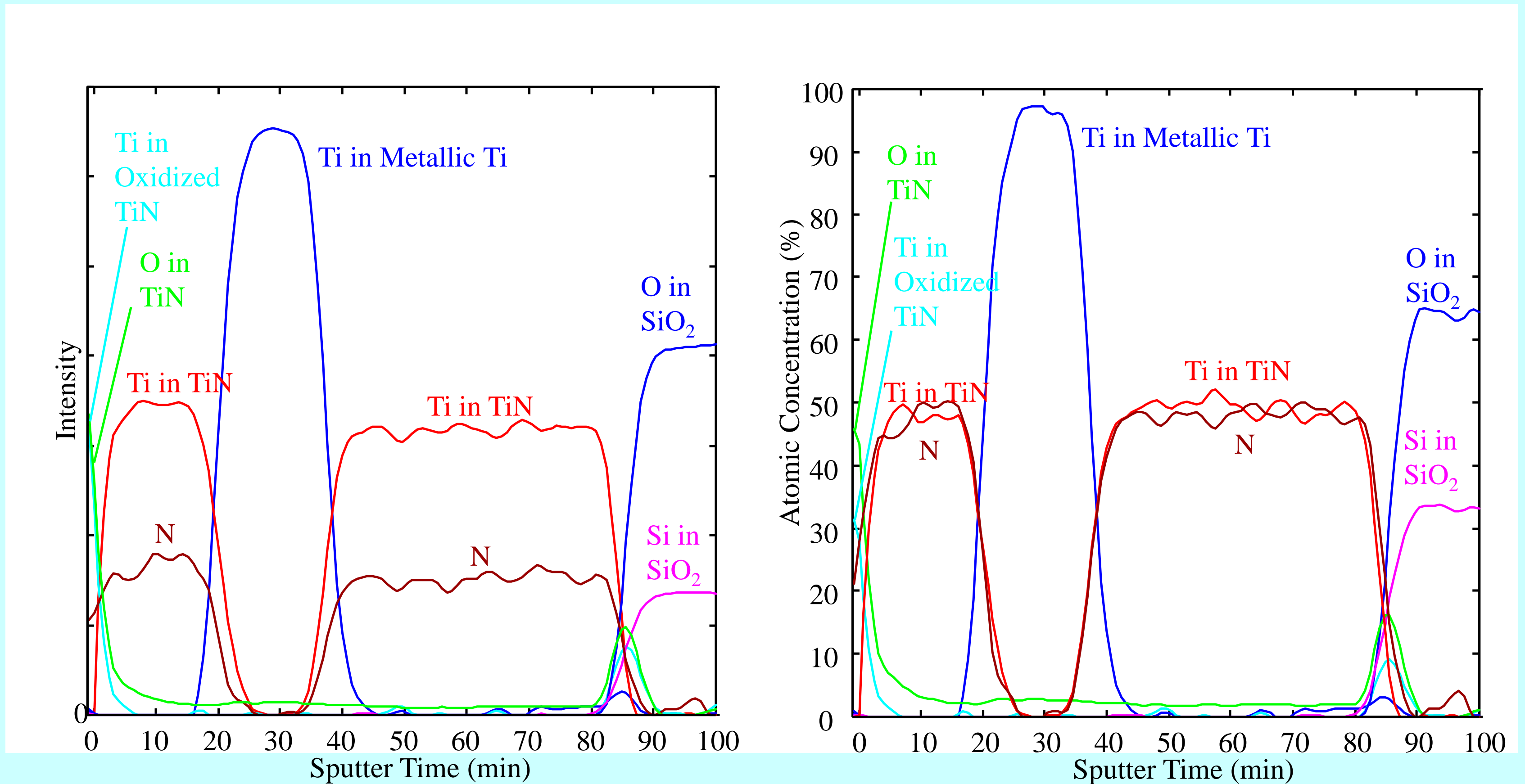
Improve depth resolution:

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



Depth Profiling of TiN/Ti/TiN on SiO_2

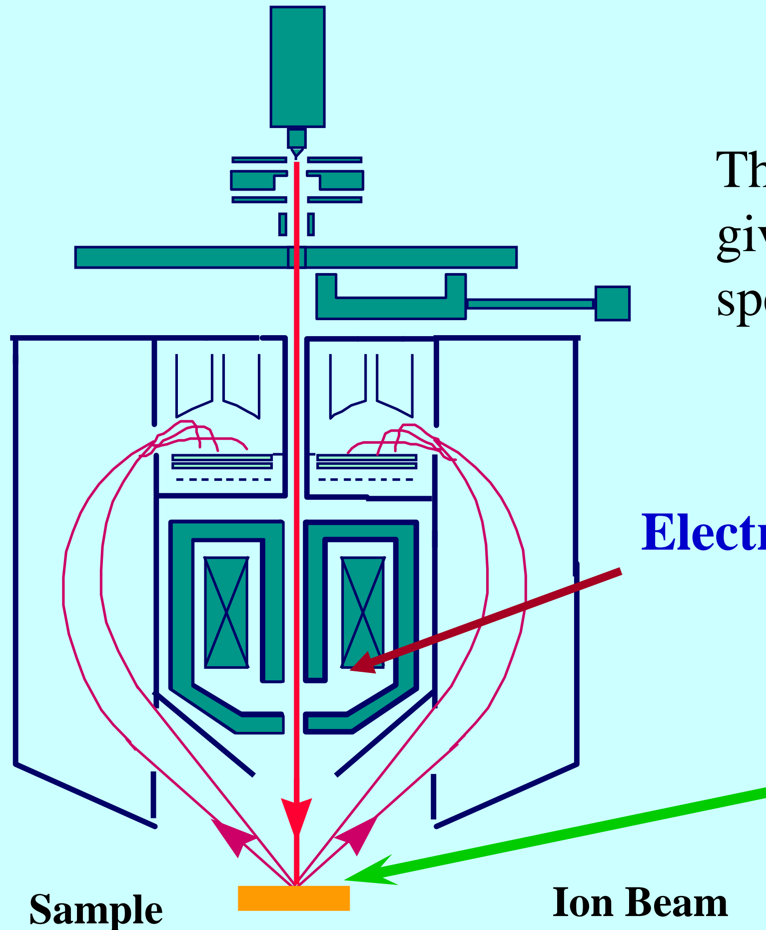
Two TiN(250Å)/Ti(375Å)/TiN(600Å) on SiO_2 samples are analyzed by Auger depth profiling to determine the film composition and thickness.



Scanning Auger Microscopy

AES Auger Electron Spectroscopy

SAM Scanning Auger Microscopy



The same instrument can give SEM images, Auger spectra and Auger maps.

Electron focusing and scanning

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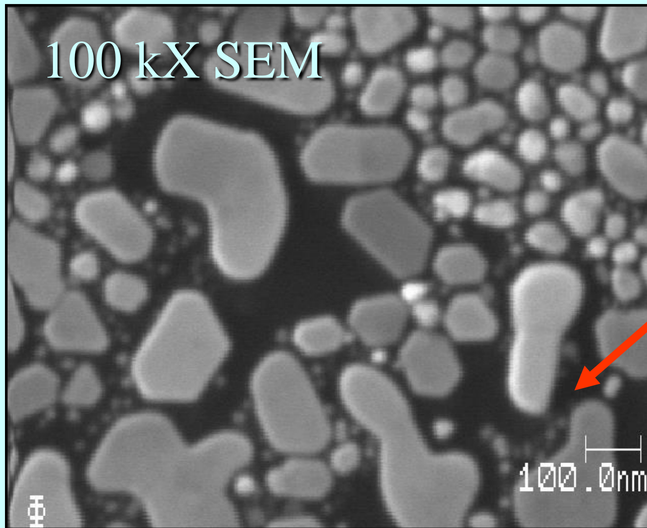
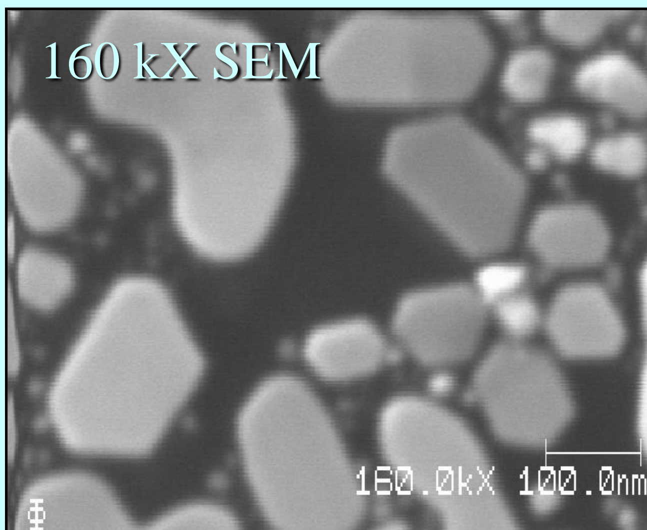
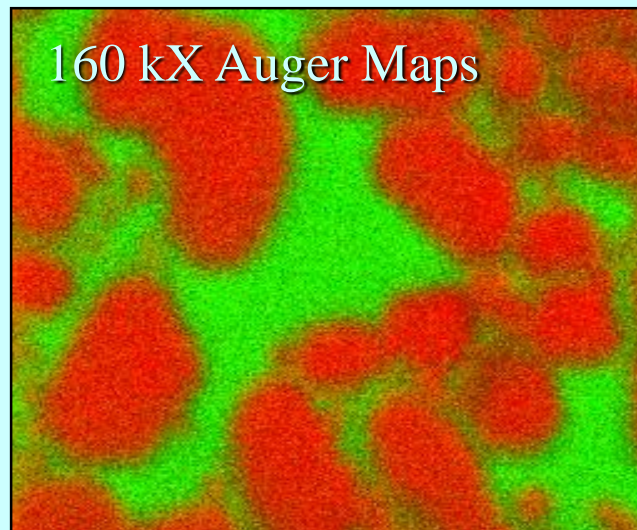
Au islands on C



Secondary electron images

Composite Auger image





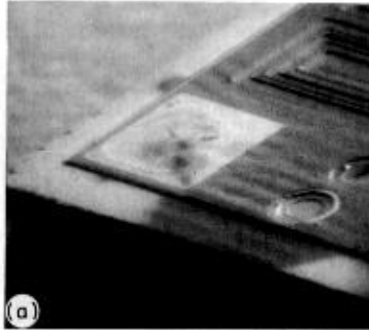
Gold

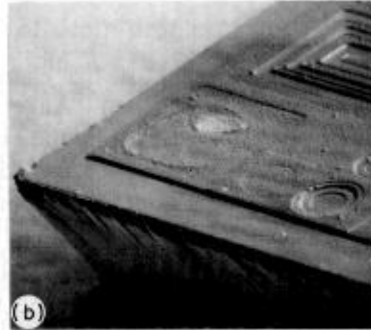
Carbon

Scanning Auger Microscopy

SEM

Sample current



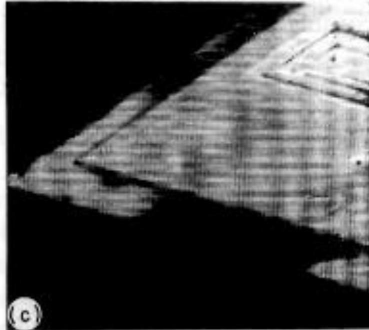


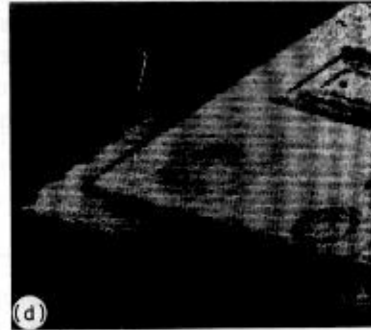
SEM

Secondary electrons

Auger

O map



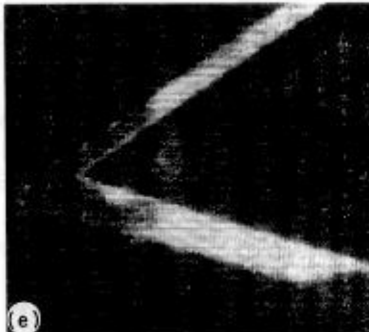


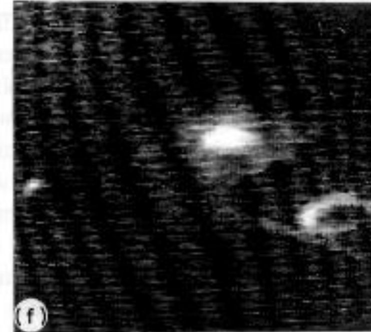
Auger

Si map (oxide)

Auger

Si map (non-oxide)





Auger

Al map

Images and Auger elemental maps from a contact pad on a semiconductor device:

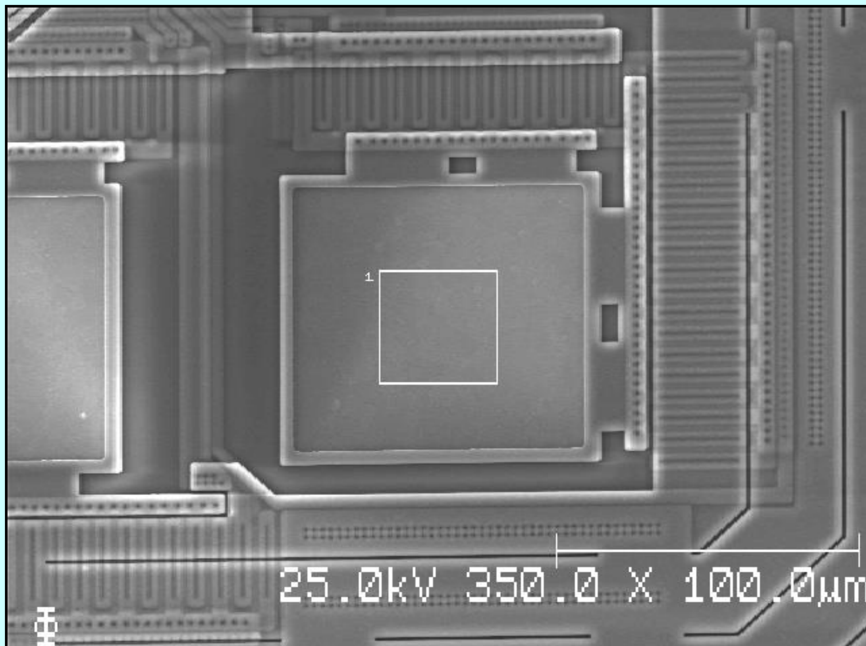
(a) Adsorbed current image;
(b) Secondary electron image;
(c) oxygen map (O KLL, 512 eV);
(d) Silicon oxide map (Si LMM, 1625 eV, oxide peak);
(e) Silicon map (Si LMM, 1625 eV, non-oxide peak);
(f) aluminum map (Al LMM, 1400 eV).

The Auger maps reveal that the oxide layer in the middle of the bond pad has been broken exposing a small area of aluminum due to bonding attempts.

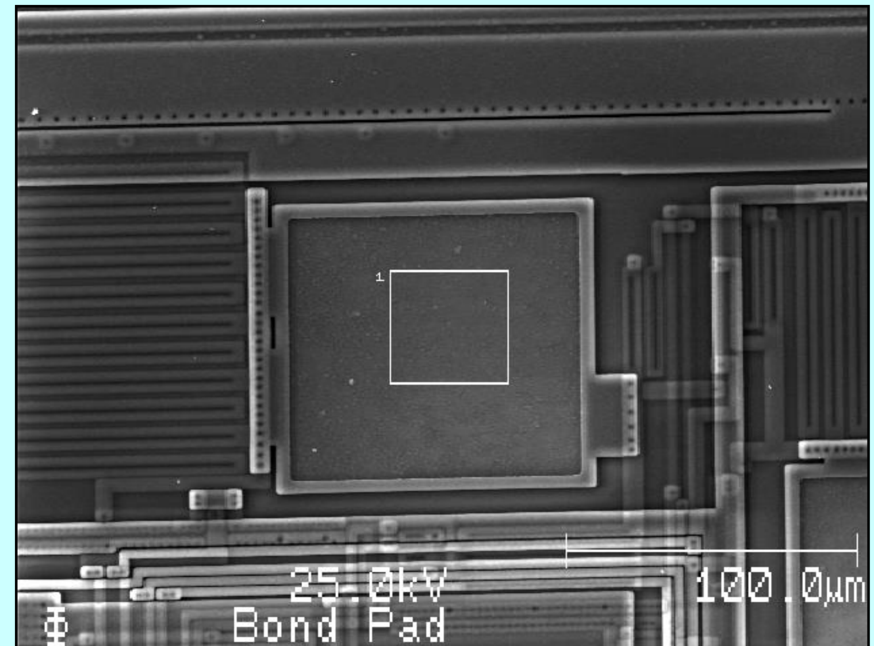
Analysis of bond pad

Two chips were supplied for analysis, a chip from a contaminated wafer and one from a "normal" or good wafer

Secondary Electron Images (Box defines analyzed area for AES)



Bond pad from normal chip



Bond pad from contaminated chip

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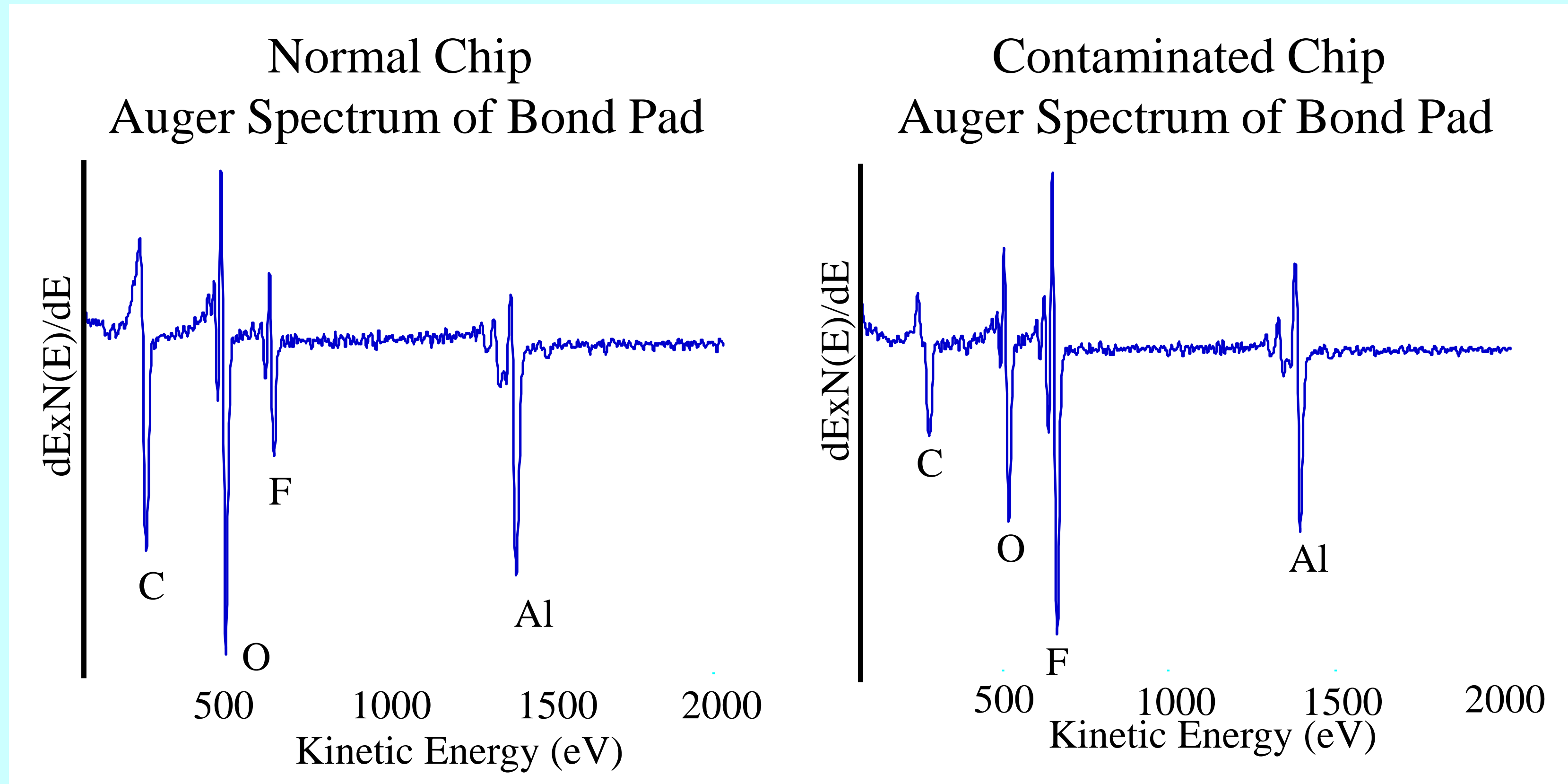
Auger electron spectra

Auger signals acquired from the areas defined in the boxes

Note the difference in F levels



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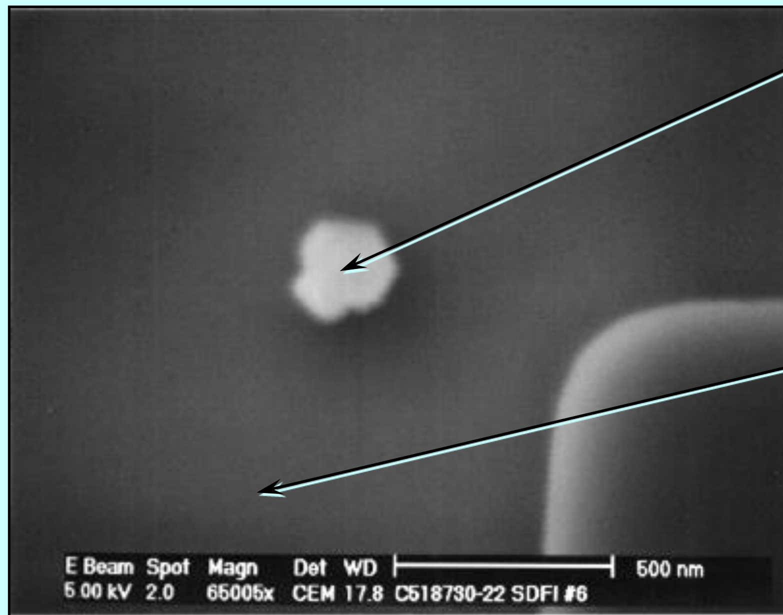
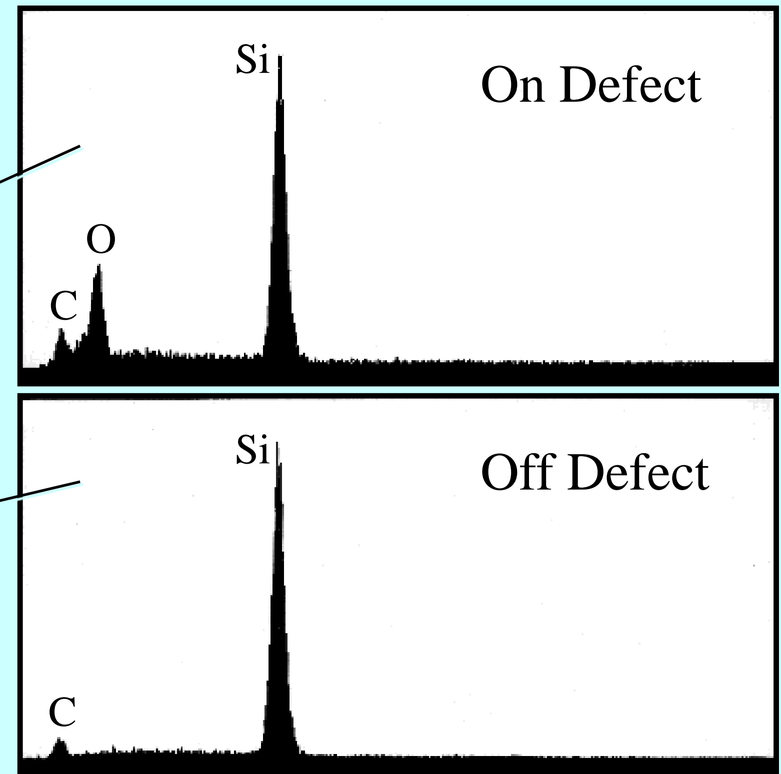
Comparison of SEM/EDX and SAM

SEM/EDX analysis of a 250 nm particle on a 200 mm Wafer

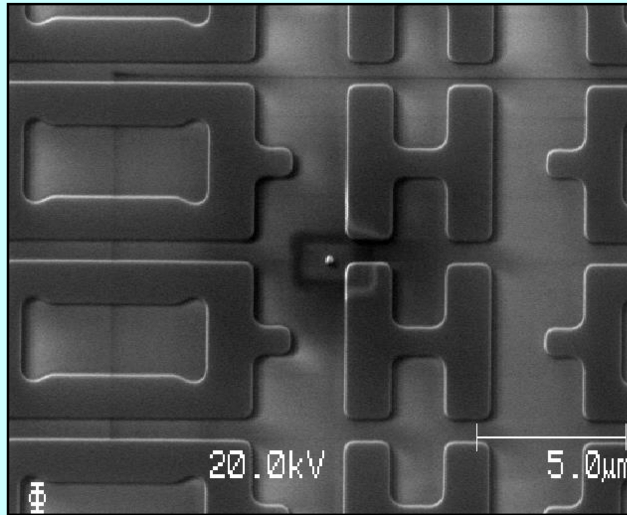
Particle found after Si oxy-nitride deposition and plasma etching

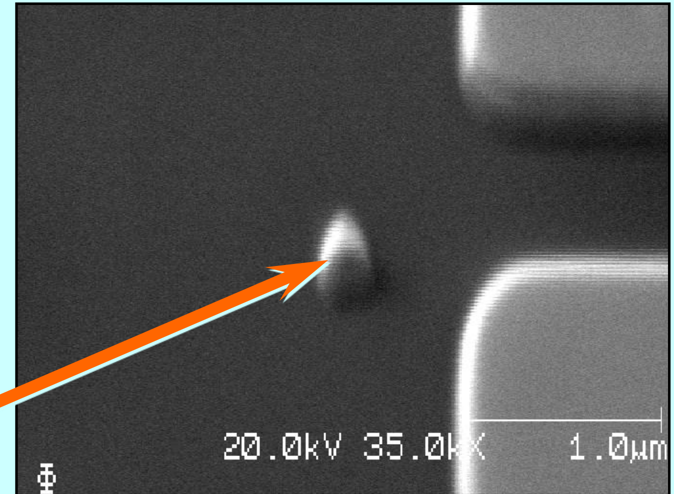


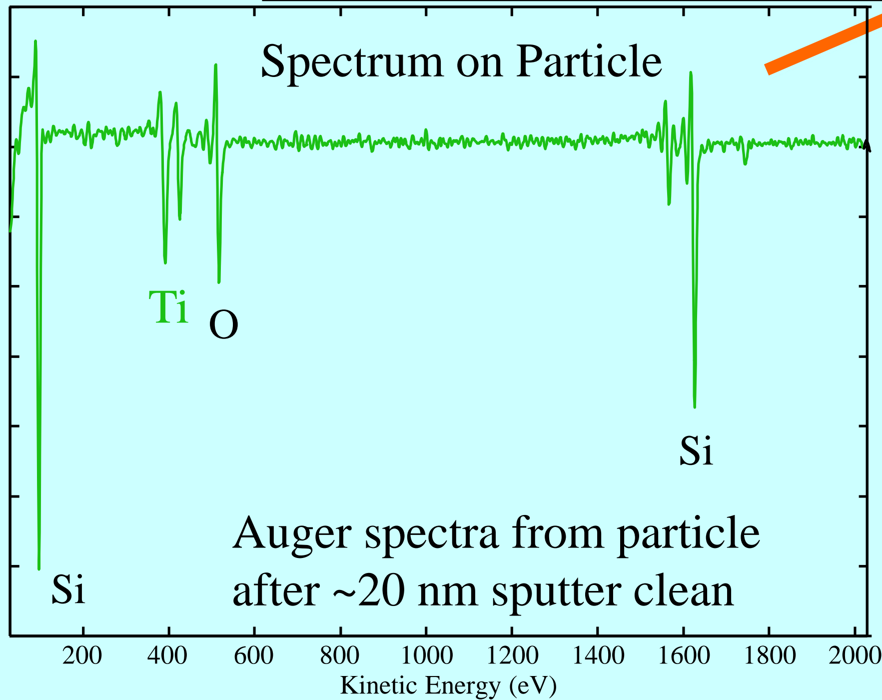


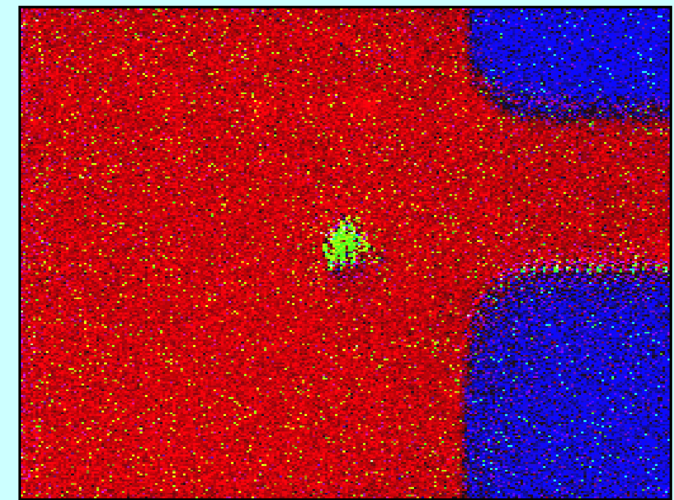
SEM/EDX

SAM analysis of the same sample









Green = Ti   Red = Elemental Si

EDS

- Defect: Si and O => Si oxy-nitride
- No Ti found
- Substrate - Si (substrate)
- C observed in both areas - from analysis tool
- Excitation volume too large to study the small particle on surface

Auger

- Defect: Si, O and Ti
- Ti - contamination from a process tool

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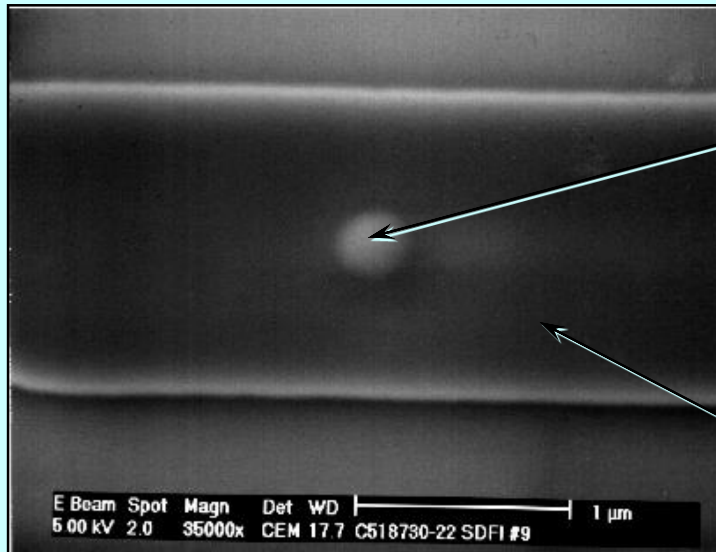
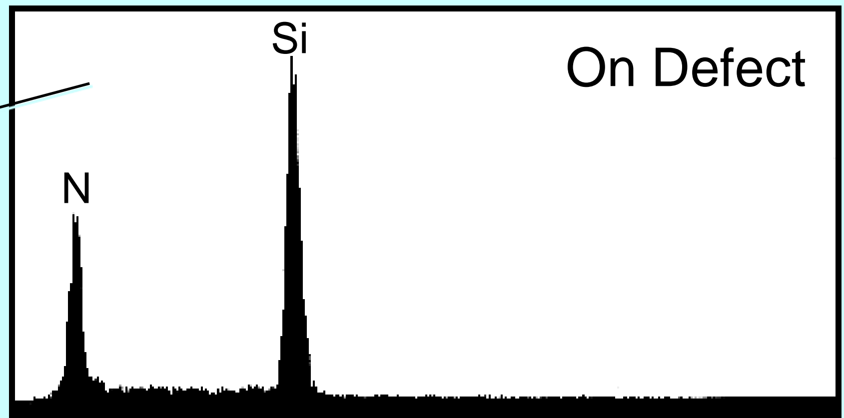
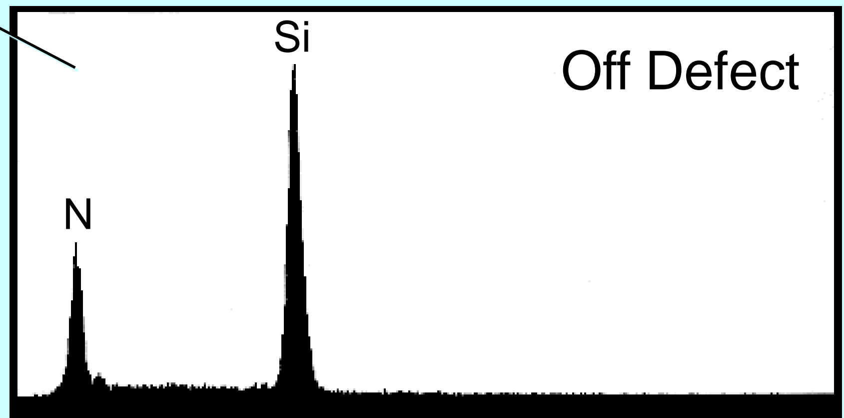
SEM/EDX analysis of a buried particle



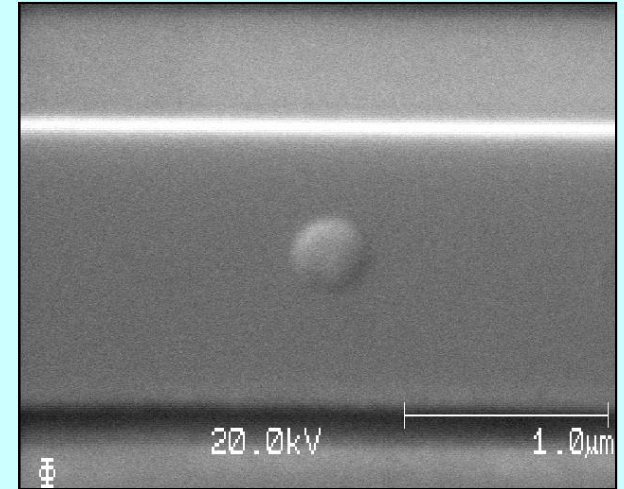
SEM/EDX



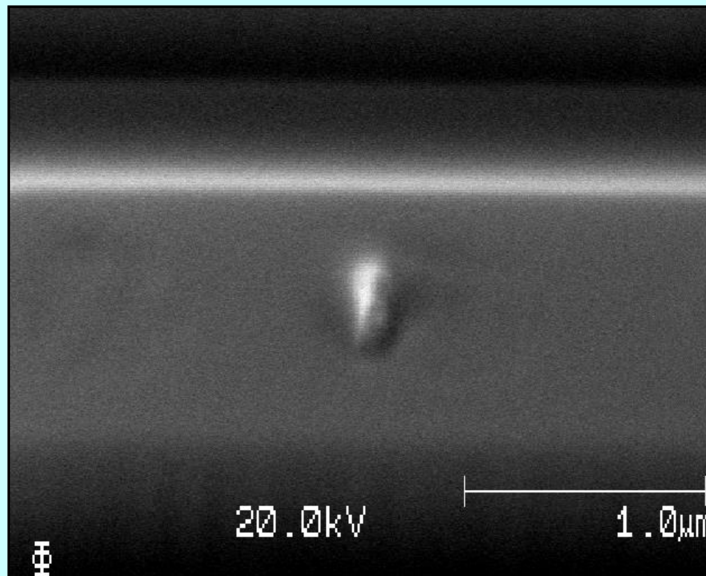


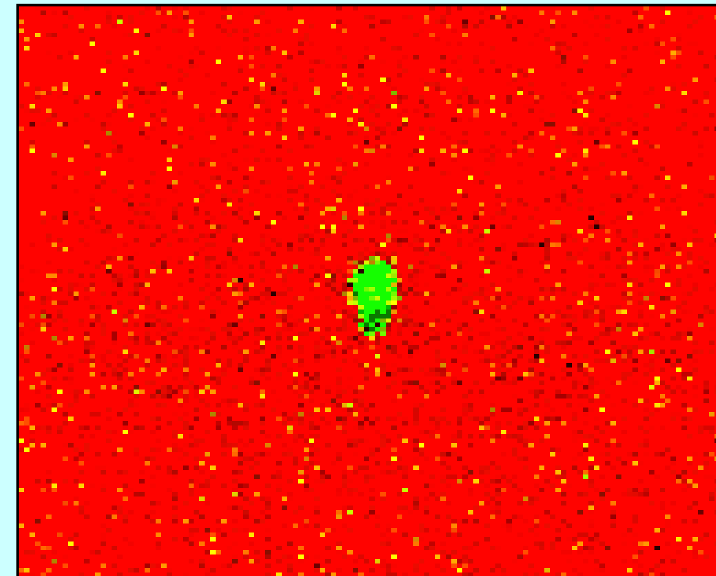
SAM of the same sample

As received (SEM)



Sputter to defect (SEM)

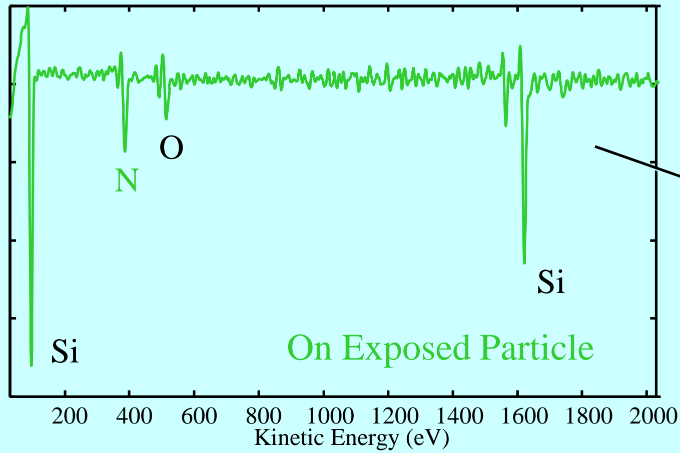


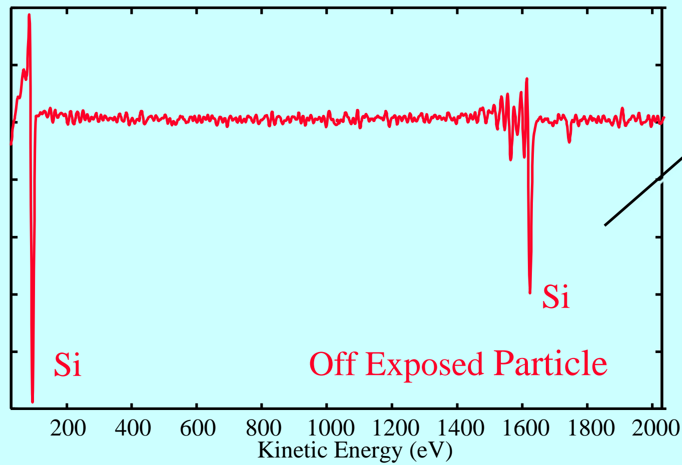


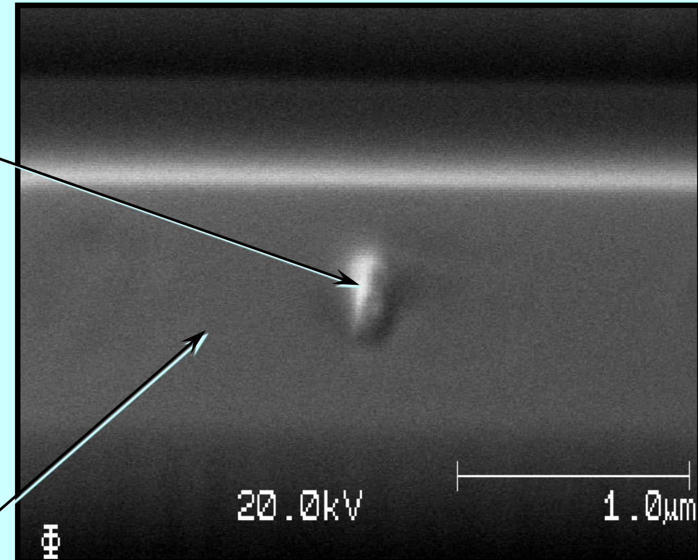
Green = N Red = elemental Si

Auger

SEM







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EDS

- Defect: Si and N
- Substrate: Si and N
- No unique contaminants found
- Excitation volume too large

Auger

- Sputter etched to defect - removing surrounding Si oxy-nitride layer
- Defect: Si, O, N
- Substrate: Si
- Confirm defect is Si oxy-nitride

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AES Summary

- AES uses a focused e-beam to excite Auger electrons
- Auger electrons have energies characteristic of the elements
- Auger electrons - reveal the elemental composition and the chemistry of the surfaces
- Chemical bonding of the atoms
- Depth profiling in conjunction with ion sputtering
- High spatial resolution of the electron beam and surface specificity allows for high resolution microanalysis
- AES attributes: high lateral resolution, reasonable sensitivity (100 ppm), semi-quantitative analysis without empirical standards, and chemical bonding information

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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, depending on the matrix
- 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

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Capabilities of SAM

- Elemental analysis
- Some chemical state information
- Quantification (sensitivity about 0.1 atomic %)
- Small area analysis
- Surface morphology (SEM mode)
- Elemental mapping
- Depth profiling

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Sample Tutorial Questions

- How are Auger electrons produced?
- Why is AES surface sensitive?
- How is depth profiling performed?
- Explain the differences between AES and EDS.
- What kinds of problems are best tackled by AES?