Auger Electron Spectroscopy

- Auger Electron Spectroscopy (AES), is a widely used technique to investigate the composition of surfaces.
- First discovered in 1923 by Lise Meitner and later independently discovered once again in 1925 by Pierre Auger [1]

Short historic of the Auger spectroscopy

- **Pierre Auger**, in 1925 observed (at first in the cloud chamber, then in photographic plates) the occurrence of electrons with precisely determined energies. These electrons have been later named *Auger electrons*) may serve to identify their parent atoms.

- **1953 J. J. Lander** – the idea of using the Auger electrons in surface analysis.
- The AES has been implemented as an analytic tool in 1967 (Larry Harris), after increasing the method sensitivity by using differential spectra to discriminate the tiny Auger peaks in the electronic spectra.
- **1968** – Auger spectrometer constructed in modern configuration.

Nowadays

- **Beam current** as low as 1 nA
- **Probing depth**: 0.5 - 10 nm, and **< 10 nm lateral resolution**(!!!)
- **Covering a wide range of elements** which can be detected (except for H and He).
- **High sensitivity**: 100 ppm for most of the elements.
**General Uses**

- **Surface composition analysis** for metals, powders, insulators.
- **Identification of particulates**, localized dopants or contaminants, visual defects.
- **Investigation of submicrometer dimension structures**.
- **Grain boundary investigations**, e.g. intergranular corrosion.
- **Analysis of surface coatings** and thin films.
- **When combined with ion sputtering**, elemental depth profiling of surface and/or interfacial layers.

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**Principle of Auger electron spectroscopy**

- AES uses electrons as primary radiation.
- Such electrons have sufficient energy to ionize all levels of the lighter elements, and higher core levels of the heavier elements.
- **The analyzed electrons are not the emitted core electrons**, but the Auger electrons that are ejected as a consequence of the return of the ionized atom to its ground state.
- The following Figure shows a schematic representation of the processes involved in the emission of an Auger electron.
The Auger process

Emission of an initial electron leads to the emission of a characteristic (Auger) electron.

It is a surface specific technique utilizing the emission of low energy electrons in the Auger process and is one of the most commonly employed surface analytical techniques for determining the composition of the surface layers of a sample.

Atomic Spectra Levels

• The non s-level peaks are doublets. This is related to the fact that when $l > 0$, two possible states characterized by $j$ arise ($j = S+L$) which arises from the spin-orbit coupling (see the following Table).
• For a single electron $j = L \pm \frac{1}{2}$
• If $L = 1$; $j = 3/2$ and 1/2 If $L = 2$; $j = 5/2$ and 3/2 but if $L = 0$ only one value $j = \frac{1}{2}$
• It is also noted that the core level peaks have different intensities and widths.
• The relative intensities are governed by the ionization efficiencies of the different core shells.
• The line width, defined as the full width at half-maximum intensity (FWHM), is a convolution of several contributions: the natural width of the core level, the width of the X-ray line and the resolution of the analyzer.
• The nomenclature employed to describe XPS and AES features is based on the momenta associated with the orbiting paths of electrons around atomic nuclei, indicated by the quantum numbers n, l, j.

• The translation into the notation is different for both techniques.

XPS uses the spectroscopic notation: first the principal quantum number \( n = 1, 2, 3, \ldots \), then \( l = 0, 1, 2, \ldots \) indicated as s, p, d, ... respectively, and finally the j value given as a suffix \((1/2, 3/2, 5/2, \ldots)\).

The AES nomenclature on the contrary usually follows the X-ray notation: the states with \( n = 1, 2, 3, \ldots \) are designated K, L,M, ..., while the combinations of l and j are given the suffixes 1, 2, 3, .... Both notations are listed in following Table.

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The Auger peaks in the spectrum, MNN peaks in the case of Ag, originate from the decay of the ionized atoms to their ground state. The principle of the Auger emission is discussed in the next paragraphs.
Introduction

- Auger process is a three electron process and leaves atom doubly-ionized.
- In Auger electron spectroscopy (AES), electrons emitted after the interaction between primary X-rays or electrons and a sample are detected.
- The amount of electrons having escaped from the sample without energy loss is typically measured in the range of 20 to 2000 eV.
- The data is represented as a graph of intensity versus electron energy.
- Due to the impact of the primary beam, the atoms in the sample are ionized, and electrons are liberated from the surface, as a result of the radiationless de-excitation in the Auger electron emission process (AES).

Principle of AES

- A fine focused electron beam bombards the sample and ejects an electron of the inner shell of the atom (e.g K-level).
- This vacancy must be refilled by an electron from a higher energy level (L_1).
- When the higher energy electron fills the hole, the release of energy is transferred to an electron in an outer orbit electron (L_2 or L_3).
- That electron has sufficient energy to overcome the binding energy and the work function to be ejected with a characteristic kinetic energy.
- Example:
  \[ E = E_k - E_{L_1} - E_{L_{2,3}} \]  (\(KL_1L_{2,3}\) excitation)
- The ejected electron is referred to as an Auger electron after Pierre Auger who first discovered it in 1925.
Auger Electron

1, 2, 3 and 4 are the order of steps in which the e\textsuperscript{}s will move in the atom when hit by the e\textsuperscript{} gun.

Two Ways to Produce Auger Electrons

1. The X-Ray source can irradiate and remove the e\textsuperscript{} from the core level causing the e\textsuperscript{} to leave the atom
2. A higher level e\textsuperscript{} will occupy the vacancy.
3. The energy released is given to a third higher level e\textsuperscript{}.
4. This is the Auger electron that leaves the atom.

The axial e\textsuperscript{} gun can irradiate and remove the core e\textsuperscript{} by collision. Once the core vacancy is created, the Auger electron process occurs the same way.
Auger Electron Spectroscopy (AES)

- Electron beam from the e⁻ gun
- e⁻ released from the top layer
- Atom layers
- Outer surface
- Inner surface

Auger Transition Notation

- Auger electrons designated by x-ray notation as KLL, KL₁L₂,3, L₂,3M₂,3M₄,5 or KVV... etc.
- First letter - initial core hole location.
- Second letter - initial location of relaxing electron.
- Third letter - location of second hole (initial location of Auger electron).

KL₁L₂,3 = \begin{align*}
\text{K} & \quad \text{location of core hole} \\
\text{L₁} & \quad \text{origin of relaxing electron} \\
\text{L₂,3} & \quad \text{Auger electron (electron that leaves ion)}
\end{align*}


\[ KVV = \begin{array}{c} K \\ \text{(is) location of core hole} \end{array} \begin{array}{c} V \\ \text{(Valence) origin of relaxing electron} \end{array} \begin{array}{c} V \\ \text{(Valence) Auger electron (electron that leaves ion)} \end{array} \]

In reality, cannot identify exact origin of Auger electron since

\[
KE = (E_A - E_B) - E_C \\
= E_A - (E_B + E_C)
\]
Regardless, Auger transition is characterized by (a) presence of core hole and (b) location of two final state holes.

For just K shell hole:

For 3 levels, $KL_1 L_1$, $KL_1 L_{2,3}$, $KL_{2,3} L_{2,3}$

For 4 levels $KL_1 L_1$, $KL_1 L_{2,3}$, $KL_{2,3} L_{2,3}$, $KL_1 M_1$, $KL_{2,3} M_1$, $KM_1 M_1$

Auger (electron or x-ray excited) spectra contain closely-spaced groups of multiple peaks!
- **KL\_1L\_1 Auger transition:**
  - initial K hole
  - filled with an L1 electron
  - simultaneously, the other L1 electron is ejected

- **L\_1M\_2M\_1 Auger transition:**
  - initial L hole (2s vacancy)

- **L\_1L\_2M\_1 Coster–Kronig transition**
  - one of the final state vacancies lies in the same shell as the primary vacancy
  - here: initial L1 hole
  - filled with electron from the same shell (but different subshell)
  - much higher rate than normal Auger transitions
  - dominant (here: reducing M to L1 vacancy transitions)
Nomenclature

- Three letters denoting the involved electron states
  - the state of the initial vacancy
  - the state of the electron that fills the vacancy
  - the state of the electron being ejected as an Auger electron
- example: KLL transition
  - initial vacancy on the K shell
  - L electron fills the vacancy
  - L electron is emitted
- indices denote subshells of the electron states (e.g. KL$_{1}$L$_{1}$, KL$_{1}$L$_{3}$, LM$_{1}$M$_{1}$)
- **strongest transitions between electrons whose orbitals are closest together:** KLL, LMM, ...
- Coster-Kronig transitions:
  - vacancy is filled by electron from the same shell.
  - example: LLM

Electronic Structure - Solid State

- In the solid state the core levels of atoms are little perturbed and essentially remain as discrete, localized (i.e. atomic-like) levels.
- The valence orbitals, however, overlap significantly with those of neighboring atoms generating bands of spatially-delocalized energy levels.
- The energy level diagram for the solid is therefore closely resemblant of that of the corresponding isolated atom, except for the levels closest to the vacuum level.
Auger transitions involving the valence band (V)
- Example: Si
- KLL transition: KL\textsubscript{1}L\textsubscript{2,3}
- LVV transition: L\textsubscript{2,3}V\textsubscript{1,2,3}

\[ V \text{ and } V_1 \text{ located at local maxima of the density of states} \]

Even in simple KLL transition, there are a large variety of final states
- \( \hat{E} \) slightly different energies of the Auger electrons
- \( \hat{E} \) slightly different lines in the spectrum
- \( \hat{E} \) final state of the atom is usually described using spectroscopic notation

We can make a rough estimate of the KE of the auger electron from the binding energies of the various levels involved.

The Auger electron has a kinetic energy given by:

\[
E_{\text{Auger}} = E_K - E_{L1} - E_{L2,3} - \phi
\]

where \( E_K \), \( E_{L1} \) and \( E_{L2,3} \) are the binding energies of the \( K_1 \), \( L_1 \) and \( L_{2,3} \) electron orbits of the atom. \( \phi \) is the work function.

Note: the KE of the auger electron is independent of the mechanism of initial core hole formation.
• The transition between different energy levels can occur with varying transition probabilities, which are characteristics for the elements.
• Auger spectra independent from original beam energy.
• For the auger process we need a minimum of two different energy levels and three electrons in an atom.
• Hydrogen and helium are not observable in auger spectroscopy.
Fig. 2.1: Schematic representation of the primary beam – sample interaction in the case of an AES analysis.

X-Ray FL and AES

Fig. 2.4: Schematic representation of the X-ray fluorescence (a) and Auger electron emission (b) processes.
For the example shown before, a hole is created on the K level in the initial ionization step. This requires a primary energy greater than the binding energy of the electron in that shell.

For the ionization to be efficient, a primary energy of about 5 times the binding energy is taken.

In practice, typical primary energies are 5 and 10 keV.

The hole can be produced by either the primary beam, or the backscattered secondary electrons.

The atom relaxes by filling the hole with an electron coming from an outer level, in the example shown as L1.

As a result, the energy difference $E_K - E_{L1}$ becomes available as excess energy, which can be used in two ways:

1) The photon emission of an X-ray at that energy may occur. (x-ray fluorescence –XRF)
   - More likely for deep core hole (high BE) high Z elements

2) Or the energy may be given to another electron, either in the same level or in a more shallow one as is the case in the example, to be ejected. (Auger emission).
   - More likely for shallow core hole (low BE) low Z elements (almost exclusively for Z<15).
   - Fortunately, the probability for Auger emission is much higher for core levels with binding energies below about 2 keV.
Table 4.2: Binding energies of some elements

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<td>Ho</td>
<td>3211</td>
<td>55</td>
<td>54</td>
<td>52</td>
<td>51</td>
<td>50</td>
</tr>
<tr>
<td>51</td>
<td>Er</td>
<td>3361</td>
<td>56</td>
<td>55</td>
<td>53</td>
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</tr>
<tr>
<td>52</td>
<td>Tm</td>
<td>3515</td>
<td>57</td>
<td>56</td>
<td>54</td>
<td>53</td>
<td>52</td>
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<tr>
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<td>3673</td>
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<td>57</td>
<td>55</td>
<td>54</td>
<td>53</td>
</tr>
<tr>
<td>54</td>
<td>Lu</td>
<td>3835</td>
<td>59</td>
<td>58</td>
<td>56</td>
<td>55</td>
<td>54</td>
</tr>
</tbody>
</table>

* 4s, 4p or 4f levels indicated, respectively
In theory, can work out approximate KE of each Auger electron from tables.

Example:

<table>
<thead>
<tr>
<th>Z</th>
<th>BE (eV)</th>
<th>1s</th>
<th>2p_{1/2}</th>
<th>2p_{3/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 Oxygen</td>
<td>532</td>
<td>24</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>9 Fluorine</td>
<td>686</td>
<td>31</td>
<td>9</td>
<td></td>
</tr>
</tbody>
</table>

Core hole ionization of 1s electron BE in O = 532 eV (E_A)

BE of 2p_{1/2} electron in O = 24 eV (E_B)

BE of 2p_{3/2} electron in O = 7 eV (E_C)

Auger electron KE (E_{ABC}) in O = 532 - 24 - 7 \approx 501 eV

The kinetic energy of an Auger electron is independent of the type of primary beam (i.e. electrons or X-rays) and its energy.

- For this reason, AES spectra are always plotted on a kinetic energy scale.
- Since the kinetic energy is only a function of the atomic energy levels, all elements of the periodic table have a unique spectrum.
The AES peaks are superimposed on an important background of different types of secondary electrons.

This is the reason why, in many cases, AES spectra are represented in the differentiated form.

The relative intensities of AES transitions are governed by their respective core shell ionization efficiencies due to the primary electron beam.

Yet, for AES the situation is more complex, since there is additional ionization due to back-scattered electrons.

The back-scattering factors depend both on the energy and the angle of incidence of the primary beam, and they influence the intensities as well as the spatial distribution of the detected Auger electrons as illustrated in Fig. below.

The sample consists of a 40 nm thick Al layer on Au. The Al KLL peak is shown.

In general, AES peaks are broader than XPS peaks. This is related to the complex multiplet splitting due to the number of final states after the transition that are permitted.

The KLL series, for example, consists of five components, i.e. $KL_1L_1$ (1 transitions), $KL_1L_{2,3}$ (2 transitions) and $KL_{2,3}L_{2,3}$ (3 transitions, of which one is forbidden).

Two elements contribute to the peak broadening in solid species: peak overlap in the multiplet structure, and solid state peak broadening.
Observe increases in KE with Z for given set of transitions (more energy available from core-hole relaxation).

Figure 3.6: Auger spectra in the differential distribution characteristic of the lightest elements. The principal peak is the $K_{L_2,M_2}$ peak. The relative intensities are not to scale. (Reproduced from Davis et al. by permission of Perkin-Elmer Corporation)
The Probability of Auger Emission

- AES usually performed using electron source not x-rays (experimentally simpler and cheaper).
- Basic steps in Auger electron creation:
  1. Creation of core hole.
  2. Creation of Auger electron by relaxation.
- For maximum sensitivity of KLL Auger electron with KE 1000 eV, set incident beam energy to ~3000 eV

Backscattered and Secondary Electrons

- Typical E, may be 3 - 30 keV - may penetrate 100's Å into solid Many inelastic collisions produce many low energy secondary electrons, additional Auger electrons or photons.

![Diagram of electron distribution](image)
Auger spectrum contains many unwanted background electrons - Auger peaks appear as small features on intense inelastic background

![Graph](image)

**Figure 4.14.** Typical survey spectrum Ta_2O_5 as a result of a point analysis

Often spectra are differentiated N(E) → N'(E) or dN(E)/dE

![Graph](image)

**Figure 3.3** Auger spectra from a contaminated molybdenum surface in the (a) undifferentiated and (b) differentiated modes. (Reproduced from Grant by permission of John Wiley & Sons)
Chemical Shifts in AES

- The equation \( KE = E_A - E_B - E_C - \phi \) is a "one-electron approximation"
- Should include hole-hole interaction energy (\( H \)) and screening or polarization energy of the surrounding atoms (\( S \))
- KE = \( E_A - E_B - E_C - H - S - \phi \)
- Energy levels sensitive to "chemical environment" of atom in solid (chemical shift).
- Source of shift can come from perturbation of \( E_A, E_B, E_C, H \) or \( S \)?
- In general, difficult to assign one chemical shift to AES spectra
- Rely on "fingerprint" spectra
Chemical shift in Si compounds

Comparison of Si, Si\textsubscript{N\textsubscript{x}}, and Si\textsubscript{O\textsubscript{2}}

Figure 5.4: Auger energy spectra of Si, Si\textsubscript{N\textsubscript{x}}, and Si\textsubscript{O\textsubscript{2}}. (a) shows the total spectrum, whereas (b) gives the KLL Auger peak and (c) the KVV peak. Incident beam current I = 6.1 nA.
Carbon KVV Auger Spectra: (underestimated mode) Each of the three electrons involved can be associated with multiple final states or relaxation effects. Peaks are broadened compared with photoemission peaks.

Difficulties

- Presence of loss features (plasmons, phonons) may confuse.
- AES data vastly complicated by multiple final states and possible intensity shifts.
- Auger spectra difficult to assign or calculate.
- Data more difficult to interpret than XPS.
- Some current theory investigations looking at Auger line shapes.
- Potentially rich spectra - may be able to get many energy levels from single Auger peak envelope.
- AES not used as much as XPS for chemical environment information.
- Used extensively for quantitative compositional analysis.
Instrumentation

**General set-up:**

(i) A primary beam source: an electron gun.

(ii) An electron energy analyzer, combined with a detection system.

(iii) A sample stage, all contained within a vacuum chamber.

- As for most techniques, the system is operated and controlled by a computer, usually provided with software allowing mathematical treatment
Multitechnique system of Physical Electronics combining XPS and AES.

Experimental arrangement
Basic components of an AES system.

Electron spectrometer

- Electron gun
- Ion gun
- Specimen
- Secondary electron detector

Schematic diagram of cylindrical mirror Auger analyser.
The vacuum system

- The electron spectrometer and sample room must be operating under ultra high vacuum (UHV), typically in the range of $10^{-8}$ to $10^{-10}$ torr.

**The reason for this is twofold:**

First: The low energy electrons are elastically and non elastically scattered by residual gas molecules leading to a loss of intensity and of energy so that not only the intensity of the peaks is affected but also the noise in the spectrum increases.

Second: Lowering the vacuum level to e.g. $10^{-6}$ torr, would immediately result in the formation of a monolayer of residual gas absorbed on the sample surface in less than a second.

A vacuum of $10^{-10}$ torr allows measurements to be carried out for about an hour before a mono film is formed. 

*Achieving a depth resolution of a few nanometer with a detection limit lower than 1 % of a monolayer, clearly establishes the high requirements on the vacuum.*

- Even in the case of a vacuum of $10^{-10}$ torr, typically carbon peaks are found as a result of surface contamination. *Therefore, often the sample is cleaned by a slight sputtering, prior to the analysis.*

- Sputtering may induce variations in the surface composition and should be handled with care, especially for a non-destructive analysis of cultural heritage material.

- Turbo molecular pumps, combined with auxiliary tools such as Ti sublimation pumps.

- **Stainless steel is often selected for the fabrication of the analysis chamber and the joints are usually made of Cu rings.**

- The trajectory of the electrons is strongly influenced by the earth’s magnetic and electric fields and consequently a screening is placed around the system.

- All UHV systems need occasionally to be baked out to remove contaminants from the chamber walls, the stage and other contact points.
The electron gun for AES:

- An AES system employs an electron gun, either based on a thermionic or on a field emitter source.
- A thermionic source uses thermal energy to give electrons of sufficient energy to escape over the work function of the source.
- While in a field emission source the work function barrier is reduced.
- The primary beam source in an AES system is comparable to that in scanning electron microscopes (SEM).
- For both techniques, there is an increasing trend of using a field emitter type electron source.
- In the case of a field emission (FE) source, the techniques of AES and SEM are respectively denoted FEAES and FESEM.

In conventional AES: the only function of the incident beam is to produce ionization in the core levels of the atoms in order to initiate the Auger transitions.

- The main characteristic of the electron gun is its brightness: It is defined as the number of electrons emitted per unit area and unit solid angle.
- The simplest form of a thermionic system is a W wire in the shape of a hairpin.
- A small electric current provokes heating in the wire, so that the electrons achieve energies higher than the work function of about 4.5 eV and are able to escape from the wire.
- Yet, most AES systems with a thermionic source use a LaB₆ filament because its brightness is higher compared to W filament sources.
Break through( Field Em.)

- **Field emission** is achieved by applying a strong electrostatic field between a filament, in the shape of a needle with a tip radius of about 50 nm, and an extraction electrode.

- **The filament** is usually a wire of a W single crystal fashioned into a sharp point.

- **The significance** of the small tip radius is that the electric field can be concentrated to extreme levels, up to $10^9$ V/m or more.

- **Applying a high field** results in narrowing the barrier as well in width as in height, allowing the electrons to tunnel directly through the barrier and omitting the requirement of thermal energy.

- **The small area of emission** from the tip into a small solid angle provides a high brightness compared to thermionic sources.

- **Cleanliness of the W single crystal** is extremely important, since adsorption of impurities will increase the work function. Therefore the gun compartment of the instrument is differentially pumped.

- **The final spot size** on the sample surface with a particular FE electron gun is a function of the beam current and the energy.
The cylindrical mirror analyzer

- The CMA, shown in the following figure, consists of two concentric cylinders, the inner cylinder at ground potential while the potential of the outer cylinder is ramped negatively.
- A proportion of the emitted Auger electrons will pass through the defining aperture (slit) in the inner cylinder.
- Depending on the potential applied on the outer cylinder, electrons of the desired energy pass through the detector aperture (exit slit) and are refocused on the electron detector and measured by a channel electron multiplier.
- By scanning the potential, a signal proportional to the number of emitted electrons is obtained as a function of the kinetic energy.
- Unfortunately, the measured spectrum not only contains Auger electrons, but also low energy (typically between 0 and 50 eV) secondary electrons and elastically and inelastically backscattered electrons, with their energies depending on the primary energy that is used (usually between 1 and 10 keV).
• The AES peaks are superimposed as weak features on a relatively intense background.
• Therefore, very often the spectrum is recorded while applying a small ac potential modulation to the analyzer, so that an analogue derivative spectrum is obtained.
• Nowadays, with the use of more sensitive multiple electron detection systems and powerful computer systems, most of the spectra are recorded in the direct mode.
• The signal to noise ratio is improved by scanning the energy over the cylinders several times so that counts are accumulated.
• After recording the spectrum in the direct mode, it can be differentiated numerically as is shown in Fig. next.

Diagram of Electron Gun

- Heated tungsten filament
  -0.1 mm diameter
  • Bent into shape of hairpin with V-shaped tip
  • maintained at potential of 1-50 kV
- Wehnelt cylinder
  • surrounds filament
  • negative bias to filament (0-3000V)
  - electric field of Gun causes electrons to converge at crossover
- Produces a beam of electrons of 1 to 10 keV
  • can be focused onto the surface with diameters of 500 to 5 μm
In order to get best focusing of electrons (minimization of aberrations), CMA’s use a fixed takeoff angle of 42° from surface normal. (typically accepts 42±3°).

\[ E_{pass} = \frac{1.31 V_{outer}}{\ln \left( \frac{r_{outer}}{r_{inner}} \right)} \]
Schematic representation of a cylindrical mirror analyzer (CMA) used in AES

AES spectrum of Ag, (a) direct spectrum, (b) differentiated spectrum. Conditions: \( E_p = 5 \text{ keV}, \Delta E/E = 0.25\% \)
• The sensitivity of the CMA is related to the analyzer transmission function, giving the effective number of electrons that are measured by the analyzer for a particular energy, and is superior compared to the HSA.

• The energy resolution of a CMA is relative to the energy of the peak. Its best relative energy resolution (about 0.25 % ΔE/E) is clearly inferior compared to that of the HSA.

• Therefore, the CMA is not often used for XPS analysis, except maybe in the past where a kind of double CMA was introduced.

• Yet this configuration is no longer considered in new systems.

Double-pass CMA with retarding field:

Two-stage design reduces background due to high-energy electrons inelastically scattered at the walls of the first stage. (Like double monochromator used for Raman spectroscopy to reject all stray light but not to improve resolution). Retarding field acts as high-pass filter, improves resolution over limited range.
The major advantage of the CMA

• Less shadowing effects when analyzing rough surfaces and small particles, which is often the case for cultural heritage materials.

• This is due to the coaxial position of the electron gun and the detector, see prev. Fig. ensuring that the collection of the electrons emitted from the surface is done coaxially around the electron gun.

• **Scanning Auger Microscopy: SAM**

• AES image is obtained by scanning of the primary lens system over the surface. At each position, the intensity of a number of AES peaks is measured, providing information on the lateral distribution of elements.

• **A drawback:** of the use of an electron gun and an analyzer operating under the same angle is that angle resolved depth profiling is not possible.

---

Images of Ni spheres on an In substrate. (a) SEM and (b) coaxial AES imaging based on the Ni mapping.
The ion gun

- Used in both AES and XPS instruments
- Sample sputtering can be performed by means of beams of energetic primary ions.

Sputtering is useful for two reasons.

The first:
- Is to clean the sample prior to the analysis, because often the surface is contaminated with dirt or residual gas from the atmosphere.

The second:
- To record depth profiles, where the composition is probed in depth by the collection of AES or XPS spectra as a function of the sputtering time.

- The ion bombardment is carried out in a sequential manner with the ion gun switched off when the spectrum is recorded.
- The depth profile is built up by the measurement of the intensity of the recorded peaks versus etching or sputtering time.
- The main parameters for sputtering are the energy and the current of the ion beam, the distribution of the current in the sputtered zone and finally the spot size.
Three different types of ion guns

- Used in both XPS and AES systems.

1. The cold static spot gun. (XPS)
2. The electron impact source.
3. The duoplasmatron type.

The cold static spot gun

- Has usually a large beam size of 5 to 10 mm and is therefore only used for large spot XPS depth profiling or for precleaning of the sample.
- The latter operation is often done in a configuration where the ion gun is mounted in a separate chamber, called preparation vacuum chamber.
- The gun is back-filled with an inert gas such as Ar having a pressure of about 10^{-6} torr, with a variable potential between 1 and 10 kV.
- A discharge to form Ar^+ is realized by an external magnet and the positively ions are accelerated and extracted by a simple focus electrode.
The electron impact source

- The ions are created by electrons emitted by a heated filament, accelerated into a cylindrical grid, where they collide with Ar gas atoms.

- The ion energy is controlled by the potential applied to the grid and ion energies up to 5 kV can be achieved.

- This ion source produces an ion beam with a narrow energy spread and spot sizes from 2 mm to 50 μm.

- It can be operated in static mode or it can be rastered over the surface to produce a larger and more uniform crater.

The duoplasmatron type

- For the rapid removal of material and etching of large areas (preferred).

- A magnetically constricted arc is used to produce a dense plasma from which the ion beam is extracted, focused and rastered across the specimen by a set of deflector plates.

- This type of gun provides intense ion beams with a narrow energy spread, very suitable for small spot focusing.

- However, due to its high price, it is not so much used in AES or XPS systems in contrast to secondary ion microscopy (SIMS) instruments.
The sample holder and stage

- The mounting of the samples on the sample holder should be done in such a way that electrical conduction is guaranteed.
- This is achieved by using metallic clips or bolt-down assemblies.
- Alternatively a metal loaded tape may also be used.
- In the case of powders, the particles can be pressed into an indium foil.
- The sample holder is mounted on a sample stage which allows for high resolution positioning in the x,y,z and θ directions.
- In new systems (and highly appreciated in industrial laboratories) remote control stages are introduced.

In this manner, in an automated fashion, different sample areas may be analyzed, and if a parking stage is available, an automatic exchange of samples is possible.

In most research instruments in use in university laboratories, the sample size is limited in area to a few cm² and in thickness to a few mm.

In some systems additional sample manipulation facilities are present such as: cooling or heating of the sample holder in situ during the analysis.

A valuable tool in materials characterization is a separate preparation chamber connected to the analysis system, enabling sample treatments such as heating or tensile testing.

After pretreatment, the sample is introduced into the vacuum chamber for analysis through a lock gate without coming in contact with the air.
• The angle between the ion beam, the primary beam and the detected electron beam may induce shadowing and re-deposition effects when sputtering rough surfaces.
• To optimize the sputtering conditions, a sample stage with tilt and rotation capabilities is useful.

Sample Requirements

• The AES method is based on the use of an primary beam of electrons.
• This means that in principle the sample has to be conductive.
• In general, a sample can be analyzed in AES if one can obtain good SEM pictures from it without coating.
• For AES investigations, isolating samples cannot be coated with a conductive C or Au layer as is commonly done in SEM-EDX analysis since the escape depth of the Auger electrons is only a few nm.
• Thus, AES is especially appreciated for the analysis of metals and passive films on metals, but there is a growing tendency to analyze semi conducting and ceramic materials with it.
• Eg: Al covered with a non conducting oxide film of about 0.1 μm is measurable.
• Both for XPS and AES, the samples should be stable in a UHV system of $10^{-10}$ torr.

• Polymers with low vapor pressure, wet samples and porous materials need to be handled with care.

• Many cultural heritage materials belong to this category.

Most operators prefer flat samples:
• Firstly because the interpretation of the data is more straightforward
• Secondly because roughness deteriorates the depth resolution in sputtering mode.

---

**Information in AES spectra**

1- *Surface analysis:*
• The primary beam has a penetration depth of a few micrometers. Auger electron (AES) can only travel a limited distance, called attenuation length $\lambda$, before being elastically scattered.
• The characteristic depth $d$ from which Auger electrons are emitted, called the escape depth, is given by:
  $$d = \lambda(E) \cos \theta$$
where $\theta$ is the angle of emission from the surface normal.
• The attenuation length varies according to the element which is emitting the electron and to the matrix, and depends on the energy of the emission.
Typical values of $\lambda$ are, in the range of 1 to 10 atom layers

Dependence of attenuation length $\lambda$ on the emitted electron energy

Qualitative analysis

- The qualitative analysis of a specimen consists in identifying the elements that are present.
- For this purpose, a survey or wide energy scan spectrum is recorded.
- Each element has a characteristic AES spectrum.
- The spectra of all elements can be found.
- Nowadays instrumentation, both for XPS and AES, is equipped with data treatment systems running automatic peak identification tools.
- The identification of the composing elements of a sample under investigation is in most cases straightforward, except if peaks are overlapping.
- The nature of the specimen is important: conductive specimens can be analyzed by AES.
Qualitative analysis

Elemental identification procedure

1. First, the main Auger peak positions are identified.
2. These values are correlated with the listed values in the Auger spectra book or standard tables. The main chemical elements are thus identified.
3. The identified element and transition are labeled in the spectrum (close to the negative jump in the differential spectrum).
4. The procedure is repeated for so-far unidentified peaks.

Example:
From the differential AES spectrum Ni, Fe and Cr have been identified.
Quantitative analysis

• The determination of the surface composition of a specimen is more complicated.
• To this purpose, data is collected in the multiplex mode.
• The relevant energy windows are selected, and the peak intensities are measured with high energy resolution and signal-to-noise ratio.
• The proportion between the peak intensity and the concentration of the emitting element depends in a complex manner: on the intensity of the primary beam, the ionization cross section, on the probability of Auger transition in the case of AES, on the attenuation length, on the spectrometer transmission efficiency and on the detector efficiency.
• A more practical approach consists in incorporating those parameters into sensitivity factors.

- The intensity of a signal from an element A, $I_A$, in a solid is proportional to its molar fraction $x_A$:

$$x_A = I_A / I_{A0}$$

where $I_{A0}$ is the intensity from a pure A sample, and may be considered as a sensitivity factor.
• By using data treatment software is a set of relative sensitivity factors, normalized to a reference element. For this reference, in most cases Cu or Ag, the sensitivity factor is set to unity.
• An additional difficulty encountered in quantitative analysis is the determination of the peak areas AES peaks area, appear on a background. Auger peaks are almost always on sloping background & Asymmetry in peak shape.
• In some cases, the background correction is not straightforward.
• In most commercial data handling systems different possibilities exist.
• The simplest one is the straight line between two suitably chosen points.
Auger spectrum - quantification

Can use peak areas or peak-to-background ratios

Quantitative surface analysis: AES
Quantitative analysis

1. Measuring the peak-to-peak height

2. Measuring the peak area (after background subtraction)

Chemical analysis

• XPS and AES not only allow to identify and quantify the constituting elements of a sample, but make it also possible to obtain information on their chemical state.

• In this respect, XPS is favored with respect to AES, and the reason for it is to be found in the nature of the respective transitions that are used in both methods.

• In AES, the situation is less promising.

• Firstly: most AES lines are by nature broader than XPS lines.

• Secondly: the Auger transition involves three electrons and the overall chemical shift is influenced by the three energy levels concerned.

• In general, similar shifts of a few eV are to be expected, especially when core electrons are involved in the transition.

• Since in AES-specific equipment, detectors with lower energy resolution are used it is clear that chemical shifts are not often measured accurately.
Moreover, peaks corresponding to transitions with valence electrons are broad and poorly defined, which makes the assignment of chemical shifts nearly impossible.

In that case, the identification of the chemical state may be done by a peak shape analysis.

In fact the shape of a CVV or CCV peak, C being a core level, is related to the density of states (DOS) in the valence band.

Since the DOS varies from one chemical environment to another, a variation in peak shape may be observed.

This effect is commonly noticed in Auger spectra of non-metallic elements such as C, S, O, N.

- Peak shape and the energy values, corresponding to maxima contain information on the nature of the environment, due to addition relaxation effects during the Auger process.
- A full theoretical model is difficult to construct.
- In practice, Auger spectra of standard samples are used and the results are drawn from spectra comparison.
Auger Spectrum

In-depth analysis

- XPS and AES can be used to provide compositional information as a function of depth.
- It can be obtained by non-destructive and destructive techniques.
- The two most commonly applied methods:
  - 1- angular resolved measurements (for XPS)
  - 2- Ion sputtering (AES)
Surface Analysis Depths

Sputter profiles:
- Sputtering is a destructive method.
- The sample is bombarded with highly energetic ions (mostly Ar\(^+\) ions with an energy of 1 to 5 keV), the surface atoms are sputtered away and the residual surface is analyzed.
- By this technique, layers up to 1 to 2 \(\mu\)m are accessible.
- AES or XPS spectra are recorded, either discontinuously after the subsequent sputter steps or simultaneously with the sputtering.
- The original data consist of signal intensities of the detected elements, mostly peak-to-peak heights in AES and peak areas in XPS, as a function of sputtering time.
- A typical example is shown:
Depth profiling - schematic

Process is fully automated, sample can be rotated (Zalar rotation).
N.B. Can also perform angle-resolved analysis.

Depth profiling CeO$_2$ buffer layer

Auger spectra of depth profile of CeO$_2$ buffer layers.
AES Imaging and Depth Profiling: An Example

Electron Beam in combination with an SDD detector allows for imaging of the sample to select the area for analysis.

Depth profile of thin elements in point electron-atom collisions in electron microscopes allows for element concentration distribution in thin profiles.

AES Depth Profiling: An Example

Al/Pd/GaN sample: as grown

Schematic of Profile

(cross section)
AES Depth Profiling: An Example

Data analysis

- Data analysis is a technique that may be helpful in interpreting multidimensional data sets with overlapping spectral features.

They are generated:

- Either in chemical analysis problems where the same spectral region is studied on different samples (e.g. metal oxide, hydroxide, sulphide, …),
- Or either in depth profiling studies where the same sample is measured under different conditions (e.g., a paint layer on top of a substrate).
- The two most commonly applied multivariate techniques are LLSF (linear least squares fitting) and FA (factor analysis).
- Both assume that each spectrum can be represented by a linear combination of component spectra.
Scanning Auger microscopy, Scanning Auger Microprobe

Electrons can be focused to a spot of < 1 nanometer
Penetration depth and scattering within solid typically limit resolution to ~ 20 nanometer. Recent instruments claim resolution of ~ 6 nm. Often use hemispherical analyzer because of its better geometric properties.

Electrons penetrate very deep
Auger electrons (~500-1000 eV) come from topmost few nanometers
Imaging

• Distributions of elements and chemical states over the surface are measurable using rastering techniques.
• Imaging in AES is also named SAM, (Scanning Auger Microscopy).
• A well focused incident electron beam is rastered over the surface, and the relevant spectra are collected.
• Peak intensities are translated into gray scale values.
• The smaller the spot size, the smaller the influence of the back-scattering.
• For spot sizes larger than 100 nm, the back-scattering phenomena may modify the images in a complex manner.
Auger mapping

Pixel-by-pixel, typically calculate;
(peak-background)/background
SEM and Auger images of an aluminium oxide surface, in absence and presence of fluorine contamination.

**AES – nm lateral and depth resolution**

Chromated aluminium alloy surface

- Chromating pretreatment
  - Corrosion protection
  - Before coating, painting, bending, etc
- Does the chromate "passivate" intermetallic particles?
- Auger spectra show that the intermetallic particles are covered by a thin layer of Cr-oxide that is invisible in the SEM images.
AES identified the composition of grain boundary particles to be Sb and Cr. These phases resulted in the embrittlement of an aged steel rotor.

Advantages and Disadvantages

**Advantages**
- Surface Sensitive
- Elemental and Chemical composition and analysis by comparing sample to known samples.
- Quantitative composition information as a function of depth below the surface
- Good for spatial distribution of elements in sample (structure).

**Disadvantages**
- Samples must be able to compatible with ultra high vacuum
- Samples must be conductive
- Possibility of beam damage for organic molecules
- Cannot detect hydrogen or helium
- Quantitative detection is dependent on the element, but accurate to high sensitivity
AES – A PERSPECTIVE

- **Elements**: Li and above.
- **Sensitivity**: 0.1 – 1 atomic %
- **Destructive**: No, some beam damage to sensitive materials.
- **Elemental Analysis**: Yes, semi-quantitative without standards, quantitative with standards, not a trace analysis technique.
- **Chemical State Information**: Yes, for some elements, sometimes requires high-resolution analyzer.
- **Depth Resolution**: 0.5 – 5 nm.
- **Lateral Resolution**: 500 nm.
- **Sample Types**: Solid UHV-compatible, conducting, semiconducting.