5.8 Auger Electron Spectroscopy (AES)

5.8.1 The Auger Process

X-ray and high energy electron bombardment of atom can create core hole
Core hole will eventually decay via either

(i) photon emission (x-ray fluorescence -XRF)
more likely for deep core hole (high BE)
high Z elements
or (ii) radiationless internal rearrangement (Auger process)
more likely for shallow core hole (low BE)
low Z elements (almost exclusively for Z<15)

Auger process is a three electron process and leaves atom doubly-ionized
- occurs independently of incident excitation (doesn't "compete" with photoemission)
• Photon not much use for surface analysis since propagates large distances in solid (but is used for x-ray microprobe analysis in SEM/TEM)

• Auger electrons produced with similar kinetic energies to photoelectrons so similar surface sensitivity

• Initial core hole can be generated by x-rays

  see Auger peaks in XPS

  or electrons (most common in AES)

  spectrum contains Auger, incident and inelastically scattered electrons

  but no photoemission peaks!

In simple, one-electron picture (ignoring relaxation or final state effects),

\[
\begin{align*}
\text{X-ray photon} & \quad h\nu \approx E_A - E_B \\
\text{Auger electron} & \quad KE \approx \underbrace{E_A - E_B}_{\text{energy gained by core-hole annihilation}} - \underbrace{E_C - \phi}_{\text{energy needed to overcome BE of Auger electron}}
\end{align*}
\]
In theory, can work out approximate KE of each Auger electron from tables

Example:

<table>
<thead>
<tr>
<th>Z</th>
<th>BE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1s</td>
</tr>
<tr>
<td>8</td>
<td>Oxygen</td>
</tr>
<tr>
<td>9</td>
<td>Fluorine</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\textsubscript{3/2} electron in O = 7 eV (E\textsubscript{C})

Auger electron KE (E\textsubscript{ABC}) in O = 532 - 24 - 7 ≈ 501 eV

Sometimes BE is "scaled" to a value between Z (O) and (Z+1) (F) to account for relaxation effects

\[ KE \approx E_A(Z) - E_B(Z + 0.5) - E_C(Z + 0.5) - \phi \]

\[ E_{ABC} \approx 532 - 27.5 - 8 = 496.5 \text{ eV} \]

Observe increases in KE with Z for given set of transitions (more energy available from core-hole relaxation)

While KE of Auger electron is \textit{independent of excitation energy}, apparent BE will change depending upon x-ray \( h\nu \) in XPS (only)

Experimental KE of O KLL Auger electron is 508.3 eV (fixed)

Apparent BE of O Auger with \( h\nu = 1253.6 \) eV is 745.3 eV

Apparent BE of O Auger with \( h\nu = 1486.6 \) eV is 978.3 eV

\[ \Delta = 233.0 \text{ eV} = h\nu(\text{Al K}\alpha_{1,2} - \text{Mg K}\alpha_{1,2}) \]
5.8.2 Auger Transition Notation

Auger electrons designated by x-ray notation as KLL, KL$_1$L$_{2,3}$, L$_{2,3}$M$_{2,3}$M$_{4,5}$ 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)

\[ \text{KL}_1 \text{L}_{2,3} = \begin{align*} &K \quad L_1 \quad L_{2,3} \\ &\text{(1s)} \quad \text{(2s)} \quad \text{(2p)} \end{align*} \]

\[ \begin{align*} &\text{KL}_1 \text{L}_{2,3} = \begin{align*} &K \quad L_1 \quad L_{2,3} \\ &\text{(1s)} \quad \text{(2s)} \quad \text{(2p)} \end{align*} \\ &\text{KL}_1 \text{L}_{2,3} = \begin{align*} &K \quad L_1 \quad L_{2,3} \\ &\text{(1s)} \quad \text{(2s)} \quad \text{(2p)} \end{align*} \]

\[ \text{KVV} = \begin{align*} &K \quad V \quad V \\ &\text{(1s)} \quad \text{(Valence)} \quad \text{(Valence)} \end{align*} \]

\[ \begin{align*} &\text{KVV} = \begin{align*} &K \quad V \quad V \\ &\text{(1s)} \quad \text{(Valence)} \quad \text{(Valence)} \end{align*} \\ &\text{KVV} = \begin{align*} &K \quad V \quad V \\ &\text{(1s)} \quad \text{(Valence)} \quad \text{(Valence)} \end{align*} \]

In reality, cannot identify exact origin of Auger electron since

\[ KE = (E_A - E_B) - E_C \]

\[ = E_A - (E_B + E_C) \]
Usual to think of left-hand process

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\textsubscript{1}L\textsubscript{1}, KL\textsubscript{1}L\textsubscript{2,3}, KL\textsubscript{2,3}L\textsubscript{2,3}

For 4 levels KL\textsubscript{1}L\textsubscript{1}, KL\textsubscript{1}L\textsubscript{2,3}, KL\textsubscript{2,3}L\textsubscript{2,3}, KL\textsubscript{1}M\textsubscript{1}, KL\textsubscript{2,3}M\textsubscript{1}, KM\textsubscript{1}M\textsubscript{1}

Auger (electron or x-ray excited) spectra contain closely-spaced groups of multiple peaks!

5.8.3 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
Probability (cross-section $\sigma$) of creating core hole electron through (1)

$$\sigma = \text{Constant} \cdot \frac{C \left( \frac{E_i}{E_A} \right)}{E_A^2}$$

where $E_i$ is incident electron beam energy, $E_A$ is core hole BE and $C$ is a constant (depends on core level)

typical values $10^{-3}$ to $10^{-4}$

many incident electrons needed for 1 ionization event

$\sigma$ reaches maximum about $3 \cdot E_A$

![Graph](image)

**Figure 4.5.** Variation of the ionization cross-section with the ratio of primary electron beam energy $E_p$ and core level energy $E_w$

For maximum sensitivity of KLL Auger electron with KE 1000 eV, set incident beam energy to $\sim 3000$ eV

Probability of Auger emission (probability $\gamma$) through process (2) following core hole creation competes with XRF
Auger emission favored for low Z elements
Probability varies with Z and core hole location (K, L, M… )

5.8.4 Backscattered and Secondary Electrons

Typical $E_i$ 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

Figure 4.6. Emission probability of an Auger electron (A) or photon (X)

Figure 4.1. Distribution (schematic) of primary, backscattered and Auger electrons together with X-rays
Such backscattered electrons contribute to spectrum - can originate from deep within solid

![Diagram of Auger spectrum](image)

**Figure 4.3.** Schematic representation of an Auger spectrum

True Auger electrons behave according to "universal curve" as in XPS

\[
I = I_0 \exp \left( \frac{-d}{\lambda \cos \theta} \right)
\]

\[
\ln \left( \frac{I}{I_0} \right) = \frac{-d}{\lambda \cos \theta}
\]

When \( \ln \left( \frac{I}{I_0} \right) = 0.05 \) (95% electrons), \( d \approx 3 \cdot \lambda \)
Consequence?

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 $\text{T}_2\text{O}_5$ as a result of a point analysis

Often spectra are differentiated $N(E) \rightarrow N'(E)$ 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\textsuperscript{1} by permission of John Wiley & Sons)
5.8.5 Chemical Shifts in AES

The equation

\[ KE \approx E_A - E_B - E_C - \phi \]

is a "one-electron approximation"

Should include hole-hole interaction energy (H) and screening or polarization energy of the surrounding atoms (S)

\[ KE = E_A - E_B - E_C - H - S - \phi \]

As in XPS, energy levels sensitive to "chemical environment" of atom in solid - chemical shift

But 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

---

**Figure 4.15.** Differentiated AES spectra of Titanium as function of their kinetic energy for: (a) TiC; (b) TiO; (c) TiO\(_2\) and (d) TiN
Can see chemical shifts in AES but

Each of the three electrons involved can be associated with multiple final states or relaxation effects

Peaks are broadened compared with photoemission peaks

![Graph showing AES peaks for different gases](Image)

Figure 3.12 Carbon KVV Auger spectra in the undifferentiated mode from gaseous methane, ethylene and acetylene, showing the differences in the fine structure. (Reproduced from Houston and Rye\textsuperscript{13} by permission of the American Institute of Physics)

Presence of loss features (plasmons, phonons) may confuse

AES data vastly complicated by \textit{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 lineshapes

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
5.9 Instrumentation for AES

Electron (or x-ray) source, sample, electron energy analyzer (monochromator), electron detector, readout and data processing

5.9.1 Electron Sources (Electron Guns)

Two common types (i) thermionic emission (ii) field emission

(i) thermionic emission is based on Boltzmann distribution of electron energies in metal

at high temperature, small fraction of electron have enough energy to escape $\phi$

typical heated filament materials include W, W(Ir) or LaB$_6$ - low $\phi$

(ii) field emission guns (FEG)

use large electric field gradients to remove electrons by tunneling

emission material fashioned to sharp point for best electron flux and beam diameter
In both type:

Lenses electrostatically manipulate beam - extract, collimate, focus and scan (deflection plates)

Minimum diameters of 20 nm can be achieved with care

Current >10 mA to <1 nA used (*space-charge effects* limit current at low beam energies and diameter)

5.9.2 Electron Energy Analyzers

Since Auger peaks are generally broader than photoemission peaks

- do not need high resolution analyzer (concentric hemispherical analyzer - CHA)

- do need good (angular) collection efficiency
Cylindrical Mirror Analyzer (CMA):

- Single or double-pass (higher resolution)
- Large angular acceptance
- Often contain integral electron gun
- Scanned by varying potentials on inner and outer cylinders
- No retarding to fixed pass energy so analyzer resolution varies with electron KE (but still less than peak FWHM)

Figure 2.29 Diagram of a double-pass CMA, used for both XPS and AES. Electrons are retarded to a constant pass energy for XPS via two spherical grids at the entrance to the first stage, centred on the source area on the sample. The exit aperture of the first stage constitutes the entrance aperture to the second stage. The entrance and exit apertures to the second stage can be changed remotely through an external rotary motion drive. For AES the retard grids are grounded, and so is the inner cylinder. (Reproduced from Palmberg by permission of Elsevier Scientific Publishing Company)
5.10 Applications of AES

5.10.1 Quantitative AES

\[ I_a = \Phi_{\text{electrons}}(x,y) \times P_{\text{backscatter}}(E, \theta, \text{material}) \]
\[ \times C_a(x,y,d) \times \sigma_a(E,n,l) \times P_{\text{Auger}}(ABC) \]
\[ \times P_{\text{no-loss}}(\text{material},d) \times A_{\text{analyzer}} \times T_{\text{analyzer}}(KE) \]

where

- \( \Phi_{\text{electrons}}(x,y) \) - incident electron flux
- \( P_{\text{backscatter}}(E, \theta, \text{material}) \) - proportion electrons backscattered causing additional Auger electrons
- \( C_a(x,y,d) \) - concentration of element a
- \( \sigma_a(E,n,l) \) - subshell (core hole) ionization cross-section
- \( P_{\text{Auger}}(ABC) \) - probability of Auger process defined by three sets of quantum numbers
- \( P_{\text{no-loss}}(\text{material},d) \) - probability of no-loss escape
- \( A_{\text{analyzer}} \) - angular acceptance of analyzer
- \( T_{\text{analyzer}}(KE) \) - transmission function of analyzer

Many factors similar to XPS

- extra terms \( P_{\text{backscatter}} \) and \( P_{\text{Auger}}(ABC) \)
- incident electron energy \( E \) is variable (1-5 keV)
- \( P_{\text{backscatter}} \) is complex function of material and incident energy - difficult to calculate
- electrons detected from outside irradiated area due to backscattered electrons

- diameter of analyzed area 2-5× irradiated area

Electron Beam

Auger electrons excited by backscattered electrons and emitted

Auger electrons excited by incident beam and emitted

Backscattered incident electrons emitted following losses

Auger electrons excited but not emitted

Empirical observations of $\sigma_a$ versus E and Z produce useable estimates for composition (though may be up to 50% inaccurate)

### Table 4.3. AES transitions and their relative sensitivity factors

<table>
<thead>
<tr>
<th>Element</th>
<th>AES rel. sensitivity at 3 keV</th>
<th>AES rel. sensitivity at 10 keV</th>
<th>AES transition</th>
<th>Atomic Number</th>
<th>Atomic Volume $V$ (×10^6 m³/mol)</th>
<th>Relative Sensitivity Factors</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>4.1</td>
<td>12</td>
<td>1H</td>
<td>1</td>
<td>0.015</td>
<td>0.075</td>
</tr>
<tr>
<td>He</td>
<td>18</td>
<td>56</td>
<td>1He</td>
<td>2</td>
<td>0.058</td>
<td>0.252</td>
</tr>
<tr>
<td>Li</td>
<td>7.1</td>
<td>21</td>
<td>7Li</td>
<td>3</td>
<td>0.032</td>
<td>0.043</td>
</tr>
<tr>
<td>Be</td>
<td>5.0</td>
<td>16</td>
<td>5Be</td>
<td>4</td>
<td>0.036</td>
<td>0.043</td>
</tr>
<tr>
<td>B</td>
<td>4.6</td>
<td>3.3</td>
<td>4.6</td>
<td>5</td>
<td>0.036</td>
<td>0.043</td>
</tr>
<tr>
<td>C</td>
<td>3.1</td>
<td>13</td>
<td>3C</td>
<td>6</td>
<td>0.036</td>
<td>0.043</td>
</tr>
<tr>
<td>N</td>
<td>13.3</td>
<td>40</td>
<td>13N</td>
<td>7</td>
<td>0.036</td>
<td>0.043</td>
</tr>
<tr>
<td>O</td>
<td>18.0</td>
<td>56</td>
<td>18O</td>
<td>8</td>
<td>0.036</td>
<td>0.043</td>
</tr>
</tbody>
</table>

- relative sensitivity factors (RSF)
\[ I_{\text{true}} = \frac{I_{\text{measured}}}{RSF} \]

- approximately compensate for \( P_{\text{backscatter}} \), \( P_{\text{Auger}} \), \( \sigma \), and \( P_{\text{no-loss}} \) at fixed \( E \)

But must be measured under identical conditions to reduce uncertainty in \( P_{\text{backscatter}} \)

Best method for quantitative AES is to standardize using known system

In the case of monolayer films it is possible to remove uncertainties in \( \sigma \) and \( P_{\text{backscatter}} \) by comparison with other techniques

- electrochemical (cyclic voltametry)
- desorption measurements
- electron diffraction (LEED or RHEED)

5.10.2 Film Growth Mechanisms

AES signals in layer-by-layer growth?

Linear decrease in \( B \) due to attenuation

Linear increase in \( A \) submonolayer as concentration increases

Slower increase in \( A \) after 1 ML due to attenuation of second layer
In principle, can determine growth mode by examining behavior of AES (or XPS) signal with exposure - ignores changes in sticking probability $S$

$$S = \frac{\text{# species that remain adsorbed}}{\text{# species that strike surface}} \quad 0 < S < 1$$
5.10.3 Elemental Mapping - The Scanning Auger Microprobe (SAM)

Electron beam can be rapidly scanned in x or y direction across surface

- line scan
- monitor intensity of Auger peaks as function of x or y position

![Diagram of electron beam scanning](image)

**Figure 4.19.** Section of a stainless steel sample covered with a layer of TiN of thickness \( d \). The vertical arrows indicate the limits of displacement of the electron beam.

![Graph of atomic concentration](image)

**Figure 4.18.** Example of a line scan over the crater edge produced by ball cratering showing the atomic concentration as a function of the displacement of the electron beam. The crater edge is located approximately at \( x = 500 \) \( \mu \text{m} \)

- need narrow primary electron beam (affects lateral resolution)

If primary beam is scanned in x and y directions
- can map elemental composition
- scanning Auger microprobe
- resolution <1 µm possible
- image acquired in <10 s (dynamic surfaces?)

Scanning electron micrograph (SEM) image of surface defect (etch pit) on stainless steel
SAM Fe LMM Auger image

SAM C KLL Auger image

SAM O KLL Auger image
5.11 Summary

Simple and inexpensive instrumentation
- electron gun and CMA
- XPS instrumentation (x-ray source and CHA)
- modified LEED apparatus (RFA)

Rapid analysis with good S/N (especially \( N'(E) \) and \( N''(E) \) spectra)
- typically faster than XPS

Sensitive to all elements except H and He, sensitivity <1% of ML for low Z elements (<\(10^{13} \) atoms·cm\(^{-2}\))
- can vary sensitivity somewhat by changing incident beam energy

Precision better than 5 %

Extensively used for elemental mapping (SAM) with < 1 \( \mu \)m resolution (minimum \(~50\ \text{Å}\))
- much easier than x-ray beam

Semi-quantitative (especially if used with standards)

Some chemical shift information

BUT

Auger spectrum must be differentiated for good sensitivity

One electron picture less reliable than XPS
- Chemical shift information embedded in complex spectra
- Multiple final states/loss features produce complex/broadened spectra

Large electron flux may induce chemistry in sensitive materials
Lateral resolution of incident beam always degraded in analyzed beam
- focus to <1 μm not trivial

Relative sensitivity factors alone produce estimates of composition only (50 %) without careful standardization