Auger Electron Spectrometry

EMSE-515

F. Ernst
Principle of AES

- electron or photon in, electron out
- radiation-less transition → Auger electron
- electron energy ⇒ properties of atom
Brief History of Auger Electron Spectrometry

1923 discovered by Lise Meitner

- reported in Zeitschrift für Physik
- two years before Pierre Auger (?)
- but: English speaking scientific (?) community came to attach Auger’s name to it

1953 J. J. Lander: idea of using electron-stimulated Auger signals for surface analysis

1967 Larry Harris: demonstrated use of spectrum differentiation for enhancing the Auger signals

today AES: very frequent analytical method for surfaces, thin-films, and interface compositions
Brief History of Auger Electron Spectrometry

Lise Meitner

Pierre Auger
Basic Concept

- escape depth of Auger electrons: 1...3 nm
- identification of elements via binding energies of electrons near the core
- energy of an Auger electron:
  - difference in binding energies between
    - the vacant state
    - the electron that fills the vacant state
  - energy loss associated with reaching the surface
Examples of Two-Electron De-Excitation

• KL\textsubscript{1}L\textsubscript{1} Auger transition:
  ◦ initial K hole, filled with an L\textsubscript{1} electron
  ◦ simultaneously, the other L\textsubscript{1} electron is ejected

• LM\textsubscript{1}M\textsubscript{1} Auger transition:
  ◦ initial L hole (2s vacancy)

• L\textsubscript{1}L\textsubscript{2}M\textsubscript{1} Coster–Kronig transition
  ◦ final state vacancy in the same shell as primary vacancy
  ◦ here: initial L\textsubscript{1} hole, filled with electron from the same shell (but different subshell)
  → much higher rate than normal Auger transitions
  → dominant (here: reducing M to L\textsubscript{1} vacancy transitions)
Examples of Two-Electron De-Exitation

M
  M₁
 L₃
  L₂
   L₁
K

AUGER
(K L₁ L₁)
K-SHELL

INITIAL
VACANCY

L₁-SUBSHELL

AUGER
(L₁M₁ M₁)

COSTER-KRONIG
(L₁L₂M₁)
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 → Auger electron

- no dipole selection rules as for photon emission

- example: KLL transition
  - initial vacancy on the K shell
  - L electron fills the vacancy
  - L electron is emitted

- subscripts denote subshells (e.g. KL₁L₁, KL₁L₃, LM₁M₁)
Nomenclature

- 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

- Auger transitions involving the valence band (V)
  - example: Si
  - KLL transition: \( KL_1 L_{2,3} \)
  - LVV transition: \( L_{2,3} V_1 V_2 \)
  - \( V_1 \) and \( V_2 \) located at local maxima of the density of states
Auger Transitions Involving the Valence Band: Si
Nomenclature

• even in simple KLL transition, there are a large variety of final states
  ⇒ slightly different energies of the Auger electrons
  ⇒ slightly different lines in the spectrum
  ⇒ final state of the atom is usually described using spectroscopic notation

• example: KL₁L₁ transition
  ◦ initial state: 1s hole
  ◦ final state: 2s shell empty (two vacancies)
  ◦ 2p shell occupied with 6 electrons
  ⇒ final state: 2s⁰2p⁶
Nomenclature

• example: KL₁L₁ transition (continued)
  ◦ states correspond to the possible allowed quantum numbers consistent with Pauli principle:

  \[ m_S = -1, 0, +1; \quad M_L = 0; M_S = 0 \]

  \( m_S \): magnetic quantum number, \( M_L \): total orbital angular momentum, \( M_S \): total spin angular momentum.

  ◦ total orbital momentum of zero → denoted as \(^1S\)

  \(^1S\) is the only allowed final state, thus this notation is redundant

  → complete description: KL₁L₁–2s⁰2p⁶ \(^1S\)
Nomenclature

- example: KL\textsubscript{1}L\textsubscript{2} or KL\textsubscript{1}L\textsubscript{3} transition
  - initial state: 1s hole
  - final state: one vacancy in 2s shell, one in 2p shell
  - 2s shell occupied with 1 electron, 2p shell with 5 electrons
  - final state: 2s\textsuperscript{1}2p\textsuperscript{5}
    - possible quantum states: \(^1\)P and \(^3\)P (spins aligned or anti-aligned)
      - P: total orbital angular momentum \(L = 1\).
    - corresponds to two states coupling to total angular momentum
      
      \[ L = 1 \]
Nomenclature

- example: KL₁L₂ or KL₁L₃ transition (continued)
  - a P state with
    - the electron spins aligned: ³P
    - the electron spins anti-aligned: ¹P
  - complete description:
    - KL₁L₂–2s¹2p⁵ (¹P), or
    - KL₁L₃–2s¹2p⁵ (³P)
Nomenclature

• example: KL₂L₂, KL₂L₃, or KL₃L₃ transition
  ◦ initial state: 1s hole
  ◦ final state: two vacancies in 2p shell
  ◦ 6 electrons remain in the L shell
→ final states can couple to total angular momenti of
  · S (L = 0)
  · P (L = 1)
  · D (L = 2)
⇒ KLL transitions yield six different final states:
  · KL₁L₁–2s⁰2p⁶ (¹S)
  · KL₁L₂,₃–2s¹2p⁵ (¹P, ³P)
  · KL₂,₃L₂,₃–2s²2p⁴ (¹D, ³P, ¹S)
Nomenclature

- spectrum showing six different states for Mg
  - KL\textsubscript{2,3}L\textsubscript{2,3}−2s\textsuperscript{2}2p\textsuperscript{4} (\textsuperscript{3}P) not observed – small intensity
Energies

• energy of Auger electrons: consider difference of the total energy before and after the transition

• empirical approach:

\[ E_{\alpha\beta\gamma}^Z = E_{\alpha}^Z - E_{\beta}^Z - E_{\gamma}^Z - \frac{1}{2} \left( E_{\gamma}^{Z+1} - E_{\gamma}^Z + E_{\beta}^{Z+1} - E_{\beta}^Z \right) \]

\( E_{\alpha\beta\gamma}^Z \): Auger energy of the transition \( \alpha\beta\gamma \) of element \( Z \).

○ first three terms: difference in binding energies of shells \( \alpha^Z, \beta^Z, \gamma^Z \)

○ correction term (small): average of increase in binding energy of
  • the \( \gamma \)-electron when a \( \beta \)-electron is removed
  • the \( \beta \)-electron when a \( \gamma \)-electron is removed
**Numerical Example:**

**KL$_1$L$_2$ Auger Transition in Ni**

- estimate for the energy of the Auger electron:

\[
E_{KL_1L_2}^{Ni} = E_K^{Ni} - E_{L_1}^{Ni} - E_{L_2}^{Ni} - \frac{1}{2} \left( E_{L_2}^{Cu} - E_{L_2}^{Ni} + E_{L_1}^{Cu} - E_{L_1}^{Ni} \right)
\]

- electron binding energies (keV):

\[
\begin{align*}
E_K^{Ni} &= 8.333 \\
-E_{L_1}^{Ni} &= 1.008 \\
-E_{L_2}^{Ni} &= 0.872 \\
-E_{L_1}^{Ni} &= 0.872 \\
\end{align*}
\]

\[
\Sigma = 0.645 \\
\Sigma = 0.079 \\
\Sigma = 0.088 \\
\]

\[
E_{KL_1L_2}^{Ni} = 6.543 \text{ keV} - 0.084 \text{ keV} = 6.369 \text{ keV}
\]

- experimental value: 6.384 keV → good agreement
Auger Energies versus Atomic Number
Auger Energies versus Atomic Number

- heavy points indicate strong transitions
  → binding energies depend strongly on $Z$
  ⇒ Auger electron spectroscopy enables straight-forward identification of elements!
Chemical Shifts

- chemical environment of an atom
  - changes in valence shell orbitals
  - binding energy of core electrons
- binding energies of K and L shells shift in the same sense
  - $K_\alpha$ X-ray emission energy does not vary significantly with chemical environment
- compare LL Auger transitions:
  - K and L shells involved as in $K_\alpha$ X-ray emission
  - however: L shell is involved twice
  - $KLL$ Auger electron energy will display chemical shift
Chemical Shifts

→ AES: chemical shifts, similar to XPS

• however: chemical shifts in Auger spectra more difficult to interpret
  ◦ process involves *two* electrons
  ◦ compare:
    chemical shift in XPS spectra involves only one electron
  ◦ Auger spectra feature larger linewidths than XPS spectra
→ less energy resolution

⇒ XPS more suitable than AES to study chemical shifts
Yield of Auger Electrons and Fluorescence Yield

- lifetime $\tau$ of an excited state is determined by
  - probability $W_X$ for radiative transition (X-ray emission)
  - probability $W_A$ for Auger transitions
  - probability $W_K$ for Coster–Kronig transitions

- consider transition to vacancy in the K shell
  - no Coster–Kronig transition
  - probability for radiative (X-ray) transition:

$$\omega_X = \frac{W_X}{W_A + W_X} = \frac{W_X/W_A}{1 + W_X/W_A}$$

$\omega_X$: “fluorescence yield.”
Yield of Auger Electrons and Fluorescence Yield

- probability for radiative decay \( \propto Z^4 \)
- Auger probability does not depend on \( Z \)
- semi-empirical relation:

\[
\frac{W_X}{W_A} = \left( -a + bZ - cZ^3 \right)^4
\]

\( a = 6.4 \cdot 10^{-2}, \quad b = 3.4 \cdot 10^{-2}, \quad c = 1.03 \cdot 10^{-6} \)
Auger Electron Yield

- versus X-ray Yield per K Vacancy as a Function of the Atomic Number $Z$
Fluorescence Yield

- for K, L₃, and M₅ Shells versus binding energy
Apger Electron versus Fluorescence Yield

→ fluorescence yield $\omega_X$ is approximately the same for comparable transition energies

$\Rightarrow$ $\omega_X$ is (nearly) independent of the electronic shell (provided that Coster–Kronig transitions do not occur)
Atomic Level Width and Lifetimes

• energy width $\Gamma$ is related to the mean lifetime $\tau$ of the excited state through Heisenberg’s uncertainty principle

$$\Gamma \tau \geq \hbar$$

• decay probability per unit time equals the sum of the transition probabilities for radiative and non-radiative decay

$\Rightarrow$ total energy width:

$$\Gamma = \Gamma_{\text{radiative}} + \Gamma_{\text{non-radiative}}$$

• each atomic process has its own probability

• however, there is only a single lifetime for the hole

• natural line width corresponds to total lifetime
Atomic Level Width and Lifetimes

• total width of atomic transition
  ○ 0.23 ... 0.8 eV in the regime of dominant Auger emission (Z < 30)
  ○ up to 30 eV for K X-ray emission in the regime of dominant X-ray emission (Z > 30)
  ○ X-ray line broadening increases with Z ⇒ Al or Mg sources for XPS
Auger Electron Spectroscopy

- AES
- ultra-high vacuum
- electron gun to generate focused electron beam
- electron energy analyzer
Principle of an Experimental Apparatus
Scanning Auger Microprobe PHI 680 System in SCSAM

- field-emission gun scanning electron microscope
  - UHV
  - Schottky emitter
  - secondary electron detector
  - axial cylindrical mirror analyzer
  - very small spot sizes $\varnothing \approx 7$ nm

- inert gas sputtering
  - PHI 06-350 ion gun
  - remove surface contamination
  - depth profiling
Scanning Auger Microprobe PHI 680 System in SCSAM
Scanning Auger Microprobe PHI 680 System in SCSAM

- modes of operation:
  - survey
  - line profile
  - elemental mapping
  - additional device permits in-situ fracture of samples (at liquid nitrogen temperature if necessary)
  - houses PHI 3600 secondary ion mass spectrometer → SIMS
Auger Electrons in Overall Spectrum of Electrons Emitted from a Solid

Energy, eV
Auger Electrons Overall Spectrum of Electrons Emitted from a Solid

→ Auger electrons superimposed on large background of secondary electrons

→ reveal by derivation $dN[E]/dE$ (inset)

• total backscattered background current typically amounts to 30% of the primary beam current at $E > 50$ eV
Differential Analysis of a Hypothetical Spectrum
Differential Analysis of a Hypothetical Spectrum

- minimizes contribution from slowly varying background

\[ AE^{-m}, \quad A'E^{-m'} \]

left and right of the Auger peak (Gauß distribution)

- note that \( EA \) corresponds to the energy of the steepest slope, not the center of the Gauß distribution

→ AES is usually carried out in “derivative mode”

- differentiation is done electronically
Example for Use of Derivative Techniques

- Co specimen, 2 keV electrons
  - derivation reveals Auger transitions
- invisible in $N[E]$
Characteristics of AES

• surface-sensitive technique

• light elements

• signal-to-noise ratio / detection limit of AES:
  ◦ noise level due to background current
  ◦ ratio of analyzer $\Delta E$ to Auger line width
  ◦ typical value: 0.1 at%
  ◦ example: 0.5 monolayers of oxygen adsorbed on Si 111

⇒ easily detected; similar for C and N

• H, however, cannot be detected
  (Auger electron transition requires 3 electrons!)
Example: 0.5 Monolayers of Oxygen Adsorbed on Si \{111\}
Characteristics of AES

- Auger signal from a substrate is sensitive to presence of surface layers
- Example: Cu versus Pd/Cu
  - (a) freshly deposited Cu
  - (b) Cu prior to Pd deposition
  - (c) after deposition of 1.35 nm Pd
- Cu signal strongly attenuated by Pd
- Cu MVV line
  - low-energy
  - completely attenuated
Example: Cu versus Pd/Cu

![Graph showing Auger signal comparison between Cu, Cu as deposited, Cu before Pd, and 1.4 nm Pd.](image-url)
Characteristics of AES

- Cu MVV line (continued)
  - substrate signal decreases as $\exp[-x/\lambda]$
  - 60 eV electrons have small escape depth

- Cu LMM line
  - high-energy
  - only partly attenuated
  - 918 eV electrons have larger escape depth
Quantitative Analysis of AES Spectra

• goal: determine absolute concentration of an element $Z$ from the yield $Y_A$ of Auger electrons

• complications:
  ◦ influence of the matrix on
    • backscattered electrons
    • escape depth

• consider KLL Auger electrons from thin layer of width $\Delta t$ at depth $t$
Quantitative Analysis of AES Spectra

• yield:

\[ Y_A = N_Z \Delta t \cdot \sigma_e[t] \cdot (1 - \omega_X) \cdot \text{Exp} \left[ -t \cos \left( \frac{\theta}{\lambda} \right) \right] \cdot I[t] \cdot T \cdot \frac{\delta \Omega}{4\pi} \]

- \( N_Z \): number of atoms per unit volume;
- \( \sigma_e[t] \): ionization cross-section at depth \( t \);
- \( \omega_X \): fluorescence yield;
- \( \lambda \): escape depth;
- \( \theta \): analyzer angle;
- \( T \): transmission of the analyzer;
- \( \Delta \Omega \): solid angle of the analyzer;
- \( I[t] \): electron excitation flux at depth \( t \).
Quantitative Analysis of AES Spectra

- separate the excitation flux into two components:
  \[ I[t] = I_P[t] + I_B[t] = I_P[t] (1 + R_B[t]) \]

  \( I_P \): flux of primary electrons at depth \( t \);
  \( I_B \): flux of backscattered primary electrons;
  \( R_B \): backscattering factor.

- assume external standards with known concentration \( N_S^Z \)

  \[ \frac{N_T^Z}{N_S^Z} = \frac{Y_T^Z}{Y_S^Z} \cdot \frac{\lambda_T}{\lambda_S} \cdot \frac{1 + R_T^S}{1 + R_B^S} \]

  \( Y \): fluorescence yields
  \( \lambda \): ionization cross-sections

  → ionization cross-sections and fluorescence yields cancel (same atom!)
Quantitative Analysis of AES Spectra

- the composition can even be determined directly from the yield ratio when
  - measurements on standard and on specimen are made under the same experimental conditions
  - the composition of the standard is similar the composition of the specimen (otherwise need to consider different backscattering yield and different escape depth)

- elemental sensitivities are acquired using pure element standards

- data are then applied to unknown determinations in multi-elemental matrices

- however, need to correct for $\lambda$
Auger Depth Profiling

- major use of AES: composition as a function of depth $t$ in thin films

- Auger signal is generated near the surface ($\approx 3$ nm)

- sputtering provides layer sectioning

- depth profiles are usually shown as Auger signal height versus sputter time

- further calibrations required
  - convert sputter time to depth
  - signal height to atomic concentration
Auger Depth Profiling

- strong approach for depth profiling: combine AES with RBS

- RBS:
  - quantitative information on depths
  - heavy-mass constituents
  - without the complications of intermixing often introduced by sputtering

- ion sputtering causes change in the composition of the surface layers
  - surface segregation
  - preferential sputtering
Auger Depth Profiling

- Auger depth profiling
  - *better* depth resolution than RBS
  - sensitive to heavy and light elements

- example: RBS and AES data for 100 nm Ni on InP \{001\}, annealed at 250 °C for 30 min

- RBS spectrum for the as-deposited case:
  - Ni signal superimposed on signal from InP substrate

- AES spectrum for the as-deposited case
  - In and P signals clearly resolved, comparable heights

- RBS: Ni/InP interface is sharp (Ni tail: sputtering artifact)
Example: RBS and AES Data for 100 nm Ni on InP {001}
Example: RBS / AES for 100 nm Ni on InP

- after annealing: layer is partially reacted with an outer layer of Ni on a layer of $\text{In}_x\text{P}_y\text{Ni}_z$

- AES:
  - Ni layer and reacted $\text{In}_x\text{P}_y\text{Ni}_z$ layer clearly seen in AES
  - P/In yield ratio: 2:1

- RBS:
  - heights of Ni and In signals nearly equal
  - indicates a Ni:In ratio of $\approx 3$
    - $(\sigma_{\text{In}}/\sigma_{\text{Ni}} \approx 3.08)$
  - analysis of the RBS spectra yields P:In ratio of 0.5
  - differs from the P-rich composition deduced from AES!
Example: RBS and AES Data for 100 nm Ni on InP {001}

- discrepancy due to preferential sputtering and segregation
- region of pure Ni in the reacted film is better resolved with AES due to its superior depth resolution
- further, AES would allow determination of e.g. C and O the interface region, which is not possible with RBS
- advantages of AES: sensitivity to low-mass impurities
  - C, O, ...
  - common contaminants at surfaces and interfaces
- presence of such interfacial contaminants plays a disruptive role in thin film reactions by retarding interdiffusion
  ⇒ degradation of interface planarity on thermal processing
Example: Sputter Depth Profile of a Ta-Si Film on Polycrystalline Si

![Graph showing sputter depth profile with Ta-Si and poly-Si regions, signal intensity over sputter time, and oxygen from interfacial oxide below detection limits.](image-url)
Example: *Sputter Depth Profile of a Ta-Si Film on Polycrystalline Si*

- shaded area: O signal from native oxide at the interface
- removal is crucial for the formation of a thin, uniform oxide layer on top of the Ta-silicide during thermal oxidation
- native oxide layer
  - retards release of Si from the poly-Si layer
  - leads to oxidation of the whole Ta-silicide layer
  - prevents desired formation of a SiO$_2$ layer on the surface
- AES with sputter depth profiling has important applications for multi-layer films
- AES enables quantitative depth-profiling
Example: Sputter Depth Profile of a Ta-Si Film on Polycrystalline Si

- however: sputtering can cause problems
  - preferential sputtering
  - surface roughness
  - rotate the sample during sputtering

- example: sputter depth profiles of a Cr/Ni multiplayer
  - Cr and Ni are nearby elements in the periodic table
  - sputtering by rastered beam of 5 keV Ar⁺
  - with and without rotation
Effect of Surface Roughness