Auger electron spectroscopy (AES) is a non-destructive electron spectroscopy technique for partial identification of elemental composition of materials. The samples can include surface, thin film, interface, etc. High surface sensitivity (analysis depth < 100 Å) and a relatively lower detection limit (~0.1 atomic percent) make AES a very popular technique for surface analyses. AES can also be used to differentiate between elements which may be adjacent in periodic table. Additionally, it can be used for almost all elements, i.e., from lithium to uranium and beyond. AES also demonstrates atomic number dependent sensitivity which may vary by up to one order of magnitude. Bonding or chemical state information can be obtained from the chemical shift and line shape observed in AES. However, AES is less accurate than XPS for obtaining bond information. AES has depth resolution of 5–25 Å, which makes it particularly attractive for depth profiling with simultaneous ion sputtering. The lateral resolution of AES (less than 100 Å) is much better than XPS. Thus, nanostructures can be readily imaged along with creating 2-D maps of elemental composition of surface via scanning Auger microscopy (SAM). AES is a rather fast technique, despite being an expensive and sophisticated technique.

Auger is a three-electron process, wherein an electron beam (having 1 to 10 keV energy) is bombarded onto a solid surface. The impact of the beam ejects an electron from inner or core shell of the surface atom, thereby creating an ionized excited atom. An electron from an outer shell can occupy the vacancy produced in the core-shell, via a non-radiative transition. The excess energy of the electron is removed via:

i. X-ray emission, this phenomenon forms the basis for X-ray fluorescence (XRF)/electron microprobe (EMP) analysis
ii. Emitting another electron from the atom. These atoms are termed as Auger electrons, after Pierre Auger, discoverer of this process in 1920s. Around the same time Lise Meitner also invented this effect in an independent investigation.

The X-ray emission of X-rays (i) creates singly ionized atoms, whereas the atoms in Auger process (ii) become doubly ionized. Interestingly, AES cannot be used to detect hydrogen and helium, as Auger involves three electrons. Further, even though lithium possesses three electrons, an individual lithium atom in its ground state does not produce Auger peaks because the atom has only two energy levels which have electrons. Nonetheless, multiply excited lithium atoms have demonstrated Auger peaks. Additionally, electrons present in valence band of solid lithium facilitate Auger transitions of type KVV.

The low energy Auger electrons have a short mean free path which is responsible for the high surface sensitivity of this technique. Even though the atomic excitations can occur up to the depths of around 10,000 angstroms beneath the surface, it is only from the depth of ~100 angstroms that Auger electrons can be emitted without losing energy. On the contrary, electron microprobe analysis (EMA), wherein X-ray photons are detected is rather a bulk technique (Figure 1). The electronic states related to Auger process have very short lifetimes, thus, according to Heisenberg’s uncertainty principle, the peaks in the spectrum are usually wide (~1 to 2 eV). Auger electrons’ kinetic energy (K.E.) is specific to the emitting atom. Consequently, particular elements can be identified by measuring these K.E. of the emitted electrons in Auger process. Since the K.E. of electrons in Auger process is determined by the binding energy (B.E.) of electronic levels, any shift in K.E. yields detail about the oxidation state and bonding environment of the atoms present at the surface. Additionally, quantitative details can also be obtained from the Auger peak intensities.
The number of electrons detected is plotted against the K.E. of electrons to obtain direct Auger spectrum. In addition to this, for distinguishing small peaks in the spectrum, usually the first derivative of the number of electrons is plotted against their K.E. The derivative Auger spectrum serves two purposes: Auger peaks are enhanced; and the background produced from secondary and backscattered electrons is suppressed. Ultra high vacuum chamber is required for AES investigations, such that electron beam can travel freely and contamination from atmosphere is avoided.

**Principle**

Figure 2 depicts the schematics of Auger phenomenon in solids. The figure shows KL\textsubscript{2}L\textsubscript{3} Auger transition which involves ionization, relaxation, and emission, and is summarized below:

a. **Ionization**: Highly energetic incident electrons remove an electron from the core shell of the atom, leading to the formation of a vacancy in K-shell. Thus, an electronically excited ion is produced.

b. **Relaxation**: The K-shell vacancy created during previous step is quickly filled by an electron coming from L\textsubscript{2} shell via nonradiative transition.

c. **Emission**: An electron (Auger electron) is emitted from L\textsubscript{3} shell, thereby releasing the extra energy of the excited ion.
Auger transitions are named on the basis of the energy levels involved in the process, e.g., the transitions involved in the above figure is named KL2L3.

In certain cases, such as atoms having high atomic numbers, many Auger transitions are available. However, most of them have low probability of occurring. Further, some of the energetically allowed transitions are also forbidden by the selection rules. If a valence electron takes part in the Auger transition, letter V is used (such as KLV, KVV, etc.). Transitions involving core level electrons use letter C (such as CVV). Transitions of ABB (such as KLL, LMM) type are strongest. Another strong transitions are AAB type (also called as Coster-Kronig) transitions. Emission of X-rays is a competing phenomenon for Auger process since the energy difference between the core and outer levels can equally be released in the form of a characteristic X-ray. Therefore, the sum of the yields of Auger emission and X-ray emission is one. AES typically operates in the energy range where the probabilities of Auger emission are much higher than that for X-ray emission. In addition to this, the cross-section for Auger transitions in elements having low atomic numbers is much higher.

Kinetic Energies of Auger Electrons

AES includes measuring the K.E. of Auger electrons which are characteristic to the elements of the sample. Uncertainties of up to 1-2 eV are tolerable in measurement of K.E. for elemental identification. However, for analysing Auger chemical shifts, this uncertainty in K.E. should not exceed 0.1-0.2 eV. Nowadays, databases are available which can be compared with the obtained results, however, earlier AES relied on measuring the K.E. of electrons. The steps involved can be summarized as follows:

K.E. of an Auger electron is expressed as the difference in energies of singly ionized initial state and doubly ionized final state. Since first principles calculations of this energy is highly complex, uncertainties up to ~10eV are acceptable in most situations, several approximations are to be made in order to determine the K.E. of Auger electrons. Suppose in a hypothetical ABC type Auger transition, a vacancy is created in A level by removing an electron from it; this vacancy gets filled by an electron from
B level; and Auger electron is emitted from C level. Let the B.E. of electrons in neutral atom for A, B, and C levels are \( E_A \), \( E_B \), and \( E_C \) respectively. When electron from B occupies vacancy in A level, an energy \((E_A - E_B)\) is transferred to the third (C level) electron, which is the Auger electron. Thus, the K.E. \((E_{ABC})\) of Auger electron can be expressed as:

\[
E_{ABC} \approx E_A - E_B - E_C
\]  

(1)

From Eq. (1), it is evident that the K.E. of Auger electron does not depend on the energy of the incident beam, rather it only depends upon the energy levels of the atoms present in the sample. Thus, the K.E. of Auger electrons represent the elemental composition at the surface of the sample. Each element shows distinct set of Auger peaks corresponding to its unique set of energy levels. For instance, the energy for \( K_{L1}L_3 \) Auger transition in aluminium can be calculated as:

\[
E_{K_{L1}L_3} \approx E_K - E_{L1} - E_{L3}
\]

\[
\approx 1560 - 118 - 73
\]

\[
\approx 1369\text{eV}
\]

The measured value of this energy is 1354 eV. Two corrections can be considered to avoid the large disparity. Eq. (1) needs to be altered to include work function of spectrometer because Auger energies are usually referenced to the Fermi level. If good electrical contact exists between the sample and sample holder, then the Fermi levels of the sample and instrument are equal. Therefore, the K.E. of ABC Auger electron is approximately given as:

\[
E_{ABC} \approx E_A - E_B - E_C - \phi_A
\]

(2)

Here, \( \phi_A \) represents the work function of spectrometer, and its typical value is \( \sim 4 \) eV. \( E_{ABC} \) come out to be 1365 eV as the energy of \( K_{L1}L_3 \) Auger transition in aluminium. This reduces the disparity in measured and calculated values to 11 eV. For a neutral atom, Eq. (1) can be further filtered by considering the change in B.E. of a level accompanying ion formation:

\[
E_{ABC} \approx E_A - E_B - E_C^* - \phi_A
\]

(3)

Here, \( E_C^* \) represents the B.E. of a level in the presence of a core hole. Eq. (3) can be employed to determine energy of Auger electrons based on various empirical approximations.

**Instrumentation**

Surface sensitivity in AES technique (Figure 3) evolves from the fact that in solid materials, emitted electrons generally possess energies in the range of 50 eV - 3 keV and relatively shorter mean free path. Therefore, escape depth of electrons is limited to few nm in the target surface which gives AES a high surface sensitivity. Due to lower energy of Auger electrons, typical AES runs under the condition of ultra-high vacuum. This prevents electron scattering from residual gas atoms and development of a thin "gas (adsorbate) layer" on the sample surface which results in degradation of the analytical performance.
A standard AES setup (Figure 3) involves the following components: (a) electron source and electron optical column forming an electron probe on the sample surface; (b) ion optical column to clean the surface and sputtering for depth profiling; (c) electron energy analyser; (d) a secondary electron detector and a pulse counter; and (e) computer control and display systems. Modules (a-d) are located inside an ultra high vacuum chamber.

a. **Electron Optical Column:** An optical column focuses the electron beam (from an electron source) to the sample surface. The electron beam must be monoenergetic, of small size, and highly bright. Electrons irradiating the sample have energy in 2-10 keV range with a beam current of $10^{-8}$ to $10^{-5}$A. Scanning Auger microscopy uses energy upto 35 keV and current $10^{-9}$A to create a beam of ~100 Å diameter. The electron source must have prolonged life and higher temporal stability. Four major types of electron source are:

(i) Tungsten thermionic emitter with ~2700 K operation temperature. They produce low current density. Owing to low brightness and large beam sizes, they are preferred for AES analysis where high lateral resolutions are required. (ii) The lanthanum hexaboride (LaB$_6$) thermionic emitter with operating temperature of ~1850 K and lower work function than tungsten, can provide high lateral resolutions since they generate high current densities. (iii) Tungsten single crystal based cold field emitter, working at room temperature in the presence of a high electrostatic field and creates high brightness. However, this emitter becomes unstable on encountering residual gases and thus ultra low pressures ($10^{-10}$torr) are needed. (iv) Hot field or ZrO$_2$/W Schottky-type field emitter, operable at ~1800 K. This type of emitter can produce high current density.

b. **Ion Optical Column:** Ion source of electron impact type are used in AES equipments for depth profiling and sputter cleaning purposes. Heated filament generates electrons which are then accelerated by cylindrical grid such that they have enough energy to ionize gas atoms upon collision. The ions thus produced are accelerated into a focusing lens column. Typically, inert gases (e.g., Ar and Xe) are used with a hot tungsten filament.
c. **Electron Energy Analyzers:** The number of electrons emitted (N) are measured as a function of their energy (E) by using electron energy analyzers. Most widely employed analyzers are: (i) RFA or retarding field analyzer; (ii) CMA or the cylindrical mirror analyzer; (iii) CHA or concentric hemispherical analyzer. Retarding field analyzers suffer from inadequate energy resolution and poor signal-to-noise ratios due to average transmission efficiency. Thus, RFA is generally employed in low energy electron diffraction investigations, and not preferred for AES. CMA has high transmission efficiencies, compact size and is simple to use, making them suitable for AES. CHA is used for AES whenever chemical state analysis is performed since they have high resolutions. CHAs include an input lens and hemispherical analyzer, and are a commonplace in XPS energy analyzers. CMA and CHA are band pass filters (BPF) while RFA is high pass filter. The BPF allows passage of electrons within a band of energy (E) at a pass energy (E), leading to the energy resolution of E/E. As RFA detects electrons having energy greater than a specific energy, E, the spectrum is differentiated once to determine N(E) spectrum.

d. **Electron Detector:** After exiting the analyser, the electrons reach the detector which amplifies and counts them using an electron multiplier (channeltron or microchannel plate, MCP). The interior of channeltron (cone-shaped dynode) is coated, such that when one electron strikes it, many secondary electrons are generated. These secondary electrons are then accelerated to the anode. Several intervening collisions cause an avalanche effect, leading to a gain of ~$10^8$ for a channeltron. MCP comprises several small channeltons joined together to create a disc. Electron intensity is measured via pulse counting.

e. **Computer and Display System:** Sophisticated computer control, data processing, and display systems are common to all modern AES instruments. The functions of computer control system are: (i) setting up conditions for analysis; (ii) efficient collection and storage of data; (iii) data processing; and (iv) displaying results in the form of spectra.

In this experimental configuration (**Figure 3**), first the focused electrons get incident on a solid sample and then the emitted electrons get deflected towards a cylindrical mirror analyzer. In detector, Auger electrons are multiplied and signal is advanced for data processing. Finally, the accumulated Auger electrons are recorded as a function of energy against broad secondary electron background spectrum. Because the Auger peaks have small intensities relative to the background noise, AES is generally operated in derivative mode that highlights Auger peaks by modulating the electron collection current by applying small AC voltage. Using setup shown in **Figure 3**, by detecting the signal at frequency ‘ω’ and plotting one can get the Auger fine structure. In this Auger electron structure, one can clearly see the little secondary peaks neighbouring the main Auger peak. The secondary peaks arise because an element may be present on the surface in different chemical states.
Review your learning

1. The characterisation of auger spectroscopy can be achieved up to which of the following depths?
   a) 1 nm
   b) 2 nm
   c) 4 nm
   d) 8 nm

2. Auger electron spectroscopy can be used for surface chemical analysis in a way similar to which of the following?
   a) ESCA
   b) SIMS
   c) ISS
   d) Ion spectroscopy

3. Qualitative chemical analysis is very often performed using which of the following?
   a) ESCA
   b) SIMS
   c) AES
   d) Ion spectroscopy

4. Electron ionization can produce which of the following?
   a) ESCA electron
   b) Auger electron
   c) Ion
   d) Photon

5. Which of the following is an Auger transition starting from a hole in 1s levels which would be filled up from the 2p level?
   a) KLM transition
   b) KLL transition
   c) LMN transition
   d) LLM transition

6. In ESCA process, the photon ejects which of the following?
   a) 1s electron
   b) 1p electron
   c) 2s electron
   d) 2p electron

7. In Auger process, an electron drops to fill which of the following?
   a) 1s hole
   b) 1p hole
   c) 2s hole
   d) 2p hole

8. In ESCA process, the photon ejects which of the following?
   a) 1s electron
   b) 1p electron
   c) 2s electron
   d) 2p electron
9. AES is more sensitive than XPS because of which of the following factors?
   a) Binding energies of electrons
   b) Kinetic energies of electrons
   c) Mass of electrons
   d) Mass to charge ratio of electrons

10. How is the specificity of Auger electron spectroscopy?
    a) Very bad
    b) Bad
    c) Good
    d) Very good

11. Which of the following denotes the sample destruction that occurs in Auger electron spectroscopy?
    a) None in 95% of sample
    b) None in 99% of sample
    c) None in 100% of sample
    d) Frequent

12. Auger electron spectroscopy involves the irradiation of the surface to be analysed with a beam of electrons of energy in the _________ range.
    a) 1-2 KeV
    b) 2-4 KeV
    c) 4-8 KeV
    d) 1-8 KeV

13. In Auger spectroscopy, beam currents are typically _____ in a beam of diameter 0.5mm.
    a) 5-10 µA
    b) 5-20 µA
    c) 5-30 µA
    d) 5-50 µA

14. AES is limited when it comes to very high resolution studies.
    a) True
    b) False

15. Electron ionisation can produce ESCA electrons.
    a) True
    b) False