Auger Electron Spectroscopy (AES)  
Scanning Auger Microscopy (SAM)  

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Adsorption Processes

(Briggs handbook of X-ray and UV photoelectron spectroscopy, Heyden 1977)

High vacua at RT: 1m$^3$ of O$_2$ at 10$^{-6}$ T weighs $\sim$ 2 mg and the mean free path is about 51 m.

Kinetic theory: $P = \frac{1}{3} N m v^2$

The theory gives the frequency of collisions of gas molecules with a surface as:

$$N = \frac{3}{5} \times 10^{22} \times P \times (M \times T)^{-2}$$

P is the partial pressure (Torr) of the gas, M the molecular weight (Sum of the atomic weighs of all the atoms in a molecule) and T gas temperature (K)

Example: O$_2$ gas $T = 20$ °C and $P = 10^{-6}$ T $N = 3.62 \times 10^{14}$ molecules

$P = 10^{-9}$ T $N = 3.62 \times 10^{11}$ molecules

Typical clean metal surfaces have about 10$^{15}$ atoms cm$^{-2}$. So, if each O$_2$ striking the surface sticks (metal/oxygen atomic ratio of 1:1).
Time for adsorption of O\(_2\) at P = \(10^{-6}\) T is \(10^{15}/3.62 \times 10^{14} \times 2 = 1.4\) s

But 24 min at \(10^{-9}\) T and 4 h at \(10^{-10}\) T.

NOTE

Gases present in HV systems are mostly H\(_2\)O vapor, C\(_x\)H\(_y\), CO, H and O\(_2\). In UHV the gases are generally H and CO with some inert gases. Oxygen concentrations in UHV are generally low because reacts with CO and C on the chamber walls to produce CO and CO\(_2\).

4 possible reactions:

1. Physiorption
2. Chemisorption
3. Chemisorption with reorganization and
4. Oxidation
Need for atomically clean surfaces

This concept is very important, for example if a 2 nm thick sample is covered with 1 ppm of C (10-20 monolayers), this is all that the spectroscopy would see.
Electron emitted from the electron source are focused on the sample via electrostatic lenses. The electrons photoemitted are collected and analyzed and counted by the detector.

One or two ion guns (Ar\(^{+}\)) are used with this technique. The Ion guns provide a way to sputter the surface of the sample and give chemical information as a function of depth (depth profiling).
Auger Electron Spectroscopy (AES)

First described by Pierre Auger in 1925. It was used to explain the radiationless relaxation of excited ions observed in cloud chambers. Only in 1953, J.J. Lander suggested to use it for chemical analysis. In 1968 L.A. Harris realized its importance as surface sensitive technique.

A specimen is irradiated with electrons, core electrons are ejected in the same way that an X-ray beam will cause core electrons to be ejected in XPS. Once an atom has been ionized, it must return to its ground state.

1. An X-ray photon is emitted, basis of electron probe microanalysis (EPMA). This is carried out in many electron microscopes by either E or λ dispersive spectrometers (Geology).

2. An electron from a higher level, the L2,3 level fills the vacancy (core level), K shell vacancy.

NOMENCLATURE

SHELL MODEL

Electron orbitals

M

L

K

Nucleus
Auger Emission

1. 1st Ionization
2. Electron "Decay"
3. Auger Electron

Initial State Energy $E_1$

$x$-ray photon

Fluorescence

$E_1 = E_2 + KE$

or $KE = E_1 - E_2$ ($= E(k) - E(L_1) - E(L_1)$)

Auger electron ($KL_1L_1$)
Survey (Wide Scan) spectrum

CasaXPS (Washington State University, Pullman, Wa)

TiO$_2$
AES is an analytical technique used to determine the elemental composition and the chemical state of the atoms in the surface of a solid material. As XPS this technique is a surface sensitive technique since the electrons have a short free path in solids. The electron escape depth ($\lambda$) is defined as the distance normal to the surface at which the probability of an electron escaping without energy loss drops to 1/e. This depends on:

1. Matrix composition (single element or composite material).
2. Energy of the Auger transition
3. Analytical geometry

For example: Auger signal from $[1-\exp(-d/\lambda)]$ where $d$ is the depth and $\lambda$ the IMFP. For $d = \lambda$ then 63.2% of the Auger signal comes from the top $1\lambda$, for $d = 2\lambda$ then 86.5% of the signal will come from the top $2\lambda$, etc …

The energy difference between the 2 states is carried away by the ejected Auger electron. The KE of the emitted electron is characteristic of the parent
Schematic diagram of an Auger emission process in a solid. The initial state is the ground state (shown on the left), singly ionized state at the center and doubly ionized final state is shown on the right.
Auger Electron Emission

Competition between X-ray fluorescence and Auger electron emission

Relative probability of Auger and x-ray fluorescence emissions. Auger and fluorescence yields as a function of atomic number. The solid lines show Auger yield; the dashed lines, fluorescence yield.

1. X-ray fluorescence (radiative decay)
2. Auger electron emission (NON-radiative decay)
Volume excited by the $e^-$ beam

X-ray resolution
Auger Electron Energy Analysis

What is the Auger electron energy? Can we determine it from energy?

The energy $E_K - E_{L1}$ can be released as a radiative decay or non-radiative transition (Auger).

Auger kinetic energy is given by

$$E = E_K - E_{L1} - E_{L2,3} - \Phi$$

NOT SO SIMPLE

Because the transition probabilities between singly ionized and doubly ionized state of the atom (NOT GROUND STATE PROPERTIES), Ref: F.P. Larkins, Applications of Surface, Science 13, 1982, 4-34

By use of the expression (1) the Auger KE is overestimated
Example: Si and P

**Case 1:** Si

\[
E_K = 1839 \text{ eV} \\
E_{L1} = 149 \text{ eV} \\
E_{L2,3} = 99 \text{ eV}
\]

Typical value for \( \Phi = 4 \pm 1 \text{ eV} \)

Then

\[
E = E_K - E_{L1} - E_{L2} - \Phi = 1587 \text{ eV}
\]

This value is too high

This equation does not take into account the interaction energies between the core holes (K and L\(_{2,3}\)) nor the intra- and extra- atomic relaxation energy which come about as a result of the additional core screening needed when there is a hole in a core level and it is achieved by an inward collapse or “relaxation” of the outer electronic orbitals towards the core.
The Intra-atomic relaxation energy is the relaxation energy appropriate to an isolated atom and the extra-atomic relaxation energy is the relaxation energy from the other atoms or from the valence band due to the ionized atom in a molecule or in a solid (Coulomb and exchange integrals).

A better approach is the “Z+1” approximation. The concept behind it is that after single ionization event the BE of all electrons is increased due to one less electron charge; *electrostatically like Z+1 atom*. Derived by Chung and Jenkins, *Surface Science*, 21, 253 (1970)

\[ E_{KL2,3} (Z) = E_K (Z) - \frac{1}{2} [E_{L1} (Z) + E_{L1} (Z + 1)] - \frac{1}{2} [E_{L2,3} (Z) + E_{L2,3} (Z + 1)] \]

**Case 2:** 
Z+1: then Si → P  
For phosphorus  
\[ E_{L1} = 189 \text{ eV} \]  
\[ E_{L2,3} = 126 \text{ eV} \]  
Then  
\[ E = E_K - E_{L1} - E_{L2} - \Phi = 1552 \text{ eV} \]

*The actual energy is 1561 eV*
Energy Distribution

Lower curve: distribution of energies of secondary electrons ejected from a graphite surface by incident electrons of energy 1000 eV. The background is made of the inelastically ejected electrons and the elastic peak is shown at exactly 1000eV (often used as energy calibration).

Upper curve: differential distribution over the energy range containing the carbon KLL Auger peaks. In the differential distribution the peak ”position” is taken to be that of the high energy minimum, by convention.
Auger spectra (Cu)

# Auger electrons vs energy

Direct Spectrum

Differentiated Spectrum

derivative # Auger electrons vs energy
4 ways to display Auger data

a) $N(E) \text{ vs } E$,  
b) $dN(E)/dE \text{ vs } E$,  
c) $d(E \times N(E)/dE \text{ vs } E$,  
d) $E \times N(E) \text{ vs } E$
Auger Si Spectrum
Oxidized Si Surface
Chemical Analysis by Auger
1\textsuperscript{st} and 2\textsuperscript{nd} derivative Si LVV Auger spectra of several silicides. Scale factors for each curves were adjusted to produce similar peak intensities.

The silicide enthalpies of formation $\Delta H_f$ expressed per metal atom per formula unit are also indicated.
Carbon Peaks

DLC (diamond like carbon), graphite and SiC

1). A distinct shoulder in the C peak of graphite was measured at KE = 280 eV.

2). The Peak –Peak width is about 22 eV for graphite and DLC. It is only 9.6 eV for SiC.

3). The peak is narrower for SiC than for graphite and DLC.
**Atomic Sensitivity Factors (ASF)**

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Voltage dependency of the Sensitivity Factors. A typical voltage used in Auger is 5kV
SAM Element Imaging

SAM element imaging provides the lateral distribution of elements in a thin film. All elements except H and He may be imaged. The “quality” and spatial resolution of SAM element images depend on the sample matrix, the quantity of the element present and the geometry of the sample. As a rule, SAM element images are of lesser quality than SEM images due to instrument and sample constraints but allows for elements analysis and element spatial distribution.
Images of a failed lead bond on a gold pad

Scanning auger microprobe images of a failed lead bond show oxide formation and the distribution of intermetallics.
Imaging – Spectrum

a) SEM image of the interface Ti (left)-fiber (right)

b) Boron Auger image – reaction of B from TiB$_2$ coating with the Ti matrix

c) Color composite of Ti Auger image (blue), B (red), and C (green). The overlap of Ti and B gives a magenta region, showing the distribution of the a Ti monoboride reaction phase. Ti and C overlap gives a sky blue region, showing the position of a TiC reaction phase.

d) Auger spectrum confirms the presence of TiC
Sputtering and Depth Profiling

Sputtering Process

Surface layer removed

Ar$^+$ ions

Crater formed

Graphs showing atomic concentration and sputtering step over time.
ESCA

1. AREA OF ANALYSIS IS ROUGHLY 5 mm IN DIAMETER
2. Elemental Map and Line scans at lower spatial resolution
3. SAMPLING DEPTH ~ 30 ANGSTROMS
4. HIGHEST SENSITIVITY FOR HEAVY ELEMENTS
5. CHEMICAL BONDING INFORMATION CAN OFTEN BE OBTAINED (QUALITATIVE AND QUANTITATIVE)
6. X-RAYS ARE GENERALLY A MORE GENTLE PROBE
7. QUANTITATION ACCURACY BETTER THAN AES IN MOST CASES
8. DATA ACQUISITIONS FREQUENTLY LONGER THAN AES
9. SPUTTER PROFILING IS NOT VERY PRACTICAL
10. SEMICONDUCTOR AND INSULATING SAMPLES RELATIVELY EASY TO ANALYZE

SAM

1. CAN FREQUENTLY ANALYZE FEATURES LESS THAN 1 MICRON IN DIAMETER
2. ELEMENTAL MAPS AND LINE SCANS CAN BE DONE
3. SAMPLING DEPTH ~ 30 ANGSTROMS
4. HIGHER SENSITIVITY FOR LIGHTER ELEMENTS
5. ATOMIC STOICHIOMETRIES AVAILABLE ONLY●
6. POTENTIAL FOR E-BEAM INDUCED DAMAGE IN SOME SAMPLES
7. PEAK AMPLITUDE CAN CHANGE WITH CHEMICAL BONDING CHANGES
8. SHORTER DATA ACQUISITION TIMES
9. AES DEPTH PROFILES ARE QUICK AND CONVENIENT
10. INSULATING SAMPLES CAN BE DIFFICULT OR IMPOSSIBLE TO ANALYZE
Applications

I. Microelectronics Technology
• TFA (thin Film Analysis). AES signal is plotted vs. sputtering etch time (Ar+). The graph composition versus the depth gives information about composition, thickness and uniformity of the film.
• The technique is used in raw material evaluation, oxidation, metallization, etc …
• SAM (scanning Auger Microscopy) looks for inhomogeneity on surfaces. It is often used with SEM to detect defects and trace of unwanted elements.

II. Metallurgy
Studies of Segregation at grain boundary (AES).

III. XPS and AES for studies of heterogeneous Catalysis

IV. Polymer Technology (XPS)
• Because of its ability to analyze relatively intractable materials without special preparation and because of its surface sensitivity. Charging neutralization.
• Shake-up satellites (6 – 7 eV) to low KE of the main peak due to the $\pi \rightarrow \pi^*$ transition indicate aromaticity in the material.
• Valence band spectra are used to distinguish between hydrocarbons polymers (LDPE, PB etc …).

V. Corrosion Science (AES)
By combining sputtering and Auger acquisition the composition and chemistry of corrosion film can be determined