EFFECTIVE APPLICATIONS OF AUGER ELECTRON SPECTROSCOPY

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Abstract : The goal of this study is to explore different aspects of the AES process and to present the new techniques which can be used effectively for analytical purposes. More emphasis is given to AES data acquisition, sensitivity factor and Auger intensity. The experimental details of a typical scanning Auger microprobe (SAM) is also presented. Applications of AES to selected systems such as microelectronic devices, supperconductors, and in metallurgy are described.

Introduction

When a sample is excited with x - ray or energetic electrons, core electrons may be ejected from an energy level E_x and core hole E_x is then filled by an internal process in which electron from energy level E_x fall into the core holes E_x. Energy blanced is achieved either by x - ray emission or by ejection of a third electron from energy energy level E_z. The energy of the third electron (Auger electron), E_A is given by :

$$E_A = E_z + E_y - E_x \qquad (1)$$

which is unique for each element. If the Auger energy spectrum frm 0-2 keV is measured, then all the elements present on be sample can be identified. AES is a surface sensitive technique because of the intense inelastic scattering that can occur for electrons in the energy range of 0-2 keV, illustrated in Fig. 1. only Auger electrons from the outmost 0.5-3 nm of a solid survive to be ejected and measured in the spectrum.

With the modified Auger electron spectrometer it is possible to obtain both Auger and secondary images of the sample under study. The modified apparatus is known as a scanning Auger Microprobe (SAM), which provides Auger spectra of localized areas of about 25 nm-1μm. A SAM system can also function as a medium - resolution SEM.

Experimental Arrangement.

A typical SAM consists of a stainless-steel ultra-high-vaccum chamber, which contains the electron gun and electron kinetic energy analyzer, a data-acquisition and analysis computer with associated displays and printer system. There are two main reasons for UHV environment, first the Auger electrons must not be scattered by the ambient gas and second the rate of sample contimination must be slow for a good analysis.

The electronic and mechanical stability of the electron gun are of utmost importance. The lack of stability, or drift, of the electron gun can severely limit the ability to analyze small samples (o.1μm) over long period of time (lh). Two types of thermoionic emitters and field emmission gun are used in AES electron gun. The developemet of the beam quality over 20 years is shown in Table 1. The electron kinetic energy analyzer is the heart of Auger spectrometer. Most systems use electrostatic analyzer and two types are the cylindrical mirror analyzer (CMA) and

the hemispherical sector analyzer (HSA).

For current detection multistage or continnuousus dynode electron mulitipliers (CDEM) are employed. A new development is the use of position sensitive detectors in electron specroscopy. As mentioned, a secondary electron detector is added to the Auger electron spectrometer which permits to be used as a SEM. A semiconductor x-ray detector is also added to the AES system which permits energy dispersive x - ray analysis (EDX) to be perfomed. However, EDX analysis is not surface sensitive, because x-ray emanate from a region 1-2μm in diameter. Thus with the combined system the number and identitiy of electrons in the sample block may be rapidly identified.

All modern spectrometers are equipped with a sputter ion gun, which allows for bombardment of the specimen surface by an energetic beam of rare gas ions. Sputter ion guns are used both to clean and erode the surface by energetic ion impact. The sample handeling includes : sample stage, sample carousel, and sample heating and cooling. It is suggested that 5 degrees of freedom in sample movement should be available (3 translationnal and 2 tilts). A carousel - type sample holder, allowing multiple samples to be located into the vaccum chamber. Sample heating may be useful (600 °C) for several hours, and cooling is usually done by liquid nitrogen. Sample fracture stages use an impact hammer or chisel to fracture the sample, which places the sample in both tension and compression. All practical fracture stages provide for liquid - nitrogen cooling of the sample to attempt a brittle fracture. Another method operating a clean surface is by mechanical removal of the original surface and its associated contimination (scribe or scratch).

Sensitivity Factor and Auger Intesity

The emitted Auger electrons are detected by an electron analyzer with a transmission efficiency T (E_A) and a detector of efficiency D(E_A). Thus,the current, I_A, may be written as

$$I_A = I_o \sigma_A(E_p) [1 + r_M(E_A, a)] T(E_A)D(E)\int N_A(Z)\exp[-Z/\lambda_m(E_A) \cos \theta] dZ \quad (2)$$

where σ_A is the ionization cross section, r_M is the backscattering term, a is the angle between the surface normal and the incident electron beam. $N_A(z)$ is the A-atom distibution with depth z into the sample surface. λ_M is the the inelastic mean free path, and θ is the angle of emission. The current is integrated over the appropriate angular enterance aperature of the electron spectrometer.

At the present Eq.(2) is not used directly for the data analysis. Instead it is used as a starting point and various simplifications are made to determine the work function of the specimen.

Considering a homogenous binary system,AB, the number of unknowns in Eq.(2) can be reduced by considering the ratio of intensities for the pure element standards I_A^∞ / I_B^∞, recorded on the same AES instruments,

$$\frac{X_A}{X_B} = F_{AB}{}^A \frac{I_A / I_A^\infty}{I_B / I_B^\infty} \quad (3)$$

where X_A and X_B are the mole fractions of A and B, respectively, in the solid AB, and $F_{AB}{}^A$ are the Auger electron matrix factors. For the case that the matrix factor are ignored, then Eq.(3) reduces to

$$X_A = \frac{I_A / I_A^\infty}{\sum_i{}^n{}_{=0} I_n / I_n^\infty} \quad (4)$$

In the absence of a large number of pure elemental standards from which values for I_A^∞ and I_B^∞ etc. may be obtained, the Auger signal from the sample may be normalized relative to both(1) the signals of all the sample Auger peaks present in the spectrum and(2)the signal of the pure sample element compared to the signal from a pure elemental target,typically silver. Thus we can write

$$X_A = \frac{I_A/S_A}{\Sigma_{i=1}^n I_n/S_n} \tag{5}$$

where I_A is the intensity of the Auger peak associated with element A, and S_A is the Auger sensivity factor for element A at the particular ionization potential employed. The choice of Auger intensities I_A and I_B is a matter of some debate, but usually peak-to background ratios are used. More recently the major sources of errors in AES measurements have been reported[1].

Data Acquisition and Analysis

1.Techniques: Data acquisition system includes AES spectrometer digital control,SAM data analysis computer and ancillary SAM capability. Digital system facilitates system automation and contributes to faster analyses and improves data accuracy. The function of the analysis computer are as follows: (1) spectral display and expansion(2) smoothing,(3)derivative spectra,(4)peak integration and area measurements,(5)analysis of overlaping spectral features,(6)addition and subtraction, of spectra and (7) noise spike removal.

AES experimental techniques include, Auger data acqusition, Auger point spectra, Auger line spectra, and Auger mapping. The electron energy distribution,N(E) vs E, is recorded by pulse counting($I_p < 10^{-7}$ A)or by current-to-digital conversion methd($I_p > 10^{-7}$ A). The most common are single or multiple point spectra, in which the electron beam remains at one point $I(x_i,y_i)$ on the sample for the duration of the data collection. Similarly multiple data points, $I_{i=1}^n(x_i,y_i)$ can be obtained in which I is the Auger signal at one point and n is the number of points. Often line scan is usefull,specially when the sample is presented such that a cross sectional view of an interface is observable.

By scanning the electron beam across the sample, and measuring intensity I (x,y), an image may be constructed in which the intensity of each pixel represents the amount of the element present. A two-dimensional view, or Auger map, of the concentration across a surface can be constructed.

2. Depth Profile Analysis: The combination of an Auger spectrometer and an ion gun can be employed to obtain a compositional depth profile of a surface. This may be done either seqentially or continuously. In the continuous method, the chemical composition of the surface at each depth , for each time, is slightly different and a simultaneous analysis is possible. Specimen rotation during sputtering has shown an improved interfacial resolution for multilayer samples[2].

The data obtained consists of Auger signal intensities,I, as a function of sputtering time,t, and must be converted to concentration C vs. depth,z. The sputter rate Z (m/s)is described by

$$Z= (M/\rho Ne) \, S \, J_P \tag{6}$$

where M is the atomic mass number, ρ is the density (kg m^{-3}),N Avogadro's number, e electron charge, S is the sputtering yield(atom/ion), and J_p is the primary ion current density(A m^{-2}). From Eq.(6) Z can be calculated by knowing S from

literature[3] and measuring J_p.

A better method to obtain Z is to measure the time required to sputter through a layer of known thickness(anodized tantalum foils). A third method is to measure the actual sputter depth after depth profiling by conventional interferometry or stylus method.

3. Depth Deconvolution Techniques: An efficient method is the factor analysis[4] which can be applied to Auger line shape spectra to determine the presence and number of new chemical states formed at interface. This technique can provide information about the number of components, qualititative analysis from overlaping spectra,and extraction of spectra for unidentified components with a good speed of analysis.

Figure 2 shows a conventional Auger depth profile of Pt-Zirconia, while it is compared with a chemical state depth profile computed from Auger line-shape information, Fig. 2b. Spectra of the three individual components Pt,Pt Zr, and Zr O_2, have been calculated by the factor analysis technique.

Depth profiling of multilayers has been accomplished by using a logistic function. For a solid/solid interface the Auger depth profiling can be determined by a logistic function of the form

$$Y = \frac{A+a(T-T_o)}{1+e^x} + \frac{B+b(T-T_o)}{1+e^{-x}} \qquad (7)$$

where Y is the surface elemental concentration of the components that defines the interface. A is a measure of the preinterface and B is for the postinterface concentration,where" pre" and "post" are taken in the sense of time. T_o is the midpoint of the interface region,and x is a dimensionless reduced time defined as $(T-T_o)/D$. D is the characteristic time for sputtering through the interface region. A least-squares fitting program has been employed which fits the Eq. (7) to the measured Auger spectral intensities.

Applications

A list of AES applicatins to a variety of problems is given in Table 2. A scanning Auger microprobe, because of its high lateral (50 - 100 nm) and depth resolutions (0.5 - 3 nm) and inherent capability to function as a SEM, is ideally suited to identify and correlate submicrometer features with elemental analysis of these features. By combining AES with ion - beams sputter etching, depth profiling on small scale (2 nm resolution in<100 - nm depths) may be performed.

There are several applications of AES in microelectronics. In metallurgy, grain - boundary segregtion, thin film interdiffusion studies and historical metallurgy can be accomplished. Alloyed superconducting Nb_3 Sn - bronze wire filaments were fractured under UHV (3×10^{-10}Torr,4×10^{-7}pa)and struture and elemenrtal composion of the individual wire filaments were examined. Other applications of AES conserns with corrosion, insulating samples and mineralogy and also surface extended energy - loss fine structures. AES also can be used as a valence - band spectroscopy that is surface sensitive. Observed changess in Auger line shapes have been useful in identifing chemical states of elements at surfaces, particulary carbon, sulfur, nitrogen, and oxygen.

A summary of the capablities of AES is presented in Table 3. In order to recognize the strong aspects of the AES and to take full advantage of the system its potentials are explained in terms of the sample form, size, topography and prepration process.

References

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Table 1. Progress in AES beam diameter.

Date	Beam diameter (μm)	Beam current (nA)	Beam voltage (keV)
Early 1970s	400	2×10^4	2.5
Mid 1970s	40	5×10^3	5
Mid 1980s	0.5	10	10
Late 1980s	0.1	1	25

Table 2. Selected applications of Auger electron spectroscopy (Ref. 5)

(1) Microelectronics	(6) Historical metallurgy
(2) Grain - boundary sgregation	(7) Corrosion
(3) Superconductors	(8) Mineralogy and insulationg samples
(4) Thin - film interdiffusion	(9) Surface extended energy - loss fine
(5) Ti - 6A1 - 4V Powder for aerospace	structure
structural components	(10) Chemical effects

Incident Electron Beam

Auger electrons - 0.5 - 3 nm

sample surface

secondary electrons - 0.5 - 50 nm

backscattered electrons - 500 nm

primary x-ray excitation - 1000 nm

100
Atomic %
Pt
O
Zr
0
0   Sputter Depth (nm)   2500
(a)

100
% Comp.
Pt
PtZr
ZrO_2
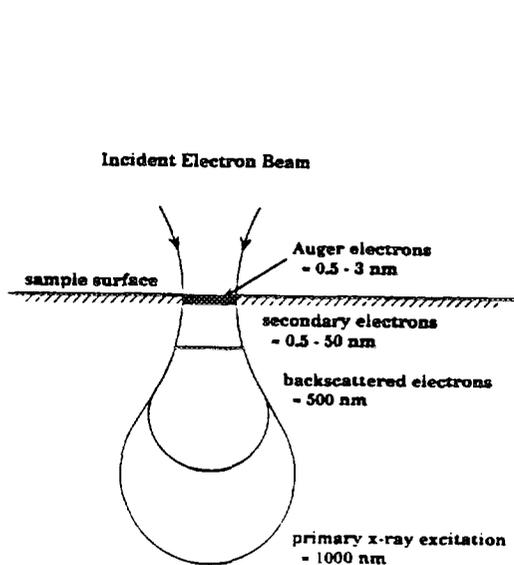0
0   Sputter Depth (nm)   2500
(b)

Fig. 1. Diagram comparing Auger electron escape with emission depths for backscattered electrons.
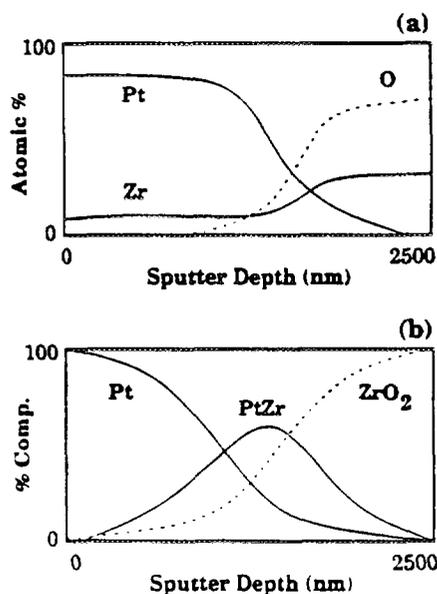
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Fig. 2. (a) Conventional Auger depth profile and (b) chemical state depth profile from Auger information.

Table3. Summary of capabilities (Ref. 5)

Use	Estimated Analysis Time
(1) 0-3 nm surface elemental analysis for all elements except H and He.	(1) Survey spectra: ≈ 5 min for a complete scan from 0-2000 eV.
(2) Depth vs composition profiling and thin-film analysis.	(2) Selected peak analyses: ≈ 15-30 min depending upon the number of peaks.
(3) 20-nm lateral resolution surface chemical analysis.	(3) Depth profiling: ≈ 30-300 min or longer.
(4) Grain-boundary and other interface analyses facilitated by sample fracture.	(4) Auger elemental imaging: ≈ 30-300 min or longer.
(5) Identification of phases in cross sections.	

Limitations	Samples
(1) Quantitative detection sensitivity is from 0.1 to 1.0 at. %	(1) Form: Solids with low vapor pressure [$<1.33\times10^{-6}$ pa(10^{-8} Torr) at 25 °C].
(2) Accuracy of quantitative analysis limited ($\pm30\%$) when calculated using sensitivity factors. Better quantification ($\pm10\%$) when standards that closely resemble the samples are available.	(2) Size: Limited by specific instrument; 2×1×1 cm is typical; powder may be analyzed.
(3) Insensitive to H and He.	(3) Topography: Flat surfaces are preferable; rough surfaces may be analyzed either in small areas (≈ 1 μm^2) or averaged over large areas (≈ 200 μm^2).
(4) Electron-beam charging may limit the analysis of insulating materials.	
(5) Electron-beam damage may limit analysis of organic and biological materials.	(4) Preparation: Frequently none; samples must be free of fingerprints, oils, and other high-vapor-pressure materials.