THEORY AND APPLICATIONS OF SURFACE ANALYSIS TO SEMICONDUCTOR RESEARCH AND DEVELOPMENT: A TUTORIAL

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The fundamental principles of three of the more common surface analytical spectroscopies-Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS)-are discussed in terms of their physics, strengths and limitations. The focus of the discussions is on the application of these characterization tools to semiconductor electronics, especially for failure analysis and preventative measurements. An application, illustrating the complementary nature of the outputs of the three methods, examines the Au-GaAs Schottky barrier, especially the nature of the interfacial reaction.

Espectroscopias de análise de superfície, semicondutores

1. INTRODUCTION

Emerging and established semiconductor technologies have critical analytical requirements for the diagnostic investigations of components. In general, the measurement needs span the optical, mechanical, electrical and chemical fields, and the sophistication of the techniques varies from simple visual inspections to complex spectroscopic examinations. Traditionally, the science of these characterization efforts has been somewhat negatively termed "failure analysis" Although this description certainly fits a majority of such studies, the field has been broadened to involve more positive approaches. These encompass process control applications, including the analysis of components/devices/materials that meet or exceed specifications in order to ascertain esired characteristics. (Of course, this latter approach is sometimes applied to a minor

number of cases to the area called "reverse engineering" in which a researcher or manufacturer attempts to make use of his competitor's success.) Of course, "failure analysis" should be viewed as a preventative technology, which provides short-term directions leading to long-term technologies. The semiconductor electronics technologies certainly have a wide range of requirements in the analytical and characterization area. This includes the process of establishing production procedures, implementing devices and components, improving the operational performance and lifetime of the product. Technology is based upon the ability to recognize, diagnose and solve problems that limit its development and implementation. Measurement and characterization, in term, provide the identification, diagnosis and solutions.

The range of analytical tools useful to semiconductor technologies is expansive. This paper introduces some of the more utilized (perhaps the more sophisticated) characterization techniques, focusing primarily on those in the compositional and chemical identification areas. The intent is to provide some understanding of the fundamental principles or physics of each of these methods, their instrumentation, their limitations and st engths, and the applications to technology development. The emphasis is on surface and interface analysis, in which the investigation of the chemical and compositional properties (including impurity distributions and gradients, trace analysis, chemical mapping) of devices and multilayer structures are discussed. The range of techniques selected for coverage includes Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) [and several alterations of these methodologies]. A summary and comparison of the more common surface analysis methods is presented in Table 1. In can be deduced from this table that the AES, XPS and SIMS represent analyses performed by three different input probes. The chemical/compositional information gained from each is different, and indeed can be complementary if applied to the same problem. It must be stressed that this paper is tutorial in nature, and that an exhaustive treatment of all approaches is not possible in the space available. The reader is encouraged to consult the wealth of literature available if further and more detailed explanations are required.

Tabela 1. Resumo de técnicas de análise de superfície selecionadas

	AES	ELS	SIMS	XPS	UPS	ESD
Sonda	elétron	elétron	ion	raios-X	ultravioleta	elétron
Espécies detectadas	elétron	elétron	ion	elétron	elétron	ion
Resolução espacial	>100 Å	>50 A	<0.5 μm	10°-10° μm	10 ³ μm	- 1000 Å
Resolução em profundidade	5-60 Å	5-60 A	>3 Å	5-60 Å	5-60 Å	~3 Å
Sensitividade de detecção	0.1 at%	0.1 at,-%	<0.001 at%	0.1 at%	0.1 at%	
Quantitativa	++	-		***	-	+
Mapeamento	+++	S INDIGHT	++	phasmostic	to Date occup	**

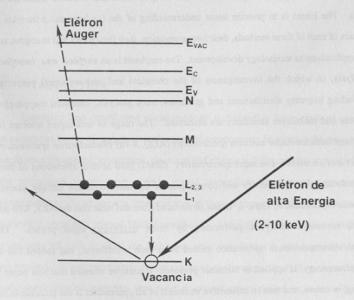


Fig. 1. Processo Auger.

2. DESCRIPTIONS AND PRINCIPLES OF THE TECHNIQUES

Surface elemental and ionic compositions, segregated impurity species at interfaces, doping profiles and gradients, interfacial chemical reactions and quantitative compositional information are fundamental measurements of primary importance to the design and performance of semiconductor electronics. The methods described in this section serve to provide such information.

Auger Electron Spectroscopy

This has emerged as one of the more useful and recognized surface-sensitive analytical techniques for the investigation of the chemical and compositional properties of electronic materials and devices. Several reasons account for the popularity and wide application of this technique. First, all elements except hydrogen and helium can be detected, with relatively rapid acquisition time, and reliable quantification of results. Second, the interpretation of data is not difficult due to the large base of scientific literature (handbooks, journal and review articles, research reports) available. Third, volume-compositional information can be obtained, on a depth resolution of 5-50Å, using simultaneous sputter etching or other material removal methods. This facilitates the identification of impurities at intra-material/device regions and interfaces. Finally, commercial instrumentation has evolved extremely rapidly, and can now provide computer-controlled data acquisition, data reduction and graphical output--with minimum danger of operator-induced analysis error.

AES involves the energy analysis of characteristic electrons, called Auger electrons, that are emitted from a solid via a radiationless process as a result of the ionization of the atomic core levels by an incident, energetic electron beam. Three fundamental mechanisms are involved in AES: (1) the ionization of the core level of the sample atoms under investigation by the electron beam, (2) the radiationless Auger transition, and, (3) the detection of the Auger electrons that escape from the sample into the vacuum. The process is illustrated in Fig. 1. The incident, 2-10 keV electron beam ionizes a core level, creating a vacancy in the inner level (i.e., the K-level in Fig. 1). This vacancy is filled immediately by another electron from a higher energy level, such as one of the L-levels. One of two process can now occur. The energy associated with the transition [K—>L] can be released

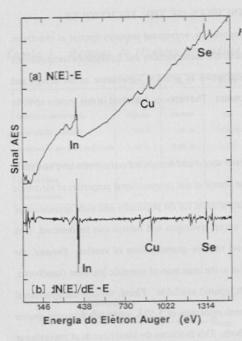
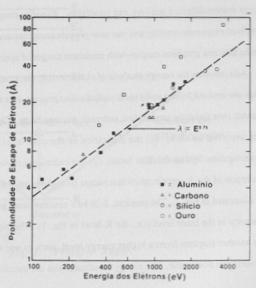


Fig. 2. Levantamentos AES:

- (a) [N(E)*E]-direto;
- (b) [dN(E)/dE].

Fig. 3. Profundidade de escape de elétron Auger para varios materiais.



in the form of radiation. If the energy difference E_K - E_L is large enough, characteristic X-rays are emitted—providing the basis for X-ray fluorescence. However, another event is probable. The energy can be transferred to another electron in the same level (or in a level close to it), and this electron can gain enough energy to escape from the atom if the différence E_K - E_L is large enough. The escaping electron, produced by the radiationless energy transfer, is called an Auger electron. Its energy is related to the difference in energy between the levels involved in its production, and thus provides an energy "fingerprint" for identification of the element. The Auger electrons emitted from a sample can be monitored by placing a suitable detector near the sample surface. A characteristic Auger survey is shown in Fig. 2 for Auger electrons detected directly [N(E)•E vs. E spectrum] or for the differentiated spectrum [dN(E)/dE vs. E spectrum].

Auger electrons created by the incident energetic electron beam must escape from the sample in order to be detected or counted. The physics of the escape of the Auger electron is the basis for the surface sensitivity of AES (as well as XPS and UPS). After Auger electrons escape from their host atoms, they undergo energy losses through collisions, plasma losses, core excitations and interband transitions. Thus, the density of emitted Auger electrons depends upon the mean free path of those carriers in the solid. Typically, mean free paths are small in semiconductors and metals, ranging from 4-40Å. The escape depth of Auger electrons is not usually the measured mean free path for a bulk sample, since the Auger electrons are influenced significantly by the surface of the material which is much different electronically and chemically in most cases than the bulk. Thus, surface composition, lattice geometry, surface roughness and incident angle of the primary beam can profoundly affect escape depths of Auger electrons. Fig. 3 shows the Auger escape depths for several materials as a function of the position of the characteristic transitions. These are generally determined empirically by depositing atomically-uniform films on metal substrates, simultaneously monitoring the Auger peak heights. The peaks usually decay exponentially, according to

$$N(z) = N_0 \exp[-z/\lambda]$$
 (1)

where λ is the Auger electron escape depth, N(z) is the density of Auger electrons originating at a depth z, and N₀ is that population at z=0. The Auger electrons which do not escape from the sample contribute to the almost uniform background "noise" upon which the AES peaks are superimposed. Since the phonon losses are nearly very small with respect to the natural widths of the Auger energy peaks, they do not significantly affect the Auger electron yield. Thus, from this consideration, low temperature measurements provide no advantage. The use of low temperatures in Auger measurements is primarily to minimize the alteration of the material being analyzed—to avoid loss or evaporation of compounds having high vapor pressure, such as HgCdTe.

There are several major contributions to the peak shape and peak energy position in an AES spectrum. The natural line width of an Auger peak is several eV, due to the short initial ionization state lifetime of about 10-16 s. Since electron emission in the Auger process always involves the binding energy of core levels and usually involves valence (outer shell) electron, the line shape and the probable peak energy are dominated by chemical environment. Peak width and shape are influenced by the density of states in the valence band, where a high density of states at a particular energy level will enhance the Auger yield from that energy level. This will cause fine structure within the wide Auger transition. Various loss mechanisms that affect the electron escaping the matrix (e.g., plasmon losses, interband excitations, core level ionization) can provide structure in the low energy side of the Auger transition peak. This specral difference makes it possible to distinguish between atoms that are absorbed on the surface from those that are bound in the bulk. Plasmons are created by energetic electrons losing discrete amounts of energy to excite collected oscillations of valence electrons under the influence of the positive cores. Thus, because plasmon energy loss is specific to certain solid, chemical changes—such as oxidation-can be noted by differences in the fine structure of certain peaks. Such is the case of the fine structure below the Si Auger transition, as shown in Fig. 4 for Si and SiO2. (Note that differentiated spectra are usually used to demonstrate peak shape differences. The direct N(E) spectrum also contains this information, but it is usually easier to discern in the differentiated case.)

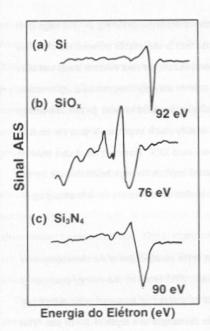
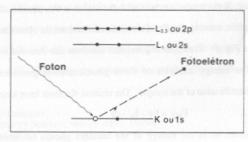


Fig. 4. Efeitos químicos em transições Si



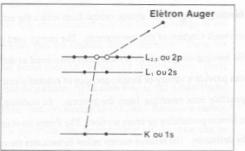


Fig. 5. Process XPS

Another difference is apparent in the two transitions presented in Fig. 4. The large shift in Auger kinetic energy (about 19 eV in this case) is observable between the chemical species. If strong bonding of two or more atoms occurs, the core electron levels can shift significantly in eV. Therefore, AES spectra contain not only compositional information, but a significant amount of chemical or bonding information as well. In fact, the energy shifts observed in the Auger transitions are usually much larger in eV than for binding energy differences found in the more commonly-used XPS. However, much care must be employed to avoid creating one's own chemical artifacts through beam damage by the incident energetic Auger probe. It is this reason that usually makes the less damaging X-ray probe desired for such chemical analysis.

X-ray Photoelectron Spectroscopy

This spectroscopy has its major application in the identification of the chemical species at the surface or interface being investigated. XPS involves the energy analysis of photoelectrons that are emitted from a solid as a result of monoenergetic, soft X-ray excitation. The usual X-ray sources penetrate the sample to a depth of 1 - 10 µm. This soft X-ray probe interacts with the atoms in this penentration region via the photoelectric effect, causing the direct emission of electrons (or photoelectrons). This process is shown in Fig. 5. These photogenerated electrons are detected by an appropriate spectrometer. The energy analysis of these photoelectrons provides the basis for the chemical identification of the sample. The emitted electrons have kinetic energies given by

$$E_{KE} = hv - E_b - \Phi \tag{2}$$

where hv is the energy of the incident photon (monoenergetic X-ray beam), E_b the binding energy of the atomic orbital from which the emitted electron originates, and ϕ is the work function of the spectrometer. The energy used to identify the chemical species is the binding energy, which is sometimes considered as the ionization energy. A given atom can provide a variety of kinetic energies of emitted electrons since there exist a number of possible ions resulting from the process. In addition, each of these processes has a different probability or cross section. The Fermi level is used as the zero binding energy by definition. The relative energy below E_f indicates the energy of the ion after the electron

emission—the binding energy of the electron. Upon ionization, it is usual for the p, d, and f-levels to split (e.g., $p \rightarrow p_{3/2}$, $p_{1/2}$; $d \rightarrow d_{5/2}$, $d_{3/2}$, etc.). Thus, the binding energy XPS spectrum provides information on the elemental composition and the chemical state of a given sample. The *composition information* is given by the energy positions of the various binding energy peaks, and the *chemical information* is gained by a knowledge of the shift in energy position from their elemental locations. A typical XPS spectrum is presented in Fig. 6.

Because the detected species are again electrons, the information depth is controlled by the escape depths of these carriers in the material being analyzed. Therefore, XPS is also a surface sensitive technique. It should also be noted from Fig. 6 that the XPS spectrum also contains Auger transitions. This is expected since Auger electrons can be created by any ionizing source—including X-rays. These transitions in the XPS spectrum are useful since they can aid in the identification of chemical species.

The major positive feature of XPS is that the technique provides little sample damage or alteration due to the nature of the input probe. This and the fact that it utilized the direct analysis of valence electrons make XPS the most reliable quantitative surface analysis method. Its major use for semiconductors is the identification of the chemical state of species at surfaces and interfaces. Combined with sputter etching, XPS can provide depth information in a manner similar to AES. Basically, the information obtained from XPS includes:

· Composition (peak energy position)

· Chemical bonding (peak energy position, energy shifts, shape)

· Quantification (area under peak)

· Auger electron transitions (positive identification)

The XPS spectrum contains major peaks that are associated with the binding energy of the electrons (photoelectron lines) in the atom and the emitted Auger electrons. These are dominant, but the spectra contain other peaks that can confuse the interpretation. These additional peaks that are sometimes observed include: (i) Satellite Peaks; (ii) Ghost Peaks; (iii) Shake-Up Lines; (iv) Valence Lines; and, (v) Energy Loss Lines. Because a variety of lines can be found in a given XPS spectrum, the interpretation of the data can be

complex and confusing. Line identification and chemical state identification require esperience.

Secondary Ion Mass Spectrometry

In the two previously discussed techniques, depth-compositional information is gained by performing the particular analysis simultaneous with removal of the material via the sputtering process. However, the interaction of the energetic ions with a solid results in the ejection of atomic and molecular species in both neutral and charges states. These positively and negatively charged particles are termed secondary ions, and are created in relatively high abundance as a result of the sputtering process. The direct detection of these secondary ions with high sensitivity mass spectroscopic techniques form the basis of secondary ion mass spectrometry or SIMS. The typical SIMS survey presents the SIMS ion current as a function of the mass to charge (m/e) ratio. This is sometimes simply interpreted as "amu", but note that the charge is involved. The predominant ion species observed in the SIMS spectrum are the singly charged atomic and molecular ions, as seen in Fig. 7. However, it is common to observe:

- Singly-charged monoatomic ions M_x[±]
- Singly-charged molecular ions M_xN_y[±], M_xN_yP_z[±]
- Multiply-charged species M+2, M+3, M+4 (dimers, trimers, etc.)
- Primary ions Ar+, Ar+2, O-, Cs+, etc.

The interpretation of SIMS spectra is divided into two considerations. The peak position at a given m/e provides the identification. The intensity of the peak relates to the concentration. Quantification is very difficult in SIMS. The method is inherently destructive. However, it has special characteristics not available in other surface analysis techniques. It complements AES or XPS in its high sensitivity to trace elements—capable of detecting ppm and ppb levels of impurities in semiconductors. For example, boron has been observed in Si at the low 10¹⁴/cm³ region. It is capable of directly detecting low atomic number elements such as H and Li. It has excellent depth resolution, which is controlled by the energy of the incident ion beam and the ionic species.

The problems and the elegance of the SIMS technique are focused in two areas. The first is the generation of the ionic species involving the sputtering process. Sputtering

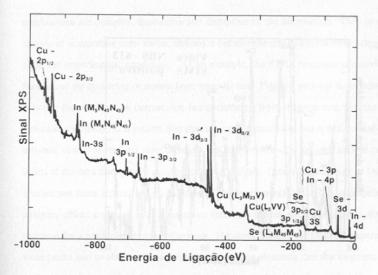


Fig. 6. Levantamento XPS para CuInSer.

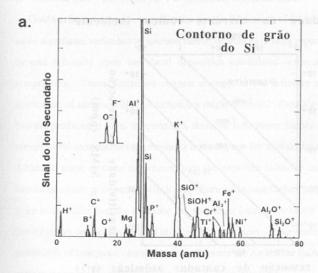


Fig. 7. Levantamento SIMS: (a) Silício

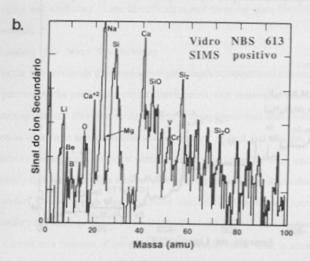


Fig. 7. Levantamento SIMS: (b) Vidro.

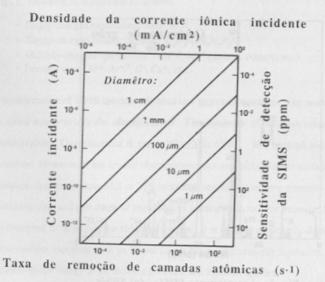


Fig. 8. Interdependencia de parametros SIMS.

mechanisms are complex, destructive and disruptive on the micro-scale. They provide a margin of interpretive error for the technique because the results are extremely dependent upon the experimental conditions. As an example, the SIMS detection sensitivity is a function of the sputtering or atomic layer removal rate. Figure 8 presents the relationships between the incident ion current, ion beam diameter, layer removal rate, and the SIMS detection sensitivity. It is evident that ultimate surface sensitivity and spatial resulation, for instance, cannot be realized simultaneously real instruments. The **second** area of concern is that of the detection systems employed for the analysis. Detection sensitivity to low-level species and mass separation is a function of the instrumentation. The quadrupole mass analyzer offers a simple and inexpensive approach in this area, and may be the most practical for a particular set of applications. However, it lacks the ability to separate isomass peaks and to obtain ultimate sensitivity to trace elements that the magnetic sector analyzer, for instance, has. Instrumentation and control of the experimental parameters are very important for this surface technique.

3. EXAMPLE: CONTACTS TO GALLIUM ARSENIDE

Gold has been a common *metallization* for the fabrication of GaAs devices. However, some significant variations in junction barrier heights have been reported, which seem to depend critically upon the metal deposition conditions—especially the substrate temperature. These variations suggest changes at the interface regions where the application of surface analytical techniques might be useful. Even for Au/GaAs Schottky barriers produced at room temperatures, there are indications that the model of a simple, abrupt metal-semiconductor junction is not adequate for explaining electrical behavior. Although some of these departures from the expected behavior can be explained by interfacial oxides or impurities which result from inadequate surface preparation procedures prior to metallization, the evidence for nonabrupt junction behavior also exists for Au parrier grown on vacuum-cleaved and ion-etched surfaces. These observations indicate the possiblility of *interfacial chemical activity* between the Au and the GaAs. Surface analysis techniques provide an excellent means to study these problems.

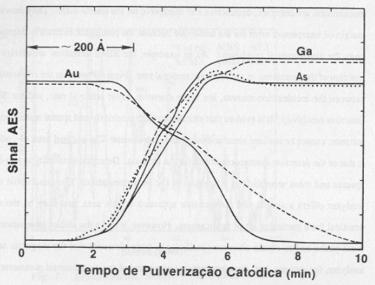


Fig. 9. Perfis AES da interfacie Au/GaAs. Linhas solidas: Antes tratamento termico; Linhas quebradas: Após tratamento termico.

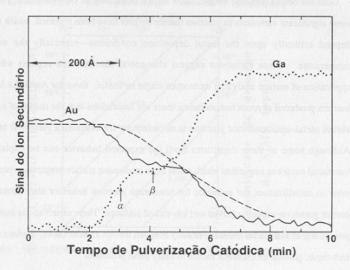


Fig. 10. Perfis SIMS da mesma interfacie da Fig. 9.

Figure 9 presents the results of several AES depth-compositional studies. The solid lines represent the transition from the 200 Å Au metallization through the GaAs substrate for a device fabricated at room temperature. It is evident that the transition region is broad, and the change in slope of the depth-profile lines indicates some degree of chemical reaction between the constituents. The chemistry of this interfacial transition region is examined more closely in the SIMS and XPS studies of Fig. 10 and 11. The solid lines in Fig. 10 represent the SIMS depth-compositional profile of the same as-deposited device shown in Fig. 9. These SIMS data complement the AES profile results very well, indicating approximately the same transition or interaction between the Au and the GaAs substrate. An apparent interrelationship between the Au and the Ga composition near the center of the transition region is indicated by the plateaus (about 30 Å in width) in the SIMS data for each of these elements. There is some indication of this region in the corresponding AES data of Fig. 9, but it is more pronounced in the SIMS profile due to the great escape depth of the Au (2024 eV) Auger electrons [about 50 Å] providing about 10 times less depth resolution than SIMS in this case. Significantly better resolution would have been gained in the AES mode if the lower energy (69 eV) transition were used in the profile. The XPS signal from the Au film itself (Fig. 12) yields the expected spectrum, with the 4f_{7/2} peak at 83.8 eV and the $4f_{5/2}$ at 87.3 eV. At point σ of Fig. 10, a double peak is observed, the elemental Au 83.8 eV peak, and another 4f7/2 peak near 85 eV which is attributed to a chemical shift due to the chemical reaction of the Au and the Ga. A double peak was also observed for the 4f_{5/2} transition, with a small peak shifted by 1.2 eV from the 87.3 eV position. This reaction is further confirmed by the XPS spectrum taken at point B, near the center of the transition region. Here, only one peak is evident, shifted to 85.1 eV from the elemental Au position. This chemical shift in the XPS Au 4f7/2 peak corresponds to Ga₂Au--a phase which has been reported only at higher temperatures.

The stability of the junction at elevated temperatures is also indicated in Figs. 9 and 10. The effects of heating at 723 K in vacuo for 20 min are shown by the broken lines. Both profiles indicate a significant amount of interdiffusion, primarily the Au into the polycrystalline GaAs. Outdiffusion of the Ga and As into the Au layer is also evident. By

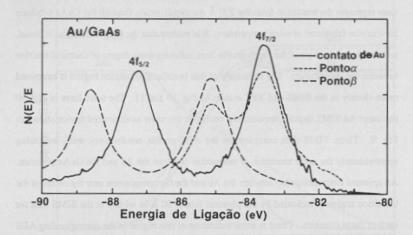


Fig. 11. Espectra XPS mostrando picos de Au nos pontos da Fig. 10.

fitting the AES or the SIMS data to an erfc representation of the diffusion process at several temperatures, the experimental dependence of the diffusion coefficient of Au into the polycrystalline substrate is calculated as

$$D = 4.6x10^{-2} \exp(-0.8eV/kT)$$
(3)

The pre-exponential term is about an order of magnitude higher than that reported for Au/single crystal Si, and the activation energy term is more than 10 times smaller. This indicates that the process of diffusion is along the grain boundaries, where the process is usually enhanced. Therefore, the surface analysis has been used to examine the chemistry of the metal-semiconductor interface and to analytical determine the diffusion parameters for the process.

4. SUMMARY

Surface analysis encompasses <u>more</u> than the three techniques discussed in this paper. All are very important tools for the solution of problems which inhibit the advancement of electronic devices. The analyst is greatly aided by the many developments in commercial equipment and the growing literature base in this area. Other techniques, such as the scanning tunneling microscope, continue to be developed. The area has *extensive* research potential for technique refinement, as well. However, the greatest impacts in the future will continue to be the progress that these methods provide in the important electronic semiconductor technologies.

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