AXIC APPLICATION REPORT

The Principle of X-ray Fluorescence Analysis in Thin Film Process Control

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Advances in thin film process analysis control have not necessarily kept pace with the generation of the thin films themselves for the magnetics and semiconductor industries. Advances in the deposition processes have been numerous in the past decade while analysis of the subject films is only now being fully addressed. In production process control it is important to be able to non-destructively determine film composition, thickness, crystal structure and boundaries among other properties. These analyses must be able to be readily carried out quickly and accurately in the manufacturing environment by the coatings practitioners themselves to allow process adjustment in a manner as close to real time as possible. With the aforementioned criteria, x-ray techniques are well suited for many applications. Major emphasis is placed on x-ray fluorescence as a viable solution for challenging analysis requirements for today as well as tomorrow.

X-ray fluorescence (XRF) is an elemental analysis technique whereby, in this case, coatings are analyzed for elements present in a given matrix. This method is efficient only for elements above atomic number 5 and becomes a primary analytical technique for elements above atomic number 11. As a primary analysis technique very low concentrations of elements (PPM range) are readily determined.

Two distinctive XRF analysis techniques are routinely carried out in academic and industrial settings. These are Wavelength Dispersive Spectrometry (WDS) and Energy Dispersive Spectrometry (EDS). Utilizing the WDS method, the given sample for analysis is radiated by an intense x-ray beam and the dispersion of characteristic x-ray radiation emitted by the elements in the sample are diffracted by means of an ordered crystal with known interplanar spacing according to Bragg's law $\lambda = 2 d \sin \theta$ where:

λ = wavelength in angstroms, (10^{-10} m)
d = interplanar spacing of the diffraction planes
θ = the angle between the incident x-ray and the diffraction plane

The WDS technique is shown in Figure 1.

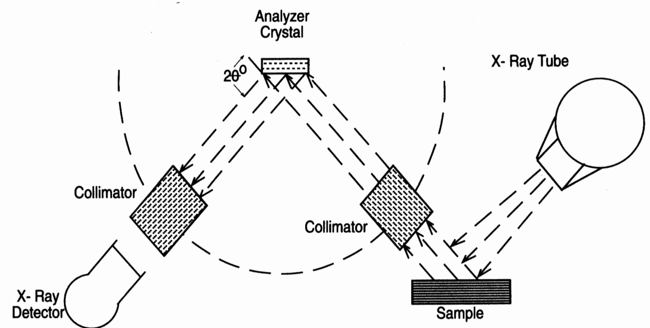

Fig. 1
Schematic diagram of wavelength dispersive x-ray fluorescence system.

X-rays are generated in a vacuum tube by impacting high voltage electrons on a metal target, generating (target) x-rays and allowing the x-rays to penetrate a thin Be window on the tube to exit into the analysis environment. The x-ray tube is depicted schematically as shown in Figure 2. Typical target elements such as tungsten and rhodium are selected for their x-ray energies to be slightly higher than the energy of the primary elements of analysis. The target x-rays are directed to the sample whereby characteristic x-rays are ejected from the atomic shell as depicted in Figure 3.

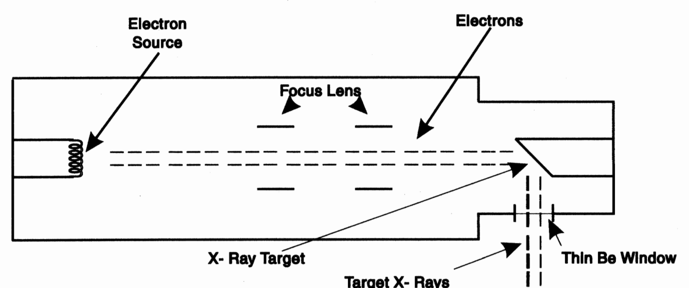

Figure 2. Schematic Diagram of X- Ray Tube

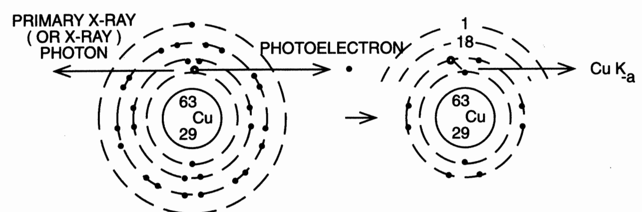

Fig. 3
X-RAY fluorescence.

The characteristic, elemental x-rays are then filtered with a parallel plate collimator to achieve a constant, solid angle, directed onto an analyzing crystal spectrometer, and separated according to Bragg's law. The single energetic x-rays are then counted by any of a number of different detector types, including silicon detectors, proportional counters, channeltrons, and phosphors etc. Most often proportional counters are selected due to high count rate (10^7 CPS) capabilities while being stable, reliable and not exhibiting dead time.

Advantages of the WDS technique include extremely high precision measurements. Disadvantages include fairly complex mechanical mechanism and ability to measure only one element at a time.

The EDS technique allows the x-ray spectrum to be separated according to their energies simultaneously. X-rays are generated in the sample in the same manner as with the WDS technique, however, the x-rays are scanned according to their energy utilizing a silicon (lithium) detector, whereby, hole-pairs are generated when the x-ray impacts the detector front face and the energy is scanned with a multi-channel analyzer and separated according to energy levels in approximately 150 eV intervals and the peak height is analyzed. Proportional counters are also used for this measurement with somewhat less energy resolution. By studying the peak height to energy in a comparative or fundamental method, the number of atoms in a unit volume are counted and thus related to the matrix. The EDS technique is depicted in Figure 4.

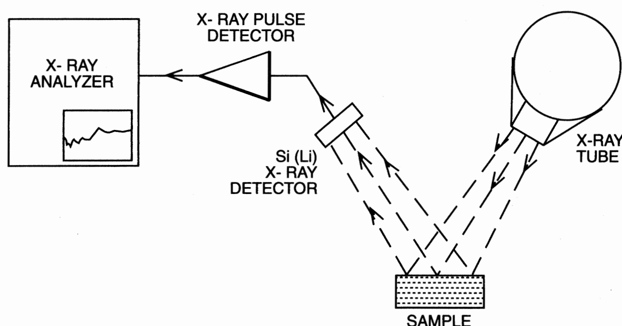

Fig. 4
Schematic diagram of EDS analysis system, by direct excitation of the sample from the x-ray tube, and detection by Si(Li) detector.

Advantages of EDS are in the speed of analysis. The entire energy spectrum can be scanned in seconds giving the signal for all elements present. By using developed data processing techniques, good approximations of the ratios of elements present to each other are obtained and concentration is calculated. Disadvantages are a sacrifice in precision and inability to separate elements with close energy levels (less than 150 eV).

Both techniques are extremely useful as materials analysis techniques and instruments combining both techniques give the best of both worlds.

Principles of XRF

A detailed discussion of this technique is beyond the scope of this note; however, there are many excellent references available. A brief summary is provided as follows. Electrons are arranged in the atom shells (energy levels). As a result of a collision between a charged particle or a photon and an electron at rest, the electron is expelled from its shell. The vacancy is immediately filled by an electron from a higher energy level. As a result of the electron transition from high to low energy level, a photon is emitted whose energy is equal to the difference between the two energy levels. This process is termed x-ray fluorescence and is further depicted in Figure 3.

A unique nomenclature system has evolved for discussing happenings in the atom. The conventional electron rings of the atomic structure K, L and M are used for spatial identification. The photon generated by an electron transition from the L to K shell is termed Kα and from the M to K shell is identified as Kβ and from M to L as L α, etc. Each element has its own characteristic XRF energy (energies). As an example SiKα and SiKβ lines have energies of 1.74 keV and 1.83 keV respectively. Likewise, iron has Fe Kα 6.4 keV and Fe Kβ 7.06 KeV. When exciting a sample film such as permalloy (80 Ni - 20 Fe) which contains some percentage of silicon, spectral peaks will be produced at all energies of Fe, Ni and Si for qualitative analysis. EDS is readily employed to provide a spectrum of elements present.

Taking the aforementioned data and performing quantitative extrapolation involves secondary effects such as differential absorption of radiation by different element concentrations and the excitation efficiencies of specific elements relative to other elements in the sample. XRF is definitely a product of the number crunching age; without the advent of modern high speed personal computers, one XRF analysis would wear out at least 3 abacuses and 4 operators. There are no simple linear relationships between XRF intensities and the elemental concentrations. It is necessary to insert correction factors, matrix absorption coefficients and excitation energy differentials to arrive at a satisfactory data fit to determine compositional analysis. Extensive efforts have been expended to integrate effective correlation for comparative analysis and fundamental determination.

Theory

X-rays are photons - a form of electromagnetic energy. They can be considered as particles with energy but without mass.

Equivalently they can be described as radiation with wavelength

$\lambda = 12.4$ E (keV) where E = Energy in keV.

X-rays are generated as a result of the transition of an electron from a higher to a lower energy level in the atom. This differs from α, β and λ radiation, which stem from the atom's nucleus.

The absorption of x-rays in matter takes place by three different processes: a) photoelectric absorption in which the x-rays deliver their energy to the electrons bound to the atoms, causing the ejection of the electrons from their orbit; b) coherent scattering (Rayleigh scattering) whereby the photon changes its direction without losing its energy; c) incoherent scattering (Compton scattering) by which the photon changes its direction and delivers part of its energy to the electron in the matter.

Most of the radiation is absorbed by the photoelectric effect in the 1st case, whilst the latter two may be considered as unwanted interference in the analysis.

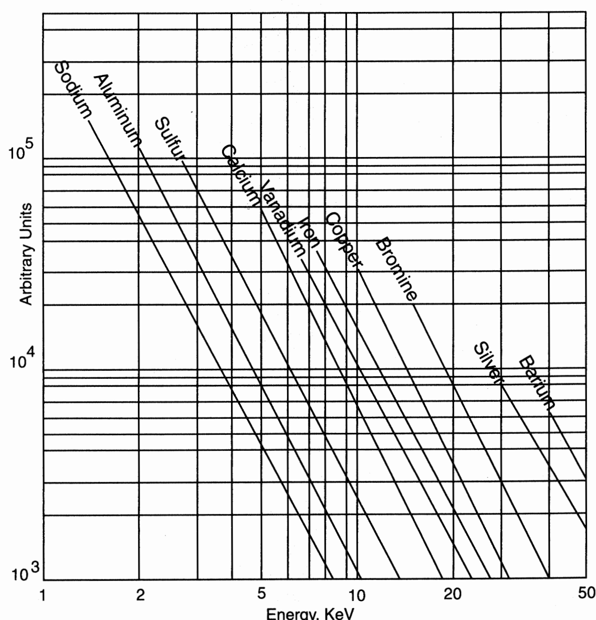

Fig. 5
Excitation probability versus energy and atomic number.

Optimal Excitation

Each element can be excited, i.e. caused to emit its characteristic x-rays, by radiation with energy higher than a certain minimum (the minimum required to eject an electron from its orbit). This energy is called the absorption edge energy and is labeled as K_{ab}, L_{ab}, which stands for ejection of an electron from the K-shell and the L-shell respectively.

Excitation is most efficient when the exciting photon energy E_p is just above the absorption edge E_{ab}. The excitation efficiency decreases as the difference E_p - E_{ab} increases. See figure 5.

The minimum concentration of an element that can be detected - Minimum Detection Limit (MDL) - depends on: a) the intensity of its XRF; b) the background mainly due to coherent and incoherent scattering. Thus, for a low MDL, it is desirable to excite the element with a radiation energy not too far from the absorption edge.

In general, when analyzing elements with concentrations of a few percent or more, the background is not a problem and a simple excitation system may suffice. When attempting to measure low concentrations of a few ppm or even less, optimal excitation conditions are essential. Care must be taken to maximize the signal to background ratio.

Inter-Element Influences

In samples where element concentrations are of the order of a few percent or more, there are inter-element influences. For instance, in stainless steel containing nickel, iron and chromium, the nickel's x-rays have enough energy to excite the iron and the chromium; the iron can also excite the chromium. Thus, the chromium's XRF becomes more intense than expected while the nickel's XRF is less intense than expected. This effect should be taken into account in calculating the concentrations in the sample.

Light and Heavy Elements

The binding energy of the internal shell electrons in the atom depends on the electrical charge of the nucleus. Higher atomic numbers, Z, produce stronger electrical forces between the electrons and the nucleus. Thus, both E_{ab} and the XRF radiation are functions of Z. For example, for gold (Z = 80), Au K_{ab} is equal to 80.7 keV. For iron (Z = 26), Fe K_{ab} is equal to 7.11 keV. It is not practical to excite the K lines of high Z elements because it requires very high excitation energy, i.e. expensive x-ray generators.

Instead, it is more practical to excite the L line of high Z elements, (L_{ab} of gold is only 14.3 keV). In this way, all high Z elements can be excited by standard x-ray generators.

The absorption of x-rays in matter depends strongly on Z. High Z elements absorb x-rays more strongly than low Z elements. The absorption is also energy dependent; i.e. more energetic x-rays penetrate deeper into matter. These two facts have very important consequences. The sensitivity of detection of high Z elements, in a low Z matrix, like traces of heavy metals in an organic matrix, is high. The opposite is true for detection of light elements in high Z matrix, like Al or Si in tungsten alloys. In most cases, better sensitivity is possible when the K line is detected instead of the L line, because the K x-ray has higher energy and is less absorbed in the sample. Very low Z elements have to be analyzed in vacuum or Helium to eliminate the XRF absorption by air. The absorption of the XRF from low Z elements by the detector entrance window limits the sensitivity of the analysis to elements of atomic numbers 11 and up.

Thin Film Composition and Thickness Measurement (Axic 100-II and Precision 1000)

Thin films are analyzed with the WDS and EDS techniques. A typical film on a substrate is schematically shown in relationship to the analysis system in Figure 6.

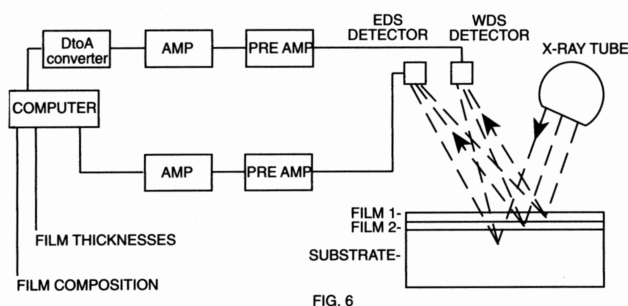

FIG. 6

Typically the EDS spectrum is analyzed and summed for film thickness. Where 2 or more films are present, the WDS signal is sequentially analyzed and processed to precisely measure the independent thickness of each film. Composition can be measured and approximated by a rough scan of the EDS system with the multi-channel analyzer. Precise elemental compositional analysis is conducted with the WDS.

The combination use of EDS and WDS yield the best of both worlds for process monitoring analysis in the control of thin films. EDS is employed for rapid qualitative determinations while WDS is simultaneously or sequentially utilized for precise determinations for film thickness and film composition. In some complex structures, EDS single channel analysis coupled with WDS sequential analysis, are employed to speed up determinations.

System Capabilities

Each film and substrate combination under analysis has its own customized analysis technique setup in memory. All the fundamental iterations previously discussed are setup in files with specific constants for all variables. Least squares fit calibration tables are setup for each analysis. The 'recipe' for the particular process under control is called from the menu. Standard procedure defaults are automatically selected. However, these are easily overridden and changed as desired. Single point analysis can be selected or up to 25 points can be mapped. The analysis can be repeated X times to insure creditability. Data is outputted to a monitor and/or printer and is permanently stored to process with established process limits as set to determine if the process is in/out of control. Full SPC is provided for composition and thickness measurements.

See Application Notes 1 through 5 for your specific analytical measurement requirements.

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