AXIC APPLICATION REPORT

Non-Destructive Composition and Thickness Analysis of Metal Films
Using Combination EDS/WDS X-Ray Fluorescence Spectrometry

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AXIC HAS DEVELOPED A DEDICATED dual detector (combined wavelength dispersive and energy dispersive) x-ray fluorescence (XRF) spectrometer system for non-destructive analysis of thin films. Metal films used in the semiconductor and magnetic media fields are addressed in this application paper. For a discussion of the analysis of silicate (PSG and BPSG) glass films and equipment description and operation, see AXIC Application Report No. 1.

The primary advantage of using a dedicated dual detector XRF system to analyze single and multilayer metal films include:

- Simultaneous analysis of film *thickness* and *composition* in one or more layers.
- Rapid non-destructive measurements can be made in a production environment by production personnel.
- Use of both wavelength and energy dispersive detectors allows analysis of light and heavy elements, avoids peak overlap problems if an EDS detector is used alone, and makes possible cross comparison of data to improve measurement accuracy.
- Calibration procedures are simple and require few standards.

The wavelength detector has an energy resolution of 10 to 15 eV, 10 to 20 times better than that of energy dispersive types and monitors one element at a time per crystal. EDS detector based systems can detect many elements simultaneously. By combining the two types of detectors in a simple dedicated system, it is possible to cover a broad range of applications each type of detector would be unable to handle, optimally, alone.

Principles of XRF Analysis of Thin Films

XRF analysis of thin films (typically from 10 Angstroms to many micrometers in thickness) is simple in principle. A beam of x-rays from an x-ray source (tube or radioactive material) of sufficient energy to pass completely through the film or films of interest is directed at the sample. In passing through the sample the incident beam fluoresces (excites) elements present in the sample, which give off characteristic x-rays unique to each element. These characteristic x-rays are detected by energy and number with either a wavelength (crystal) or energy dispersive (lithium drifted silicon diode or proportional counter) detector system. By counting the characteristic x-rays from each element in the sample and/or the substrate, it is possible to determine film composition and thickness. The process of quantifying film thickness and composition from the raw data is frequently quite complicated and will be discussed later in detail.

The x-rays used (in energy and flux intensity) to excite the sample are chosen by application requirements; i.e., by the composition and thickness of the film and substrate to be analyzed. The energy of the probing x-rays is determined by the choice of the x-ray tube target material and the total incident flux by the tube power and the system geometry. For example, if one wished to analyze an AlSi film on boron nitride, rhodium would be a good tube target choice, for the **L lines** of **Rh** at 2.7 keV are sufficiently energetic to excite efficiently the **Al K lines** at 1.5 keV and the **Si K lines** at 1.7 keV. In the case of a NiFe film, a rhodium target could also be used, even though the **Rh K lines** lie at 20.2. keV; however, germanium would be a better target choice, for the **Ge K lines** at 9.9 keV lie just above the **Fe** and **Ni K lines** at 6.4 and 7.5 keV, respectively. In short, the ionizing incident x-rays must be higher in energy, above the absorption edge of the characteristic elemental lines of interest **(K, L, or M)** coming

from the sample, in order for fluorescence to occur. The most efficient sample excitation occurs when the x-ray tube target chosen produces radiation just above the absorption edge of the elemental lines of interest.

Once raw data have been acquired, some spectral processing may be required before quantitative routines may be employed, particularly if a silicon EDS detector is being used. First artifact peaks need to be identified and removed and the spectral background determined and removed. Also, if there are serious peak overlaps, as may often occur when using an EDS detector (either silicon or proportional), it may be necessary to separate or deconvolute the peaks of interest. Once net peak intensities have been determined, they may be entered into algorithms for determining film thickness and composition. The algorithms may be least squares or multiple regression curve fitting routines or fundamental parameter logarithmic functions relating three key variables (film composition, density, and thickness) to net peak intensity. They also include matrix correction programs to cover absorption and secondary fluorescence effects, for net peak intensities are generally not directly proportional to film thickness and composition.

Film Thickness Measurement

Determination of film thickness can be done by two methods, depending on substrate composition; by emission of characteristic x-rays from the film of interest or by absorption of characteristic x-rays from the substrate in the overlying film. For example, to measure the thickness of an Al film on a silicon substrate, the thickness of the aluminum film can be logarithmically related to the aluminum **K line** net peak intensity or to the absorption of silicon **K line** intensity from the substrate in the aluminum film. With a wavelength dispersive system, which can easily separate the **Al** and **Si K lines** which overlap in an EDS system, it is possible to measure film thickness by both approaches simultaneously, if more than one crystal is available, or sequentially by moving the detector from the Al to the Si x-ray emission line of interest.

The two methods for film thickness measurement are described in Figure 1 and as follows:

Film Emission Method

The element in the film that is being studied must be absent in the substrate, Fig. 1B. With the foregoing, one measures the direct intensity of the line of interest using the following:

$$\log_e[1 - (I_{F,t}/I_{F,\infty})] = - \overline{(\mu/\rho)}\rho t$$

where:

$$\overline{(\mu/\rho)} = (\mu/\rho)_{\lambda\text{pri}} \csc \blacklozenge + (\mu/\rho)_{\lambda L} \csc \psi$$

- ♦ is the angle between the central ray of the primary cone and the specimen.

- ψ is the angle between the central ray of the secondary cone and the specimen—the takeoff angle.

A plot of $I_{F,t}$ or of $1 - (I_{F,t}/I_{F,\infty})$ *versus* thickness may be prepared from standards.

Cameron and Rhodes[2] define the maximum thickness that can be determined by this method in terms of the mass-absorption coefficients of the element for the primary and analyte-line x-rays as:

$$t_{max} = \frac{3}{(\mu/\rho)_\lambda + (\mu/\rho)_{\lambda_A}} = \frac{3}{\overline{(\mu/\rho)}}$$

The minimum thickness is determined by the background.

Substrate Attenuation Method

This method is defined by the measurement of the attenuation of a substrate element line passing through the overlaying film, Fig. 1A, by the following:

$$\log_e(I_s/I_{s,F}) = \overline{(\mu/\rho)}\rho t$$

where ρ is film density in g/cm³. A plot of Is,F or Is/Is,F versus thickness may be prepared from standards having a known film thickness.

The following notation is used:

I_0 is the intensity of the incident primary beam

$I_{F,t}$ is the intensity of the film-element line from a film thickness t

I_F is the intensity of the film element line from infinitely thick film metal

$I_{s,F}$ is the intensity of the substrate element line after emerging through the overlaying film

I_s is the intensity of the substrate-element line from an uncoated substrate

t is thickness

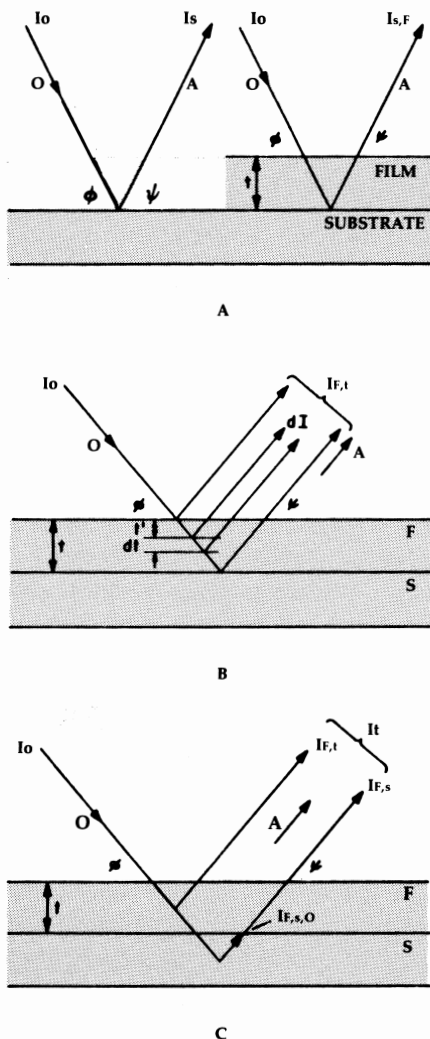μ is the mass absorption coefficient of the specimen (cm^2/g)

FIG. 1. **Basic methods for x-ray spectrometric determination of film thickness.** A. Attenuation of the line of a substrate element absent in the film. B. Emission of the line of a film element absent in the substrate. C. Emission of the line of a film element also present in the substrate.

Calibration can be accomplished with multiple type standards covering the range of film thicknesses to be measured, in conjunction with least squares or multiple regression routines; or by using an empirical fundamental parameter approach using a bulk and one thin film standard for all key elements in the film matrix and substrate, if necessary.

When determining the thickness of multi-element compound films, things become a bit more involved. For complicated matrix, corrections are often required in addition to dealing with the standard variables — film thickness, composition, and density — in order to make accurate thickness determinations. If film composition does not vary, film thickness can be related to the net peak emission intensity of one element present in the film or by absorption in the film of a signal from the substrate. For example, if one were measuring the thickness of a NiFe film on silicon, the film thickness could be determined by either measuring the net peak intensity of the Ni $K\alpha$ or Fe $K\alpha$ lines, or by measuring the net silicon $K\alpha$ intensity (assuming the thickness of the overlying NiFe film is not too great) after absorption in the NiFe film.

If film composition varies and there are two or more elements in a film, as in oxide superconductor films, measurement procedures become even more complicated. Generally, when dealing with unknown multielement films (particularly for nonmetals and oxides), it is desirable to weigh accurately the substrate with an analytical balance before and after film deposition and determine film thickness by profilometry or some other method, if possible, to determine average film density. Also, it is necessary with complex films to use a strict fundamental parameters' approach without standards, or a modified fundamental parameter calibration with pure bulk and thin film material for each element in the sample matrix in order to quantify film thickness and composition. Also, with several variables to deal with simultaneously, and not enough equations for every unknown, an iterative calculation process must often be used.

Film Composition Measurment

Measurement of the composition of simple all-metal films (such as AlSi, AlCu, NiCr, TiW, NiFe, CoCr, etc.) can be accomplished a couple of ways — by ratioing net peak intensities if film thickness does not vary—or by using an iterative fundamental parameter, with or without standards, type approach. For more complex single and multilayer multielement films, the fundamental parameter approach is the only practical method. The number of standards that would be required for calibration is prohibitive in cost and time.

Measurement of films with a common element in two or more layers and/or the substrate is a major difficulty, which cannot always be resolved. For example, analysis of the composition of AlSi alloys and silicides on silicon by XRF is not feasible. However, if another suitable substrate can be found, such as pyrolitic graphite, boron nitride, or Ge coatings over silicon, then it is possible to measure both film thickness and composition. A composite wafer of Ge deposited over silicon has been found to be particularly useful as an alternate substrate for it can be made in the same dimensions as a standard silicon wafer (4, 5, 6, or 8 inches). It is a high purity material, and can be recycled repeatedly (after chemically etching the previous deposition off) through a production process for monitoring purposes.

It is also possible to measure the thickness and composition of a film with a common element in an over- or underlying layer, if the composition and thickness of one layer are known. For example, it has been possible to measure the thickness and composition of many multilayer magnetic films with a common element in two layers — CoCr/Cr/NiP, CoP/NiP, and others. . . .

Measurement Precision, Accuracy and Detection Limits

Measurement precision is a function of three key factors — counting statistics, overall instrument stability, and sample placement reproducibility. It is generally expressed statistically as ± 1, 2, or 3 Standard Deviations (Sigma) or as %RSD (Relative Standard Deviation) at the 1, 2, or 3 Sigma level; e.g., the measurement precision for phosphorus in PSG can be expressed as 7.8 Wt. % ± 0.1 (2 Sigma) or 1.3% RSD (2 Sigma). Measurement accuracy is a function of overall measurement precision and the uncertainty in the composition and thickness values of the standards used. **Measurement accuracy can never be any better than the statistical uncertainty in the measured values for the standards.** Measurement precision for all film applications presented in the following material is clearly noted. Accuracy figures are also shown, when suitable standards have been available.

Typical measurement detection limits for thickness and composition depend on several variables — counting time, peak to background ratio, and film and substrate composition. Accurate detection limits must be calculated for each film matrix type. In general, however, it is possible by XRF to measure pure metal film thickness to less than 10 Angstroms and elemental concentrations from about 0.1 percent by weight, depending on film thickness and composition.

Standards

Accurate thin film composition and thickness measurement requires well characterized standards, regardless of the analytical method used. Thin film standards are not readily available, for they require that a broad range of cross correlated analytical techniques be used to determine film uniformity as well as composition and thickness. For a discussion of the importance of thin film standards for manufacturing quality control, see Reference 3.

Typical Analyzed Films for Thickness and Composition

Al-Si — Composition and Thickness

SAMPLE	SUBSTRATE	RUN	COMPOSITION WT. % Si	FILM THICKNESS ANGSTROMS
1	2 μ Ge Film over Silicon	1	.45	8261
		2	.43	8434
		3	.41	8425
			Avg .43 $\pm$ .02 (σ)	Avg 8377 $\pm$ 92 (σ)

WSi$_x$ — Composition and Thickness

SAMPLE	SUBSTRATE	RUN	COMPOSITION WT. % Si	FILM THICKNESS ANGSTROMS
1	Silicon	1	25.4	2350
		2	25.0	2370
		3	25.1	2340
			Avg 25.3 $\pm$ .2 (σ)	Avg 2350 $\pm$ 40 (σ)

TiW — Thickness

SAMPLE	SUBSTRATE	RUN	GIVEN THICKNESS ANGSTROMS	MEASURED THICKNESS ANGSTROMS
1	Silicon	1	715	705
		2		698
		3		712
				Avg 705 $\pm$ 7 (σ)
2	Silicon	1	1262	1278
		2		1293
		3		1265
				Avg 1278 $\pm$ 14 (σ)
3	Silicon	1	1640	1622
		2		1643
		3		1636
				Avg 1634 $\pm$ 11 (σ)
4	Silicon	1	2033	2016
		2		2018
		3		2057
				Avg 2030 $\pm$ 23 (σ)

Al-Si-Cu — Composition and Thickness

SAMPLE	SUBSTRATE	RUN	COMPOSITION WT. % Si	COMPOSITION WT. % Cu	FILM THICKNESS ANGSTROMS
1	2 μ Ge over Silicon	1	.63	.50	10,140
		2	.61	.40	10,235
		3	.69	.44	10,123
			Avg .64 $\pm$ .04 (σ)	Avg .45 $\pm$ .05 (σ)	Avg. 10,166 $\pm$ 100 (σ)

Cr/Au — Stack, Thickness

SAMPLE	SUBSTRATE	RUN	MEASURED THICKNESS ANGSTROMS	
			Cr	Au
1	Silicon	1	95	1900
		2	75	1910
		3	61	1910
		4	70	1904
		5	62	1900
			Avg 73 $\pm$19 (σ)	Avg 1905 $\pm$5 (σ)
2	Silicon	1	313	1869
		2	300	1856
		3	333	1866
		4	319	1875
		5	309	1873
			Avg 315 $\pm$20 (σ)	Avg 1867 $\pm$12 (σ)

Cr/Co — Stack, Thickness

SAMPLE	SUBSTRATE	RUN	GIVEN THICKNESS ANGSTROMS		MEASURED THICKNESS ANGSTROMS	
			Cr	Co	Cr	Co
1	Aluminum	1	2500	360	2514	360
		2			2490	371
		3			2520	364
					Avg 2514 $\pm$25 (σ)	Avg 363 $\pm$10 (σ)

Summary

In summary the AXIC-100 with energy dispersive and wavelength dispersive spectrometers is readily employed to measure the composition and thickness of single and multiple element films in single and multiple layers. Elements above atomic number 11 are readily analyzed. Compositional analysis precision ranges from .1 to 1 wt.% depending on the element and film thickness and thickness precision measurements range from $\pm$ several Angstroms to $\pm$ several hundred Angstroms dependent on the elements being measured and the film thickness.

In many cases, combination EDS/WDS x-ray fluorescence is the only method to non-destructively determine metal film compositions and thicknesses. This is particularly relevant in very thin films (less than 500 Angstroms) and in stacks of films.

References

1. Bertin, E.P., ''Principles and Practices of X-Ray Spectrometric Analysis,'' Plenum Press, pp. 811-814, 1984.

2. Cameron, J.F. and J.R. Rhodes, ''Coating Thickness Measurement and Chemical Analysis by Radioisotope X-Ray Spectrometry''; in ''Encyclopedia of X-Rays and Gamma Rays,'' G.L. Clark, ed.; Reinhold Publishing Corp., N.Y., pp. 150-6, 1983.

3. Augenstine, J., G. Kladnik, and L. Bernard, ''Thin Film Standards for Process Monitoring,'' Microelectronic Manufacturing and Testing, August 1987.

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