

Application Note: XRF

Coating Thickness and Composition Analysis by Micro-EDXRF



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Introduction:

The use of coatings in the modern manufacturing world continues to increase in an effort to improve product performance and reduce product cost. Coatings are used in a variety of applications including electrical/electronics, anti-corrosion and wear resistance. New layer systems are developed and these are often multi-layer systems, which may include very thin layers. Furthermore, layers are deposited over varying regions of interest – for example, very small areas, such as individual electrical contacts to an IC chip; and larger areas, such as the entire field of a plasma coater. It is of great interest to determine the thickness/composition parameters of individual electrical contacts as well as the coating homogeneity of a plasma coater.

Energy-Dispersive X-ray Fluorescence (ED-XRF) has been used for many years to characterize the thickness and composition of various coatings. XRF analysis is an ideal method for many types of coating structures due to the fact that the technique is non-contact, non-destructive, and requires little if any sample preparation. Micro-EDXRF, with its capability to measure thickness/composition parameters within a very small area or to measure individual points over a larger area, is well suited for the analysis of many coatings used in today's manufactured products.

The basic principle behind XRF coating analysis can be explained as depicted in Figure 1. Given a simple example of a pure layer of Zn coated on a base of steel, exciting X-rays penetrate through the Zn layer and into the Fe substrate (Figure 1a) generating Zn and Fe X-ray signals detected by the ED-XRF spectrometer. In Figure 1(b), an example of an ED-XRF spectrum is shown. The intensity of the relevant spectral peaks are calculated and plotted in Figure 1(c) as a function of Zn layer thickness. As the Zn layer gets thicker, the Zn intensity increases as more Zn X-rays are generated. Eventually, intensity becomes relatively insensitive to thickness as the curve plateaus, because Zn X-ray signals originating from greater depths within the layer are completely absorbed within the thick Zn layer itself. (See EDAX Application Note: *Analysis Depth for micro-EDXRF Methods*). This is known as the “Saturation Thickness” or “Infinite Thickness”. Conversely, the Fe intensity decreases as the Zn layer thickens because Fe X-rays are absorbed within the Zn layer. Eventually, the Zn layer becomes thick enough to absorb most or the entire Fe X-ray signal being generated. This kind of function can be characterized by standards or modeled in some cases to yield direct results on the mass coverage [mass per unit of area, e.g. $\mu\text{g}/\text{cm}^2$] of each detected element. Mass coverage can be converted to thickness, given the density [g/cm^3] of the material in the layer or, for an alloy layer, the mass coverage for each element in the alloy, can be combined to give alloy composition.

The Orbis micro-EDXRF spectrometer simply uses a small XRF beam to analyze the coating thickness and composition over a small area or the distribution of these parameters over a larger area. Large area analysis is done by moving the sample under the analytical beam.

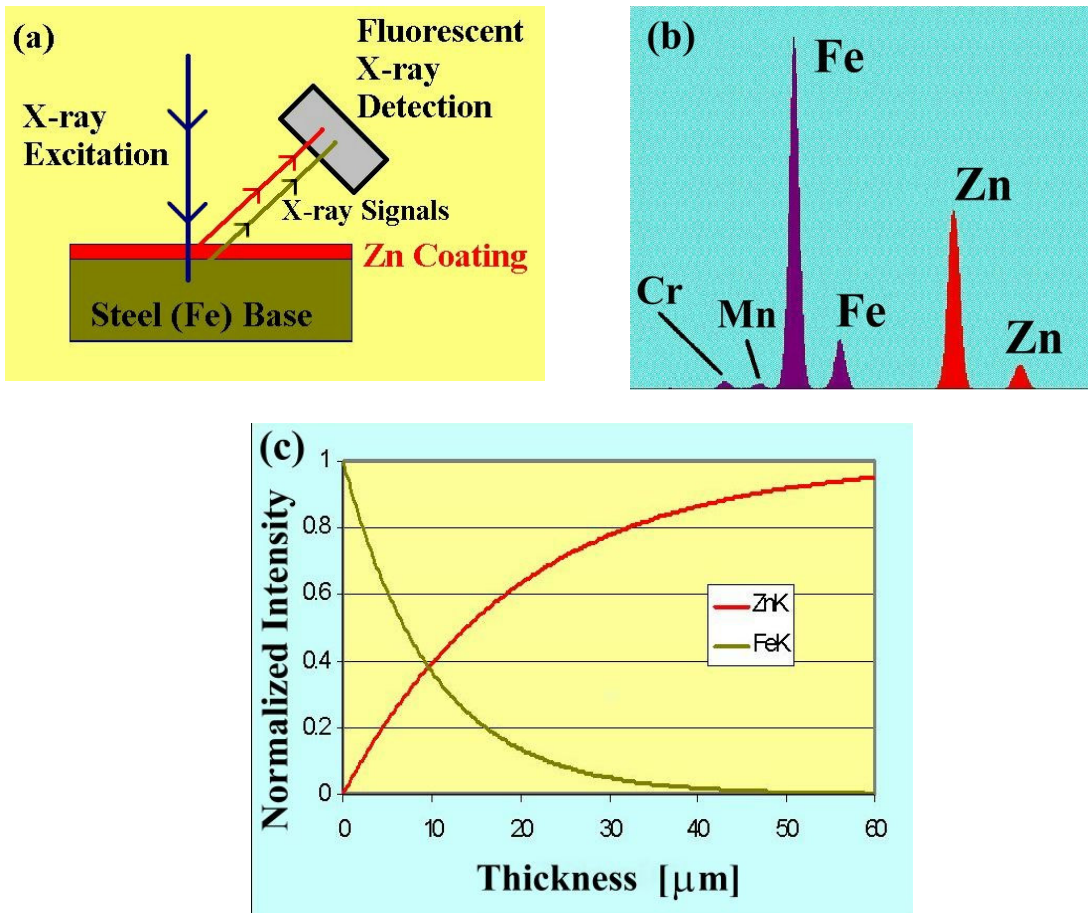


Figure 1: (a) XRF excitation & detection of Zn plated on Steel
 (b) XRF spectrum of Zn and Fe signals
 (c) Theoretical plot of Zn and Fe intensities as a function of Zn thickness

Coating Thickness and Composition Analysis:

At the end of this application note, an example of the Orbis micro-XRF analysis of a complex coating structure will be given. At first, however, a description of the capabilities of the XRF coating analysis technique is provided.

Types of Coating Systems: XRF analysis of layered systems is quite versatile in that it can handle the analysis of simple to complex coating structures. For example, it is possible to measure:

<u>Coating System</u>	<u>Result</u>
Single layer: “pure” metal	Thickness
Single layer: “pure” oxide, nitride, etc	Thickness
Single layer: alloy	Thickness & Composition
Multiple layers: “pure” layers	Thickness of each layer
Multiple layers: “pure” and alloy layers	Thickness & Composition of each layer

For the best accuracy (which is often required to control the performance of high-tech devices), standards are required to calibrate the XRF coating models. The number of standards depends on the thickness range to be covered. Referring back to Figure 1(c), the first portion of the intensity curve is approximately linear, which is known as the “thin film region”. As the film gets thicker, this function becomes increasingly non-linear, which is known as the “thick film region”. The minimum requirements are listed in Table 1. Of course, the more standards that are available, the better the calibration that can be made.

Table 1: Minimum # of Standards for Coating Calibration

Limit	Requirements
Thin Film	<ul style="list-style-type: none"> • 2 – 3 standards for each layer • “pure / infinite” material for each element in the layer system
Thick Film	<ul style="list-style-type: none"> • 3- 4 standards for each layer • “pure / infinite” material for each element in the layer system

As an example, given an Fe:Ni alloy layer, nominal 20wt% Fe, (thin film limit), then, 2 standards covering the thickness range to be covered with a composition of roughly 20wt% Fe will be needed. In addition, “pure” (> 99.8%), “infinitely” thick pieces of Fe and Ni are required to normalize the calibrations. In most situations, a foil 200 to 300 μm (i.e. 0.008 to 0.012”) thick would easily satisfy the condition for “infinite” thickness.

Where accuracy in the range of 5% to 10% is acceptable, then modeling methods can be used. In this case, only the pure / infinitely thick materials are needed to normalize the model calibration and a wax block (free of XRF signal generating impurities) is needed to collect an X-ray scatter spectrum. The wax block should be at least 2.5 cm (i.e. 1”) thick. For alloy layers, where both thickness and composition can vary, it is necessary to use a calibration with standards to analyze the alloy layer.

Detected Elements: XRF coating analysis is limited to elements detected by the XRF spectrometer, which is typically Na through U for micro XRF systems with vacuum capability (i.e. the EDAX Orbis). For example, it is possible to determine the thickness of a TiN layer given the TiN density. But, it is not possible to determine the composition of the TiN layer, since the signal for N cannot be detected. In the case of TiN, the layer is assumed to be of constant composition. A similar situation occurs for oxide layers like SiO₂.

Thickness Range: The maximum thickness measurable by XRF is determined by physics and depends on 3 basic factors: (1.) Observed X-ray line energy; (2.) Density of layer(s); (3.) X-ray absorption in same layer or layer(s) above. The limit of detection (LOD) for a thickness measurement is determined also by instrument parameters. In Table 2, estimated saturation thickness and LODs are shown for some single layer applications:

Table 2: Saturation and LOD Thickness of Au, Zn and Al layers

Layer (Density [g/cm ³])	Observed Line (Energy [keV])	Saturation Thickness [μm]	LOD Thickness [μm] (3σ criteria)
Au (19.370)	Au L-line (9.71)	8	---
	Au M-line (2.12)	0.3	~0.0005 ^a
Zn (7.140)	Zn K-line (8.64)	50	
SiO ₂ (~2.2)	Si K-line (1.74)	10	~0.0005 ^b

^a Coated on PCB electrical contact

^b Coated on thin plastic foil

Multiple Layer Systems: For complex coating systems with layer on top of layer, a unique element must typically be associated with each layer in order to measure thickness via XRF methods. For an alloy layer, each element in the alloy should only occur in that alloy layer for proper measurement of both thickness and composition. For example in a multiple layer system, suppose there is a layer of Ti and a layer of TiN. The measured Ti intensity would be a combination of signals from both the Ti and the TiN layers. XRF coating algorithms do not have the capability to determine how much Ti intensity comes from the Ti layer and how much comes from the TiN layer.

Example: Analysis of a Solar Cell Module

Introduction: Solar energy conversion has proven to be a promising technology in the field of renewable energy science. Solar cells (devices which convert the sun's energy into electricity) can be made by coating various materials on top of one another. Due to the complex nature of the energy conversion process, it is important to know the layer thickness and composition of each layer with a high degree of accuracy.

The structure of the solar cell coating system measured in this example is depicted in Figure 2. Each layer of the solar cell has a specific function. ZnO and Mo layers act as electrodes and contacts. The CdS is a diffusion barrier. The actual energy conversion process takes place in the CuInGaSe layer (abbreviated CIGS).

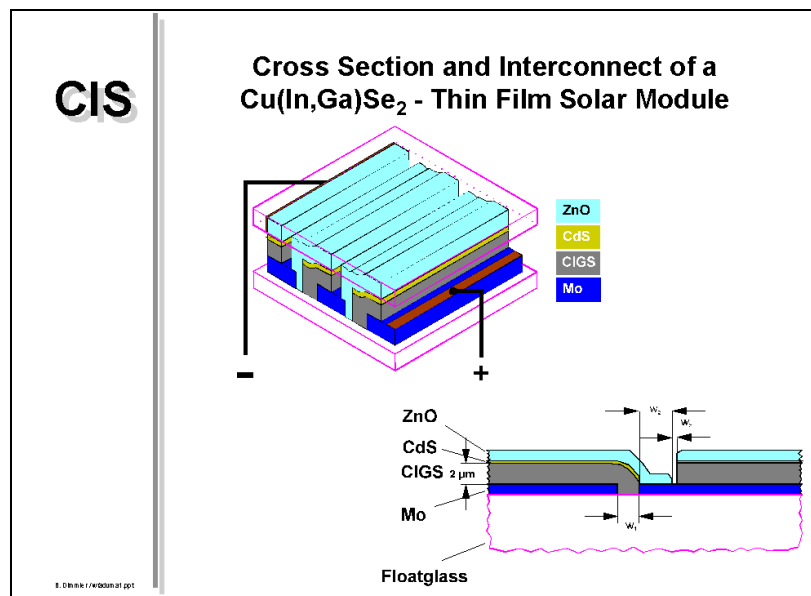


Figure 2: Structure of a Solar Cell Module

Instrumentation: The EDAX Orbis XXL was used to measure coating thickness and composition on square solar panels as large as 300 mm x 300 mm. The instrument configuration and measurement conditions were as follows:

- X-ray Anode: Rh
- 50 kV, 1 mA
- 1 mm collimator
- 80 mm² Si(Li) detector
- Measurement time: 450 sec

To accommodate large solar cell wafers, the Orbis XXL has a large sample chamber (capable of vacuum) with the following dimensions (Table 3):

Table 3: Orbis XXL Sample Chamber Dimensions

	Size [mm]
Sample Chamber	700 x 700 x 400
Max. Sample Size	600 x 600 x 220
XYZ Stage Movement	310 x 310 x 220

Analysis and Results: The coating model for this complex system was built using two standards each for the ZnO, CdS and Mo thin layers to establish a roughly linear calibration. Modeling was also used to support the two standard calibrations for each of these layers. For the alloy layer (CIGS), a “standards-only” calibration using four standards was employed in this study. Table 4 shows the calibration ranges for each layer in the structure.

Table 4: Layer Thickness Calibration Range

Layer	Thickness [μm]
ZnO	0.80 – 1.80
CdS	0.05 – 0.10
CuInGaSe	1.50 – 2.00
Mo	0.30 – 0.40

In conventional analysis, profilometry was used to determine layer thickness and Energy Dispersive Spectroscopy on a Scanning Electron Microscope (EDS-SEM) was used to analyze the alloy layer composition. Substantial sample preparation was required for the desired analysis using these methods which would destroy the solar cell panel. Therefore, these two methods were only suitable during the intermediate processing of an incomplete layer system. ED-XRF, being non-destructive, was more suitable for the process control of the final product.

In Table 5, results for EDS-SEM (composition) and profilometry (thickness) as measured on the “in-process” solar cell are compared to the Orbis XRF measurements made both “in-process” and on the final product. To compare the Orbis’s performance fairly with the other two methods, the CIGS and Mo layers were coated first. The layers were then measured for thickness (Mo, CIGS) and composition (CIGS). After each additional layer was added on top of the CIGS layer, the samples were re-measured. This gives 3 sections of Orbis results in the table: CIGS/Mo, CdS/CIGS/Mo and the final results – ZnO/CdS/CIGS/Mo. Numbers in normal type are repeat measurements while the bold numbers in the blue rows are the mean values for the Orbis measurements.

Table 5: Orbis XRF Results in Comparison to EDS-SEM and Profilometry

Layer	Composition (Wt%)				Thickness (µm)			
	Se	In	Ga	Cu	Mo	CIGS	CdS	ZnO
CIGS/Mo	53.0	19.3	8.9	18.8	0.27	1.50		
	52.7	19.5	9.0	18.8	0.26	1.50		
	52.3	20.1	8.8	18.8	0.27	1.53		
Mean	52.7	19.6	8.9	18.8	0.27	1.51		
CdS/CIGS/Mo	52.4	20.2	8.8	18.6	0.27	1.54	0.12	
	52.5	20.0	8.8	18.8	0.26	1.52	0.09	
	52.6	19.9	8.8	18.7	0.27	1.52	0.12	
	52.4	20.0	8.9	18.8	0.26	1.52	0.09	
Mean	52.5	20.0	8.8	18.7	0.27	1.53	0.10	
ZnO/CdS/CIGS/Mo	53.3	19.8	8.7	18.2	0.27	1.55	0.10	1.45
	53.3	19.6	8.8	18.3	0.28	1.59	0.11	1.52
	53.0	20.5	8.5	18.1	0.28	1.59	0.10	1.51
	53.0	20.4	8.6	18.0	0.28	1.61	0.10	1.50
Mean	53.1	20.1	8.7	18.1	0.28	1.58	0.10	1.50
EDS-SEM	52.1	20.0	9.0	18.8				
Profilometry						1.5		

The results from the Orbis XRF measurements are quite comparable to EDS-SEM and profilometry measurements.

Over the entire area of the 300 mm by 300 mm panel, the Orbis can measure thickness and composition to study a variety of factors such as the homogeneity of individual layers and correlations between different layers. An example is shown in Figure 3. Again, it is worthwhile to note that this distribution data has been collected on the finished module. Before using the Orbis, this information was unavailable.

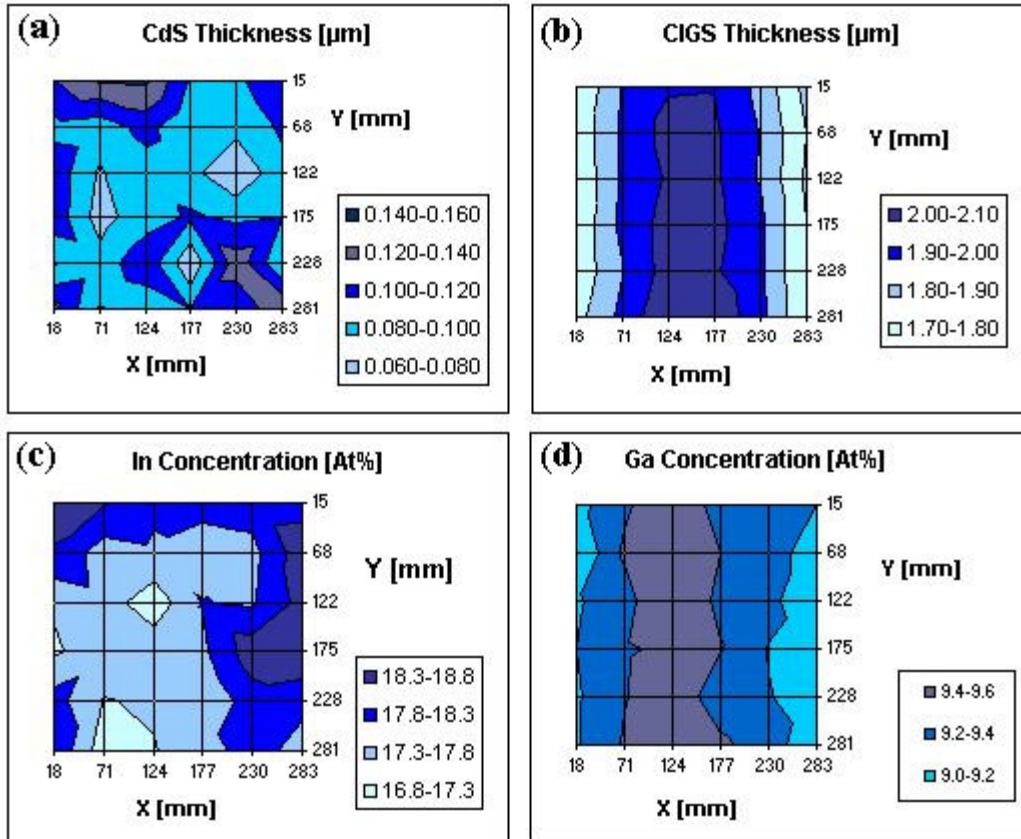


Figure 3: Thickness and Composition Distributions
 (a) CdS Thickness
 (b) CIGS Thickness
 (c) In Composition in CIGS Layer
 (d) Ga Composition in CIGS Layer

Summary:

X-ray Fluorescence is an established method to measure coating thickness and composition. The technique is non-destructive and non-contact. In conjunction with collimators or capillary optics, the Orbis micro-XRF systems allow this technique to be extended to the analysis of small structures and homogeneity analysis over larger areas while providing excellent accuracy. As demonstrated, the Orbis is capable of analyzing the complex layer structures found in the current and future high-technology markets.