Calibration Strategies for Coating Measurements on the XLNCE X-ray Metrology Product Line

Introduction

In making coating composition and thickness measurements, particularly in an industrial environment for quality and process control, questions regarding the accuracy of results are very common. These are often difficult to answer because in many instances there are no reference standards available to gauge the accuracy of the results, particularly when the material studied is a proprietary formulation. To begin to address the issue, it is important to understand the calibration methodology for X-ray Fluorescence (XRF) coating measurements as there is often a focus on making "standardless" measurements.

The quantitative algorithm used for coating analysis on the XLNCE XRF product line is essentially the same type of routine as is used for bulk materials. Quantification of a bulk material assumes that the material is homogeneous. Various instrumentation factors such as geometry, X-ray tube type and detector characteristics are either entered or modeled. The algorithm then attempts to calculate all the physical interactions that take place within the sample when X-rays excite the sample and scattered photons and fluoresced characteristic X-rays travel to the detector. These types of algorithms are commonly referred to as "Fundamental Parameter" routines because the physical modeling of the measured sample is facilitated by a database of fundamental atomic parameters which characterizes the X-ray physics of each atomic element. A coating algorithm requires some additional information, i.e. the number and order of layers in the coating structure and assignment of all elements either to a specific layer or to the substrate. In addition, as the coating calculations are much more sensitive to the instrument's geometry, coating routines are typically "calibrated" by measuring a single, pure element. In the XLNCE product series, this last step would take the form of measuring any element and assuming the calculated calibration coefficient is the same for all elements involved in the calculation.

In theory, the calibration coefficients are the same for all elements for a given set of excitation conditions; however, in practice this is not the case, which leads to the implementation of various calibration methodologies to improve the accuracy of the coating calculations. For the XLNCE product line, these calibration methodologies involve the use of either pseudo-standards or type standards. The simplest example of pseudo-standards involves measuring a pure element of "infinite" thickness to generate a calibration coefficient for every element involved in the coating structure. The term, infinite, signifies that the thickness of the pure element standard is such that further increase in thickness produces no further increase in count rate of the relevant X-ray signal. This type of pure element calibration is achievable for many elements, but obviously becomes problematic in cases where the material is toxic, unstable or in a non-solid state at room temperature. In these cases, it is possible to measure the element in a stable compounded form, e.g. measuring potassium in the compounded form of potassium carbonate, K_2CO_3, to get a calibration coefficient for potassium. Another strategy is to use what could be referred to as a "nearest neighbor" element. One might measure an available pure element with signal energy near to the element which is not available, e.g. measuring the calibration coefficient of tin and using this for tellurium or using hafnium or tungsten to estimate the rare-earth coefficients.

In practice, pure element calibrations seem to work most accurately in the "thin" film regime, where "thin" is defined as that portion of the XRF signal response curve where increase in film thickness yields a somewhat linear response. Beyond the "thin" regime, unit increases in thickness yield less than unit increases in signal response until the point of saturation, i.e. where the material is infinitely thick.

Table 1 provides the results from a homogeneity study of an indium coated silicon wafer using the XLNCE SMX-BEN benchtop analyzer. Type standards, a standard which matches the sample to be measured in terms of layers and layer ordering, were not available in-house for this study, but a type standard of sorts was developed by cross-sectioning the indium film with a Focused Ion Beam (FIB) electron microscope. The FIB result (Table 1, "FIB (μm)" column) at the center of the wafer was

used as the type standard and an SMX-BEN measurement at the center was set to 6.61 µm, highlighted with green in Table 1.

Wafer Measurement Position	FIB (µm)	Type Std (µm)	Pure In(K) CC (µm)	Pure Sn(K) CC (µm)
Nominal Center	6.61	6.61 (from FIB)	6.56	6.44
6 mm off nominal center		6.65	6.60	6.48
12 mm off nominal center		6.71	6.65	6.53
68 mm off nominal center	6.7	6.52	6.47	6.35
90 mm off nominal center	6.22	6.42	6.37	6.25
95 mm off nominal center		6.29	6.25	6.13

Table 1. FIB and XRF thickness measurements of Indium deposition on a 200 mm Si wafer.

Three sets of results are shown for the same data collection with three different calibrations applied: the "Type Std" column with a calibration as previously described; "pure In(K)" with a calibration based on a measurement of a pure, infinite sample of indium; and "pure Sn(K)" with a calibration based on a measurement of a pure, infinite sample of tin. Indium and tin are atomic numbers 49 and 50, respectively, in the periodic table. The difference between type standard results and calibration by pure indium is < 1% relative, while the difference using pure tin is about 2.6 to 2.7% relative. The FIB results don't completely track with the XRF measurements at 68 mm and 90 mm off center; however, the FIB layer thicknesses are measured in cross-sections about 5 µm wide, while the XRF measurements are made over an area of about 2.5 mm in diameter allowing for variations in FIB results that may be averaged by the XRF measurement area. The main idea here is simply to show how well type standard, matching pure element, and nearest neighbor pure element calibrations agree when making measurements in this thin film regime. (The limit of indium metal film XRF measurements using the In(K) line is approximately 90 µm.)

As the layer thickness increases beyond the thin film regime, the calculations of the X-ray physics become more complicated and the errors increase. The same is true of multi-layer structures where the calculation errors in the upper layers propagate into the calculations on the subsurface layers. For optimum accuracy in these situations, it is best to apply single- and multi-layer type standard calibrations. For simple, single layer metal films, there are commercially available standards (e.g. www.calmetricsinc.com), both free-standing stackable metal foils and hard-plated standards. Stackable foils allow flexibility to stack them in varying order, while hard-plated standards are more durable. Hard-plated standards are typically available for very common industrial applications, such as electrical contact layer structures.

In many industrial metrology applications, measurements are made on performance coatings with proprietary formulations. The same rules apply between calibration strategies for thin film versus thick film measurements. Type standards will still provide the best accuracy and it is in this environment where the best accuracy is typically required. However, standards are not available for proprietary formulations. In this case, type standards are developed in-house using destructive testing methods or EDAX can provide support assistance in characterizing proprietary materials to make type standards for the customer under a confidentiality agreement.

In making type standards for proprietary performance coating structures, these materials are often optimized by tuning the deposition processes. For example, the introduction of dopants into photovoltaic layers is often varied until the best photovoltaic conversion efficiency has been achieved. Variations in deposition processes can also impact the accuracy that a type standard provides in a calibration and it is best to use the same deposition process to produce the type standards as the final product. Experience has shown that matching deposition conditions in a multi-layer structure that appears essentially the same from an X-ray physics perspective can improve the accuracy of the type standard calibration from 2 to 3% relative down to about 1% relative.

Conclusion

Essentially, standard-less coating measurements are possible with the XLNCE X-ray Metrology product series. However, there may be a concern about the accuracy of these measurements as today's performance coating structures are often tuned for best performance within a limited range of composition and thickness. Calibration strategies with the XLNCE X-ray Metrology product line range from simple, durable pure elements to type standards depending on the accuracy demanded. It is important to understand the need for measurement accuracy up front when implementing a calibration strategy because the accuracy demands of one customer can be completely unacceptable for another.