Thickness and composition analysis of thin film samples using FP method by XRF analysis

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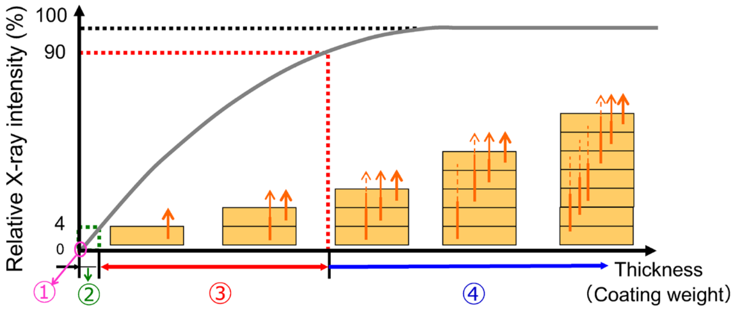
1. Introduction

X-ray fluorescence spectroscopy (XRF) is an elemental quantification analysis method for inorganic and metallic compounds. Sample preparation is simple and does not require solid samples to be dissolved, as is necessary for wet chemical analysis techniques. The fundamental parameter (FP) method implements quantitative analysis without type standards. The XRF technique has been widely accepted not only for bulk analysis but for thin film analysis in plating and electronic materials. With the thin film FP method, the thickness and composition of a thin film can be simultaneously determined, and the software is able to handle even complex multilayers. This article explains the basic principles of XRF thin film analysis; the depth of an XRF measurement and an overview of the thin film FP method. An ITO (indium tin oxide) thin film is analyzed as an example, and software parameter settings and reference material settings are also described.

2. Relationship between fluorescent X-ray intensity and sample thickness

The fluorescent X-ray intensity of the analyte is correlated to its concentration in the sample. In the empirical calibration method, the relationship between the X-ray intensity and the concentration is obtained from standard samples with known concentrations, known as a calibration curve. The concentration of an analyte in an unknown sample is then determined using the calibration curve. The fluorescent X-ray intensity is also related to the thickness of a thin film. The thickness and composition of the analyte layer are determined based on these relationships. Figure 1 illustrates the relationship between thickness (or coating weight) and fluorescent X-ray intensity. As a layer thickness increases, the fluorescent X-ray intensity increases as well, but only up to a point. Above a certain thickness, the X-rays from deep regions can no longer escape from the sample, and an increase in thickness does not increase X-ray intensity. In XRF analysis, the thin film range is defined as a sample where the analyte X-ray intensity changes with thickness, and the bulk range is defined as a sample thickness where any analyte X-ray intensity does not change with thickness. In the range #1 (Fig. 1), the thickness is too thin to detect any X-ray intensity. In the range #2, X-ray intensity changes with film thickness linearly because the film is so thin that matrix effects caused by coexisting components are ignorable. The film thickness is relatively easily determined with the calibration curve method using a



Range	Empi-rical	FP	Thin film analysis by XRF
①	×	×	Not possible due to insufficient X-ray intensity
②	○	○	Possible by both empirical calibration and FP methods. Linear relationship thanks to ignorable matrix effect.
③	△	○	FP method is advantageous. Empirical calibration methods can be used for single element film.
④	×	×	Not possible due to the saturation of X-ray intensity

Fig. 1. The relationship between film thickness and X-ray intensity. The concept of thin film and bulk regions.

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few standard samples. In the range #3, the film thickness can also be determined. The empirical calibration curve is not linear due to self-absorption. It also includes unignorable error for multi-component film, since the X-ray intensity is affected by matrix effects that are caused by the absorption and excitation of coexisting components. The thin film FP method described below is useful in this range. Range #4 is the bulk region, where X-ray intensity is constant regardless of any variation in film thickness; therefore, thickness analysis is not possible in this range. For thickness ranges #2 and #3, the thin film FP method can be applied to determine both thickness and composition simultaneously.

The applicable film thickness analysis range can vary from 0.01 nm to a few tens of μm depending on the film type, as shown in Fig. 2. The reason for such a wide variation is because the depth of XRF measurement, meaning the sample thickness contributing to X-ray intensity, differs with the sample composition and the energy of the analytical line. Figure 3(a) plots thickness dependence of the relative intensity of Fe-Kα to the bulk intensity for solder, copper metal, copper oxide, aluminum oxide, and polyethylene. Here, bulk intensity is defined as the X-ray intensity where increasing sample thickness does not change intensity. Depth of measurement is defined as the sample thickness corresponding to over 99% of bulk intensity. The depth of measurement is shallow for solder because a sample matrix composed of heavy elements has higher X-ray absorption. In case of a sample matrix composed of lighter elements such as aluminum oxide, the depth of measurement is more than a few tens of μm for Fe-Kα due to the lower X-ray absorption by the sample matrix. Thus the depth of measurement is deeper in light element materials than in heavy element materials. Figure 3(b) shows the thickness dependence of the relative intensity to the bulk intensity for various analytical lines. Low energy analytical lines such as Si-Kα are more easily absorbed by the sample matrix and the depth of measurement is as shallow as a few μm. In contrast, the higher energy lines are less absorbed, so that the depth of measurement becomes a few hundred μm for Zr-Kα and Cd-Kα.

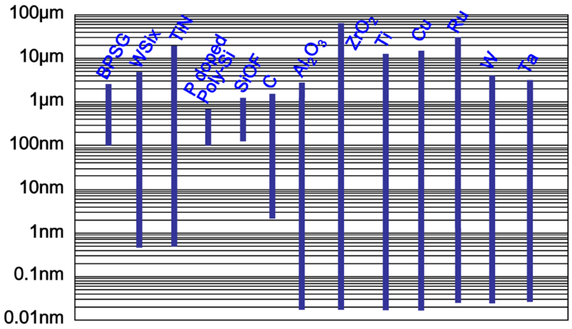


Fig. 2. Thin film analysis ranges for various film types.

The concept of depth-of-measurement should be a guide for the thin film range of the analysis sample, since thickness analysis is possible only when the fluorescent X-ray intensity of the analyte changes with sample thickness. In practical analysis, the thin film analysis range of the sample composition should be confirmed beforehand by spectral measurement and theoretical intensity simulation. This procedure is described later in section 4.

3. Thin film FP method(1)

If the film composition is known, X-ray intensities can be calculated theoretically using fundamental parameters (physical constants) specified with the measurement conditions. The theoretical calculation is based on the assumptions listed below.

(1) Elements are distributed homogeneously in each layer.
(2) The amount of generated fluorescent X-rays correlates to the concentration of the analyte in each layer. The absorption and enhancement of the X-rays occur by co-existing elements.
(3) The influence of co-existing elements can be modeled by using physical constants such as absorption coefficients.
(4) Spectrometer and measurement conditions influence the generated X-ray intensities and counted X-ray intensities.

Due to assumption (4), measurements of standard materials in advance is necessary to obtain the relationship between measured and theoretical

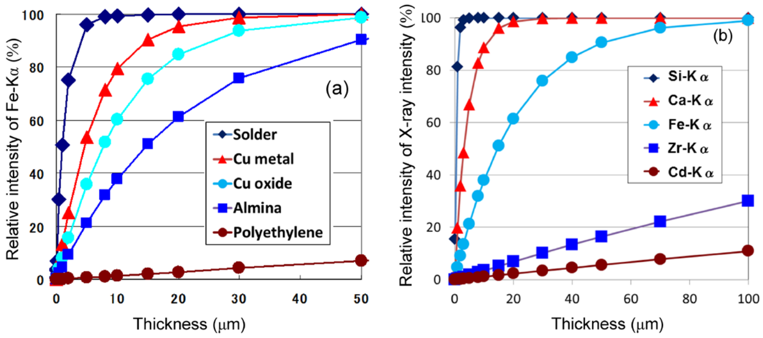
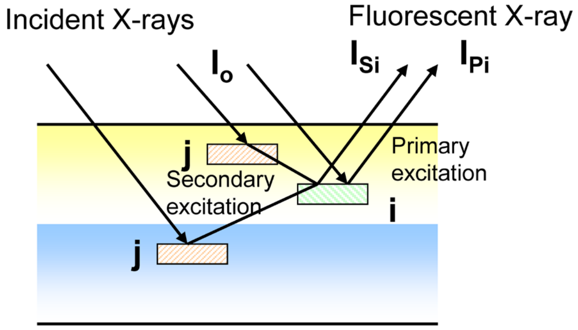


Fig. 3. (a) Relative intensity of Fe-Kα dependence on thickness of various matrices. (b) Relative intensity dependence of various analytical lines on thickness of aluminum oxide.



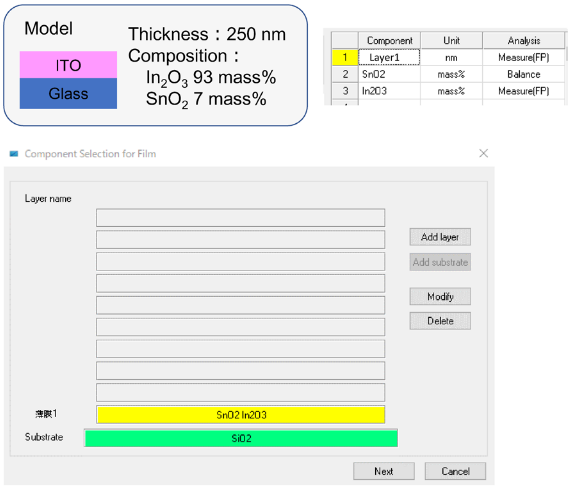
$I_i = I_{Pi} + I_{Si}$

I_i: Fluorescent X-ray of element *i*

I_{Pi}: Primary excitation X-ray of element *i*

I_{Si}: Secondary excitation X-ray of element *i*

Fig. 4. Model of fluorescent X-ray generation in a two layered film in the thin film FP method.



	Component	Unit	Analysis
1	Layer1	nm	Measure(FP)
2	SnO2	mass%	Balance
3	In2O3	mass%	Measure(FP)

Fig. 5. A model specified in thin film FP application.

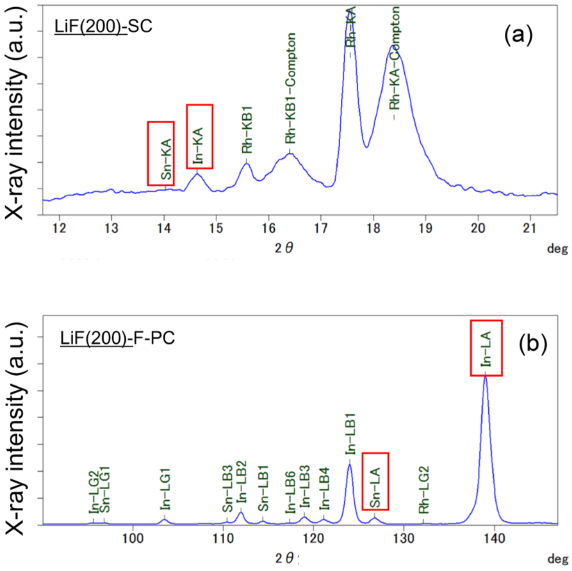


Fig. 6. Spectral charts of K and L lines for In and Sn.

fluorescent X-ray intensities. This is known as the spectrometer's sensitivity calibration. Better results will be obtained using standard samples whose layer structure, thickness and composition are similar to the test samples. In the theoretical calculation, coating weight is calculated and converted to a layer thickness value making use of the layer density.

Figure 4 shows a model of fluorescent X-ray generation in a two layered sample. The theoretical fluorescent X-ray intensity equation involves primary excitation and secondary excitation within the layer, and secondary excitation between the layers. The thin film FP method calculates layer thickness and composition based on the specified layer model and determine the thickness and composition where the theoretical X-ray intensity matches the measured X-ray intensity. The software of the Rigaku ZSX Primus series of XRF spectrometers is able to calculate theoretical intensities for multi-layer models for up to ten layers. In the software, set up a quantitative application by specifying a layer model, analysis parameters and measurement of standard samples, then measure thin film samples. When setting up analysis parameters, the depth of the XRF measurement and the selection of analysis lines can be decided with the aid of a theoretical intensity simulation program.

4. Thickness and composition analysis of ITO thin film(1)

The procedure and details of thin film analysis are described using ITO (indium tin oxide) thin film as an example.

(1) Setting up the layer model

In the first step of thin film application setup, the layer model is chosen. An ITO thin film sputtered on an SiO_2-based glass substrate is used as an example. The ITO layer consists of In_2O_3 and SnO_2, and the target thickness and composition in sample preparation are specified as initial values for the FP calculation. The X-ray intensities of In and Sn are measured and the thickness and composition are determined. Figure 5 shows the layer model set up in the software. In this model, the sum of the percentages of contents of In_2O_3 and SnO_2 is assumed to be 100%. Therefore, either In_2O_3 or SnO_2 can be specified as the measured component and the other is set as the balance component.

(2) Setting up analysis parameters

In thin film analysis, the analysis line should be carefully chosen for each element. Generally, Kα, Kβ, Lα, or Lβ lines are used. Check the spectral chart and theoretical intensity simulation to study the possibilities for thin film analysis and the optimal analysis line. The optimal analysis line should have sufficiently high fluorescent X-ray intensity, no or low peak overlap with other lines, and high sensitivity to thickness variation in the range covering the target thickness of the sample. Since In and Sn are heavy elements, the measurable K and L lines are investigated here. Figure 6 shows

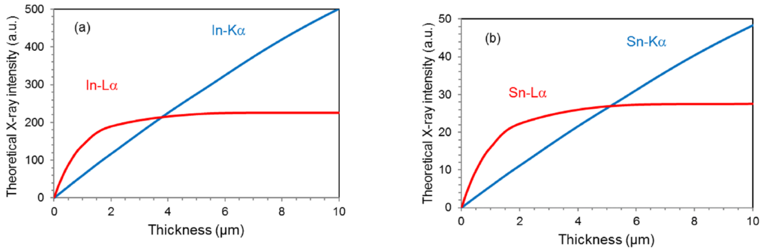
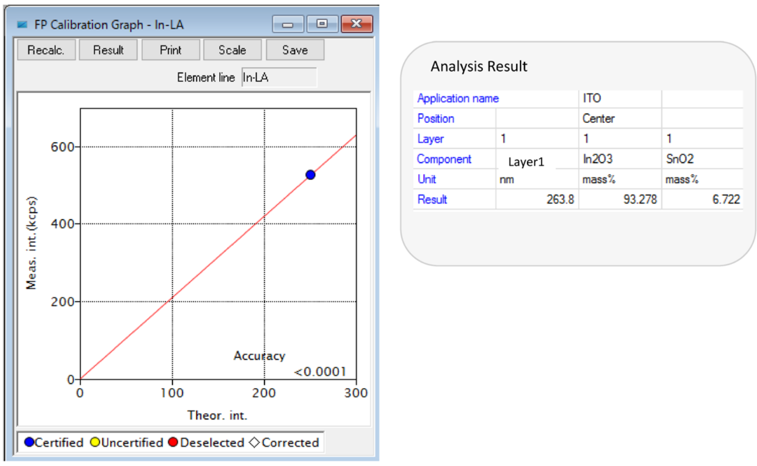


Fig. 7. Theoretical intensity simulation results of Kα and Lα intensity dependences on the layer thickness for In (a) and Sn (b).



Analysis Result

Application name		ITO	
Position		Center	
Layer	1	1	1
Component	Layer1	In2O3	SnO2
Unit	nm	mass%	mass%
Result	263.8	93.278	6.722

Fig. 8. FP calibration curve of In-Lα and analysis result of ITO film.

a spectral chart of K and L lines for In and Sn. The Kα lines of Sn and In are located near the scattering primary X-ray peaks of a Rh X-ray tube anode. The high background intensity causes poor PB (peak to background) ratio, and the Sn-Kα intensity is very low. On the other hand, both In-Lα and Sn-Lα lines likely show high enough intensities.

Figures 7 (a) and (b) show theoretical simulation results of Kα and Lα intensity dependences on layer thickness for In and Sn respectively. In-Kα intensity increases linearly up to a few 10μm (Figure 7(a) shows range only below 10μm). This indicates the possibility of thin film analysis in a wide order range of a few 10μm. In contrast, In-Lα intensity increase and reaches bulk intensity around 2μm, implying the In-Lα line is not applicable for thicknesses greater than 2μm. The higher slope below 2μm, however, indicates that the sensitivity for thinner thickness is higher for In-Lα than for In-Kα intensity. The same trend is shown in theoretical intensity simulation for Sn-Kα and Sn-Lα lines in Fig. 7(b). Since the target thickness of the present sample is 250 nm, Lα lines of In and Sn can be expected to be applicable for thickness analysis. Generally, the L line is surface sensitive because irradiation X-rays contributing to the excitation of L lines is high due to the low energy. For this reason, the L line is oftentimes chosen for thin film analysis. In ZSX Guidance, the latest software of the ZSX Primus series, the auto searching function for analysis lines in thin film applications can be helpful.

(3) Standard samples and FP calibration curves

Using standard samples with similar layer structure, thickness, and composition as the analysis samples can give better results. However, when such standards are not available, pure metallic bulk standard samples can also be used to set up FP calibration curves. When neither thin films nor metallic bulk standard samples are available, factory registered sensitivities can be used for FP calculation. Figure 8 shows an FP calibration curve for In-Lα setup with an indium metallic standard sample. The analysis results of the thickness and composition were obtained using In and Sn metallic standard samples. Even though they use common bulk standards, the analysis results are in good agreement with the target thickness and composition shown in Fig. 5.

5. Conclusion

X-ray fluorescence analysis is an elemental analysis method widely used not only for inorganic compounds and metallic materials but plating and thin films. Thickness and composition of thin films is determined by the correlation with the X-ray fluorescent intensities of the components. The thin film FP method is advantageous when appropriate standard samples are not available, for example for research and development, because it can simultaneously determine the thickness and composition of a thin film by theoretical calculation. The aim of this article is to explain the basic principle of XRF thin film analysis. The depth of an XRF measurement and an overview of the thin film FP method are discussed. As an example, an ITO thin film sample is analyzed, explaining the details of the actual software parameter settings and reference material measurements.

Reference

(1) Y. Kataoka and T. Arai: *Advances in X-Ray Analysis*, **33**, (1990), 213–223.