

Application News

Energy Dispersive X-ray Fluorescence Spectrometer

Measuring the Film Thickness of ITO and Perovskite Layers in Perovskite Solar Cells

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User Benefits

- ◆ EDXRF spectroscopy enables simple, rapid, and nondestructive measurement of film thicknesses on the order of nanometers.
- ◆ EDXRF can provide film thickness analysis results comparable to those obtained with the OLS laser microscope.
- ◆ By specifying layer information, the thicknesses of multiple layers can be quantified.

■ Introduction

As larger perovskite solar cells with higher efficiencies continue to be achieved, it has become increasingly important to control the quality of ITO (indium tin oxide) films used as transparent electrodes. ITO films are transparent conductive films that offer a combination of both high visible-light transmittance and electrical conductivity. They allow incident light to pass through the film while also transmitting charges generated by photoelectric conversion to an external circuit. The thickness of the ITO film affects transmittance, sheet resistance, and other properties, which consequently influences device performance. Therefore, appropriate film-thickness control is essential.

Energy dispersive X-ray fluorescence (EDX) spectrometers can measure the thickness of this ITO film nondestructively, without any pretreatment, and with a simple analytical procedure.

This article describes analyzing the following samples:

1. ITO films
2. Perovskite/ITO films

In addition, to evaluate the quantitative accuracy of the EDXRF system, Sample 1 (the ITO film) was also measured using the OLS5500 laser microscope (OLS) and the results were compared.

1. ITO Film

■ Sample

A sample consisting of an ITO film deposited on a glass substrate by lithography was used for the analysis. An enlarged diagram of the analysis area is shown in Fig. 1. The EDXRF and OLS measurement positions are also indicated in Fig. 1.

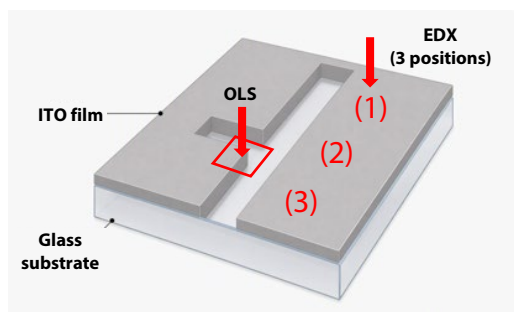


Fig. 1 Enlarged Diagram of Analysis Areas

■ Film Thickness Measurement by EDXRF

The film FP method is used to quantify thickness in terms of the quantity of material deposited (weight per unit area). Film thickness can be calculated by dividing the deposition quantity by the density (see the equation below).

$$\text{Film thickness [nm]} = \frac{\text{Deposition quantity } [\mu\text{g}/\text{cm}^2]}{\text{Density } [\text{g}/\text{cm}^3]} \times 10$$

Accordingly, to quantify film components in terms of film thickness, information about the layer density is required. If an element contained in the target layer is present in elemental form, the software uses its preset density value for that element, so no user input is required. In contrast, if the element is present as a compound, such as an oxide, the density must be entered.

■ Selection of Analytical Lines

If an element is contained in multiple layers and also the base, the instrument cannot determine from which layer the signal originates and, therefore, in principle, the film thickness of respective layers cannot be calculated. However, if information about the layers containing the same element as the layer targeted for thickness quantification—specifically its elemental composition, film thickness, and film density—is known, then quantification becomes possible by specifying those values in the measurement condition settings.

Alternatively, if the target layer contains an element that is not present in the other layers, the film thickness can be quantified by using that element as the quantitative element and specifying the elemental composition and film density information in the measurement condition settings.

For the sample used in this study, Sn was present in both the glass substrate and the ITO layer. Therefore, the thickness of the ITO layer was quantified using the latter approach, with In selected as the quantitative element. The elemental composition and film density of the ITO film specified in the measurement conditions are indicated in Fig. 2. The theoretical value of the film density was calculated as follows.

$$\begin{aligned} &\text{ITO film density (theoretical value)} \\ &7.18 (\text{In}_2\text{O}_3) \times 0.9 + 6.95 (\text{SnO}_2) \times 0.1 \\ &= 7.16 [\text{g}/\text{cm}^3] \end{aligned}$$

(Layer 1)	ITO 90 % In ₂ O ₃ and 10 % SnO ₂ Density of Layer: 7.16 g/cm ³
(Base)	Glass substrate (SiO ₂)

Fig. 2 Layer Structure Settings

■ Analysis Conditions

The analysis conditions are summarized in Table 1.

Table 1 Analysis Conditions

Instrument	EDX-7200
Element	In
Analytical Line	InKα
X-Ray Tube	Rh target
Tube Voltage	50 kV
Tube Current	Auto [μA]
Integration Time	60 s
Dead Time	Max. 30 [%]
Primary Filter	None
Detector	SDD
Atmosphere	Air
Collimator	3 mm dia.
Analysis Group	Film FP method

■ Quantitative Analysis Results

The quantitative analysis results for the ITO layer thickness by the film FP method are indicated in Table 2 and the overlaid profiles are shown in Fig. 3.

With a measurement time of 60 s, film thickness measurements on the order of nanometers were possible, where EDXRF spectroscopy determines the average film thickness within the collimator (3 mm dia. in this case). Although measurements were performed at three positions, the results indicate that there were no significant differences in ITO layer thickness among those positions. The qualitative profiles also confirm that nearly identical intensities were measured regardless of the measurement position.

Table 2 Quantitative Analysis Results

Measurement Position	ITO
(1)	212nm
(2)	213nm
(3)	210nm

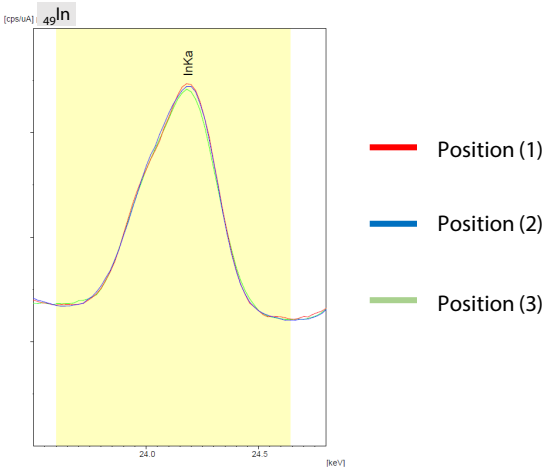


Fig. 3 Overlaid Profiles

■ Film Thickness Measurements by OLS5500

OLS is an instrument that uses laser light to measure the fine surface topography of a sample with high precision. When the step between the film and the substrate is clearly defined, the film thickness can also be calculated from the height of that step.

The measurement results obtained with the OLS microscope from the lithographically applied pattern area are shown in Fig. 4. That determined an ITO film thickness of 214 nm.

The OLS measurement results also provide information about the surface condition. When ITO is deposited on a glass substrate, fine surface irregularities (roughness) may form. If the roughness is significant, it can affect the deposition of the layer formed on top of the ITO. Therefore, the surface condition of the ITO film is important. In fact, Fig. 4 confirms the presence of fine roughness on the ITO film surface.

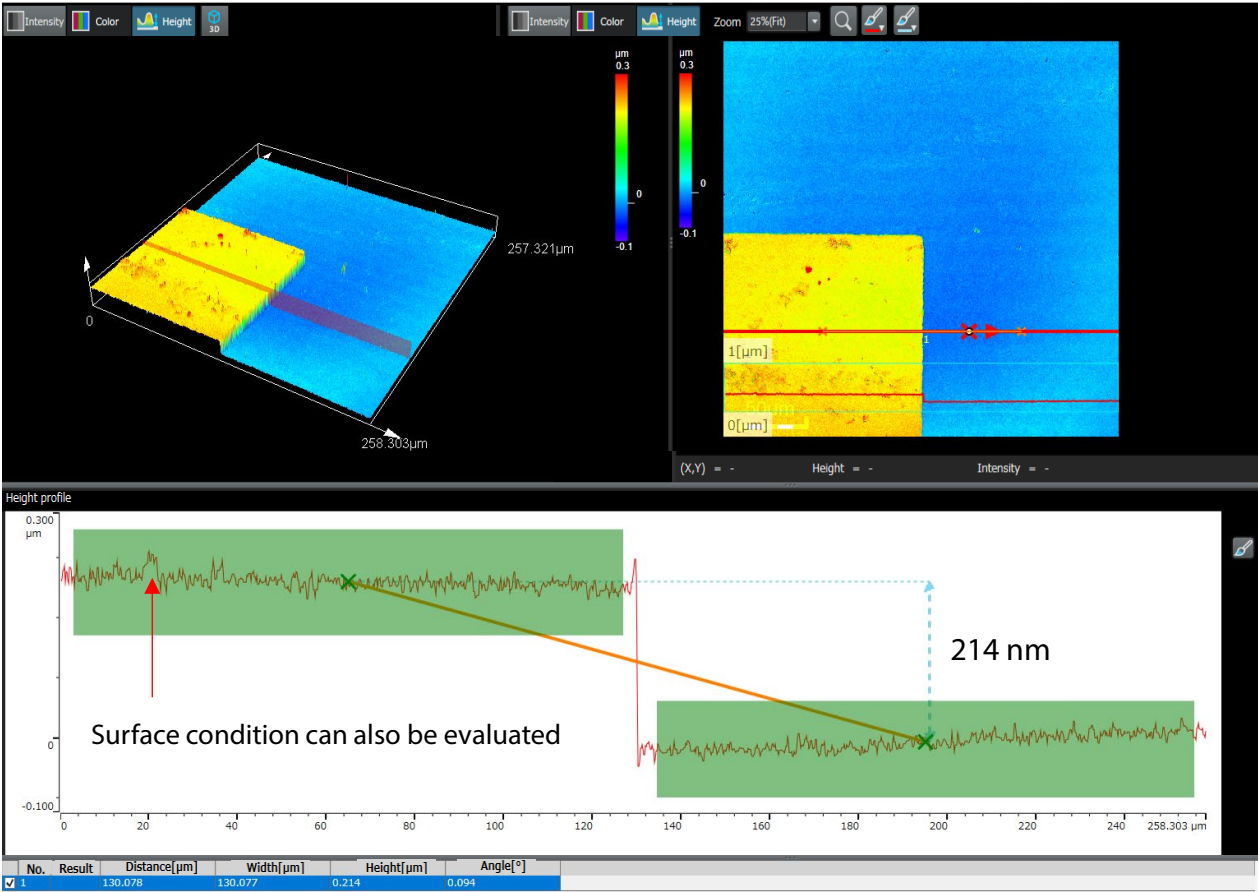


Fig. 4 Measurement Results Obtained from the Lithographically Applied Patterned Area by OLS

2. Perovskite/ITO Film

EDXRF systems can simultaneously and nondestructively analyze the thicknesses of multiple layers.

■ Samples

The layer structure of the samples is shown in Fig. 5.

These samples were prepared by depositing an additional formamidinium lead iodide perovskite (FAPbI₃) layer on the sample described in section 1. Two samples (Samples A and B) with different layer thicknesses were prepared. Pb was used as the quantitative element for measuring the thickness of the FAPbI₃ layer. In addition, the chemical formula and film density of FAPbI₃ (Fig. 5) were prespecified in the measurement conditions.

(Layer 1)	FAPbI ₃ 100 % CN ₂ H ₅ PbI ₃ Density of Layer: 4.00 g/cm ³
(Layer 2)	ITO 90 % In ₂ O ₃ and 10 % SnO ₂ Density of Layer: 7.16 g/cm ³
(Base)	Glass substrate (SiO ₂)

Fig. 5 Layer Structure Settings

■ Analysis Conditions

The analysis conditions are summarized in Table 3.

Table 3 Analysis Conditions

Instrument	EDX-7200	
Element	Pb	In
Analytical Line	PbLβ ₁	InKα
X-Ray Tube	Rh target	
Tube Voltage	50 kV	
Tube Current	Auto [μA]	
Integration Time	60 [s]	60 [s]
Dead Time	Max. 30 [%]	
Primary Filter	#4	None
Detector	SDD	
Atmosphere	Air	
Collimator	10 mm dia.	
Analysis Group	Film FP method	

■ Quantitative Analysis Results

The results of quantitative analysis are indicated in Table 4 and the overlaid profiles are shown in Fig. 6.

Table 2 Quantitative Analysis Results

Sample	FAPbI ₃	ITO
A	957 nm	161 nm
B	325 nm	128 nm

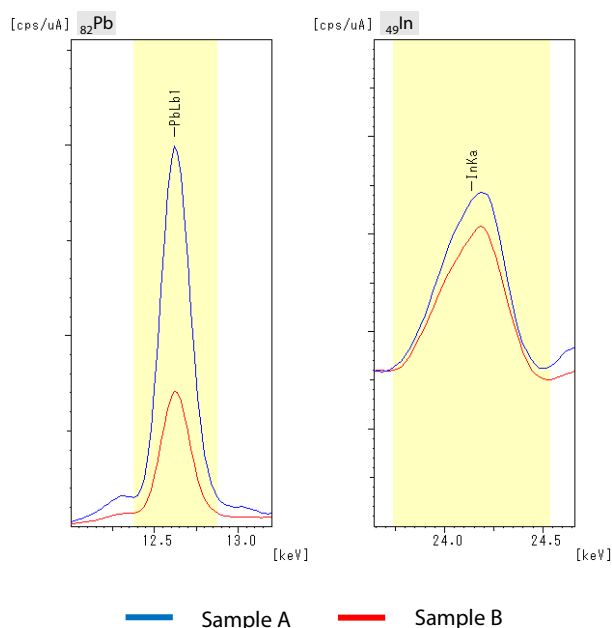


Fig. 6 Overlaid Profiles

■ Conclusion

This Application News article describes measuring similar samples using an EDX-7200 spectrometer and OLS5500 microscope, which confirmed that comparable measured values could be obtained with both methods. These results indicate that EDXRF spectroscopy is an effective technique for simple, rapid, and nondestructive analysis of film thicknesses on the order of nanometers. Film thickness can also be quantified without pretreatment at locations where no cross section is exposed and no lithographic processing has been applied. In addition, by specifying layer information, it is also possible to quantify the thicknesses of multiple layers.

As increasingly precise film thickness control is required for R&D and quality control applications, EDXRF spectroscopy holds new promise as a useful tool in the field of perovskite solar cells.

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