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Application News

No. X266

X-Ray Analysis

Quantitative Analysis of Film Thicknesses of Multi-Layer Plating Used on Cards

A three-layer plating of gold (Au), nickel (Ni), and copper (Cu) is often applied to the contact areas of electronic devices and IC chips. The amount of plating material deposited (film thickness) can be measured non-destructively by using X-ray fluorescence (XRF) spectrometry.
This article introduces a simple quantitative analysis of Au, Ni, and Cu film of a three-layer plating by employing the thin-film fundamental parameter (FP) method without using standard samples.

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Sample

1. Certified Reference Material:
   NMIJ CRM 5208-a, 20 mm × 20 mm
2. IC chip, SIM card

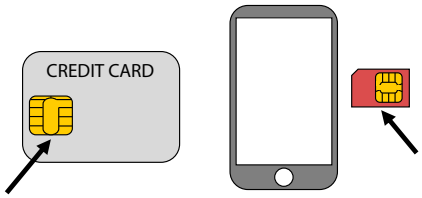

Fig. 1 IC Chip (Left) and SIM Card (Right)

Elements and Layers of Plating

The elements and layers of the plating are shown in Fig. 2.

Fig. 2 Elements and Layers of Plating

Sample Pretreatment

The samples were directly set on the sample stage without any pretreatment.

Quantitative Analysis of Film Thickness and Amount of Deposition

The layer of each metal, Au, Ni, and Cu, was quantitated by the thin-film FP method. The analysis diameter was set to 1 mmϕ.

1. Certified Reference Material NMIJ
   The analysis results of each layer's central point are shown in Table 1. A good result was obtained that the error of the quantitative value of each layer was within 5 % of the certified value.

Table 1 Results of the Quantitative Analysis of NMIJ CRM 5208-a

[μg/cm²]

Element/Layer	Au	Ni	Cu
Quantitative Value	192	862	852
Certified Value	184	869	880
(Uncertainty)	(5)	(17)	(14)

2. IC Chip (IC) and SIM Card (SIM)
   The analysis results of one central point on the IC and the SIM are shown in Table 2.

Table 2 Quantitation Results of IC and SIM

[μg/cm²]

Element/Layer	Au	Ni	Cu
IC	71.0	1,700	25,275
SIM	76.3	1,673	23,941

<Formula for the Amount of Deposition and Film Thickness>
In XRF spectrometry, the analysis result is quantitated as the amount of deposition and then the film thickness is calculated by the following formula using an assumed density.

$$\text{Film thickness } [\mu m] = \frac{\text{Amount of deposition } [\mu g/cm^2]}{\text{Density } [g/cm^3]} \times 10^{-2}$$

In this measurement test, the density [g/cm³] of Au, Ni, and Cu was assumed as 19.3, 8.90, and 8.94, respectively. Table 3 shows the film thicknesses calculated from the values of Table 2.

Table 3 Film Thickness of IC and SIM

[μm]

Element/Layer	Au	Ni	Cu
IC	0.037	1.91	28.3
SIM	0.040	1.88	26.8

With a thickness of approx. 30 μm, the Cu layer was the thickest among the three layers. Sufficient quantitation accuracy cannot be obtained in such a thick layer area as this Cu layer (see the next section for details), so we re-calculated the film thickness of the Au and Ni layers on the assumption that the the thickness of Cu layer was infinite. The results are shown in Table 4 as the final results of the amount of deposition and the film thickness.

Table 4 Amount of Deposition and Film Thickness at a Central Point with the Cu Layer Having an Infinite Thickness

Element/Layer	Au	Ni	Cu
	Amount of deposition [μg/cm²]		
IC	70.9	1,782	∞
SIM	76.3	1,756	∞
	Film thickness [μm]		
IC	0.037	2.00	∞
SIM	0.040	1.97	∞

3. Spectra
   Spectra of the analytical lines of each layer are shown in Fig. 3. While the thickness of the Au layer was thin at a few dozen nm, the peak was clear, demonstrating the high sensitivity of the analysis.
   Standard X-ray emission lines were used for analytical lines: AuLα, NiKα, and CuKα. Kβ and Lβ lines could be used when the analytical lines of each layer's element are close to each other.

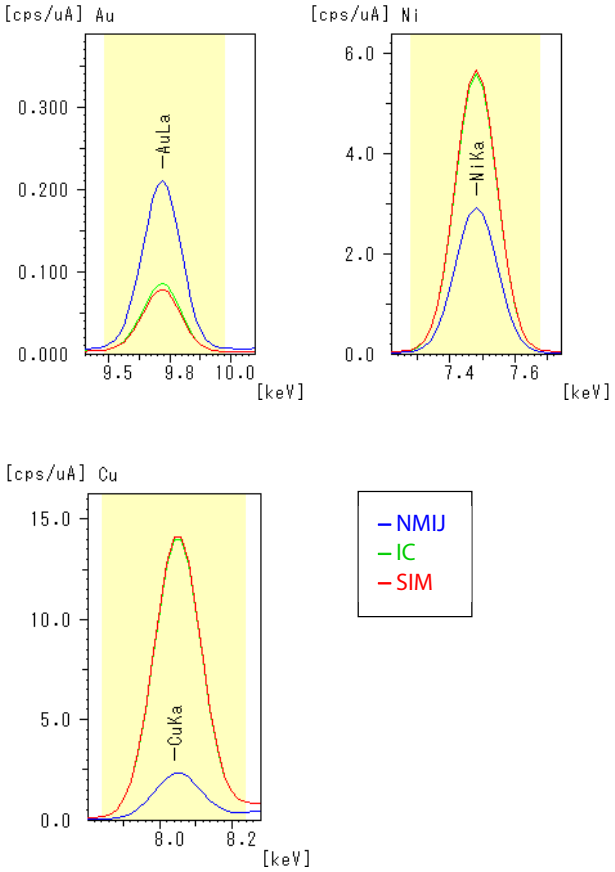

Fig. 3 Spectra of Analytical Lines

Repeatability

A repeatability test was performed by analyzing the IC chip repeatedly for 10 times with an analysis diameter of 1 mmϕ and 3 mmϕ. The amount of deposition of Au and Ni layer were analyzed on the assumption that the the thickness of Cu layer was infinite. The results are shown in Table 5.

Table 5 IC Chip Quantitation Repeatability [μg/cm²]

	Au	Ni	Analysis Diameter
Average	70.0	1,709	1 mmϕ
Standard Deviation	0.38	3.2	
Coefficient of Variation [%]	0.55	0.19	
Average	69.5	1,723	3 mmϕ
Standard Deviation	0.41	3.0	
Coefficient of Variation [%]	0.59	0.17	

Relationship between Theoretical X-ray Intensity and Thickness of Cu Film

The relationship between the theoretical X-ray intensity and the thickness [μm] of Cu film is shown in Fig. 4. When the intensity of the saturation thickness is defined as 90 % of the saturation intensity that is obtained when the Cu film has an infinite thickness (JIS H 8501), the upper quantitation limit is about 18 μm.

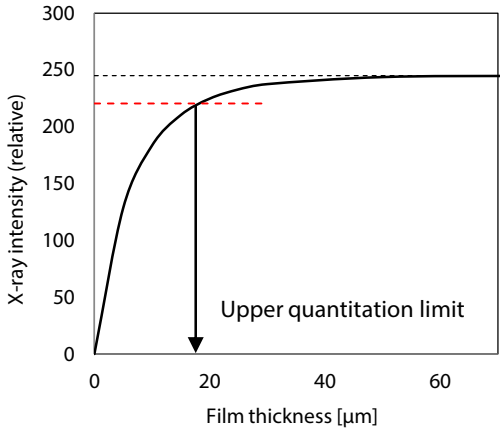

Fig. 4 Relationship between X-ray Intensity and Thickness [μm] of Cu Film

Conclusion

Film thicknesses of a three-layer plating of gold, nickel, and copper were analyzed with ease, high sensitivity and precision in the order of nm to μm using small analysis diameters of 1 mmϕ and 3 mmϕ. Quantitation of even thinner areas may be possible by using the standard analysis diameter of 10 mmϕ. As demonstrated in this research, XRF spectrometry is effective for film thickness measurement.

Furthermore, XRF spectrometry can also easily analyze the elements and their amounts used in the material. For example, it can be employed to manage the used amount and grasp the recovered amount on recycling of precious metals such as gold, platinum (Pt), palladium (Pd) and rhodium (Rh) that are used in films of plating and physical vapor deposition.

(Reference)
Estimated mass and price of gold used for the plating of the SIM card measured in this study

Mass	80 μg (80 μg/cm² × area 1 cm²)
Price	Approx. 0.37 yen (USD 1,302.3 per troy ounce) (London Metal Exchange price, Oct. 13, 2017)

Measurement Conditions

Instrument	: EDX-8000 / (7000)
Element - Analytical Line	: AuLα, NiKα, CuKα
Analysis Method	: Thin-film FP method
X-Ray Tube	: Rh Target
Detector	: SDD
Tube Voltage - Current	: 50 [kV] - Auto [μA]
Collimator	: 1, 3 [mmϕ]
Primary Filter	: None
Measurement Atmosphere	: Air
Integration time	: 100 [s]
Dead Time	: Max. 30 [%]

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