Association Connecting Electronics Industries

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IPC-TM-650
TEST METHODS MANUAL

Number
2.3.44

Subject
Determination of Thickness and Phosphorus Content in Electroless Nickel (EN) Layers by X-Ray Fluorescence (XRF) Spectrometry

Date
03/16

Revision

Originating Task Group
Plating Processes Subcommittee (4-14)

1 Scope The purpose of this test method is to measure the thickness and phosphorous (P) concentration of chemically (electroless) deposited nickel (Ni) coatings by (energy dispersive) X-ray fluorescence (XRF) analysis.

The measurement is nondestructive and noncontact, and can be performed either in ambient atmosphere or under vacuum. Measurements **shall** be made on a defined feature (equivalent to a typical SMT pad) of 1.5 mm x 1.5 mm [0.060 in x 0.060 in] or equivalent area, using a 0.6 mm diameter collimator. This equates to a measuring spot size (analysis area) of 1 mm diameter.

This test method is designed primarily for failure analysis, process qualification and process auditing. It is not intended for daily production control, due to the complexity and cost of the equipment required.

2 Applicable Documents

IPC-4556 Specification for Electroless Nickel/Electroless Palladium/Immersion Gold (ENEPIG) Plating for Printed Circuit Boards

IPC-4552 Specification for Electroless Nickel/Immersion Gold (ENIG) Plating for Printed Circuit Boards

3 Test Specimen This test method is primarily designed for measurement of the phosphorus content in ‘‘as plated’’ ENIG PWBs. Other ENIG or electroless nickel (EN) plated substrate materials may also be tested using this method, including flexible circuits, silicon wafers, aluminum or steel. The typical thickness range of the NiP layer on PWB substrates is 3 to 6 µm [118.1 to 236.2 µin]. The Phosphorous content can range from 0 % to 14% by weight. Minimum and maximum thickness for single layers of electroless nickel required for accurate determination of the P content is 0.5 µm to 25 µm [19.7 µin to 984 µin]. The maximum thickness of gold present on the surface of the specimen when tested **shall** be less than 0.10 µm [0.004 µin]. For samples with thicker gold, the gold must be removed by chemical stripping or Ion milling prior to evaluation.

While this test method is also suitable for evaluating phosphorus content in ENEPIG samples, the thickness of both the gold (Au) and palladium (Pd) layers needs to be considered. The maximum thicknesses of the layers over the electroless nickel on ENEPIG specimens when tested **shall not** exceed 0.05 µm [0.002 µin] of Au and 0.10 µm [0.004 µin] of Pd on top of the EN layer. This constraint will impact measurement of ENEPIG samples plated on the higher side of the current IPC-4556 specification. For samples with gold thicknesses above 0.05 µm [0.002 µin], chemical or Ion milling stripping may be carried out prior to evaluation. With the gold removed, the maximum thickness of palladium on a specimen when tested **shall** be 0.25 µm [0.0098 µin].

Note: Electroless palladium deposits may also contain phosphorus and its contribution to the total phosphorus content must be taken into account when reporting the phosphorus content of the deposit.

The sample to be tested should be flat and ideally not populated with components in the area of measurement. If testing is done on populated boards, consideration has to be given to measurement location, such that none of the electronic components block the fluorescent radiation from reaching the detector, as described in Section 5.4.

The test specimen requires no other sample preparation.

4 Apparatus An X-ray fluorescence spectrometer consisting of the following:

- A radiation source (X-ray tube with adjustable HV power supply from 10 kV to 50 kV).
- A primary beam filter and safety shutter assembly.
- A video camera.
- An X-ray collimator or a polycapillary X-ray optic.
- An energy dispersive Silicon Drift Detector SDD (a device in which charge carriers created by the incidence of X-ray photons on a high purity silicon substrate are directed to a measuring electrode by an applied transverse electric field), including electronics.
- Evaluation software capable of simultaneously measuring coating thickness and composition of multiple layers. The software of the instrument **shall** have the capability of multiple excitation modes. It is necessary to apply different excitation conditions; a soft excitation for the excitation of P-K at 10 kV and a hard excitation for Ni-K at 50 kV.
- A programmable X-Y positioning stage (accurate positioning is required especially if small areas are to be analyzed).
- The instrument must be able to record the Intensities of the individual radiation components of the Phosphorous K energy line (I_{P-K}) and the Nickel K energy line (I_{Ni-K}) with sufficient precision.

A Certified Reference Material (CRM) covering the measuring range of the application as described in 5.2.

A typical instrument layout is shown in Figure 1.

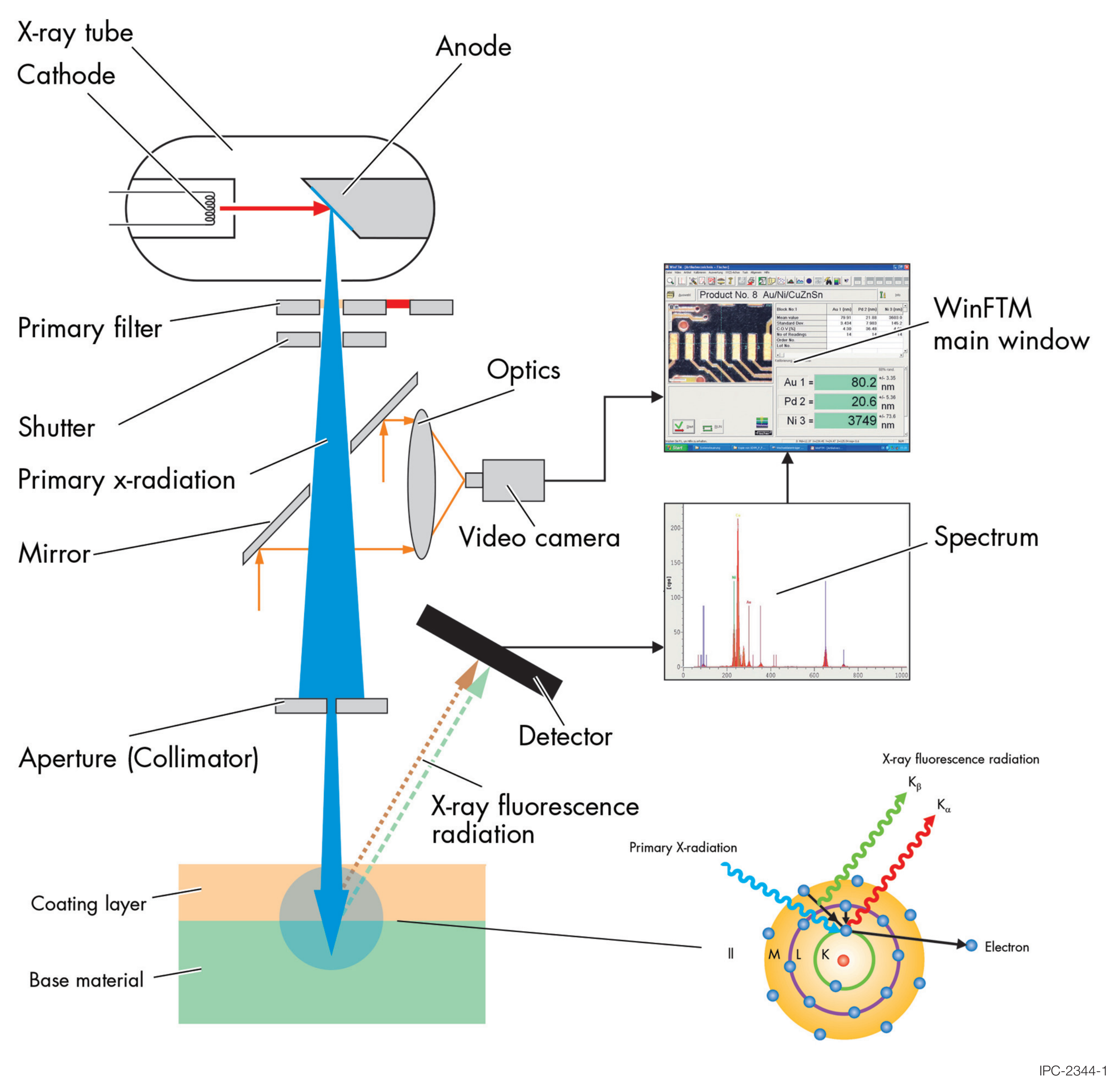

Figure 1 XRF Instrument Layout

5 Procedure

5.1 Instrument Setup Prior to the purchase of the Certified Reference Materials (CRMs), confirm with the XRF manufacturer that the instrument is capable of measuring phosphorus content and obtain details of the recommended machine set-up and operational procedures.

Instrument setups usually contain a product file that contains the required measurement specific hardware and software settings for the application. In addition, the product file contains a calibration file which defines the calibration settings and certified reference material to be used.

5.2 Typical Instrument setup conditions and measuring ranges are as follows:

- Aperture Size: 1 mm for both 10kV and 50kV applications.
- Anode Current (I): I=1 mA for 10kV and I=0.15 mA for 50kV (Anode current setup maximizing achievable instrument count rates will yield best instrument repeatability, reference 5.3).
- Primary Beam Filter: NO filter for 10 kV and Ni Filter for 50 kV.
- Measurement Time: 120 s for 10kV and 20 s for 50kV.

5.3 Instrument Calibration Calibration **shall** be performed with CRM's according to the instrument manufacturer instructions. The CRM's **shall** be traceable to national laboratories. The structure of the reference material **shall** be similar to the samples under investigation, i.e., NiP/Cu/PCB, Au/NiP/Cu/PCB or Au/Pd/NiP/Cu/PCB. Individual calibration foils **shall not** be used for multilayer coatings. The certified reference standards **shall** have compositions and thicknesses similar to the samples to be measured. If desired, it is possible to calibrate an instrument over the full (low to high) phosphorous range. However, optimum accuracy can be achieved by calibrating each phosphorous range (low, mid, and high) separately. Each phosphorous content range should be calibrated with no less than 4 standards per range. No less than 3 measurements per calibration standard **shall** be performed. Calibration checks should be performed after each calibration and periodically by re-measuring the calibration standards. If the results are within the measurement uncertainty of the standards and the uncertainty of the measurement itself, no action is required. If not, a recalibration of the instrument is required. Typical CRM standards used and results obtained are summarized in Table 1.

5.4 Sample Placement There are some basic rules for positioning specimens. For each measurement, it **shall** be ensured that the X-ray fluorescence radiation can reach the detector without obstruction. For flat, unpopulated PCB boards, this is not a problem.

If populated boards are being measured, the operator **shall** note the position of the detector and position the sample such that no components are present in locations that would prevent the radiation emanating from the measurement location from reaching the detector, as illustrated schematically in Figure 2.

The area measured should be flat and not tilted.

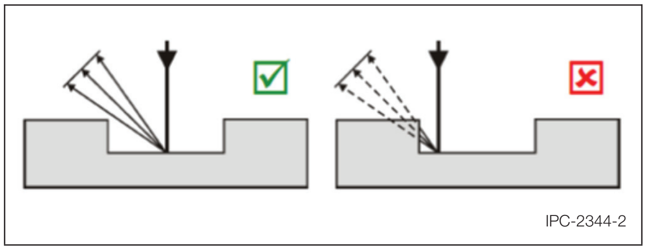

Figure 2 Sample Placement with Respect to Detector

5.5 Measurement XRF equipment operation is instrument specific and **shall** be in accordance with the instrument manufacturer's instructions. Always ensure that the correct measurement file is selected for the application to be measured. Typically, instruments will slide the measuring stage out of the instrument when the measurement chamber is opened. The test sample is then positioned on the programmable X-Y stage such that the laser pointer points at the measurement location. When the measurement chamber is closed, the stage will automatically retract into the chamber.

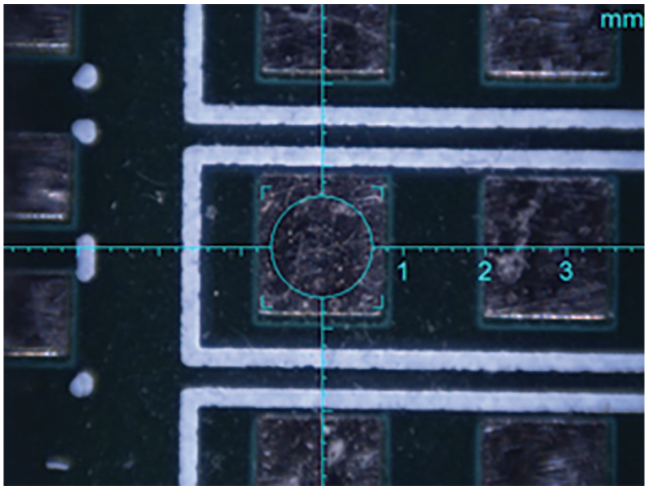

Figure 3 Positioning of a 1 mm Ø Collimator on a 1.5 mm x 1.5 mm [0.060 in x 0.060 in] ENEPIG Pad

The measurement location can then be observed on the video camera image and adjusted if necessary. The collimator area indicated on the video image should fit entirely within the test area of the sample specimen as seen in Figure 3. The sample image is then focused with the autofocus feature of the instrument.

A minimum of 5 measurements **shall** be made per measurement location (0.060 in x 0.060 in pad). Using a polycapillary instrument, the 5 measurements **shall** be made at different locations on the pad or the instrument should be used in a scanning mode across the pad. On each side of the test specimen on which an electroless nickel coating has been applied, three pads **shall** be measured. The Measurement Report **shall** include as a minimum:

- Instrument used
- Size of the collimator
- Measurement time
- Excitation conditions
- Individual measurement results
- Statistical measurement parameters such as mean, standard deviation and relative standard deviation
- Specification Limits as required
- Operator, time and date

6 Notes

6.1 Measurement Results:

Table 1 Measurement of Coating Thickness and Phosphorus Content: Typical achievable results for NiP/Cu/PCB samples (1 mm collimator; measuring time 120 s)

	Specified Values		Measured Values	
CRM	**d (µm)**	**%P**	**d (µm)**	**%P**
CRM 1	5.20 (0.1)	0	5.29 (0.1)	0.0 (0.3)
CRM 2	7.35 (0.2)	0	7.43 (0.1)	0.1 (0.3)
CRM 3	1.2 (0.1)	8 (0.4)	1.2 (0.1)	7.7 (0.3)
CRM 6	2.89 (0.1)	10.6 (0.4)	2.88 (0.1)	10.7 (0.4)
CRM 4	6.9 (0.2)	9.0 (0.4)	6.5 (0.1)	8.9 (0.3)
CRM 5	5.90 (0.2)	11.2 (0.4)	5.7 (0.1)	11.1 (0.3)
CRM 7	11.20 (0.2)	11.3 (0.4)	11.2 (0.1)	11.4 (0.3)

Table 2 Evaluation of Measurement Repeatability using a Polycapillary XRF: 5 Readings of the ENEPIG Sample shown in Figure 3.

	Au	Pd	NiP	wt-%P
Mean	0.049 µm	0.096 µm	3.2 µm	9.3
Standard deviation	0.002 µm	0.002 µm	0.026 µm	0.413
50 nm Au/96 nm Pd/3.2 µm NiP9.3/Cu/PCB (Small spot polycapillary instrument, measuring time 60 s)				

Table 2 demonstrates the excellent standard deviation achievable (0.4 wt.-% for 60 s measuring time) for measurement of P-concentration. It should be noted that a high total spectral intensity of more than 50,000 cps is the result of very high flux excitation by an instrument using a polycapillary X-ray optic emitted from a relatively small measuring spot of less than 50 µm Ø.

In the case of standard aperture beam collimation, the total measuring time for similar precision is expected to be a factor of 2-3 X longer.