Characterization of reference materials with thin gold and palladium layers by means of gravimetric analysis, ED-XRF and Rutherford Backscattering

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1. Motivation

ED-XRF is a well established method for measuring the coating thicknesses of gold and palladium on nickel on copper on a substrate material (e.g. epoxy resin) in the printed circuit board industry [1, 2].

Recently, also very thin coatings of gold and palladium of less than 100 nm have to be measured. This places greater demands on the instrument technology, the evaluation software and, of course, on the reference materials [3].

For such thin coatings the available reference materials are not suitable, because their thicknesses are not of the same order of magnitude as the thin layers to be measured. Stacking several foils should be avoided, as this will increase the uncertainty of the measurement due to small air gaps between the foils. New reference materials which are similar to samples in production have been developed and quantified using independent methods.

Figure 1. *The thickness of Au, Pd, Ni and Cu is measured with a FISCHERSCOPE® X-RAY instrument.*

2. Experimental

Non-structured pc-board material (nickel on copper on fiberglass-reinforced epoxy resin, containing bromine compounds) was coated with different gold and palladium layers (Table 1). The coated material was tested for homogeneity and cut into individual pieces for further analysis and for the use as "Master Standards". Rutherford backscattering (RBS) and ED-XRF in combination with gravimetric analysis (an accredited method under DKD-K 33101 at the Deutsche Kalibrierdienst *[German Calibration Service]*) were used as independent quantification methods. Both methods are non-destructive, therefore it was possible to use them for the same sample piece.

Table 1. *Reference materials with thin gold and palladium coatings. Measurement uncertainty stated for a confidence level of 68.3 %.*

Ref. Mat.	Au [nm]	u [nm]	Pd [nm]	u [nm]	Ni [nm]	u [nm]
1	213.8	2.6			103.6	4.1
2	486.8	4.7			250.4	8.5
3	117.5	1.3			2510	35
4	114.1	1.3			5710	46
5			21.6	0.6	2101	35
6			87.3	0.9	2363	33
7			333.2	2.6	2263	29
8	48.1	0.7	21.1	0.8	2211	33
9	44.0	0.7	92.1	0.9	2354	35
10	45.8	0.7	331.7	2.7	2693	30
11	11.8	0.2	18.7	0.4	2425	34
12	28.4	0.6			2217	32

3. Quantification

a) Gravimetric analysis and ED-XRF

Self-supporting gold and palladium foils are weighed and their area is measured. This provides the global mass per unit area. The foils are separated into squares with side lengths of 1 cm. The mass per unit area assigned to each partial piece is corrected using ED-XRF (used here as a relative method) with regard to lateral inhomogeneity. The gravimetrically measured foils and a "zero sample" are measured standardless with XRF. The linear interpolation between the mass per unit area (XRFA) and the mass per unit area (gravimetric analysis) (Fig. 2) is used to correct the standardless ED-XRF results of the different samples shown in table 1.

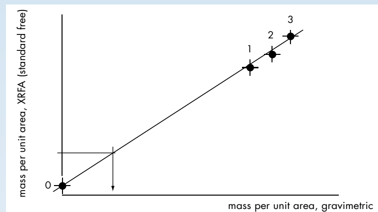


Figure 2. *Linear Correlation between the mass per unit area (XRFA; standardless) and mass per unit area (gravimetric analysis).*

b) Rutherford Backscattering (RBS)

Accelerated He ions hit the sample perpendicularly. The backscatter probability can be calculated for known experimental conditions (energy and number of ions, scattering angle, solid angle of the detector). If the atomic number of the coating Z_2 is sufficiently large compared to the atomic number of the substrate Z_1, then the peak assigned to Z_2 is clearly separated from the spectrum of the base material. The mass per unit area of the coating element Z_2 can be determined from the number of detected backscattered He ions (peak area) if the initial energy E_0 is known. The deceleration of the ions in the coating ("stopping power") must also be taken into account.

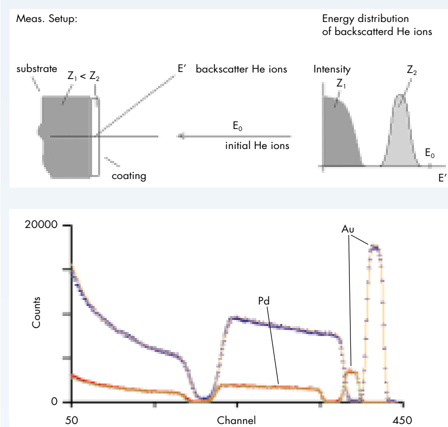
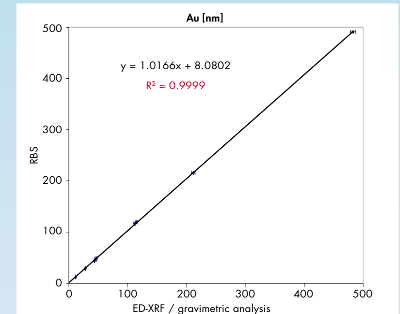


Figure 3. *Principle of the mass per unit area determination from the backscatter spectrum of He ions (top) and backscattering spectra (from [4]; bottom): Intensity (counts) as a function of the particle energy (channel) for reference material No. 10 with 46 nm Au/332 nm Pd/2693 nm Ni/about 30 µm Cu/substrate with Br. (Surrey University England, 2MV Tandetron accelerator of High Voltage Engineering Europe, 1.562 MeV 4He+, backscatter angle = 173° and 148°).*

4. Results

An excellent correlation between the results of RBS and ED-XRF/gravimetric analysis has been observed.



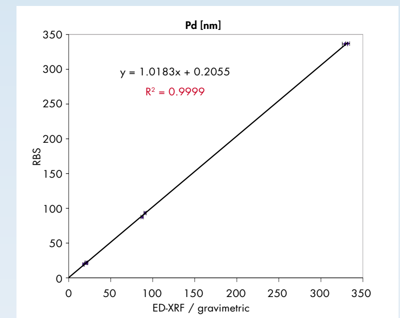


Figure 4. *Correlation between the results of Rutherford backscattering and ED-XRF / gravimetric analysis for the coating thicknesses of Au (top) and Pd (bottom).*

5. Summary

New certified reference materials with thin Au and Pd coatings on printed circuit board in the nanometer range have been developed by the Helmut Fischer GmbH. Their quantification is traceable to ED-XRF, gravimetric analysis and Rutherford Backscattering. For the region below 100 nm, the uncertainty of the reference materials is less than 1 nm.

Figure 5. *Certified reference materials with thin Au and Pd coatings on Ni/Cu/PCB (with cerificate).*

5. References

[1] S. Korsch, H. Kleinbach, P. Neumeier, Qualitätskontrolle unbestückter Leiterplatten, Galvanotechnik 10 /2008 , Leuze Verlag, Bad Saulgau 2008, 2386-2295.
[2] V. Rößiger, B. Nensel, Analyse von Schichtdicken mit Röntgenfluoreszenz, Jahrbuch Oberflächentechnik, Leuze Verlag, Bad Saulgau 2004, 195-225.
[3] S. Dill, V. Rößiger, Schichtdickenmessung dünner Gold- und Palladiumschichten auf Leiterplatte mit Röntgenfluoreszenz, Galvanotechnik 5/2010, Leuze Verlag, Bad Saulgau 2010, 999-1004.
[4] C. Jeynes, "Report on thickness determinations of 18 Pd and Au thin films ..", Job No. 2083, August 2009 (priv. notification).