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X-Ray Fluorescence for Measuring Plating Thickness

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X-RAY FLUORESCENCE
FOR
MEASURING PLATING THICKNESS

1. PURPOSE

There are a number of techniques currently being used for measuring plating thickness. All have peculiar application and also limitations. Basic economics, however, demands that for measuring gold thicknesses in the commonly used plating thickness ranges, a system must be highly reliable, accurate, repeatable and fast. Over the past several years X-ray Fluorescence systems, more than any other, have been found to meet that requirement. There are, however, many facets of operation involved with x-ray techniques with which the operator should be acquainted. The purpose of this paper is to highlight these subtleties so that x-ray users are aware of them and can implement procedures for their instrument operation which will provide measurements of highest possible levels of accuracy and repeatability.

2. INTRODUCTION

X-rays are electromagnetic waves, generally thought of as particles of light or photons of very high energy levels. They travel at a very high frequency and are of short wave length. X-ray radiation occurs naturally, such as in the form of a radioisotope or can be generated artificially as in an x-ray tube. The advantage of an x-ray tube is that it produces a high x-ray flux which does not decay and is generated only as long as power is applied. The radioisotope in contrast cannot be turned off and unless a large quantity of the material is used, it generates only a small flux of x-rays.

Consequently, the x-ray tube is the more stable and safest system for generating x-rays in applications for measuring plating thickness. This is accomplished in the tube by applying a high voltage across the gap between a heated cathode filament and a tungsten target causing the electrons to bombard the target at high energies which in turn emits x-rays. In application these incident x-rays must be focused into a fine beam capable of being directed into extremely small areas. This is done by passing the x-rays through a long narrow tube made with strongly absorbing or reflective walls which permit only radiation traveling parallel to the tube axis to traverse its entire length. This tube, known as a "Collimator", can direct x-rays in a beam as narrow as 0.08 mm (.003") in diameter, allowing access to very small areas.

3. X-RAY FLUORESCENCE

The atoms which make up an element consist of a central nucleus surrounded by electrons orbiting the nucleus at various energy levels, known as shells. If an incident photon, a quanta of energy, strikes an electron in a given shell that electron will gain energy from the striking photon and becomes excited. In this state it leaves the atom, creating a vacancy in the shell from which it originated. To fill the vacancy an upper level electron, one with a higher energy will fall into the vacancy. The excess energy which this electron possesses will then be released as the emission of a photon, in this case, an x-ray photon. This is known as x-ray fluorescence.

Each atom possesses an electron distribution and arrangement peculiar to itself, see Periodic Table, page 7. The energy of the fluoresced x-rays for a given emission line increases with the atomic number of the particular atom. In other words, the wave length or energy of the fluoresced x-rays characterizes the particular atom emitting them. So, it can then be seen that by examining the distribution and energies of the fluoresced x-rays from materials, the nature of these materials may be determined. Further, by the monitoring of the relative quantities or intensities of the x-ray fluorescence throughout the spectrum the proportional quantities of the materials present can be determined as well.

4. MEASURING THICKNESS

To determine coating thicknesses, spectral or energy peaks are generated representing the intensity or count rate of x-ray fluorescence at energy levels for the base material and for the coating material to be measured. For a substrate with only a thin coating the x-ray spectrum will show a high peak for the substrate and a small peak for the coating material. As more of the coating is added the size of the substrate peak decreases and the peak in the coating region of the spectrum will increase. The substrate peak decreases as the coating increases simply because the x-rays are being absorbed by the coating. This will continue as more coating thickness is added until there no longer is any difference in the detected x-ray fluorescence from the substrate and the coating material reaches a point of saturation. To redefine, this point of saturation can be considered as the point where the coating material approaches a thickness such that the intensity of the x-rays fluoresced from the coating no longer increases with the increase in coating thickness.

To make a measurement there are 2 methods which can be employed. The first is described as the excitation mode in which a window is established around the region of interest for the coating material. When the measurement is complete a computer (an integral part of the instrumentation) integrates all the counts of all the x-rays which were detected within this window. A wide variety of coating and base combinations can be measured. As the coating thickness increases, so does the intensity or count rate of the fluoresced x-rays within the window until a point of saturation is reached. This is known as the upper thickness limit which is specific to each coating. An example of some of these limits is shown in the table that follows:

Combination	Approx. Upper Limit (in)
gold/nickel	300
nickel/copper	950
tin/copper	3000
60/40 solder/copper	1500
palladium/nickel	1900

The second method for making measurements is the absorption mode which is an alternate method when the excitation mode is not suitable, such as in the case of coatings with very low atomic number. In this absorption mode, the window or region of interest is established around the substrate material and so the coating thickness increases, the intensity of the x-rays from the substrate will decrease.

In both measuring modes, the intensity (count rate) is translated into direct measurements by means of a mathematical relationship between "normalized counts" from the sample and the coating's thickness. The term "normalized counts" is the count rate data from a sample expressed as a percentage of the range between a bare sample and a sample of the coating material at saturation thickness.

Many instruments are available for making measurements using the X-ray Fluorescence system. Each may have built in features peculiar to make and model which may improve the ease or speed of the required operating mechanics. Regardless, there are basic requirements to be aware of, whether performed automatically in the instrument or manually by external controls.

5. CALIBRATION

Calibration is the first and most important step in the use of any measurement instrument, including x-ray fluorescent types. Most significant factors influencing the accuracy and repeatability are the following:

5.1 Accurate and reliable thickness standards must be obtained. Most sources certify the accuracy to be +/-5% of the stated value. Standards should be verified by comparison to other techniques. This is done primarily for the detection of any bias. Limitations and possible error sources of each technique must be taken into account when attempting to perform a calibration.

5.2 Each calibration requires a base and an infinite standard. These provide the end points of the calibration curve. The base should consist of the basis metal substrate and the appropriate plating that will be applied as the undercoating on the specimen to be measured. The infinite standard should consist of the measurement coating at a thickness such that the x-ray beam cannot penetrate to the basis metal or undercoat. This is the saturation point at which the count rate will not increase with an increase in thickness.

5.3 Variations in the basis metal will not affect the accuracy and repeatability of the measurement unless its characteristic peak interferes with that of the coating to be measured. The prime example of a basis metal interference is the measurement of nickel over copper. In this case, the interference is handled by using a cobalt filter which selectively screens the copper counts from the detector but allows the nickel counts to pass through. Other interferences can be calibrated out through a base adjustment program available on many units. Refer to manufacturers' guidelines for specific procedures.

5.4 The calibration count time has a direct influence on the variability of the resulting calibration. A count time should be chosen by the user to provide the confidence level desired. Measurement repeatability is improved as calibration count times are increased.

6. MEASUREMENT TIME

The measurement time selected will affect the accuracy and repeatability of the resulting thickness measurement. The required count time should be established by the user to obtain the desired level of precision. This can be accomplished by performing count time studies; i.e., measure the same product at various count times and evaluate the results for precision. Many of the units available today are equipped with software programs that will predict the percent uncertainty of a measurement at various count times.

7. DENSITY

As with all mass-per-unit-area techniques, the x-ray measurement is based on a conversion of mass to thickness. Therefore, the density of the plate must be considered.

For many electro-deposited coatings, such as nickel, the density is fairly straightforward and the value employed is consistent throughout the industry. Gold, however, is a different story with many densities reported. Military specifications for hard gold specify, by grade and type, acceptable purity and hardness - but not density.

Densities ranging from 15.7 to 19.3 G/CC have been reported for gold, with hard gold electrodeposits at the lower end of the scale. The density of the plate will vary with bath chemistry and current density. When performing thickness measurements and comparisons an agreed upon density should be established based on the plating conditions.

8. DRIFT

The x-ray tube and detector are subject to some degree of drift over time. This drift must be corrected for at some frequency. The correction procedure is handled differently by each unit manufacturer but the general principle involves the realigning of specific spectral peaks and count rates in comparison to initial calibration conditions.

The frequency at which this correction will need to be performed should be established by each user based on accuracy and repeatability requirements.

9. SAMPLE CONDITION

The geometrical configuration and condition of the sample should be considered before taking measurements. If the sample has surface damage or poor adhesion, the measurements will not be accurate. If the sample is significantly curved, the unit may need to be calibrated with standards of the same geometrical configuration.

10. LOCATION AND POSITIONING

Most connector products today are selectively plated. Therefore, the thickness measurement must not only show that the thickness is correct but that the coating is in the proper location for product functionality.

Many x-ray units do not have an easy, accurate means of determining location. The user should consider, if location accuracy is a concern, retrofitting these units with electronic, digital x-y stages.

11. GENERAL USE PRECAUTIONS

As with any instrumentation there are always a number of general rules or precautions which must be followed in order to obtain optimum results. Listed below are some general use guidelines to incorporate into any x-ray fluorescence testing techniques.

11.1 As mentioned earlier, the collimator is the mechanism by which the x-ray beam is aimed onto the correct measurement area. Therefore, the alignment of this collimator to the microscope is critical and should be verified at a frequency that the user feels is adequate to ensure proper alignment.

11.2 Along with the collimator alignment, another factor to consider is the size of the collimator in relation to the size of the measurement area. The area that the x-ray beam is striking must be totally covered by the sample being measured. The user should also be aware of the fact that the x-ray beam will spread from the time it exits the collimator until it strikes the part.

11.3 The orientation of the sample in relation to the detector is also important. The general rule is that nothing should be between the measurement area and the detector that would block the path of the x-rays. (ex., detector shadowing).

11.4 Samples must be flat on the staging area and must be in clear focus. Individual eyesight may affect the focal length significantly enough to give inaccurate readings on some instruments. Each user should test their eyesight (i.e., focusing ability) on a known sample or thickness standard.

TABLE 1

PERIODIC TABLE OF THE ELEMENTS

Ia	2a	3b	4b	5b	6b	7b	8			1b	2b	3a	4a	5a	6a	7a	0	Orbit
1 +1 H -1 1.00797 1		Atomic Number → 50 +2+4 Symbol → Sn +4 KEY TO CHART Atomic Weight → 118.69 -18-18-4 ← Oxidation States ← Electron Configuration															2 0 He 4.0026 2	K
3 +1 Li 6.939 2-1	4 +2 Be 9.0122 2-2						Transition Elements					5 +3 B 10.811 2-3	6 +2+4 C +4 -4 12.01115 2-4	7 +1+2 N +3+4 +5 -1-2-3 14.0067 2-5	8 -2 O 15.9994 2-6	9 -1 F 18.9984 2-7	10 0 Ne 20.183 2-8	K-L
11 +1 Na 22.9898 2-8-1	12 +2 Mg 24.312 2-8-2			Transition Elements			Group 8				Transition Elements	13 +3 Al 26.9815 2-8-3	14 +2+4 Si -4 28.086 2-8-4	15 +3+5 P -3 30.9738 2-8-5	16 +4+6 S -2 32.064 2-8-6	17 +1+5+7 Cl +3 -1 35.453 2-8-7	18 0 Ar 39.948 2-8-8	K-L-M
19 +1 K 39.102 -8-8-1	20 +2 Ca 40.08 -8-8-2	21 +3 Sc 44.956 -8-9-2	22 +2+3 Ti +4 47.90 -8-10-2	23 +2+3 V +4+5 50.942 -8-11-2	24 +2+3 Cr +6 51.996 -8-13-1	25 +2+3 Mn +4+6+7 54.9380 -8-13-2	26 +2 Fe +3 55.847 -8-14-2	27 +2 Co +3 58.9332 -8-15-2	28 +2 Ni +3 58.71 -8-16-2	29 +1 Cu +2 63.546 -8-18-1	30 +2 Zn 65.37 -8-18-2	31 +3 Ga 69.72 -8-18-3	32 +4 Ge 72.59 -8-18-4	33 +3+5 As -3 74.9216 -8-18-5	34 +4+6 Se -2 78.96 -8-18-6	35 +1+5 Br -1 79.904 -8-18-7	36 0 Kr 83.80 -8-18-8	L-M-N
37 +1 Rb 85.47 -18-8-1	38 +2 Sr 87.62 -18-8-2	39 +3 Y 88.905 -18-9-2	40 +4 Zr 91.22 -18-10-2	41 +3+5 Nb 92.906 -18-12-1	42 +6 Mo 95.94 -18-13-1	43 +4+6+7 Tc (97) -18-13-2	44 +3 Ru 101.07 -18-15-1	45 +3 Rh 102.905 -18-16-1	46 +2+4 Pd 106.4 -18-18-0	47 +1 Ag 107.868 -18-18-1	48 +2 Cd 112.40 -18-18-2	49 +3 In 114.82 -18-18-3	50 +2+4 Sn 118.69 -18-18-4	51 +3+5 Sb -3 121.75 -18-18-5	52 +4+6 Te -2 127.60 -18-18-6	53 +1+5+7 I -1 126.9044 -18-18-7	54 0 Xe 131.30 -18-18-8	M-N-O
55 +1 Cs 132.905 -18-8-1	56 +2 Ba 137.34 -18-8-2	57* +3 La 138.91 -18-9-2	72 +4 Hf 178.49 -32-10-2	73 +5 Ta 180.948 -32-11-2	74 +6 W 183.85 -32-12-2	75 +4+6+7 Re 186.2 -32-13-2	76 +3+4 Os 190.2 -32-14-2	77 +3+4 Ir 192.2 -32-15-2	78 +2+4 Pt 195.09 -32-16-2	79 +1+3 Au 196.967 -32-18-1	80 +1+2 Hg 200.59 -32-18-2	81 +1+3 Tl 204.37 -32-18-3	82 +2+4 Pb 207.19 -32-18-4	83 +3+5 Bi 208.980 -32-18-5	84 +2+4 Po (209) -32-18-6	85 At (210) -32-18-7	86 0 Rn (222) -32-18-8	N-O-P
87 +1 Fr (223) -18-8-1	88 +2 Ra (226) -18-8-2	89** Ac +3 (227) -18-9-2																O-P-Q

*Lanthanides	58 +3+4 Ce 140.12 -19-9-2	59 +3 Pr 140.907 -20-8-2	60 +3 Nd 144.24 -22-8-2	61 +3 Pm (145) -23-8-2	62 +3 Sm 150.35 -24-8-2	63 +3 Eu 151.96 -25-8-2	64 +3 Gd 157.25 -25-9-2	65 +3 Tb 158.924 -26-9-2	66 +3 Dy 162.50 -28-8-2	67 +3 Ho 164.930 -29-8-2	68 +3 Er 167.26 -30-8-2	69 +3 Tm 168.934 -31-8-2	70 +2+3 Yb 173.04 -32-8-2	71 +3 Lu 174.97 -32-9-2	N-O-P
**Actinides	90 +4 Th (232) -18-9-2	91 +4+5 Pa (231) -20-9-2	92 +3+4+5+6 U (238) -21-9-2	93 +3+4+5+6 Np (237) -22-9-2	94 +3+4+5+6 Pu (244) -23-9-2	95 +3+4+5+6 Am (243) -24-9-2	96 +3 Cm (247) -25-9-2	97 +3+4 Bk (247) -26-9-2	98 Cf (251) -28-8-2	99 Es (254) -29-8-2	100 Fm (257) -30-8-2	101 Md (256) -31-8-2	102 No (254) -32-8-2	103 Lr	O-P-Q

Numbers in parentheses are mass numbers of most stable isotope of that element.

Symbols:

Ag = Silver	Pb = Lead
Au = Gold	Pd = Palladium
Cu = Copper	Sn = Tin
Ni = Nickle	Sn/Pb = Tin/Lead Solder

11.5 Cylindrical parts should be positioned with their length perpendicular to the detector.

11.6 Sampling frequency should be considered if using x-ray fluorescence as a process control. Frequency should be adequate enough to detect shifts in the process. SPC programs tied into x-ray fluorescence measurements are very effective for this purpose.

12. REFERENCES

1.   "The Key to Plating Process Control", P. L. Hoffman, DuPont Electronics Division of E. I. DuPont Company, Emigsville, Pennsylvania.

2.   Fluoroderm™ Users Manual, VEECO/UPA Technology, Inc., Syosset, New York.

3.   ASTM A754-79, Standard Test Method for Coating Thickness by X-ray Fluorescence.