eurofins | EAG Laboratories

APPLICATION NOTE

# Determining Density of Thin Films

By Dr. Daniel J. D. Sullivan, Patrick Davis, Greg Strossman, and Dr. Daniel Tseng

## INTRODUCTION

Thin films are widely used in many high-tech devices and consumer products.[1,2] The reasons for their use varies widely but is predominantly due to their physical, mechanical, electrical, thermal or decorative properties.[3,4]

The quality and consistency of these films is of great interest to manufacturers and users of these materials. One of the key film properties of interest is density.[5,6] This paper addresses the processes best used to measure the density of such films. The elemental composition and film thickness can also be determined and are also discussed.

The use of X-ray Fluorescence Spectroscopy (XRF) to determine film thickness and composition is coupled with Rutherford Back Scattering Spectrometry (RBS) which determines the film's areal density and elemental composition. The third technique of interest is Dual Beam Focused Ion Beam (DB FIB) which can directly measure film thickness.[7,8,9] These techniques combine to provide the film's elemental composition, thickness and density.

## SAMPLE PREPARATION

The sample we used in this study is a US 10 cent coin that was coated with a thin layer of gold. This film is used for demonstration purposes only and is not as uniform as state-of-the-art films used for demanding electronic or semiconductor applications, but it is a good example for the techniques and measurements that can be made on real films and film stacks. No sample preparation was required for any of the techniques.

XRF measurements were made on both sides of the coin at several locations. The RBS measurement and the DB FIB cross section were made in one location only.

## INFORMATION OBTAINED

Optical microscopy allows inspection of devices for major defects such as large cracks, discolorations, and gross contamination. It is often used to document the samples prior to analysis. Bright field and dark field or a mix can be used to examine and document specific surface features of different types, e.g. pits, scratches or particles.

XRF uses X-rays to excite fluorescence in materials. The wavelength of the fluorescence shows the species present in the sample and the intensity of the fluorescence can be used to determine the elemental composition. Layer thicknesses can also be determined on flat samples. Detection limits are typically in the PPM (parts per million) range for most elements, but this varies with atomic number.

In Rutherford Back Scattering Spectrometry (RBS) MeV alpha particles (He nuclei) bombard the sample and the energy of the

**Table 1: Test Matrix**

| Method | Information acquired | Comments |
|---|---|---|
| **Optical microscopy** | Color images of sample, dimensional measurements. | Limited to ~ 2500×. Only detects visible light. |
| **WDXRF** | Elemental composition and film thickness | Minimum sampling area is 0.5 mm diameter |
| **RBS** | Elemental composition up to 2 microns depth. Elemental areal density and calculated film thickness. | No standards required. |
| **DB FIB** | Allows direct imaging of a cross section of the sample. Grey scale images with high depth of field with magnifications up to 100,000× on standard tools. | Small area cut. Only shows that one plane in the sample. Limited depth of approximately 50 microns. |

**Figure 1: Optical images of the sample after DB FIB**

COPYRIGHT © 2020 EUROFINS SCIENTIFIC I REV. 10.20.21

scattered ions are measured. The date obtained are modeled to determine the elemental composition and layer structure. The areal density of the film can also be determined. With this technique, if the film thickness is known, then the density can be determined and vice versa: if the density is known, then the film thickness can be calculated.

Dual Beam FIB can be used to cross section through the thin film layers to directly measure the film thickness(es) using subsequent in situ SEM inspection. The interface and the entire film can also be imaged to investigate the sharpness of the interface and to determine if any voids/defects are present. DB FIB cross-sections can be made at any accessible location on a sample.

## RESULTS OF EACH TEST

Optical imaging in this case was used just to document the sample and inspect it prior to analysis.

XRF is used to detect the elements present in the film and also in the underlying substrate, with ppm detection limits. With this data and knowing the gold is in the overlying film, calculations can be made to determine the thickness of the film. Several locations were analyzed to determine the overall uniformity of the gold coating.

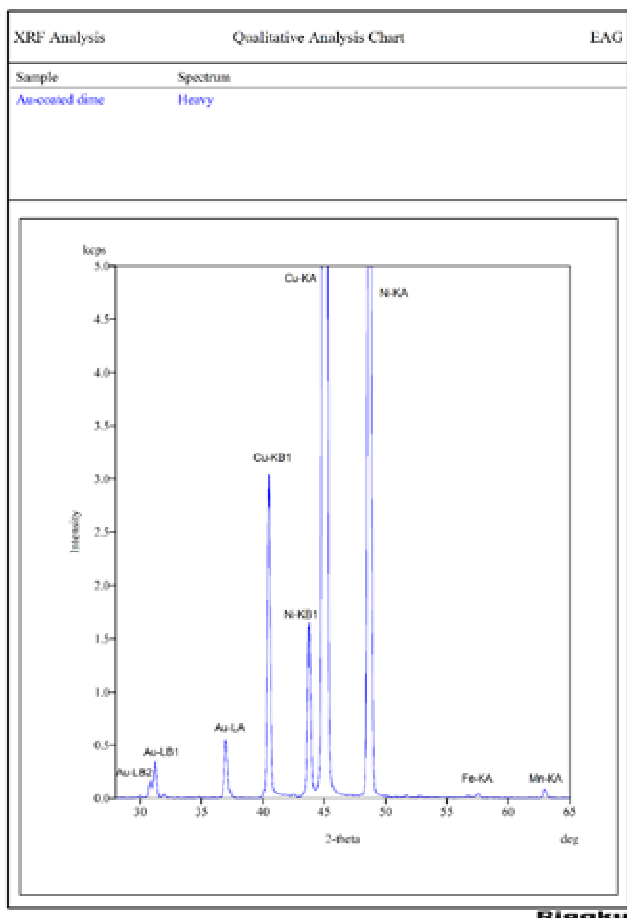


**Figure 2: The XRF scan shows the elements present in the sample**

Table 2. Gold coating (front side)

| Element | Coating (wt%) | Substrate (wt%) |
|---|---|---|
| Au | 100 | |
| Cu | | 73.9 |
| Ni | | 25.7 |
| Co | | 0.019 |
| Fe | | 0.059 |
| Mn | | 0.30 |
| Zn | | 0.042 |

**Table 3: Elemental composition of the surface layer and the substrate, the coating is pure Au.**

| | Film | | | Substrate | Substrate |
|---|---|---|---|---|---|
| | Au | | | Cu | Ni |
| | nm | St. Dev. | RSD (%) | wt% | wt% |
| **Spot 1** | 98 | 0.29 | 0.30 | 75.4 | 24.6 |
| **Spot 2** | 87 | 0.49 | 0.56 | 75.1 | 24.9 |
| **Spot 3** | 112 | 0.33 | 0.29 | 75.2 | 24.8 |

**Table 4: Quantified using calibration from Au thickness standards over a 1mm area**

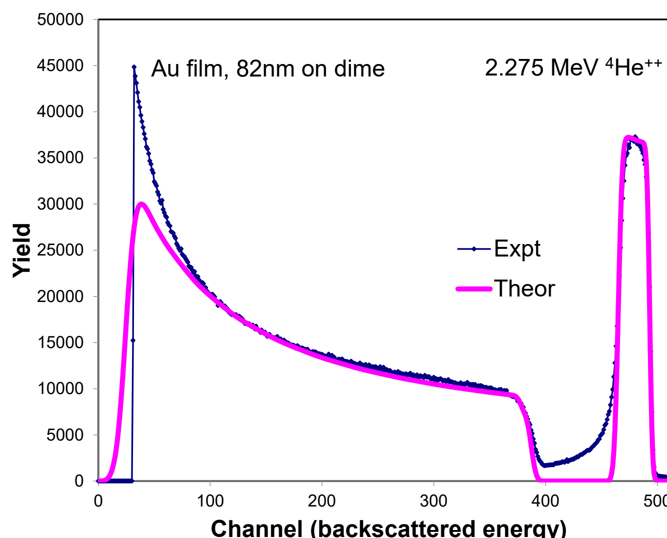


**Figure 3: RBS data with the best fit modeled data. Using the best fit to the data, a depth profile of the film and the areal density are then calculated.**

The coating thickness is nonuniform. Each analysis was repeated 3 times at each location (note the RSD determined from the repeat measurements). WDXRF has excellent precision and can measure sub-nm scale differences in thickness.

COPYRIGHT © 2020 EUROFINS SCIENTIFIC I REV. 10.20.21

# Determining Density of Thin Films

| | RBS Thickness [nm] | Atomic Concentrations [at%] | | | Assumed Density [at/cc] |
|---|---|---|---|---|---|
| | | Ni | Cu | Au | |
| **Layer 1** | 82 | - | - | 100 | 5.90E22 |
| **BULK** | - | 26.5 | 73.5 | - | 8.63E22 |

**Table 5: RBS elemental composition, showing an aerial density of 4.85e17 atoms/cm²**

The average thickness for this film was measured to be 70 nm by Dual Beam FIB. The film is rough with a standard deviation of 8 nm, as measured directly using the SEM mountd on the DB FIB.

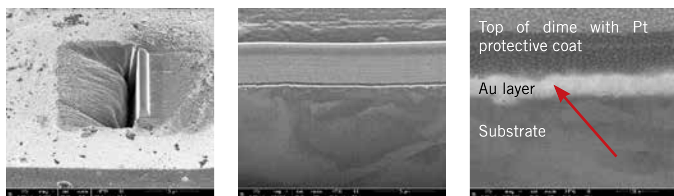


**FIgure 4: A DB FIB cross section of the gold layer (see red arrow) on the sample allows measurement of the layer thickness.**

The density of the gold film can be calculated using the areal density obtained from RBS and the layer thicknesses from either XRF or DB FIB. The XRF gives an average thickness over a larger area while the DB FIB shows the film thickness and variation in a much smaller specific location.

Using the atomic mass of gold, $3.2707 \times 10^{-22}$ g/atom, this results in a range of 22.6-24.0 g/cm$^3$ which compared to the common density of gold of 19.3 g/cm$^3$ (see table below).

| Aerial density (atom/cm$^2$) | Thickness | Atom Density (atm/cm$^3$) | Calculated Density g/cm$^3$ |
|---|---|---|---|
| $4.85 \times 10^{17}$ | 70-87 nm | 6.91 X$10^{22}$ | 22.6-24.0 |

## SUMMARY:

The use of thin films in products requires a knowledge of the film properties. This paper illustrates a procedure to determine the composition, thickness and density of a film. The Three techniques used on different locations on the sample provided a range of thicknesses. This sample was checked and the gold coating thickness ws found to be very variable. The analyses of the techniques were repeated and the individual locations provide very repeatable results however the sample variation across the analyzed regions showed the non-uniformity of the coating.

While there are alternative techniques to determine film thickness and composition this approach has the advantages of direct measurement of the thickness (via DB-FIB) at a particular location and elemental composition determination with excellent detection limits (via XRF) along with averaged thickness over a larger area. The RBS then adds the capability to measure the aerial density and ultimately provide a film density. This combination of techniques enables average thickness measurements and specific area measurements to be made to better understand the thickness variations in the film(s).

Additional properties of thin films can be investigated with additional techniques: roughness with AFM, Stress and texture by XRD, trace contaminations with SIMS, grain structure with EBSD and surface composition with XPS or Auger Electron Spectroscopy.

## REFERENCES


1. A. A. Voevodin and J. S. Zabinski, Thin Solid Films 370 (2000) 223
2. Tomoaki Matsushima, ... Kiyotaka Wasa, in Handbook of Sputtering Technology (Second Edition), 2012.
3. Carretero, E.; Alonso, R. Semitransparent Decorative Coatings Based on Optical Interference of Metallic and Dielectric Thin Films for High Temperature Applications. Coatings 2018, 8, 183.
4. Gould R.D., Kasap S., Ray A.K. (2017) Thin Films. In: Kasap S., Capper P. (eds) Springer Handbook of Electronic and Photonic Materials. Springer Handbooks. Springer, Cham.
5. Gould R.D., Kasap S., Ray A.K. (2017) Thin Films. In: Kasap S., Capper P. (eds) Springer Handbook of Electronic and Photonic Materials. Springer Handbooks. Springer, Cham
6. LOVELL, S., ROLLINSON, E. Density of Thin Films of Vacuum Evaporated Metals. Nature 218, 1179–1180 (1968).
7. Thin-film characterization by x-ray fluorescence, T. C. Huang, Invited paper presented at the Federation of Analytical Chemistry and Spectroscopy Societies Annual Meeting, Chicago, IL, 1–6 October, 1989.
8. Abiodun E. Adeoye, Emmanuel Ajenifuja, Bidini A. Taleatu, and A. Y. Fasasi, “Rutherford Backscattering Spectrometry Analysis and Structural Properties of Thin Films Deposited by Chemical Spray Pyrolysis,” Journal of Materials, vol. 2015, Article ID 215210, 8 pages, 2015.
9. ] J. Orloff, M. Utlaut, L. Swanson, High Resolution Focused Ion Beams: FIB and its Applications, first ed., Kluwer Academic/Plenum Publishers, New York, 2003


COPYRIGHT © 2020 EUROFINS SCIENTIFIC I REV. 10.20.21