Characterization of electronic materials using fundamental parameter micro X-ray fluorescence

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Abstract
Increasingly complex coating structure on electronic samples for functional purposes include multiple layers, ultra-thin coating and alloy coating. Such combinations have prohibited straightforward characterization by most techniques today. With the robust quantifying method offered by fundamental parameter approach and technologies available from energy-dispersive X-ray fluorescence (XRF), both thickness and chemical composition of the layers can be measured fast and non-destructively. Furthermore, the combination of micro-spot XRF also allows such analysis to be carried out on small parts, typically down to tens of micrometres. In this paper, application examples are presented with the advantages and challenges of this approach addressed.

1. Introduction
X-ray fluorescence (XRF), a sub-field of X-ray spectroscopy, is today a mature technology of its own with both academic and industrial applications including electronics [1], jewelries [2], chemicals [3,4], catalysts [5], biotechnology [6] and renewable energy [7]. Coating thickness and elemental composition are the information extractable from quantitative analysis of a typical XRF spectrum. After rigorous development of such quantitative approaches in the past decades which is still ongoing today, as well as corresponding advances in the hardware design, current detection limits can reach a few nanometer for thickness and a few parts-per-million (ppm) for elemental concentration.

Dealing with electronic samples require both high instrument sensitivity and small lateral resolution (beam spot size). Achievement in the former is partially attributed to the breakthrough in energy-dispersive spectroscopy (EDS) technology – silicon drift detectors (SDD) today supports enhanced sensitivity to light elements and high count rate in excess of 100,000 cps [8]. Increasing need for the latter also spurred development in polycapillary focusing systems that are nowadays commonly coupled to XRF systems and have focal spot size (FWHM) at the order of tens of micrometers [9]. Despite the relatively bigger beam size (order of μm) as compared to SEM-EDS (order of nm) which utilizes electron beam rather than X-ray beam, this complements the SEM-EDS as the depth information of the latter is typically limited to only a few micrometer due to the lower penetration power of electron beams [10]. X-ray beams are also generally better at exciting heavier elements and thus give lower detection limit for these elements. A schematic setup of a XRF system is shown in Figure 1. Finally, discussions here touch only on XRF systems based on polychromatic x-ray tube source and SDD.

2. Working principles
Similar to other X-ray spectroscopy techniques, the core of quantitative XRF relies on the software capability to interpret the acquired spectrum. It logically follows that the quality of spectrum - in terms of signals intensity, handling of artefact peaks, and energy resolution – is also of utmost importance. As an example, signal intensity relates to counting statistics and dominantly determines the precision of the measured parameter.

Perhaps not surprisingly, any researcher working with X-ray diffraction systems would be familiar with the process of “fitting” a spectrum. The principles behind some of the most advanced commercial XRF softwares today rely on the same principle: define a model for the sample and let the software alter the free parameters (either thickness or concentration or both) until the generated theoretical spectrum matches the experimental one. Typically such a spectrum would be divided into “channels” (Fig. 2), each covering a finite energy range. A quantity, sometimes referred to as “mq” (in short for measurement quality) can then be computed according to the following equation [11]:

\[mq^2 = \left(\frac{1}{N}\sum \frac{s_{exp}^2 - s_{theor}^2}{\mu_i^2}\right)

Fig 2: A typical quantitative analysis of XRF spectrum involves generating a theoretical spectrum that fits the experimental spectrum best. The residue spectrum aids in locating regions in spectrum with poor fitting.
is in effect a quantity that measures how closely fitted are the two spectra, where the difference between theoretical value \( s_i^{\text{theor}} \) and measured value \( s_i^{\text{exp}} \) is calculated and normalized with respect to the corresponding Poisson uncertainty \( u_i \) and summed over all channels.

The above-mentioned method is sometimes also known as “fundamental parameter” [11] as it is possible to produce measurement results from a set of known physical constants without the need of calibration standards. The formulation of the problem is very much equivalent to the “minimization problem” in mathematics, where in the ideal situation a unique solution refers to the global minimum in \( mq \). For simple cases, an unique solution is obtainable from a single spectrum measured at one condition. In cases where one excitation condition favors one element but disfavors the other, it is necessary to acquire several spectra at different conditions, each optimized for the excitation of a particular set of elements.

The author also wishes to point out at this point that depth-profiling capability is not inherent in XRF analysis, unlike in other technique such as Rutherford backscattering spectroscopy (RBS). Unless a modification of both hardware and software is involved, such as the confocal system demonstrated by Šmit et. al. [12], a single XRF spectrum generally does not provide any information on depth profile. While in principle more information can be obtained by taking spectra at different conditions (including different geometry arrangements), future XRF softwares intending to tackle this problem would undoubtedly have to face the challenges of finding an algorithm which is capable of handling the vast input information while remains computationally affordable.

### 3. Applications

Micro-XRF systems are today widely used in leadframe applications, where the challenges are getting sufficient fluorescence intensity from ultra-thin coating layers (such as Au and Pd) on very small sample area (< 100 µm). The latter immediately demands polycapillary focusing system where a small beam size with high intensity is possible. Figure 3 shows the optical image of the measurement spot on a AuAg/Pd/Ni/CuFe lead-frame tip using a XDV-mue Fischerscope. Analysis of spectrum is done using Fischer WinFTM software without the need of any standards (fundamental parameter approach) All the parameters of interest can be defined and measured concurrently in a single measurement. Measurement results are shown in Table I.

![Fig 3: Measurement spot (shown in inset figure) is sufficiently small for the leadframe-tip.](image)

<table>
<thead>
<tr>
<th>AuAg</th>
<th>Au</th>
<th>Ag</th>
<th>Pd</th>
<th>Ni</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>[nm]</td>
<td>[%]</td>
<td>[%]</td>
<td>[nm]</td>
<td>[nm]</td>
<td>[%]</td>
<td>[%]</td>
</tr>
<tr>
<td>Mean</td>
<td>15.4</td>
<td>35.4</td>
<td>64.6</td>
<td>5.54</td>
<td>719</td>
<td>97.6</td>
</tr>
<tr>
<td>Std. dev.</td>
<td>0.8</td>
<td>1.4</td>
<td>1.4</td>
<td>0.38</td>
<td>2</td>
<td>0.0</td>
</tr>
</tbody>
</table>

It is worth noting that for such polycapillary systems, the intensity at the higher energy region of the spectrum (20-30keV) suffers dramatically as compared to conventional pinhole collimation design due to the lower transmission efficiency at shorter wave-length x-rays [13]. Figure 4 shows partially the analysis outcome of the leadframe sample. For such low intensity signals, longer measurement time is necessary to improve the counting statistics.

![Fig 4: XRF spectrum fitting for Pd and Ag signals using WinFTM. Black, blue and green spectrum indicates measured, theoretical and residue spectrum respectively.](image)

When it comes to trace element analysis such as lead-free requirements, especially on small samples, micro-XRF system is also highly desirable. Besides the obvious advantage of higher intensity, such small beam size allows high resolution mapping across a small sample. Figure 5 shows a mapping of 20 points across a hard-disk component which is made of stainless steel (contaminated with lead). With the availability of programmable sample stage, such mapping is automatic and takes less than half an hour. Figure 6 shows the measurement results.

![Fig 5: Crosses in the diagram indicate mapping points programmed on the stainless steel parts on a hard disk component. More points can be programmed depending on the area to be covered and density of the mapping.](image)
Such an approach is available in the WinFTM software and is known as “multi-excitation” method. We use the example of a particular sample – Pd/NiP/TiW/Wafer – to demonstrate this. In this application, 50kV excitation settings are generally favored for most of the elements. However, to obtain high signal to background ratio for P signal, it is necessary to utilize 10kV excitation settings. It is noted that the substrate in this case, Si wafer, need not be quantified. Table III shows the measurement results.

Table III: Measurement results on Pd/NiP/TiW/Wafer, where Si wafer is the substrate.

<table>
<thead>
<tr>
<th></th>
<th>Pd</th>
<th>NiP</th>
<th>Ni</th>
<th>P</th>
<th>TiW</th>
<th>Ti</th>
<th>W</th>
</tr>
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<tbody>
<tr>
<td>[nm]</td>
<td>[nm]</td>
<td>[%]</td>
<td>[%]</td>
<td>[nm]</td>
<td>[%]</td>
<td>[%]</td>
<td>[%]</td>
</tr>
<tr>
<td>Mean</td>
<td>205</td>
<td>2882</td>
<td>89.5</td>
<td>10.5</td>
<td>265</td>
<td>6.8</td>
<td>93.2</td>
</tr>
<tr>
<td>Std. dev.</td>
<td>4</td>
<td>32</td>
<td>0.4</td>
<td>0.4</td>
<td>5</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

To understand the necessity of using multi-excitation further, it is helpful to look at the signal-to-background ratio for phosphorous under both 10kV and 50kV settings (Figure 8). It is clear that 10kV preferentially excites the phosphorous (and other elements with fluorescence in the lower energy region such as Pd-L lines). By solving for P% in the 10kV settings, this information can be transferred to the 50kV settings to calculate the remaining parameters such as NiP thickness, Pd thickness, TiW thickness and TiW composition. This process is iteratively repeated until the mq reaches a minimum (note that in this case the calculation of mq involves summation over all the channels used in both spectra).

3. Conclusion

In summary it has been demonstrated that fundamental parameter micro-XRF is a valuable tool to tackle various measurement applications in the electronics industry. Its non-destructive nature, fast measuring time, and robust setup are especially useful. While it is today unclear about the ultimate limitation of this technique, new and existing industry partners are constantly joining the push for greater instrument capability, in terms of both hardware and software. It is the author’s belief that XRF will continue to evolve and remain highly relevant in many fields including electronics in the near future.
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References