X-Ray Fluorescence in Thin film Solar Cell Manufacturing:

Improving cell efficiency and production yield

Production quality of thin film solar cells can be accurately and precisely monitored using the X-Ray Fluorescence (XRF) methodology. Specifically tailored inline measurement instruments are available that fulfil the robustness requirements in production environment. Clever software features enable simple setup and handling of the measurement instruments whilst ensuring stable measurement and maintaining comparability between them.

The main driver for continued PV growth is that a path to grid parity is now visible as production cost per watt continues to decline. The use of larger and more efficient production facilities is creating the economies of scale required for its competitiveness other sources of energy [4]. Whilst in 2007 the worldwide Silicon (Si)-based Solar Cell production dominated the global PV-market at approx. 94 percent market share [5], its market share is expected to decline to 80 percent in 2010 [4]

Thin film technologies mainly use compound semiconductors, namely CIS, CIGS and CdTe (Cadmium Telluride). CIS and CIGS consist of copper indium selenide and copper gallium selenide providing polycrystalline thin films. CIGS solar cells are not as efficient as crystalline silicon solar cells, but they are expected to be substantially cheaper. CIGS efficiency is by far the highest compared with those achieved by other thin film technologies such as CdTe or amorphous silicon (a-Si). These technologies are being commercialised rapidly and production facilities are ramped up.

About 10 different methods for thin film manufacturing

Worldwide over 30 companies are known to actively develop thin film CIGS technologies, using about 10 different deposition methods for growing the thin film absorber layers. The most common CIGS products are built on glass, stainless steel or plastic foil substrates.

Thin film cells are manufactured using either co-evaporation or the two-stage process such as deposition of the precursors by sputtering followed by selenization. Their back contact material is sputtered Mo and usually ZnO is used as the front contact material, as well deposited either by sputtering or chemical vapour deposition [5].

Thin film PV system: A fairly complex stack of layers

Finally a typical thin film PV system ends up as a fairly complex stack of layers. The following system may serve as an example (top to bottom): TCO(InSnO or AlZnO) / CdS / CIGS/ Mo / Glass. CdTe technology today already achieves 10.7 percent efficiency in mass production.

Today's CIGS efficiency is quite similar but believed to carry the potential to get close to 20 percent in the future [4]. This is commercially interesting, as increasing PV cell efficiency is a main lever for further cost reduction [6].

According to [5] some of the major critical issues for significant progress in achieving low cost and reliable CdTe / CIS / CIGS products are:

- higher module efficiencies
- thinner absorber layers of less than 1 µm
- absorber film stoichiometry and uniformity over large areas.

Innovations leader in layer thickness analysis

The german company **Helmut Fischer GmbH Institut für Elektronik und Messtechnik** is well known for its highly precise measuring instruments for coating thickness measurement, material analysis, material testing and micro hardness.The company was founded more than 55 years ago and considers itself as innovations leader in the field of layer thickness analysis.

More than 10.000 x-ray spectrometers have been sold to date. Helmut Fischer is present in almost all countries with own subsidiaries and distribution partners. R&D and production are based at the headquarters in Sindelfingen near Stuttgart, Germany.

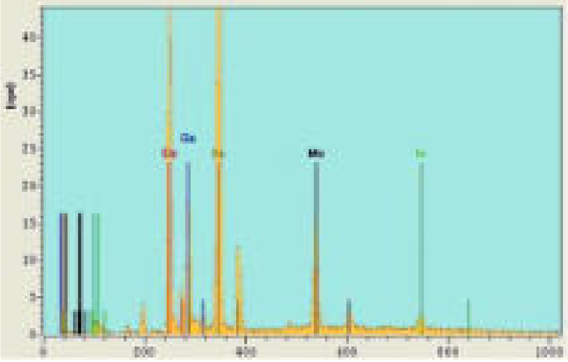


Fig. 1

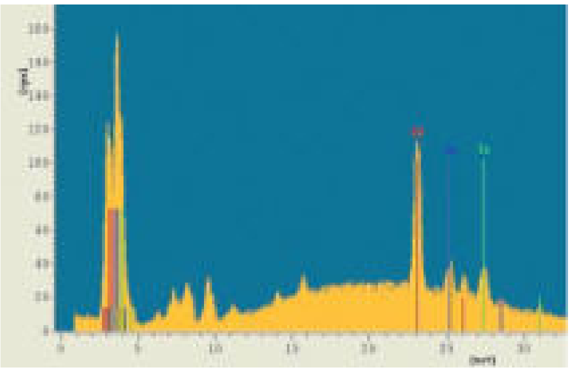


Fig. 2

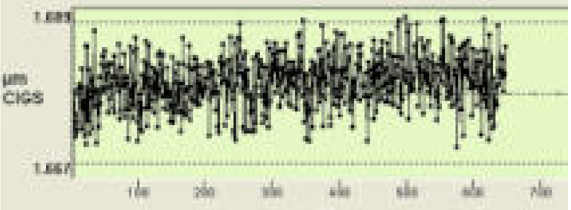


Fig. 3

XRF spectrum of typical CIGS/Mo/Glass sample (above) and of typical CdTe/Glass sample. The third figure shows measurement of CIGS thickness in 8-day long-term trial with FISCHERSCOPE® X-RAY 5000

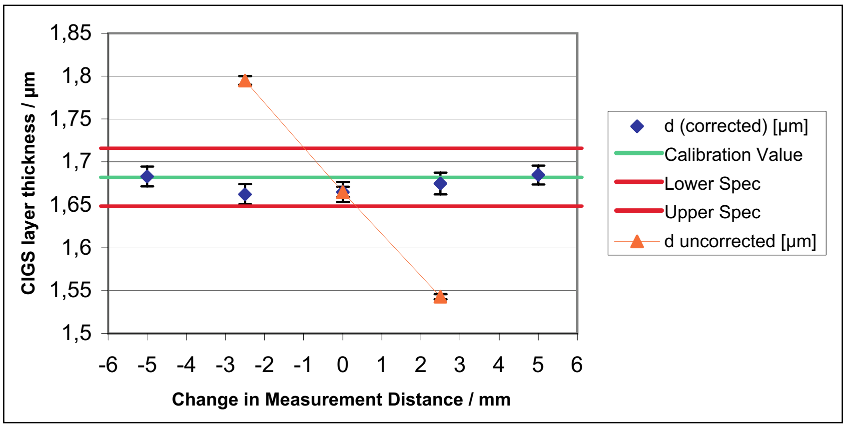
X-Ray-Fluorescence (XRF) Measurement

This is where measurement technology comes into play: Uniformity and stoichiometry can be measured non-destructively with mature technology thus helping to improve cell efficiency and production yield. Layer thicknesses and composition of CIS / CIGS / CdTe thin film systems can be accurately and precisely measured using the XRF technique[1]. *(Fig. 1, 2)*

According to the typical requirements of manufacturers running industrial processes two different types of equipment, each supporting specific measurement strategies are being supplied by XRF manufacturers and widely used.

Table top and inline instruments often used in parallel

Table top or laboratory instruments with moveable, programmable stages such as the Fischerscope XDV-SD are used for off-line measurement and in-depth qualification of discrete samples. Those instruments allow for large area automatic surface-scanning in two dimensions. Such samples often originate from process optimisation in the development phase or in machine start-up.



Change of CIGS thickness reading vs. change in measurement distance. The blue data points are with distance compensation, the red points without
Fig. 4

Continuous inline measurement during the production process (sometimes even at various stages) can be carried out using single or multiple XRF measuring heads such as FISCHERSCOPE® X-RAY 5000. They are mounted via cooled standard interfaces (eg. ISO250F flange) to the vacuum chamber system and can be used in production machinery at zones where substrate temperatures up to 500°C are encountered.

Stability and Precision of Measurement

As PV manufacturers often use table-top and inline instruments in parallel, measurements should be fully comparable between them. Thus a key requirement is the long-term stability of the measurement. *Fig. 3* displays results of a long-term trial, measuring the CIGS layer in a sample on glass substrate. No unwanted drift was observed and the observed scattering is purely random. [1] Each data point represents a mean value of 10 single readings. During the 8-day long-term trial with FISCHERSCOPE® X-RAY 5000 no re-baselining or calibration had to be performed.

Following the rule of thumb that the instrument must not scatter more than 1/40 of the process tolerance window [3], the active material layer thickness and its composition sometimes has to be measured with a precision of as little as 1 percent relative Standard Deviation (COV%). *Tab.1* represents the statistics of 6500 single readings for CIGS film thickness (d1), its percent-composition for Cu, In, Ga, Se and the Mo back contact thickness (Mo2).

One can see that all COV percent-results are easily passing the above requirement, even the Indium percentage which is known to be the most difficult to measure.

Distance compensated measurement

XRF measurement results are known to vary with fluctuating measurement distance. Inline measurement heads are mounted in a fixed position on the machine, but movement or bulging of the product does occur in the production process. This – at first sight – seems to be in contradiction to the precision requirements of the measurement.

Solutions to compensate for this potentially falsifying effect are either

- the use of a separate distance sensor (at additional cost) or a
- more intelligent use of the information already contained in the measured XRF-spectra.

The latter method was recently implemented in Fischer's WinFTM Software and enables reliable distance compensation without any moving parts thus making secondary sensors in many cases completely superfluous. *Fig. 4*. With this software feature activated, the measurement distance can be altered by up to +/- 6mm without affecting the measurement readings significantly.

	d1 (µm)	**Cu 1 (%)**	**In 1 (%)**	**Ga 1 (%)**	**Se 1 (%)**	**Mo 2 (µm)**
Mean value	1.680	23.20	19.08	9.183	48.54	0.491
Standard Dev.	0.012	0.048	0.167	0.066	0.155	0.004
C.O.V.[%]	0.70	0.21	0.87	0.72	0.32	0.77
Min. Reading	1.635	23.00	18.43	8.938	48.04	0.477
Max. Reading	1.723	23.38	19.65	9.431	49.23	0.506
No of Readings	6500	6500	6500	6500	6500	6500

Tab. 1

Fast and simple calibration procedure

The measurement tasks in question are usually quite well defined in terms of (1) the elements contained in the samples and (2) a narrow bandwidth of their composition – only fluctuating by a few percent. The WinFTM software now provides – in addition to the full Fundamental Parameter method[2] – a much faster, parametrized approach as an option. This method does not impair the measurement accuracy for samples produced within the process window.

The reference point for this fast computing approximation is the ensemble of the calibration standards. Very few standards are sufficient, which may be of significant advantage. Of course, the WinFTM software utilizes its "physical background" in order to compute the characteristic values of this linear model from the fundamental parameters. Thus, in extreme cases one single calibration spectrum is sufficient for backing the analysis. Benefits are significant time savings in installing and setting up the measurement equipment thus avoiding machine downtime.

XRF provides precise monitoring of production Quality

Production quality of thin film solar cells can be accurately and precisely monitored using the XRF methodology. Specifically tailored inline measurement instruments are available that fulfil the robustness requirements in production environment. Clever software features enable simple setup and handling of the measurement instruments whilst ensuring stable measurement and maintaining comparability between them.

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