

Measurement of Atomic Fractions in Cu(In,Ga)Se₂ Films by Auger Electron Spectroscopy (AES) and Energy Dispersive Electron Probe Microanalysis (ED-EPMA)

Vasile-Dan Hodoroaba¹, Thomas Wirth¹, Ralf Terborg², Kyung Joong Kim³ and Wolfgang E. S. Unger¹

¹ BAM Federal Institute for Materials Research and Testing, Division 6.8 Surface Analysis and Interfacial Chemistry, Berlin 12200, Germany.

² Bruker Nano GmbH, Am Studio 2D, 12489 Berlin, Germany.

³ Korea Research Institute of Standards and Science, Division of Industrial Metrology, Daejeon 305-340, Republic of Korea.

A pilot study (PS) has been performed under the Consultative Committee for Amount of Substance (CCQM) / Surface Analysis Working Group (SAWG) with the objective to compare the atomic fractions of Cu, In, Ga and Se in CIGS alloy films. Four polycrystalline CIGS films with different atomic fractions were fabricated by variation of the relative atomic fraction of Ga on 100 mm x 100 mm soda-lime glass (SLG) substrates. Similar to real solar cells the atomic fractions of the four elements (Cu, In, Ga, Se) are not homogeneous with depth. For the analysis of the CIGS layers of about 2 μm thickness depth profiling with surface analysis techniques such as XPS, AES and SIMS was recommended. A CIGS alloy reference sample with atomic fractions certified by isotope dilution ICP-MS at KRISS has been also put at disposal by the coordinator of the comparison. The certified values were close to the atomic fractions of the samples to be analyzed. Hence, the atomic fractions of Cu, In, Ga and Se in the CIGS films could be determined by the relative sensitivity factors (RSF) derived from the reference CIGS film. The total ion intensities of the constituent elements were obtained by the total number counting (TNC) method [1].

In this paper the results obtained in our lab by AES (Auger electron spectroscopy) depth profiling, see Fig. 1a, are described in conjunction with the results of ED-EPMA (Electron Probe Microanalysis with Energy Dispersive X-Ray Spectroscopy, or simply SEM-EDX).

It was demonstrated recently that accurate quantitative EDX analysis of atomic fractions of metallic alloy elements in homogeneous thin layers is feasible [2]. For samples like those in this study where the elemental concentration is not homogeneous through the entire depth of the layer, EDX line scan analysis over the cross-sectioned samples might be an option. However, the poor spatial resolution of EDX relative to the layer thickness makes the technique not competitive with the conventional surface sensitive methods operating in depth profiling mode [3]. By means of Monte-Carlo simulation programs, e. g. [4], it can be demonstrated that for the elemental concentration and the thickness of the CIGS layers like those in the present study the interaction volume at 30 kV electron beam voltage still “remains” mainly in the 2 μm thick layer. Hence, the emitted X-ray spectrum (see Fig. 1b) is not significantly influenced by the SLG substrate and - if quantified against a reference CIGS layer of rather close elemental composition - can be treated as supplying valuable integral information on the whole inhomogeneous CIGS layer.

The results obtained by the two different techniques, AES depth profiling with TNC method, and EDX point analysis quantified both against the supplied reference CIGS layer are shown in Table 1 for two

CIGS samples of different concentrations, T1 and T4. Note the excellent agreement between the determined atomic fractions characterizing the integral layer depth which leads to the conclusion that quick nondestructive EDX analysis with an appropriate reference material can supply very accurate results. Also the standardless EDX analysis supplies acceptable results. However, in-depth gradients of elemental concentrations can be measured only by more costly surface sensitive techniques operated in the depth profiling mode such as AES.

The complete PS report including also results of other analytical techniques is still in progress.

References:

- [1] J S Jang, H H Hwang *et al.*, *Metrologia* **49** (2012), p. 522.
- [2] V-D Hodoroba, K J Kim *et al.*, *Surf. Interface Anal.* **44** (2012), p. 1459.
- [3] D Abou-Ras, R Caballero *et al.*, *Microsc. Microanal.* **17** (2011), p. 728.
- [4] CASINO software package for Monte Carlo simulation of electron trajectories in solids, <http://www.gel.usherbrooke.ca/casino/What.html>

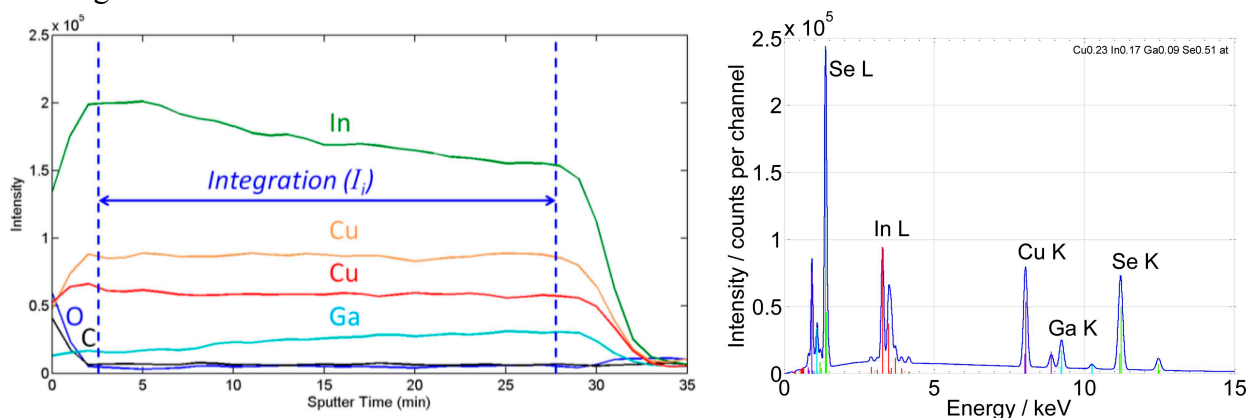


Figure 1. An AES depth profile of a CIGS test specimen with marked range of steady state conditions for determination of integral intensities by the TNC method (left) and a corresponding 30 kV EDX spectrum with the characteristic X-ray lines (Cu K, In L, Ga K and Se K) considered for quantification.

	Cu		In		Ga		Se	
	AES	EDX	AES	EDX	AES	EDX	AES	EDX
T1	23.9 ±0.1	23.6 ±0.1	20.1 ±0.3	20.2 ±0.1	6.0 ±0.1	5.6 ±0.1	49.9 ±0.4	50.6 ±0.2
T4	24.7 ±0.2	24.8 ±0.1	17.9 ±0.2	18.0 ±0.1	7.5 ±0.2	7.1 ±0.1	50.0 ±0.3	50.1 ±0.3

Figure 2. AES and EDX quantification results for two (of four) test CIGS films, T1 and T4, expressed in at.-% and having associated the standard deviation of the mean of *N* repeated measurements (*N*=4 for AES and *N*=7 for EDX).