Comprehensive comparison of various techniques for the analysis of elemental distributions in thin films – additional techniques

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Abstract

In a recent publication (D. Abou-Ras et al., Microscopy & Microanalysis **17** (2011) 728-751), various techniques for the analysis of elemental distributions in thin films were compared, using the example of a 2 µm thick $Cu(In,Ga)Se_2$ thin film, applied as absorber material in a solar cell. The authors of this work found that similar relative Ga distributions perpendicular to the substrate across the $Cu(In,Ga)Se_2$ thin film were determined by 18 different techniques. Their spatial and depth resolutions, their measuring speeds, their availabilities, as well as their detection limits were discussed. The present work adds two further techniques to this comparison: laser-induced breakdown spectroscopy and grazing-incidence X-ray fluorescence analysis.

Introduction

In a recent publication, Abou-Ras et al. (2011), performed elemental distribution analyses on 2 µm thick $Cu(In,Ga)Se_2$ thin films by use of wavelength-dispersive and energy-dispersive X-ray spectrometry (EDX) in a scanning electron microscope, EDX in a transmission electron microscope, X-ray photoelectron, angle-dependent soft X-ray emission, secondary ion-mass (SIMS), time-of-flight SIMS, sputtered neutral mass, glow-discharge optical emission and glow-discharge mass, Auger electron, and Rutherford backscattering spectrometry, by use of scanning Auger electron microscopy, Raman depth profiling and Raman mapping, as well as by use of elastic recoil detection analysis, grazing-incidence X-ray and electron backscatter diffraction, with the main objective to determine the Ga gradient perpendicular to the substrate. The relative Ga distributions determined by these techniques across $Cu(In,Ga)Se_2$

thin films (fabricated in the same identical deposition run) were similar. The more than 20 techniques were compared with respect to their spatial and lateral resolutions, their measuring speeds, their availabilities and their detection limits.

The present work adds two further measurement techniques to the comparison study. The analyzed specimens were the same identical $Cu(In,Ga)Se_2$/Mo/glass stacks, which were already used for the previous study. The corresponding details on materials fabrication and specimen preparation are given in [Abou-Ras et al, 2011].

Additional methods and results

Laser- induced breakdown spectroscopy

This technique is based on the irradiation of a specimen by a laser at a fixed wavelength and intensity, measuring the corresponding plasma emission spectrally resolved. Since this laser irradiation is accompanied by ablation of the specimen material, a depth profile can be recorded (St-Onge and Sabsabi, 2000; Kim et al., 2013). The laser-induced breakdown spectroscopy (LIBS) system as well as the experimental procedure used in the present study were described in previous reports (In et al., 2013a; In et al., 2013b; Kim et al., 2013).

The LIBS system is equipped with an Nd-YAG laser (532 nm, 5 ns, top-hat profile) and a six-channel charge-coupled device (CCD) spectrometer. The CCD gate delay and gate width were 0.2 μs and 1 ms. The laser energy and spot size were set to 1.18 mJ and 150 μm, at which the laser flux became 6.68 J/cm^2. Ar gas was supplied obliquely to the sample surface (about 45°) using a 1/4 inch tube at the rate of 20 l/min. The depth of the ablation crater at increasing shot number was measured using a scanning confocal microscope (μSurf, NanoFocus Inc.), and the depth resolution was about 140 nm. The ablation depth increased almost linearly with respect to increasing shot number (Kim et al., 2013). Each of the total 30 measurement points was irradiated until the Mo signal from the substrate appeared.

From LIB spectra acquired at each laser shot, the intensity ratios of In/Cu, Ga/In, and Se/In were evaluated using the lines at 325.6, 325.9 (In), 324.6, 327.4 (Cu), 403.3, 417.2 (Ga), 410.2 (In), 196.1, 204.0, 206.3 (Se), and 303.9 nm (In). The ablation mass of CIGS per pulse was assumed to be proportional to the summation intensity of Cu lines at 324.6 and 327.4 nm. The intensity ratios of measured LIB spectra were calibrated by the concentration ratios of reference CIGS samples. The integral composition of each reference sample was determined by first dissolving the CIGS film in nitric acid solution and subsequently measuring elemental concentration by inductively coupled plasma optical emission spectrometry (ICP-OES, 720-ES, Varian, Inc.) for In, Ga, and Se, and by atomic absorption spectroscopy (AAS, iCE 3000, Thermo Fisher Scientific, Inc.) for Cu. The quantification procedure of the LIBS intensity distributions was described by In et al. (2013a). Fig. 1 shows the resulting elemental distribution profiles for the matrix elements Cu, In, Ga, and Se from the depth profiling in the investigated $Cu(In,Ga)Se_2$ thin film. For each element, the average values and standard deviations of the predicted concentration values of the 30 measurement points were calculated for each shot number (or ablation depth). However, we found that the systematic error related, e.g., to the quantification of the LIBS data by use of the ICP-OES and AAS measurements are

much larger than the standard deviations, estimated to about ±2 at.%. These errors are given in the viewgraph of Fig. 1.
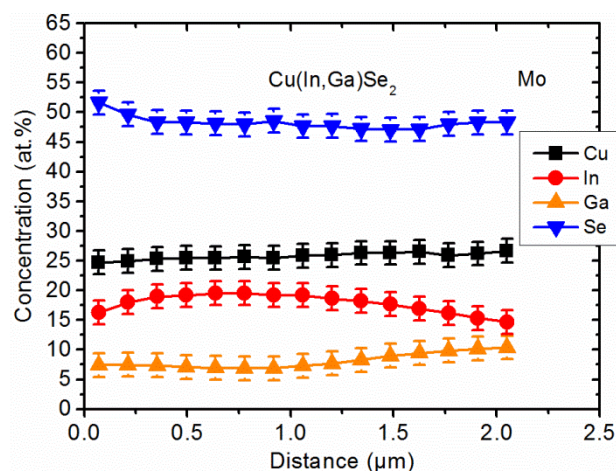

Fig. 1. Depth profiles of Cu, In, Ga, and Se, as obtained by LIBS, including the measurement errors..

Reference-free grazing-incidence X-ray fluorescence

This analysis technique provides a non-destructive access to compositional depth profiles in thin films (Streeck et al., 2010; Streeck et al., 2013). Applying well-determined synchrotron radiation and calibrated instrumentation allows for a physically traceable quantification based on the knowledge of all relevant experimental and instrumental parameters as well as of the atomic fundamental parameters involved (Hönicke et al. 2014), such as photoionization cross-sections, transition probabilities, and fluorescence yields. With this approach, no additional calibration samples or reference materials are needed for instrumental precalibration (Beckhoff, 2008). Varying the angle of incidence of the exciting radiation the matrix-dependent and energy-dependent information depth of the measured characteristic fluorescence lines can be equally tuned, and differential information about the compositional depth profiles obtained.

For $Cu(In,Ga)Se_2$ thin films with thicknesses of only a few micrometers, best detection sensitivities for the elemental distribution perpendicular to the substrate are reached at very shallow angles of incidence of below about 3° when using an excitation energy of about 11 keV (Streeck et al., 2010). Reference-free grazing-incidence X-ray fluorescence (GIXRF) measurements were performed at the four-crystal monochromator (FCM) beamline in the PTB laboratory (Beckhoff et al., 2009) at the electron storage ring BESSY II. The angle of incidence was varied from 0 to 5°. A photon energy of the incident radiation of 11 keV was chosen to excite the Cu-K, Ga-K, and In-L fluorescence lines which all were used for the GIXRF quantification. The incidence photon flux was determined by means of a calibrated photodiode (Beckhoff et al., 2009). The synchrotron beam profile exhibits an extension of approximately 300 µm x 200 µm. Owing to the rotation of the sample in the incoming beam, one of the footprint dimensions on the excited sample surface varies up to a few mm. For the detection of fluorescence radiation, an energy-dispersive silicon drift-detector with known detection efficiency and response behavior was employed (Kumrey & Ulm, 2001; Scholze & Beckhoff, 2009).

All spectra were deconvoluted by means of both, detector response functions and physically modeled background contributions originating from Bremsstrahlung and resonant Raman scattering (Müller et al., 2006, Hönicke et al., 2014). In Fig. 2, the normalized fluorescence intensities are shown, taking into account the incoming photon flux, the effective solid angle of detection, and the efficiency of the energy-dispersive detector. At shallow incidence angles, the fluorescence intensities of the surface-near region dominate, whereas with increasing incidence angle, regions deeper within the Cu(In,Ga)Se$_2$ layer significantly contribute to the fluorescence intensities detected.
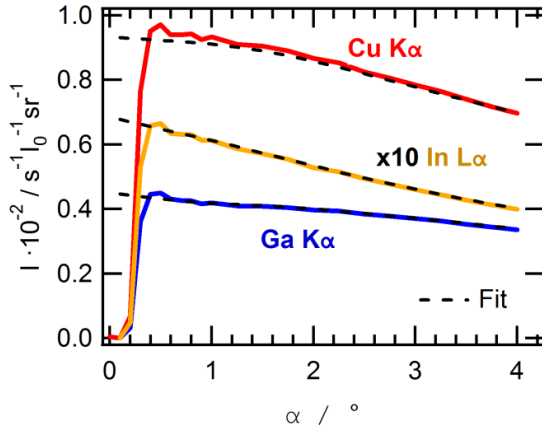

Fig. 2: Grazing-incidence X-ray fluorescence intensities for Cu-Kα, Ga-Kα, and In-Lα in dependence of the angle of incidence α.

For the determination of an elemental concentration distribution (Streeck et al., 2013) from the GIXRF data shown in Fig. 2, a least square method using the Levenberg-Marquardt algorithm (Marquardt, 1963) was employed. The elemental distributions were reconstructed by using a simple model gradient, which approximated the Ga and In gradients as double-linear ones (found fo the Ga/In elemental distributions in the previous report, Abou-Ras et al., 2011). The corresponding Cu, In, Ga and Se elemental distribution profiles are shown in Fig. 3.

The Cu and Se concentrations were assumed to be constant throughout the Cu(In,Ga)Se$_2$ thin film. According to the double-linear model, the Ga concentration is allowed to have a minimum or a maximum between the surface and the bottom of the film. For the calculation of the angular dependent fluorescence intensities, the film is divided into 25 sublayers with increasing thicknesses for increasing depth. This accounts for the decreasing sensitivity of the method with increasing distance from the film surface.

The quantification of the elemental distribution adopting the double linear behavior of the In and Ga concentration is implemented by a three-step fit, which was described elsewhere (Streeck et al., 2013). These steps transfer the angular-dependent increase of the information depth to the fitting procedure. For the highest angle of incidence, the average composition is determined, which provides the Cu and Se concentrations. Measurements at shallow angles determine the Ga and In compositions at the surface. This stepwise approach enables a numerically stable fit for the total error square χ^2 of the calculated and measured intensities. The total, relative uncertainties range from 0.06 to 0.15, which is related to the uncertainties of the atomic fundamental, the experimental, and the instrumental parameters, with main

contributions from atomic fundamental parameters, such as fluorescence yields (ranging from 0.03 to 0.1), photoionization cross sections, and transition probabilities (Beckhoff et al., 2007; Zschornack, 2007), as well as from the uncertainties of the least-square fit. For the elemental concentrations, total errors sum up to about 1-2 at.%, where we take the upper limit for error bars in the viewgraph of Fig. 3.
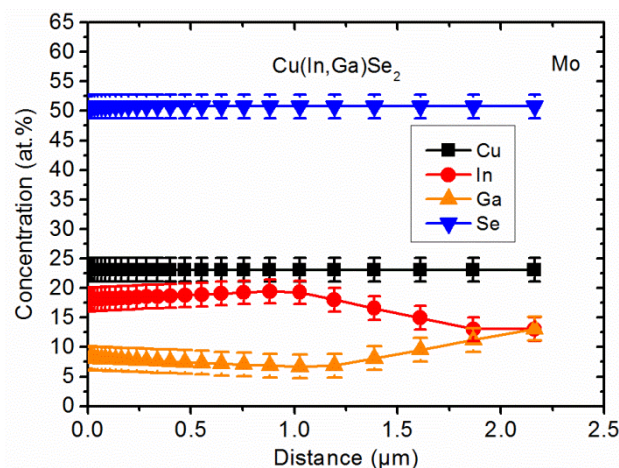

Fig. 3: Elemental distribution profiles resulting from the fit of GIXRF data given in Fig. 2.

It is clear that for a precise GIXRF analysis of depth profiles deviating from a double linear shape, an extended depth-distribution model with a larger number of free parameters is needed, including more robust fitting strategies. In order to be able to increase the number of parameters describing the depth profiles, further information concerning the measurement and adjustment procedure may be needed. For example, fluorescence line intensities of additional shells of the elements and variation of the incidence radiation energy may have to be included. An increase of the number of parameters can reduce or eliminate the necessity of any previous knowledge of the elements and of the phases present in the sample. Thus, if the accuracies of the measurements and of the numerical calculations are further increased, quantitative characterization of samples with completely unknown composition and element distributions may become possible with the GIXRF method (Streeck et al., 2013).

Discussion

The Ga distributions obtained by LIBS and GIXRF, given in Figs. 1 and 3, are in good agreement with the ones determined by the 18 different techniques in the recent work by Abou-Ras et al. (2011). For both techniques, no specimen preparation is necessary. LIBS and GIXRF feature poor spatial resolutions of 10^5-10^6 nm and good depth resolutions of 10-140 nm.

The great advantage of LIBS is its measurement speed. In the present work, the acquisition of the LIB spectra took only about 2 min, which makes the technique very attractive for industrial application. However, it is a destructive method (on the measurement spot) and it needs calibration of the matrix composition by, e.g., ICP-OES and AAS.

On the other hand, GIXRF is a reference-free, non-destructive method giving decent elemental distributions across a thin film. As a disadvantage, the parameters for the fit model

limit the accuracy of the technique. Also, the technical requirements for the measurement setup and the quantitative evaluation of the analysis are extensive.

Table 2 of the previous report, Abou-Ras et al., 2011, was extended by the corresponding entries for LIBS and GIXRF. Now, Table 1 of the present work gives an overview of 20 techniques for elemental distribution analysis in thin films, highlighting their advantages and disadvantages.

Table 1: Techniques applied for the analysis of elemental distributions in thin films and their characteristics. DP: depth profiling (destructive), Surf: analysis from the surface (non-destructive), CS: analysis on cross-section. Note that all given values correspond to the measurement conditions used for the present work; they may differ substantially for other analysis parameters applied. The lateral resolutions refer to the minimum areas of acquisition for the DP and Surf techniques, and for the CS analyses to the minimum distance between to features still to be distinguished. The availability is divided into techniques frequently (good), in fewer numbers (medium), and rarely (rare) present in research labs. Accuracy of quantitative results refers to whether a technique needs calibration by reference samples or reference measurements (standard), which may be *difficult* in some cases (i.e., since the fitting of the model to the experimental data requires a large number of parameters), or whether a technique is entirely standard-less. In any case, the accuracy of the determined atomic concentration of a matrix element within an elemental distribution profile (in contrast to an integral compositional measurement) is hardly smaller than 1 at.%.

Technique	Analysis mode	Lateral resolution (nm)	Depth resolution (nm)	Duration (min)	Availa-bility	Detec-tion limits (at.%)	Quantifi-cation of results
SIMS	DP	5×10^3	4	45	good	10^{-7}-10^{-3}	standard
SNMS	DP	10^6	1	120	medium	0.05	standard
GD-OES	DP	10^6	3-100	5	good	10^{-5}-10^{-3}	standard
GD-MS	DP	10^7	10	10	medium	10^{-7}-10^{-5}	standard
AES	DP	10^5	10	45	good	0.3	standard
XPS	DP	10^5	1-10	120	good	0.1	standard-free
Raman depth-profiling	DP	10^5	100	50	medium	1	standard
LIBS	DP	10^5	140	2	good	1	standard
RBS	Surf	10^7	10	10	rare	1	standard-free
ERDA	Surf	10^7	10	30	rare	10^{-4}	standard-free
GIXRD	Surf	10^6	100	420	good	1	difficult
Reference-free GIXRF	Surf	10^6	10-100	30	rare	10^{-4}-10^{-1}	standard-free

AXES	Surf	10^5	10-80	420	rare	1	standard
Ellipsometry	Surf	10^6	1	30	medium	0.2-2	difficult
TEM-EDX	CS	5	specimen thickness	30	good-medium	0.5	standard
SEM-EDX	CS	150	few 100	20	good	0.5	standard
SEM-WDX	CS	150	few 100	60	good	3	standard
Scanning Auger	CS	10	1	137	good	3	standard
TOF-SIMS	CS	100	1	2	medium	10^{-6}	standard
Raman mapping	CS	400	100	120	medium	1	standard

Conclusions

The present contribution adds two further techniques to the comparison for the analysis of elemental distributions in thin films. We note that LIBS represents a fast and reliable method for depth profiling, whereas reference-free GIXRF can be applied non-destructively on thin films using monochromatized synchrotron radiation and calibrated instrumentation, in particular for the qualification and characterization of reference materials or calibration samples. Nevertheless, also these techniques alone can not be identified as suitable for an unambiguous and quantitative elemental distribution analysis of a thin film with unknown compositional in-depth distribution.

Acknowledgements

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