Thin Solid Films 579 (2015) 89–94

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Rapid quantitative analysis of elemental composition and depth profile of $Cu(In,Ga)Se_2$ thin solar cell film using laser-induced breakdown spectroscopy

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ARTICLE INFO

Article history:
Received 29 July 2014
Received in revised form 12 February 2015
Accepted 23 February 2015
Available online 1 March 2015

Keywords:
Copper Indium Gallium Selenide
Elemental analysis
Depth profile
Laser-induced breakdown spectroscopy
Thin film solar cell

ABSTRACT

Laser-induced breakdown spectroscopy (LIBS) is reported as a method for rapid quantitative analysis of elemental composition and depth profile of $Cu(In,Ga)Se_2$ (CIGS) thin film. A calibration model considering compositional grading over depth was developed and verified with test samples. The results from eight test samples showed that the average concentration of Cu, In, Ga and Se could be predicted with a root mean square error of below 1% and a relative standard deviation of also below 1%. The depth profile of each constituent element of CIGS predicted by LIBS was close to those by Auger electron spectroscopy and secondary ion mass spectrometry. The average ablation depth per pulse during depth profiling was about 100 nm.

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1. Introduction

The compound semiconductor $Cu(In,Ga)Se_2$ (CIGS) is a promising material for thin film solar cell and CIGS solar cell has shown a steady improvement in efficiency with the highest value among thin film type solar cells. To achieve high efficiency, the composition of Cu, In, Ga and Se constituting the CIGS layer is required to be precisely controlled [1]. Thus, the need for rapid quantitative analysis of CIGS thin film is increasing in the development and production sites of CIGS thin film solar cells.

For rapid quantitative analysis of CIGS thin film, X-ray fluorescence (XRF) is one of the available technologies under use [2]. Whereas depthwise elemental grading is known to be important for high efficiency CIGS solar cell [3], XRF can provide average composition only with a limitation in detecting light trace elements such as Na. Recently, glow discharge optical emission spectroscopy (GD-OES) was introduced as an alternative fast quantitative analysis method (a few tens of second) [4]. However, GD-OES measurement requires a relatively large sample size (a few cm^2) for vacuum holding, which is a disadvantage for repetitive measurement for product assessment due to increased loss of cell area.

Laser-induced breakdown spectroscopy (LIBS) is a promising technique for rapid quantitative analysis of CIGS thin film, especially at the production sites, because it does not need sample preparation or vacuum. Also, LIBS measurement can be done with a small test area (within a spot diameter of about 0.1 mm) and is much faster (a few seconds) than other techniques. Multiple measurements along the depth or surface of a CIGS thin film can be easily done with the use of appropriate optics or stages.

Previously, we reported the optimal spectral lines of Cu, In, Ga for LIBS elemental analysis of CIGS thin films [5,6] and demonstrated that LIBS analysis was highly reproducible [1]. In this work, the LIBS calibration model for quantitative analysis of all four constituent elements including Se is introduced. Depthwise elemental grading over CIGS thickness is also considered in the model. It is shown that the composition of CIGS thin film can be predicted with high precision and accuracy using LIBS. The depth profiling results were compared with those by Auger electron spectroscopy (AES) and secondary ion mass spectrometry (SIMS).

2. Experimental setup

2.1. CIGS samples

Six CIGS thin film samples for calibration (C1–C6) and nine test samples for validation were fabricated on Mo-coated soda-lime glass substrates by co-evaporation method. Among the nine test samples, eight samples (T1–T8) were used for average concentration analysis and one sample (T9) was used for depth profiling. The reference composition of these samples was measured by inductively coupled plasma optical emission spectrometry (ICP-OES; Varian, 720-ES) for

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http://dx.doi.org/10.1016/j.tsf.2015.02.061
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Table 1
Composition of calibration (C) and test (T) CIGS samples.

No.	Cu (at.%)	In (at.%)	Ga (at.%)	Se (at.%)	Thickness (μm)
C1	25.75	23.34	3.06	47.85	1.72
C2	25.31	20.91	4.82	48.95	1.89
C3	25.50	19.40	7.41	47.69	2.18
C4	25.77	17.27	9.14	47.81	1.89
C5	25.43	15.18	10.91	48.49	1.36
C6	26.32	13.12	12.97	47.59	1.34
T1	25.62	22.69	3.78	47.91	1.70
T2	25.89	18.00	8.35	47.76	1.45
T3	25.59	16.82	8.16	49.43	2.02
T4	25.48	17.03	9.53	47.96	1.46
T5	25.18	14.72	11.17	48.93	1.54
T6	25.24	13.69	12.85	48.22	1.34
T7	24.19	19.72	8.38	47.71	2.17
T8	24.67	17.12	8.16	50.02	2.11
T9	25.91	18.16	8.72	47.21	2.14

Table 2
Spectral lines used for the calibration of LIBS signal intensity ratios.

	Element	Spectral lines (nm)
In/Cu	In	325.6, 325.9
	Cu	324.6, 327.4
Ga/In	Ga	403.3, 417.2
	In	410.2
Se/In	Se	196.1, 204.0, 206.3
	In	303.9

In, Ga, and Se and atomic absorption spectroscopy (AAS; Thermo Fisher Scientific, iCE 3000) for Cu and the results are summarized in Table 1. The thicknesses of the CIGS thin films were measured from the scanning electron microscope (Hitachi, S-4800, 15 kV) images of the cross-section as shown in Fig. 1. In and Ga concentrations of these samples were varied over a wide range, whereas Cu and Se concentrations were changed only slightly.

For depth profile analysis, the aforementioned test sample T9 (A) and a commercial CIGS solar cell (B) fabricated on stainless steel foil substrate by co-evaporation process were utilized. For the commercial sample, the transparent conductive layer and buffer layer were removed by dipping in a dilute hydrochloric acid solution for 2 min prior to the analysis. The thicknesses of CIGS layer of sample A and sample B were about 2.1 and 1.8 μm, respectively. The depth profiling results by LIBS were compared with those by AES (PerkinElmer, SAM4300, electron beam voltage 15 kV, ion gun voltage 3 kV) and SIMS (AMETEK, CAMECA IMS 7f, Cs+, acceleration voltage 5 kV).

2.2. Experimental conditions

The LIBS system used in this study was the same as that described in our previous studies [1,5,6], equipped with an Nd:YAG laser (532 nm, 5 ns, top-hat profile) and six channel CCD spectrometer. The CCD gate delay and gate width in experiments were 0.2 μs and 1 ms, respectively. The laser pulse energy and spot diameter were set to 1.63 mJ and 200 μm, respectively, at which the corresponding laser fluence became 5.19 J/cm^2. An impinging Ar jet was supplied to the sample surface (~45° from the surface) using a 1/4 inch tube at the rate of 20 L/min for signal enhancement. LIBS signal was measured at 30 points on each CIGS sample (see the inset in Fig. 1) and each measurement point was irradiated until Mo signal appeared.

3. Calibration model and spectral lines

3.1. Calibration model

The ratio of spectral line intensities rather than absolute intensity was used for the calibration because the intensity ratio between elements remains consistent even when experimental parameters change. First, the LIBS signal intensity ratio of element A to element B at the *i*-th shot on one measurement point of the *j*-th sample is denoted by

$$R_{A/B,i,j} = I_{A,i,j}/I_{B,i,j} \tag{1}$$

where $I_{A,i,j}$ and $I_{B,i,j}$ are the spectral line intensities of A and B, respectively. Then, the concentration ratio between these elements is represented by a polynomial function of the measured LIBS signal intensity ratio as

$$C_{A/B,i,j} = \sum_{k=1}^{Q} a_k \left(R_{A/B,i,j}\right)^k \tag{2}$$

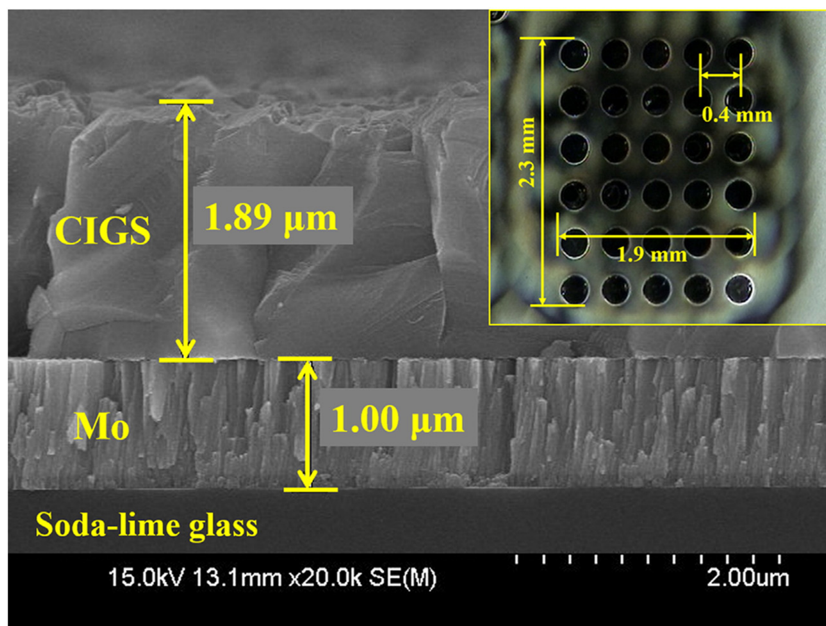

Fig. 1. Cross-sectional image of the CIGS sample (C2). The inset shows an optical micrograph of the CIGS thin film after LIBS measurement.

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