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Effects of spot size variation on the laser induced breakdown spectroscopy analysis of Cu(In,Ga)Se_2 solar cell

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ABSTRACT

The effects of spot size variation on the results of laser induced breakdown spectroscopy (LIBS) analysis of Cu(In,Ga)Se_2 (CIGS) thin film solar cell using a scanning laser beam (λ = 532 nm, τ = 5 ns, top-hat spatial profile) are reported. The spot diameter of laser beam was reduced from 150 μm to 35 μm, below the laser P2 scribing pattern width, at the fixed laser fluence of about 4.5 J/cm^2 and overlap ratio of 79%. The results showed that the measured LIBS signal intensity ratio rather than intensity could be nearly independent of laser spot diameter if the spectral lines are properly selected. It is demonstrated that the concentration ratio of CIGS layer can be predicted within 5% error from the average concentration ratio measured by inductively coupled plasma optical emission spectroscopy by LIBS analysis with a spot diameter of 50 μm.

1. Introduction

Thin film solar cells have several advantages compared with crystalline silicon based solar cells such as low material consumption, simple manufacturing processes, and the possibility to use flexible substrates [1, 2]. It has long been expected that the potential of low cost, high volume manufacturing of thin film solar cells based on streamlined manufacturing technologies such as a roll-to-roll process would enhance cost competitiveness and lead to the replacement of crystalline silicon based solar cells by thin film ones, which however lags significantly behind the expectation. The growth of thin film solar cell market primarily relies on the improvement of cell efficiency which has been showing a gradual but steady increase until recently. Among the different types of thin film solar cells, Cu(In,Ga)Se_2 (CIGS) thin film solar cell recorded the highest cell efficiency (22.6%) up to date and thus is regarded as the most promising one [3]. Another critical issue for the thin film solar cell industry is the development of stable low cost manufacturing technologies. Scribing the back contact layer (P1), absorber layer (P2), and the transparent conducting layer plus absorber layer (P3) are the key processes in thin film solar cell manufacturing. The laser scribing process has been considered one of the most promising techniques that can enhance thin film solar cell productivity by solving the tool wear problem of mechanical tip scribing [4, 5]. Accordingly, laser scribing has been investigated by many researchers and was demonstrated that all laser scribing of the P1, P2, and P3 patterns could be achieved if laser parameters are properly controlled [6, 7]. The width of scribing patterns typically lies in the range of 40–60 μm and the nonactive region between the P1 and P3 patterns (often called by 'dead zone') vary from 100 to 500 μm as shown in Fig. 1 [8].

On the other hand, the efficiency of CIGS thin film solar cell is known to be highly affected by the elemental composition of the constituent elements or their ratios [2, 3]. Therefore, it is necessary to ensure that the products under manufacturing are of proper compositions [9]. In our previous studies, we reported that the composition or composition ratio of the constituent elements of CIGS thin film solar cells could be accurately measured by laser-induced breakdown spectroscopy (LIBS) [10, 11]. With properly selected emission lines and LIBS measurement parameters (λ = 532 nm, spot diameter = 200 μm, fluence = 5.2 J/cm^2, gate delay = 0.2 μs, gate width = 1 ms), an accurate calibration model could be developed and quantitative prediction of CIGS concentration with a root mean square error below 1% could be achieved [10]. Due to the short measurement time of LIBS, on the order of seconds or shorter, it was suggested that LIBS could be effectively applied for the monitoring of fabrication processes or product quality at manufacturing sites. Since a waste of active solar cell area should be minimized during LIBS measurement, it would be most appropriate if the LIBS analysis can be performed over the dead zone, possibly along the scribing pattern or between patterns. For this purpose, LIBS analysis may be carried out either using the plasma generated during laser P2 scribing or using a second laser that independently ablates the CIGS

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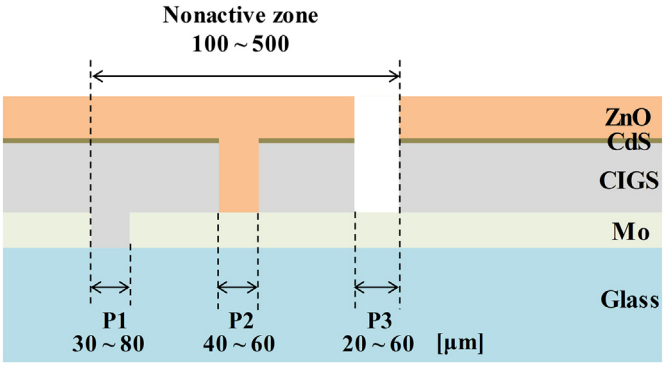

Fig. 1. Schematic diagram of the typical pattern widths of P1, P2 and P3 scribing on CIGS solar cell.

along the scribing pattern or on the dead zone area. The former approach is more advantageous in terms of system and process simplicity but could be difficult to match the scribing and LIBS measurement conditions simultaneously, whereas the latter approach requires more complex system while providing certainty for both processes.

Unlike most LIBS analyses in which a sufficiently large spot diameter is selected to attain strong emission signals, LIBS measurement along a scribing pattern needs to be carried out with a laser spot below the pattern size. In general, a reduction of laser spot size is accompanied by the decrease of emission intensity and plasma life time. Although it has been understood that LIBS signal could be affected by the changes of focusing conditions [12] or sample vibration [13], the effects of laser spot diameter change on LIBS signal has been little investigated in previous studies.

In this study, we report the results for LIBS analysis of CIGS solar cell with laser spot diameters comparable to that of laser scribing pattern. The variations of LIBS signal intensity and intensity ratio of the major elements of CIGS thin film were investigated, while changing the spot diameter from well above (150 μm) to below (35 μm) the scribing pattern. The optimum LIBS measurement conditions at spot sizes close to the scribing pattern width were determined and the concentration ratios at these spot sizes were predicted.

2. Experiments

2.1. CIGS samples

A commercial CIGS solar cell fabricated on stainless steel foil substrate by co-evaporation method was used as the experimental sample (thickness of the CIGS layer = 1.89 μm). Since the LIBS measurement was intended to analyze the composition of CIGS absorber layer only, the layer that converts incident sunlight into electricity, the protective cover layer of the commercial CIGS solar cell was removed and the transparent conduction oxide layer and cadmium sulfide buffer layer were also etched away in dilute hydrochloric acid to expose the CIGS layer. The average composition of the CIGS layer is shown in Table 1 which was measured by inductively coupled plasma optical emission spectrometry (ICP-OES; Varian, 720-ES) for In, Ga, and Se and atomic absorption spectroscopy (AAS; Thermo Fisher Scientific, iCE3000) for Cu.

Also, four reference CIGS thin film samples with varying In and Ga concentrations were fabricated on Mo-coated soda-lime glass substrates by co-evaporation technique and utilized for the generation of a calibration curve. Composition of the four reference samples (R1~R4) measured by ICP-OES and AAS are also shown in Table 1.

Table 1
Composition of the commercial and reference (R) CIGS samples measured by ICP-OES and AAS.

	No	Cu (at.%)	In (at.%)	Ga (at.%)	Se (at.%)	In/Cu
Commercial sample		22.461	14.755	8.859	53.925	0.656916
Reference samples	R1	25.618	22.693	3.776	47.914	0.885829
	R2	25.479	17.029	9.533	47.959	0.668367
	R3	25.244	13.693	12.848	48.215	0.542412
	R4	25.499	19.404	7.411	47.685	0.760993

2.2. LIBS measurement

For LIBS analysis, the sample was ablated by a second harmonic Q-switched Nd:YAG laser (λ = 532 nm, τ = 5 ns, top-hat spatial profile) while being translated along a straight line by utilizing a motorized stage. The Nd:YAG laser was part of a commercial LIBS system (Applied Spectra Inc., RT250EC) and the laser beam is delivered to the sample through a beam expander and an objective lens. The laser spot diameter at sample surface was adjusted by varying the distance between the two lenses of the beam expander, and the actual spot diameter at sample surface was verified from the diameter of ablation crater produced on silicon wafer at threshold ablation energy. The profile of ablation craters was measured with a scanning confocal microscope (NanoFocus Inc., μsurf).

Five different spot sizes (35 μm, 50 μm, 70 μm, 100 μm, 150 μm), beginning from 150 μm to a size below the typical P2 scribing pattern width of 50–60 μm, were selected for the investigation. For each of these spot sizes, laser fluence (energy per unit area) was kept nearly the same as shown in Table 2 so that the effect of laser energy difference could be ruled out during the interpretation of the data. The laser irradiation of CIGS sample was carried out in atmospheric conditions. For signal enhancement, argon gas was injected in an approximately 45° direction from the sample surface at the flow rate of 3 L/min through an orifice (inner diameter = 3.8 mm) located 0.8 cm away from the laser spot. It was known that the use of argon buffer gas could enhance LIBS signal by as much as 10 fold [14]. Besides signal enhancement, Ar gas jet was also known to produce a smooth crater bottom [15]. Different scan speeds of 58.4, 83.5, 116.5, 166.5 and 250 μm/s were used for the spot diameters of 35, 50, 70, 100 and 150 μm, respectively, in order to keep the overlap ratio (79%) to be the same for all spot diameters, while keeping the repetition rate of the laser at 5 Hz. The overlap ratio is expressed by

$$Overlap = \frac{2}{\pi}\left(\theta - \frac{V\sin\theta}{DR}\right) \quad (1)$$

where V is scan speed, R is repetition rate, D is laser spot diameter and $\theta = \cos^{-1}(V/DR)$. Similarly, LIBS measurement at fixed repletion rate but at varying overlap ratio was also carried out to check the signal variation with scan speed. In general, the ablation depth increases with increasing overlap ratio. However, Zhao et al. [16] reported that the ablation depth became saturated when overlap ratio increased beyond a certain value, depending on laser fluence: for example, 81–84% for 3 J/cm^2 and 78–81% for 4.5 J/cm^2. An overlap ratio of 79% within this suggested range was selected in this study.

The emission from LIBS plasma was collected with a collection optics consisting of two lenses (1:1 magnification) and delivered to a six channel CCD spectrometer (spectral range: 187–1041 nm, resolution:

Table 2
Laser pulse energy and corresponding fluence for varying spot size.

Spot size (μm)	Energy (mJ)	Fluence (J/cm^2)
35	0.044	4.57
50	0.092	4.69
70	0.184	4.78
100	0.345	4.39
150	0.820	4.64