SHIMADZU

Application News

Inductively Coupled Plasma Atomic Emission Spectrometry   No.J91

Analysis of CIGS Solar Cell by ICPE-9000

■ Introduction

Solar cells based on compounds that do not include silicon are receiving increased attention. The CIGS solar cell that uses Cu, In, Ga and Se is one such example. The ratio of these substances is important from the standpoint of improving power generation efficiency. An EDX (energy dispersive X-ray fluorescence spectrometer) allows nondestructive, direct measurement of this CIGS thin film, but when accuracy becomes a priority, a more reliable method of quantitation is by putting the thin file into solution, and generating a calibration curve using standard solutions of certified concentration. ICP emission spectrometry, which allows simultaneous analysis at multiple wavelengths, is an effective method for analyzing this sample placed in solution.

Here we introduce an example of analysis of the Mo rear electrode layer and CIGS layer of thin film on a glass substrate using the Shimadzu ICPE-9000 Multitype ICP Emission Spectrometer.

■ Pretreatment

This time, we used 4 types of 25 mm × 40 mm glass substrates with a Mo rear electrode layer and a CIGS layer under different conditions, and processed them as described below. The samples consisted of films produced by Kojundo Chemical Laboratory Co., Ltd., using sputtering targets.

First, each of these substrates was inserted into a 200 mL tall beaker one by one, and after adding 5 mL hydrochloric acid (1 + 1), the beaker was heated on a hotplate at 180 °C. In addition, 1 mL concentrated nitric acid was added, and heating was continued until the thin film peeled off the glass substrate and completely dissolved (about 1 hour). After it cooled down, the solution in the beaker was transferred to a 50 mL volumetric flask, taking care not to drop the glass substrate. The beaker was then rinsed 3 times with a small amount of distilled water, each time transferring the rinse solution to the volumetric flask. Finally, the solution volume was brought to 50 mL using distilled water, and this became the measurement source solution. A 10-fold dilution of this source solution (using distilled water) was used for actual measurement.

■ Analytical Method and Conditions

Measurement was conducted by the calibration curve method. The basic instrument conditions are shown in Table 1, and the concentration and wavelength used for each element in the mixed standard solution are shown in Table 2. The mixed standard solution was prepared by mixing atomic absorption standard solutions.

Table 1 Instrument and Analytical Conditions

Instrument	: ICPE-9000
RF Power Output	: 1.2 kW
Plasma Gas Flowrate	: 10 (L/min)
Auxiliary Gas Flowrate	0.6 (L/min)
Carrier Gas Flowrate	: 0.7 (L/min)
Sample Introduction	: coaxial nebulizer
Chamber	: cyclone chamber
Plasma Torch	: mini torch
Observation Method	: axial

Table 2 Standard Solution Concentration (Unit: mg/L) and Wavelength Used for Each Element

Element	Wavelength (nm)	STD 1	STD 2	STD 3	STD 4
Cu	324.75	0	2	4	10
In	230.61	0	2	4	10
Ga	417.21	0.0	0.2	0.4	1.0
Se	203.99	0	2	4	10

■ Results

The calibration curves for the measured elements are shown in Fig. 1 to 4. The measured element concentration in each of the measurement solutions was converted to an absolute quantity, and then, the mole number divided by the atomic weight of each element was obtained. By determining that mole ratio, we were able to compare it with ratio of the designed value. An example of the calculation for one sample is shown in Table 3, and the measurement result for each sample is shown as a mole ratio of the element with respect to Cu, as a value of 1. In all cases, the result coincided well with the designed value. In this example, we also calculated the amount corresponding to 1 sheet of glass substrate, or 1 cm^2, but if the mole ratio is known, the mole number can be calculated from the absolute amount, and the amount can be calculated from this ratio.

With the EDX, if there is no standard substance, it may not be possible to obtain an accurate ratio due to the matrix effect. In contrast, if correction is conducted using this ICP measurement result, accurate measurement is possible with the EDX for a thin film having the same composition.
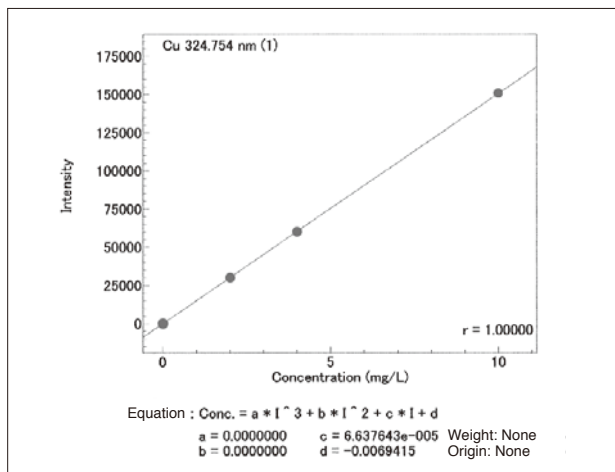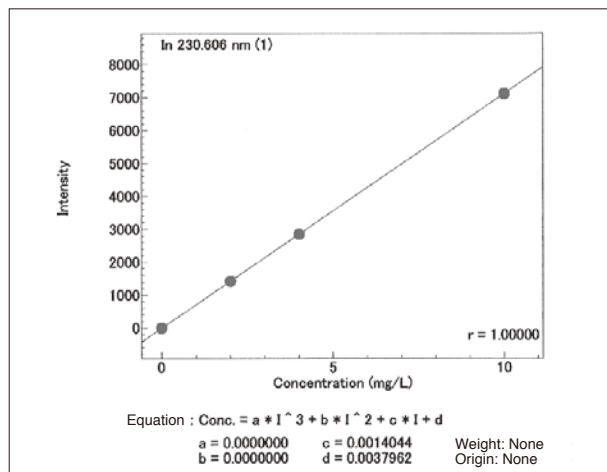
Fig. 1 Calibration Curve for Cu
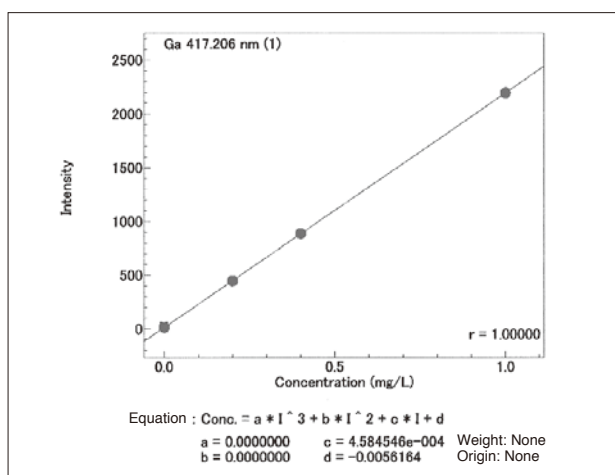

Fig. 2 Calibration Curve for In

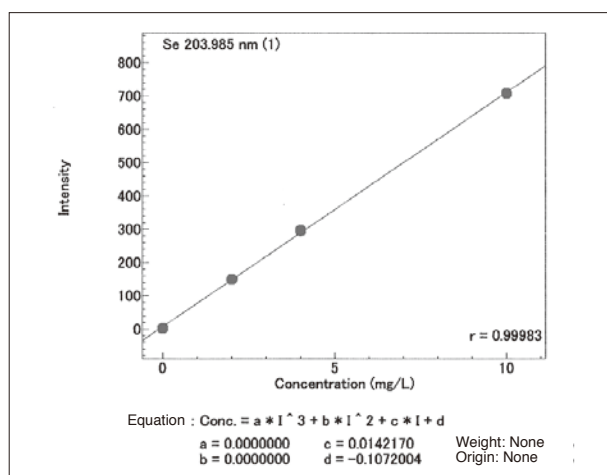**Fig. 3 Calibration Curve for Ga**

Fig. 4 Calibration Curve for Se

Table 3 An Example of Conversion from the Concentration to the Mole Ratio

	Item and Conversion Method	Cu	In	Ga	Se	Total
(1)	Concentration during measurement (mg/L)	3.02	4.40	0.654	7.76	
(2)	Concentration in source solution (50 mL) (mg/L = μg/mL) [10 × value of (1)]	30.2	44.0	6.54	77.6	
(3)	Absolute quantity (μg) per sheet [50 × value of (2)]	1510	2200	327	3880	7917
(4)	Absolute quantity (μg) per 1 cm^2 (1 sheet, 10 cm^2) [value of (3) divided by 10]	151	220	32.7	388	791.7
(5)	Atomic weight of each element	63.55	114.82	69.72	78.96	
(6)	Absolute quantity (per sheet) μmol number [value of (3) divided by respective atomic weight]	23.8	19.2	4.7	49.1	96.75
(7)	Mole ratio (= atom %) [100 × (each absolute quantity (6) divided by total of (6))]	24.6	19.8	4.8	50.8	
(8)	Ratio when Cu is 1 [each mole ratio of (7) divided by Cu mole ratio 24.6]	1.000	0.805	0.197	2.065	

Table 4 The Mole Ratio Results for Samples and Designed Value

	Cu	In	Ga	Se
Sample 1	1.000	0.805	0.197	2.065
Sample 2	1.000	0.791	0.196	2.064
Sample 3	1.000	0.791	0.199	2.063
Sample 4	1.000	0.797	0.198	2.065
Designed Value	1.000	0.800	0.200	2.000