In situ optical monitor system for CIGS solar cell applications

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An *in situ* process monitor for the $CuIn_xGa_{1-x}Se_2$ (copper indium gallium selenide) (CIGS) coating system is a very important tool that produces repeatable, high-quality CIGS coatings. This letter provides an overview of the current state of application of *in situ* process monitor systems for co-evaporation CIGS coatings. A comparison between different *in situ* monitoring systems is given and a novel multiple-elements rate monitor system is introduced.

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Copper indium gallium selenide (CIGS)-based thin film photovolatic (PV) modules exhibit the highest efficiency of all thin film PV materials (α-Si, Tandem-Si, CdTe)[1]. The best energy conversion efficiency of a CIGS standard cell is 19.9±0.6%. Currently, a large area commercial module can provide a conversion efficiency of 15.22%[2,3]. As such, CIGS standard cells have the potential of becoming the best candidates for replacing silicon wafer-based PVs in the future. All the potential benefits of a CIGS PV module, such as high efficiency and low material and energy consumption, are combined and it can be mass produced with high levels of reliability, throughput, yield, and quality. *In-situ* precision control of CIGS layers is the key to the mass production of this kind of solar cell.

Several process sensors for CIGS coatings have been reported over the past 20 years, many of which were based on different diagnosis principles. For example, a quartz crystal microbalance (QCM) and quadrupole mass spectroscopy (QMS)[4] can be used to detect the evaporation rate of different materials. A thermocouple (TC)[5], pyrometer[6,7], and an infrared monitor[8] can be used to measure different levels of heat radiation of CIGS coatings with different copper/(indium+gallium) (Cu/(In+Ga)) compositions. Spectroscopic light scattering (SLS)[9] can also be introduced to investigate the structural changes of CIGS during deposition using different Ga/(In+Ga) compositions. A spectroscopic ellipsometer (SE)[10] can be used to characterize the optical constants, thicknesses, and compositions of CIGS films. Electron impact emission spectroscopy (EIES)[11] and atomic absorption (AA)[12] can be used to monitor the flux of Cu, In, and Ga simultaneously, since each element has a characteristic wavelength, while x-ray fluorescence (XRF) can be integrated in evaporation systems to analyze the composition and thickness of CIGS in real time[13]. QCM, QMS, TC, the pyrometer, SLS, and EIES are all good process sensors for laboratory batch systems, and SE, AA, and XRF are very suitable monitoring systems for industrial inline systems. Repins *et al.* gave a very good summary and comparison of each kind of process sensor for CIGS deposition and manufacture in 2005[14]. To date, researchers continue to search for new process monitors for CIGS coating systems that will improve the yield, quality, and repeatability of CIGS coatings.

In this letter, a brief description of the critical requirements for CIGS process sensors is given. In addition, the current state of application of *in situ* process monitors in laboratory and industrial co-evaporation systems is summarized. A novel, optical-based, multiple-elements rate monitor system is introduced.

The CIGS absorber layer is a compound made of Cu, In, Ga, and Se. In order to obtain high conversion efficiency, the composition depth profile of each element in the CIGS absorber layer must be well-controlled. The process monitor for a CIGS co-evaporation system should meet the following critical requirements:

1) The process monitor must work both *in situ* and in real time;

2) The process monitor must be able to control the state of multiple elements at the same time;

3) The process monitor must be operated at high temperatures. Typically, the surround temperature should be from 350 °C to 550 °C;

4) The process monitor must be able to sustain Se corrosion during evaporation;

5) For industrial systems, the process monitor must work inline without contact and be non-intrusive.

A summary of the different process monitors described above is shown in Table 1.

From Table 1, we can find that only TC, SE, AA, and XRF have the potential to be used for industrial systems. A spectroscopic ellipsometer requires a complex interpretative algorithm to control the CIGS coating process, which is still not commercially available. Atomic absorption with multiple hollow cathode lamps can monitor the flux of multiple elements at the same time. However, a special background correction system must be introduced since optical path misalignment, contamination of windows, and scattering of Se can affect the accuracy of the system. Alternatively, X-ray fluorescence is a mature technology that can monitor the composition and thickness of CIGS coatings. However, during CIGS

Table 1. Summary of Process Monitors Currently Used in CIGS Co-Evaporation

Method	Probe	Features	System	Cost	Commercially Available
TC	Source Temperature	Rate of One Element	Lab, Industry	$	Yes
QCM	Quartz Crystal	Rate of One Element	Lab	$$	Yes
QMS	Mass Ion	Flux of Multiple Elements	Lab	$$$	Yes
TC	Heat Radiation	Composition	Lab	$	Yes
TC Pyrometer	Heat Radiation	Composition, Thickness	Lab	$$	Yes Yes
Infrared Monitor	Heat Radiation	Composition, Thickness	Lab	$$	Yes
SLS	White Light	Composition, Thickness, Surface Structure, Band gap	Lab	$$$	No
SE	Polarized Light	Composition, Thickness, Surface Structure, Band gap	Lab, Industry	$$$	No
EIES	Atomic Emission	Flux of Multiple Elements	Lab	$$$	Yes
AA	Atomic Absorption	Flux of Multiple Elements	Lab, Industry	$$$	Yes
XRF	X-ray	Composition, Thickness	Lab, Industry	$$$	Yes

co-evaporation, two In and Ga evaporation sources are required, and XRF is unable to control these separately.

All process monitors for CIGS co-evaporation have their own unique merits and limitations. Currently, researchers continue to search for new process monitors to improve the yield, quality, and repeatability of CIGS co-evaporation systems. To this end, a novel high-resolution continuum source atomic absorption spectroscopy (HR-CS AAS) rate monitor was developed by Optorun Co., Ltd. This monitor is aimed at being used in CIGS co-evaporation systems.

As mentioned above, an AA rate monitor with multiple hollow cathode lamps can monitor the evaporation rate of multiple elements at the same time, although a special background correction system must be introduced. The high price and short lifetime of hollow cathode lamps, however, restrict the widespread use of this rate monitoring technique.

In 1952, Alan Walsh investigated the possibility of using a continuum light source for recording atomic absorption spectra (CS AAS)[15]. He came to the conclusion that a resolution of approximately 2 pm would be required if a continuum source was used. This, however, was far beyond the capabilities of the best spectrometer available at the time. The turning point of the CS AAS was the introduction of a high-resolution echelle spectrometer. Echelle spectrometers make use of a prism and a perpendicularly mounted grating to separate light in two-dimensional (2D) image planes. It is now very easy to achieve 2 pm resolutions with the current charge-coupled devices (CCD) digital camera technology. Based on this principle, Optorun Co., Ltd. developed an HR-CS AAS rate monitor. The system diagram of this monitor is shown in Fig. 1.

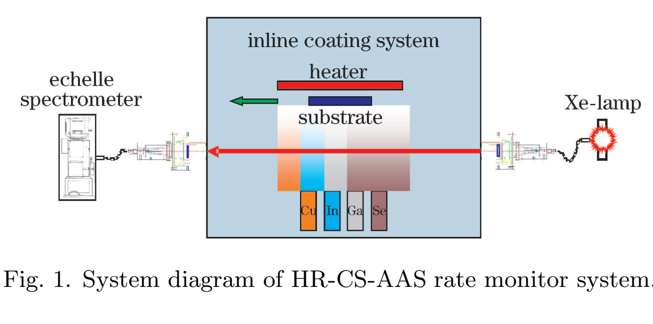

Fig. 1. System diagram of HR-CS-AAS rate monitor system.

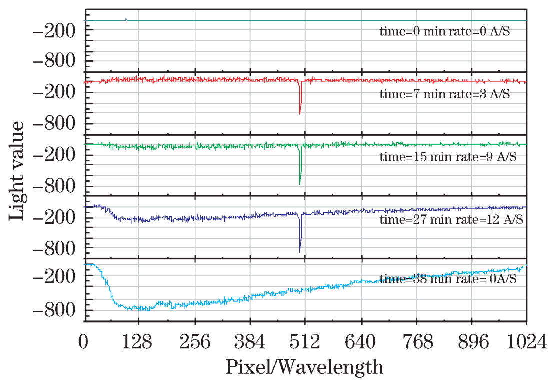

Fig. 2. Cu atomic absorbance signal change during evaporation.

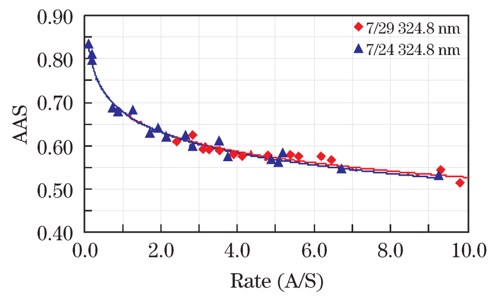

Fig. 3. Twice HR-CS AAS rate monitor experiment result of Cu evaporation.

The HR-CS AAS rate monitor system uses a Hamamatsu super-quiet Xe lamp as a light source. The radiation spectrum of this Xe lamp covers the wavelength range between 185 to 2000 nm. The life span of the Xe lamp is more than 3000 h. It is significantly cost-saving, especially when multiple elements have to be analyzed at the same time. The continuum white light is first introduced into the inline CIGS co-evaporation chamber via optical fibers. Light beams then pass over the Cu, In, Ga, and Se evaporation source and send the atomic absorption spectra information of these elements toward the echelle spectrometer. The spectrometer separates the light and gives the continuum spectrum of each element. The atomic absorption lines of Cu, In, and Ga are 324.8, 303.9, and 294.5 nm, respectively. Figure 2 shows the Cu atomic absorbance signals obtained from the inline CIGS co-evaporation system.

Based on the figure, we can observe that the background changes during Cu coating. Since we consider the entire range of spectral information, including that from the beginning of evaporation, it is very easy to correct the background deformation and obtain the correct absorbance of Cu. Figure 3 shows the twice experimental results of Cu evaporation. The absorption of Cu at different rates displays good repeatability, proving that the HR-CS AAS rate monitor can be used in inline co-evaporation systems and can monitor the rate of multiple elements at the same time.

In conclusion, the key to CIGS process monitors is *in situ* monitoring of the composition of Cu, In, Ga, and Se materials and the precise control of the deposition rate of each material. The HR-CS AAS rate monitor uses a continuum light source and a high-resolution echelle spectrometer to simultaneously monitor the atomic absorption of all elements involved in the system. It provides a real time, *in situ*, no-contact, and non-intrusive process sensor for CIGS co-evaporation and has proven to be suitable for monitoring the evaporation rate of multiple elements in industrial systems that use CIGS technology.

Future CIGS process sensors may include a combination of an HR-CS AAS rate monitor and inline XRF composition detector. Inline XRF composition detectors analyze the composition of CIGS coatings and provide the desired evaporation rate to the HR-CS AAS rate monitor. The HR-CS AAS rate monitor then controls each evaporation source and functions at the desired rate during co-evaporation. Hence, a closed-loop control system is formed, which could well improve the yield, quality, and repeatability of CIGS co-evaporation systems.

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