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Quantitative analysis of graded $Cu(In_{1-x},Ga_x)Se_2$ thin films by AES, ICP-OES, and EPMA

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ABSTRACT

The overall composition and the compositional profile of the quaternary semiconductor $Cu(In_{1-x},Ga_x)Se_2$ (CIGS) have strong effects on the performance of photovoltaic devices based on it. Recent work that has yielded ~20% efficient solar cells based on CIGS has forced extra attention on quantitative analysis of the absorber layers. In this paper we present details of the procedures used to generate detailed compositional profiles of graded $Cu(In_{1-x},Ga_x)Se_2$ thin films by Auger electron spectroscopy (AES) that when integrated, agree quantitatively with inductively-coupled plasma optical emission spectrometry (ICP-OES) data on the same films. The effects of sample rotation during sputter depth profiling on the quantification results are described. Details of the procedures used for the ICP-OES and wavelength-dispersed electron probe microanalysis (EPMA) analyses are also presented. Finally, we show why X-ray microanalysis techniques alone should not be used to argue that specific windows of copper and gallium concentrations can yield high performance devices.

1. Introduction

Steady progress in the understanding of $Cu(In_{1-x},Ga_x)Se_2$-based thin film solar cells has seen their efficiencies approach 20% in the laboratory [1]. Although many factors go into the production of these high efficiency devices, one key aspect of obtaining these results has been rigorous control over the composition of the selenide absorber layers, including the grading in relative copper and gallium concentrations. In CIGS films, grading of the gallium to indium ratio induces band-gap grading and electrical fields that can either improve or degrade the performance of solar cells, and are especially significant in the design of cells utilizing thin absorber layers [2]. The latter topic has been of increasing importance due to concerns about limited world reserves of indium [3]. Grading of the ratio of copper to Group III elements near the metallurgical junction with the n-type layer (usually CdS) can also have strong effects on final device performance. A high Cu/Group III ratio often signifies the presence of a $CuSe_x$ phase, a degenerate p-type semiconductor that harms device performance unless removed chemically, usually with cyanide compounds [4]. On the other hand, a Cu/Group III ratio of about 0.3 at the absorber surface is typically found in high performance devices and is thought to facilitate doping by cadmium and the formation of a buried homojunction [1,5].

Because of the strong effects that CIGS composition has on device performance, at our laboratory there has been an ongoing effort to quantify the absorber composition after deposition using AES, EPMA, and ICP-OES. All three techniques are widely used to characterize thin films of various types, and each has its own advantages and disadvantages. AES, used in conjunction with sputter depth profiling, can provide highly depth-resolved compositional profiles of films with varying composition. On the other hand, because the amplitude of an Auger transition in a spectrum depends on the chemical state of the element, the use of pure elements as standards can cause large matrix-dependent errors. EPMA results are more easily quantified by using elemental standards. Yet with this and related X-ray-based analytical techniques such as energy-dispersive X-ray spectroscopy (EDX), details of composition profiles in thin (~2 μm) films such as the CIGS layers in high efficiency solar cells are masked because of electron beam and X-ray-solid interactions that extend deep into the film depending on sample morphology and composition, angle of incidence, beam energy, and X-ray energy [6]. Nevertheless both EPMA and EDX data have been used to argue for specific windows of overall film composition that yield high efficiency devices [7–9].

ICP-OES is a mature technique and can be extremely sensitive and quantitative, but data obtained by dissolution of a film is also an averaging technique and cannot supply detailed information about

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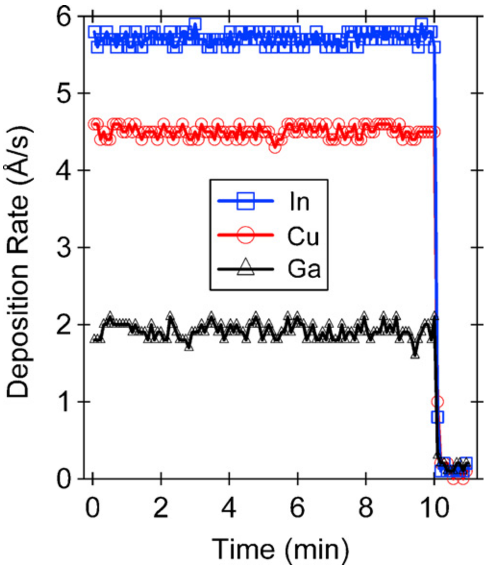

Fig. 1. Metal fluxes measured during deposition of the nominally ungraded standard film.

CIGS compositional grading that appears necessary to obtain high efficiency solar cells.

In the past, our procedure for determining the composition of graded CIGS films using AES followed the simple procedures outlined by previous workers [10]. Sensitivity factors (SFs) for indium, gallium, and selenium are derived from AES spectra of a nominally ungraded CIGS thin film of known composition using the following:

$$S_a = \left(\frac{I_a}{X_a}\right)\left(\frac{X_{ref}}{I_{ref}}\right)S_{ref}, \quad (1)$$

where S_a is the sensitivity factor for element A, I_a is the peak-to-peak AES intensity of element A, X_a is the mole fraction of element A, X_{ref} is the mole fraction of the reference element, I_{ref} is the peak-to-peak AES intensity of the reference element, and S_{ref} is the reference element sensitivity factor. In our case, the copper sensitivity factor was used as S_{ref} and thus was kept constant throughout this work. I_a and I_{ref} values were obtained from those portions of the depth profile in which the AES signals had reached a steady state. It is important to note that this latter part of the procedure folds in the contributions to the AES signals that come from the thin, non-stoichiometric layer formed at the surface due to preferential sputtering, the sputter-altered layer [11].

For an unknown homogeneous sample then, the atomic concentration C_a of element A is simply:

$$C_a = \frac{I_a/S_a}{\sum I_i/S_i}, \quad (2)$$

where I_i and S_i refer to the ith element in the compound. Relative to elemental standards, advantages of using a CIGS film of known composition to derive AES sensitivity factors include the minimization of errors due to chemical state effects, matrix-dependent changes in electron inelastic-mean-free paths, and surface roughness. Typically the CIGS standards that are used in our laboratory are nominally ungraded in the sense that they are grown using metal fluxes that are constant in time. The lack of compositional grading is important because EPMA is used to determine the mole fractions X_a and X_{ref} in Eq. (1). With a graded film, the surface sensitivity of EPMA, although low relative to electron spectroscopic methods such as AES, would result in a poor representation of the overall film composition and in erroneous AES sensitivity factors.

Using the above procedure, semi-quantitative AES results for a wide range of CIGS compositions can been obtained. We have observed however that integrated AES sputter profiles calibrated as described above show a systematic deviation from overall compositions derived from carefully performed ICP-OES measurements. Recently the origins of this deviation have been identified. This paper describes details of an improved procedure for quantification of AES sputter profile data of CIGS thin films, with the result being that integrated AES sputter depth profiles agree well with ICP-OES results even for films heavily graded in composition.

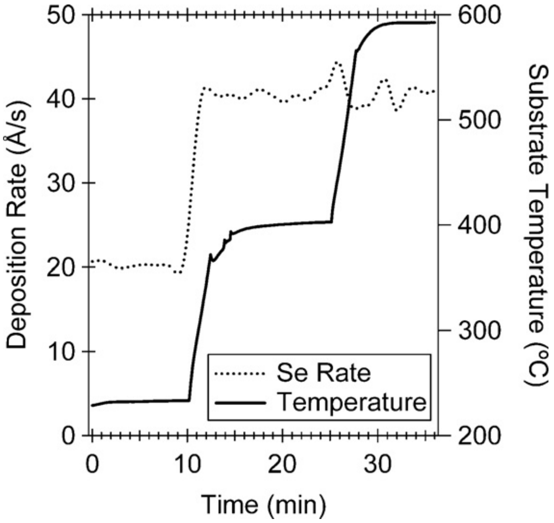

Fig. 2. Selenium flux and temperature profile of AES standard film.

2. Materials and methods

AES spectra and sputter depth profiles were taken on a Physical Electronics PHI 670 Scanning Auger Microscope that has been updated with the 5-axis motorized manipulator more commonly found on the PHI 680 instrument. For CIGS studies, a 5 kV, 20 nA electron beam was rastered over a 2400 μm^2 area. Unless noted otherwise, during data acquisition and ion sputtering, the sample was rotated at 0.4 rpm. Sputter depth profiling was performed using a 3 kV Ar^+ beam at ~20 $\mu A/cm^2$ and with the sample tilted such that the angle between the sample normal and the electron beam/analyzer axis was 30°. With our instrument this corresponds to an ion beam angle of 59° with respect to the surface normal. AES spectra were acquired in the direct mode and numerically smoothed and differentiated with the PHI MultiPak V8.2B software package. AES intensities were taken as the peak-to-peak amplitudes of the differentiated Cu LMM transition at 922 eV, the In MNN transition at 412 eV, the Ga LMM transition at 1071 eV, and the Se LMM transition at 1313 eV.

Electron inelastic-mean-free paths were calculated for the particular composition of $Cu(In_{0.7}, Ga_{0.3})Se_2$ using the relationship developed by Tanuma et al. [12,13] and assuming a density of 5.75 g/cm^3.

Interleaved measurements of relative sputter yields during AES sputter profiles were conducted with a Stanford Research Systems RGA300 quadrupole mass spectrometer mounted on a spare port of the AES vacuum system. The RGA300 ionizer was kept off for all measurements. The sample to probe distance was approximately 3 in. The most abundant isotopes of copper (Cu^{63}), indium (In^{115}), and gallium (Ga^{69}) were followed continuously, but the intensities of these ions were determined only for times when the argon ion beam was on and by averaging over a 40 s interval centered on each 60 s sputtering cycle.

Inductively-coupled plasma (ICP) measurements were performed as follows: a Varian Liberty 150 ICP emission spectrometer