Sputter Rate Measurements of Cu(In,Ga)Se₂ Absorber Layers with Varied Ga Ratios, Primary Voltage, and Angle of Incidence by Secondary Ion Mass Spectrometry

Jesse Claypoole¹, Steve Novak¹, Mark Altwerger¹, Dan Dwyer¹, Pradeep Haldar¹, Matt Eisaman^{2, 3, 4}, and Harry Efstathiadis¹

¹State University of New York Polytechnic Institute, Colleges of Nanoscale Science and Engineering, 257 Fuller Rd., Albany, NY 12203, USA

²Sustainable Energy Technologies Department, Brookhaven National Laboratory, Upton NY 11973

³Department of Physics and Astronomy, Stony Brook University, Stony Brook NY 11790

⁴Department of Electrical and Computer Engineering, Stony Brook University, Stony Brook NY 11790

Abstract

Thin film Cu(In,Ga)Se₂ (CIGS) layers were deposited by a 1-stage and 3-stage co-evaporation process on Mo/Glass substrates at various Ga/(Ga+In) ratios (Ga ratio). The sputter rate and the depth profile of 1-stage CIGS absorber layers at various Ga ratios were measured using secondary ion mass spectrometry (SIMS) using different primary voltages and angles of incidence of a Cs beam in order to study how the Ga ratio of CIGS affected the sputter rate. It was determined that there was up to 50% variation in film sputter rate depending on the Ga ratio range, SIMS primary voltage, and angle of incidence. A point-by-point correction method was then developed to correct for relative sputter rate differences in 3-stage CIGS samples with a graded Ga ratio profile.

Keywords: Secondary Ion Mass Spectrometry (SIMS), Absorber Layer, Semiconductors, Thin Films, Photovoltaics, Sputter Rate

Corresponding Author:

Email: hefstathiadis@sunypoly.edu

Tel: 518-4378605

Postal: State University of New York Polytechnic Institute,
Colleges of Nanoscale Science and Engineering

257 Fuller Road

Albany, NY 12203

1. Introduction

In order to reduce the cost of solar panels from that of crystalline silicon panels, several different thin-film technologies are being developed. One of the most promising of these is $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ (CIGS), with a record small scale efficiency at 22.3 %, approaching that of conventional silicon solar cells.^{1, 2} CIGS thin-film devices are an attractive alternative to silicon because they have a direct band gap and high absorption coefficient.³ CIGS also has a tunable band gap from 1.0 - 1.7 eV and adjustable lattice parameters that can be readily adjusted by changing the Ga content in the absorber layer. The solar cell device layered structure consists of $\text{ZnO}:\text{Al}/\text{ZnO}/\text{CdS}/\text{CIGS}/\text{Mo}/\text{Soda-lime glass}$.⁴ The highest efficiency CIGS cells use 3-stage co-evaporation in order to grade the gallium distribution in the cell and optimize the band gap with respect to depth. This reduces recombination at the rear contact and also increases the range of wavelengths the device can absorb.⁵

In order to measure the grading of the bandgap and hence the composition of the CIGS film, a technique like dynamic SIMS is used. Dynamic SIMS uses an ion beam to collide with the surface of a sample and then measures the mass and amount of the secondary ions that come off the sample through mass spectrometry. A reference standard with similar composition to the unknown is used for quantification of each mass measured using MCs^+ clusters. In order to reduce well-known matrix effects due to the large compositional changes in graded films, MCs^+ ions are typically measured in SIMS profiling CIGS.^{6, 7} In the process of the primary ions colliding with the sample surface a crater is formed the final depth of which is measured using a profilometer. That depth is then used to determine the average sputter rate for the entire profile. The problem with using an average sputter rate is that because the composition of the CIGS

changes significantly with respect to depth, the average sputter rate will not give an accurate depth profile.

The sputter rate of a material is affected by several parameters, including beam current, primary voltage, crystal orientation, raster size, and angle of incidence. Beam current is the number of primary ions colliding with the surface of the sample per unit area. By increasing the beam current, the sputter rate of the sample will increase. The primary voltage describes the accelerating voltage the ion beam experiences and is how much energy the primary beam ions have when they collide with the surface. The crystal orientation can weakly affect the sputter yield because different crystal faces can have different numbers of bonds associated with each crystal face. The raster size is the linear dimension over which the ion beam is scanned. Decreasing the raster size will result in an increased sputter rate by the square of the linear dimension. The angle of incidence at which the beam strikes the surface, usually measured with respect to surface normal, generally increases the sputter yield as the angle of incidence up to near 60 degrees.^{8,9}

This work presents how the sputter rate of 1-stage CIGS absorber layers with Ga ratios between 0 and 0.5, primary Cs beam voltages between 2-5 kV, and angles of incidence of 45 and 60 degrees affect the sputter rate. It also demonstrates a point-by-point correction of a graded CIGS absorber layer based on Ga ratio.

2. Experimental

The 1-stage and 3-stage CIGS samples were prepared by co-evaporation from elemental Cu, In, Ga, and Se sources. This deposition system is described elsewhere.¹⁰ The films were deposited on approximately 600 nm Mo coated soda lime glass substrates. The 1-stage CIGS

samples with Ga ratios of 0.00, 0.14, 0.19, 0.28, 0.37, 0.39, 0.487, and 0.49 were deposited in order to measure the film sputter rate using SIMS. Three 3-stage CIGS samples were prepared with different Ga ratio grading to determine the difference in composition with respect to depth between the measured depth profile and the actual depth profile using SIMS. To determine the actual depth profile, the three 3-stage CIGS samples had multiple depth profiles at increasing two minute time intervals until the Mo layer was reached. The composition and the crater depths of the increasing time intervals crater bottoms were used to plot the actual profile. The sputter rate data from the 1-stage CIGS films and the difference in composition with respect to depth between the actual and measured profile in the 3-stage CIGS films was used to create a point-by-point correction method to correct for the dependence of sputter rate based on the Ga ratio in 3-stage CIGS films.

The MS (Mass Spectrometry) SIMS characterization of the CIGS sample was carried out on the Physical Electronics 6650 Quadrupole SIMS. The samples were first loaded into the sample exchange chamber and then pumped down to 10^{-8} Torr before being inserted to the main chamber. Cesium bombardment with a 45 and 60 degree angle of incidence and accelerating voltages of 2 to 5 kV was used at 10^{-9} Torr in order to create the ions. The area scanned by the cesium beam had a raster size of 500 x 500 μm and a 10% gate detection area. An electron multiplier detector was used to detect the positive secondary ions. Concentration calibration of the 1-stage CIGS samples with Ga ratios between 0.0 and 0.5 were calibrated using S11 Nano Technology, Model SEA 2210A Element Monitor XRF tool. Depth calibration of the SIMS craters was accomplished using a Veeco Dektak 150 Profilometer. Each crater was measured 4 times at 0, 45, 90, and 135 degrees in order to verify the depth of the craters. Percent relative standard deviations of these repeat measurements were within 10%.

3. Results & Discussion

The sputter rate of CIGS absorber layers with different primary voltages ranging from 2 to 5 kV and at 45 and 60 degrees were determined using 1-stage CIGS absorber layers with varied Ga ratios. The sputter rates with respect to composition, beam energy, and angle are listed in Figures 1 to 2. Figures 1 and 2 show the combined normalized sputter rate data at a given angle of incidence, have a compositional range from Ga ratio 0.0 to 0.5, and contain error bars with a 3 percent possible error in the measurements. In the Ga ratio range from 0.0 to 0.5, there is a linear change in sputter rate with respect to Ga ratio, this means that the Ga ratio may not be accurately determined with respect to depth using just a final crater measurement and an average sputter rate in 3-stage samples. This is important because high efficiency 3-stage samples, which have Ga ratios near 0.3, need to have a properly engineered band gap with respect to depth in order to optimize cell efficiency.¹¹ If the average sputter rate is assumed to be the only sputter rate throughout absorber layer, a CIGS absorber layer with a Ga grading dip of at least 0.1 – 0.15 in Ga ratio will be measured with the dip shifted deeper into the absorber layer than it actually is. In order to correct for this, we can use the relative sputter rates at a given beam energy and angle in the linear region in order to create a model to provide a point-by-point correction for the depth profile to make it match the actual profile.

Figure 1. Combined sputter rate data for 60 degree angle of incidence from 2 to 5 kV primary voltage.

Figure 2. Combined sputter rate data for 45 degree angle of incidence from 2 to 5 kV primary voltage.

Beam Energy (kV)	Beam Angle of Incidence (Degrees)	Sputter rate ($\mu\text{m}/(\text{sec} \cdot \text{nA})$)	R ²
5	60	$Y = 3\text{E-}6 X + 3\text{E-}6$	0.98
4	60	$Y = 3\text{E-}6 X + 2\text{E-}6$	0.94
3	60	$Y = 2\text{E-}6 X + 2\text{E-}6$	0.76
2	60	$Y = 1\text{E-}6 X + 1\text{E-}6$	0.86
5	45	$Y = 2\text{E-}6 X + 2\text{E-}6$	0.89
4	45	$Y = 3\text{E-}6 X + 3\text{E-}6$	0.90
3	45	$Y = 2\text{E-}6 X + 2\text{E-}6$	0.82
2	45	$Y = 1\text{E-}6 X + 2\text{E-}6$	0.84

Table 1. Sputter rate equation with respect to beam energy and angle where Y is the sputter rate in ($\mu\text{m}/(\text{sec nA})$) and X is the Ga ratio in the linear region from 0.0 to 0.5.

Single Stage Sample Number	Ga/(Ga+In) Ratio	Cu/(Ga+In) Ratio	Se/(Se+In+Ga) Ratio
1	0.00	2.35	0.71
2	0.14	3.23	0.71
3	0.19	1.31	0.68
4	0.28	1.22	0.68
5	0.37	1.64	0.62
6	0.39	0.77	0.59
7	0.49	1.65	0.68
8	0.49	1.72	0.64

Table 2. Composition ratios of single stage CIGS absorber layers used to calculate sputter rates.

The point-by-point correction method works in the Ga ratio range from 0.0 to 0.5 with a linear change in sputter rate which can be seen in Figures 1 and 2 and table 1. The equations that describe the sputter rates in Figures 1 and 2 are shown in Table 1 in order to show how the sputter rate changes with respect to beam energy and angle of incidence and also confirms that the assumption of linear change of sputter rate used in the model is accurate under a variety of conditions. It can be seen that the sputter rate increases with beam energy and decreases slightly with increasing beam angle. By using the average sputter rate, which is obtained from the profile time and final crater depth, and knowing the composition with respect to depth using the average sputter rate we can do a correction on each depth point based on its Ga ratio with respect to the

average Ga ratio with depths with a lower than average Ga ratio not sputtering as fast as depths with higher than average Ga ratio.

Table 2 describes the composition of the 1-stage samples that were used to generate the data shown Figures 1 and 2 and table 2. It can be seen that there is a small difference in Se/(Se+In+Ga) ratio between the 1-stage samples with the Se/(Se+In+Ga) ratio not significantly affecting the linear sputter rate trend. The Cu/(Ga+In) ratio between the 1-stage samples in table 2 has a much larger range of variation compared to the Se/(Se+Ga+In) ratios but by comparing the Cu/(Ga+In) ratio sample 5 and 6 it appears that the Cu/(Ga+In) ratio does not significantly affect the sputter rate and any affect is within the margin of error of the measurement.

Using the point-by-point correction method equations below, the sputter rate difference with respect to composition is compensated for using equation 1, 2, and 3 listed below,

$$\rho_{Ga} = \frac{Ga\ ratio\ (point)}{Average\ Ga\ ratio} \quad (1)$$

$$Corrected\ Depth = t_{interval} * Average\ Sputter\ Rate(\rho_{Ga} + Grading\ Factor \times (1 - \rho_{Ga})) + Previous\ Depth\ Point \quad (2)$$

Here the “Ga ratio” is the Ga/(Ga+In) ratio at the measured time interval; the “Average Ga ratio” is the averaged Ga ratio over the entire profile; the ρ_{Ga} is the Ga ratio at measured interval divided by the overall average Ga ratio; the “Corrected Depth” is the actual depth using the correction method; the $t_{interval}$ is the time of the later data point minus the time from the previous data point in order to get the time interval between points; the “Average Sputter Rate” is the sputter rate over the entire profile calculated using the profilometer crater measurement divided by total time of the experiment. Equation 3 describes the terms that make up the grading factor which is used to help fit the equation to the actual profile.

$$\textbf{Grading Factor} = \frac{\textit{Upper depth}}{\textit{Lower depth}} * \frac{\textit{Upper Ga ratio}}{\textit{Lower Ga ratio}} \quad (3)$$

A graphical depiction of what the terms that make up the grading factor in Equation 3 are shown in Figure 3. The “Upper depth” and “Upper Ga ratio” is the x and y coordinate where the Ga grading is fairly level or the highest point before the dip. The Lower depth and Lower Ga ratio is the x and y coordinate where the bottom of the Ga grading occurs.

Three 3-stage samples have been grown and measured by SIMS to show the amount of correction produced by application of the above correction procedure (Figures 4, 5, and 6). In these Figures, the measured profile is the data collected by the SIMS tool using the total crater depth measurement. The actual profile is the real profile generated by making multiple separate craters in the same sample at different regular time intervals and measuring each of these craters individually. The data with compensation is the corrected profile using equation 2 to modify the depth of the data points in the measured profile based on the composition. The error of the crater measurements is 3%, roughly the size of the error bars that make up the actual profile in Figures 3, 4, and 5. The first part of equation 2, the ρ_{Ga} compensates for the dependence of the sputter rate on the Ga ratio. The $(1 - \rho_{\text{Ga}}) * \text{Grading factor}$ is the term that accounts for the difference in sputter rate based on the width of the Ga grading and the change in Ga ratio in the sample.

Figure 3. Graphical depiction of the terms in Equation 3.

Figure 4. 3-stage SIMS profile of Ga ratio with respect to depth using the relative sputter rate to modify the measured profile.

Figure 5. 3-stage SIMS profile of Ga ratio with respect to depth using the relative sputter rate to modify the measured profile.

Figure 6. 3-stage SIMS profile of Ga ratio with respect to depth using the relative sputter rate to modify the measured profile.

As can be seen from Figures 4, 5, and 6, the amount of profile adjustment varies depending on the Ga gradient. There is little difference in the Ga ratio with respect to depth in Figure 4 so the measured and compensated profiles nearly line up. In sample B (Figure 5), there is a larger Ga ratio change in the sample so the difference in sputter rate is greater and thus will exaggerate the difference in profile between the measured and the compensated. Sample C

(Figure 6) has the greatest difference in sputter rate because of the largest range of Ga ratios. We can see that the compensated profile lines up well with the actual profile meaning that the model works well.

The SIMS data for the 3-stage samples shown in Figures 7, 8, and 9 shows that the Cu and Se contents in the samples are nearly uniform within the film and that the parameter varies is the Ga ratio. Figure 10 shows how the grading dips of the three 3-stage CIGS compare to each other with sample A having a wide shallow grading, sample B having a wide deeper grading, and sample C having a narrow deep grading. Looking at equation 3, we can see that sample C in Figure 6 will have the largest grading factor and hence need the most compensation from the model.

Figure 7. SIMS profile of a 3-stage sample A.

Figure 8. SIMS profile of a 3-stage sample B.

Figure 9. SIMS profile of a 3-stage sample C.

Figure 10. Comparative Ga/(Ga+In) ratio for the three 3-stage samples: A, B, and C.

4. Conclusions

We demonstrated how the sputter rate changes with respect to Ga ratio from CGS to 0.5 CIGS, primary voltage, and angle of incidence. We then used the fact that the sputter rate changes linearly in the compositional range from 0.0 to 0.5 Ga ratio at 2-5 kV and 45 and 60 degrees angle of incidence to create a point-by-point correction method to correct for the sputter rate differences in three 3-stage samples with graded Ga ratios. The model can increase the accuracy of the profile by 10% and shift the Ga ratio profile by more than 100 nm if the Ga ratio grading dip has a change in Ga ratio of 0.2 or more.

Acknowledgments

This work was partially supported by the U.S. Department of Energy, Sustainable Energy Technologies Department under Contract No. DE-SC0012704, and Brookhaven National Laboratory's Laboratory Directed Research and Development (LDRD) Program.

Special thanks is given to Isaiah Mori and Shane McMahon for their contributions to this project.

References

-
- ¹ J. Gifford, Solar Frontier hits 22.3% on CIGS Cell, PV Magazine, Dec, 8 2015.
 - ² P. Jackson, D. Hariskos, R. Wuerz, O. Kiowski, A. Bauer, T. M. Friedlmeier, Phys. Status Solidi-RRL 9, No. 1, 28-31 (2015)
 - ³ Green, Martin A., et al. "Solar cell efficiency tables (version 46)." Progress in Photovoltaics: Research and Applications 23.7 (2015): 805-812.
 - ⁴ I. Repins, S. Glynn, J. Duenow, T. J. Coutts, W. Metzger, and M. A. Contreras, "Required materials Properties for High-Efficiency CIGS Modules." NREL.CP-520-46235, (July 2009)
 - ⁵ M. A. Contreras, J. Tuttle, A. Gabor, A. Tennant, K. Ramanathan, S. Asher, A. Franz, J. Keane, L. Wang, T. Noufi, "High efficiency graded bandgap thin-film polycrystalline Cu(In,Ga)Se₂ – based solar cells". Sol Energ Mat Sol C. 41/42, 231-246 (1996)
 - ⁶ J. Lee, A. H. Kim, K-B Lee, B. K. Min, Y. Lee, "Improved quantitative analysis of Cu(In,Ga)Se₂ thin films using MCs⁺-SIMS depth profiling." Appl Phys A. 115: 1355-1364 (2014)
 - ⁷ K. Kaufmann, S. Wahl, S. Meyer, C. Hagendorf, "Quantitative elemental analysis of Photovoltaic Cu(In, Ga)Se₂ thin films using MCs⁺ clusters." Surf Interface Anal, 45, 1, 434-436. (Jan 2013)
 - ⁸ R. G. Wilson, F. A. Stevie, C. W. Magee; Secondary Ion Mass Spectrometry: A Practical Handbook for depth Profiling and Bulk Impurity Analysis, 1989, pp. I-1 – 1.6-5
 - ⁹ V. Cherepin, Secondary Ion Mass Spectrometry of Solid Surfaces, 1-30. (1987)
 - ¹⁰ D. Dwyer, S. Schujman, J. Novak, D. Metacarpa, P. Haldar, "Selenium flux effects on Cu(In,Ga)Se₂ growth rate, and control by in-line X-ray fluorescence" Proc. of the 39th IEEE Photovoltaic Specialists Conference, June 16-21, 2013, Tampa, FL, pp. 1957-1960
 - ¹¹ K. Ramanathan, J. keane, R. Noufi; Properties of High-Efficiency CIGS Thin-Film Solar Cells, 2005, 31st IEEE Photovoltaics Specialists Conference and Exhibition