EFFECT OF MAXIMUM CU RATIO DURING THREE-STAGE CIGS GROWTH DOCUMENTED BY DESIGN OF EXPERIMENT

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ABSTRACT

The impact of a Cu-rich growth period during three-stage CIGS co-evaporation on device performance was examined. Design of experiments was utilized to determine effect magnitudes and statistical significance. It was found that a Cu-rich growth period yields a statistically significant benefit for device performance. By varying film thickness, the number of moles deposited in stage 3 was also included as a variable. The latter did not produce a significant effect on efficiency. Comparison of these conclusions to other studies, and the application to manufacturing, are also discussed.

INTRODUCTION

Several studies have examined the impact of a Cu-rich growth period during three-stage CIGS co-evaporation [1]-[5]. Some of these studies have linked the Cu-rich growth period to larger grain growth and beneficial effects on device performance, while others have defined these benefits as limited to depositions at reduced temperatures or times. In general, conclusions in these studies are based on several pair-wise comparisons of depositions (e.g. comparisons of a sample with Cu-rich growth and another without for several deposition conditions) and have not included a statistical analysis of uncertainties. In this study, a designed [6] experiment utilizing 12 substrates and 144 devices was performed. Design of experiments is the discipline dedicated to planning optimal experiments and analyzing the results. The techniques are useful for a number of reasons, including allowing one to draw the strongest conclusions regarding a large number of factors with the fewest possible observations, objectively attaching magnitude and statistical significance level to all effects, providing a framework for statistical analysis via standard software packages, and randomizing the order of experiments to avoid impact from deceptive drifts.

EXPERIMENTAL

CIGS films were deposited by three-stage co-evaporation [7] onto 3” × 3” Mo/glass substrates. A thermopile was used to monitor film emissivity and thereby deduce Cu-ratio (i.e. the atomic ratio Cu/[In+Ga]) in real time [8]. Electron impact emission spectroscopy rate monitoring was used to control the number of moles deposited in stage 3. CIGS films were deposited on glass at 575°C over approximately 20 minutes. Devices were finished utilizing standard bath CdS, sputtered resistive ZnO, and sputtered ITO. Ni/Al grids and mechanical scribes were applied to form 1.16 cm^2 devices. All quoted device parameters are based on AM1.5, total-area measurements. No anti-reflective coating was applied to the devices in this study.

RESULTS

A summary of deposition conditions, CIGS properties, and device results for the samples in this study is given in Table 1. The samples form a three-level factorial experiment design with two factors (maximum Cu ratio, and moles in third stage) and several replicas; the order of sample fabrication was randomized. Final Ga ratio was controlled to 0.45 ± 0.05, while the final Cu ratio was controlled to 0.8 ± 0.07 and film thickness was kept between 2.1 and 3.4 µm. Some variations in thickness and final Cu ratio are necessary to achieve the desired combinations of maximum Cu ratio and third-stage atoms. In Table 1, maximum Cu ratio is abbreviated as “R2”. Each row of Table 1 represents one CIGS substrate on which 12 devices were measured. The table lists both average and best-device parameters for each substrate. Evaluating deposition conditions by either choice of parameter is essentially equivalent, as the average and best-device parameter values are highly correlated.

ANALYSIS AND DISCUSSION

Results of the factorial experiment were analyzed using Statistica® software [9]. The most important outputs from this analysis include, for each parameter listed in columns 2 through 9 of Table 1, an estimate of the magnitude of the two factors on the parameter, and level of statistical significance for these effects. Both linear and quadratic relationships between the factors and device parameters were explored. The level of statistical significance (“p-level”) describes the probability for the particular relationship between the factors and device parameters, with lower p-levels indicating higher statistical significances. A p-level of 5% (0.05) is a typical threshold for concluding a relationship to be statistically significant at the 95% confidence level.

Table 1: Sample and device characteristics.

Sample	Best device η (%)	Best device V_{oc} (V)	Best device J_{sc} (mA/cm^2)	Best device ff (%)	Avg η (%)	Avg V_{oc} (V)	Avg J_{sc} (mA/cm^2)	Avg ff (%)	Cu/ (In+Ga)	Ga/ (In+Ga)	thick-ness (µm)	R2	Atoms ($10^{15}/cm^2$)
Low atoms - Low R2	8.7	0.533	24.7	66	7.9	0.543	23.3	62	0.73	0.39	2.1	0.85	354
Low atoms - Ctr R2	8.5	0.619	21.2	64	7.9	0.613	20.4	63	0.76	0.49	2.2	1.05	365
Low atoms - Ctr R2	10.3	0.591	26.9	65	8.1	0.580	22.9	61	0.8	0.44	2.2	1.04	367
Low atoms - Hi R2	10.2	0.622	27.1	60	8.6	0.624	27.2	51	0.85	0.5	2.1	1.25	369
Ctr atoms - Low R2	8.8	0.525	31.3	54	7.9	0.540	25.7	58	0.85	0.43	3	0.95	420
Ctr atoms - Ctr R2	9.2	0.545	28.8	58	8.7	0.556	28.3	55	0.87	0.47	2.4	1.07	424
Ctr atoms - Ctr R2	8.8	0.560	26.7	59	7.7	0.547	24.9	56	0.85	0.49	3.4	1.03	468
Ctr atoms - Hi R2	10.3	0.598	27.3	63	9.5	0.603	25.3	62	0.87	0.48	2.4	1.11	466
Hi atoms - Low R2	7.9	0.553	23.7	60	6.6	0.587	21.0	53	0.74	0.5	3.2	0.94	647
Hi atoms - Ctr R2	9.7	0.566	26.1	66	8.6	0.527	27.1	60	0.83	0.45	2.1	1.05	591
Hi atoms - Ctr R2	8.4	0.542	27.8	56	7.6	0.555	25.4	55	0.76	0.41	2.4	1.07	594
Hi atoms - Hi R2	9.9	0.564	27.8	63	9.3	0.574	26.7	61	0.76	0.48	2.2	1.12	585

The statistically significant relationships are listed in Table 2. Effect magnitudes are defined as follows by the best fit surface for a parameter j to the data:

$$F(j, \text{low } k) \equiv \text{the value of the fit to parameter } j \text{ at the low value of factor } k \quad (1)$$

Then for linear relationships,

$$\text{Effect of factor } k \text{ on parameter } j \equiv F(j, \text{high } k) - F(j, \text{low } k) \quad (2)$$

and for quadratic relationships

$$\text{Effect of factor } k \text{ on parameter } j \equiv F(j, \text{center } k) - \tfrac{1}{2}\left[F(j, \text{low } k) + F(j, \text{high } k)\right] \quad (3)$$

Thus, a positive linear effect means the parameter increases with the factor, and a negative linear effect represents parameter increase with factor decrease. Table 2 identifies a linear dependence of efficiency and V_{oc} on maximum Cu ratio. An efficiency improvement of about 2% out of 10% is associated with an increase in maximum Cu ratio from 0.95 to 1.15. A weaker tendency of V_{oc} to decrease linearly with third-stage atoms is also identified. However, this dependence does not translate significantly to efficiency. The lack of translation of moles in stage 3 dependency from V_{oc} to efficiency may indicate that the improvement in V_{oc} is somewhat offset by changes in J_{sc} and ff, or that the effect magnitude (35 mV between the extremes) is simply not large enough to convert significantly to efficiency based on the deviation of the population tested. The best fit surfaces for these significant dependencies are shown in Figure 1. Some curvature is apparent in the surfaces, however, these quadratic terms are not statistically significant and therefore are not listed in Table 2.

Table 2: List of statistically significant relationships from this study's data.

Parameter	Is a function of:	Form	Effect Magnitude	p-level
Average η	Maximum Cu ratio	Linear	2.11	0.036
Best device η	Maximum Cu ratio	Linear	1.67	0.011
Best device V_{oc}	Maximum Cu ratio	Linear	0.058	0.009
Best device V_{oc}	Stage 3 atoms	Linear	-0.035	0.042

Comparing this study with others in the literature requires consideration of both statistics and film growth kinetics. Shafarman et al [4] conclude that the Cu-rich growth period is beneficial only for devices deposited at reduced temperatures. However, two-stage, rather than three-stage growth was utilized. The simultaneous deposition of group I and III atoms during the two-stage process may provide more time for the necessary reactions and lessen the benefit of the Cu-rich growth period, since the benefit of the Cu-rich growth period has been surmised to come from a fluxing of the CIGS grains by excess liquid Cu_2Se [3]. Other conditions that affect film kinetics, such as the presence and amount of Na, are also expected to have an impact on the benefit of the Cu-rich growth period. It also should be noted that only six samples in the two-stage study (three at each of two temperatures) were used to draw conclusions. Different groups have reported varying roles for Na during film growth, including enhancing mobility of constituent elements [12], impeding diffusion and CIGS formation [13], modifying potential barriers [14], or passivating defects [15]. It is, thus, difficult to predict whether the presence of Na should make the Cu-rich growth stage more or less beneficial. Nishiwaki et al [5] present an impressive data point quoting a 16.6% efficient device formed by three-stage deposition without the Cu-rich growth period, but provide neither data from samples with Cu-rich growth nor data from replicas without Cu-rich growth. The optimized conditions suggested by the present study (i.e. use of a Cu-rich growth period, and application of just under 400 x 10^{15} $atoms/cm^2$ in the third stage) are roughly consistent

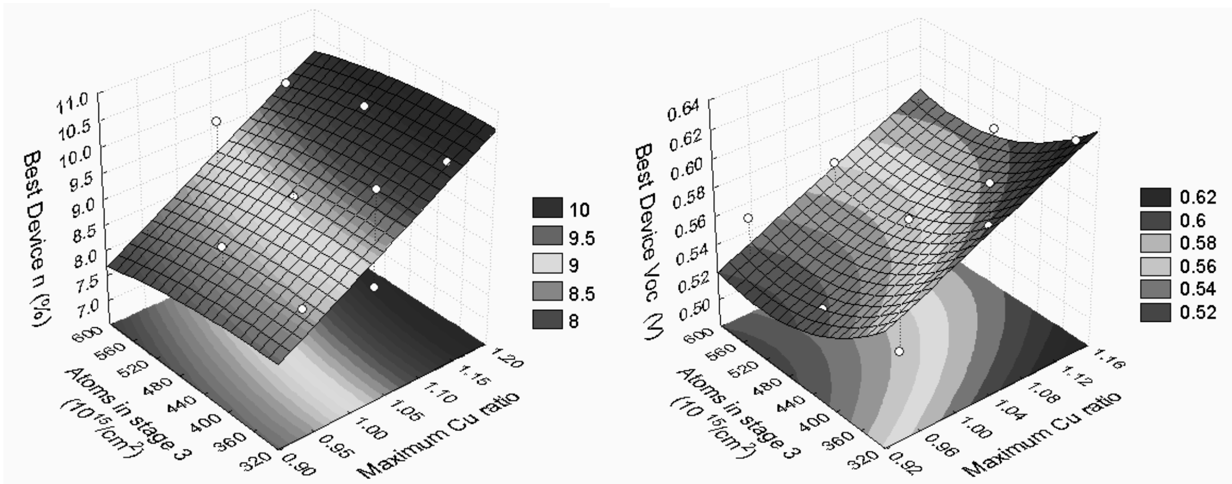


Figure 1: Best-fit surfaces for a) efficiency and b) V_{oc} as a function of maximum Cu ratio and atoms in stage 3.

with those utilized to make record CIGS devices at the National Renewable Energy Laboratory (NREL) [10][11]. This similarity exists despite an almost two-fold extension in deposition time for the NREL deposition, and the average Ga content being almost 10% less than used here.

APPLICATION TO MANUFACTURING

Given the sensitivity of bell jar devices to maximum Cu ratio, tests of the impact of maximum Cu ratio were also performed at Global Solar Energy in production roll-coaters [16]. A two-level screening test of maximum and final Cu ratio was executed. The 2×2 matrix was replicated one time for a total of eight test conditions with the planned levels for Cu-rich excursion being 1.0 and 1.1, as measured by in-situ XRF. The targets for final absorber composition (Cu/(Ga+In)) were 0.81 and 0.91. The web was processed according to baseline manufacturing process conditions yielding large area devices (total area 78 cm^2). Three thirty-cell sample panels were extracted from each condition and outliers well outside the normal distribution were removed prior to analysis.

The mean efficiency of each condition is plotted on the interaction chart in Figure 2. For films processed without a Cu-rich excursion (in process Cu/(Ga+In) ~ 1.0), the final composition had a significant effect on final efficiency; a final Cu/(Ga+In) of 0.91 was superior to 0.81.

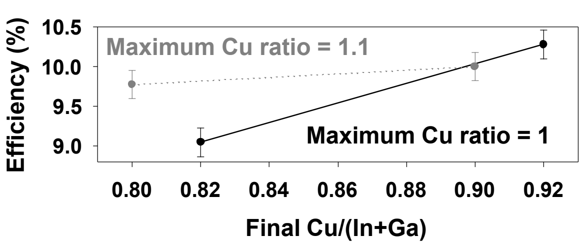


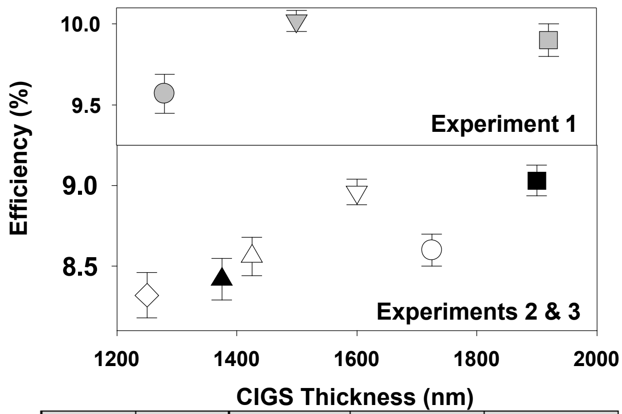
Figure 2: Interaction chart summarizing device efficiency from roll-to-roll deposited CIGS as a function of maximum and final Cu ratio.

All IV parameters (V_{oc}, J_{sc}, and fill factor) improved. For films that experienced a Cu-rich excursion (in process Cu/(Ga+In) ~ 1.1), the efficiency was much less dependent on the final Cu/(Ga+In). The latter process was more robust, although the mean efficiency under the best conditions may be slightly lower than the case where the film did not transition through a Cu-rich growth regime.

As somewhat different conclusions were reached from the bell jar and roll-coater experiments, further examination of conditions in the roll-coater were performed. In these follow-up experiments, deposition temperature and film thickness (as varied either by source temperature or deposition time) were included as factors. Both 1 variable at a time and 2×2 DOE matrices – both with multiple replicas – were employed. Interpretation is more complex than for the earlier experiments, as – even for a constant maximum Cu ratio – thickness and resultant Ga profile (as determined by SIMS and/or AES) impact performance. Substrate temperature is also a factor. These results are summarized in Figure 3, which shows efficiency as a function of the newly-introduced factors, for constant maximum Cu ratio. The legend lists the process conditions for each symbol.

CONCLUSIONS

A designed experiment was utilized to examine the effect of maximum Cu ratio and moles deposited during stage 3. A Cu-rich growth period was found to yield a statistically significant benefit for device performance through open-circuit voltage. An increasing number of moles deposited during stage 3 was found to cause a slight decrease in V_{oc}, but this dependency did not translate significantly to efficiency. These conclusions are consistent with some studies in the literature and at odds with others. Differences are likely related to the film growth kinetics of the different processes, including reaction time, temperature, and the presence and amount of Na. Small sample sets may also have influenced the conclusions in some studies.



Data Point	Web T	Source T	Web Speed	Max. Cu ratio
●	High	High	High	Constant
▼	High	High	Medium	Constant
■	High	High	Low	Constant
▲	High	Low	Medium	Constant
■	High	High	Medium	Constant
○	Low	High	Medium	Constant
▽	High	High	Medium	Constant
◇	High	High	High	Constant
△	Low	High	High	Constant

Figure 3: Results from experimental design varying deposition temperature and CIGS thickness (by source temperature or web thickness) at the roll-to-roll production scale under constant Cu ratio.

Designed experiments performed at the production roll-to-roll level revealed the effect of maximum Cu ratio to be convoluted with film thickness, temperature, and time. DOE based efforts are currently underway to fully optimize conditions and assign the dependencies to physical mechanisms such as Ga profile.

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REFERENCES

[1] D. S. Albin, G.D. Mooney, A. Duda, J. Tuttle, R. Matson, R. Noufi, *Solar Cells* **30**, 47, (1991).

[2] A.M. Gabor, J.R. Tuttle, D.S. Albin, M.A. Contreras, R. Noufi, A.M. Herman, "High-efficiency $CuIn_xGa_{1-x}Se_2$ solar cells made from $(In_x,Ga_{1-x})_2Se_3$ precursor films", *Applied Physics Letters*, **65**(2), (1994), pp. 198-200.

[3] B. M. Keyes, P. Dippo, W. Metzger, J. AbuShama, R. Noufi, "$Cu(In,Ga)Se_2$ Thin Film Evolution During Growth – A Photoluminescence Study", *Conference Record of the Twenty-Ninth IEEE Photovoltaics Specialists Conference*, (2002).

[4] W.N. Shafarman, J. Zhu, "Effect of Substrate Temperature and Deposition Profile on Evaporated $Cu(In,Ga)Se_2$ films and devices", *Thin Solid Films* **361-362**, (2000), pp. 473-477.

[5] S. Nishiwaki, T. Satoh, S. Hayashi, Y. Hashimoto, T. Negami, T. Wada, "Preparation of $Cu(In,Ga)Se_2$ thin films from In-Ga-Se precursors for high-efficiency solar cells", *Journal of Materials Research* **14** (12) , (1999), pp. 4514-4520.

[6] See, for example, G.E.P. Box, W.G. Hunter, J.S. Hunter, *Statistics for Experimenters*, John Wiley & Sons, (1978), pp. 289 ff.

[7] M.A. Contreras, J. Tuttle, A. Gabor, A. Tennant, K. Ramanathan, S. Asher, A. Franz, J. Keane, L. Wang, J. Scofield, R. Noufi, "High Efficiency $Cu(In,Ga)Se_2$-Based Solar Cells: Processing of Novel Absorber Structures," *Proceedings of the First World Conference on Photovoltaic Energy Conversion*, (1994), pp. 68-75.

[8] I.L. Repins, D. Fisher, W.K. Batchelor, L. Woods, M.E. Beck, "A Non-Contact Low-Cost Sensor for Improved Repeatability in Co-Evaporation of High-Quality CIGS", *Progress in Photovoltaics*, May, 2005, in press.

[9] http://www.statsoft.com/textbook/stathome.html

[10] K. Ramanathan, M. A. Contreras, C.L. Perkins, S. Asher, F. S. Hasoon, J. Keane, D. Young, M. Romero, W. Metzger, R. Noufi, J. Ward, A. Duda, "Properties of 19.2% Efficiency $ZnO/CdS/CuInGaSe_2$ Thin-film Solar Cells," *Progress in Photovoltaics: Research and Applications*, **11**, (2003), pp.225-230.

[11] Logged flux data from NREL deposition S2051.

[12] M. Bodegard, L. Stolt, J. Hedstrom, "The Influence of Sodium on the Grain Structure of $CuInSe_2$ films for Photovoltaic Applications," *12th European PVSEC*, (1994), pg. 1743.

[13] D. Rudmann, D. Bremaud, H. Zogg, A.N. Tiwari, "Na Incorporation for Low-Temperature $Cu(In,Ga)Se_2$ Growth," *Proceedings of the 19th European PVSEC*, (2004).

[14] J. Holz, F. Karg, H. von Philipsborn, "The Effect of Substrate Impurities on the Electronic Conductivity in CIS Thin Films," *12th European PVSEC*, (1994), pg. 1592.

[15] M. Ruckh, D. Schmid, M. Kaiser, R. Schaffler, T. Walter, and H.W. Schock, "Influence of Substrates on the Electrical Properties of $Cu(In,Ga)Se_2$ Thin Films," *First World Conference on Photovoltaic Energy Conversion*, (1994), pg. 156.

[16] S. Wiedeman, M.E. Beck, R. Butcher, I. Repins, N. Gomez, B. Joshi, R.G. Wendt, and J.S. Britt, "CIGS Module Development on Flexible Substrates," *Proceedings of the 29th IEEE Photovoltaics Specialists Conference*, (2002), pp. 575-578.