

Na Diffusion and Device Performance of AgBr Treated CuGaSe₂ Thin Films

Elizabeth Palmiotti^a, Polyxeni Tsoulka^b, Thomas Lepetit^b, Nicolas Barreau^b, and Angus Rockett^a

^aColorado School of Mines, Department of Metallurgical and Materials Engineering, Golden, CO, U.S.A.

^bUniversité de Nantes, CNRS, Institut des Matériaux Jean Rouxel, IMN, F-44000, Nantes, France

Abstract—Previous work demonstrated that uniform CuGaSe₂ (CGS) thin films with large grains could be grown using a short AgBr vapor treatment during growth. Devices made with this treated CGS showed better performance compared to devices made with standard material. Here, it is shown that AgBr treated CGS device performance worsens over time and is attributed to the suppression of Na diffusion. A NaF post-deposition treatment is shown to effectively introduce Na into the AgBr treated CGS film and prevent device degradation.

Keywords— *Copper Gallium Diselenide, Post-Deposition Treatment, Co-Evaporation, Thin Film*

I. INTRODUCTION

The development of tandem photovoltaics with a silicon bottom cell and wide band gap top cell is a path to quickly increase efficiency while utilizing existing manufacturing lines. CuGaSe₂ (CGS) is a top cell candidate due to its band gap (1.7 eV) which is well matched to silicon. Typical co-evaporation deposition procedures optimized for CuIn_{1-x}Ga_xSe₂ (CIGS) are often used for CGS deposition, resulting in devices with limited efficiencies due to Cu₂Se phase formation and grain size non-uniformities [1], [2]. This is likely attributed to the slower rate of formation of CuGaSe₂ compared to CuInSe₂ [3], [4], [5], meaning CIGS deposition procedures are not suitable for CGS.

This was first addressed by a modified co-evaporation procedure which introduced two, thirty-minute anneals at a high substrate temperature [1]. Although the modified procedure improved CGS material properties and device performances, the long process is not suitable for manufacturers. In our previous work we demonstrated that the long anneals in the modified procedure could be replaced by a short AgBr vapor treatment after the second stage of the co-evaporation process [6]. The AgBr treatment resulted in large grains, removal of the Cu₂Se phase, and enhanced device properties driven by V_{oc} in half the time of the previous modified procedure [6].

Typically, laboratory-scale CIGS devices improve with ageing. Characterization of the AgBr treated devices after many weeks showed a decay of performance and significant efficiency losses. In this work it is noted that AgBr treated films had suppressed Na diffusion from the soda-lime glass substrate. The ageing and Na diffusion of AgBr treated CGS devices were studied and a NaF post-deposition treatment tested to solve this problem.

II. EXPERIMENTAL

A. Sample and Device Fabrication

CGS films were deposited from elemental Cu and Ga sources by co-evaporation under a Se overpressure onto molybdenum-coated soda-lime glass (SLG) substrates held at 575°C. The co-evaporation deposition followed standard and modified versions of the Cu-poor/Cu-rich/Cu-off (CuPRO) [7] procedure. Reference samples followed a standard CuPRO procedure and were labelled as ‘CuPRO.’ The modified procedure included two thirty-minute anneals in Se overpressure as described in [1] and were labelled ‘CuPRO(M).’ Samples undergoing AgBr treatment were introduced to AgBr vapor in a Se overpressure as described in [6]. AgBr treated samples were labelled as ‘CuPRO+AgBr’ and ‘CuPRO(M)+AgBr’, respectively. Some films received a NaF post-deposition treatment (PDT).

Devices were completed with the following architecture: SLG/Mo/CGS/CdS/ZnO/ZnO:Al. After the CGS deposition, the samples were dipped in a 0.05 M KCN solution for two minutes. The CdS buffer layer was grown by chemical bath deposition. The ZnO/ZnO:Al window layer was deposited using rf-sputtering. The 0.5 cm² devices were completed with Ni-Al-Ni metallic grids and separated by mechanical scribing.

B. Characterization

Elemental depth profiling was studied by time-of-flight secondary ion mass spectroscopy (TOF-SIMS) with an Ion TOF 5 SIMS. Depth profiling was performed using a 1 kV Cs⁺ ion beam and analysis using a 30 kV Bi₃ beam. Current density voltage (J-V) data was collected under standard testing conditions (STC). The sample was placed on a metal plate which was held at 25°C using a thermoelectric cooler and illuminated under AM1.5 using a solar simulator at 1000 W/m².

III. RESULTS

A. TOF-SIMS

The elemental distribution through the CGS films was studied by positive ion TOF-SIMS. To compensate for minor drift in the analyzer beam intensity, elemental intensity was normalized to the total ion yield. Cu, Ga, and Se normalized intensities were mostly constant through all films and devices in this study though the Na signal varied per sample; a representative example is shown in Appendix A. This work

investigates the influence of Na on CGS device performance, thus, only the Na^+ signal is plotted.

Figure 1 shows the Na^+ ion signal on a logarithmic scale for the standard CuPRO with and without AgBr treatment (Figure 1(a)) and CuPRO(M) with and without AgBr treatment (b). The low sputter time region of all samples shows the Na^+ signal in the CGS film. The increase at ~ 5000 s sputter time in Figure 1(a) is at the CGS/Mo interface and the second step at ~ 7000 s shows the Mo/SLG interface. Note that the same sputtering parameters were used for all samples.

The high intensity Na^+ signals for the CuPRO and CuPRO(M) samples are typical for films grown on SLG at elevated temperatures. Both films that received a AgBr treatment show significantly less Na^+ in the film. The Na^+ signal for CuPRO+AgBr is approximately three orders of magnitude less than that for CuPRO. The CuPRO(M)+AgBr Na^+ signal is approximately one order of magnitude less than CuPRO(M). Although a AgBr treatment to a CuPRO(M) sample is not standard, it shows that introducing two, thirty-minute anneals does not promote Na diffusion as seen in the samples without AgBr treatment.

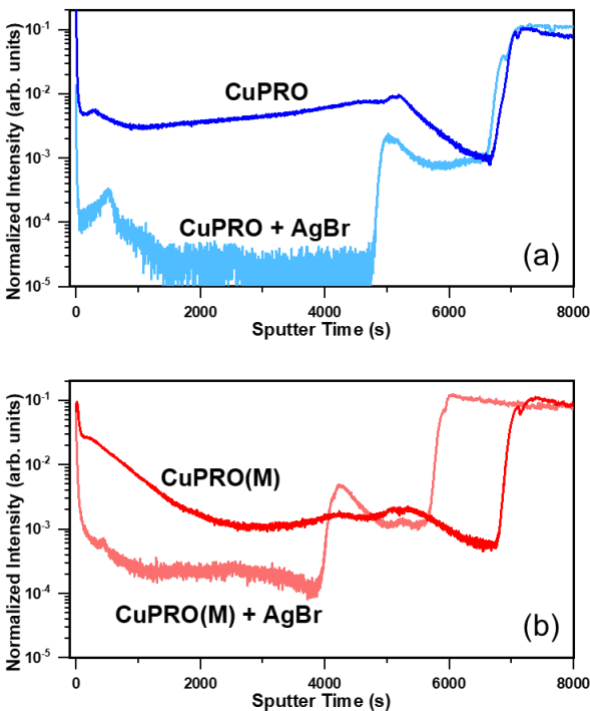


Fig. 1. Positive ion Na^+ TOF-SIMS scans collected for (a) CuPRO with (light blue) and without (blue) AgBr treatment and (b) CuPRO(M) with (light red) and without (red) AgBr treatment.

Na diffusion in CIGS films is dominated by grain boundary diffusion as shown using atom probe tomography [8], [9]. The AgBr vapor treatments were inspired by the CdCl_2 treatment of CdTe films, which acts through Cl segregation into grain boundaries [10]. If it is assumed that the AgBr treatment of CGS films similarly works through grain boundaries, we propose that the AgBr displaces Na in the grain boundaries. The increased Na^+ signal at the CGS/Mo interface for both AgBr treated

samples suggests the Na may be displaced to and collects at this interface.

A NaF post-deposition treatment was performed on a CuPRO+AgBr CGS film. The Na^+ signal for this CuPRO+AgBr+NaF CGS films was overlaid on Figure 1(a) and is shown in orange in Figure 2. CuPRO+AgBr+NaF has two orders of magnitude more Na compared to CuPRO+AgBr and slightly less than CuPRO. Notably, the Na barrier at the CGS/Mo interface of CuPRO+AgBr disappears.

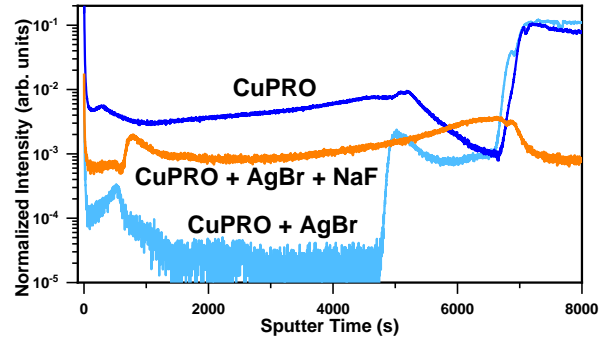


Fig. 2. Positive ion Na^+ TOF-SIMS scans collected for CuPRO with (light blue) and without (blue) AgBr treatment. The scan in orange is the CuPRO sample prepared with AgBr treatment and NaF post-deposition treatment.

B. Device Results

Devices were completed using the CuPRO+AgBr and CuPRO+AgBr+NaF films studied in Figure 2. The highest efficiency device per sample was studied using J-V and device parameters were extracted (Figure 3). Device parameters were collected when the devices were completed (Week No. 0) and weekly thereafter. The initial CuPRO+AgBr+NaF device has a higher efficiency, as expected [11], [12], due to a high J_{sc} and V_{oc} .

All device parameters decrease on a weekly basis for CuPRO+AgBr. The decrease in efficiency is largely driven by decreases in J_{sc} and Fill Factor. The CuPRO+AgBr+NaF device parameters fluctuate, but generally do not change over time.

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REFERENCES

- [1] P. Tsoulka, A. Rivalland, L. Arzel, and N. Barreau, "Improved CuGaSe₂ absorber properties through a modified co-evaporation process", *Thin Solid Films*, 709, 2020. DOI: 10.1016/j.tsf.2020.138224.
- [2] P. Tsoulka, N. Barreau, I. Braems, L. Arzel, and S. Harel, "Detrimental copper-selenide bulk precipitation in CuIn_{1-x}Ga_xSe₂ thin-film solar cells. A possible reason for the limited performance at large x?", *Thin Solid Films*, 712, 2020. DOI: 10.1016/j.tsf.2020.138297.
- [3] M. Purwins, A. Weber, P. Berwian, G. Müller, F. Hergert, S. Jost, and R. Hock, "Kinetics of the reactive crystallization of CuInSe₂ and CuGaSe₂ chalcopyrite films for solar cell applications", *Journal of Crystal Growth*, 287, 408-413, 2006. DOI: 10.1016/j.jcrysgro.2005.11.054.
- [4] S. Kim, W.K. Kim, R.M. Kaczynski, R.D. Acher, S. Yoon, T.J. Anderson, and O.D. Crisalle, "Reaction kinetics of CuInSe₂ thin films grown from bilayer InSe/CuSe precursors", *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 23, 310-315, 2005. DOI: 10.1116/1.1861051.
- [5] W.K. Kim, E.A. Payzant, S. Kim, S.A. Speakman, O.D. Crisalle, and T.J. Anderson, "Reaction kinetics of CuGaSe₂ formation from a GaSe/CuSe bilayer precursor film", *Journal of Crystal Growth*, 310, 2987-2994, 2008. DOI: 10.1016/j.jcrysgro.2008.01.034.
- [6] E. Palmiotti, P. Tsoulka, D. Poudel, S. Marsillac, N. Barreau, A. Rockett, and T. Lepetit, "Homogeneous CuGaSe₂ Growth by the CuPRO Process with In-Situ AgBr Treatment", unpublished.
- [7] J. Kessler, C. Chityuttakan, J. Lu, J. Schödlström, and L. Stolt, "Cu(In,Ga)Se₂ Thin Films Grown with a Cu-Poor/Rich/Poor Sequence: Growth Model and Structural Considerations", *Progress in Photovoltaics: Research and Applications*, 11, 319-331, 2003. DOI: 10.1002/ppi.495.
- [8] F. Couzinie-Devy, E. Cadel, N. Barreau, L. Arzel, and P. Pareige, "Atom probe study of Cu-poor to Cu-rich transition during Cu(In,Ga)Se₂ growth", *Applied Physics Letters*, 99, 2011. DOI:10.1063/1.3665948.
- [9] A. Stokes, M. Al-Jassim, D. Diercks, A. Clarke, and B. Gorman, "Impact of Wide-Ranging Nanoscale Chemistry on Band Structure at Cu(In,Ga)Se₂ Grain Boundaries", *Scientific Reports*, 7, 1, 1-11, 2017. DOI: 10.1038/s41598-017-14215-0.
- [10] M. Kim, S. Sohn, and S. Lee, "Reaction kinetics study of CdTe thin films during CdCl₂ heat treatment", *Solar Energy Materials and Solar Cells*, 95, 8, 2295-2301, 2011. DOI:10.1016/j.solmat.2011.03.044.
- [11] D. Rudmann, A. da Cunha, M. Kaelin, F. Kurdesau, H. Zogg, A. Tiwari, and G. Bilger, "Efficiency enhancement of Cu(In,Ga)Se₂ solar cells due to post-deposition Na incorporation", *Appl. Phys. Lett.*, 84, 7, 1129-1131, 2004. DOI: 10.1063/1.1646758.
- [12] F. Pianezzi, P. Reinhard, A. Chiril'a, B. Bissig, S. Nishiwaki, S. Buecheler, and A. Tiwari, "Unveiling the effects of post-deposition treatment with different alkaline elements on the electronic properties of CIGS thin film solar cells", *Phys. Chem. Chem. Phys.*, 16, 8843-8851, 2014. DOI:10.1039/c4cp00614c.

APPENDIX A

Figure A.1 shows an example of the Cu, Ga, Se, versus Na elemental distributions for CGS films prepared by CuPRO(M)+AgBr and CuPRO(M). The Cu, Ga, and Se signals are mostly constant through these films which is representative of all films and devices in this study.

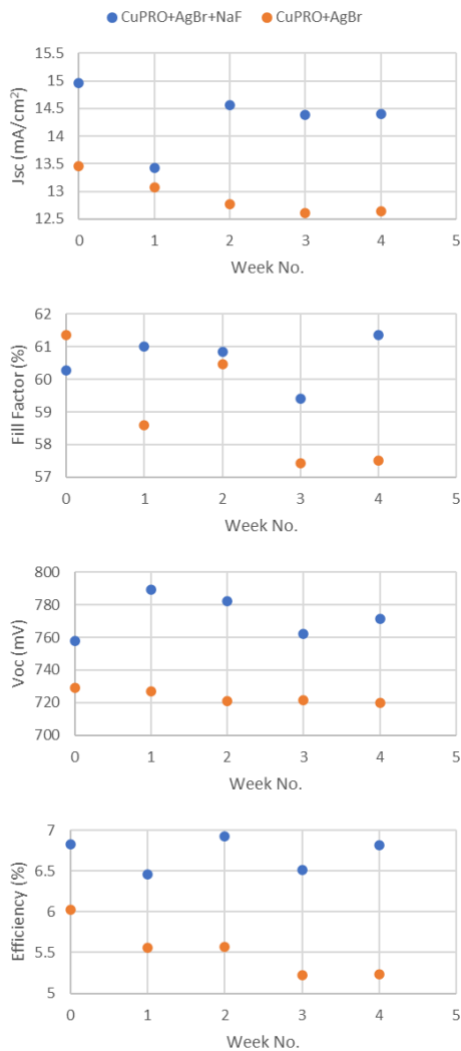


Fig. 3. Device parameters extracted from current density-voltage measurements for CuPRO+AgBr and CuPRO+AgBr+NaF collected weekly for four months.

IV. CONCLUSION

It is hypothesized that the Na barrier at the CGS/Mo interface caused by the AgBr treatment causes the device to degrade rapidly with time. In this work we have demonstrated that a NaF PDT can re-introduce Na into the AgBr treated CGS film, remove this Na barrier, and prevent device degradation. Weekly EQE data was also collected and will be reported at the conference. This work shows that further deposition and PDT optimization is necessary for metal halide treated CGS films and devices.

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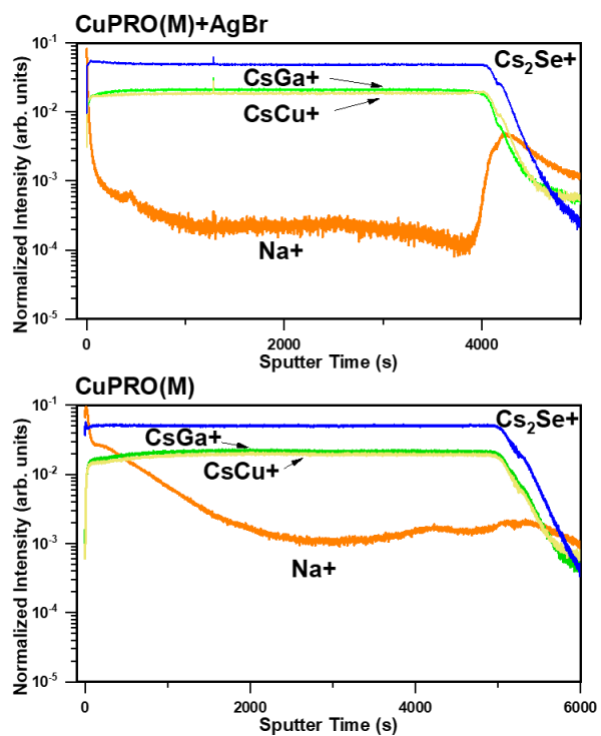


Fig. A1. Positive ion TOF-SIMS Cu, Ga, Se, and Na signals for CGS films prepared by CuPRO(M)+AgBr and CuPRO(M).