Effect of Metal Halides Treatment on High Throughput Low Temperature CIGS Solar Cells

Deewakar Poudel[1], Benjamin Belfore[1], Adam Masters[1], Elizabeth Palmiotti[2], Angus Rockett[2] and Sylvain Marsillac[1]

[1]Virginia Institute of Photovoltaics, Old Dominion University, Norfolk, VA 23529, USA

[2]Dept. of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401, USA

***Abstract*— Copper indium gallium diselenide (CIGS) semiconductor thin films were deposited at high rate and low temperature using single-stage thermal co-evaporation process on molybdenum back contact. A post deposition treatment was done by flashing AgBr at 350 ºC to induce recrystallization. Changes in morphology were confirmed by SEM, with an observed increase in grain size, as well as by XRD measurements, with a decrease in FWHM. Device results show an improvement of the performance after the AgBr vapor treatment, as all the photovoltaic parameters enhanced. Overall, AgBr seems to be a suitable transport agent and beneficial for device fabrication.**

Keywords*— *Cu(In,Ga)Se₂, recrystallization, AgBr

I. Introduction

CIGS high absorption coefficient and tunable band gap makes it a good candidate in the field of thin film photovoltaic technology [1]. Conventional deposition processes for this technology often require high substrates temperature (up to 600 ºC) to get large grain size and are also time consuming. The economic viability of CIGS solar modules is affected by this duration and high temperature process. A single-stage process (where all source temperatures are kept constant) is simple to operate and faster as compared to the traditional three stage process, potentially providing high throughput for industrial applications [2]. Furthermore, using a recrystallization process, enhancing grain growth, might be a suitable approach to get high quality film and better device performance [3]. This recrystallization and grain growth could be achieved by the post deposition treatment of CIGS semiconductor thin films by metal halides.

In this work, we studied the post deposition treatment by silver bromide vapor of CIGS semiconductor thin films, deposited by single-stage process at a high rate and low temperature.

II. Experimental methods

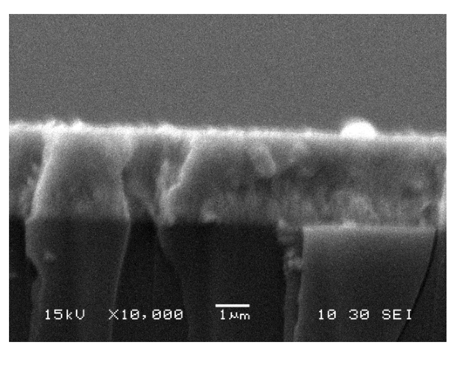
A single stage co-evaporation process was used to fabricate the CIGS semiconductor thin films. The final device structure is the following: SLG/Mo/CIGS/CdS/i-ZnO/ITO/Grids. The back contact molybdenum bilayer was deposited by dc sputtering magnetron. The Cu-poor films were grown at substrate temperature of 350 ºC for both as-deposited and AgBr treated samples. The substrate and source temperatures were kept constant throughout the process. The silver bromide post deposition treatment was done by flashing 60 mg in 2 minutes. Half of the samples were set aside for characterization, while the other half were converted to completed devices.

The crystallographic structure analysis was done by symmetric θ-2θ X-ray diffraction and analyzed using the International Center for Diffraction Data (ICDD) database. Cross-section morphological analyses were performed by scanning electron microscope (SEM). The surface roughness was measured by atomic force microscopy (AFM). The photovoltaic characteristics were evaluated by external quantum efficiency (QE) measurements (QEX7, PV measurements Inc.) and current density-voltage (J-V) measurements (IV5, PV measurements Inc.) done under AM 1.5G with a light intensity of 100 mW/cm^2 at 25°C.

III. Results and discussions

The CIGS samples were recrystallized at 350 °C in an AgBr environment by flashing 60 mg for 2 minutes after CIGS deposition. Samples with no treatment, named as-deposited, were also prepared separately.

Figure 1 shows the cross-sectional SEM images of as-deposited and recrystallized samples. A change in grain structure can be observed as small grain changes into larger ones after the treatment. The grains for the recrystallized films seemed to be compact and uniform, as compared to the as-deposited samples. The AFM images of the as-deposited and recrystallized samples are shown in Figure 2. The roughness of the surface increases slightly after the treatment as the rms roughness increases from 20.1 nm (as-deposited) to 26.7 nm (AgBr treated).



This research was supported by the Department of Energy Contract No. DE-EE0007551.

indicating potentially a redistribution of the gallium content in the films. This phenomena was observed previously, whereby the rerystallization process leading to an increase in grain size, is also associated with a redistribution of the elements in the films. This will be further studied by SIMS.

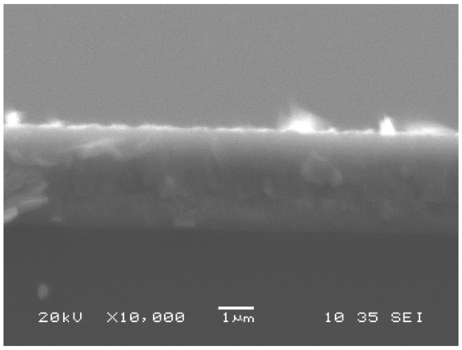


Fig. 1. Cross-section scanning electron microscopy micrographs of CIGS films: as-deposited (top) and recrystallized (bottom) at 350 °C by AgBr vapor treatment.

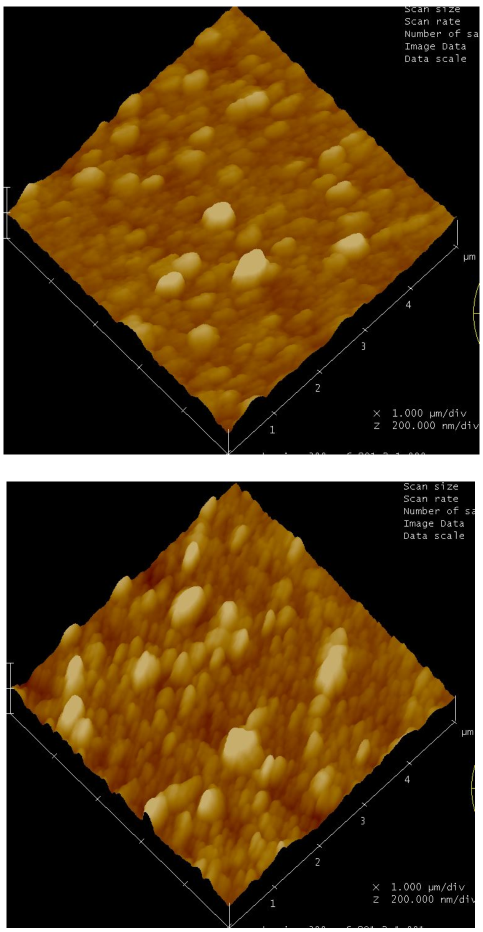


Fig. 2. Atomic Force Microscope images of CIGS films: as-deposited (top) and recrystallized (bottom) at 500 °C by AgBr vapor treatment.

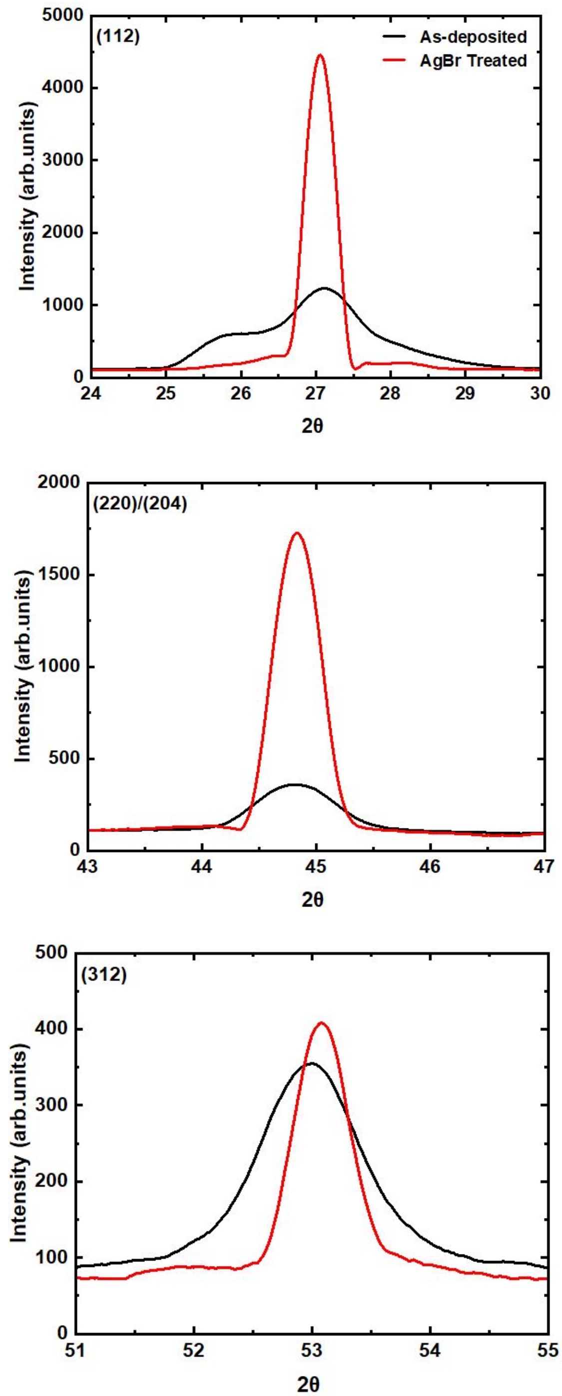


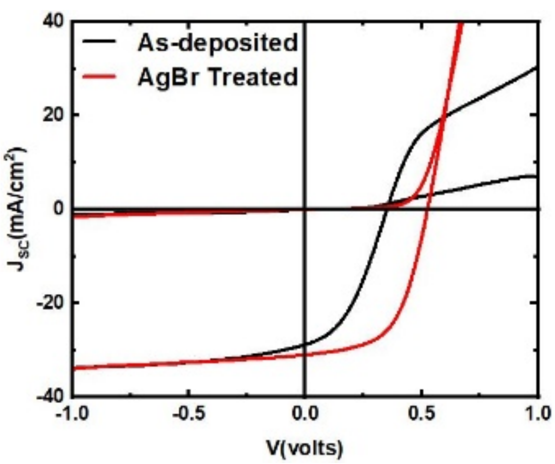
Fig. 3. XRD plots (full spectrum, (112), (204) and (312) peaks) for as-deposited (black) and AgBr treated (red) CIGS samples.

Figure 3 shows the XRD measurements for the as-deposited and recrystallized films. As one can see Table 1, an increase in peak intensity and decrease in full width half maxima (FWHM) was observed for all the major peaks ((112), (220)/(204) and (312)) suggesting an increase in crystallinity which is consistent with the SEM results. One can also see Figure 3 that for the (112) peak, the as-deposited films seem to have two peaks, while only one peak is observed for the AgBr treated samples,

TABLE I. XRD RESULTS FOR AS-DEPOSITED AND AGBR TREATED SAMPLES AT 350 °C

	As-deposited			AgBr-Treated		
Peaks	(112)	(204)	(312)	(112)	(204)	(312)
Angles (deg)	26.9	44.7	52.8	27.2	44.7	53.2
FWHM (deg)	1.27	0.63	0.85	0.23	0.29	0.16
Int. I (cps deg)	1284	357	355	4454	1725	408

Representative current-voltage and external quantum efficiency curves for the devices are shown Figure 4. The solar cell devices were completed for as-deposited and AgBr treated samples. After the post deposition treatment by AgBr, the device shows significant improvements in device performance. All the photovoltaic parameters, V_{OC} , J_{SC} and FF increases from 0.35 V to 0.53 V, 28.5 mA/cm^2 to 30.3 mA/cm^2 and 40.2 % to 56.1 % respectively. The overall efficiency increases from 4 % to 8.9 %. The diode parameters were extracted by fitting a single diode model to the dark J-V curves. The reverse saturation current density decreased (from 5.2E-04 mA/cm^2 to 4.4E-05 mA/cm^2), the series resistance decreased (from 5.7 Ω.cm^2 to 2.5 Ω.cm^2), the diode ideality factor decreased (from >2 to 1.88) whereas the shunt resistance increased (from 800 Ω/cm^2 to 1100 Ω/cm^2) after the AgBr treatment. All these changes in parameters correlate well with an increase in performance for the device after AgBr treatment. The QE curve confirm a small increase in current collection at all wavelengths.



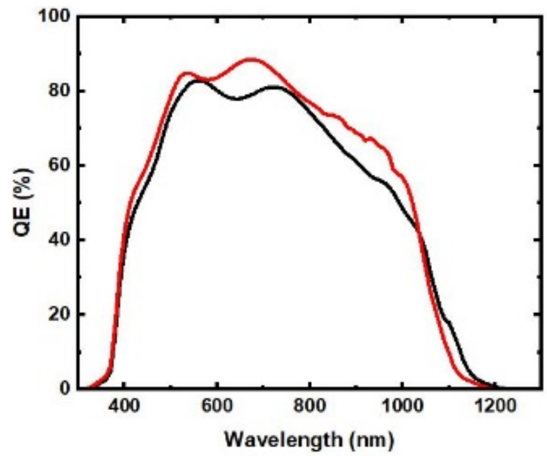


Fig. 4. Representative I-V and QE curves for the as-deposited and AgBr treated CIGS samples.

IV. CONCLUSION

The post-deposition treatment and recrystallization by AgBr of CIGS thin films deposited at low temperature and high rate by single stage process was studied. Changes in morphology were observed by SEM and confirmed by XRD measurements, with a decrease in FWHM and an increase in peak intensity. The surface roughness does not seem much affected by the treatment. Device performance increases after the AgBr treatment as V_{OC}, J_{SC} and FF all increase. These results indicate that AgBr acts as a good transport agent even in case of low temperature CIGS deposition. Further characterization will be needed to understand fully the effect of AgBr, including secondary ion mass spectrometry to assess how the elements are redistributed in the films, and Hall effect measurements to assess the impact of the treatment on electrical properties.

ACKNOWLEDGMENT

This research was supported by the Department of Energy Contract No. DE-EE0007551.

REFERENCES

[1] T. Kato, "Cu (In, Ga)(Se, S) 2 solar cell research in Solar Frontier: Progress and current status," *Japanese Journal of Applied Physics,* vol. 56, no. 4S, p. 04CA02, 2017.

[2] H. Wang *et al.*, "Effect of substrate temperature on the structural and electrical properties of CIGS films based on the one-stage co-evaporation process," *Semiconductor science and technology,* vol. 25, no. 5, p. 055007, 2010.

[3] H. Rodriguez-Alvarez *et al.*, "Recrystallization of Cu (In, Ga) Se2 thin films studied by X-ray diffraction," *Acta Materialia,* vol. 61, no. 12, pp. 4347-4353, 2013.