Grain Enhancement in Polycrystalline $CuGaSe_2$ by AgBr Vapor Treatment

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***Abstract*— Copper Gallium diselenide ($CuGaSe_2$ or CGS) thin film were deposited using a three-stage thermal co-evaporation process on molybdenum coated soda lime glass. Recrystallization was carried after the second stage by flashing AgBr for 2 mins. The change in morphology, structure and depth profile were studied after the treatment. SEM and XRD showed an increase in grain size and enhanced crystallinity. A decrease in sodium profile after the treatment was observed through SIMS measurements. Overall, AgBr treatment of CGS seems to be promising for the improvement of film quality, which could help with enhanced device fabrication in the future.**

***Keywords*— $CuGaSe_2$, recrystallization, AgBr**

I. Introduction

The use of wide bandgap chalcopyrite material devices could potentially allow the fabrication of high efficiency photovoltaic devices in tandem structure. Due its bandgap values, comparatively high absorption coefficient and cost, CGS with a direct bandgap of 1.7 eV is thought to be one of the most important contenders for top cell fabrication in thin films solar cells, as its with low band gap $CuInSe_2$ in tandem devices promises high efficiency. The highest efficiency reported for CGS solar cells to date remain somewhat low, reaching value of 11.9 % and thus additional development in enhancing material properties and device performance are necessary to achieve potential application. The control of defects present at the surface, interfaces, and bulk with alkali-metal doping along with Cu-deficient phases at grain boundaries is essential to improve this photovoltaic device performance [1, 2]. It is important to note that the microstructure of these chalcopyrite thin films can change significantly after recrystallization due to change in orientation and grain growth [3].

We have previously shown that metal halides can act as transport agents to recrystallize CIGS and enhance grain growth [4]. High-rate depositions were achieved by post-deposition vapor treatment by alkali and metal halides, and recrystallization of CIGS thin films. In this work, we studied various experimental conditions allowing post deposition recrystallization with AgBr vapor treatment of CGS films fabricated at 500 ºC.

II. Experimental Methods

A bilayer of molybdenum film was deposited by dc magnetron sputtering on soda lime glass (SLG) substrates, with a first layer at low pressure for adhesion and a second layer at high argon pressure for conductivity. A three stage CGS deposition was performed on these SLG/Mo substrates at a high deposition rate (around 10 µm/hr). The CGS grown was about 1.5 µm thick. The first, second and third stage temperatures were kept at 350 ºC, 500 ºC and 500 ºC respectively. The substrate temperature was observed using a thermocouple positioned at the back of the substrate and a pyrometer targeted at the growing film. The recrystallization was performed between the second and third stage. 40 mg of AgBr was flashed over 2 minutes. The flux was varied by changing the AgBr source temperature. As-deposited samples were also fabricated without AgBr treatment.

Time of flight secondary ion mass spectrometry (SIMS) was used to measure the compositional variation as a function of depth in the device. The crystallographic structures analysis was done by symmetric θ-2θ X-ray diffraction and analyzed using the International Center for Diffraction Data (ICDD) database. Cross-section morphological analysis were performed by scanning electron microscope (SEM). The surface roughness was measured by atomic force microscopy (AFM). The composition was measured by X-ray fluorescence (XRF).

III. Results and Discussions

The CGS samples were recrystallized at 500 °C, by flashing AgBr for 2 minutes at the end of the 2nd stage. The Ag halide was introduced in between the 2nd and 3rd stages to control the composition of group I, and avoid having group I rich films. The cross-section of the films as-deposited and after recrystallization was observed by SEM as shown in Figure 1. Significant changes were observed after the AgBr vapor treatment. The small grains observed for the as-deposited films transformed into larger grains of about a micrometer size, indicating that the AgBr acts as a suitable transport agent to generate large grains. Looking at the AFM (Figure 2), one can see that the surface roughness increases slightly after the treatment, as the rms roughness increases from 35.4 nm (as-deposited) to 39.3 nm (AgBr treated). This is in good agreement with the SEM images, where the as-deposited films appear

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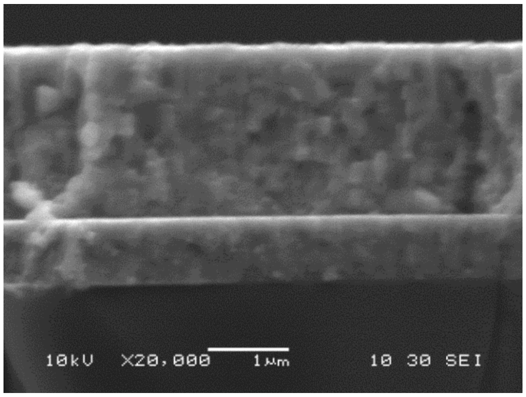
quite smooth while the recrystallized films have some non-uniformities associated with some larger grains.



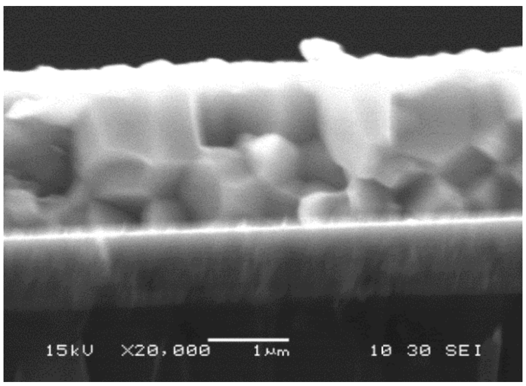
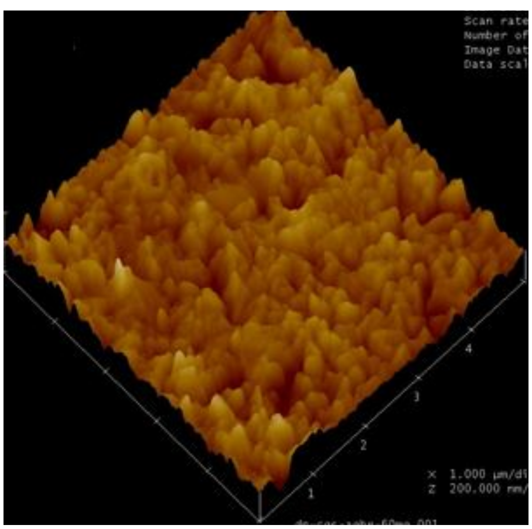


Fig. 1. Cross-section Scanning Electron Microscopy micrographs of CGS films: as-deposited (top) and recrystallized (bottom) at 500 °C by AgBr vapor treatment.



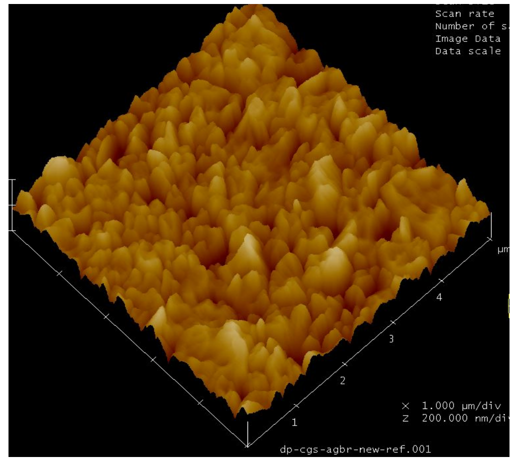


Fig. 2. Atomic Force Microscope images of CGS films: as-deposited (top) and recrystallized (bottom) at 500 °C by AgBr vapor treatment.

XRD measurements were completed on the as-deposited and recrystallized films to understand how the crystalline structure of the films changed with AgBr treatment. For the four main peaks observed ((112), (220)/(204) and (312)), one can observe a decrease in full width at half maxima (FWHM) in all the peaks, which is consistent with an increase in grain size observed with SEM. One can also notice the increase in peak intensity in the case of the (220)/(204) peak, with a decrease in the other directions, which indicates a change in preferred orientation towards the (220)/(204) peak after recrystallization. There is a small shift in peak position between the as-deposited and the recrystallized films, with slightly higher angles for the recrystallized films. Such behavior was previously observed for CGS films with slightly different gallium content [2]. The authors mentioned also that as the gallium content increases, the (220)/(204) doublet becomes less resolved. This seems to be the case for our work too, as a secondary peak is not clearly seen. Composition measurements by X-ray fluorescence did not indicate a modification of the composition between the as-deposited and the recrystallized films, and a Cu/Ga ratio between 0.92 and 1. Higher resolution scans will be perform to try to resolve the two peaks. Interestingly, higher efficiency devices are often obtained in CIGS solar cells when the films are oriented along the (220)/(204) direction as is the case here.

TABLE I. XRD RESULTS FOR AS-DEPOSITED AND AGBR TREATED SAMPLES AT 500 °C

	As-deposited			AgBr Treated		
Peaks	(112)	(220)/(204)	(312)	(112)	(220)/(204)	(312)
Angle (deg)	27.7	45.7	54.3	27.8	45.8	54.3
FWHM (deg)	0.29	0.25	0.32	0.17	0.13	0.13
Int.I (cps deg)	1190	6402	508	396	9815	470

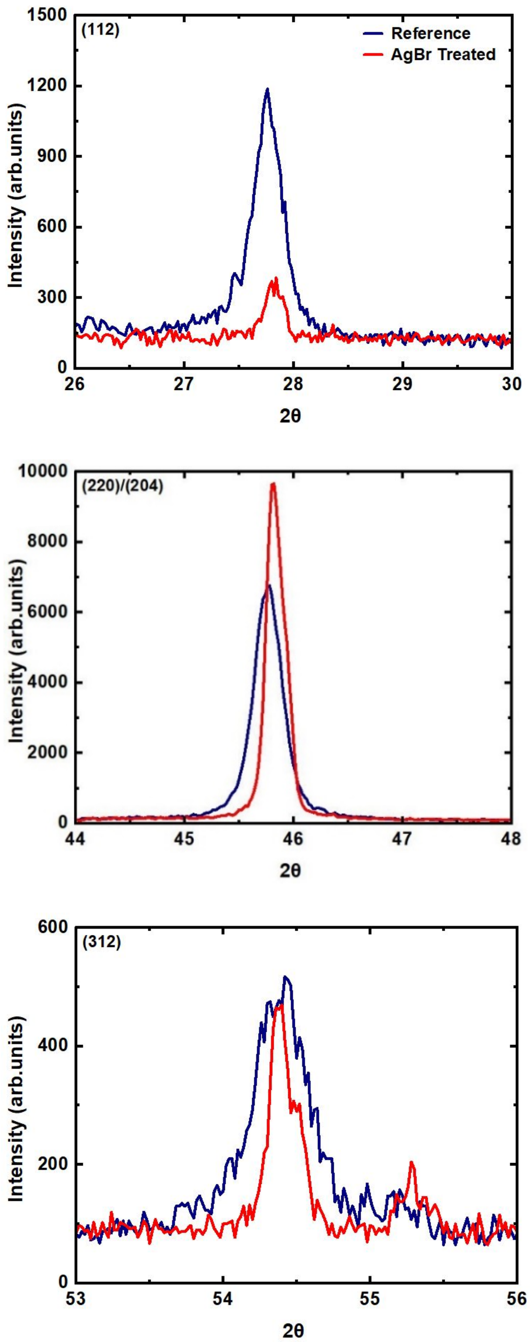


Fig. 3. XRD plots (full spectrum, (112), (204) and (312) peaks) for as-deposited (blue) and AgBr treated (red) CIGS samples.

To assess the effect of AgBr treatment on the elemental depth profile, the samples were investigated by SIMS. The main elements profiles (Cu, Ga and Se) remain the same after the AgBr treatment, as can be seen in Figure 4. On the other hand, the sodium profile was modified after the treatment, with a lower concentration for the recrystallized film compared to the as-deposited. It is possible that the increase in grain size for the recrystallized films decreases the grain boundaries density. Since sodium has been hypothesized to mostly resides at the grain boundaries, this could be correlated with a decrease in the sodium content.

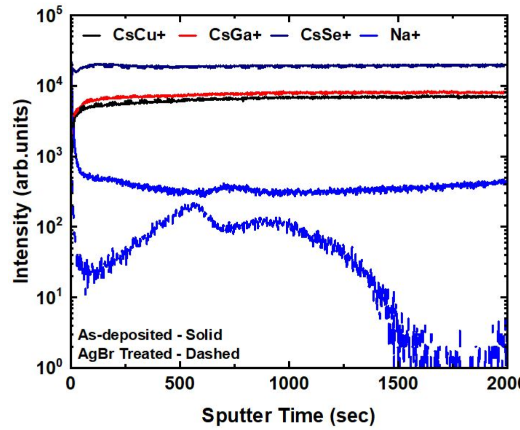


Fig. 4. Secondary Ions Mass Spectroscopy (SIMS) depth profile (positive ions) of the main elements for the as-deposited (solid) and AgBr treated (dashed) CGS samples.

IV. Conclusion

A three-stage thermal co-evaporation process was used to deposit $CuGaSe_2$ thin films and the effects of AgBr vapor treatment on the CGS films were studied. The structural and elemental depth profile properties were analyzed, indicating that the AgBr treatment results in larger grain throughout the film, as confirmed by SEM and XRD. No change in the main elements distribution was observed by SIMS, while the sodium profile changed drastically with a decrease in content after AgBr treatment. Electrical measurements will be performed to assess fully the effect of the treatment on the films. Additional research is still required in terms of AgBr doses and substrate temperature for potential application in solar cells device fabrications

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References

[1] S. Ishizuka and P. J. Fons, "Polycrystalline CuGaSe2 thin film growth and photovoltaic devices fabricated on alkali-free and alkali-containing substrates," *Journal of Crystal Growth,* vol. 532, p. 125407, 2020.

[2] G. Orsal, N. Romain, M.-C. Artaud, and S. Duchemin, "Characterization of CuGaSe/sub 2/thin films grown by MOCVD," *IEEE Transactions on Electron Devices,* vol. 46, no. 10, pp. 2098-2102, 1999.

[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.

[4] D. Poudel *et al.*, "Studying the Recrystallization of Cu (InGa) Se 2 Semiconductor Thin Films by Silver Bromide In-situ Treatment," in *2021 IEEE 48th Photovoltaic Specialists Conference (PVSC)*, 2021: IEEE, pp. 2307-2311.