Post-deposition Metal Halide Treatment of CuGaSe$_2$ for Photovoltaic Application

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Abstract— **Copper gallium diselenide (CGS) semiconductor thin films were deposited by three-stage thermal co-evaporation process. Post-deposition treatments and recrystallization were performed at various AgBr doses of 40 mg, 60 mg, and 80 mg after the 2nd stage. The changes in surface morphology were confirmed by SEM. The electrical properties were also modified, as the resistivity of the film decreases with increasing doses. The device performance after the treatment did not change as expected, as the overall device performance only slightly increases in the case of 60 mg of AgBr. Substantial changes in the fabrication process will therefore be required for better device results.**

Keywords— CuGaSe$_2$, recrystallization, AgBr

I. INTRODUCTION

Chalcopyrite materials are critical materials for achieving high efficiency and low-cost polycrystalline thin film solar cells, thanks to their attractive properties such as their high absorption coefficient, appropriate bandgap energy and tunable band edges [1]. As compared to Cu(In,Ga)Se$_2$ and CuInSe$_2$, the reports on CuGaSe$_2$ are fewer and the maximum recorded efficiency is only 11.9 % [2]. One of the constraining aspects of CGS is its low conductivity. To overcome this limitation, it is important to investigate the materials properties in detail to attain the optimum device performance. One reason for such research is that tandem solar cells with wide bandgap top cell and high efficiency bottom cell have drawn substantial interests. Based on the required properties, CGS with a band gap of 1.67 eV and its high absorption coefficient is considered as an excellent candidate for the top cell of the tandem solar cell [3]. To fabricate this suitable wide bandgap absorber layer, a recrystallization process might be required to enhance the grain growth and provide a high-quality absorber layer.

Previously, we have demonstrated that various metal halides post-deposition treatment can act as excellent transport agents in CIGS, generating larger grain and uniform layers. In this work, we studied silver bromide as a transport agent for the recrystallization of CGS thin film deposited at temperature of 500 ºC using various doses and investigated its effect on photovoltaic devices.

II. EXPERIMENTAL METHODS

DC magnetron sputtering was used to deposit the molybdenum back contact on soda lime glass substrate. The molybdenum layer is a bilayer with the bottom layer deposited at low Ar pressure resulting in a tensile stress, whereas the top layer was deposited at high Ar pressure resulting in compressive stress. Traditional, three-stage thermal co-evaporation deposition process was used to deposit the CGS layers. The 1st stage temperature was 300 ºC, whereas the 2nd and 3rd stages temperature were maintained at 500 ºC. The vapor treatment and thereafter recrystallization process was carried out in between the 2nd and 3rd stage of the CGS deposition. Different AgBr doses were used, ranging from 40 mg, 60 mg to 80 mg. The AgBr was flashed over 2 minutes. As-deposited samples were also fabricated. After completion of the CGS deposition, half of the samples were set aside for characterization, while the other half were converted into completed devices using our standard process, resulting in a SLG/Mo/CGS/CdS/ZnO/ITO/grids structure.

Surface morphological analysis was performed by scanning electron microscope (SEM). Electrical properties of the film were measured by Hall effect measurements performed on films deposited on glass. Spectroscopic ellipsometry measurements were performed to further analyze the optical properties of the films. 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

CGS samples were recrystallized at 500 °C in an AgBr environment by flashing either 40 mg, 60 mg or 80 mg of AgBr for 2 minutes at the end of the 2nd stage. The surface morphology of the films was observed by SEM before and after recrystallization as shown in Figure 1. Slight variations in the surface morphology were observed after the 40 mg and 60 mg AgBr treatments as compared to the reference, while clear and significant changes on the surface were observed in the case of the 80 mg dose.
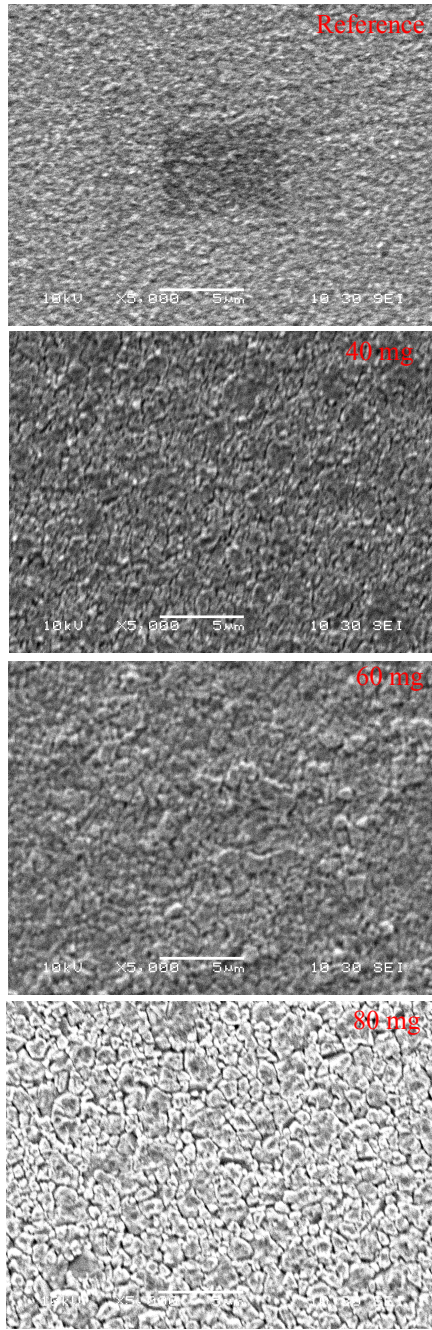
Fig. 1. Surface Scanning Electron Microscopy micrographs of CGS films: as-deposited and recrystallized at 500 °C by 40 mg, 60 mg, and 80 mg AgBr vapor treatment.

The film optical properties of the CGS film were analyzed by spectroscopic ellipsometry (Figure 2). The observed features in (n,k) are associated with interband transitions that appear at the van Hove singularities or critical points (CPs) of the joint density of states. These features were fitted assuming parabolic bands (PBs), yielding CPPB oscillators. Here the fundamental transitions were fitted with excitonic CPs and the higher energy transition points were fitted with 2-dimensional CPs. This fitting procedure revealed that there is no significant shift in the $E_0(A,B)$ or $E_0(C)$ CP energies with the AgBr treatment.
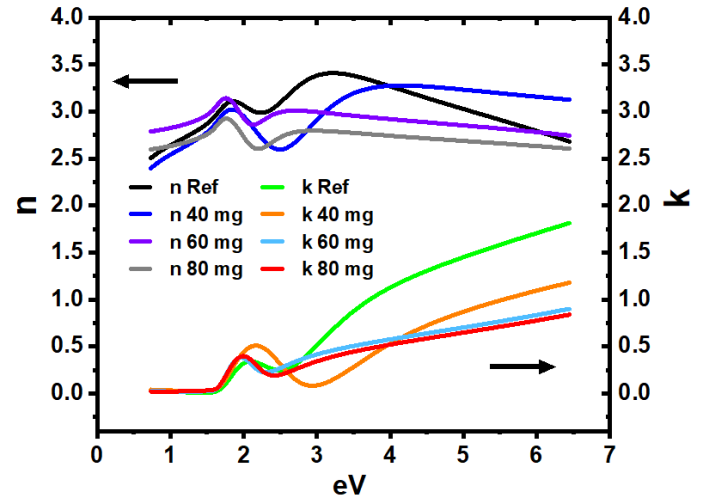

Fig. 2. Dielectric functions for the as-deposited and AgBr treated CGS samples.

Hall effect measurements were also performed to assess the electrical properties, such as carrier concentration, mobility, and resistivity, as shown in Table I. This shows that the electrical properties of the film are enhanced with an increase in the amount of AgBr dose, due both to a modification of the mobility and of the carrier concentration, with the higher dose yielding the best properties.

TABLE I.   ELECTRICAL PROPERTIES OF CGS FILMS FOR AS-DEPOSITED AND AGBR TREATED SAMPLES AT 500 °C WITH 40 MG, 60 MG AND 80 MG DOSES.

Samples	Carrier concentration (cm^{-3})	Mobility (cm^2/s)	Resistivity (Ω cm)
As-deposited	6.9E +13	4.4	2.0E +4
AgBr 40 mg	2.7E +15	5.6	4.1E +2
AgBr 60 mg	5.5E +15	6.7	1.7E +2
AgBr 80 mg	7.8E +15	7.7	1.0E +2

After the CGS fabrication process, devices were completed by depositing ~50 nm of CdS by chemical bath deposition, followed by i-ZnO (~50 nm) and ITO (~250 nm) by r.f. sputtering, and Ni/Al/Ni grids by e-beam evaporation. Figure 3 shows representative current-voltage and external quantum efficiency curve for the devices as a function of the AgBr doses, while Table II shows the corresponding photovoltaic parameters. All devices have a voltage dependent current collection, indicative of a high level of trap density. The major problem observed with the treatment is that some of the samples are shunted (40 mg and 80 mg samples). This result is not correlated with a specific change in morphology, optical or electrical properties of the films so is likely to be due to a problem in processing or scribing the device rather than the AgBr effect. Interestingly, for the devices that were not shunted (60 mg dose), we can observe an enhancement for all parameters (open circuit voltage, fill factor, short circuit current

density). The diode parameters were extracted from the dark J-V curves for the two most efficient devices (as-deposited and 60 mg samples). The reverse saturation current density changed from 3.1E-3 mA/cm^2 to 5.3E-4 mA/cm^2, the series resistance from 9.7 Ω.cm^2 to 5.5 Ω.cm^2, the shunt resistance from 500 Ω/cm^2 to 900 Ω/cm^2 and the diode ideality factor from 2.4 to 2.1 after the AgBr treatment. All these parameters indicate a slight enhancement of the overall device after AgBr treatment.

TABLE II.   PHOTOVOLTAIC PARAMETER FOR AS-DEPOSITED AND AGBR TREATED SAMPLES AT 500 °C FOR 40 MG, 60 MG AND 80 MG DOSES.

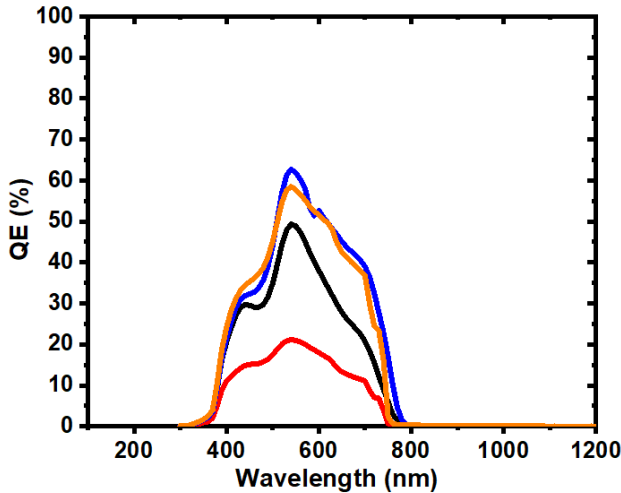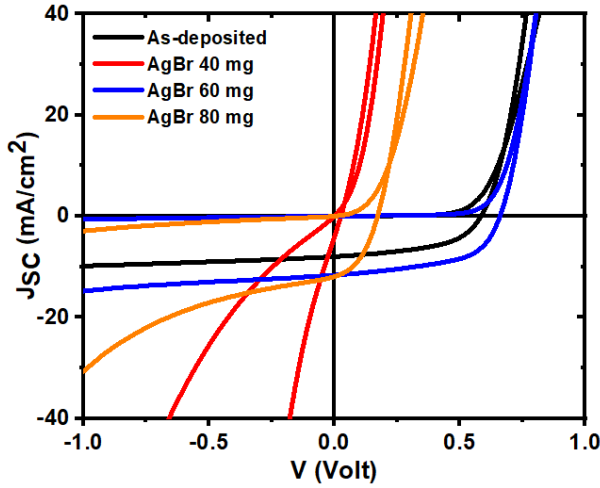| Samples	V_{OC} (volt)	J_{SC} (mA/cm^2)	FF (%)	η (%)
As-deposited	0.58	7.2	50.8	2.3
AgBr 40 mg	0.03	3.4	24.3	0.03
AgBr 60 mg	0.66	10.0	54.9	4.23
AgBr 80 mg	0.18	9.6	43.2	0.86

FIG 3. REPRESENTATIVE I-V AND QE CURVES FOR THE AS-DEPOSITED AND AGBR TREATED CGS SAMPLES.

The quantum efficiency correlates well with the spectroscopic ellipsometry measurements, where no change in the bandgap was observed. One can see a clear enhancement of QE at all wavelengths for the 60 mg and 80 mg devices.

IV. CONCLUSION

The effects of various doses of silver bromide treatment on CGS semiconductor thin films deposited by 3-stage were analyzed. The recrystallization was done by flashing three different doses of 40 mg, 60 mg, and 80 mg of AgBr for 2 minutes. The change in surface morphology was observed with increased surface roughness with increasing doses. The increase in conductivity was also observed after the treatment with higher conductivity at higher doses. In the case of devices, several issues were observed both before and after treatment. The reference sample efficiency was very low, indicating a fundamental problem in the way we fabricated these devices. This will need to be addressed to properly study the effect of AgBr treatment. Nevertheless, one can observe that potential benefits of this AgBr treatment are present, notably an enhancement of the electrical properties. An increase in efficiency was observed for the films deposited with a 60 mg dose, with an improvement of all the device parameters. Additional characterizations will be performed on the samples, including X-ray diffraction for structural analysis, and secondary ion mass spectrometry for elemental depth profile.

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