Improvement in the electronic quality of pulsed laser deposited $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ thin films via post-deposition elemental sulfur annealing process

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Abstract

We synthesized $\text{CuIn}_{0.7}\text{Ga}_{0.3}\text{Se}_2$ thin films on soda lime glass substrates using pulsed laser deposition and post-annealing under different conditions. Increasing substrate temperature during deposition and vacuum annealing after deposition both increased grain size but had negligible effect on the electronic properties of the films. As-deposited films demonstrated P-type conductivities with high carrier concentrations and low Hall

mobilities, but annealing in elemental sulfur environment significantly improved the electronic properties of the films. We found that the incorporation of even small quantities of sulfur into the films reduced carrier concentrations by over three orders of magnitude and increased Hall mobilities by an order of magnitude. This resulted in films with resistivity $\sim 5\Omega\text{-cm}$ suitable for photovoltaic applications.

Keywords: Cu(In,Ga)(Se,S)₂ absorber; pulsed laser deposition; elemental sulfur annealing; Hall effect; Raman spectroscopy; Rutherford backscattering

1 Introduction

Thin film solar cells using Cu(In,Ga)Se₂ (CIGSe) absorber layers have achieved high efficiencies, both in laboratory cells as well as in commercial modules [1, 2]. Although the CIGSe material system has been studied for over two decades and commercial products are available on the market, a complete understanding of the defects, crystal grains and junction physics of CIGSe remains lacking [3].

Research into the CIGSe material system remains relevant not only for continuing investigation into its fundamental defect and grain properties but also because it serves as a standard against which the next generation Cu₂ZnSnS₄ (CZTS) material system can be evaluated. Pulsed laser deposition (PLD), particularly valuable for multi-component systems like CIGSe and CZTS, represents a laboratory-scale synthesis tool that enables rapid evaluation of material combinations and layer interfaces. Previous studies have investigated the growth of CIGSe and CZTS thin films by pulsed laser deposition from single multi-element targets; see for example [4-6].

However, existing literature [7-9] shows that PLD of CIGSe and CIGSe thin films typically yielded materials with high carrier concentrations ($>10^{18} \text{ cm}^{-3}$) and low hole mobilities ($<10 \text{ cm}^2/\text{V-s}$) not adequate for use in photovoltaic (PV) device and interface studies. It has been reported that for PV applications, optimum free hole concentrations of $10^{15} - 10^{17} \text{ cm}^{-3}$ and hole mobilities of $20 - 200 \text{ cm}^2/\text{V-s}$ are desired [1, 2]. High hole concentrations have been correlated with large Cu:[In+Ga] ratios (>1) and attributed to acceptor-type Cu_{In} or V_{In} defects, as well as the formation of Cu_{2-x}Se phases on the film surface [7-10].

This work explores pulsed laser deposition of CIGSe thin films with thermal annealing under varying conditions, with the intent to understand the effects of various defects on the electronic behavior of the material and to achieve device quality films for use as reference standards in studies of CZTS films.

2 Experimental details

Single layer films of CIGSe, 100 – 150nm thick, were deposited onto soda lime glass substrates by pulsed laser deposition from a single, hot-sintered $\text{CuIn}_{0.75}\text{Ga}_{0.25}\text{Se}_2$ target. The 5.1cm diameter, 0.57cm thick target was commercially fabricated by American Elements. Material composition data was provided by the manufacturer, and no additional measurements were performed. Films were deposited for 2hrs in vacuum ($\sim 5 \times 10^{-5}$ torr) using a 248-nm wavelength KrF excimer laser with fixed laser energy of $\sim 110\text{mJ}$ and a repetition rate of 7Hz. During deposition, the target was rotated, in order to minimize drilling effects. The target was not polished between depositions, but prior to every deposition the target was ablated for several minutes while the substrate was shuttered, in order to remove any oxides or chamber contaminants from the target surface. For each deposition, four pieces of $0.8 \times 0.8\text{cm}$ glass were mounted on the substrate holder using DuPont 4929N silver paste, located approximately 10cm from the target. The substrates were cleaned ultrasonically in acetone, alcohol, and ultra-high purity water ($18\text{M}\Omega\text{-cm}$) then blown dry with nitrogen gas prior to deposition.

Substrate temperatures were varied between room temperature (RT) and 450°C using a resistively heated mounting block, and substrates were allowed to cool passively back to room temperature after deposition. Vacuum annealing was performed in the deposition chamber at vacuum $< 5 \times 10^{-5}$ torr. Substrates were mounted on the heater block and heated for 2hr at

temperatures ranging from 300 – 500°C, then allowed to cool passively back to room temperature. The substrates required less than 2hrs to cool from the deposition or annealing temperatures to less than 100°C. Films used for the vacuum annealing study were initially deposited at 450°C.

Sulfur annealing was performed in a 5cm diameter, sealed thermal-vacuum chamber that included a small quantity (~13mg) of elemental sulfur with the sample. The chamber was then evacuated to $< 10^{-3}$ torr and sealed using a vacuum valve. Samples were heated for 1hr at temperatures ranging from 300 – 500°C, then allowed to cool passively back to room temperature. The substrates required less than 2hrs to cool from the annealing temperatures to less than 100°C. With a chamber size of approximately 772cm^3 , 13mg of elemental sulfur, and temperatures of 300 – 500°C, the sulfur vapor is expected to consist primarily of S_2 molecules at a pressure of approximately 10torr [11, 12]. Due to condensation in some colder parts of the chamber, however, the sulfur vapor likely remains well below 10torr. Films used for sulfur annealing study were initially deposited at 450°C.

Film compositions and thicknesses were characterized using Rutherford back scattering (RBS) analysis. Using a National Electrostatics Corporation 5SDH pelletron tandem accelerator, RBS measurements were performed with a 3.05MeV $^4\text{He}^{++}$ ion beam, detected at a 165° scattering angle. Film compositions were modeled using SIMNRA 6.06 [13] and fitted to the raw RBS data. Measurement uncertainty was estimated according to the range of visually acceptable fits, and subsequently, uncertainty values vary according to signal intensities. Since the scattering cross section in RBS is proportional to the square of the atomic number, detection of light elements is always more difficult [14]. In our case, we enhance the detection limit of O by performing our experiment using a 3.05MeV alpha beam, making use of the $^{16}\text{O}(\alpha,\alpha)^{16}\text{O}$

resonance reaction. In this case the detection limit of O in the film is about 1%; however, quantitative analysis of the concentration using this method is not accurate [15]. On the other hand, heavier elements (Cu, In, Ga, Se, and S) can be quantitatively measured and the ratios among these elements are well-defined. Here we assume that no significant amount of other light elements such as H and C are present, and therefore O provides the balance of film composition when atomic percentages total less than 100%. Note that, while it is presumed that some Sodium has diffused from the SLG substrate into the film in accordance with established literature, the quantities expected in our films (typically < 1at% reported [16]) cannot be reliably detected with RBS, due to the low atomic number of Na. Calculated film thicknesses are intended as a relative guide only, and we do not provide error estimates.

Film crystal structures were analyzed by x-ray diffraction (XRD), using a Siemens D500 x-ray diffractometer with Cu anode (Cu-K α wavelength 0.154 nm). Additional phase identification was performed by Raman spectroscopy using a Horiba Jobin-Yvon LabRam Raman confocal microscope with 1800 grating and interference filter, and excitation by a 0.5mW (after attenuation), 488nm wavelength Coherent Argon laser. Carrier concentrations, carrier type, and mobilities were evaluated by Hall effect in the van der Pauw geometry using an Ecopia HMS-3000 device. Film morphologies were evaluated using scanning electron microscopy (SEM) with a Hitachi S-4300 SE/N, as well as a Jeol field emission SEM JSM-7500F. The band gaps of the samples were measured by photomodulated reflectance (PR) at room temperature. Radiation from a 300W halogen tungsten lamp dispersed by a 0.5m monochromator was focused on the samples as a probe beam. A chopped HeCd laser beam ($\lambda=442$ nm) provided the photomodulation. PR signals were detected by a Ge photodiode using a phase-sensitive lock-in amplification system.

3 Results and discussion

The effects of substrate temperature (ST), vacuum annealing (VA), and sulfur annealing (SA) on the film composition, structure and opto-electronic properties are investigated in the following sections. Note that all films measured P-type conductivity in this study.

3.1 Effects of Substrate Temperature (ST)

Using the CIGSe sputtering target and the laser parameters detailed in Section 2, films were grown with substrate temperatures varied between room temperature and 450°C. The deposition rate decreased slightly with substrate heating, but all film thicknesses remained near ~100nm.

Table 1 Composition and electronic properties of films in substrate temperature (ST) study

T_{sub}	Atomic %				Hole	Hall
	Cu	In	Ga	Se	Density (cm^{-3})	Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)
Target	25.0	18.8	6.20	50.0	-	-
RT	26.0	17.8	6.90	49.2	3×10^{20}	1.2
250°C	26.0	17.7	7.00	48.6	8×10^{19}	1.1
350°C	25.9	18.2	7.00	48.9	8×10^{19}	0.2
450°C	26.0	17.4	7.30	47.6	7×10^{19}	1.2

The CIGSe sputtering target composition was chosen with stoichiometric element ratios and an In:Ga-alloying ratio of $\text{Ga}:[\text{In}+\text{Ga}] = 0.25$ typically used in high-performing devices [1-3]. The compositions of the as-deposited ST films, and the associated carrier concentration and transport properties, are summarized in Table 1. In films totaling < 100at%, O provides balance of composition.

The relevant element ratios are summarized below in Fig. 1 (dashed line indicates stoichiometric ratios). The as-deposited ST films are Cu-rich and Se-deficient, with the deviation from stoichiometry showing no strong correlation with deposition temperature. The

high Cu:[In+Ga] and low Se:metal ratios relative to the target composition are consistent with the previously reported PLD results [5, 7, 9, 17]. In general in PLD, lighter elements exhibit slightly greater forward-peaking in the plume [18], and this may account for the relatively higher Cu content in the films compared to the sputtering target. Further, Se has a higher vapor pressure and lower sticking coefficient than the metal elements, and in physical vapor deposition methods, Se typically requires an evaporation in excess to maintain stoichiometry and mitigate (In,Ga)₂Se re-evaporation losses [1]. The Se-deficiency may therefore be attributed to the lack of Se excess in the plume, which may also contribute to the increase in relative Cu concentration by increasing In and Ga re-evaporation losses. CISE and CGSe phases are formed through the reaction of binary precursor phases, which in addition to Cu_xSe phases include In_xSe_y and Ga_xSe_y, respectively [19, 20]. Subsequently, (In,Ga)₂Se phases may be evolved from these binary precursor phases or directly from CuInSe₂ and CuGaSe₂ phases [20].

Fig. 1. Element composition ratios for ST films

Fig. 2 shows x-ray diffractograms for each of the as-deposited ST films. Only a single diffraction peak at around 20~27° is observed in all ST films. This peak corresponds to the (112) diffraction peak from the chalcopyrite structure (JCPDS 35-1102). Fig. 2 reveals that all ST films have chalcopyrite grains with strong (112) preferred orientation. We note that CuSe

and Cu_2Se have diffraction peaks at $26.6\text{--}26.7^\circ$ (JCPDS 89-7391 and 88-2044) that may be masked by the $\text{CuIn}_{0.7}\text{Ga}_{0.30}\text{Se}_2$ (112) peak near 26.9° (JCPDS 35-1102). Hence the presence of a small fraction of secondary phases cannot be ruled out. Indeed, Raman spectroscopy reveals the presence of a small amount of Cu_{2-x}Se phases in films deposited at 450°C , as shown in Fig. 3 (also see Fig. 5 and Fig. 9). Raman measurements were not performed on the other ST films. The Raman spectrum for the as-deposited film, shown in Fig. 3, exhibits the characteristic A1 chalcopyrite mode ($\sim 175\text{cm}^{-1}$) and secondary B2/E (214 and 226cm^{-1}) modes associated with CIGSe [21], as well as a distinct peak at 260cm^{-1} attributed to Cu_{2-x}Se [2].

Fig. 2. X-ray diffractograms for as-deposited ST films

As expected, grain sizes increase significantly with increasing deposition temperatures, evident as increasing (112) diffraction peak intensities and decreasing peak widths. Grain sizes were estimated using the Debye-Scherrer equation [22], ignoring other broadening effects. As the substrate deposition temperature increases from room temperature to 450°C , grain sizes increase from approximately 10nm to 50nm, respectively.

Although crystallinity of the CIGSe thin films improves significantly with increasing substrate temperature, free hole concentrations do not change significantly with deposition

temperature. As tabulated in Table 1, hole concentrations for as-grown films deposited at all temperatures remain greater than 10^{19} cm^{-3} . The high carrier concentrations can be attributed to the Cu-rich film stoichiometries through the formation of Cu_{In} antisite defects [10] or high conductivity Cu_{2-x}Se phases [8, 23]. Hole mobilities also show no strong correlation with substrate deposition temperatures, remaining less than $1.2 \text{ cm}^2/\text{V}\cdot\text{s}$ for all as-deposited ST films. Grain sizes of the films increased with increasing substrate temperature, but hole mobilities did not increase. This stagnation of mobility with increasing grain size suggests that scattering by defects or possibly secondary phases, and not scattering by grain boundaries, primarily limits the mobilities in as-deposited films. Se-vacancies and Cu_{2-x}Se likely contribute to this detrimental scattering behavior.

Fig. 3. Raman spectra for as-deposited (450°C) and KCN-etched CIGSe films

It has been reported that Cu_{2-x}Se and Cu_{2-x}S phases tend to precipitate on film surfaces during the growth of copper-rich $\text{CIG}(\text{Se},\text{S})$ thin films, and KCN has been used to selectively etch and remove these unwanted phases [2]. To investigate the possibility that Cu_{2-x}Se phases were contributing the excessive carrier concentrations and low mobilities, an as-deposited film (deposited at 450°C) was etched in 1.5M KCN for 3 minutes. Raman spectra in Fig. 3 confirm

the removal of the Cu_{2-x}Se phases by KCN etching. Fig. 4 shows SEM images for the as-deposited and KCN-etched films.

After etching, the film conductivity decreased dramatically, such that Hall effect measurements were not possible. This suggests that the Cu_{2-x}Se phases existed mainly on the surface and also decorated the CIGSe grains, such that their removal by etching disrupted the lateral transport and made the Hall measurement inconclusive.

Fig. 4. SEM images of a) as-deposited CIGSe film, b) KCN-etched CIGSe film

3.2 Effects of Vacuum Annealing (VA)

Using films deposited at 450°C , annealing was performed for 2hr at 300 to 500°C in vacuum, as detailed in Section 2. Note the as-deposited samples used for this section were slightly thicker ($\sim 130\text{nm}$) and had slightly different compositions than films reported in Section 3.1. This is attributed to laser energy instabilities in the deposition system. The film thickness exhibits minimal change with vacuum annealing, indicating negligible evaporation losses up to 500°C .

Table 2. Composition and electronic properties of films in vacuum annealing (VA) study

T_{anneal}	Atomic %				Hole Density (cm^{-3})	Hall Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)
	Cu	In	Ga	Se		
None	26.6	17.8	8.10	47.5	2×10^{20}	1.1
300°C	26.5	17.2	7.10	47.4	2×10^{20}	0.7
400°C	27.1	17.6	7.00	48.5	2×10^{20}	0.7
500°C	28.8	17.5	6.60	47.4	2×10^{20}	0.5

The compositions of the VA films, and the associated carrier concentration and transport properties, are summarized in

Table 2. The Cu concentration monotonically increases and the Ga concentration monotonically decreases with increasing annealing temperature, evident as increasing Cu:[In+Ga] and decreasing Ga:[In+Ga] ratios, respectively. The relative increase in Cu also infers the loss of In and Ga. This loss of In and Ga is attributed to the re-evaporation of volatile (In,Ga)₂Se phases as detailed in Section 3.1.

For all VA films, x-ray diffractograms (not shown) indicate only the presence of chalcopyrite (112) peaks associated with CIGSe. Raman spectroscopy was used to detect secondary Cu_{2-x}Se phases that may impact the electronic properties of the films but that may not be identifiable by x-ray diffraction, as previously discussed. Fig. 5 shows the Raman spectra taken for VA films using single-spot measurements. Spectra are normalized to the primary mode peak intensity.

Raman spectra for all films exhibit the characteristic A1 chalcopyrite mode ($\sim 175\text{cm}^{-1}$) and secondary B2/E (214 and 226cm^{-1}) modes associated with CIGSe [21]. The Raman spectrum for the as-deposited film also shows a well-defined peak at 260cm^{-1} (with weaker shoulder near 240cm^{-1}) attributed to Cu_{2-x}Se [2]. This peak grows monotonically with increasing anneal temperature, consistent with the increasing Cu:[In+Ga] ratios exhibited in the films.

Fig. 5. Raman spectra for VA films

After vacuum annealing, films remain highly conductive with hole concentrations of $\sim 10^{20} \text{ cm}^{-3}$, which do not show any variation with anneal temperature. Hall mobilities, on the other hand, show a small monotonic decrease from 1.1 to $0.5 \text{ cm}^2/\text{V}\cdot\text{s}$ as the anneal temperature increases to 500°C . The Se:metals ratio increases and then decreases with anneal temperature, which is attributed either to variations of Se-content in the as-deposited films or to deviations associated with $(\text{In,Ga})_2\text{Se}$ loss. Notably, the fraction of Cu_{2-x}Se phase present in the film increases monotonically with increasing anneal temperature. These trends suggest that Cu_{2-x}Se plays a more significant role than Se-deficiencies in the decreasing mobilities demonstrated in these films.

3.3 Effects of Sulfur Annealing

Using films deposited at 450°C , sulfur annealing was performed for 1hr at 300 to 500°C , as detailed in Section 2. As-deposited samples used for this section were similar to those used in the VA studies. The film thickness exhibits minimal change with sulfur annealing, indicating

negligible evaporation losses. The compositions of the SA films, and the associated carrier concentration and transport properties, are summarized in Table 3.

Table 3. Composition and electronic properties of films in sulfur annealing (SA) study

T_{anneal}	Atomic %				Hole Density (cm^{-3})	Hall Mobility ($\text{cm}^2/\text{V}\cdot\text{s}$)
	Cu	In	Ga	Se/S		
None	26.2	17.1	6.90	47.1/ -	2×10^{20}	1.1
300°C	26.2	17.1	6.80	44.0/ 4.30	7×10^{16}	16.6
400°C	25.0	17.0	6.90	36.0/ 8.50	5×10^{16}	19.3
500°C	25.7	17.1	6.70	35.5/ 14.0	1×10^{17}	8.5

Annealing in elemental sulfur environment dramatically modified the material properties. First, we notice that SA yielded graded composition films with the maximum sulfur concentrations located at the film surfaces (note the Se and S values shown in Table 3 correspond to the surface-most layer). Fig. 6 shows the sulfur concentration profiles through the films, in which the relatively large error bars arise from the weak sulfur signals in RBS measurements (due to low elemental concentrations and the low atomic number of S). The surface concentration of sulfur increased with increasing annealing temperature, consistent with increasing sulfur gas pressures. Note that the sulfur distributions are in good agreement with the complementary error function fit of the data (solid lines), suggesting the diffusion of S from the ambient into the thin film.

Fig. 6. Elemental sulfur concentrations in SA films (solid lines represent erfc fits of the indicated data)

The relevant element ratios are summarized below in Fig. 7 (dashed line indicates stoichiometric ratios). The total chalcogen concentration [S+Se]:metals generally increased after sulfur annealing, indicating that the incorporated S must have occupied some of the Se-vacancies. With increasing S incorporation, however, the Se content correspondingly decreased, suggesting that a large fraction of the S likely occupied the films as Se-sublattice substitutions.

Fig. 7. Element composition ratios for SA films (weighted-average values shown)

The substitution of S into the Se-sublattice should yield an increase in the band gap, since CIS has a larger band gap than CISE [2]. Based on the band gap behavior, however, the S incorporation mechanism remains unclear. Photomodulated reflectance (PR) measurements shown in Fig. 8 indicate negligible effect of sulfur annealing on the band gap (at ~1.17 eV) of the

material. However, we point out that the regions of significant sulfur incorporation remain limited to small surface layers ($< 40\text{nm}$), likely resulting in the mitigated effect on the band gap measured by PR, which probes film depths up to $\sim 200\text{ nm}$. The measured band gap of 1.17eV is in excellent agreement with the predicted band gap for $\text{Ga:}[\text{In+Ga}] \sim 0.28$ in the literature [1].

Fig. 8. PR measurements for SA films

For all SA films, x-ray diffractograms (not shown) indicate only the presence of chalcopyrite (112) peaks associated with CIGSe. As for VA films, Raman spectroscopy was used for SA films to detect secondary Cu_{2-x}Se phases that may not be identifiable by x-ray diffraction. Fig. 9 shows the Raman spectra for sulfur annealed films, averaged over film surface areas of approximately $20 \times 20 \mu\text{m}$ ($\sim 0.75 \mu\text{m}$ spacing) and normalized to the primary mode peak intensity.

Raman spectra for all films exhibit the characteristic A1 chalcopyrite mode ($\sim 175\text{cm}^{-1}$), as well as secondary B2/E (214 and 226cm^{-1}) modes, associated with CIGSe [21]. The Raman spectrum for the as-deposited film also shows a well-defined peak at 260cm^{-1} attributed to Cu_{2-x}Se . This is consistent with previous reports that showed the presence of Cu_{2-x}Se phases in Cu-rich CIGSe films synthesized by PLD [7, 9, 24]. The 300°C SA film demonstrates a small red (right) shift of the Cu_{2-x}Se peak (266cm^{-1}) and the appearance of a well-defined Cu_{2-x}S (460cm^{-1}) peak [25]. As the sulfur anneal temperature increases to 500°C , the Cu_{2-x}Se peak decreases and

further red shifts, while the Cu_{2-x}S peak dramatically decreases and then disappears, as shown in Fig. 9b and c. Notably, at 500°C a small Cu_{2-x}Se peak remains, but at 400°C the Cu_{2-x}Se peak disappears completely. Further, a characteristic A1 mode for CuInS_2 peak (293cm^{-1}) appears at 500°C [26].

Fig. 9. Raman spectra for SA films

In contrast to vacuum annealing, sulfur annealing yields a dramatic reduction in film conductivity. Fig. 10 summarizes the electronic properties of the SA samples. Hole concentrations decreased by more than three orders of magnitude, and mobilities increased by at least one order of magnitude, for all sulfur annealed samples.

A decrease in carrier concentration with sulfurization of CIGSe films has been attributed to an increase in the ionization energies of the acceptor levels associated with the Se-sublattice substitution by S [27]. However, in our case the SA films indicated no substantial widening of the band gap and hole concentrations do not show a dependence on the amount of sulfur incorporated in the films; subsequently, shifting of the ionization energies does not appear to properly account for the decreases in hole concentrations.

Fig. 10. P-Type carrier concentrations and Hall mobilities for SA films

Notably, the highest electronic quality film (e.g. minimum hole concentration and maximum mobility) corresponds to the least Cu-rich composition with the smallest Cu_{2-x}Se Raman peak. The concentration of Cu_{2-x}S phases decreases with increasing anneal temperature, as evidenced by decreasing Raman peak intensity, but these variations do not appear to influence the electronic behavior.

Both Cu_{2-x}Se and Cu_{2-x}S phases exhibit low resistivities ($< 1\Omega\cdot\text{cm}$) and high carrier concentrations ($10^{19} - 10^{20}\text{cm}^{-3}$), depending on their stoichiometric deviations [28]. The presence of these phases in similar quantities in films with very high hole concentrations, as well as films with the desired hole concentrations, suggests that these phases are not predominately responsible for the changes in hole concentration behavior observed. In the vacuum annealed and sulfur annealed films, small decreases in the mobilities ($\sim 2\times$) were observed to correspond with increasing concentrations of Cu_{2-x}Se phases. The dramatic drop in film conductivity with KCN etching demonstrated in Section 3.1 likely indicates that Cu_{2-x}Se phases decorate the grain boundaries, such that their removal by etching disrupts the lateral transport between grains, particularly in the very thin films ($\sim 100\text{nm}$) investigated here. We conclude, then, that the Cu_{2-x}Se phases form on the grain boundaries in small quantities and mildly degrade the mobility of the films. These phases are not, however, responsible for the overall very high hole concentrations and low mobilities observed in the as-deposited and vacuum annealed films.

The observation that orders of magnitude changes in the hole concentrations and hole mobilities are independent of both the amount of sulfur incorporation and the amount of secondary phases suggests that the incorporation of sulfur, in any amount, improves the electronic properties of the film. Thermal annealing of CIGSe absorbers in sulfur environment has been shown to quench electrically active deep level defects [2, 29], although the defect involved and the nature of the passivation have not been definitively identified. The order of magnitude increase in mobilities with sulfur annealing is consistent with the view of deep level defect passivation by the S atoms. While it is noted that sulfur-containing CIGSeS alloys have demonstrated low hole concentrations, it is expected that these decreases would be accompanied by shifts in the band gap, which we do not observe. In the sulfur annealed films, the coincidental

reduction of hole concentration and increase of mobility with incorporation of sulfur suggests, however, that the defects being passivated are acceptors.

4 Conclusions

We have investigated the structural and electrical properties of thin chalcopyrite-phase CIGSe films synthesized by pulsed laser deposition and annealed under varying conditions. As-deposited films demonstrated Cu-rich, Se-deficient composition with high hole carrier concentrations and low Hall mobilities. Increasing the substrate temperature, either during deposition or through vacuum annealing, increased the grain size but had negligible effect on the electronic performance of the films. This independence of grain size and electronic performance suggests that scattering by defects or secondary phases, not grain boundaries, dominate the electronic quality of these films. The incorporation of sulfur into the films via sulfur annealing, even in small quantities, substantially decreased the carrier concentration and increased the Hall mobility. This is mainly attributed to a reduction in stoichiometry-related defects, defect passivation, and improved film connectivity associated with sulfur incorporation.

The results of this study indicate that sulfur annealing represents a feasible processing route for improving the electronic quality of pulsed laser deposited CIGSe thin films for use in photovoltaic device studies. After sulfurization, films demonstrated hole carrier concentrations and Hall hole mobilities within the range of values typically associated with device-quality films.

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