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Properties of Cu(In,Ga,AI)Se₂ thin films fabricated by magnetron sputtering

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Cu(In,Ga,Al)Se₂ (CIGAS) thin films were studied as an alternative absorber layer material to Cu(In_xGa_{1-x})Se₂. CIGAS thin films with varying Al content were prepared by magnetron sputtering on Si(100) and soda-lime glass substrates at 350 °C, followed by postdeposition annealing at 520 °C for 5 h in vacuum. The film composition was measured by an electron probe micro-analyzer while the elemental depth profiles were determined by secondary ion mass spectrometry. X-ray diffraction studies indicated that CIGAS films are single phase with chalcopyrite structure and that the (112) peak clearly shifts to higher 2θ values with increasing Al content. Scanning electron microscopy images revealed dense and well-defined grains, as well as sharp CIGAS/Si(100) interfaces for all films. Atomic force microscopy analysis indicated that the roughness of CIGAS films decreases with increasing Al content. The bandgap of CIGAS films was determined from the optical transmittance and reflectance spectra and was found to increase as Al content increased. © 2015 American Vacuum Society. [http://dx.doi.org/10.1116/1.4913863]

I. INTRODUCTION

Chalcopyrite Cu(In_xGa_{1-x})Se₂ (CIGS) solar cells currently have the highest efficiency among polycrystalline thin film cells. This efficiency has reached ~20% in lab-scale devices¹ and was reported to be ~17% in commercial modules with 30 × 30 cm² area.² A major factor that contributes to achieving high efficiency in CIGS solar cells is the strong photon absorption of CIGS material in the solar spectrum combined with ease of tuning its direct bandgap over the range from 1.04 eV (Ga-free) to 1.67 eV (In-free) by changing the [Ga/(In + Ga)] ratio.³ The high absorption coefficient of CIGS and its polycrystalline thin-film structure facilitate its fabrication on flexible substrates. Solar cells fabricated from CIGS grown on metal foils and high melting point polymers have reached efficiencies of ~17% and 18%, respectively.^{4,5}

The optimal bandgap for absorbing the solar spectrum is 1.37 eV.^6 This bandgap is obtained in CIGS with a Ga/ (In + Ga) ratio of ~0.6.⁷ However, the efficiency of CIGS solar cells starts to drop when this ratio is increased above ~0.3, which corresponds to a bandgap of ~1.2 eV. Such reduction in efficiency as Ga concentration is increased, which results in interface states formed at the CIGS/CdS interface.⁸ It is desirable to increase the bandgap of the

absorbing layer while maintaining interface quality. This led to investigating alternative alloys of CuInSe₂. For example, Cu(In_{1-x}Al_x)Se₂ thin films have been studied as the absorber material in solar cells. Its bandgap was found to increase with Al content and a device efficiency of 11% was demonstrated.⁹ In another study, a Cu(In_{0.87}Al_{0.13})Se₂ thin-film solar cell demonstrated an efficiency of 16.9%.¹⁰ These results indicate that alloying CIGS with Al could result in increased bandgap while reducing In content. Another consideration is that the cost of In in CIGS solar cells is considered a major cost factor for scaling these types of solar cells and reduction of In content will be beneficial.¹¹

CIGS thin films have been fabricated by a variety of deposition techniques, such as coevaporation, chemical vapor deposition, chemical solution deposition, and electrodeposition.^{12–15} However, these methods often involve multiple steps and are complicated, while simplified processes are always desired for large-scale mass production. During the past few years, efforts have been made to develop simplified sputtering processes using single quaternary targets for fabricating CIGS thin films.^{16–18} Compared to other deposition techniques, sputtering has been widely employed in the semiconductor industry for depositing a wide range of thin films. Hence, it can be readily integrated into the manufacturing processes for fabricating CIGS-based solar cells. Additionally, sputtering provides a fast means for prototyping new material systems when target materials, e.g., Al in the present study, are readily available.

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| Sample | Al sputtering time (min) | Cu (%) | In (%) | Ga (%) | Al (%) | Se (%) | Al/(In + Ga + Al) |
|----------|--------------------------|--------|--------|--------|--------|--------|-------------------|
| Al(0%) | 0 | 23.3 | 15.2 | 6.2 | 0.0 | 55.3 | 0.00 |
| Al(2.0%) | 2 | 21.9 | 14.8 | 6.1 | 2.0 | 55.2 | 0.09 |
| Al(3.7%) | 6 | 21.5 | 14.3 | 6.0 | 3.7 | 54.5 | 0.15 |
| Al(5.5%) | 10 | 20.9 | 13.4 | 5.9 | 5.5 | 54.3 | 0.22 |
| Al(7.3%) | 14 | 20.1 | 13.1 | 5.8 | 7.3 | 53.7 | 0.28 |

TABLE I. Composition of CIGAS thin films on Si(100).

We report on the incorporation of Al into CIGS thin films, i.e., Cu(In,Ga,Al)Se₂ (CIGAS) thin films, using magnetron sputtering. The dependence of surface morphology, microstructure, and optical properties of CIGAS films on Al content is studied.

II. EXPERIMENT

CIGAS thin films were deposited using an ATC Orion-5 magnetron sputtering system (AJA International, Inc., USA) on Si(100). For optical characterization, CIGAS films were also deposited on soda-lime glass (SLG) substrates. A 2 in. quaternary CIGS target (American Elements, USA) with the composition of Cu, In, Ga, and Se of 0.24, 0.20, 0.06, and 0.50 at. %, respectively, was used as the RF sputtering source for CIGS films, and a 2 in. Al target (99.999%, Kurt J. Lesker, USA) was used as the DC sputtering source for incorporating Al into CIGS. The base pressure of the deposition chamber was kept in low 10^{-6} Pa range, and the deposition was performed at 4×10^{-1} Pa with an argon (99.999% purity) flow rate of 20 sccm. The substrate temperature was

kept at 350 °C. For all films, the CIGS was sputtered for a total of 60 min using an RF sputtering gun operating at 85 W. After 30 min of CIGS deposition and while the CIGS sputtering was proceeding, Al was sputtered for either 2, 6, 10, or 14 min into CIGS films using a DC gun operating at 10 W. Finally, CIGS sputtering was continued to result in a total CIGS deposition of 190 nm plus the added Al. Note that the film thickness used in the present study is less than the film thickness in actual CIGS-based solar cells (commonly 1.5–2.5 μ m). This is because the focus of this study is to study the incorporation of Al into CIGS and its effect on chemical composition, structure evolution, and optical properties. Material properties obtained from a 200 nm film are expected to be similar to that from thicker films. All asdeposited samples were then annealed at 520 °C for 5 h in vacuum to improve the distribution of Al across the CIGS film thickness.

The depth profile of the CIGAS films was determined by a TOF-SIMS 5 time-of-flight secondary ion mass spectrometry (ION-TOF GmbH, Germany) with dual beam operation



Fig. 1. (Color online) SIMS depth profiles of Al, Ga, In, Cu, Se, and Si for the Al(5.5%) sample: (a) as-deposited and (b) annealed at 520 °C for 5 h.



FIG. 2. (Color online) (a) XRD patterns of CIGAS thin films deposited on Si(100). (b) Enlarged portions of the XRD patterns in (a) showing the shift of (112) peak with Al content.

for depth profiling. A 25 keV Bi⁺ ion (0.5 pA, 50 μ m \times $50\,\mu\text{m}$) for analysis, while a 10 keV Cs ion beam (5 nA, $140 \,\mu\text{m} \times 140 \,\mu\text{m}$) was used for sputtering. Two reproducible depth profiles were acquired for each sample. A Cameca SX100 electron probe microanalyzer (EPMA, Cameca, France) was used to determine the overall composition of the film. The crystal structure was studied by x-ray diffraction (XRD, MiniFlex II, Rigaku, Japan) using a CuKα radiation $(\lambda = 1.54 \text{ Å})$ and by high-resolution transmission electron microscopy (HRTEM, JEM-2100F, JEOL, Japan). The TEM specimens were prepared by depositing CIGAS thin films directly on carbon-coated Cu grids using the same deposition conditions described above except for a shorter deposition time. The surface morphology and cross-sectional images were obtained by field-emission scanning electron microscopy (FESEM, S-4700, Hitachi, Japan), and the surface roughness was measured using an atomic force microscope (AFM, Dimension 3100, Veeco, USA). CIGAS films deposited on SLG were used for optical transmission and reflection measurements. The spectra were acquired in the wavelength range of 200–1200 nm using a double-beam UV/ Vis spectrophotometer (LAMBDA 45, PerkinElmer, USA).

III. RESULTS AND DISCUSSION

Table I summarizes the composition of CIGAS thin films deposited on Si(100) substrates, as determined by EPMA measurements. The Al content exhibited roughly linear dependence with the sputtering time, and the In and Ga content decreased with increased Al content. Moreover, it was observed that Se content showed a reduction with Al addition to the films. Similar results were also reported in previous studies on Al incorporation into CuInSe₂ materials.¹⁹ Note that the calculated Ga/(In + Ga) ratio from Table I is 0.29 for sample Al(0%), which is deviated from that of the target [Ga/(In + Ga) ratio 0.23] mainly due to the sticking coefficient difference for different elements.

Figures 1(a) and 1(b) show the SIMS depth profile obtained for the as-deposited and annealed Al(5.5%) samples, respectively. From the SIMS profile, it is clearly seen



FIG. 3. (Color online) AFM image of CIGAS thin films on Si(100): (a) Al(0%), (b) Al(2.0%), (c) Al(3.7%), (d) Al(5.5%), and (e) Al(7.3%). (f) Variation of RMS roughness with Al content.

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that for the as-deposited film, Al concentration has a gradient throughout the depth of the sample and peaks at the middle where the Al was deposited. The Al concentration remains relatively unchanged for the thickness of about 60-100 nm away from the surface, then drops significantly near the Si interface and at the surface. The In and Ga concentration is lower where the Al concentration is higher, indicating that some In and Ga atoms are substituted by Al. Also, the spikes in counts near the CIGAS/Si interface are expected to be due to the native oxide covering the Si surface. There is a slight reduction in the Cu concentration up to \sim 30 nm away from the surface. In contrast, the SIMS profile in Fig. 1(b) shows a much improved Al distribution across the film thickness after the sample was annealed at 520 °C for 5 h. Similarly, In and Ga distribution also becomes almost uniform upon annealing, indicating that the concentration gradient in the sputtered film can be effectively minimized using the right annealing treatment.

Figure 2(a) shows the XRD patterns of CIGAS thin films deposited on Si(100) substrates. Since there is no ICDD file for CIGAS, standard CIGS file (PDF card No. 00-035-1120) is used to identify the diffraction peaks. All peaks are identified as CIGAS chalcopyrite phase or the Si substrate with no secondary phase detected. The (112) peak position exhibits clear shift toward higher 2θ values as the Al content increases, as illustrated in Fig. 2(b). The $d_{(112)}$ values were calculated to be 3.35, 3.33, 3.32, 3.31, and 3.30 Å for Al(0%), Al(2.0%), Al(3.7%), Al(5.5%), and Al(7.3%), respectively. The deviation of d values may be attributed to the substitution of Al atoms for In atoms in the CIGS matrix, causing reduction of *d*-spacing because of the difference in atomic radii between Al and In. Similar results were also reported on Cu(In,Al)Se₂ thin films with varying Al contents.^{9,19}

The mean crystallite size of polycrystalline CIGAS thin films can be estimated by Scherrer equation²⁰

$$D = \frac{K\lambda}{\beta\cos\theta},\tag{1}$$

where *D* is the mean crystallite size, λ is the x-ray wavelength ($\lambda = 1.54$ Å for CuK α radiation), β is the full width at half maximum (FWHM), θ is the Bragg angle, and *K* is the shape factor. The FWHM of (112) peaks is 0.010, 0.012, 0.013, 0.015, and 0.019 rad for Al(0%), Al(2.0%), Al(3.7%), Al(5.5%), and Al(7.3%), respectively, giving rise to corresponding mean crystallite sizes of 16.57, 15.95, 15.02, 14.10, and 12.03 nm. Clearly, the CIGAS crystallite size decreases as the Al content increases.

A similar trend was also observed on the surface roughness of CIGAS films, which was measured from the AFM images shown in Fig. 3. The measured root mean square (RMS) roughness for Al(0%), Al(2.0%), Al(3.7%), Al(5.5%), and Al(7.3%) is 4.80, 3.97, 3.87, 3.53, and 3.47 nm, respectively, showing a clear reduction as the Al content increases. Since surface roughness affects the shunt paths in thin-film solar cells,²¹ the incorporation of Al may help reduce the shunt resistance in solar cell devices and,

hence, improve their efficiency. Additionally, all CIGAS films exhibit well-defined and uniformly distributed grains, as shown in Fig. 3. The surface morphology and cross-section of CIGAS films on Si(100) were also characterized using FESEM. Figure 4 shows the FESEM images of two samples, Al(0%) and Al(7.3%), which exhibit similar surface morphologies observed by AFM. Moreover, FESEM cross-sectional images (insets of Fig. 4) revealed columnar grains in CIGAS films, as well as sharp interfaces between the films and Si(100) substrates. The measured CIGAS film thickness is ~190 nm for sample Al(0%) and ~220 nm for sample Al(7.3%). The thickness for the Al(7.3%) measured by FESEM is in very good agreement with the SIMS results shown in Fig. 1.

The structure of CIGAS films was further investigated using HRTEM. Figure 5(a) shows a low magnification HRTEM image of the sample Al(7.3%). The film has welldefined small grains of a few tens of nm as also observed by AFM and FESEM, shown in Figs. 3 and 4, respectively. Moreover, the measured lattice spacing of 3.35 Å from a high magnification HRTEM image, as shown in Fig. 5(a) inset, matches well with $d_{(112)}$. Figure 5(b) illustrates a selected area diffraction (SAD) pattern acquired from the same sample. All diffraction rings are identified and labeled as belonging to a single chalcopyrite phase according to ICDD standards (PDF card No. 00–035-1102) with no



FIG. 4. FESEM images of CIGAS thin films: (a) Al(0%); (b) Al(7.3%). Insets are corresponding cross-sectional images.

FIG. 5. (a) HRTEM image of sample Al(7.3%). The inset is high magnification showing lattice spacing corresponding to $d_{(112)}$. (b) SAD pattern with diffraction rings labeled as pure chalcopyrite structure.

secondary phases observed, which is in good agreement with XRD data.

The dependence of optical bandgap (E_g) on Al content was studied using the optical data, including transmittance and reflectance spectra acquired from CIGAS films on SLG substrates. The optical absorption coefficient, α , was calculated using the following equation:²²

$$\alpha = \frac{1}{d} \ln \left[\frac{\left(1-R\right)^2}{2T} + \frac{\left(1-R\right)^4}{4T^2} + R^2 \right)^{1/2} \right],$$
 (2)

where *d* is the film thickness, *R* is the reflectance, and *T* is the transmittance. Since chalcogenide compounds are direct gap semiconductors,²² the following equation can be used:²³

$$\alpha h \upsilon = A_a (h \upsilon - E_g)^{1/2}, \tag{3}$$

where A_a is a constant that depends on the transition nature, the effective mass, and the refractive index; and hv is the incident photon energy. The bandgap was then determined by extrapolating the linear portion of $(\alpha hv)^2$ versus hv curve to the abscissa. Figure 6 shows the $(\alpha hv)^2$ versus hv plots for CIGAS films with varying Al content. The measured bandgap of 1.20 eV for sample Al(0%), i.e., Cu(In_{0.69}Ga_{0.31})Se₂, is comparable to values for Cu(In_{1-x}Ga_x)Se₂ thin films with x = 0.30.⁷ Moreover, the bandgap of CIGAS films increases with increasing Al content, as shown in Fig. 6 inset, which is also in good agreement with previously reported results for Cu(In,Al)Se₂.¹⁰ Due to the Al content gradient inside the

Fig. 6. (Color online) $(\alpha h\nu)^2$ vs $h\nu$ plot for CIGAS thin films with varying Al content. Inset shows the dependence of bandgap with Al content.

CIGS matrix, the bandgap here refers to an effective bandgap for these particular samples.

IV. CONCLUSION

Polycrystalline single phase CIGAS thin films with varying Al content were fabricated by magnetron sputtering. XRD data showed shift of the (112) peak toward higher 2θ values with increasing Al content. SIMS results show that the concentration of In and Ga in as-deposited films is reduced for higher Al concentrations, suggesting some Al atoms are substituted for In as well as Ga. After annealing, the Al distribution across film thickness became almost uniform. In and Ga also exhibited almost uniform distribution across the film thickness. AFM analysis showed that CIGAS films exhibited well-defined and uniformly distributed grains with decreasing surface roughness as Al content increased. Cross-sectional FESEM images revealed columnar grains of the films and sharp interfaces between the films and Si(100) substrates. The optical bandgap of each film, determined from transmittance and reflectance spectra, increased from 1.20 to 1.28 eV as the Al content increased from 0 to 7.3 at. %. Our results demonstrate that by incorporating Al the bandgap of CIGS can be increased, which may benefit the development of high-efficiency CIGS-based solar cell devices.

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