Optimization of vertical and lateral distances between target and substrate in deposition process of CuGaSe₂ thin films using one-step sputtering

Jae-Cheol Park¹, Mowafak Al-Jassim², and Tae-Won Kim^{1,*}

¹Advanced Photoenergy Laboratory, Applied Optics and Energy Research Group,
Korea Institute of Industrial Technology, Gwangju, 500-480, Korea

²National Renewable Energy Laboratory, National Center for Photovoltaics, Golden, CO, 80401, USA

ABSTRACT

Copper gallium selenide (CGS) thin films were fabricated using a combinatorial one-step sputtering process without an additional selenization process. The sample libraries as a function of vertical and lateral distance from the sputtering target were synthesized on a single soda-lime glass substrate at the substrate temperature of 500 °C employing a stoichiometric CGS single target. As we increased the vertical distance between the target and substrate, the CGS thin films had more stable and uniform characteristics in structural and chemical properties. Under the optimized conditions of the vertical distance (150 mm), the CGS thin films showed densely packed grains and large grain sizes up to 1 μm in scale with decreasing lateral distances. The composition ratio of Ga/[Cu+Ga] and Se/[Cu+Ga] showed 0.50 and 0.93, respectively, in nearly the same composition as the sputtering target. X-ray diffraction and Raman spectroscopy revealed that the CGS thin films had a pure chalcopyrite phase without any secondary phases such as Cu–Se or ordered vacancy compounds, respectively. In addition, we found that the optical bandgap energies of the CGS thin films are shifted from 1.650 to 1.664 eV with decreasing lateral distance, showing a near-stoichiometric region with chalcopyrite characteristics.

Keywords: CuGaSe₂, Solar Energy, One-Step Sputtering, Sputter Yield, Optical Bandgap.

1. INTRODUCTION

Cu(In,Ga)Se₂ (CIGS) thin-film solar cells have reached a high level of performance because of CIGS' controllable bandgap ($E_g = 1.0\sim 1.6$ eV) and apparent high absorption coefficient ($\alpha \geq 10^5$ cm⁻¹).⁽¹⁾ CIGS thin films have been optimized from I–III–V₂ ternary semiconducting materials such as CuInSe₂ (CIS) and CuGaSe₂ (CGS), which have different electrical and optical properties. Relating to the co-evaporation process, CIS thin films have been steadily improved by controlling their bandgaps, which can be easily adjusted by adding Ga element, and the optimized solar cells have exhibited conversion efficiencies above 20% in

laboratory scale.⁽²⁾ However, under the optimized conditions of CGS device structures, the highest CGS cell efficiency showed the maximum cell efficiency of 9.7% for a single crystal device and 9.5% for a polycrystalline thin film device, respectively.⁽¹⁸⁾ For that reason, CGS thin film has not been used alone in device fabrication because it has a large bandgap energy of 1.67 eV, which can limit collection from the long-wavelength spectrum. Nonetheless, CGS thin films with large bandgap energy have shown potential through a co-deposition process with CIS materials to fabricate high-quality CIGS thin films. In addition, CGS thin films have contributed to improved solar cell performance with tandem structure as the top absorber layer to collect selectively from the short-wavelength spectrum. It is reported that the CIGS solar cells with this structure

*Author to whom correspondence should be addressed.
Email: twkim90@kitech.re.kr

theoretically exhibit a cell efficiency of 33.3%.⁽³⁾ Obviously, the Ga component of the related thin film plays an important role in CIGS solar cells, which can be beneficial to cell efficiency as a jointly used material. To date, several fabrication techniques for making CGS thin films have been studied, including co-evaporation, sputtering, electro-deposition, and other techniques.^(4–9) Among them, the sputtering method has been widely used to fabricate thin films due to its advantages of being scalable and cost effective. However, most of the sputtering methods are two-stage processes, where the first deposition step is of a metal precursor, which is then selenized by H_2Se ambient gases. This selenization process has shortcomings in several deposition steps: it uses toxic gases, and it is difficult to control composition during film growth. Hence, further research should be done to develop a simpler and scalable process to achieve high-quality absorber layers.

In this study, we suggest a simple one-step sputtering method that can fabricate CGS thin films by using a Se-containing CGS single target. Despite the above several advantages, one-step sputtering should precisely optimize growth parameters because three different kinds of atoms (Cu, Ga, and Se) are simultaneously deposited on the substrate to meet the compositional and structural uniformity of CGS thin films. Generally, it is widely reported that sputter yield is considerably affected by angle of ion incidence and atomic weight.^(16,17) In other words, the sputter yields of atoms ejected from the sputtering target are varied with those conditions. The different sputter yields of compound materials might especially affect the physical properties of the deposited films. So, we have systematically investigated the effects of vertical and lateral distance from the center of the sputtering target on the CGS thin films. Finally, using a one-step sputtering process without an additional selenization process, the sputtering conditions for high-quality CGS thin films have been optimized to improve the structural and optical properties of well-organized CGS thin films.

2. EXPERIMENTAL DETAILS

The CGS thin films were deposited on soda-lime glass (SLG) substrate using a combinatorial one-step sputtering system that employs a CGS target with an 1:1:2 stoichiometry. The targets had a 4-inch diameter and were purchased from High Purity Chemical Co., Japan. By using the combinatorial one-step sputtering method, CGS thin films were deposited directly from a compound chalcopyrite target onto the SLG substrate without any additional selenization process. To fabricate the CGS films, RF magnetron sputtering was employed, which consists of a vacuum chamber reactor (ULVAC MB07-4501) equipped with a 4-inch sputtering gun. Prior to film growth, the sputtering chamber was evacuated to a base pressure of 2×10^{-6} Pa. The SLG substrate was prepared in four steps: the substrate was first cleaned in a soap bath to eliminate organic materials,

then isopropyl alcohol (IPA) and deionized (DI) water was sequentially used, and the substrate was finally heated at 100 °C for 10 min. The optimized deposition conditions were as follows: RF power (300 W), ambient gas (argon), gas flow rate (30 sccm), working pressure (0.43 Pa), substrate temperature (500 °C), and SLG substrate with $180 \times 50 \text{ mm}^2$ area. By using this technique, the CGS sample libraries were fabricated as a function of film thickness, which have different sample positions from the target to the substrate.

Figure 1 shows the schematic diagram of the one-step sputtering process and the sample configuration having different film thickness as a function of distance from the target to the substrate. The CGS thin films were deposited on the SLG substrate without substrate rotation; but they were grown with a thickness gradient that has different vertical and lateral distance from the CGS sputtering target. The former has the distance of 110, 130, and 150 mm between the center of the target and surface of SLG substrate. And the latter has the distance of (I) 180 mm, (II) 150 mm, (III) 110 mm, (IV) 70 mm, and (V) 30 mm, where the lateral length is measured at each sample position (I to V) from the center of the sputtering target with only x -component, respectively. To investigate the morphological changes as a function of the vertical and lateral distance, the CGS thin-film libraries were fabricated by using the one-step process, as shown in Figure 1. As shown in Figure 1, the sputtering target is positioned at the out-of-SLG substrate to deposit the particles sputtered from the erosion region with higher kinetic energy (KE). Generally, sputter yields are considerably affected by ion incidence angle even in identical ion-beam energies.⁽¹⁶⁾ The sputter yields increase with increasing ion incidence angle and then have

Fig. 1. Schematic diagram of one-step sputtering process and sample configuration between the target and substrate as a function of lateral and vertical distance from the target.

Fig. 2. Schematic diagram of the expected coverage of the particles sputtered from the target as a function of vertical and lateral distance.

a maximum value at a certain angle and finally decrease when it gets close to the target normal. Again, the particles sputtered at the specific angle with the high sputter yield mean that they have sufficient KE to deposit high-quality thin films on the substrate. On the contrary, it is assumed that the particles sputtered at the out-of-erosion region have a relatively low KE, resulting in inferior morphological properties such as island growth and irregular facets.

Figure 2 shows the schematic diagram of the particle coverage sputtered from the target as a function of vertical and lateral distance. At the vertical distance of 110 mm, the particles with sufficient KE can be deposited on the limited area of the SLG substrate. However, the sputtered particles with sufficient KE can be deposited on the whole area of the SLG substrate with increasing vertical distance.

Five kinds of CGS samples with a size of $12 \times 12 \text{ mm}^2$ have been deposited on the SLG substrate with a size of $180 \times 50 \text{ mm}^2$ using a patterned shadow mask. In order to increase the reliability of the analysis of CGS thin films, all analysis were carried out using the same samples in the order of Raman, Transmittance, XRD, and SEM. Plan-view and cross-section images of CGS films were examined by field-emission scanning electron microscopy (FE-SEM, Quanta 200). Crystal structure was analyzed by X-ray diffractometry (XRD, Panalytical X'pert MPD). The phase analysis was performed by Raman spectroscopy with a He-Ne laser with a wavelength of 632 nm (JOVIN YVON SAS). Optical properties of films were measured using a UV-VIS-IR spectrometer (Varian Cary 5000).

3. RESULTS AND DISCUSSION

3.1. Effect of Target-Substrate Distance

The RF power (200 W) and the process pressure (0.43 Pa) are mentioned as the growth conditions for CGS thin

films by using one-step sputtering process in experimental section. These optimized growth conditions are to generate sputtering particles from the target with the higher kinetic energy. In particular, we confirmed that the process pressure had a great influence on the surface morphology and compositional distributions during the film growth in previous study (not shown here). After changing the process pressure from 0.19 to 1.95 Pa, CGS thin films were fabricated and characterized in structural and compositional properties. As a result, it was confirmed that a secondary phase was formed in the CGS film when the process pressure was 0.19 and 1.95 Pa. This phenomenon is considered to be the change of the mean free path (MFP) of the sputtered particles depending on the pressure of the process chamber. That is to say that the MFP distance decreases as the process pressure increases, which causes particle energy reduction. In the opposite case, the particle energy is increased but the process time is greatly increased due to the decrease of the amount of the sputtered particles. The process pressure of 0.43 Pa used in this experiment is the optimized condition considering the kinetic energy of the sputtered particles and the amount of sputter yields.

Figure 3 shows the SEM plan-view images of CGS thin films as a function of vertical and lateral distance from the center of the CGS sputtering target. The surface morphologies of CGS thin films have irregular grain growth as the lateral distance increases, whereas the CGS thin films at the short lateral distance of 30 mm show smooth and densely packed grain growth regardless of vertical distances. The CGS thin films grown at the vertical

Fig. 3. Plan-view images of CGS thin films as a function of vertical and lateral distance from the center of CGS sputtering target.

distance of 150 mm show smooth and regular surface morphologies regardless of the lateral distances. Meanwhile, CGS thin films deposited at the vertical distance of 110 and 130 mm have irregular island growth, demonstrating that variations in surface morphologies are in good agreement with our expectations by changing the distance from the target. In addition, composition ratios of CGS thin films are analyzed by X-ray fluorescence (XRF) measurement to confirm the relationship between the protrusion and matrix in the CGS thin films. As mentioned in the experimental section, the CGS thin films are fabricated using a Se-contained CGS target with a 1:1:2 stoichiometry. Accordingly, $\text{Ga}/[\text{Cu} + \text{Ga}]$ (GCG) and $\text{Se}/[\text{Cu} + \text{Ga}]$ (SCG) ratios of the CGS thin films are depicted to determine compositional deviations between the target and film. Figure 4 shows the GCG and SCG ratios of the CGS films had 0.5 and 0.93 at the lateral and vertical distances of 30 and 150 mm, respectively. But the GCG and SCG ratios of the CGS films have a fairly big difference in the vertical distance of 110 and 130 mm, whereas those of composition ratios have relatively constant values irrespective of lateral distances in the vertical distance of 150 mm. That is to say, our expectation as a function of sputtering distance corresponds well to the experimental results, demonstrating that the morphology and composition ratio of the CGS thin films are more stable and have uniform properties as vertical distances increase. Under the optimized conditions of vertical distance (150 mm), the compositions of CGS thin-film libraries are further investigated as a function of lateral distance as shown in the Table I. The Se composition of the CGS thin films deposited at the different lateral distance was found to be lower than the target composition, which might be caused by lower vapor pressure of the Se element. And the compositions of Cu and Ga are not completely matched with the target composition but showed a relatively stable composition distribution regardless of the lateral distance. As described above, the results of whether the compositional deviation of the CGS thin

Table I. Compositions of CGS thin films as a function of the lateral distance at the constant vertical distance of 150 mm measured by X-ray fluorescence.

No.	Cu (at.%)	Ga (at.%)	Se (at.%)	Sum (at.%)	Ga/(Cu+Ga)	Se/(Cu+Ga)
I	26.31	27.52	46.17	100	0.51	0.86
II	25.30	25.81	48.89	100	0.50	0.96
III	24.40	26.61	48.99	100	0.52	0.96
IV	25.10	26.31	48.59	100	0.51	0.95
V	25.71	26.01	48.29	100	0.50	0.93

film produces a secondary phase such as Cu–Se will be discussed in detail in the following section.

3.2. SEM Analysis

Cross-section and plan-view images in Figure 5 show the variations in grain size and morphology as a function of sample position. The thicknesses of CGS films ranged from 540 nm to 2,200 nm with different sample positions from the CGS sputtering target. The CGS films show the dense and compact adhesion to the SLG substrate without any voids or cracks. However, the grain size and morphology of the films are largely different as a function of sample position. The samples of (I) and (II) show round-shaped facets and have a small grain size of ~ 200 nm. In contrast, the samples of (III), (IV), and (V) exhibit densely packed large grains and smooth surfaces, as shown in Figure 5. In the three-stage co-evaporation process, it is generally reported that the substrate temperature influences grain size and surface morphology.⁽¹⁰⁾ In other words, large grain sizes are observed at a substrate temperature of ~ 600 °C whereas small grains are found at ~ 350 °C. In our case, the CGS films show a dramatic increase in grain size up to the $1\text{-}\mu\text{m}$ scale, maintaining excellent surface morphology for all samples even at the low growth temperature of 500 °C. In addition, the film thickness and morphology of CGS thin films are strongly influenced by a combination of vertical and lateral distance during the

Fig. 4. Composition ratios of (a) $\text{Ga}/[\text{Cu} + \text{Ga}]$ and (b) $\text{Se}/[\text{Cu} + \text{Ga}]$ for CGS thin films as a function of vertical and lateral distance measured by X-ray fluorescence.

Fig. 5. Cross-section (Top) and plan-view (Bottom) of the CGS thin films grown on SLG substrate as a function of lateral distance of (I) 180 mm, (II) 150 mm, (III) 110 mm, (IV) 70 mm, and (V) 30 mm at the constant vertical distance of 150 mm.

film growth, as mentioned above in Figure 3. All the samples grown at the vertical distance of 150 mm show the regular and smooth surface morphology; but some differences of grain shapes are observed as a function of lateral distances. The samples (I) and (II) with the large lateral distance of 180 and 150 mm show small grains compared to other samples (III, IV, and V), assuming that the incident particle energies may be reduced by collisions when the particles move toward the substrate. But the surface morphologies in each film are not changed such as in the island structure or irregular facets. From this result, it is confirmed that high-quality CGS films can be fabricated by the one-step sputtering process, which has advantages of being a simple and scalable process compared to the evaporation method.

3.3. XRD Analysis

The CGS thin-film libraries showed uniform morphologies in each film (I to V) under the optimized DTS conditions. But, the CGS thin-film libraries had some different features in the grain size and surface morphologies. Hence, a more-detailed investigation was conducted to study structural properties in regard to crystallography and to see whether or not the sample libraries have the distinctive characteristics as a function of lateral distance. Figure 6 shows the XRD patterns and full width at half maximum (FWHM) values corresponding to the (112) diffraction plane as a function of sample position. The only chalcopyrite structure observed is at the diffraction plane of (112), (220)/(204), and (312)/(116) without secondary phases such as Cu–Se or ordered vacancy compounds (OVCs). One of the secondary phases, Cu_2Se (111), occurs at the diffraction angle of 27.1° near the CGS (112) peak position.⁽¹¹⁾ Also, diffraction peaks of $2\theta_{112}$ values are separated at the similar peak position, in which the (111) cubic structure is determined below 27.7° and

the (112) tetragonal structure is observed above 27.7° .⁽¹²⁾ In our films, there are no relevant peaks along with the CGS (112) plane, showing (112) diffraction angles ranging from 27.75° to 27.78° with no remarkable angle shifts.

Fig. 6. XRD patterns (a) and FWHMs and crystallite sizes (b) of CGS thin films as a function of lateral distance of (I) 180 mm, (II) 150 mm, (III) 110 mm, (IV) 70 mm, and (V) 30 mm at the constant vertical distance of 150 mm.

In addition, the CGS films show a clear doublet diffraction plane of (220)/(204) and (312)/(116), demonstrating superior structural quality as compared to OVC phases without any doublet characteristic. Furthermore, the FWHM for the (112) orientation plane is depicted to investigate crystallinity of the CGS films, as shown in Figure 6. The FWHM of the (112) plane decreases with decreasing lateral distances, indicating that the increased crystallinity is correlated with the densely packed surface morphology. These can be expected to be the sputtered particles with the higher kinetic energy to deposit the CGS film having smooth and densely packed structures. Namely, the crystallinity of CGS thin films via XRD patterns correspond to surface morphologies by demonstrating the reduction in FWHM values with decreasing lateral distances. As shown in the SEM result, the grain size of CGS thin films showed the irregular island growth as increasing lateral distances. In other words, it is considered that the lateral distance between target and the substrate have a great influence on the crystal growth of the CGS thin film. Particularly, the samples I and II with large lateral distances showed poor crystallinity such as irregular grains and high FWHM values compared to other samples (III to V). So, crystallite sizes of the CGS thin films by using scherrer equation ($\tau = K\lambda/\beta \cos \theta$) are compared with morphological properties. As a result, the crystallite size tends to increase as the lateral distance from the target increases, which is also consistent with the SEM results.

3.4. Raman Analysis

Figure 7 shows the Raman spectra and its variations in FWHMs as a function of sample position to study structural changes such as binary phases or non-stoichiometric properties. The Raman spectra on CGS single-crystals with stoichiometry show the dominant A_1 mode at 186 cm^{-1} and other scattering modes at B_2 -273 (257 cm^{-1}) and E_1 -252 (249 cm^{-1}), indicating the various vibration directions caused by that of cations and anions in the chalcopyrite crystal.⁽¹³⁾ Importantly, during film growth, the existence of binary and OVC phases are considered eliminated due to degraded absorber and device properties. One of them, non-stoichiometric CGS films, have the A_1 mode shifted toward higher frequency; for example, CGS films with OVC phases are observed at the A_1 mode frequency of $193\sim 199 \text{ cm}^{-1}$.⁽¹⁴⁾ Also, a Cu-Se phase is observed at 261 cm^{-1} when the films have defects related to composition, crystal structure, and other growth parameters. In this regard, a Se-containing stoichiometric CGS single target is used to form only chalcopyrite structures and to avoid any other structures in the CGS film. As seen in Figure 7(a), the chalcopyrite characteristic peaks of A_1 , $B_2(\text{LO})$, and $E_1(\text{TO})$ are observed at 185 cm^{-1} , 272 cm^{-1} , and 249 cm^{-1} , respectively, for all of the CGS films. Although all the peaks observed are shifted slightly toward lower frequency compared to theoretical values, this means that there is in-phase movement of Cu and Ga

Fig. 7. Raman spectra (a) and FWHM values (b) of CGS thin films as a function of lateral distance of (I) 180 mm, (II) 150 mm, (III) 110 mm, (IV) 70 mm, and (V) 30 mm at the constant vertical distance of 150 mm.

against Se anions but not secondary phases. Additionally, the FWHMs of A_1 and $B_2(\text{LO})$ scattering modes for CGS films are illustrated in Figure 7(b). The FWHMs of A_1 mode peaks are changed as a function of sample position, showing poor crystallinity in sample (III) with the value of 11.04 cm^{-1} and sample (V) has the lowest FWHM value of 8.31 cm^{-1} with good crystallinity. Similarly, Raman spectra and FWHM values are in good agreement with the XRD results, showing that the dominant peaks are little changed as a function of lateral distance, and the crystallinity increases with decreasing lateral distances.

3.5. Transmittance and Bandgap Energy

Figure 8 shows the transmittance and optical bandgap energy of CGS films deposited at various film thicknesses. The bandgap energies of the films are calculated from the transmittance and determined by extrapolating the linear portion of $(\alpha h\nu)^2$ versus photon energy ($h\nu$). The absorption coefficient (α) was calculated by dividing

Fig. 8. Transmittance (a) and optical bandgap energy (b) of CGS thin films as a function of lateral distance of (I) 180 mm, (II) 150 mm, (III) 110 mm, (IV) 70 mm, and (V) 30 mm at the constant vertical distance of 150 mm.

the transmittance of each sample (I to V) by the film thickness since each sample had a different film thickness. All the CGS films exhibit a good linear fit over the photon energy and are easily extrapolated to obtain the bandgap values. In the case of CGS film with near-stoichiometry, fundamental transitions are limited to the range of photon energy between 1.66 and 1.72 eV due to the existence of additional inter-band absorption at 1.75 eV.⁽¹⁵⁾ This means that the bandgaps of CGS films can be shifted slightly as a function of compositions in films, maintaining the chalcopyrite crystal structures. As shown in Figure 8(b), bandgap energies range from 1.650 to 1.658 eV with increasing film thickness. It is worth mentioning that CGS films remain close to near-stoichiometry with decreasing lateral distances from the target. Similarly, the improvement in film quality was already confirmed by SEM images, XRD patterns, and Raman spectra as a function of lateral distance. The optical bandgap energies are also in good agreement with effects of sputtering distances, showing chalcopyrite characteristics without secondary phases.

4. CONCLUSION

In summary, we presented the structural and optical properties of CGS thin films fabricated by a combinatorial one-step sputtering process employing a CGS ternary compound target. Most importantly, the CGS thin films are considerably affected by vertical and lateral distances from the target through the changes in the structural and compositional properties of CGS thin films. The CGS thin-film qualities are improved because the sputtered particles with sufficient KE can be deposited on the whole substrate with increasing vertical distances. Some deviations in physical properties were observed as a function of lateral distance under the optimized vertical distance from the target. But all the CGS thin films revealed a chalcopyrite characteristic and there were no phase changes in CGS thin films. Overall, we demonstrated that one-step sputtering has excellent potential to be an effective fabrication process for high-quality CGS thin films. In the future, more research motivated by this result could be expected to improve the growth mechanism through the combinations of other chalcopyrite materials.

Acknowledgment: This study was supported by Korea Institute of Industrial Technology (KITECH) under the international cooperative R&D project number of EO160024 and NK140080 and National Renewable Energy Laboratory (NREL) under the subcontract number of DE-AC36-08G028308.

References and Notes

1. S. M. Kong and C. W. Chung; Characterization of Cu(In,Ga)Se₂ thin films prepared by RF magnetron sputtering using a single target without selenization; *J. Ind. Eng. Chem.* 19, 1320 (2013).
2. Y. K. Liao and S. Y. Kuo; Observation of unusual optical transitions in thin-film Cu(In,Ga)Se₂ solar cells; *Opt. Express* 20, A836 (2012).
3. K. T. Ramakrishna Reddy and P. Jayarama Reddy; Fabrication and performance of a polycrystalline ZnCdS/CuGaSe₂ thin-film solar cell; *J. Mater. Sci. Lett.* 10, 439 (1991).
4. B.-T. Jheng, P.-T. Liu, M.-C. Wu, and H.-P. D. Shieh; A non-selenization technology by co-sputtering deposition for solar cell applications; *Opt. Lett.* 37, 2760 (2012).
5. M. Marudachalam and H. Hichri; Preparation of homogeneous Cu(In,Ga)Se₂ films by selenization of metal precursors in H₂Se atmosphere; *Appl. Phys. Lett.* 67, 3978 (1995).
6. S. Niki and M. Contreras; CIGS absorbers and processes; *Prog. Photovolt. Res. Appl.* 18, 453 (2010).
7. C. J. Hibberd, E. Chassaing, and A. N. Tiwari; Non-vacuum methods for formation of Cu(In,Ga)(Se,S)₂ thin film photovoltaic absorbers; *Prog. Photovolt. Res. Appl.* 18, 434 (2010).
8. X. H. Tan, S. L. Ye, and X. Liu; Increasing surface band gap of Cu(In,Ga)Se₂ thin films by post depositing an In-Ga-Se thin layer; *Opt. Express* 19, 6609 (2011).
9. Q. Guo, S. J. Kim, and H. W. Hillhouse; Development of CuInSe₂ nanocrystal and nanoring inks for low-cost solar cells; *Nano Lett.* 8, 2982 (2008).
10. K. Ramanathan and M. A. Contreras; Properties of 19.2% efficiency ZnO/CdS/CuInGaSe₂ thin-film solar cells; *Prog. Photovolt. Res. Appl.* 11, 225 (2003).

11. F.-J. Haug, M. Krejci, and A. N. Tiwari; Characterization of $\text{CuGa}_x\text{Se}_y/\text{ZnO}$ for superstrate solar cells; *Thin Solid Films* 362–362, 239 (2000).
12. D. Albin and R. Noufi; Composition-structure relationships for multisource evaporated CuGaSe_2 thin films; *J. Appl. Phys.* 64, 4903 (1988).
13. I. V. Bodnar and L. V. Golubev; Raman Scattering in CuGaSe_2 ; *Phys. Status Solidi B* 105, K111 (1980).
14. D. Papadimitriou and N. Esser; Structural properties of chalcopyrite thin films studied by Raman spectroscopy; *Phys. Status Solidi B* 242, 2633 (2005).
15. J. Tuttle and R. Noufi; Effects of composition and substrate temperature on the electro-optical properties of thin-film CuInSe_2 and CuGaSe_2 ; *Solar Cells* 24, 67 (1988).
16. H. Hofsass and K. Zhang; Simulation of ion beam sputtering with SDTrimSP, TRIDYN and SRIM; *Appl. Surf. Sci.* 310, 134 (2014).
17. H. Oechsner; Sputtering-a review of some recent experimental and theoretical aspects; *Appl. Phys.* 8, 185 (1975).
18. S. Ishizuka and S. Niki; Structural tuning of wide-gap chalcopyrite CuGaSe_2 thin films and highly efficient solar cells: differences from narrow-gap Cu(In,Ga)Se_2 ; *Prog. Photovolt. Res. Appl.* 22, 821 (2014).

Received: 23 September 2016. Revised/Accepted: 1 January 2017.

Delivered by Ingenta to: National Renewable Energy Lab (NREL)
IP: 192.174.37.50 On: Wed, 24 May 2017 19:41:07
Copyright: American Scientific Publishers