Influence of Ag Layer Location on the Performance of $\text{Cu}_2\text{ZnSnS}_4$ Thin Film Solar Cells

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In this work, the $(\text{Ag,Cu})_2\text{ZnSnS}_4$ (ACZTS) thin films were fabricated via sputtering with a multi-target to form different layer stacks, i.e., (S1) ZnS/Sn/Cu/Ag/Mo, (S2) ZnS/Sn/Ag/Cu/Mo and (S3) ZnS/Ag/Sn/Cu/Mo. The stacked precursors were sulfurized through a soft annealing, followed by a two-step sulfurization in a chamber filled with N_2 at standard atmospheric pressure. The x-ray photoelectron spectroscopy elemental profile showed a vertical non-uniform distribution of Ag in the film. Based on the results of scanning electron microscopy and electron probe microanalysis, Ag enrichment of the upper surface was beneficial for the grain size. Moreover, a dense, uniform surface could be obtained and the stability of the elemental composition could be maintained. After optimizing the order of the Ag layers, the efficiency of the solar cells increased from 1.30% to 3.65%, an improvement of 181%. The open circuit voltage is increased from 448 mV to 630 mV because of the reduced voids, increased grain size, and reduced Cu_{Zn} antisite defects.

Key words: Magnetron sputtering, multi-target, two-step sulfurization, Ag-doped CZTS solar cells

INTRODUCTION

The kesterite, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), has attracted wide attention as an absorber material because of its suitable band gap energy (E_g) of 1.4–1.5 eV, environmentally friendly composition, and low-toxicity processing techniques.^{1–4} To date, CZTS solar cells fabricated via co-sputtering Cu/ZnS/SnS have achieved the highest efficiency of 11.0%.⁵ However, this efficiency remains far below the theoretically predicted photo-conversion efficiency of 32%,⁶ and its high open-circuit voltage deficit is one of the key issues.⁷ Since Cu and Zn have similar ionic radii,

Cu_{Zn} antisite defects can be easily formed.⁸ The presence of a large number of Cu_{Zn} antisite defects lead to band tailing that decreases the open circuit voltage.⁷

Many researchers have tried to incorporate impurities, such as Ge, In, and Cd, to improve the optical and electrical properties of CZTS.^{9–11} Among them, the incorporation of Ag has significantly improved the performance of CZTS. Chen et al. found that the formation energy of Ag_{Zn} antisite defects was higher than Cu_{Zn} antisite defects.⁸ Therefore, partial substitution of Cu by Ag can decrease the concentration of Cu_{Zn} antisite defects. Kumar et al. found that incorporation of Ag increased the grain size of CZTS. The larger grain size is beneficial in reducing the number of grain boundaries, and therefore decreasing carrier recombination.¹² Cui et al.

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deposited 20 nm of Ag on Mo-coated soda lime glass before the deposition of the $\text{Cu}_2\text{ZnSnS}_4$ absorber¹³; Ag was expected to function as a barrier layer in the same manner as TiN,¹⁴ ZnO,¹⁵ and TiB_2 ,¹⁶ and was considered to aid in suppressing the decomposition of CZTS at the CZTS/Mo contact surface.^{13,17} Qi et al. studied the gradient distribution of Ag in the $(\text{Cu}, \text{Ag})_2\text{ZnSn}(\text{S}, \text{Se})_4$ absorber layer. The content of Ag at the back and front surfaces was higher, while the content in the middle portion was lower. A higher concentration of Ag in the CdS/absorber interface hinders the Fermi level pinning and the higher Ag content near the Mo back contact suppresses recombination and improves the utilization of long-wavelength incident light. They achieved an efficiency of 11.2%, and this is the highest efficiency demonstrated for Ag-substituted CZTSSe solar cells.² However, the solution processing method is not suitable for the preparation of uniform CZTS absorption layers over a large area. Moreover, the evaporation of solvents can cause environmental pollution. In this paper, Ag was sputtered at different locations. The Raman spectroscopy, x-ray diffraction, backscattered electron, and scanning electron microscope (SEM) were used to investigate how the location of the Ag layer in the precursor influences the growth mechanism, microstructure, and device performances of the CZTS solar cells.

Table I. Thicknesses of precursor component layers

Precursor	ZnS (nm)	Cu (nm)	Ag (nm)	Sn (nm)
S1	254	98	19	195
S2	254	98	19	195
S3	254	98	19	195

EXPERIMENTS

Materials

Copper (Cu, 99.99%), silver (Ag, 99.99%), zinc sulfide (ZnS, 99.9%), tin (Sn, 99.8%) zinc oxide (i-ZnO, 99%), and indium tin oxide (ITO, 99.9%) targets were purchased from MAT-CN; sulfur (S,99.95%), ammonium acetate ($\text{CH}_3\text{COONH}_4$, 99%), cadmium acetate ($\text{C}_4\text{H}_6\text{CdO}_4\cdot 2\text{H}_2\text{O}$, 99%) and thiourea ($\text{CH}_4\text{N}_2\text{S}$, 99%) were purchased from Aladdin Co.

Methods

A substrate based on Mo coated soda-lime glass was deposited by a DC-magnetron sputtering. The Cu-Ag-Sn-ZnS metallic stacks were deposited by RF-sputtering. The stacked sequential design is shown in Fig. 1. Table I shows the metallic layer thickness of the precursors. These values were calculated by the deposition rate of each target and time. Before depositing the precursors, the sputtering chamber was evacuated to a pressure of 5.0×10^{-4} Pa. Then, the precursors were alloyed at 260°C for 30 min in a tube furnace filled with N_2 about 1×10^5 Pa. After that, the samples were cooled down to room temperature naturally. Finally, 60 mg of S powder was added and heated up to 560°C for 45 min. To the complete device (ITO/i-ZnO/CdS/ACZTS/Mo), a ~ 50–60 nm CdS buffer layer was deposited via a chemical bath. The solution was prepared by dissolving $\text{C}_4\text{H}_6\text{CdO}_4\cdot 2\text{H}_2\text{O}$ (0.01 mol L^{-1}), $\text{CH}_4\text{N}_2\text{S}$ (1 mol L^{-1}), and $\text{CH}_3\text{COONH}_4$ (1 mol L^{-1}) into deionized water (450 mL) and stirred in a 83°C water bath for 12 min to get a clear orange solution. The window layer was 45–55 nm i-ZnO and 250–300 nm ITO were deposited by RF-magnetron sputtering at 80 W. Finally, Ni-Al metal grids contacts

Fig. 1. Schematic illustration of the stacks of the Ag-incorporated CZTS thin film: (a) Ag layer located on the Mo layer; (b) Ag layer located on the Cu layer; (c) Ag layer located on the Sn layer.

were fabricated via electron beam evaporation. The active area of each ACZTS solar cell was $\sim 0.22 \text{ cm}^2$ as determined by mechanical scribing and an optical microscope. No etching was used for device fabrication in this work.

Characterization

The thickness of the films was measured with a KLA Vencor *p*-6 surface step profiler. The composition of the ACZTS thin films was determined with JOEL *JXA-8230* (20 kV) electron probe microanalysis (EPMA). The crystal structures were examined by Rigaku Ultima IV multipurpose x-ray diffraction (XRD) with a $\text{Cu-K}\alpha$ ($\lambda = 0.15406 \text{ nm}$) source. Raman spectroscopy measurements were conducted using the 514 nm line of an Ar^+ laser with a 50 mW excitation source. A scanning electron microscope (SEM; FEI *Nova Nano450*) was used to characterize the morphology, depth profiles, and chemical composition of the sulfurized materials. Elemental depth profiles were obtained by sputtering the CZTS surface with 1 keV Ar^+ ions over an etching area of $2 \times 2 \text{ mm}$ and a Thermo Fisher Scientific *K-Alpha+* was used for the x-ray Photoelectron Spectroscopy (XPS) analysis. The current density–voltage (*J*–*V*) measurements were made under the standard AM1.5 G spectrum with an illumination intensity of 1000 W/m^2 at room temperature (Keithley 2420).

RESULTS AND DISCUSSION

Structural Characterization

Although a stack of discrete metal layers was deposited, inter-diffusion of the metal layers occurred to form alloys. Figure 2a shows the XRD θ – 2θ scans of the precursor films after alloying at 260°C . For all the films, the main diffraction peaks are consistent with Cu_5Zn_8 (JCPDS: 25-1228), Cu_3Sn (JCPDS: 01-1240), Cu_6Sn_5 (JCPDS: 45-1488), and Cu_{2-x}S . The formation of these second phases is accompanied by a volume expansion, which releases the residual stress of the metal stack and provides a significant improvement in the crystallinity of the ACZTS thin film during subsequent vulcanization.¹⁸ The Cu–Sn alloy mainly exists in the form of Cu_6Sn_5 as previously reported.^{6,19–22} In this work, a very strong peak is observed at $\sim 41.82^\circ$ corresponding to the Cu_3Sn phase. The Cu_6Sn_5 is generated at a low temperature in a Sn-rich environment, and Cu_3Sn is formed at high temperatures in a Cu-rich environment.²³ Ag does not stabilize at the deposition site, but spreads rapidly at high temperatures and binds to Sn to form the solid solution Ag_3Sn (Fig. 2a). The melting point of the ternary eutectic phase $\text{Sn}+\text{Ag}_3\text{Sn}+\text{Cu}_6\text{Sn}_5$ was 217°C . In contrast, the melting points of $\text{Sn}+\text{Cu}_6\text{Sn}_5$ and β -Sn are slightly higher, approaching 227°C .²⁴ Ag acts as a “fluxing agent” in the Sn–Cu–Zn alloy system, which

promotes the formation of the liquid phase and the inter-diffusion of the metal stack.

Figure 2b shows the XRD patterns of the sulfurized thin films. The diffraction peaks of all the samples correspond to the tetragonal kesterite phase (JCPDS: 26-0575). The intensity of the (112) diffraction peak of S3 sample is higher than that of the S1 and S2 samples, and the full width at half maximum (FWHM) of the diffraction peak is also narrow. This indicates that the stack structure of the S3 sample has a significantly improved crystal quality.

It is difficult to distinguish ZnS and Cu_2SnS_3 from CZTS by XRD because their crystal structure and lattice constant are similar.^{25,26} To further confirm the phase constitution of the CZTS thin films, Figure 3a shows the Raman spectroscopy of the ACZTS thin films, the main peaks for all the samples are at 251 cm^{-1} , 287 cm^{-1} , 337 cm^{-1} and 371 cm^{-1} , which is in accordance with the CZTS phase.²⁷ However, there is a broad peak between

Fig. 2. (a) XRD diffraction patterns of precursors S1, S2 and S3 after 260°C alloying and (b) XRD patterns of the sulfurized films S1, S2 and S3 which were annealed at 560°C .

Fig. 3. (a) Raman spectroscopy of the ACZTS thin films at an excitation wavelength of 514 nm and (b) backscattered electron and Raman spectroscopy, the white point is the elemental content sampling point.

351 cm⁻¹ and 352 cm⁻¹ in the S2 sample, which is consistent with the peaks reported for Cu₂SnS₃ (352 cm⁻¹) and ZnS (351 cm⁻¹).^{28,29} The upper corner of Fig. 3b shows the backscattered electron image of the S2 sample, where many white dotted areas can be found. The results of the white point element test showed that the Zn content was high; thus, we speculate that the 351 cm⁻¹ peak of the S2 sample corresponds to ZnS. In the S2 sample, the Ag layer is located between the Cu and Sn layers. Since the Ag layer is very thin, sufficient inter-diffusion occurred before heating to the melting point of the Sn-Ag-Cu ternary eutectic. As reported in the literature, the already melted Sn+Ag₃Sn+Cu₆Sn₅ tend to be absorbed into the un-melted β-Sn and Sn+Cu₆Sn₅ phases. This hinders the spreading behavior in the subsequent melting process and reduces the wettability.²⁴ Lateral segregation of the elements into islands of stable phases could occur, leading to a non-uniform composition at small length scales. The secondary phase of the isolated

Table II. Elemental constituent ratios of the precursors and sulfurized samples determined from EPMA measurements

Sample	(Cu+Ag)/(Zn+Sn)	Zn/Sn	S/M
Precursors	0.79	1.03	–
Sulfurized film S1'	0.92	1.13	0.99
Sulfurized film S2'	0.94	1.22	0.97
Sulfurized film S3'	0.88	1.04	1.01

region failed to react with ZnS during the sulfurization process. Under high temperature conditions, SnS is extremely volatile so a part of the ZnS secondary phase remained. Therefore, the deposition of an Ag layer between Cu and Sn could be detrimental to the formation of ACZTS.

Composition

The elemental content of the metallic precursors and sulfurized thin films were measured via EPMA. All the samples satisfy the characteristics of “Cu-poor and Zn-rich”, which is commonly used for making high efficiency CZTS solar cells.³⁰ It can be seen from Table II that the ratio of Zn/Sn increases after sulfurization. As reported in previous work, CZTS thin films using stacked metallic precursors showed problems with Zn and Sn losses during the annealing process in a sulfur atmosphere.³¹ In this work, ZnS replaced Zn and reduced the Zn-loss. So, the amount of Sn-loss can be taken as the basis of reference for Zn/Sn. Table II show that the amount of Sn-loss is different in the three samples. The position of Ag in the lamination may be an important reason for the difference in Sn-loss.

Sn-loss usually occurs in two stages: (1) the temperature rise process and (2) the dynamic equilibration process. Before reaching a dynamic balance, the synthesis of CZTS mainly includes the following steps: (1) the metal layers mix with each other to form a binary alloy phase, such as Cu-Sn and Cu-Zn; (2) The metal alloy phase decomposes at high temperature and then reacts with S to form the Cu-S, Sn-S, and Zn-S binary sulfides; and (3) Cu-Sn-S forms a ternary compound Cu₂SnS₃ and reacts with ZnS to form CZTS.³² Scragg et al. determined that the equilibrium reaction of CZTS can be decomposed into a two-step reaction^{33,34}:

It can be seen from the dynamic equilibrium reaction equation that if the solid SnS does not react with the other intermediate phases in time, it can easily aggregate and be converted into gas and escape from the surface. Ag was deposited on the upper layer of Sn in the S3 sample, the formed

Ag_3Sn or Ag_2S acted as a temporary barrier to reduce the volatilization of SnS during the annealing process. In contrast, for the S2 sample, Ag was located between Cu and Sn. The intermediate Ag_3Sn was too dense and may hinder the formation of Cu_2SnS_3 , which led to SnS aggregation that escaped from the sample easily. In the S1 sample, Ag deposition at the bottom has no significant effect on SnS volatilization.

ACZTS Thin Films Morphology

Figure 4a, b and c shows the SEM surface morphologies of ACZTS thin films. The grain size of S1 sample is uneven, the average grain size is $\sim 0.5\text{--}1.5\ \mu\text{m}$ and some voids could be observed. These voids are considered to be the channels left by the volatilization of the elements Sn. Compared with S1 sample, S3 has a more uniform surface and a larger grain size, and these the results are consistent with the XRD measurements. The white area on the surface of the S2 sample may be a secondary phase of ZnS , which had not sufficiently reacted.

Figure 5a, c and e shows the cross-sectional morphologies of the ACZTS thin films. Obvious morphological differences can be seen between the samples. The S1 sample has small grains from the top to bottom, and a large number of grain boundaries are present. The upper half of the S2 sample is a dense film composed of large grains, while the lower half of the sample had finely separated broken grains. The S3 sample has large grain sizes that almost span the thickness of the whole absorber layer. Figure 5b, d and f are the XPS elemental depth profiles of samples S1, S2 and S3, respectively. It can be seen from Fig. 5. (b), that Ag in the S1 sample is mainly concentrated at the bottom. Although Ag has a very fast diffusion rate, it combines with Sn to form the Ag_3Sn alloy, which may be stabilized in the alloy phase. In addition, the amount of incorporated Ag is very low, so no more elemental Ag diffuses after the formation of the Ag_3Sn alloy phase; therefore, Ag rarely enters the outermost layer. In the S2 sample, the content of Zn was higher than Sn as determined by the XPS elemental depth profile line (Fig. 5a), which is in accordance with the EPMA test results. Ag is mainly concentrated in the middle, which may be the reason for Cu and Sn not combining well. From Fig. 5d, Ag is mainly concentrated on the surface and the distribution of the other elements in S3 sample is more uniform, which effectively increased the grain size at the surface. These results show that the stacking position of Ag has a significant effect on the crystal growth of Ag-doped CZTS. The upper layer of Ag in the upper layer of Sn can function as a temporary barrier that suppresses the rapid volatilization of SnS during the temperature ramp phase. The surface Ag rich portion is beneficial for enhancing the crystallinity and uniformity of ACZTS. The fact that Ag is located in the middle

Fig. 4. (a), (b), and (c) are the SEM morphologies of the sulfurized films S1, S2 and S3.

of Cu and Sn hinders their uniform mixing and increases the loss of Sn. The Ag on the bottom layer has little effect on the surface topography, and the

Fig. 5. (a), (c) and (e) are SEM images of the cross-sectional morphologies of the sulfured films S1, S2 and S3; (b), (d) and (f) are the XPS elemental depth profiles of the S1, S2 and S3 samples. (Red circle indicates that Ag has a higher content distribution at this depth) (Color figure online).

performance of CZTS is not as good as that on the upper layer.

Device Characterization

Figure 6 shows the current–voltage (J – V) curves of the ACZTS solar cells under AM 1.5G illumination. As shown in Table III and Fig. 6, the highest efficiency of 3.65% was obtained from the device made from the S3 sample, prepared with a ZnS/Ag/Sn/Cu/Mo stacking order. Compared with the S1 sample, the efficiency of the S3 sample is increased by 82.5%. The S3 sample has a larger surface grain size and better surface uniformity (very few voids), which effectively reduces the recombination of carriers between the ACZTS/CdS heterojunctions. In addition, the Ag-rich surface has a low carrier concentration and Cu_{Zn} anti-defects. This facilitates the transport of carriers and increases the fill factor and open circuit voltage of the solar cells. Compared with sample S2, the open circuit voltage (V_{oc}), short circuit current (J_{sc}), and fill factor (FF) of S3 sample were increased by 40.6%, 50%, and 33.8%, respectively. Although the S2 sample also has larger grains, a part of the ZnS secondary phase was present on the surface and several hundred nm of broken crystal grains are present at the bottom. ZnS has a high resistance value which increases the series resistance of the device. On the other hand, there are many grain boundaries and the large number of defect states seriously affected carrier

transport. This has a strongly negative impact on the electrical performance of the solar cells. From the above results, the stable elemental composition and crystals have a large influence on the electrical properties of the CZTS battery device. The Ag doping position in the S3 sample is the structurally optimized design.

Table III shows the electrical characteristics of the sample determined via Hall measurements and J – V measurements. The results show that: (1) carrier concentration follows: $\text{S3} < \text{S1} < \text{S2}$. (2) Carrier mobility follows: $\text{S2} < \text{S1} < \text{S3}$. Li et al. found that when the ratio of Zn/Sn increases, the carrier concentration and the defect concentration of the CZTSe absorber layers also increases significantly, and the depletion region width of the battery was remarkable smaller.⁴ The lower Zn/Sn ratio of the S3 sample is a key factor for the resulting low carrier concentration. On the other hand, Ag and ZnS are adjacent in the S3 sample. The XPS elemental depth measurement shows that the surface layer was an Ag-rich layer, which helps reduce the density of Cu_{Zn} anti-defects. Additionally, a low defect density state helps reduce the carrier concentration and increase mobility. In conclusion, the electrical properties of the S3 (ZnS/Ag/Sn/Cu/Mo) prefabricated layer structure were greatly improved.

CONCLUSIONS

In this work, CZTS with different Ag-doping locations were prepared via multi-target sequential sputtering. The different Ag positions had a large influence on CZTS, which can be summarized as follows:

1. Ag was not stabilizing at the deposition site, but rapidly diffuses between the metal layers and acts as a “flux” for the alloy system.
2. After alloying, Ag combines with Sn to form Ag_3Sn ; the diffusion rate slows and tends to concentrate at the deposition site. This causes an uneven distribution of the Ag element. When Ag was concentrated on the surface, it beneficially reduced Sn-loss and formed larger grains, and the performance of the solar cell was significantly improved.
3. The Ag deposited between Cu and Sn hinders diffusion during the subsequent melting process and reduces the wettability. A lateral segrega-

Fig. 6. J – V curve for the ACZTS solar cells under AM 1.5G illuminations.

Table III. Electrical properties of S1, S2 and S3 samples after annealing

Sample	Mobility $\text{cm}^2 (\text{V s})^{-1}$	Carrier concentration/ cm^{-3}	Resistivity $\Omega \text{ cm}$	V_{oc} (mV)	J_{sc} (mA/ cm^2)	FF (%)	η (%)
S1	5.469	8.118×10^{17}	1.406	502.95	12.24	32.43	2.00
S2	1.646	2.115×10^{18}	1.793	448.00	9.60	30.15	1.30
S3	10.148	4.381×10^{17}	1.404	630.00	14.38	40.35	3.65

tion of the elements into islands with stable phases, leads to a non-uniform composition at small length scales.

Overall, the produced ACZTS thin film solar cell had a maximum efficiency of 3.65%, which was still very low. There are numerous factors that affect the efficiency of thin film solar cells, such as the Mo electrode, the CdS buffer layer, and the window layer (i-ZnO:ITO), which all have a strong impact on the device performance. In addition, we did not design a layer without Ag layer as a preference due to previous work has already reported the benefits of Ag-doping in detail. Our future work will focus on optimizing the ACZTS/CdS heterojunction interface.

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REFERENCES

1. X. Liu, R. Hao, Q. Zhao, F. Chang, Y. Li, K. Gu, L. Wang, B. Liu, and J. Guo, *Zeitschrift Fur Naturforsch. - Sect. A J. Phys. Sci.* 73, 957 (2018).
2. Y.F. Qi, D.X. Kou, W.H. Zhou, Z.J. Zhou, Q.W. Tian, Y.N. Meng, X.S. Liu, Z.L. Du, and S.X. Wu, *Energy Environ. Sci.* 10, 2401 (2017).
3. W. Li, X. Liu, H. Cui, S. Huang, and X. Hao, *J. Alloys Compd.* 625, 277 (2015).
4. J. Li, S.Y. Kim, D. Nam, X. Liu, J.H. Kim, H. Cheong, W. Liu, H. Li, Y. Sun, and Y. Zhang, *Sol. Energy Mater. Sol. Cells* 159, 447 (2017).
5. C. Yan, J. Huang, K. Sun, S. Johnston, Y. Zhang, H. Sun, A. Pu, M. He, F. Liu, K. Eder, L. Yang, J.M. Cairney, N.J. Ekins-Daukes, Z. Hameiri, J.A. Stride, S. Chen, M.A. Green, and X. Hao, *Nat. Energy* 3, 764 (2018).
6. Q. Zhao, R. Hao, S. Liu, M. Yang, X. Liu, F. Chang, Y. Lu, and S. Wang, *Phys. B Condens. Matter* 523, 62 (2017).
7. T. Gokmen, O. Gunawan, T.K. Todorov, and D.B. Mitzi, *Appl. Phys. Lett.* 103, 2 (2013).
8. Z.K. Yuan, S. Chen, H. Xiang, X.G. Gong, A. Walsh, J.S. Park, I. Repins, and S.H. Wei, *Adv. Funct. Mater.* 25, 6733 (2015).
9. S. Shanmuga Priya, A. Rao, I. Thirunavukkarasu, and V. Nayak, *Int. J. ChemTech Res.* 9, 261 (2016).
10. C. Wang, S. Chen, J.H. Yang, L. Lang, H.J. Xiang, X.G. Gong, A. Walsh, and S.H. Wei, *Chem. Mater.* 26, 3411 (2014).
11. T. Gershon, D. Bishop, P. Antunez, S. Singh, K.W. Brew, Y.S. Lee, O. Gunawan, T. Gokmen, T. Todorov, and R. Haight, *Curr. Opin. Green Sustain. Chem.* 4, 29 (2017).
12. J. Kumar and S. Ingole, *J. Alloys Compd.* 727, 1089 (2017).
13. H. Cui, X. Liu, F. Liu, X. Hao, N. Song, and C. Yan, *Appl. Phys. Lett.* 041115, 2 (2014).
14. B. Shin, Y. Zhu, N.A. Bojarczuk, S.J. Chey, S. Guha, B. Shin, Y. Zhu, N.A. Bojarczuk, S.J. Chey, and S. Guha, *Appl. Phys. Lett.* 053903 (2012).
15. W. Li, J. Chen, H. Cui, F. Liu, and X. Hao, *Mater. Lett.* 130, 87 (2014).
16. F. Liu, K. Sun, W. Li, C. Yan, H. Cui, L. Jiang, X. Hao, and A. Martin, *Appl. Phys. Lett.* 051105 (2015).
17. F. Liu, J. Huang, K. Sun, C. Yan, Y. Shen, J. Park, A. Pu, F. Zhou, X. Liu, J.A. Stride, M.A. Green, and X. Hao, *NPG Asia Mater.* 9, e401 (2017).
18. J. Li, Y. Zhang, H. Wang, L. Wu, J. Wang, W. Liu, Z. Zhou, Q. He, and Y. Sun, *Sol. Energy Mater. Sol. Cells* 132, 363 (2015).
19. M. Yang, S. Wang, Z. Jing, Z. Li, S. Liu, R. Guo, Y. Tang, R. Hao, and P. Yang, *Bull. Chin. Ceram. Soc.* 34, 222 (2015).
20. H. Yoo and J. Kim, *Thin Solid Films* 518, 6567 (2010).
21. M.G. Gang, K.V. Gurav, S.W. Shin, C.W. Hong, J.H. Min, M.P. Suryawanshi, S.A. Vanalakar, D.S. Lee, and J.H. Kim, *Phys. Status Solidi Curr. Top. Solid State Phys.* 12, 713 (2015).
22. Y. Feng, T.K. Lau, G. Cheng, L. Yin, Z. Li, H. Luo, Z. Liu, X. Lu, C. Yang, and X. Xiao, *CrystEngComm* 18, 1070 (2016).
23. J.F. Li, P.A. Agyakwa, and C.M. Johnson, *Acta Mater.* 59, 1198 (2011).
24. Y. Liu, F. Sun, and J. Wang, *Trans. China Weld. Inst.* 32, 25 (2011).
25. D.B. Mitzi, O. Gunawan, T.K. Todorov, K. Wang, and S. Guha, *Sol. Energy Mater. Sol. Cells* 95, 1421 (2011).
26. K. Sato, M. Fujiyoshi, M. Date, T. Shoji, and K.N. Tu, *J. Mater. Res.* 19, 2887 (2005).
27. F. Yang, R. Ma, W. Zhao, X. Zhang, and X. Li, *J. Alloys Compd.* 689, 849 (2016).
28. D.M. Berg, R. Djemour, L. Gütay, S. Siebentritt, P.J. Dale, X. Fontane, V. Izquierdo-Roca, and A. Pérez-Rodríguez, *Appl. Phys. Lett.* 100, 192103 (2012).
29. P.A. Fernandes, P.M.P. Salomé, and A.F. da Cunha, *Thin Solid Films* 517, 2519 (2009).
30. W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, and D.B. Mitzi, *Adv. Energy Mater.* 4, 1 (2014).
31. S.W. Shin, S.M. Pawar, C.Y. Park, J.H. Yun, J.H. Moon, J.H. Kim, and J.Y. Lee, *Sol. Energy Mater. Sol. Cells* 95, 3202 (2011).
32. A. Fairbrother, X. Fontané, V. Izquierdo-Roca, M. Espíndola-Rodríguez, S. López-Marino, M. Placidi, L. Calvo-Barrio, A. Pérez-Rodríguez, and E. Saucedo, *Sol. Energy Mater. Sol. Cells* 112, 97 (2013).
33. J. Scragg, T. Ericson, T. Kubart, M. Edoff, and C. Platzer-Bjorkman, *Chem. Mater.* 204, 4625 (2011).
34. A. Redinger, D.M. Berg, P.J. Dale, and S. Siebentritt, *J. Am. Chem. Soc.* 10, 3320 (2011).

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