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DTU Journal of Science and Technology 5(60) (2023) 58-63

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Fabrication of $Cu_2ZnSn(S_xSe_{1-x})_4$ thin film solar cell using spray pyrolysis method

Chế tạo pin mặt trời màng mỏng $Cu_2ZnSn(S_xSe_{1-x})_4$ bằng phương pháp phun nóng

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(Ngày nhận bài: 26/4/2023, ngày phản biện xong: 14/6/2023, ngày chấp nhận đăng: 03/9/2023)

Abstract

A kesterite $Cu_2ZnSn(S_xSe_{1-x})_4$ (CZTSSe) thin film is fabricated on a Mo-coated glass substrate by a non-vacuum spray pyrolysis method from an aqueous precursor solution containing $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Sn(CH_3SO_3)_2$ and thiourea followed by sulfurization and selenization at 600°C. The fabricated CZTSSe thin film shows high crystallinity with optimal Cu-poor and Zn-rich compositions, which is confirmed by the X-ray diffraction pattern, Raman spectrum, and Energy dispersive X-ray spectroscopy results. Based on the thus-obtained CZTSSe absorber, a solar cell device with Al/ITO/ZnO/CdS/CZTSSe/Mo/glass structure exhibits a conversion efficiency of 4.34% with J_{SC}, V_{OC}, and FF of 39.47 mA/cm^2, 0.31 V, and 0.36, respectively.

Keywords: $Cu_2ZnSn(S_xSe_{1-x})_4$; thin-film solar cells; spray pyrolysis method.

Tóm tắt

Màng mỏng kesterite $Cu_2ZnSn(S_xSe_{1-x})_4$ (CZTSSe) được chế tạo trên đế Mo bọc thủy tinh bằng phương pháp phun nóng từ dung dịch tiền chất chứa $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Sn(CH_3SO_3)_2$ và thiourea cùng với quá trình lưu huỳnh hóa và selen hóa ở nhiệt độ 600°C. Màng mỏng CZTSSe chế tạo được có sự kết tinh cao và thành phần tối ưu, được xác nhận bởi các kết quả nhiễu xạ X-ray, Raman và phổ tán xạ năng lượng tia X. Từ lớp hấp thụ CZTSSe, chúng tôi tiến hành chế tạo pin mặt trời với cấu trúc Al/ITO/ZnO/CdS/CZTSSe/Mo/thủy tinh, hiệu suất chuyển đổi đạt được là 4.34% với các giá trị J_{SC}, V_{OC}, và FF lần lượt là 39.47 mA/cm^2, 0.31 V và 0.36.

Từ khóa: $Cu_2ZnSn(S_xSe_{1-x})_4$; pin mặt trời màng mỏng; công nghệ phun nóng.

1. Introduction

Compound semiconductor thin film solar cells have attracted numerous interest from many research groups due to their low production cost from the cheaper materials and flexible fabrication methods [1,2]. Among the current thin film solar cells, cadmium telluride (CdTe) and copper indium gallium selenium

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($Cu(In,Ga)Se_2$ or CIGS) are the most popular with the high conversion efficiencies of more than 20% achieved [3,4]. Despite the good performance of the CdTe and CIGS solar cells, they contain a toxic cadmium element and rare elements of In and Ga resulting in the limitation of their production capacity because of harmful factors and material shortages. For these reasons, kesterite $Cu_2ZnSn(S_xSe_{1-x})_4$ (CZTSSe) is a potential alternative material, in which all components are not only non-toxic but also earth-abundant. Besides the high coefficient of more than 10^4 cm^{-1}, the bandgap energy of the CZTSSe could be varied by changing the S and Se ratio to obtain the optimal bandgap energy of 1.0 eV to 1.5 eV [5,6]. Therefore, the kesterite CZTSSe has emerged as one of the most promising candidates for low-cost and high-efficiency thin film solar cells.

The high power conversion efficiency (PCE) of CZTSSe solar cells of 12.62% was achieved by DC sputtering, a vacuum-based process[7]. It should be more advantageous to use low-cost and non-vacuum technologies for later industry applications. Therefore, several non-vacuum methods such as spin coating, spray pyrolysis, and electrodeposition could be considered [8-10]. Among them, spray pyrolysis is widely used for fabricating thin films due to its simplicity and ease of handling in the fabrication process, it even can deposit the thin film on a large scale, which are great advantages for industrial applications.

In this work, we present the fabrication of the CZTSSe thin film solar cell. The composition and crystallinity of the thin film will be investigated by using energy dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), and Raman spectroscopy. Then a complete device with Al/ITO/ZnO/CdS/CZTSSe/Mo/glass structure is fabricated to study its photovoltaic performance.

2. Experimental

2.1. Materials: Copper (II) nitrate ($Cu(NO_3)_2$), zinc (II) nitrate ($Zn(NO_3)_2$), tin (II) methanesulfonate ($Sn(CH_3SO_3)_2$), thiourea ($SC(NH_2)_2$) and elemental sulfur and selenium powders are used as received from Sigma-Aldrich.

***2.2. Preparation of CZTSSe thin films*:** As-deposited thin films are grown by spray pyrolysis technique onto Mo-coated glass substrates heated at 380°C with a distance from the atomizer to the substrate of 30 cm in 15 min of deposition time. For the spray precursor solution, an aqueous solution is prepared by dissolving 0.019 M copper nitrate ($Cu(NO_3)_2$), 0.009 M zinc nitrate ($Zn(NO_3)_2$), 0.0125 M tin methanesulfonate ($Sn(CH_3SO_3)_2$) and 0.06 M thiourea ($SC(NH_2)_2$) in deionized water as a copper-poor and zinc-rich precursor composition. We also control the pH of the precursor solution by adding a few drops of concentrated HCl acid. The CZTS thin films are obtained after the sulfurization by annealing in an evacuated borosilicate glass ampoule together with 20 mg Sulfur powder at 600°C for 20 min. Then these CZTS thin films are further selenized by annealing in a vacuum with 20 mg Selenium powder at 600°C for 10 min to obtain CZTSSe thin films.

***2.3. Device fabrication*:** To fabricate a complete thin film solar cell, CdS is used as a buffer layer, which was prepared by chemical bath deposition. Then ITO/ZnO bilayer is coated on the top of the CdS layer using radio frequency (RF) magnetron sputtering. Finally, Al as a top contact layer is fabricated by thermal evaporation for a complete device structure of Al/ITO/ZnO/CdS/CZTS/Mo/glass.

***2.4. Characterization*:** The metallic composition of the fabricated thin films is analyzed by using energy dispersive X-ray spectroscopy (EDS) at several positions to obtain the average composition. X-ray diffraction (XRD) using a Rigaku MiniFlex X-ray diffractometer and Raman spectroscopy using a JASCO NRC 3100 laser Raman spectrophotometer are performed for the crystalline structures of the films. The fabricated CZTSSe solar cell device is characterized by current density-voltage (J-V) characteristics and external quantum efficiency (EQE) under a simulated amplitude modulation of AM1.5G irradiation using a Bunhoh-Keiki CEP-015 photovoltaic measurement system.

3. Results and Discussion

Table 1: Compositions of the as-deposited and annealed CZTSSe thin film.

Sample	Cu	Zn	Sn	S	Se	Cu/(Zn +Sn) ratio	Zn/Sn ratio
As-deposited	26.0	16.5	13.8	43.7	0	0.86	1.20
CZTSSe	25.6	15.2	12.2	19.3	27.8	0.93	1.25

Firstly, the stoichiometry of the as-deposited and annealed CZTSSe films was investigated by EDS measurement. The atomic percentages of Cu, Zn, Sn, and the atomic ratios of Cu/(Zn + Sn) and An/Sn are listed in Table 1. Although the precursor solution contained excess amounts of Sn component, the Sn content was reduced significantly in the as-deposited film. This indicated the evaporation of Sn during spray deposition and annealing processes. It is well-known that the chemical composition of an absorber layer has a significant effect on the performance of the solar cell devices and high-efficiency kesterite solar cells can be achieved from Cu-poor (Cu/(Zn + Sn) ratios of 0.75 - 0.95) and Zn-rich compositions (Zn/Sn ratios of 1.1 – 1.4) [7,9]. Hence, for our fabricated films, it can be noted that both as-deposited and annealed CZTSSe films are confirmed to have optimal Cu-poor and Zn-rich compositions, which are beneficial for kesterite solar cells as reported in the literature.

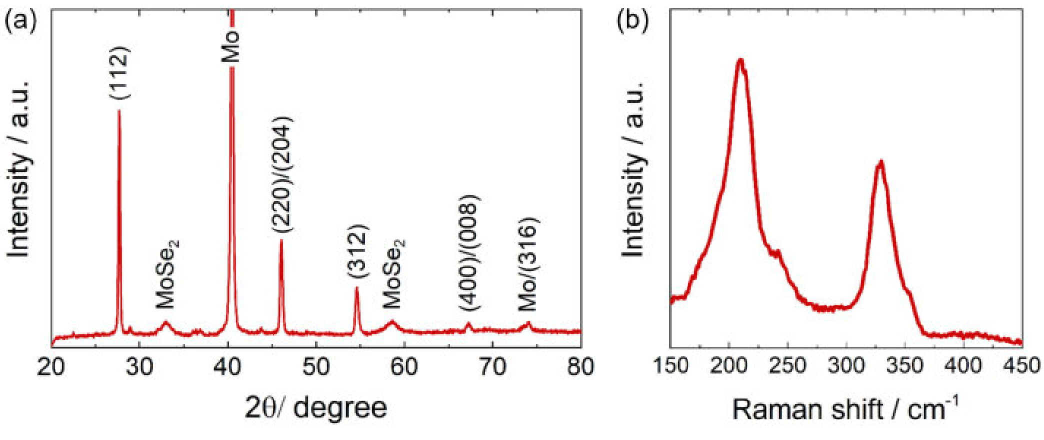

Figure 1. (a) XRD pattern and (b) Raman spectrum of the fabricated CZTSSe film.

The phases and crystal structures of the fabricated film were examined by XRD pattern and Raman spectrum. As shown in Figure 1a, the XRD pattern of the CZTSSe film exhibits intense diffraction peaks at 27.7 °, 46.1°, 54.6°, 67.3° and 74.1° assignable to (112), (220)/(204), (312), (400)/(008) and (316) of the kesterite CZTSSe structure [11-12]. It is also observed the presence of Mo peaks from the Mo substrate and $MoSe_2$ peaks from the partial selenization during the annealing process. No other secondary peaks are observed, indicating the high crystallinity of the fabricated thin film. In addition to XRD diffraction, Raman measurement is also performed, Figure 1b shows the Raman spectrum of the fabricated film. Two main peaks at 208 and 329 cm^{-1} are observed, corresponding to the kesterite CZTSSe crystal [13]. Thus, the XRD and Raman results confirm the formation of kesterite CZTSSe of our fabricated film.

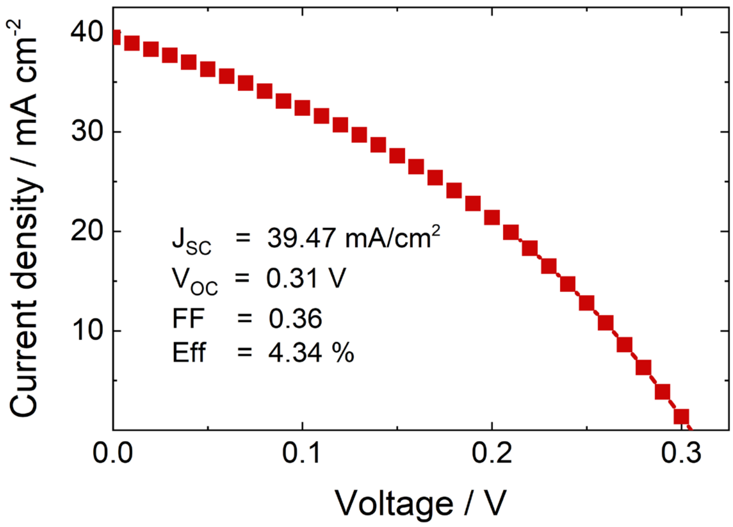

Figure 2. J-V characteristics of Al/ITO/ZnO/CdS/CZTSSe/Mo/glass solar cells made from the fabricated CZTSSe film.

The fabricated film is processed to make a solar cell device with a structure of Al/ITO/ZnO/CdS/CZTSSe/Mo/glass. The photovoltaic performance is investigated by using the current-voltage characteristics under irradiation of simulated sunlight (AM1.5G) of the device and the cell parameters of short-circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF), and power conversion efficiency (Eff) are summarized in the inset of Figure 2. The J-V curve indicated that our fabricated solar cell has a conversion efficiency of 4.34% with J_{SC}, V_{OC}, and FF of 39.47 mA/cm^2, 0.31 V, and 0.36, respectively. Compared with the cell parameters of other reports [14, 15], the J_{SC} value in this study is quite high, but the V_{OC} and FF values are still low, indicating the recombination in the bulk and/or the interface of the absorber, leading to the low V_{OC} and FF.

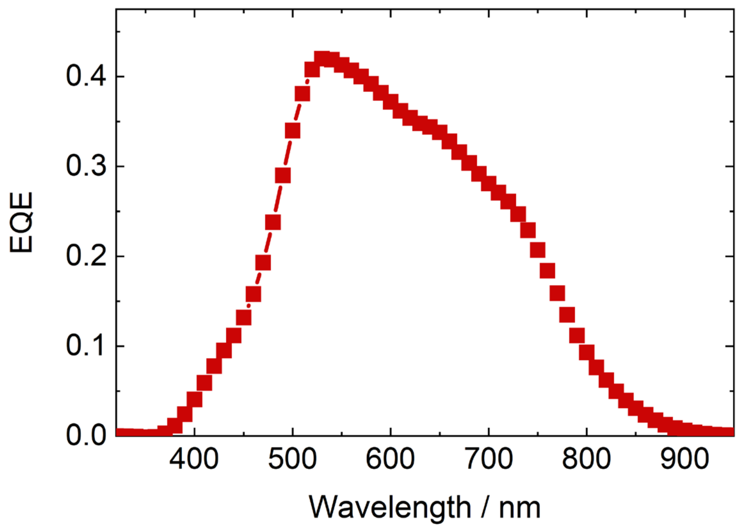

Figure 3. EQE spectrum of the solar cell device based on the fabricated CZTSSe film.

Finally, the EQE spectrum of the fabricated device is measured in wavelengths ranging from 300 to 950 nm as presented in Figure 3. It is easy to observe that the spectrum gradually increases from *ca.* 360 nm to *ca.* 460 nm and rapidly increases to *ca.* 530 nm and then gradually decreases to the onset wavelength of *ca.* 900 nm. The un-sharp onset at long wavelengths suggests the presence of band tails in the CZTSSe solar cell. The loss in the spectrum in the short wavelength region is caused by the absorption losses of the CdS buffer layer, while the loss in the long wavelength region is related to the loss of absorbed photons in the absorber layer. These losses lead to insufficient solar cell performance compared to the reported efficient CZTSSe solar cells in the literature. Therefore, it is necessary to have further studies to improve the device qualities and suppress the recombination.

4. Conclusion

In this study, we have demonstrated the deposition of the CZTSSe thin film solar cells using the spray pyrolysis method and investigated their photovoltaic performance. The XRD pattern and Raman spectrum confirm that high crystalline CZTSSe thin film is successfully fabricated with the optimal Cu-poor and Zn-rich compositions. Finally, the solar cell based on the obtained CZTSSe absorber with Al/ITO/ZnO/CdS/CZTSSe/Mo/glass structure achieves a conversion efficiency of 4.34% and J_{SC}, V_{OC}, and FF of 39.47 mA/cm^2, 0.31 V, and 0.36, respectively. Although the J_{SC} value in this study is quite high, the V_{OC} and FF values are still low, leading to the low performance of the solar cell device. We expect further studies to suppress the recombination in the bulk and/or the interface of the absorber as well as to optimize the complete device structures to improve the V_{OC} and FF values, resulting in the enhancement of the power conversion efficiency.

Acknowledgment

Dr. Nguyen Thi Hiep would like to acknowledge the support from Prof. Michio Matsumura and Prof. Shigeru Ikeda for the experiments which were performed at Research Center for Solar Energy Chemistry, Osaka University, Japan. This work has also been supported by Vietnam Academy of Science and Technology under grant No. TĐHYD0.04/22-24.

References

[1] F. Liu, Q. Zeng, J. Li, X. Hao, A. H. Baillie, J. Tang, M. A. Green. (2020). Emerging inorganic compound thin film photovoltaic materials: Progress, challenges, and strategies. *Mater. Today*, 41, 120-142.

[2] S. Ishizuka, J. Nishinaga, K. Beppu, T. Maeda, F. Aoyagi, T. Wada, A. Yamada, J. Chantana, T. Nishimura, T. Minemoto, M. M. Islam, T. Sakurai, N. Terada. (2022). Physical and chemical aspects at the interface and in the bulk of $CuInSe_2$-based thin-film photovoltaics. *Phys. Chem. Chem. Phys.*, 24, 1262-1285.

[3] R. S. Hall, D. Lamb, S. J. C. Irvine. (2021). Back contacts materials used in thin film CdTe solar cells - A review. *Energy Sci. Eng.*, 9, 606-632.

[4] Y. Osman, M. Fedawy, M. Abaza, M. H. Aly. (2020). Solar cell performance enhancement with optimized CIGS absorber bandgap and buffer layer. *J. Phys.: Conf. Ser.*, 1447, 012057.

[5] K. J. Yang, J. H. Sim, D. H. Son, D. H. Jeon, D. K. Hwang, D. Nam, H. Cheong, S. Y. Kim, J. H. Kim, D. H. Kim, J. K. Kang. (2017). Comparison of chalcopyrite and kesterite thin-film solar cells. *J. Ind. Eng. Chem.*, 45, 78-84.

[6] M. He, C. Yan, J. Li, M. P. Suryawanshi, J. Kim, M. A. Green, X. Hao. (2021). Kesterite Solar Cells: Insights into Current Strategies and Challenges. *Adv. Sci.*, 8, 2004313.

[7] D. H. Son, S. H. Kim, S. Y. Kim, Y. I. Kim, J. H. Sim, S. N. Park, D. H. Jeon, D. K. Hwang, S. J. Sung, J. K. Kang, K. J. Yang, D. H. Kim. (2019). Effect of solid-H_2S gas reactions on CZTSSe thin film growth and photovoltaic properties of a 12.62% efficiency device. *J. Mater. Chem. A*, 7, 25279-25289.

[8] S. B. Patel, J. V. Gohel. (2018). Optimization of sol–gel spin-coated Cu_2ZnSnS_4 (CZTS) thin-film control parameters by RSM method to enhance the

solar cell performance. *J. Mater. Sci.*, 53, 12203-12213.

[9] T. H. Nguyen, S. Fujikawa, T. Harada, J. Chantana, T. Minemoto, S. Nakanishi, S. Ikeda. (2016). Impact of Precursor Compositions on the Structural and Photovoltaic Properties of Spray-Deposited Cu_2ZnSnS_4 Thin Films. *Chemsuschem*, 9, 2414-2420.

[10] M. I. Khalil, R. Bernasconi, A. Lucotti, A. L. Donne, R. A. Mereu, S. Binetti, J. L. Hart, M. L. Taheri, L. Nobili, L. Magagnin. (2021). CZTS thin film solar cells on flexible Molybdenum foil by electrodeposition-annealing route. *J, Appl. Electrochem*., 51, 209-218.

[11] S. Oueslati, G. Brammertz, M. Buffiere, H. Elanzeery, D. Mangin, O. Eldaif, O. Touayar, C. Koble, M. Meuris, J. Poortmans. (2015). Study of alternative back contacts for thin film Cu2ZnSnSe4-based solar cells. *J. Phys. D: Appl. Phys.*, 48, 035103.

[12] L. Sravani, S. Routray, K. P. Pradhan, M. C. Piedrahita. (2021). Kesterite Thin-Film Solar Cell: Role of Grain Boundaries and Defects in Copper-Zinc-Tin-Sulfide and Copper-Zinc-Tin-Selenide. *Phys. Status Solidi A*., 218, 2100039.

[13] S. Tripathi, B. Kumar, D. K. Dwivedi. (2020). Study on formation and characterization of kesterite CZTSSe thin films deposited by thermal evaporation technique for solar cell applications. *J. Mater. Sci: Mater. Electron.*, 31, 8308-8315.

[14] W. Wang, M. T. Winkler, O. Gunawan, T. Gokmen, T. K. Todorov, Y. Zhu, D. B. Mitzi. (2014). Device Characteristics of CZTSSe Thin-Film Solar Cells with 12.6% Efficiency. *Adv. Energy. Mater.*, 4, 1301465.

[15] J. M. D. Sanchez, I. L. Bravo. (2021). High Vapor Transport Deposition: A Novel Process to Develop $Cu_2ZnSn(S_xSe_{1-x})_4$ Thin Film Solar Cells. *Sol. RRL*, 6, 2100835.