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Preparation and Properties of Cu_2ZnSnS_4 Thin Films Based on Spraying Method

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Abstract. CZTS(Cu2ZnSnS4) based thin film solar cells have attracted interest for their excellent performance, non-toxicity, and abundant raw materials. As an efficient, flexible and economical thin film preparation technology, the spraying method is widely used in the field of thin film preparation. This experiment presents the preparation of CZTS thin films using spraying method. This study analyzes the impact of air-annealing temperature on the CZTS samples. The results show that the optimal film performance is achieved with the sample annealed at 475 ℃ for 10 minutes. The morphology of the film displayed a homogeneous nanoparticle composition with high crystallinity, the Cu:Zn:Sn:S ratio of 2.3:1:1.1:4.7 and an ideal bandgap of ~1.68 eV. The prepared samples show potential application prospects in the field of photovoltaic devices.

Keywords: CZTS, Thin films, Spraying method, Air-annealing.

1. Introduction

Fuel energy has always been the mainstay of human energy use. However, fuel energy is a non-renewable resource, which will produce pollution during combustion[1]. Therefore, with the increasing attention to energy and the environment, research on efficient and low-cost solar energy absorbing materials is constantly receiving attention. Thin film solar cells (TFSCs) are one of the important types of photovoltaic devices. CuInGaSe2 (CIGS), CdTe, and GaAs possess high conversion efficiencies and stability[2]. However, their development will be limited due to the presence of toxic and rare elements (In, Ga and Cd)[3]. Cu2ZnSnS4 (CZTS) is a quaternary compound of the kesterite mineral structure, belonging to the I2-II-IV-VI4 type semiconductor material. CZTS is a P-type direct bandgap semiconductor material with excellent optical and electrical properties. It has a high absorption coefficient, (up to 10^4 cm^{-1}) and its bandgap width (1.5 eV)[4]. In addition, CZTS does not contain rare or toxic elements. Due to these advantages, it has become a promising choice for solar cell absorber layers.

There are many preparation methods for CZTS thin films, which can be divided into two categories: vacuum technologies and non-vacuum technologies. Vacuum technologies mainly include sputtering[5], thermal evaporation[6], and pulse laser deposition[7]. Non vacuum technologies mainly include electrochemical[8], spraying approach pyrolysis[9], sol-gel method[10], and screen printing[11]. In 2007, Jimbo et al. reported a 5.74 % conversion efficiency of solar cells based on 480 nm high-quality CZTS thin films using sputtering method[5]. In 2011, Shin et al. reported that the efficiency of solar cells based on the CZTS layer was 8.4%, with the thermal deposition method[6]. These vacuum methods can prepare high-performance thin films, but expensive equipment and complex processes both affect the production cost. Therefore, non-vacuum technology had received extensive attention. Among non-vacuum methods, spraying approach has the advantage of easy operation and simple production equipment.

2. Experimental Details

First, preparation of precursor solution: 2.5 mmol thiourea (0.190 g), 0.75mmol of CuCl2 (0.100 g) 0.5 mmol of $Zn(CH_3COO)_2(H_2O)_2$ (0.110 g) and 0.5mmol of SnCl2 • 2H2O (0.110 g) were added to 100 ml of ethanol. At room temperature, the solution was stirred by a magnetic stirrer

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until the chemical is dissolved, approximately one hour. Next, spraying method for sample film deposition: The glass substrate was placed on a heating platform at 300 ℃, and the precursor solution was uniformly sprayed onto it using a spray gun. Finally, annealing of sample films: the films were annealed at different temperatures and the annealing temperature was varied from 400 ℃ to 500 ℃.

3. Results and Discussion

In this study, to investigate the relationship between the properties of CZTS films and the different annealing temperature, the annealing temperature was varied from 400 ℃ to 500 ℃. The XRD images of CZTS thin films are presented in Figure 1a. The diffraction peaks appeared at 2 θ value of 28.45°, 47.30°, and 56.25° corresponds to the (112), (220), and (312) planes of CZTS (JCPDS 26-0575). Weak peaks can be observed in the unannealed samples. As the annealing temperature increases from 400 ℃ to 475 ℃, the peaks become more and more obvious and sharp. In Figure 1b, the crystal sizes of the prepared thin films for samples at 400, 420, 450, 475, and 500 ℃ are approximately 8.6, 9.1, 9.8, 11.7, and 9.5 nm, respectively, according to the Scherrer equation[12] of the (112) crystal plane. This indicates that as the increase in annealing temperature, the crystallinity of the obtained sample increases. When the annealing temperature reaches 475 ℃, the FWHM of the peak is the narrowest, indicating the best crystallinity. The peak at 28.45° did not decrease significantly in intensity for samples annealed at 500 ℃, but the FWHM is obviously wider than that of the 475 ℃ sample. This could be due to the high temperature causing the evaporation of chemical substances, which is detrimental to the reaction and leads to a decrease in crystallinity.

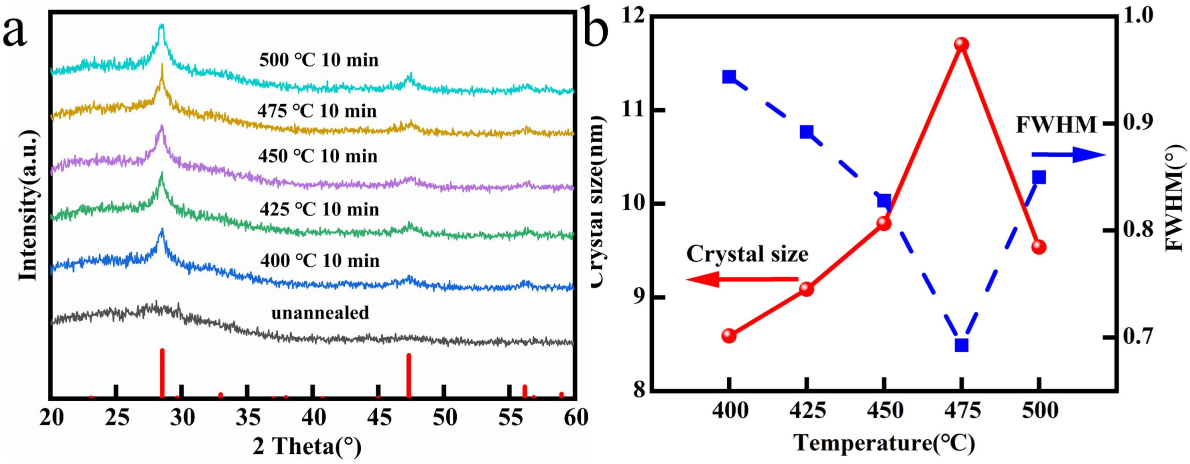

Fig. 1 a) XRD patterns, b) crystallite size and FWHM of the thin films prepared at different annealing temperatures

The optical properties of CZTS are determined by the transition from the Cu 3d/S 3p state (valence band) to the Sn 5s/S 3p state (conduction band)[12]. It can be seen from the Figure 2a that the slope of the absorption edge for the unannealed sample is very low within the visible light range, which may be due to its poor crystallinity. And in the Figure 1a it is observed that the slope of the absorption edge continues to increase with the annealing temperature increases, indicating that annealing within a certain temperature range improves the crystallinity of the samples. However, when the annealing temperature reaches 500 ℃, the slope of the absorption edge decreases, which is consistent with the above XRD analysis.In this experiment, the UV-Vis-NIR spectroscopy was utilized to investigate the effect of annealing temperature on the bandgap (Eg) of CZTS thin films. The Eg values of unannealed, 400, 425, 450, 475 and 500 ℃ were observed to be 2.39, 2.16, 2.04, 1.80, 1.68, and 1.74 eV. In Figure 2b,with the increase of annealing temperature, it can be clearly seen that the band gap of the sample decreases, which is advantageous for the manufacturing of

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optoelectronic devices. The optimal band gap is 1.68 eV at 475 ℃, but it is still higher than the ideal band gap of 1.5 eV. This may be due to the fact that the experimental intermediate products, such as ZnS (3.65 eV) and SnS2 (2.6 eV), are not completely converted into CZTS[12]. The band gap increases slightly at 500 ℃, which may be due to the high temperature not conducive to the conversion of CZTS.

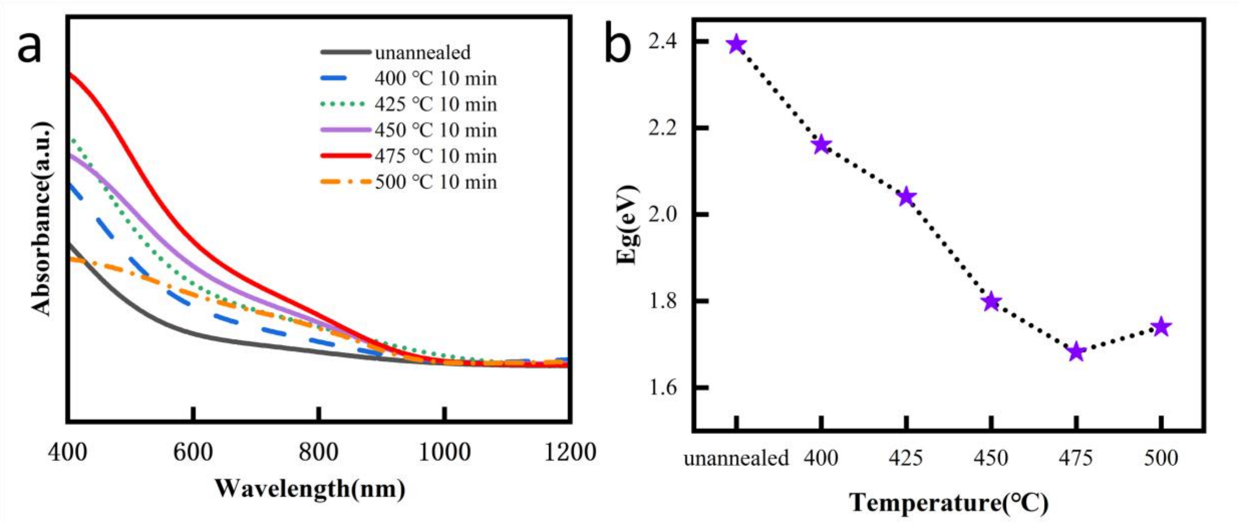

Fig. 2 Optical properties of the samples. a) absorption spectra, b) Eg c) (Ahν)2 vs.(hν) plots

In Figure 3a, compared with the unannealed sample, the content of Cu increases and the content of Sn and Zn decreases in the sample annealed at 400 ℃. This may be due to the higher reactivity of copper relative to zinc and tin[13]. The atomic content of the annealed samples changes slightly within 400 ~ 450 ℃. After annealing at 475 ℃, the Cu content decreased, while the S, Zn, and Sn contents increased.The atomic ratio of this sample (Cu:Zn:Sn:S = 2.3:1:1.1:4.7) is closest to the ideal ratio (2:1:1:4). In this experiment, Cu, Zn, and Sn were added to the precursor solution in a ratio of 1.5 : 1 : 1, and it was found that the reactivity order of Cu, Zn, and Sn is Cu > Sn > Zn, which is similar to previous reports[13]. At 500 ℃, the decrease in S content may be due to evaporation of S caused by high temperature, which is not conducive to the reaction. Figure 3b depicts the atomic ratios of Cu / (Zn + Sn), Zn / Sn, and S / (Cu + Zn + Sn). It can be observed that these ratios gradually approach the ideal value 1 as the temperature increases. This indicates that annealing is beneficial to the conversion of CZTS when the temperature reaches an appropriate level.

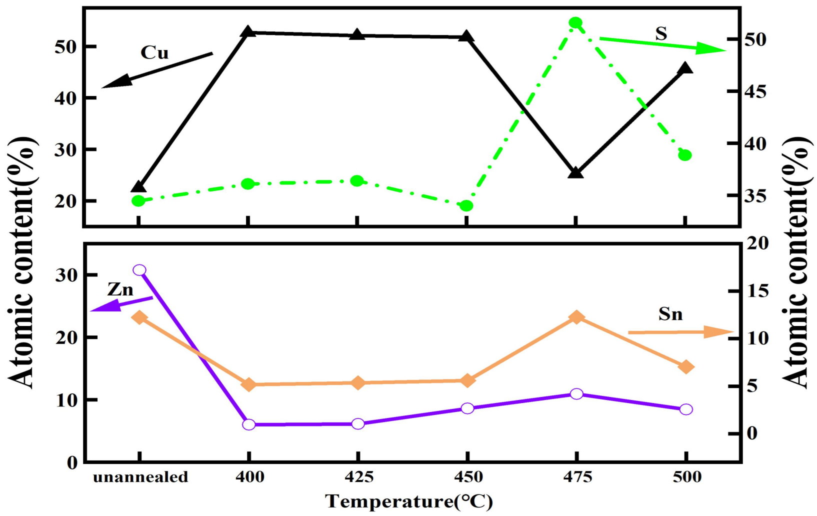

Fig. 3 Chemical composition of the samples prepared at different annealing temperatures: a) compositional ratios of the elements b) atomic content

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The image in Fig. 4 is the SEM morphology image of the sample. It can be seen from the image that the unannealed sample is deposited on a glass carrier, distributed as a whole block. As the annealing temperature rises, it is found that the large structured compounds break down into irregular particles. But the nanoparticles are uneven and have large inter-particle gaps, which is unfavorable for the synthesis of photovoltaic materials. With the further increase of annealing temperature, the particles of various sizes progressively transforming into spherical particles. After annealing at 475 ℃, the nanoparticles became fuller and more uniform, which resulted in the ideal surface morphology. When the temperature rises to 500, the surface nanoparticles are not dense, which may be attributed to decomposition and evaporation caused by high temperature.

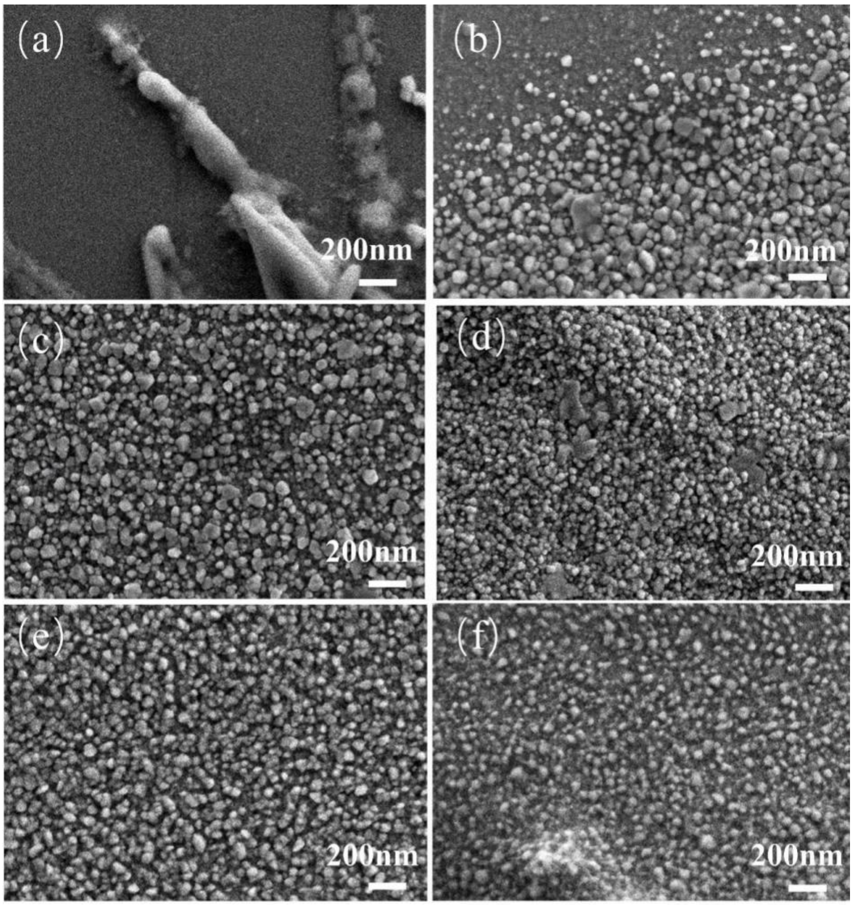

Fig. 4 SEM images of the thin films prepared at different temperatures: a) as-deposited, b) 400 ℃, c) 425 ℃, d) 450 ℃, e) 475 ℃, f) 500 ℃

4. Conclusion

In summary, CZTS thin films are successfully prepared by spraying method combined with annealing process. And this experiment discussed the relationship between the samples prepared by spray spraying properties and annealing temperature. The results show that the crystallinity, chemical composition, absorption and morphology of the samples are positively correlated with the annealing temperature in a certain temperature range (400-475 ℃), when the annealing time is 10 min. The sample prepared by annealing at 475 ℃ has better comprehensive properties. The obtained sample has excellent crystallinity, close to the ideal chemical composition, better absorption and has an acceptable uniform granular morphology. This method not only has low requirements on the preparation environment, but also has simple process and low cost, which is conducive to the large-scale preparation of CZTS thin films. It is helpful to expand the application of CTZS thin film solar cells in photovoltaic field.

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References

[1] S. C. Dhawale, R. V. Digraskar, A. V. Ghule, and B. R. Sathe, "Noble metal-free CZTS electrocatalysis: synergetic characteristics and emerging applications towards water splitting reactions," Frontiers in Chemistry, vol. 12, 2024.

[2] F. Wang et al., "Influences of rapid thermal annealing on Cu2ZnSnS4 thin film fabricated by spraying approach," Journal of Materials Science: Materials in Electronics, vol. 32, no. 6, pp. 7153-7161, 2021.

[3] B. Salhi, "The Photovoltaic Cell Based on CIGS: Principles and Technologies," Materials, vol. 15, no. 5, 2022.

[4] A. Walsh, S. Chen, S. H. Wei, and X. G. Gong, "Kesterite Thin-Film Solar Cells: Advances in Materials Modelling of Cu2ZnSnS4," Advanced Energy Materials, vol. 2, no. 4, pp. 400-409, 2012.

[5] K. Jimbo et al., "Cu2ZnSnS4-type thin film solar cells using abundant materials," Thin Solid Films, vol. 515, no. 15, pp. 5997-5999, 2007.

[6] B. Shin, O. Gunawan, Y. Zhu, N. A. Bojarczuk, S. J. Chey, and S. Guha, "Thin film solar cell with 8.4% power conversion efficiency using an earth-abundant Cu2ZnSnS4 absorber," Progress in Photovoltaics: Research and Applications, vol. 21, no. 1, pp. 72-76, 2011.

[7] Z. Oulad Elhmaidi, M. Abd-Lefdil, and M. A. El Khakani, "Photoconversion Optimization of Pulsed-Laser-Deposited p-CZTS/n-Si-Nanowires Heterojunction-Based Photovoltaic Devices," Nanomaterials, vol. 10, no. 7, 2020.

[8] E. M. Mkawi, Y. Al-Hadeethi, B. Arkook, and E. Bekyarova, "Impact of 1,8-Diiodooctane (DIO) Additive on the Active Layer Properties of Cu2ZnSnS4 Kesterite Thin Films Prepared by Electrochemical Deposition for Photovoltaic Applications," Materials, vol. 16, no. 4, 2023.

[9] S. Lie et al., "Improving Carrier-Transport Properties of CZTS by Mg Incorporation with Spray Pyrolysis," ACS Applied Materials & Interfaces, vol. 11, no. 29, pp. 25824-25832, 2019.

[10] A. A. Ahmad, A. B. Migdadi, A. M. Alsaad, I. A. Qattan, Q. M. Al-Bataineh, and A. Telfah, "Computational and experimental characterizations of annealed Cu2ZnSnS4 thin films," Heliyon, vol. 8, no. 1, 2022.`

[11] Y. Wang, Y. Huang, A. Y. S. Lee, C. F. Wang, and H. Gong, "Influence of sintering temperature on screen printed Cu2ZnSnS4 (CZTS) films," Journal of Alloys and Compounds, vol. 539, pp. 237-241, 2012.

[12] J. Chen et al., "Molecular-solution printing of Cu2ZnSnS4 (CZTS) thin film," Ceramics International, vol. 46, no. 17, pp. 26660-26667, 2020.

[13] B. Flynn, I. Braly, P. A. Glover, R. P. Oleksak, C. Durgan, and G. S. Herman, "Continuous flow mesofluidic synthesis of Cu2ZnSnS4 nanoparticle inks," Materials Letters, vol. 107, pp. 214-217, 2013.