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Solution-processed Cu_2FeSnS_4 thin films for photovoltaic application

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ABSTRACT

Highly-condensed thin films of Cu_2FeSnS_4 (CFTS) nanoparticles are prepared on FTO substrates by spin-coating CFTS precursor solution followed by a short thermal annealing at low temperature for the first time. The CFTS film has a band gap of 1.53 eV and an absorption coefficient higher than 10^4 cm^{-1} in the wavelength range of 300–1100 nm. The thin film solar cells structured as FTO/CFTS/CdS/Al are fabricated and it is demonstrated that the optimized CFTS film thickness for such devices is around 125 nm.

1. Introduction

Due to its high absorption coefficient (>10^4 cm^{-1}) and suitable band gap (1.0–1.5 eV), quaternary Cu_2FeSnS_4 (CFTS) semiconductor consisting of earth abundant elements has recently attracted increasing attention in the field of thin film solar cells, with an achievement of the state-of-the-art power conversion efficiency (η) close to 3% [1–6]. Up to now, a variety of methods have been developed to fabricate CFTS thin films for photovoltaic application, such as magnetron sputtering combined with sulfurization [1,2], doctor blade coating of CFTS nanoparticle ink followed by sulfurization [3], successive ionic layer absorption and reaction [4], spin-coating of molecular precursor solution [5] etc. Among those methods, spin-coating is a versatile and effective approach to fabricate thin films on a large scale. Ghosh and coworkers [5,7] prepared CFTS thin films by spin-coating the molecular precursor solution of simple inorganic compounds, with 2-methoxyethanol as solvent and ethanolamine as a stabilizer; however, they only obtained porous films of CFTS nano-flakes (ca. 3–4 μm) over ITO/ZnO/ZnS nanoarrays for solar cells or CTFS nanoparticles (ca. 60 nm) on ITO substrates. Herein, we demonstrate, for the first time, a solution-processing strategy to controllably prepare the condensed thin films of CFTS nanoparticles over FTO surfaces, which features spin-coating a transparent and stable molecular precursor solution consisting of simple inorganic salts as metal sources and thiourea as sulfur source in N,N-dimethylformamide solvent, followed by a short thermal annealing at 350 °C for chemical reaction and crystallization. Our results show that the as-prepared CFTS thin films exhibit an absorption coefficient (α) of >10^4 cm^{-1} within 300–1100 nm and a great potential for photovoltaic application. Compared to the previous reports [5,7], our synthesis method does not use any special organic additives and results in the condensed films of CFTS nanoparticles (ca. 10 nm) with a controllable thickness on FTO substrates.

2. Experimental

A clear and dark-brown CFTS precursor solution was prepared by sequentially mixing 3.0 mmol $Cu(CH_3COO)_2{\cdot}H_2O$, 1.85 mmol $FeSO_4{\cdot}7H_2O$, 1.65 mmol $SnCl_2{\cdot}2H_2O$ and 13.0 mmol thiourea in 8 mL N,N-dimethylformamide, under vigorous stirring at 50 °C. The color changes in preparing the precursor solution are shown in Fig. S1 in Supplementary Information (SI).

FTO (SnO_2:F) coated glass sheet (14 Ω/sq, 400 nm FTO in thickness, Nippon Sheet Glass Co.) was patterned and cleaned as described elsewhere [8]. A CFTS precursor film was prepared on the patterned FTO substrate by spin-coating (2000 rpm for 30 s) the precursor solution three times on a patterned FTO coated glass that has been further cleaned with UV-Ozone for 10 min prior to spin-coating, followed by the annealing at 350 °C for 5 min on a hot plate in a glove box filled with N_2 atmosphere, which is referred to as one CTFS film growth number (n). In order to obtain

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the desired thickness of CFTS films, the patterned FTO substrate was subject to a given CFTS film growth number (i.e., n = 1–3).

The FTO/CFTS/CdS/Al solar cells are fabricated as follows. A CdS layer (ca. 50 nm) was first deposited on the as-prepared CFTS film as reported elsewhere [9], and annealed at 175 °C for 30 min in N_2 atmosphere. Then, an Al electrode was thermally evaporated under vacuum (5×10^{-4} Pa) through a shadow mask (1×4 mm^2), which defined the active area of each device. The solar cells were encapsulated in a glove box (O_2 < 1 ppm, H_2O < 1 ppm).

The details of the chemicals used and the sample characterizations are provided in SI.

3. Results and discussion

The XRD patterns of the as-prepared CFTS films with different n values are shown in Fig. 1a. Except for the information of FTO substrate, all the diffraction peaks of thin film samples agree well with the stannite CFTS (JCPDS 44-1476). The average grain sizes of the CFTS films are calculated to be 5–10 nm by using Scherrer's formula, on the basis of the XRD peak for (1 1 2) plane. With the increase in n values, the diffraction peaks of CFTS get enhanced, suggesting more CFTS has been deposited on FTO substrate. The Raman spectra of the samples (Fig. 1b) only display a strong peak at about 318 cm^{-1} due to the A_1 symmetric vibrational motion of sulfur atoms in CFTS, indicating a high purity of the CFTS films [10,11].

Fig. 2a–d shows the SEM data of the CFTS films with different n values. All of the films consist of spherical nanoparticles of 10 nm in size in agreement with XRD data, they are densely compact and have an extremely smooth surface without evident pin holes. With increasing n values, the thicknesses of CFTS films increase linearly, that is, 65 nm for n = 1, 125 nm for n = 2 and 190 nm for n = 3

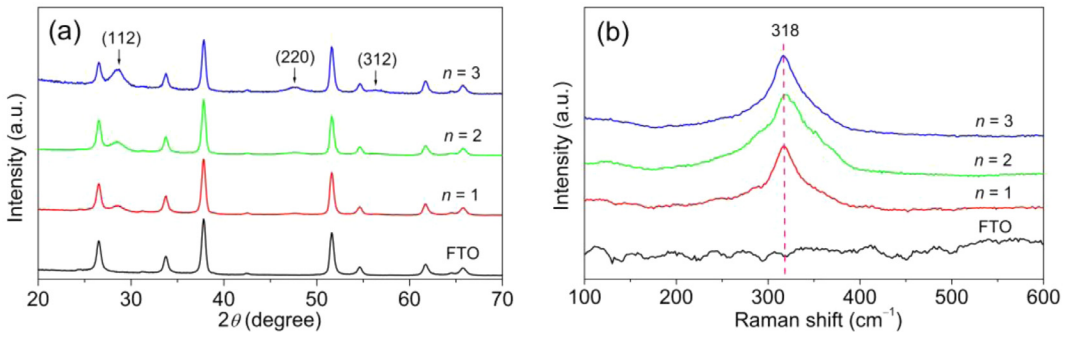

Fig. 1. (a) XRD patterns and (b) Raman spectra of as-prepared CFTS thin films on FTO substrate.

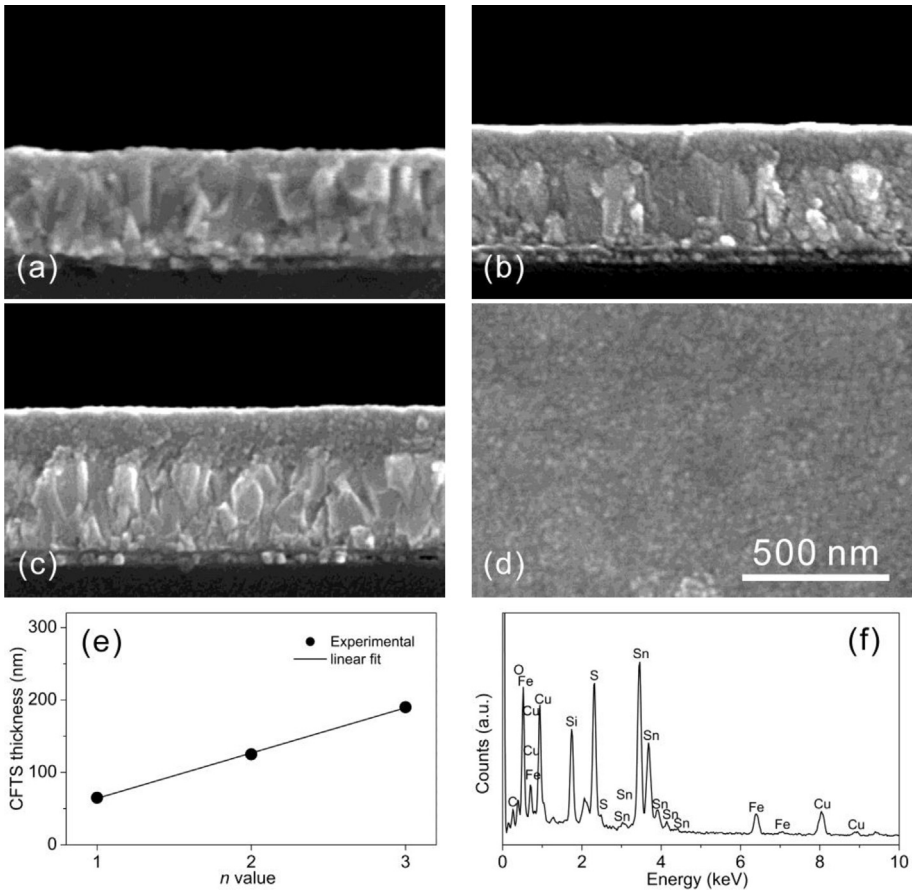

Fig. 2. Cross-sectional (a–c) and top-view (d) SEM images of CFTS films with n values of 1 (a), 2 (b, d) and 3(c), where the scale bar is for all the SEM images. (e) shows the dependence of the CFTS film thicknesses on CFTS film growth number n. (f) EDX spectrum of CFTS (n = 2) film.

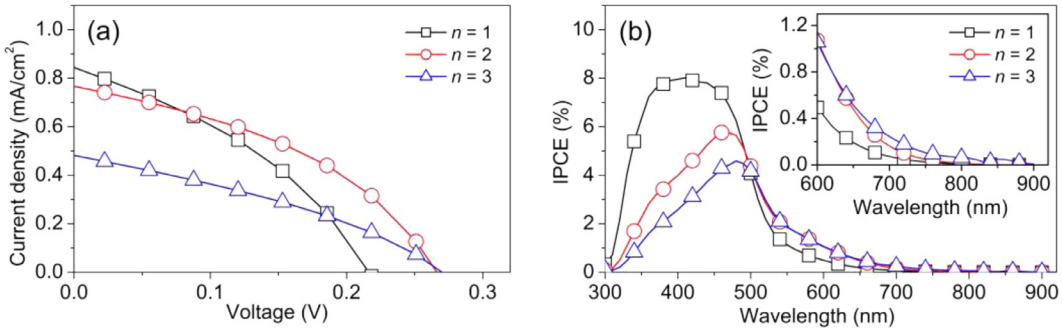

Fig. 3. (a) *J–V* curves and (b) IPCE spectra of FTO/CFTS/CdS/Al solar cells with n = 1–3. The inset to (b) shows the magnified IPCE spectra within 600–900 nm.

(Fig. 2e). EDX result (Fig. 2f) confirms that atomic ratio of Cu:Fe:Sn:S is 2:0.95:1.68:3.95, close to the stoichiometry of 2:1:1:4, in which the excess Sn content is accounted for by the contribution from FTO substrate [12]. XPS results (Fig. S2) further confirm that the main chemical states of Cu, Fe, Sn and S elements in CFTS film are +1, +2, +4 and −2, respectively, agreeing well with the element states in Cu_2FeSnS_4. Fig. S3 shows the optical absorption coefficient (α) of CFTS film is higher than 10^4 cm^{-1} in the wavelength range of 300–1100 nm. Using the direct band gap method, the band gap of CFTS film is evaluated to be ca. 1.53 eV, which is very close to the earlier reports [4,13,14] and matches the optimal value (1.1–1.7 eV) for ideal solar cell materials [15]. Note that, similar to Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ [16], the band gap of CFTS film may get reduced by partially replacing S with Se.

We fabricated the solar cells with a structure of FTO/CFTS/CdS/Al. Fig. 3a shows the *J–V* curves of the best solar cells with n = 1–3 under illumination (AM 1.5G, 100 mW/cm^2). The device performance is of a high reproducibility (Table S1). With increasing CFTS thicknesses (i.e., changing n from 1 to 3), the V_{oc} increase initially but saturated afterwards, a continuous decrease trend in J_{sc}, and an initial increase followed a decrease in FF, resulting in a champion η of 0.08% for n = 2 (i.e., the thickness of 125 nm). This efficiency of our solar cells is comparable to that of similarly structured Mo/CFTS/CdS/ZnO/Al:ZnO devices in which the CFTS was prepared by magnetron sputtering in combination with sulfurization [1,2]. However, our devices still have a poorer performance than the reported Mo/CFTS/CdS/ZnO/Al:ZnO/Ni/Al devices [3], which have CFTS films consisting of larger crystal grains obtained by sulfurization of preformed CFTS nanocrystals. Compared to those previous reports, our solar cells are mainly prepared by solution-processing method and much simpler in structure, which are convenient for scaled preparation.

In order to get insight into the photocurrent generation related to CFTS thickness, incident photon-to-current efficiency (IPCE) spectra of solar cell devices were measured (Fig. 3b). All the devices exhibit two IPCE bands: 300–550 nm from CFTS and CdS absorptions and 550–900 nm from only CFTS absorption (Fig. S4). With increasing n from 1 to 3, the IPCE in the whole range gets reduced, which is consistent with the changes in J_{sc} (Fig. 3a). Since the CdS layer in all the devices have the same thickness, the IPCE results indicate that the CFTS with a thickness higher than 65 nm (i.e., n = 1) does not favor the photocurrent generation, for which the short exciton diffusion length in CFTS might be responsible.

4. Conclusions

Compact nanocrystalline CFTS thin films with a controllable thickness are prepared by spin-coating CFTS precursor solution followed by a thermal annealing process. The CFTS films exhibit an absorption coefficient of $\alpha > 10^4$ cm^{-1} in 300–1100 nm range and a band gap of E_g = 1.53 eV. Furthermore, the FTO/CFTS/CdS/Al solar cells based on the CFTS films exhibits the highest efficiency of η = 0.08% for the optimized CFTS thickness of 125 nm. This work provides a novel solution-processing method for preparing CFTS films for low-cost thin film solar cells, photocatalysts and other optoelectronics. In order to get efficient solar cells, the nanoparticles in as-prepared CFTS films may be increased by sulfurization for example to reduce the resistances for charge transport, which is in progress.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.matlet.2017.12.032.

References

[1] X. Meng, H. Deng, J. He, L. Sun, P. Yang, J. Chu, Mater. Lett. 151 (2015) 61–63.
[2] X. Meng, H. Deng, J. Tao, H. Cao, X. Li, L. Sun, P. Yang, J. Chu, J. Alloys Compd. 680 (2016) 446–451.
[3] B. Ananthoju, J. Mohapatra, M.K. Jangid, D. Bahadur, N.V. Medhekar, M. Aslam, Sci. Rep. 6 (2016) 35369.
[4] S. Chatterjee, A.J. Pal, Sol. Energy Mater. Sol. Cells 160 (2017) 233–240.
[5] A. Ghosh, D.K. Chaudhary, A. Biswas, R. Thangavel, G. Udayabhanu, RSC Adv. 6 (2016) 115204–115212.
[6] C. Dong, W. Meng, J. Qi, M. Wang, Mater. Lett. 189 (2017) 104–106.
[7] A. Ghosh, A. Biswas, R. Thangavel, G. Udayabhanu, RSC Adv. 6 (2016) 96025–96034.
[8] W. Yue, F. Wu, C. Liu, Z. Qiu, Q. Cui, H. Zhang, F. Gao, W. Shen, Q. Qiao, M. Wang, Sol. Energy Mater. Sol. Cells 114 (2013) 43–53.
[9] H. Xin, J.K. Katahara, I.L. Braly, H.W. Hillhouse, Adv. Energy Mater. 4 (2014) 1301823.
[10] D.B. Khadka, J.H. Kim, J. Alloys Compd. 638 (2015) 103–108.
[11] K. Mokurala, S. Mallick, P. Bhargava, J. Power Sources 305 (2016) 134–143.
[12] Z. Yan, A. Wei, Y. Zhao, J. Liu, X. Chen, Mater. Lett. 111 (2013) 120–122.
[13] R.R. Prabhakar, N.H. Loc, M.H. Kumar, P.P. Boix, S. Juan, R.A. John, S.K. Batabyal, L.H. Wong, ACS Appl. Mater. Interfaces 6 (2014) 17661–17667.
[14] M. Adelifard, J. Anal. Appl. Pyrol. 122 (2016) 209–215.
[15] A. Goetzberger, C. Hebling, H.-W. Schock, Mater. Sci. Eng. R 40 (2003) 1–46.
[16] A.H. Reshak, K. Nouneh, I.V. Kityk, J. Bila, S. Auluck, H. Kamarudin, Z. Sekkat, Int. J. Electrochem. Sci. 9 (2014) 955–974.