Crystallization temperature investigation of Cu$_2$ZnSnS$_4$ by using Differential scanning calorimetry (DSC)

Dagang Miao[a,*], Jiangtao Xu[b], Shouxiang Jiang[b,*], Xin Ning[a], Jie Liu[a], Songmin Shang[b]

[a] Industrial Research Institute of Nonwovens and Technical Textiles, College of Textiles and clothing, Qingdao University, Qingdao, China
[b] Institute of Textiles and Clothing, the Hong Kong Polytechnic University, Hong Kong, China

A B S T R A C T

The Cu$_2$ZnSnS$_4$ (CZTS) powder was systematically investigated by energy dispersive X-Ray spectroscopy (EDX), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Ramam spectrometer, and further studied by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA). The Ramam and XRD results showed that the sample is a structure of Kesterite type under a condition of Cu-rich and Zn-poor with few impurity phases. The DSC results show that incubation time, peak time and end time of crystallization are all reduced with the increasing temperature; and the temperature of 550 ℃ will be more suitable for annealing treatment of CZTS. A CZTS film is also fabricated and annealed at 550 ℃ to confirm the result of the research. The systematic investigation of CZTS by using differential scanning calorimetry provided a fundamentally dynamic reference for the temperature selection of anneal during the fabrication of CZTS.

1. Introduction

As a absorber in thin-film solar cell devices, quaternary compound Cu$_2$ZnSnS$_4$ (CZTS) has attracted steady increasing attention due to its low cost, earth-abundant elements, non-toxic, direct band gap energy of ~1.5 eV and large absorption coefficient of $> 10^4$ cm^{-1} [1–3]. Nevertheless, it is not so easy to fabricate a high quality single phase compound restricted by its element stoichiometry [4,5]. There are more ternary and binary secondary phases, such as Cu$_2$S, SnS$_2$ and CTS, formed during the fabrication [6,7]. The phase structure and crystallization of the compound would affect the properties and efficiency of the solar cell devices directly. Therefore, it is essential to investigate and optimize the fabrication of CZTS for further, these fundamental investigations are supposed to contribute to help understand the phase formation and improve the stability and reproducibility of the fabrication of CZTS.

During the fabrication of CZTS, it could form many different structures, such as kesterite structure, stannite structure and primitive mixed CuAu-like structure [8]. The kesterite structure is the desired crystalline phase, with stable structure and lower energy, which was used as an absorber of solar cell devices [9,10]. CZTS film or nanoparticles could be fabricated by several different techniques based on vacuum and non-vacuum methods, such as RF sputtering [11,12], co-evaporation [13], pulsed electrodeposition [14], sol-gel deposition [15], spray pyrolysis [16], screen printing [17] and so on. Most of the films or nanoparticles prepared by the above methods should be post-treated to obtain the single kesterite phase CZTS. Olgar et al. fabricated CZT film by sputtering and annealed the film in sulfur atmosphere by RTP method at 500 °C, 550 °C and 600 °C, the results showed that the annealing temperature of 600 °C and treating time of 3 min was proposed [18]. Lin et al. deposited CZTS films by RF sputtering and sulfur annealed at 570 °C for 1 h to get the Cu$_{24.15}$Zn$_{14.73}$Sn$_{10.75}$S$_{50.37}$ thin film which was close to ideal stoichiometric ratio of 2:1:1:4 [12].

As presented above, a lot of valuable researches have been acquired. However, there are few fundamental studies of the isothermal crystallization kinetics which would provide a guidance of the range of the annealing temperature selection. Thermal analysis methods, such as Differential scanning calorimetry (DSC), Thermogravimetric analysis (TG), and Differential thermal analysis (DTA) are often used for kinetic analysis of solids crystallization processes [19–21]. In this study, the CZTS powder is evaluated by EDX, SEM and Ramam firstly, and then the recrystallization process of CZTS is investigated by DSC. The DSC results illuminate the change of crystallization parameters during the isothermal process, including incubation time, end time and peak time of crystallization. Moreover, a CZTS film with a thickness of 1 μm was fabricated and annealed at an optimized condition; the elements change of the film is systematically investigated as well as its structure and morphologies.

2. Experimental

2.1. Material

The CZTS powder used for tests was scraped from a commercial CZTS target purchased from Qijin New Material Technology Ltd (purity: 99.99%; Quanzhou, China).

2.2. Fabrication of CZTS film

The CZTS film was deposited on a cleaned slide with the commercial target by using RF magnetron sputtering system at 150 ℃, with a power of 150 W, a target-substrate distance of 10 cm and Argon flow rates of 100 sccm, for 180 min. The film thickness of 1 μm was obtained by a P-10 Surface Profiler. The annealing process was conducted by using a tube annealing furnace at 550 ℃ for 15 min, with a N_2 flow rate of 50 sccm.

2.3. Chemical composition

EDX was performed by using a JEOL model JSM-6490 in an ultra-high-vacuum system with a base pressure of about 1.5×10^{-4} Pa.

2.4. Surface morphology

The surface morphology of the coated fabric was observed by using emission scanning electron microscope (JSM-6490).

2.5. Ramam

The Ramam spectrum of CZTS sample was collected in the range of 200–600 cm^{-1} using a Ramam spectrometer (NomadicTM 3-in-1 Raman Microscope, Bay Spec, U. S.) with an excitation wavelength of 785 nm and resolution of 2.2 cm^{-1} at 150 mW laser power.

2.6. Thermal and isothermal process

The crystallization process was investigated by using TGA/DSC 1 STAR[e] System (METTLER TOLEDO) and Power compensated Perkin–Elmer DSC-8000. The temperature scanning program was performed at a scanning rate of 10 ˚C/min in a temperature range of 50 ˚C to 550 ˚C under a nitrogen purge of 50 ml/min. The isothermal program was conducted at temperature of 450 ℃, 470 ℃, 490 ℃, 510 ℃, 530 ℃ and 550 ˚C under a nitrogen purge of 50 ml/min for 40 min respectively.

3. Results and discussion

3.1. Chemical composition analysis

The EDX spectrum of the CZTS power is shown in Fig. 1(a). The elements S (2.308 keV, 2.464 keV), Cu (0.93 keV, 8.048 keV and 8.905 keV), Zn (1.012 keV, 8.639 keV and 9.572 keV) and Sn (3.444 keV, 3.666 keV) are detected without any other impurities.

The atomic percentage of the above four elements is shown in Table 1. The atomic ratio of Cu/Zn/Sn/S is 2.76: 1: 1.37: 4.01, which is close to the standard stoichiometric of 2: 1: 1: 4. The powder also shows a higher ratio of Cu/ (Zn + Sn) and lower ratio of Zn/Sn, indicating that it is Cu-rich and Zn-poor.

The EDX elemental mapping was recorded from the CZTS powder, shown in Fig. 1(b). It can be found that the elements are distributed uniformly, and the Zn contents seems less than other elements, which is consistent with the analysis of the elements ratio.

3.2. Crystallization analysis

The Ramam spectrum of the CZTS powder is shown in Fig. 1(c). A strong peak at 338 cm^{-1} is observed, which belongs to the kesterite CZTS phase [22,23]. Moreover, other minor peaks related to the kesterite phase at 287 cm^{-1} and 368 cm^{-1} are also detected [24]. However, a small peak appeared at 321 cm^{-1} corresponding to CTS (Cu_2SnS_3) phase is also observed [25]. This may be caused by the elemental composition of Cu-rich and Zn-poor.

The structure property is also evaluated by XRD spectrum. As shown in Fig. 1(d), diffraction peaks at expected positions of 2θ =18.20˚ (101), 28.53˚ (112), 32.98˚ (200), 47.33˚ (220), 56.17˚ (312) and 76.44˚ (332) are well detected, indicating the formation of Kesterite type CZTS [18,26,27]. Nevertheless, a small peak at 2θ = 26.66˚ can be contributed to CTS Mohite phase (JCPDS 35–0684). Therefore, the XRD result is in accordance with Ramam analysis. These results imply that the CZTS sample is a structure of Kesterite type under a condition of Cu-rich and Zn-poor with few impurity phases, combing with the chemical composition analysis.

3.3. Crystallization dynamic analysis

The TGA and DSC spectrum were recorded in order to investigate the crystallization dynamic of CZTS, presented in Fig. 2(a). As shown in the figure, only one peak is detected in the DSC curve and no weight loss is found in the TGA curve, indicating that it is a single crystallization stage during the heating process. However, the result is conflicted with the analysis results of Ramam and XRD, which may be owing to relatively small weight percentage of impurity phase. The exothermic curve ranged from 450 to 550 ℃ with a exothermic peak at 534 ℃ reveals the completion of CZTS crystallization process.

For further study, the isothermal curves of the sample at the temperature ranged from 450 to 550 ℃ are exhibited in Fig. 2(b). As shown, the isothermal curves at different temperature of the sample are in accordance with the analysis results of the temperature scanning curves that the crystallization process is a single stage.

The data (heat flow) collected from a power compensated differential scanning calorimetry is the power difference between the sample and the reference (dH/dt). The heat quantity released by time t is proportional to the volume fraction of crystallization χ (t) during the crystallization process [28], as shown in Eq. (1):

$$\frac{dH(x)}{dt} \propto \frac{d\chi(t)}{dt} \tag{1}$$

Where $dH(x)/dt$ is the integration of heat flow to time; $d\chi(t)/dt$ is the integration of volume fraction of crystallization.

Fig. 2(c) shows the crystallized volume fraction versus isothermal temperature. The curves are S-shaped and the volume fraction of crystallization goes steeper with the increasing time, indicating that the crystallization process is accelerated. However, the increase rate of the volume fraction of crystallization is closely to each other among the temperature from 450 ℃ to 550 ℃.

Incubation time of crystallization (τ) is defined as the time when the crystallized volume fraction is 0.5%. The peak time of crystallization (t_p) is the time when the crystallization rate ($d\chi(t)/dt$) reaches its maximum value, and the end time of crystallization (t_e) is the time when the process completed.

The incubation time, end time and peak time of crystallization of the sample are presented in Fig. 2(d). As shown in Fig. 2(d), the incubation time of crystallization is shortened from 11.8 to 5.7 min with the increasing temperature. This indicates that the incubation time of the crystal particles is shortened due to the increase in the amount of energy that can be gained in an instant. Similarly, with the increase of the temperature, the time consumed to reach the maximum rate of crystallization is shortened from 12.8 to 4.4 min. Moreover, the efficiency of annealing process will also be improved with the increasing