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THE INFLUENCE OF SUBSTRATE TEMPERATURE ON SPRAY-DEPOSITED $CuSbS_2$ THIN FILMS

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Ternary $CuSbS_2$ thin films were deposited on glass slides at substrate temperatures in the range 280-400 ºC via the spray pyrolysis deposition approach from methanol solutions. The structure, morphology, composition and optical properties were characterized by XRD, SEM, EDAX and UV-Vis spectroscopy. XRD patterns show the orthorhombic structure films in polycrystalline nature. No secondary phases are observed for the films deposited at 320 ºC and 360 ºC. SEM images reveal the homogenous films in the form of densely packed nanoparticles. EDAX analysis confirms the presence of copper, antimony and sulphur elements with the feature of copper-rich and sulphur-poor. According to Tauc plots, optical band gaps of $CuSbS_2$ films are estimated to be 1.72-1.75 eV.

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Keyword: $CuSbS_2$; CAS; Thin films; Spray pyrolysis deposition; Solar cells.

1. Introduction

Ternary copper antimony sulphide $CuSbS_2$ (CBS) has mostly been studied as one of the most promising absorber materials in thin film solar cells because of its near-optimal bandgap (0.91-1.89 eV), high absorption coefficient (>10^4 cm^{-1}) and proper electrical conductivity [1,2]. Also, $CuSbS_2$ is considered as an emerging alternative to $Cu(In,Ga)Se_2$ (CIGS) and CdTe owing to its relatively abundance and non-toxic compositions [1-3]. Very recently, photovoltaic device with an AZO/CdS/$CuSbS_2$/Mo/glass structure has achieved a preliminary conversion efficiency of 3.1% [3].

Various deposition techniques for $CuSbS_2$ thin films have been reported, *e.g.*, chemical bath deposition [4-6], heating Sb_2S_3/Cu layers [7], thermal evaporation [8-11], spray pyrolysis deposition [12,13], electrodeposition [3,14,15], and hydrazine solution process [16], *etc*. Compared with the other methods, the spray pyrolysis approach possesses the merits of simplicity, commercial viability, and potential for cost-effective mass production [17,18]. Although the spray pyrolysis deposition of $CuSbS_2$ thin films from the aqueous media has been published [12,13], the non-aqueous media and the effect of substrate temperature on the $CuSbS_2$ film properties in the spray pyrolysis process have never been reported.

Herein, ternary copper antimony sulphide $CuSbS_2$ thin films were deposited on glass slides at different substrate temperatures via the spray pyrolysis deposition approach from methanol solutions. The as-prepared $CuSbS_2$ thin films was investigated by XRD, SEM, EDAX and UV-Vis spectroscopy in details.

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2. Experimental description

2.1. Deposition of $CuSbS_2$ films

$CuSbS_2$ thin films were deposited by the chemical spray pyrolysis (CSP) technique from methanol solutions of copper(II) chloride $CuCl_2$ (0.05 M), antimony(III) chloride $SbCl_3$ (0.05 M), and thiourea (0.2 M) using compressed air as the carrier gas at a pressure of 2.0 bar. Several drops of HCl were added for insuring the solubility of the antimony precursor. Excess thiourea was necessary to compensate for sulphur loss during thermal deposition. The methanol solutions were sprayed by airbrush onto the clean glass slides (20 mm x 20 mm x 2 mm) heated at the substrate temperatures of 280, 320, 360, or 400 °C.

2.2. Characterization

The crystal structure of $CuSbS_2$ films deposited on the glass slides was analyzed by X-ray diffraction (XRD) using a Bruker D8 ADVANCE. The surface morphologies and chemical compositions of the films were characterized by a scanning electron microscope (SEM) (Hitachi S-4800) coupled with an X-ray microanalysis system (HORIBA EX-350) for acquiring the Energy Dispersive X-Ray Spectroscopy (EDAX). UV-Vis absorption spectra were obtained on a Shimadzu UV-2450 spectrophotometer at room temperature.

3. Results and discussion

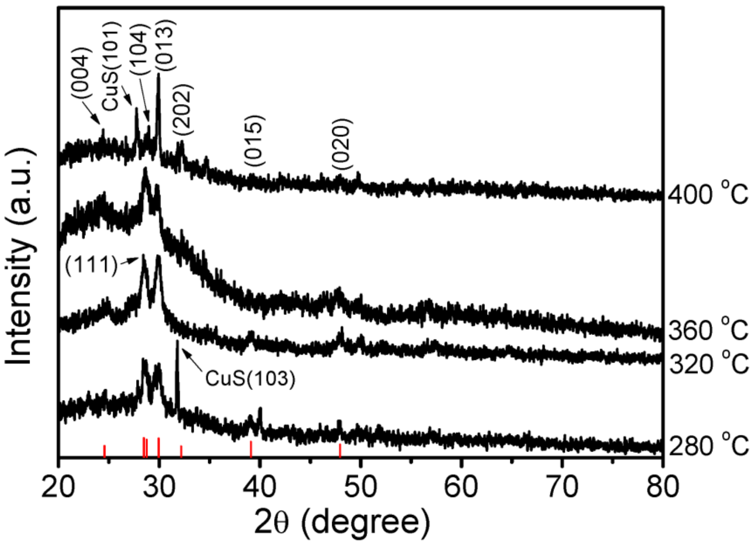

Fig. 1. XRD patterns of $CuSbS_2$ films deposited at different substrate temperatures.

Fig. 1 displays the typical XRD patterns of the as-prepared $CuSbS_2$ thin films grown at different substrate temperatures. The diffraction peaks centered at 2θ values of approximately 4.6º, 28.5º, 28.7º, 29.9º, 32.2º, 39.1º, and 48.0º are indexed to the (004), (111), (104), (013), (202), (015), and (020) planes of orthorhombic $CuSbS_2$ structure (JCPDS Card No.: 65-2416). The sharp peaks of a secondary phase at 27.7º and 31.8º for the films deposited at 280 ºC and 400 ºC, respectively, can be attributed to (101) and (103) plane of hexagonal CuS structure (JCPDS Card No.: 65-3588). At the deposition temperature of 320 ºC and 360 ºC, no crystal impurity is detected. It implies that the moderate reaction temperatures are required for the spray pyrolysis deposition of $CuSbS_2$ from the non-aqueous media. In brief, purity-free $CuSbS_2$ thin films are successfully synthesized at the substrate temperatures of 320 ºC and 360 ºC through the spray pyrolysis approach from methanol solutions.

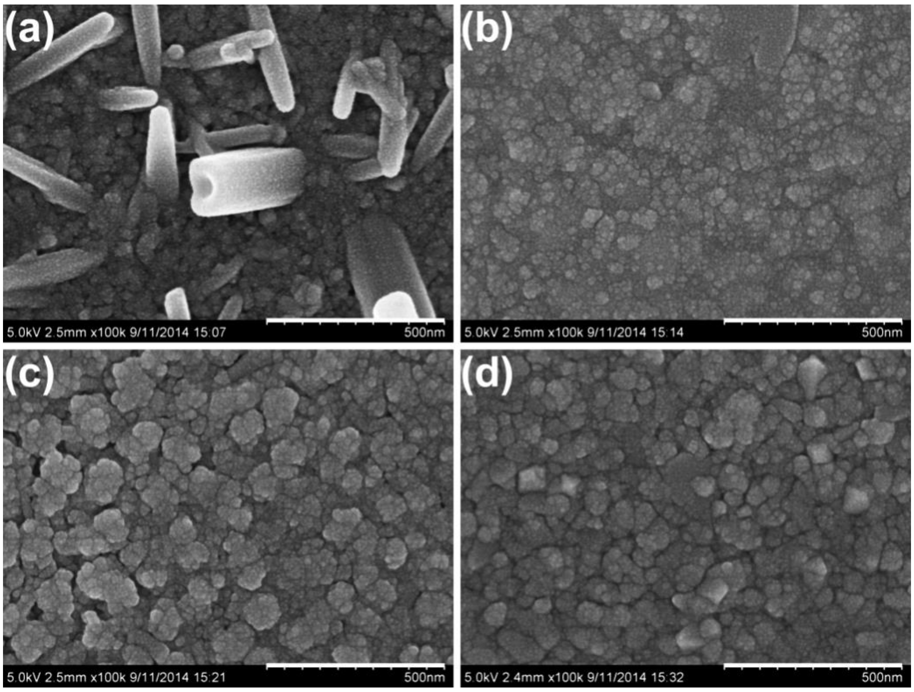

Fig. 2. SEM images of $CuSbS_2$ thin films deposited at the substrate temperature of (a) 280 ºC; (b) 320 ºC; (c) 360 ºC; (d) 400 ºC.

Fig. 2 shows the representative SEM images of $CuSbS_2$ thin films grown at different substrate temperatures. It is observed that all the as-prepared films are constituted by densely packed submicro-sized grains, which are also composed of very fine nanoparticles on a smaller scale. The films deposited at 280 ºC exhibits lots of irregular grain morphologies, such as rods or top-holed rods, which can be distinguished to be comprised of nanoparticles from rods' rough surfaces. More studies are needed to understand the formation of such rods in the deposition process. When the substrate temperature rises up to 320 ºC, the fairly homogeneous and compact films, which only contain rare cracks or pinholes, are clearly viewed.

Fig. 3 shows the EDAX analysis of the film which indicates the presence of copper, antimony and sulphur. The average atomic contents of Cu, Sb and S in the as-deposited films are 35.02%, 26.02% and 38.96%, respectively. Compared with the stoichiometric value of 1:1:2 for $CuSbS_2$, the as-prepared films are evidently copper-rich and sulphur-poor. The copper-rich may come from the impurity of CuS in the crystalline form which was found in Fig. 1 or in the amorphous form which cannot be ruled out even though it is not detected by XRD. The sulphur-poor may resulted from the thermal loss of volatile sulphur element during the spray pyrolysis process.

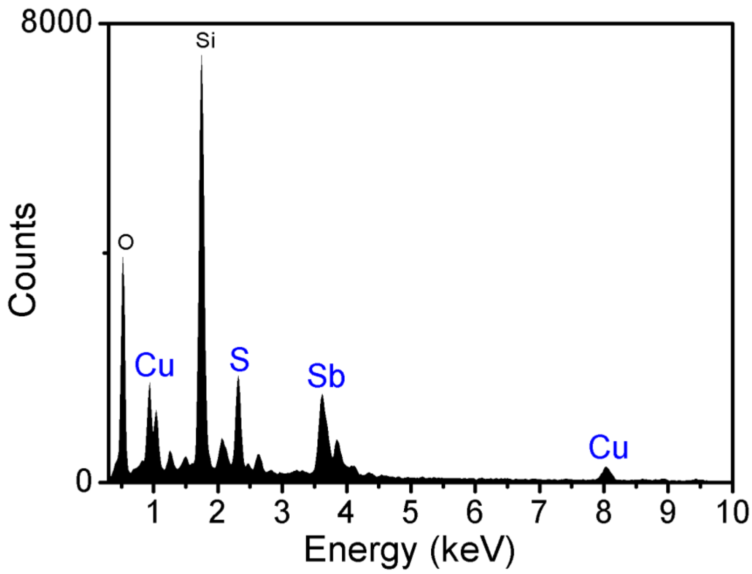

Fig. 3. EDAX spectrum of the as-prepared $CuSbS_2$ films. The signals of Si and O elements come from the glass substrate.

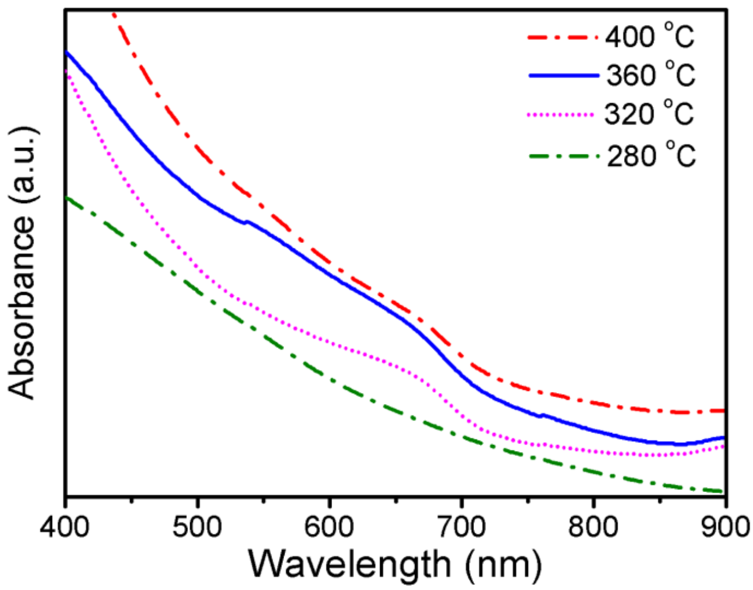

Fig. 4. UV-Vis absorption spectra of $CuSbS_2$ films deposited at various substrate temperatures.

UV-Vis absorption spectra of $CuSbS_2$ films are displayed in Fig. 4. Optical band gaps of $CuSbS_2$ films are determined using Tauc formula for the direct band gap semiconductors,

$$(\alpha h\upsilon)^2=A(h\upsilon-E_g)$$

where α is the absorption coefficient, A is a constant, E_g is the optical gap energy, υ is incident photon frequency and h is the Planck's constant.

As shown in Fig. 5, the optical band gaps of the films are estimated to be between 1.72 and 1.75 eV, which are in good agreement with published values [1,8]. The slight alteration in values means that the substrate temperatures between 280 ºC and 400 ºC have little impact to the optical band gaps of the as-prepared films.

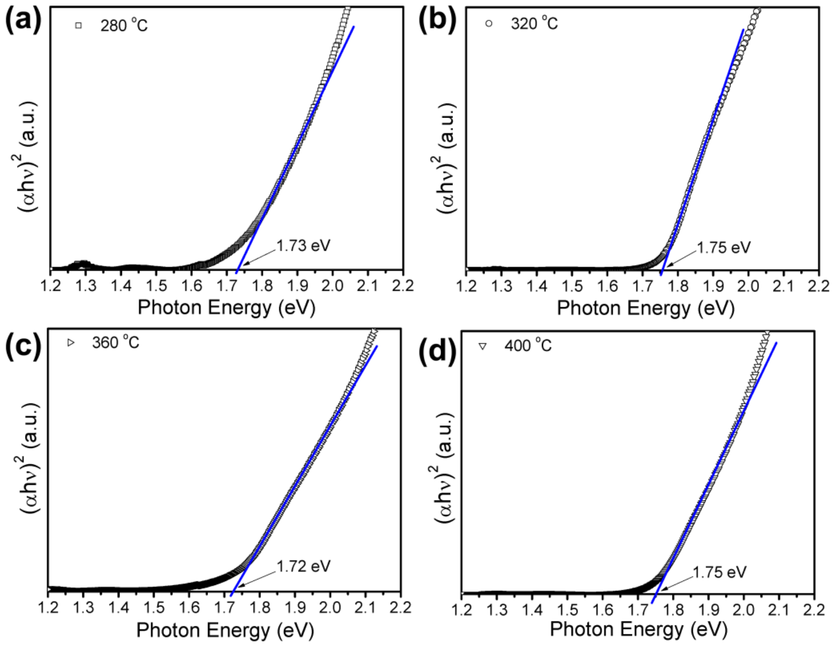

Fig. 5. Tauc plot of $(\alpha h\upsilon)^2$ vs. $h\upsilon$, displaying a linear trend for a direct transition, for $CuSbS_2$ films deposited at (a) 280 ℃; (b) 320 ℃; (c) 360 ℃; (d) 400 ℃.

4. Conclusions

Ternary $CuSbS_2$ thin films were successfully deposited on glass slides at different substrate temperatures via the spray pyrolysis deposition approach from methanol solutions. The effects of substrate temperature on the structural, morphological and optical properties of $CuSbS_2$ thin films in the spray pyrolysis process were investigated in details. XRD patterns show the orthorhombic structure films in polycrystalline nature. SEM images reveal the homogenous films in the form of densely packed nanoparticles. EDAX analysis confirms the presence of copper, antimony and sulphur elements with the feature of copper-rich and sulphur-poor. According to Tauc plots, optical band gaps of $CuSbS_2$ films are estimated to be 1.72-1.75 eV.

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