GROWTH, STRUCTURE AND OPTICAL CHARACTERIZATION OF $CuGaS_2$ THIN FILMS OBTAINED BY SPRAY PYROLYSIS

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CuGaS2 thin films were deposited on soda lime glass substrates at various substrate temperatures through spray pyrolysis. Growth, structure, and optical characterization of the films were recorded by XRD, SEM, EDAX and UV-Vis absorption spectroscopy. The as-prepared films with a chalcopyrite structure have a loose surface morphology consisting of large island-like grains. EDAX analysis confirms the presence of copper, antimony and sulphur elements with a copper-rich and sulphur-poor composition. Direct optical band gaps of $CuGaS_2$ films were estimated to be 2.07-2.25 eV according to UV-Vis absorption spectra.

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Keyword: $CuGaS_2$; CGS; thin films; spray pyrolysis.

1. Introduction

As a member of the chalcopyrite family, Copper gallium sulfide $CuGaS_2$, a ternary compound that has a relatively low toxicity, broad band gap and high absorption coefficient [1], has been expected to be a candidate for short wavelength opto-electronic applications such as Cd-free window layer for $Cu(In_{1-x}Ga_x)Se_2$ solar cell [2], green light-emitting material [3-5], and photocatalyst [6,7]. Moreover, $CuGaS_2$ has been considered as a promising material for high efficiency tandem solar cells [8] and intermediate-band solar cells [9-11].

$CuGaS_2$ thin films have been produced by numerous techniques, *e.g.*, modulated flux deposition [12], metal-organic vapor-phase epitaxy [3,5,13-15], electron beam evaporation [16], metal-organic chemical vapor deposition [17], vacuum thermal evaporation [18,19] and electrodeposition [20-22]. However, they are not suitable for large-scale production due to their expensive cost. Thus, it remains appealing to develop a non-vacuum and low cost approach for large-scale deposition of $CuGaS_2$ thin films.

In this study, $CuGaS_2$ thin films were deposited on soda lime glass substrates at various substrate temperatures through spray pyrolysis. The composition, structure and optical characteristics of the as-prepared $CuGaS_2$ thin films has been thoroughly analyzed by XRD, SEM, EDAX and UV-Vis absorption spectroscopy.

2. Experimental description

2.1. Deposition of $CuGaS_2$ films

$CuGaS_2$ thin films were deposited onto glass slides by using chemical spray pyrolysis (CSP) method. Spray solution containing copper(II) chloride $CuCl_2$ (0.05 M), gallium (III) chloride $GaCl_3$ (0.05 M), and thiourea (0.25 M) dissolved in methanol was used. Excess thiourea was necessary to compensate for the loss of sulfur during pyrolysis. The solution was sprayed by airbrush with a spray

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rate of 5 ml min^{-1} at a substrate temperature of 290, 320, 350, or 380 °C. Compressed air with a pressure of 1.5 bar was used as the carrier gas.

2.2. Characterization

Crystal structures of the films were 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

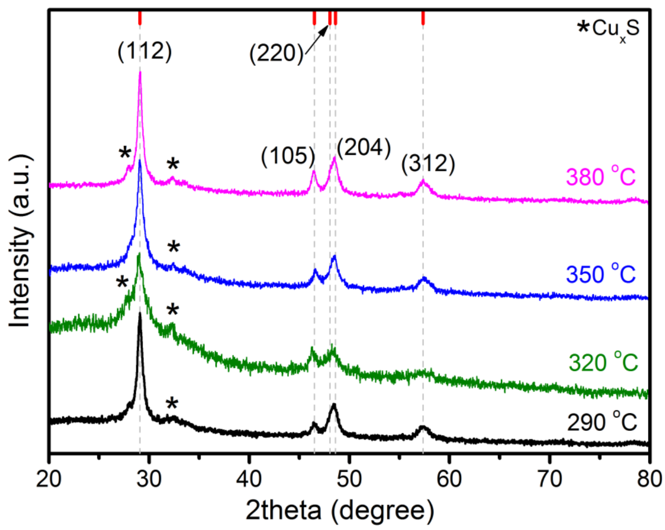

Fig. 1. XRD patterns of $CuGaS_2$ films deposited at various substrate temperatures.

The representative XRD patterns in Fig. 1 illustrate phase structures of $CuGaS_2$ thin films produced at various substrate temperatures. The diffraction patterns confirm the formation of chalcopyrite structure of $CuGaS_2$ (JCPDS Card No.: 65-1571) as the prominent diffraction peaks centered at 2θ values of 29.1°, 46.5°, 48.1°, 48.6°, and 57.4° corresponding to the (112), (105), (220), (204), and (312) planes. The weak diffraction peaks at approximately 28.0° and 32.3° can be attributed to a secondary phase Cu_xS structure. The average grain size of the crystal phase formed at 290, 320, 350 and 380 °C are similar and estimated to be about 14 nm calculated from the full-width at half-maximum of the main XRD peaks according to Scherrer equation.

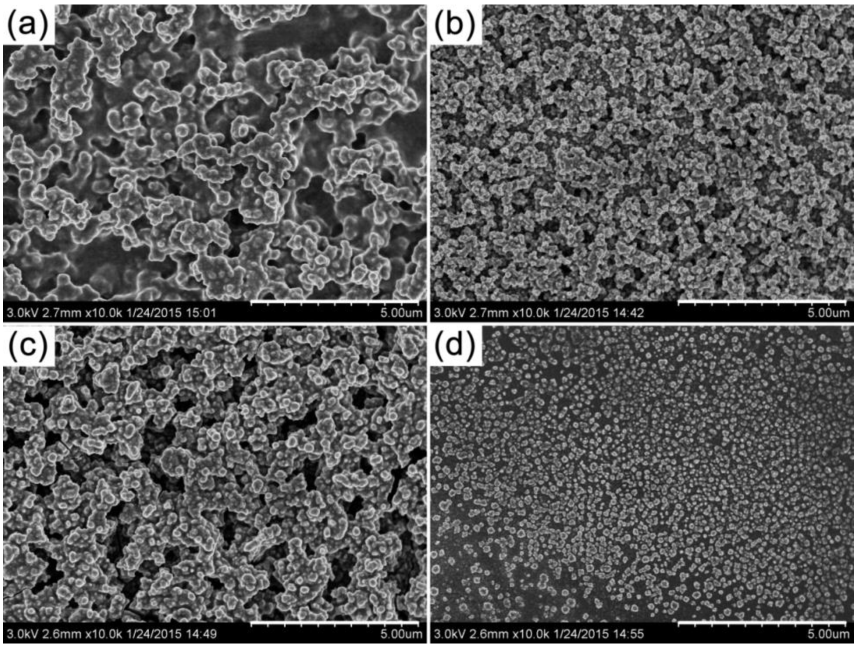

Fig. 2. SEM images of $CuGaS_2$ thin films deposited at the substrate temperature of (a) 290 ºC; (b) 320 ºC; (c) 350 ºC; (d) 380 ºC.

Figure 2 displays the typical SEM images of $CuGaS_2$ thin films deposited at different substrate temperatures. Loose surface with large island-like grains are observed for all the as-prepared films. Surface morphologies obtained at different points of the film are similar. As the substrate temperature increases from 350 ºC to 380 ºC, appearance of the film is found to be less rough but agglomeration of the grains is clearly viewed.

EDAX analysis of the film in Figure 3 indicates the presence of copper, gallium and sulfur elements with an average atomic contents of 35.41%, 18.99% and 45.60%, respectively. Accordingly, atomic ratios of Cu/Ga and S/(Cu+Ga) is calculated to be 1.90 and 0.83. Compared with the stoichiometric value of 1:1:2 for $CuGaS_2$, the films exhibit a copper-rich and sulphur-poor composition. The excessive copper in the films may come from a secondary phase Cu_xS structure which is discovered by XRD in Figure 1. Sulfur deficiency in the films may be caused by an easy loss of volatile sulfur element during thermal pyrolysis. The evident signal of Cl should stem from an incomplete decomposition of cation precursors.

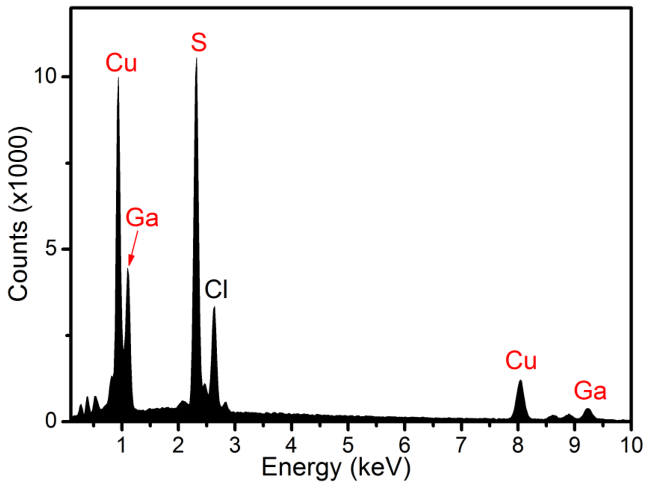

Fig. 3. EDAX spectrum of the as-prepared $CuGaS_2$ films.

To acquire optical properties of $CuGaS_2$ films, UV-Vis absorption spectroscopy was used at room temperature. To avoid effect of film thickness on absorbance, normalized UV-Vis absorption spectra of the films were recorded in Figure 4.

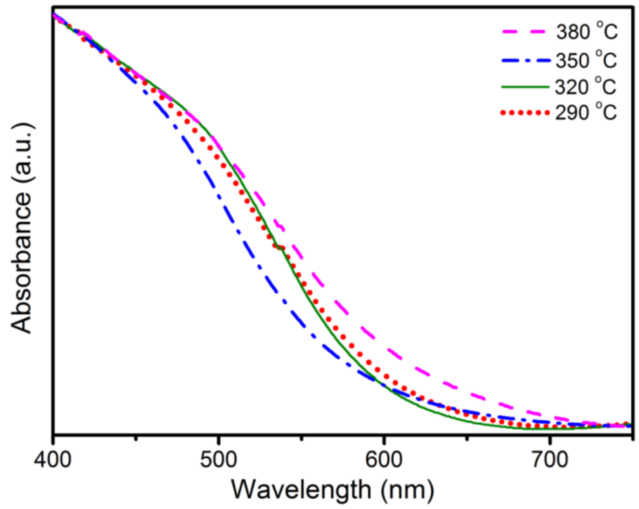

Fig. 4. Normalized UV-Vis absorption spectra of $CuGaS_2$ films deposited at various substrate temperatures.

Optical band gaps of the as-prepared $CuGaS_2$ films are determined by 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.

The fitting results are shown in Figure 5. Direct optical band gaps of the films are estimated to be 2.07-2.25 eV, which are slightly lower than 2.49 eV for the bulk [17,23], but in good agreement with the previously published value of 2.24 eV [24]. The reason for the lower band gaps of the as-prepared films may be due to the presence of defect states resulted from the copper-rich composition, which is also supported by XRD and EDAX results.

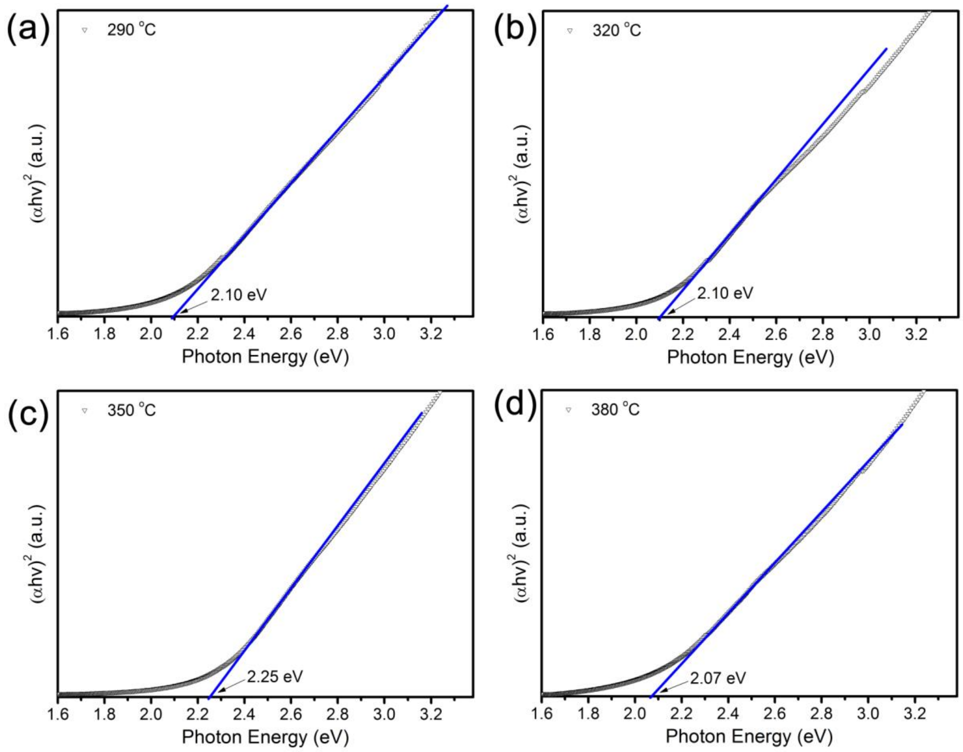

Fig. 5. The square of the product between absorption coefficient and photon energy plotted as a function of photon energy displaying a linear trend for a direct transition, for the typical $CuGaS_2$ films deposited at (a) 290 ºC; (b) 320 ºC; (c) 350 ºC; and (d) 380 ºC.

4. Conclusions

Chalcopyrite structure $CuGaS_2$ thin films were deposited on soda lime glass at various substrate temperatures via spray pyrolysis approach. The as-prepared films consist of large island-like grains which results in a loose surface morphology. EDAX analysis confirms the presence of copper, antimony and sulphur elements with a copper-rich and sulphur-poor composition. According to Tauc formula, direct optical band gaps of $CuGaS_2$ films are estimated to be 2.07-2.25 eV.

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