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Effects of the sulfurization temperature on sol gel-processed Cu_2ZnSnS_4 thin films

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Abstract

As a promising and alternative solar absorber material, the copper–zinc–tin–sulfide compound (Cu_2ZnSnS_4) has been drawing attention in recent years for the production of cheap thin-film solar cells owing to the high natural abundance and non-toxicity of all the constituents, a tunable direct-band-gap energy and a large optical absorption coefficient. In addition, to overcome the problem of expensive vacuum-based methods, solution-based approaches are being developed for Cu_2ZnSnS_4 deposition. In this study, we have produced Cu_2ZnSnS_4 thin films via the sol–gel technique and subsequent sulfurization. The effects of the sulfurization temperature on the structural, morphological, compositional and optical properties of the films were investigated. X-ray diffraction and Raman spectroscopy analyses confirmed the formation of phase-pure CZTS films. The crystallinity of the films increased with an increasing sulfurization temperature. From the surface images and the results of the composition analysis, it was found that the films are uniform, composed of homogenously distributed grains and have compositions with Cu deficit. The values of the optical absorption coefficients for the films were found to be 10^4 cm^{-1} based on absorbance spectroscopy. The optical band-gap values were estimated to be between 1.32 and 2.27 eV depending on the sulfurization temperature.

Keywords: A. Films; A. Sol–gel process; B. Spectroscopy; B. X-ray methods

1. Introduction

The development of green-energy resources as an alternative to carbon-based fuels has become one of the most important duties assigned to researchers in recent years. Among the diverse forms of renewable energy sources, solar energy is the best option, as it can meet the energy demands of modern society [1]. Lately, the production of solar cells has increased significantly due to a rapid increase in demand for renewable energy sources. In order to make photovoltaic devices more widespread, cheaper, more efficient, green solar cells have to be developed [2]. Silicon is the most commonly used material in commercial solar cells: about 80% of the photovoltaic market is silicon-based devices. The production of highly efficient silicon solar cells requires the use of monocrystal silicon wafers, which dramatically increases the production costs. Moreover, silicon is an indirect-band-gap semiconductor and its absorption coefficient is relatively low, requiring the absorption layer to be at least 100 μm thick in order to absorb a significant fraction of the incoming solar spectrum. As a result of these problems, the electricity produced by solar cells is still expensive compared to that produced by fossil fuels [2,3].

Thin-film chalcogen materials, especially $CuInSe_2$ (CIS), $CuInGa(S,Se)_2$ (CIGS) and CdTe, are currently used in the production of large-scale, commercial photovoltaic devices. However, the scarcity of indium and tellurium in the earth's crust limits the future of CIGS- and CdTe-based solar cells. In addition, the price of In and related solar-cell production

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costs will increase in the near future due to the extensive use of indium in display technologies and opto-electronic devices. Another problem with CdTe-based solar cells is that the cadmium (Cd) is very toxic to health and the environment. This problem has led researchers to search for more abundant and greener materials. Because of its similar properties to the CIGS compound, the I_2–II–IV–VI_4 group has been receiving attention as a new-generation absorber material. The Cu_2ZnSnS_4 (CZTS) compound is a good candidate for photovoltaic applications as an absorber layer [4–7]. CZTS has a direct band gap ranging from 1.4 to 1.6 eV which is close to the optimum value required for a single junction solar cell's absorber layer, a high absorption coefficient at the visible solar spectrum wavelengths and a p-type conductivity [8]. However, even though it is a promising absorber material, the studies on CZTS-based solar cells are at an early stage [3]. An efficiency of 9.6% has been reported for CZTS-based solar cells in laboratory conditions [9]. But in view of the fact that the theoretical efficiency of CZTS is about 32.2% [10], more studies are required to increase the efficiency and to develop economical production methods, which would ensure successful commercialization [11]. CZTS thin films have been prepared via various methods such as physical vapor deposition [3,5,7,12–20], electrochemical deposition [2,21–23], sol–gel [24–33] and successive ionic layer adsorption-reaction methods [34–38]. Aqueous solution deposition methods have several advantages, very important one being that a variety of thin films can be grown at low temperatures using cheap manufacturing equipment. The sol–gel method is a very simple and low-cost process based on hydrolysis and poly-condensation reactions. Sulfide films can be directly obtained by sulfurizing oxyhydrate precursors. To date, several groups have reported CZTS thin films produced via the sol–gel method. To the best of our knowledge, the first sol–gel-grown CZTS films were reported by Tanaka et al. [31]. They prepared CZTS films by annealing oxyhydrate precursors in a N_2+H_2S toxic gas atmosphere. Yeh et al. [32] prepared CZTS films by using metal chlorides with thiourea and investigated the effects of annealing between 160 and 320 °C in air. Fischereder et al. [29] deposited CZTS films on ITO-coated glass substrates by using thioacetamide as a source of sulfur. They studied the influence of vacuum annealing temperatures (180–450 °C) and the concentration of thioacetamide in precursor solutions. Park et al. [31] fabricated CZTS thin films via the sol–gel method and then annealed the samples at temperatures above 500 °C in a N_2 atmosphere without any sulfur source. However it is still necessary to improve the quality of sol–gel-processed CZTS films and to find non-toxic ways to tolerate sulfur loss during annealing. In our study, we prepared high-quality, dense CZTS thin films on quartz-glass substrates using the sol–gel spin-coating method. To tolerate sulfur loss during annealing, the annealing process was carried out in a vacuumed quartz tube containing elemental sulfur which is a non-toxic material. We investigated the effects of sulfurization temperature on the structural, morphological, compositional and optical properties of the films.

2. Experimental

The CZTS precursor solution was prepared by dissolving copper (II) acetate monohydrate (0.3 M, 98+%), zinc (II) acetate dihydrate (0.3 M, 99.99%), tin (II) chloride (0.3 M, 98%) from Sigma Aldrich and thiourea (1.2 M, 99.0+% from Sigma Aldrich) into 2-methoxyethanol (20 ml, 99.8% from Sigma Aldrich). The final solution was stirred at 45 °C, 850 rpm for 1 h to dissolve the metal compounds completely. During stirring, 2 ml of diethanolamine (DEA) was dropped slowly into the solution as a stabilizer. A quartz glass slide was used as a substrate which was ultrasonically cleaned in turn with detergent, nitric acid (1:4), acetone and ethanol for 10 min.

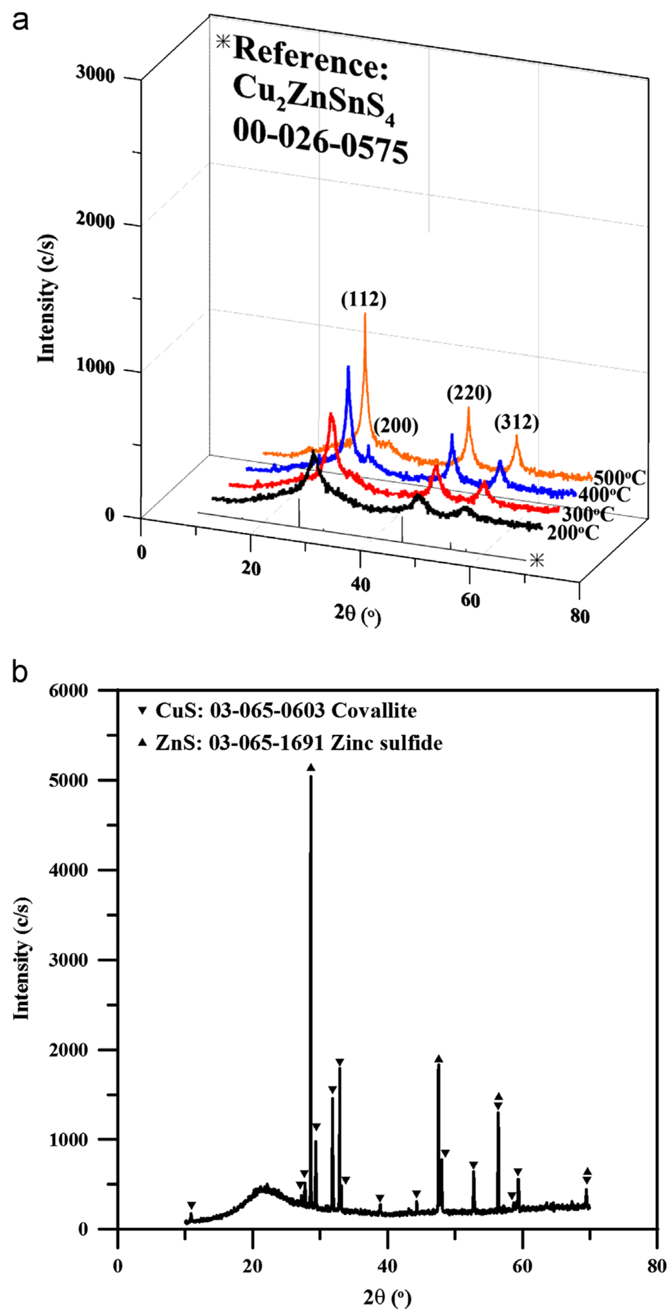

Fig. 1. XRD patterns of the CZTS samples sulfurized at (a) 200 °C, 300 °C, 400 °C and 500 °C and (b) 700 °C.

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