



High open-circuit voltage of ternary Cu_2GeS_3 thin film solar cells from combustion synthesized Cu-Ge alloy



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ABSTRACT

Ternary chalcogenide semiconductor copper germanium sulfide (Cu_2GeS_3) composed of earth-abundant and non-toxic elements is considered to be a suitable light harvesting material for photovoltaics. In this study, Cu_2GeS_3 thin film solar cells are creatively fabricated based on combustion method. XRD and Raman analyses reveal that the combustion synthesized product is composed of Cu-Ge alloy rather than metal oxides. The structural, morphological, optical and electrical properties of CGS films are analyzed in detail. The best power conversion efficiency of Cu_2GeS_3 thin film solar cell achieve 2.67% with a high open-circuit voltage of 592 mV. The experiment results reveal that the p-type semiconductor Cu_2GeS_3 is an extremely promising light harvesting material for photovoltaics due to its suitable band gap and carrier concentration.

1. Introduction

With the decrease of fossil energy and the aggravation of environmental pollution, utilizing clean solar power via photovoltaic (PV) devices is of great realistic significance for social sustainable development. During recent years, the non-toxic quaternary compound $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) has received increasing attention as a promising light absorption material for thin film solar cells due to its large optical absorption coefficient of above 10^4 cm^{-1} and suitable band gap of 1.5 eV [1,2]. The record efficiency of 12.6% was reported by Wang et al. using mixed $\text{Cu}_2\text{ZnSn(S, Se)}_4$ absorber layer through hydrazine-based solution method [3]. According to the first principle calculation, however, the stable chemical potential range for forming pure CZTS phase is so narrow, easily leading to the formation of many undesired secondary phases such as CuS, ZnS, Cu_2SnS_3 and SnS_2 [4]. Besides, as the number of elements increases, composition control of the compound is still challenging. So searching for new absorber material with simpler composition has important significance in large-scale application of low-cost and non-toxic thin film solar cells.

Recent advancements in absorber layer alternatives turns to ternary system like Cu-Sb-S [5,6] and Cu-Sn-S [7,8] since it has less number of elements that are nontoxic and earth-abundant. Among them, the ternary semiconductor Cu_2SnS_3 (CTS), which was formed as a secondary phase during CZTS deposition, was most thoroughly studied by various methods including spray pyrolysis [9], liquid coating [10], pulsed laser deposition [7], magnetron sputtering [11] and electro-

deposition [12]. It has been reported that CTS has a direct band gap energy of 0.95–1.15 eV depending on the crystal structure and absorption coefficient greater than 10^4 cm^{-1} [13]. To date, the highest efficiency of CTS solar cell achieved 4.63% by sequential evaporation method [14]. However, as the research move along [15], several issues regarding narrow band gap value, higher carrier concentration and low mobility of CTS became the major obstacles to further enhance cell performance. As far as we know, all the reported solar cells based on CTS generally have a low open circuit voltage smaller than 300 mV.

More recently, modifying the electronic properties of CTS by Ge (same family as Sn) doping was confirmed to be an effective way to improve those issues, which can not only widen the band gap [13], but also reduce the carrier concentration [16]. What's more, Araki et al. found that the pure Cu_2GeS_3 (CGS) also showed favorable optical properties with band gap value of around 1.5 eV and achieved a preliminary conversion efficiency of 1.7% [17]. However, little is understood about the electrical properties of CGS, further investigation is needed to improve the device performance. Previously, we have fabricated a 1.6% CZTS thin film solar cell by combustion method [18] which is an extremely powerful tool to synthesize various composites (usually in the form of mixed metal oxides) using the corresponding metal salts-fuel mixtures. In addition, homogeneous mixtures with several components at atomic level can be achieved in precursor solution. Compared with other fabrication technologies, combustion method shows several significant advantages for application on thin film solar cells including: (1) Easy and precise control of composition

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by only changing the starting materials; (2) Good universality for Cu-based ternary and quaternary chalcogenides (e.g. $\text{Cu}_2\text{X}^{\text{IV}}\text{S}_3$ and $\text{Cu}_2\text{M}^{\text{II}}\text{X}^{\text{IV}}\text{S}_4$, $\text{M}^{\text{II}}=\text{Mn, Fe, Co, Ni, Cd, Hg}$; $\text{X}^{\text{IV}}=\text{Si, Ge, Sn}$); (3) Homogeneous distribution of chemical elements in precursor films; (4) Low production cost for large-scale application. In this study, the combustion method is introduced to fabricate Cu_2GeS_3 thin film solar cells. The precursor films were deposited on Mo-coated glass substrate by doctor blade method which is a low-cost and non-vacuum process that suitable for mass production. The structural, morphological, optical and electrical properties of CGS were investigated in detail. The experiment results reveal that the p-type semiconductor Cu_2GeS_3 is an extremely promising light harvesting material for photovoltaics due to its suitable band gap and carrier concentration, comparable to that of CZTS but having simpler composition. What's more, our study proves for the first time that ternary Cu-based solar cell can also achieve a high open circuit voltage of nearly 600 mV.

2. Experimental

2.1. Preparation of Cu_2GeS_3 thin films by combustion method

All the chemical reagents used in the experiment were of analytic grade without any further purification. Fig. 1 shows the schematic of fabricating Cu_2GeS_3 thin films by combustion method. 6 g $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (purity > 99.5%) and 13 g citric acid (CA, fuel) were first dissolved into 40 mL deionized water. In order to ensure sufficient oxidizer for combustion, 25 mL HNO_3 was added to compensate NO_3^- . Then under constant stirring, 1.52 g GeO_2 (purity > 99.9%) was added. All the species were totally dissolved when the pH value achieved 7 by adding ammonia and a blue transparent solution eventually formed. The obtained metal salt solution continued to be stirred for 2 h and then transferred to a heated evaporating dish. When sufficient water was evaporated, the solution converted into gel with large amounts of foam and the color changed from blue to brown. Finally, self-propagating combustion happened along with releasing of massive amounts of heat, yielding a red product. It should be noted that the entire process has no visible flames and just lasted for about 10 s. To fabricate available precursor films, the as-prepared powder was dissolved into ethanol solvent after grinding and stirred for three weeks. The precursor film was deposited on Mo-coated glass by doctor blade method. The subsequent sulfurization process was carried out in a two heating zone tube furnace of which the precursor film and sulfur powder were placed at the two ends.

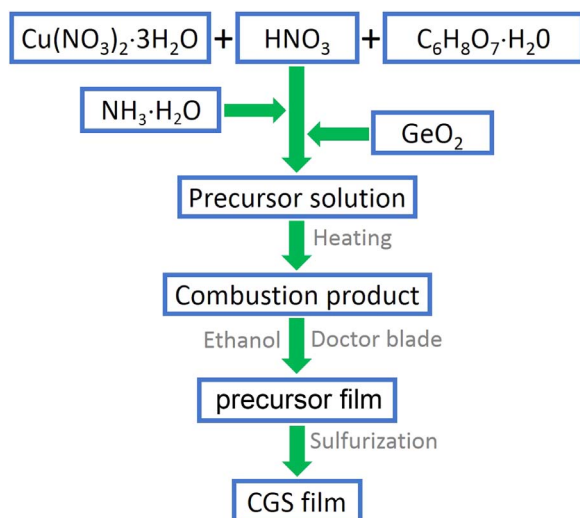


Fig. 1. Schematic of fabricating Cu_2GeS_3 thin films by combustion method. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

2.2. Solar cell structure

Solar cell devices with structure Al/AZO/ZnO/CdS/CGS/Mo/SLG substrate without any anti-reflection layer were prepared. The CdS buffer layer (~50 nm) was deposited using chemical bath deposition (CBD) method, which was carried out in an open system containing 25 mL CdSO_4 (15 mM) and 12.5 mL thiourea (1.5 M) at 65 °C. The pH of the solution was adjusted to 10 by adding 32.6 mL $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25%). After 15 min the samples were removed from the solution, rinsed with deionized water and dried with nitrogen gas. The 50 nm i-ZnO window layer was deposited by rf sputtering (50 W, 10 min) under mixed atmosphere of Ar (60 sccm) and O_2 (6 sccm), followed by depositing 350 nm Al-doped ZnO (AZO) transparent conducting layer (150 W, 40 min) under Ar atmosphere (60 sccm). The top Al metal electrode (~800 nm) was deposited via thermal evaporation approach under 5×10^{-4} Pa.

2.3. Characterization

The thermal gravimetric and differential thermal analysis (TG-DTA) profiles were recorded by a thermal analyzer (Shimadzu DTG-60H) with a heating rate of 5 °C min^{-1} under continuous-flow of air atmosphere. The crystal structure characterization of precursor and CGS thin films was conducted using X-ray diffractometer (XRD, D/Max-rA) with Cu-K α radiation ($\lambda=1.5406$ Å). The X-ray photoelectron spectroscopy (XPS) spectra were carried out on thermo ESCALAB 250 spectrometer. The Raman spectra of CGS films were performed at room temperature using a LABRAM-HR micro-Raman system in the back scattering configuration with laser sources of 514 nm. The surface morphology and elemental composition were determined by field emission SEM (FE-SEM Sirion 200) equipped with an energy dispersive spectrometer (EDS). The optical absorption spectrum was recorded on a UV-vis-365-type spectrophotometer in range of 200–1600 nm. The electrical properties were characterized by Hall effect measurement (Vander Paw configuration) operated at room temperature. The current density-voltage (J-V) characterization was carried out using a Keithley 2400 source measurement unit under simulated AM 1.5 irradiation (100 mW cm^{-2}) with a standard xenon-lamp-based solar simulator (Oriel Sol 3A). External quantum efficiency (EQE) was carried out with an ORIEL Intelligent Quantum Efficiency 200 Measurement system established with the tunable light source.

3. Results and discussion

Dried gel was obtained by heating the precursor solution at 110 °C for two days. Fig. 2 shows the thermal gravimetric and differential thermal analysis (TG-DTA) profiles of the dried gel. In order to accurately record the reaction temperature, the gel was heated up with a slow rate of 5 °C min^{-1} in air atmosphere. At low temperature region,

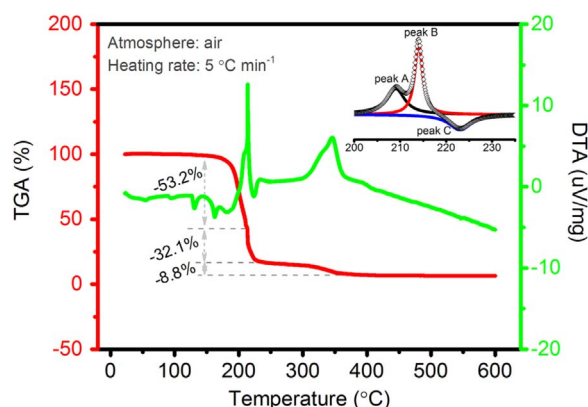


Fig. 2. TG-DTA curve of dried gel in air atmosphere.

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