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One–step synthesis of Cu_3BiS_3 thin films by a dimethyl sulfoxide (DMSO)–based solution coating process for solar cell application

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ABSTRACT

A large–grain and highly crystalline Cu_3BiS_3 thin film is successfully prepared by a dimethyl sulfoxide (DMSO)–based solution coating process. Without involving post sulfurization, Cu_3BiS_3 absorber with grain size of ~ 1 μm has been achieved via a short-time drying of spin–coated precursor film on a hot plate at relatively low temperatures (< 300 °C). Our Cu_3BiS_3 film exhibits a direct band gap of 1.47 eV with high absorption coefficients (~ 7×10^4 cm^{-1}). Hall effect measurements reveal a p–type conductivity with hole concentration of ~ 10^{16} cm^{-3} and mobility of 52.83 $cm^2/(V\,s)$. Moreover, an initial Cu_3BiS_3 thin film solar cell with the device structure of glass/Mo/Cu_3BiS_3/CdS/ZnO/ITO/Al is fabricated, achieving a definite conversion efficiency of 0.17%. The mild preparation condition promises great potential of current method in realizing Cu_3BiS_3 solar cells on temperature-sensitive substrates such as flexible polymer through an energy efficient way. The Cu_3BiS_3 has thus been presented as a promising absorber material for solar cell applications.

1. Introduction

As competitive alternatives to silicon–based photovoltaic technologies, copper indium gallium selenide (CIGS) and cadmium telluride (CdTe) based thin film solar cells have already demonstrated considerable conversion efficiencies (> 22%) [1]. Nevertheless, the growing production capacity towards the terawatt level requires developing low–toxicity, earth–abundant, and cost–effective absorber materials, which is restricted by the toxicity of Cd and the scarcity of In and Te raw materials [2,3].

Cu_3BiS_3 (wittichenite), a relatively less explored ternary I–V–VI chalcogenide, has been proposed as an potential absorber material for photovoltaics [4]. The reported direct optical band gap in the range of 1.4–1.5 eV is close to the optimum value for efficient solar energy conversion [5]. A high optical absorption coefficient ($\alpha > 10^4$ cm^{-1}) enables the sufficient light absorption within a thin absorber layer [6]. Furthermore, bismuth (Bi) is low–toxic and has been employed in areas where toxicity is a concern, including in pharmaceuticals and as a replacement for lead in solders and ammunition [7]. Compared to Te and In, Bi is also readily available and relatively cheap. The current global reserve of bismuth listed in the US Geological Survey is over 330,000 metric tons, while 21,000 metric tons for tellurium and merely 2500 metric tons for Indium [8]. With promising characteristics, Cu_3BiS_3 thin films have been tentatively prepared by various techniques, including reactive sputtering [9], solid state reaction [10], co–evaporation [11], chemical bath deposition [12], electro–deposition [13], and hot injection [14]. Unfortunately, even a prototype cell with convincing conversion efficiency has not been demonstrated so far. Besides, the solution processing method has already been proved particularly suitable for high–throughput, low–cost deposition of chalcogenide thin films onto the desired substrates. In fact, solution process would be more effective in controlling the Cu/Bi ratio by simply applying appropriate amounts of Cu/Bi chemicals in the precursor, which is quite critical for the pure–phase formation of ternary compound [15]. To our knowledge, however, a facile, low–toxic, and versatile solution approach to fabricate high–quality Cu_3BiS_3 thin film has not been reported yet.

This work illustrates the successful preparation of high–quality Cu_3BiS_3 thin film by the one–step and environmentally friendly DMSO–based solution method without involving high–temperature annealing and post sulfurization processes. The compositional, structural, optical, and electrical properties of Cu_3BiS_3 films were systematically studied. More importantly, a Cu_3BiS_3 solar cell device with definite conversion efficiency was demonstrated for the first time. The results confirm the extraordinary promise of Cu_3BiS_3 as an absorber material for thin film solar cell applications.

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2. Experimental

2.1. Materials

Cuprous chloride (CuCl, 97%), bismuth chloride ($BiCl_3$, AR), thiourea (Tu, ≧ 99%), and dimethyl sulfoxide (DMSO, > 99%) were obtained from Aladdin Industrial Corporation. All chemicals were of analytical grade and were used without further purification.

2.2. Preparation of Cu_3BiS_3 precursor solution

Cuprous chloride (CuCl), bismuth chloride ($BiCl_3$), and thiourea (Tu) were used as the source chemicals for the precursor solutions. Thiourea (Tu), which is a versatile metal–ion complexing agent, was used as both the source of sulfur and the stabilizer of Cu_3BiS_3 precursor solutions. Typically, 0.99 g CuCl and excess thiourea were dissolved in 5 mL DMSO to prepare the Cu–Tu stock solution. Analogously, 1.05 g $BiCl_3$ and excess Tu were dissolved in 5 mL DMSO to produce a clear yellow Bi–Tu solution. The final precursor solution was prepared by mixing the Cu–Tu and Bi–Tu stock solution together, yielding a clear yellow solution with proper viscosity. Excess thiourea was utilized to guarantee both the sufficient supply of sulfur during the drying–induced sulfurization reaction and the complete coordination with cuprous and bismuth metal ions as the form of metal–thiourea complexes to avoid the precipitation of metallic sulfides and hydroxides [16]. The precursor solution was then stirred for at least 4 h before being used for thin film deposition.

2.3. Films deposition and device fabrication

Fig. 1 depicts the fabrication procedure of Cu_3BiS_3 films, involving only a simple drying step. After being spin–coated onto 2 × 2 cm^2 molybdenum–coated soda–lime glass substrates at 3000 rpm for 30 s, the precursor films were dried on a hot plate at 240, 260, 280, 300 and 340 °C for 2 min in nitrogen atmosphere. Repeating above process cycle another 10 times resulted in an absorber film with the final thicknesses of about 1 μm. No additional sulfurization and/or high–temperature annealing are required. Subsequently, Cu_3BiS_3 films produced with the optimal conditions were utilized to fabricate a solar cell device. A CdS buffer layer was deposited onto Cu_3BiS_3 film by a typical chemical bath deposition method [17], which was followed with the bilayer construction of intrinsic ZnO and ITO by RF and DC magnetron sputtering, respectively. Thermal evaporation was then used to deposit Al grid electrodes on top of the ITO layer to form top contact fingers through a shadow mask. After the device fabrication, it was mechanically scribed to define a total device area of 0.11 cm^2.

2.4. Materials and device characterization

The precursor powder, which was obtained from drying the precursor solution at 90 °C, was characterized by thermal gravimetric analysis (TGA, NETZSCH STA449C, ramp rate 10 °C/min, N_2 flowing environment). The Cu_3BiS_3 thin films prepared on molybdenum–coated soda–lime glass were characterized by field–emission scanning electron microscope (FE–SEM, JSM–6701), energy dispersive spectroscopy (EDS, JSM–6701F field–emission scanning electron microscope), and X–ray diffraction (XRD, PANalytical EMPYREAN X–ray diffractometer with Cu Kα radiation, λ = 0.154 nm). The Cu_3BiS_3 thin films prepared on soda–lime glass were characterized by X–ray photoelectron spectroscopy (XPS, PHI–5702), UV–vis absorption spectra (Shimadzu UV–2600 spectrometer) and Hall effect measurement (Ecopia HMS–3000). Current density–voltage (*J–V*) characterization of the solar cell was performed under AM 1.5G illumination using a Newport solar simulator and KEITHLEY 4200SCS.

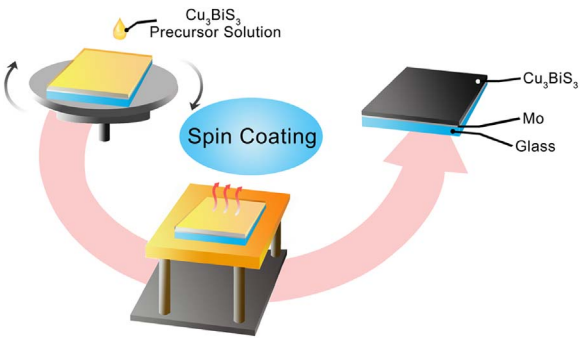

Fig. 1. Schematic illustration for the fabrication of Cu_3BiS_3 thin films.

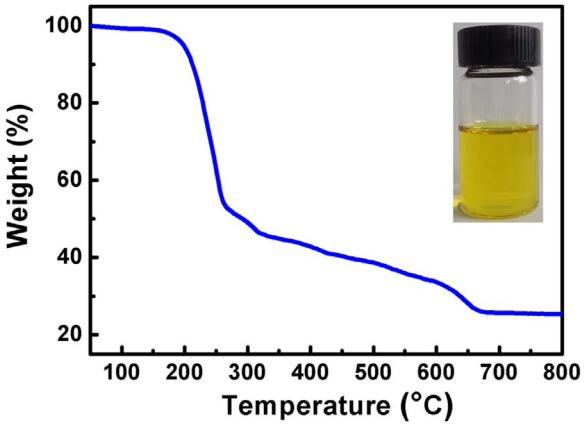

Fig. 2. TGA curve of the precursor powder from drying the solution at 90 °C for several days to evaporate most solvent. The inset shows the Cu_3BiS_3 precursor solution obtained by dissolving metal salts and thiourea in DMSO.

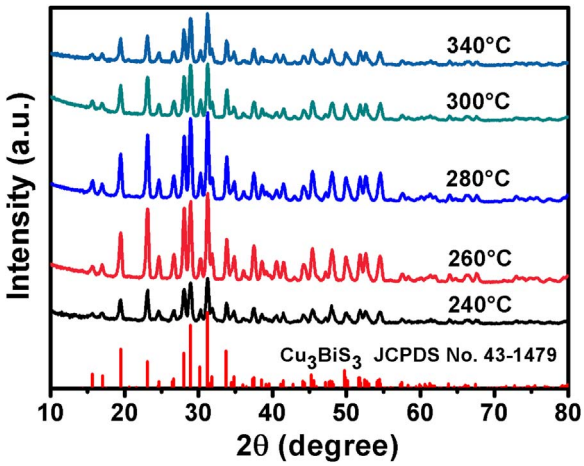

Fig. 3. XRD patterns of the as–prepared Cu_3BiS_3 films being dried at 240, 260, 280, 300 and 340 °C. Reference diffraction peaks of orthorhombic Cu_3BiS_3 (JCPDS NO. 43-1479) are displayed at the bottom.

3. Results and discussion

Thermogravimetric analysis (TGA) of the precursor powder was performed in a N_2 atmosphere to determine the optimum drying conditions. As shown in Fig. 2, the weight loss starts from about 180 °C, which corresponds to the boiling point of DMSO. The sharp 45% weight loss over the range of 189–260 °C is attributed to the volatilization of residual DMSO and the thermal decomposition of excess thiourea. The following weight loss with a relatively moderate rate from 260 to 320 °C is caused by the thermal decomposition of metal–thiourea complexes and the formation of Cu_3BiS_3 phase. Metal–thiourea