Research Article

Preparation of $\text{Cu}_2\text{Sn}_3\text{S}_7$ Thin-Film Using a Three-Step Bake-Sulfurization-Sintering Process and Film Characterization

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$\text{Cu}_2\text{Sn}_3\text{S}_7$ (CTS) can be used as the light absorbing layer for thin-film solar cells due to its good optical properties. In this research, the powder, baking, sulfur, and sintering (PBSS) process was used instead of vacuum sputtering or electrochemical preparation to form CTS. During sintering, Cu and Sn powders mixed in stoichiometric ratio were coated to form the thin-film precursor. It was sulfurized in a sulfur atmosphere to form CTS. The CTS film metallurgy mechanism was investigated. After sintering at 500°C , the thin film formed the $\text{Cu}_2\text{Sn}_3\text{S}_7$ phase and no impurity phase, improving its energy band gap. The interface of CTS film is continuous and the formation of intermetallic compound layer can increase the carrier concentration and mobility. Therefore, PBSS process prepared CTS can potentially be used as a solar cell absorption layer.

1. Introduction

For thin-film solar cells, copper indium gallium selenide (CIGS) materials are expensive, and thus copper zinc tin sulfide (CZTS) materials have been developed [1, 2]. Studies [3, 4] have shown that it is difficult to control the Cu, Zn, Sn, and S atomic ratio of the four-element CZTS system. For upper ZnS junction solar modules, interactions during the crystallization process cause Zn atoms to easily diffuse into the CZTS system (insufficient or excess Zn). The present study uses the Cu, Sn, and S (CTS) ternary system, mainly formed by colloidal baking and powder sintering, as a light absorbing layer material [5, 6].

Studies have reported that CuS and SnS_2 coevaporation [7, 8] and sputtering [9] can be used to form CTS ternary films whose energy band gap is close to the ideal energy band gap of $\text{Cu}_2\text{Sn}_3\text{S}_7$ (1.2~1.3 eV). However, this process is easy to produce much secondary degradation like $\text{Cu}_{10}\text{Sn}_2\text{S}_{13}$ and Cu_4SnS_4 of nature, reducing the energy conversion efficiency. This study coated Cu and Sn powders at a set atomic percentage mix on a Mo substrate with spin-coater and formed powder film. Baking, sulfurizing (sulfur vapor), and liquid-phase sintering were then applied to form

the Cu-Sn-S compound and a crystalline thin film. The powder, baking, sulfur, and sintering (PBSS) process can reduce the solar film process (sputtering and deposition) costs [10] and avoid the reliability problems of chemical solutions such as forming oxide phase and atomic ratio control problem [11].

Comparing with other literatures processes [12, 13], PBSS process has potential applications due to its easy fabrication, lower cost, and easy-controlling atomic ratio procedure. In addition, no previous studies have been conducted on CTS/Mo metallurgy and the interfacial diffusion mechanism. This research determines the CTS crystalline phase and optical and electrical properties. The PBSS process was adopted according to temperature effects. The interface diffusion behavior of atoms between absorption layer and Mo substrate was explored to understand relationship between structure and optoelectric properties. The results may be used as a reference for solar cell manufacturing.

2. Experimental Procedure

Cu (~500 nm) and Sn (~1000 nm) powders were mixed in a 2 : 3 molar ratio in colloid and deposited onto Mo substrates with spin coater (3000 rpm). Cu-Sn prefilms were obtained

FIGURE 1: Schematic procedure of CTS film.

FIGURE 2: Morphology of CTS films sintered at (a) 200, (b) 300, (c) 400, (d) 500, (e) 600, and (f) 700°C.

by vacuum baking (200°C, 10^{-2} Torr, 8 h). Subsequently, the films were subjected to sulfur vapor in an oven (240°C, 1 h) and followed by different sintering temperatures at 300, 400, 500, 600, and 700°C (4 h for each) to form CTS film in vacuum process. All the procedure is schematically shown in Figure 1.

The specimens were observed using scanning electron microscopy (SEM, Hitachi SU8000), energy-dispersive X-ray spectroscopy (EDS), and atomic-scale surface topography. X-ray diffraction (XRD, Bruker AXS, Germany) was conducted at a scanning rate of $1^\circ/\text{min}$ in the 2θ range of 20° – 60° to determine phase composition. A photoluminescence-

FIGURE 3: XRD patterns of CTS sintered at (a) 200, (b) 300, (c) 400, (d) 500, (e) 600, and (f) 700°C.

(PL-) ultraviolet (UV) spectrometer (ULVAC) was used to determine the sintering temperatures and the absorption layer specifications. Hall measurements were conducted for samples sintered at 200, 500, and 600°C to determine the resistance value and carrier mobility. The interfacial diffusion behavior study of samples sintered at 500°C was chosen because the sample had flattening surface and less second phases. It possessed the best morphology and phase composition. The sample sintered at 500°C was observed by transmission electron microscopy (TEM, JEM-2100F). The interface structure characteristics caused by atoms diffusion between absorption layer and Mo substrate are discussed by the atomic and structure change between CTS and Mo.

3. Results and Discussion

In the PBSS process (vulcanization condition), for sintering temperatures of 200°C to 400°C, the specimen surface was coarse and Sn particles had not completely melted. The particle size was approximately 3–5 μm (Figure 2). When the sintering temperature was increased to 500°C, melting and solidification film were evenly distributed on the substrate surface. When the temperature was 600°C or 700°C, the surface of the sample had sheet-like deposition on CTS film surface which was regarded as CuS precipitates. The XRD patterns (Figure 3) for samples sintered at between 200°C and 400°C show that CuS and $\text{Cu}_{10}\text{Sn}_2\text{S}_{13}$ formed, without the $\text{Cu}_2\text{Sn}_3\text{S}_7$ phase. At 500°C, $\text{Cu}_2\text{Sn}_3\text{S}_7$ began to become the main phase. At 600°C or 700°C, most of the CuS transformed into a liquid phase that coagulated and precipitated on the surface. The XRD patterns show multiple CuS diffraction peaks. The phases of specimens sintered at various temperatures identified from XRD patterns are shown in Table 1. The films are divided into three broad categories: (I), (II), and (III), corresponding to the experiment in the choice of 200, 500, and 600°C specimens. The chosen specimen with best optical properties is regarded as ideal sintering condition for CTS. And it will be taken in interface characteristics discussion.

In the analysis of spectral absorption and excitation properties of Cn-Sn-S materials, the conversion results of UV spectrometer measurements are shown in Figure 4. The specimens sintered at 200, 500, and 600°C have energy band gaps of about 3.77, 1.25, and 2.08 eV, respectively. The energy band gap of the specimen sintered at 500°C is close to the ideal range of a solar absorption layer (1.3–1.5 eV). To determine the absorption of various wavelengths of light, PL measurements (Figure 5) were taken. The PL spectra show three absorption peaks. The specimens sintered at 200, 500, and 600°C have absorption peaks at a short wavelength (607.1 nm) near a clear continuous peak region, a long wavelength (859.0 nm) near the infrared region, and short wavelengths (577.1 and 611.5 nm) and a long wavelength (871.7 nm), respectively. From the phase composition (Table 1), the $\text{Cu}_{10}\text{Sn}_2\text{S}_{13}$ and CuS phases contributed to the short wavelength absorption waves. The long wavelength absorption is contributed by $\text{Cu}_2\text{Sn}_3\text{S}_7$. Overall, the UV and

FIGURE 4: CTS band gap of 200, 500, and 600°C sintering temperatures.

TABLE 1: Phase composition of samples sintered at various temperatures.

	(I)			(II)		(III)	
	200°C	300°C	400°C	500°C	600°C	700°C	
$\text{Cu}_2\text{Sn}_3\text{S}_7$				○	○	○	
SnO_2	○	○	○	○	○	○	
CuS	○	○	○		○	○	
Cu_4SnS_4	○	○	○	○			
$\text{Cu}_{10}\text{Sn}_2\text{S}_{13}$	○	○	○	○	○	○	

PL spectra show similar trends, confirming that the specimen sintered at 500°C possesses an ideal band gap.

In addition to the light absorption characteristics, the characteristics of the absorption layer and substrate interface affect the material conversion efficiency. Figure 6 shows TEM image and selected area electron diffraction (SAED) pattern of the specimen sintered at 500°C. The structure change of the intermetallic compound (IMC) layer was showing at the interface that the SAED pattern changed from (b) and (c) Morich IMC to (d) and (e) CTS layer and from (d) and (e) CTS layer to (f) and (g) Mo layer. At the IMC interface, there is a face centered cubic (FCC) structure (thickness: about 38 nm), the upper CTS is orthorhombic, and the lower Mo substrate has a body centered cubic (BCC) structure. Therefore, we got the whole structure of “CTS/IMC (38 nm)/Mo” by PBSS processes.

Hall measurement values of samples are shown in Table 2. The average thickness of the CTS films was approximately 50 μm . Each specimen was measured by four probes on sample surface corners. The formula $[\rho = R_s \times T = [\text{C.F.} \times (V/I)] \times T]$ was used to calculate bulk resistivity, where ρ is resistivity ($\mu\omega\text{-cm}$); R_s is sheet resistance (ω); T is thickness (cm); C.F. is correction factor (=4.532); V is voltage; I is current.

FIGURE 5: PL characteristics of specimens. (a) 200°C and visible light, (b) 200°C and infrared, (c) 500°C and visible light, (d) 500°C and infrared, (e) 600°C and visible light, and (f) 600°C and infrared.

TABLE 2: Hall 4-point measurements of CTS after sintering at various temperatures.

CTS	200°C	500°C	600°C
Bulk resistivity (Ohm·cm)	3.3899×10^{-2}	1.6038×10^{-1}	1.8678
Sheet resistivity (Ohm·Sq.)	3.3899	1.6038×10	1.8678×10^2
Bulk carrier concentration (cm^{-3})	2.6494×10^{20}	2.1088×10^{17}	9.7608×10^{15}
Sheet carrier concentration (cm^{-2})	2.6494×10^{18}	2.1088×10^{15}	9.7608×10^{13}
Mobility (cm^2/Vs)	6.9590×10^{-1}	1.8479×10^2	3.4282×10^2
Conductivity	P-type	P-type	P-type

(a)

(b)

(c)

(d)

(e)

(f)

(g)

FIGURE 6: TEM morphology and SAED patterns of CTS sintered at 500°C. (a) Morphology of CTS-Mo interface and SAED patterns, (b) and (c) Mo-rich IMC, (d) and (e) CTS layer, and (f) and (g) Mo layer.

The sample sintered at 200°C has the lowest carrier mobility. With increasing sintering temperature, the carrier mobility significantly increases. The ideal migration rate is $10^1 \sim 10^2 \text{ cm}^2/\text{Vs}$ [14]. The specimen sintered at 600°C has a lower carrier concentration than that of the specimen sintered at 500°C and the highest resistance value mainly due to the formation of CuS. Therefore, CuS not only affected light absorption, but also affected carrier concentration and resistance. It could be presumed that the specimen sintered at 500°C melted evenly and contained more $\text{Cu}_2\text{Sn}_3\text{S}_7$ phase than the other sintering conditions. Also, the CTS/IMC (38 nm)/Mo structure improves carrier mobility which can be found that 500°C and 600°C specimens were both better than 200°C specimen.

4. Conclusion

CTS material was obtained by the PBSS process. For a given sulfurizing condition, sintering at 500°C led to surface melting and formation of $\text{Cu}_2\text{Sn}_3\text{S}_7$ possesses positive benefits in spectral absorption and electrical properties. When temperatures are too high, forming sheet specimen surface structure (CuS) deteriorates characteristics. Thus, an appropriate sintering temperature is needed for absorption layer preparation. From the study, the 500°C temperature possessed the best morphology and optoelectric properties which is ideal for further research.

The PBSS process is continuous formation at the absorption layer and substrate interface. The cross-section structure is CTS/IMC/Mo. The crystal structure of the IMC layer is rich-Mo and has a face centered cubic arrangement (nonvoid doped). This interface mechanism is dominated by Cu and Sn thermal diffusion and leads to improvements in optoelectric properties.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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