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Research Article

Effects of Sulfurization Temperature on Properties of CZTS Films by Vacuum Evaporation and Sulfurization Method

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Copper zinc tin sulfur (CZTS) thin films have been extensively studied in recent years for their advantages of low cost, high absorption coefficient ($\geq 10^4$ cm^{-1}), appropriate band gap (~1.5 eV), and nontoxicity. CZTS thin films are promising materials of solar cells like copper indium gallium selenide (CIGS). In this work, CZTS thin films were prepared on glass substrates by vacuum evaporation and sulfurization method. Sn/Cu/ZnS (CZT) precursors were deposited by thermal evaporation and then sulfurized in N_2 + H_2S atmosphere at temperatures of 360–560°C to produce polycrystalline CZTS thin films. It is found that there are some impurity phases in the thin films with the sulfurization temperature less than 500°C, and the crystallite size of CZTS is quite small. With the further increase of the sulfurization temperature, the obtained thin films exhibit preferred (112) orientation with larger crystallite size and higher density. When the sulfurization temperature is 500°C, the band gap energy, resistivity, carrier concentration, and mobility of the CZTS thin films are 1.49 eV, 9.37 Ω · cm, 1.714×10^{17} cm^{-3}, and 3.89 cm^2/(V · s), respectively. Therefore, the prepared CZTS thin films are suitable for absorbers of solar cells.

1. Introduction

Cu_2ZnSnS_4 (CZTS) is one of the promising materials for absorbers in thin film solar cells because of its excellent properties for obtaining high efficiency; that is, it has a direct band gap of 1.51 eV, very close to optimum band gap of semiconductor used for photovoltaic conversion, and high absorption coefficient ($\geq 10^4$ cm^{-1}) [1]. At the same time, it has versatile electrical properties which can suitably be tailored and tuned to the specific need in a given device structure [2–5]. Various methods have been reported to fabricate the CZTS thin films including thermal evaporation [6], sputtering [7], pulsed laser deposition [8], electroplating [9], and hydrazine process [10]. The best efficiencies reported for the pure CZTS solar cells so far have been 8.4% using thermal evaporation and sulfurization [11]. In the study, the CZTS thin films were deposited using a 150°C vacuum thermal evaporation process and subsequent short (5 min) high-temperature (570°C) atmospheric pressure annealing. Though the efficiency of the solar cells is high, the annealing temperature is a little high and it does not correspond to the designing rule of solar cells. Therefore, choosing a lower sulfurization temperature to produce CZTS thin films is important.

In our study, we also use thermal evaporation and sulfurization method to produce CZTS thin films. And the effects of the sulfurization temperature on the structural, optical, and electrical properties of the CZTS films are investigated.

2. Experiment Details

We fabricated CZTS thin films on floating glasses substrates by vapor-phase sulfurization of thermal and electron-beam (E-B) evaporated precursors. This process consisted of two stages with the sequential evaporation of precursors followed by the vapor-phase sulfurization. We formed the stacked precursors on the substrates by depositing ZnS layers with E-B evaporation, Cu and Sn layers with thermal evaporation orderly. The thickness of each layer was controlled by a film thickness monitor (FTM) on the evaporation equipment. And the thicknesses of the three layers are shown in Table 1 according to the ratio of the constituents. We sulfurized the precursors in an annealing furnace in the atmosphere

Table 1: The parameters of the CZT precursors.

Precursors	d_{Sn} (nm)	d_{Cu} (nm)	d_{ZnS} (nm)	n_{Zn}/n_{Sn}	$n_{Cu}/(n_{Sn}+n_{Zn})$
CZT	145	120	360	1.70	0.704

Table 2: Samples at different sulfurization temperatures (T_s).

Sample	S11	S12	S13	S14	S15
T_s (°C)	360	400	450	500	560

of $N_2 + H_2S$ (5%) at temperatures of 360°C–560°C for 2 hours. After sulfurization of the precursors, CZTS thin films were formed. The samples obtained at different sulfurization temperatures are listed in Table 2.

The film thickness was measured by a stylus profiler (TENCOR D100). The crystallinity of the CZTS thin films was ascertained by an X-ray diffractometer with Cu Kα radiation (λ = 1.5406 Å). The optical characteristics of the CZTS films were performed by a PerkinElmer Lambda 900 UV/VIS/NIR spectrometer in the wavelength range from 300 nm to 1400 nm at room temperature. The surface morphology was observed by a scanning electron microscope (SEM) (HITACHI S-4800) and an atom force microscope (AFM) (Bruker). A HMS-3000 hall measurement system was used to carry out the carrier concentration, mobility, and resistivity.

3. Results and Discussions

3.1. Structure and Morphology. Figure 1 shows the XRD patterns of the CZTS films obtained at different sulfurization temperatures. For the films sulfurized at 360°C and 400°C, in the XRD patterns, there exist peaks from CZTS (JCPDS-ICDD no. 00-026-0575). However, there are also several peaks from SnS (JCPDS-ICDD no. 01-073-1859) and CuS (JCPDS-ICDD no. 01-075-2233). When the sulfurization temperature is 450°C, the phases of CuS and SnS disappear but there are some XRD peaks from SnS_2 (JCPDS-ICDD no. 00-022-0951) besides those from CZTS. When the sulfurization temperature is about 500°C and 560°C, the peaks from secondary phases disappear, and there are only the XRD peaks of CZTS. The result indicates that the CZTS thin films sulfurized below 500°C are a mixture of CZTS polycrystals with SnS, CuS, and SnS_2 as intermediates, and there is only the CZTS phase with the sulfurization temperature above 500°C. The films have the preferred (112) orientation, and the intensity of peak (112) is increased with the increase of the sulfurization temperature.

The size D_{hkl} of the crystallites is determined from XRD data by the Scherrer formula:

$$D_{hkl} = \frac{K\lambda}{\beta \cos\theta}, \quad (1)$$

where K is a constant, β is full width at half maximum (FWHM) in radians, λ is the wavelength of X-ray, and θ is the Bragg angle [12]. The K, λ values are taken as 0.89, 1.5406 Å for the calculations, respectively.

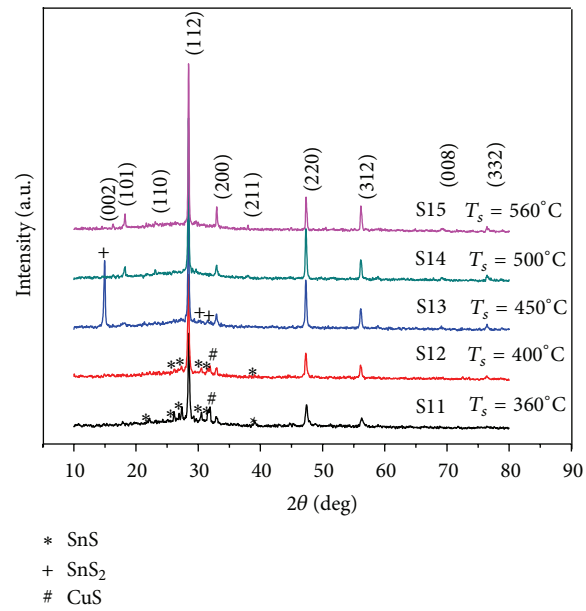

Figure 1: The XRD patterns of the CZTS films obtained at different sulfurization temperatures.

Table 3: The FWHM values and grain sizes of (112) orientation of the CZTS thin films obtained at different sulfurization temperatures.

Sample	S11	S12	S13	S14	S15
T_s (°C)	360	400	450	500	560
FWHM (°)	0.1968	0.1574	0.1378	0.1200	0.1181
Grain size (nm)	39.92	49.91	57.01	65.47	66.52

Table 4: The R_{ms} values of the CZTS thin films obtained at different sulfurization temperatures.

Sample	S11	S12	S13	S14	S15
R_{ms} (nm)	167.2	157.7	116.4	81.0	75.2

Table 3 shows the variation of the grain size from (112) orientation with the sulfurization temperature. With the increase of the sulfurization temperature from 360°C to 560°C, the grain size becomes larger and larger (from 39.92 nm to 66.52 nm).

Figures 2(a)–2(e) show the SEM graphs of the CZTS thin films obtained at different sulfurization temperatures. Figure 2(f) only shows the AFM image of sample S15 for simplification, and Table 4 shows the mean root roughness (Rms) of the CZTS films. We can see that, with the increase of the sulfurization temperature, the grain sizes of the CZTS samples become larger, and the surfaces of the thin films become smoother and denser, which is in agreement with Tables 3 and 4. When the sulfurization temperature is less than 500°C, the CZTS may not be completely synthesized, and thus there are some secondary phases like SnS, SnS_2, and CuS as shown in the XRD patterns. When the temperature is 500°C, the film is the most compact. When the temperature is higher than 500°C, the secondary phases disappear and the grain size of the film becomes larger, as seen in Figure 2(e).

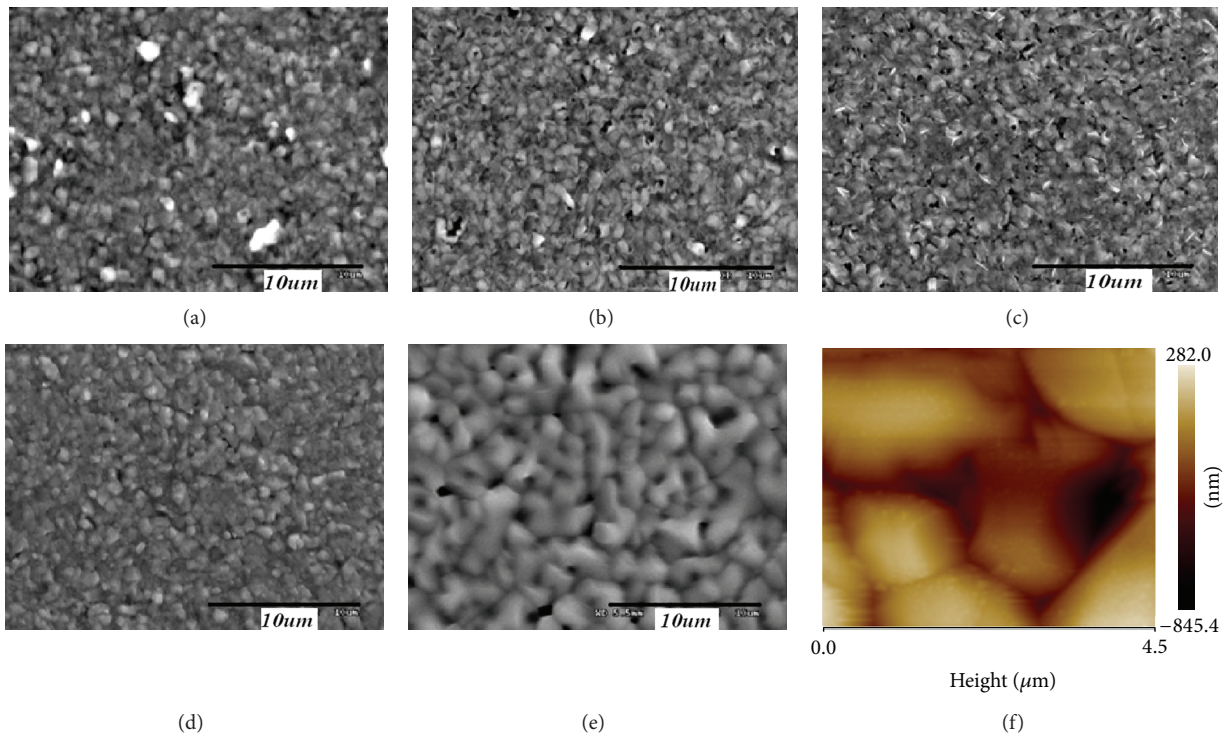

Figure 2: The SEM images of the CZTS thin films samples obtained at different sulfurization temperatures: (a) S11 (360°C), (b) S12 (400°C), (c) S13 (450°C), (d) S14 (500°C), (e) S15 (560°C), and (f) AFM image of sample S15.

Table 5: The values of E_g and α of the CZTS thin films obtained at different sulfurization temperatures.

Sample	T_s (°C)	E_g (eV)	λ_0 (nm)	$\alpha(\lambda_0)$ (cm^{-1})
S11	360	1.38	898.6	3.25×10^4
S12	400	1.40	885.7	4.43×10^4
S13	450	1.45	855.2	2.66×10^4
S14	500	1.49	832.2	2.19×10^4
S15	560	1.57	789.8	1.18×10^4

But there are some voids on the surface of the CZTS thin films. It may be due to the loss of Sn at higher sulfurization temperature (≥500°C) [13]. It is obvious that the sulfurization temperature has some effects on the phase and crystallinity of the CZTS thin films. Therefore, the suitable sulfurization temperature of CZTS films should be no less than 500°C.

3.2. Optical Properties. Figure 3 shows the optical properties of the CZTS thin films obtained at different sulfurization temperatures. And Table 5 shows the values of E_g and α of the CZTS thin films. From Figures 3(a) and 3(b), we can see that, with the decrease of the sulfurization temperature, the transmittance and reflectance of the CZTS films decrease. The reasons may be as follows. One could be due to the surface roughness and the crystallinity. From the SEM graphs and Table 4, it can be seen that, with the decrease of the sulfurization temperature, the surfaces become rougher, resulting in more light scattering. The other one may be due to the secondary phases because the secondary phases are increased with the decrease of the sulfurization temperature. However, most of these compounds have lower energy gap; thus they can absorb light with longer wavelength. Therefore, in the near-infrared waveband, the lower the sulfurization temperature is, the smaller transmittance and reflectance of the CZTS thin films are.

Figure 3(c) shows the absorptance versus the photon energy ($h\nu$) of the CZTS thin films with different sulfurization temperatures. With the decrease of the sulfurization temperature, the absorptance of the samples in the near-infrared waveband increases. The main reason may be due to the existence of the secondary phases. Figure 3(d) shows that the absorption coefficient (α) versus $h\nu$ of the CZTS thin films. From Figure 3(d), we can see that the absorption edge and the stable α are increased with the increase of the sulfurization temperature. Figure 3(e) gives that the energy bandgap (E_g) of the CZTS thin films becomes larger with the increase of the sulfurization temperature; the detailed data are listed in Table 5. Therefore, the temperature has some effects on the crystallinity, phase, and optical properties of the CZTS thin films. When the sulfurization temperature is below 500°C, there are some secondary phases, resulting in the worse crystallinity, rougher surface, and smaller E_g. When the sulfurization temperature is above 500°C, not only the grain size becomes larger, but also the E_g is very close to the optimum bandgap of semiconductor used for photovoltaic conversion.

3.3. Electrical Properties. Figure 4 shows the electrical properties of the CZTS thin films obtained at different sulfurization temperatures. All the films are of p-type conductivity.

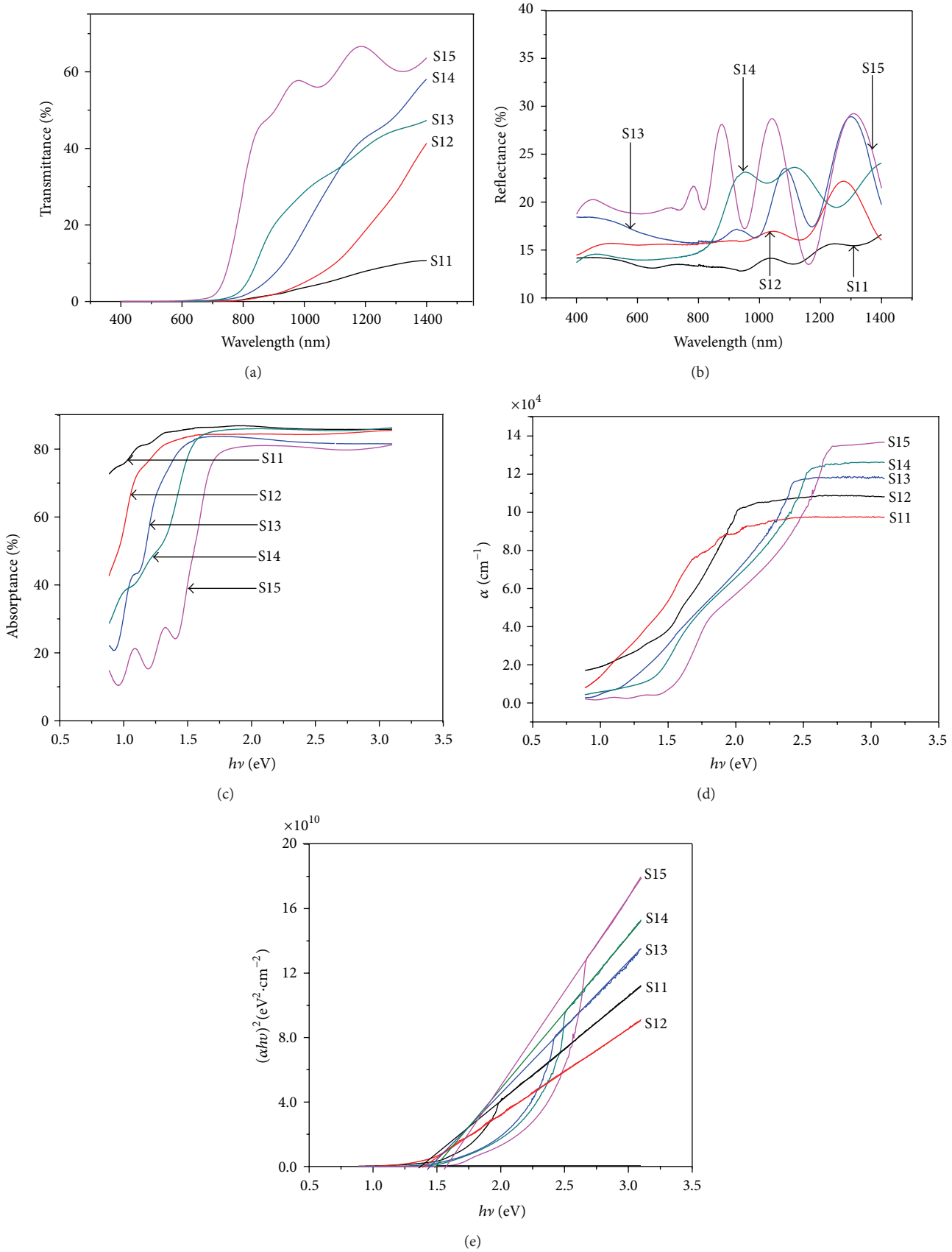

FIGURE 3: The optical properties of the CZTS thin films obtained at different sulfurization temperatures: (a) T, (b) R, (c) absorptance, (d) α, and (e) E_g.

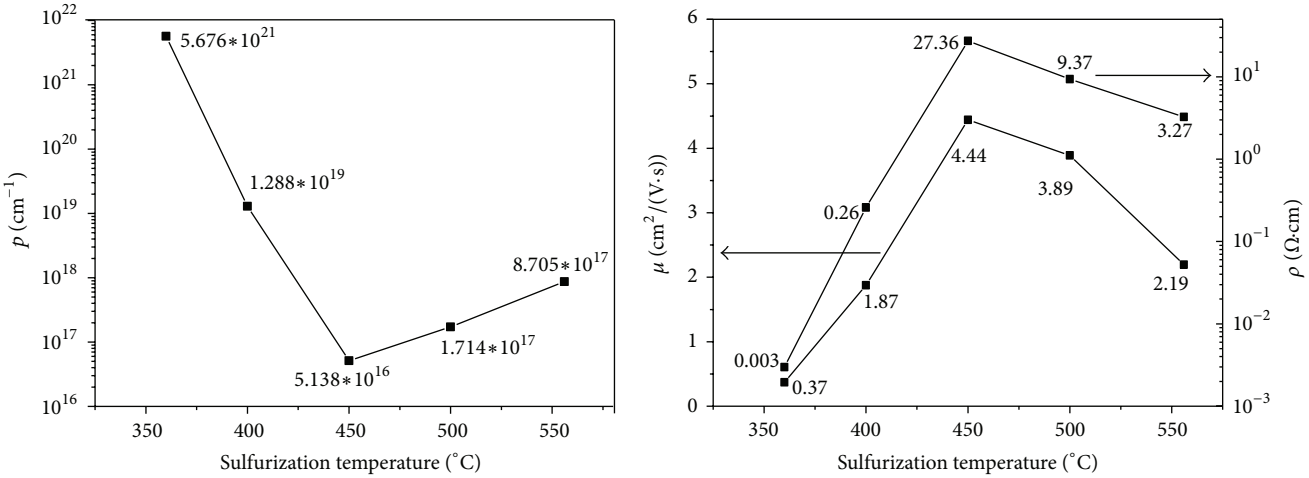

FIGURE 4: The electrical properties of the CZTS thin films obtained at different sulfurization temperatures: (a) carrier concentration (p), (b) mobility (μ) and resistivity (ρ).

With the increase of the sulfurization temperatures, the carrier concentration is decreased firstly and then increased slowly. But the variation tendency of the mobility and the resistivity are opposite to those of the carrier concentration. Because there are still some binary and ternary compounds in the samples under the low sulfurization temperature, these compounds make the carrier concentration increase. At the same time, they would result in the appearance of some defects and grain boundaries, so the mobility is decreased gradually. With the increase of the sulfurization temperature, the mixed phases are declined. When the temperature is 450°C, we can judge the existence of SnS_2 phase according to the XRD patterns. Whereas SnS_2 is a kind of compound with high resistivity, it may result in the highest resistivity (27.36 Ω·cm) and the lowest carrier concentration (5.138×10^{16} cm^{-1}) of the films. With the increase of the sulfurization temperature, Sn and Zn are lost seriously, resulting in the enlargement of $n_{Cu}/(n_{Sn} + n_{Zn})$. Thus, the carrier concentration is increased, and the resistivity is decreased gradually. From the above discussion, we can conclude that the CZTS thin films sulfurized at 500°C have the best electrical properties.

4. Conclusions

The CZTS films were deposited on the glass substrates by thermal and E-B evaporation following sulfurization. With the increase the sulfurization temperature, the crystalline grain size becomes larger, and thereby the crystallinity of the CZTS thin films becomes better. With the increase of the sulfurization temperature, the E_g of the samples is close to the optimum band gap of the semiconductor used for photovoltaic conversion. At the sulfurization temperature of 500°C, the CZTS thin films have the best electrical properties for PV application.

Acknowledgments

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