Research Article

Optical and Electrical Properties of Ag-Doped In_2S_3 Thin Films Prepared by Thermal Evaporation

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Ag-doped In_2S_3 ($\text{In}_2\text{S}_3:\text{Ag}$) thin films have been deposited onto glass substrates by a thermal evaporation method. Ag concentration is varied from 0 at.% to 4.78 at.%. The structural, optical, and electrical properties are characterized using X-ray diffraction (XRD), spectrophotometer, and Hall measurement system, respectively. The XRD analysis confirms the existence of In_2S_3 and AgIn_5S_8 phases. With the increase of the Ag concentration, the band gap of the films is decreased gradually from 2.82 eV to 2.69 eV and the resistivity drastically is decreased from $\sim 10^3$ to $5.478 \times 10^{-2} \Omega\cdot\text{cm}$.

1. Introduction

Indium sulfide (In_2S_3) is a promising semiconductor material for photovoltaic applications. Though solar cells with CdS buffer layers have had the highest efficiency among the chalcogenide solar cells, people are looking for the alternative materials of CdS because of its toxicity. Due to the stability, wide band gap, and little toxicity, In_2S_3 is considered a potential material to replace CdS as the buffer layer of a solar cell. The efficiency of 16.4% was obtained for $\text{CuInGa}(\text{S},\text{Se})_2$ thin film solar cells using ALCVD-deposited In_2S_3 as the buffer layers [1, 2].

Recent studies of In_2S_3 were mostly concentrated on the preparation of the In_2S_3 thin films [3–6]. Only very few works were reported on the doping of the In_2S_3 films to modify their optical and electrical properties. Our group has investigated the band alignment at the $\text{In}_2\text{S}_3/\text{Cu}_2\text{ZnSnS}_4$ heterojunction interface [7]. According to our study, the ΔE_c of the $\text{In}_2\text{S}_3/\text{CZTS}$ heterojunction is calculated to be 0.82 ± 0.1 eV, which is too high for chalcogenide solar cells. The doped In_2S_3 films may have a lower band gap to drop down the ΔE_c of the $\text{In}_2\text{S}_3/\text{CZTS}$ heterojunction. Mathew et al. studied the $\text{In}_2\text{S}_3:\text{Ag}$ films [8]. They concluded that Ag doping could improve the optical and electrical properties of the $\text{In}_2\text{S}_3:\text{Ag}$ films and obtained samples with low resistance of $0.06 \Omega\cdot\text{cm}$ ($1260 \Omega\cdot\text{cm}$ for the undoped sample). But they

didn't investigate the effect of annealing on photoelectrical performance of the $\text{In}_2\text{S}_3:\text{Ag}$ films. However, annealing is crucial for modifying the photoelectrical performance of the doped samples [9]. Mathew also studied the $\text{In}_2\text{S}_3:\text{Sn}$ films [10]. He proved that wider band gap and better conductivity of In_2S_3 could be achieved by Sn doping.

In this work, we deposited $\text{In}_2\text{S}_3:\text{Ag}$ thin films by thermal evaporation in order to analyze the dopant mechanism and investigate the influence of the Ag-doped concentration on the optical and electrical properties.

2. Experiment

Float glasses were used as substrates and cleaned in an ultrasonic bath containing deionized water, acetone, and ethanol, respectively. Ag films and In_2S_3 thin films were successively deposited on the substrates using thermal evaporation technique. The deposition was achieved in a DMDE-450 deposition equipment. The In_2S_3 powder with 99.98% purity and Ag patch with 99.9% purity were used as the source materials and loaded into molybdenum boats, respectively. The chamber pressure during evaporation was $\sim 2 \times 10^{-3}$ Pa. The distance between the source material and the substrate was kept 11.5 cm. All the samples were annealed in Ar at 300°C for 1 hour. The doped concentration was estimated by the weight of the source material. These doped samples

TABLE 1: The optical and electrical properties of the $\text{In}_2\text{S}_3:\text{Ag}$ films deposited with different dopant levels.

Sample	Ag at. %	E_g	Resistivity ($\Omega \cdot \text{cm}$)	Carrier concentration (10^{18} cm^{-3})
IS	0	2.82	~ 1000	$\sim 1.0 \times 10^{-5}$
IS1	0.55	2.77	0.2100	2.311
IS2	1.09	2.67	0.2127	3.615
IS3	1.58	2.72	0.2797	2.752
IS4	1.62	2.70	0.1679	2.241
IS5	1.90	2.73	0.2637	2.424
IS6	2.15	2.70	0.3691	2.655
IS7	3.31	2.69	0.3255	1.419
IS8	4.21	2.69	0.3448	2.289

TABLE 2: Average grain size of the Ag-doped In_2S_3 films with different dopant levels.

Sample	IS	IS3	IS6	IS8
Dopant level (at. %)	0	1.58	2.15	4.21
Grain size (nm)	31.77	40.52	41.07	41.10

were named as IS1 to IS8 for Ag concentration from 0.08 at.% to 4.21 at.% as shown in Table 1, and the pristine sample was named as IS. The structures of the samples were confirmed by an XRD with a Cu-K α radiation source ($\lambda = 1.5406 \text{ \AA}$). The morphology was characterized using a Philips XL30E scanning electron microscopy (SEM). The optical transmittance and reflectance spectra were measured in the range of 350–1200 nm with a Cary 5000-Scan UV-vis-NIR Spectrometer. The thicknesses of the films were measured by a TENCOR D100 stylus profiler. The resistivity and carrier concentration of the films were determined by a HMS-3000 Hall measurement system.

3. Results and Discussion

Figure 1 shows the XRD patterns of the Ag-doped In_2S_3 films with different dopant levels. All the XRD peaks of the samples match to those of cubic In_2S_3 (PDF# 01-084-1385). In addition, with the increasing of the Ag concentration, the 2θ values of peaks (111), (220), and (311) become smaller as Figure 2 shows. This may also be caused by the diffusion of Ag.

According to the strongest diffraction peak, we can estimate the average size of the crystalline grains by the Scherrer equation. The calculated grain size of the samples is shown in Table 2. The ionic radius of Ag^{1+} is $1.26 \text{ \AA}$, which is greater than that of In^{3+} ($0.8 \text{ \AA}$). Therefore, the grain size of the samples becomes larger with the increasing of the Ag concentration.

Figure 3 shows the XRD pattern of the In_2S_3 film annealed at 400°C . Besides the In_2S_3 phase, there are some peaks of InS phase. And there is a peak from another structure of In_2S_3 . That shows annealing at 400°C would lead to the instability of In_2S_3 phase.

FIGURE 1: XRD patterns of the $\text{In}_2\text{S}_3 : \text{Ag}$ films with different dopant levels.

FIGURE 2: The blowup of (220), (311), and (222) peaks.

FIGURE 3: The XRD pattern of In_2S_3 film annealed at 400°C .

FIGURE 4: Optical transmittance spectrum (a) and the band gap (b) of sample IS3.

FIGURE 5: The variation of carrier concentration (a) and resistivity (b) with the Ag concentration.

The transmittance and reflectance spectra of the samples show little difference. Therefore, Figure 4(a) only shows the optical transmittance spectrum of sample IS3 for simplification. The thickness of the film is about 250 nm. With the transmittance, reflectance, and the thickness, the absorption coefficient can be obtained, and the relationship between the absorption and the optical band gap obeys the following formula:

$$(\alpha h\nu)^2 = A(h\nu - E_g), \quad (1)$$

where A is a constant related to the effective mass and $h\nu$ is the photon energy. The plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Figure 4(b). Table 1 shows the band gap of the $\text{In}_2\text{S}_3:\text{Ag}$ films with different Ag concentrations. It can be seen that the band gap of the films is decreased gradually from 2.82 eV to 2.69 eV with the increasing of the Ag doping concentration. We think that Ag ions incorporate into the lattice sites as the donor

levels, thus, making the semiconductor in the degenerate state. As a result, the conduction band extends into the gap and reduces the band gap.

Table 1 also shows the electrical properties of the Ag-doped In_2S_3 films with different dopant levels. The undoped and Ag-doped In_2S_3 thin films are of n -type conductivity. Because the resistivity of all the samples (IS1 to IS8) does not change obviously, we prepared some samples with smaller dopant levels. The electrical properties of these samples are shown in Table 3. Figure 5(a) shows the variation of the carrier concentration with the Ag-doped concentration. It can be seen that, with the Ag-doped concentration increasing, the carrier concentration is increased till reaching a maximum value of $4.5 \times 10^{18} \text{ cm}^{-3}$, and then it is decreased. It is interesting that the resistivity has a sharp drop with a very low Ag concentration. Similar observation has been reported for $\text{In}_2\text{S}_3:\text{Ag}$ films by Mathew [8]. This can be

TABLE 3: Electrical properties of the $\text{In}_2\text{S}_3\text{:Ag}$ films with different dopant levels.

Ag at. %	Resistivity ($0.1 \Omega \cdot \text{cm}$)	Carrier concentration (10^{18} cm^{-3})
0	$\sim 1.0 \times 10^4$	$\sim 1.0 \times 10^{-5}$
0.08	3.387	0.8918
0.12	2.920	1.047
0.20	1.467	2.083
0.27	6.691	3.780
0.29	0.5478	4.529
0.36	0.7449	2.450
0.48	1.258	2.516
0.57	2.056	2.114
0.64	2.120	2.403

explained as follows. For In_2S_3 has high degree of vacancies of In sites [11], the Ag ions can be easily doped into the In sites as donors [12], thereby leading to the increase of the carrier concentration. With the further increase of the Ag-doped concentration, some Ag ions may be doped into the interstitial positions. Since the ionization energies of the interstitial Ag ions are higher than those of the substitutional Ag ions, the energy levels of the interstitial Ag ions are lower than those of the substitutional Ag ions and near the middle of the band gap. As a result, the interstitial Ag ions can act as recombination centers which decrease the carrier concentration. The existence of substitutional Ag ions can be supported by XRD analysis.

Figure 5(b) shows the variation of the resistivity with the Ag-doped concentration. The variation trend can also be analyzed by the above doped mechanism.

4. Conclusion

In_2S_3 thin films doped with different Ag concentrations have been synthesized by thermal evaporation deposition. The optical and electrical properties of the $\text{In}_2\text{S}_3\text{:Ag}$ thin films were studied. From the above results, we can conclude that the Ag atoms are doped into In sites as donors when the doped concentration is low. With the increase of the Ag concentration, some Ag atoms are doped into the interstitial positions as the recombination centers. The two different dopant mechanisms explain the variation trend of optical and electrical properties of $\text{In}_2\text{S}_3\text{:Ag}$ thin films with the Ag-doped concentration.

Conflict of Interests

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

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