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Effect of anneal temperature on electrical and optical properties of SnS:Ag thin films

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ABSTRACT

SnS and Ag films were deposited on glass substrates by vacuum thermal evaporation technique successively, and then the films were annealed at different temperatures (0-300℃) in N_2 atmosphere for 2h in order to obtain silver-doped SnS (SnS:Ag) films. The phases of SnS:Ag films were analyzed by X-ray diffraction (XRD) system, which indicated that the films were polycrystalline SnS with orthogonal structure, and the crystallites in the films were exclusively oriented along the（111）direction. With the increase of the annealing temperature, the carrier concentration and mobility of the films first rose and then dropped, whereas their resistivity and direct band gap E_g showed the contrary trend. At the annealing temperature of 260℃, the SnS:Ag films had the best properties: the direct bandgap was 1.3 eV, the carrier concentration was up to 1.132×10^{17} cm^{-3}, and the resistivity was about 3.1 Ωcm.

Keywords: Sns:Ag Films; Thermal Evaporation; Annealing; Electrical And Optical Properties

1. INTRODUCTION

Emphasis on cost-competitive photovoltaic cells has been involved in the study of low-cost, non-toxic materials. SnS could be of interest for photovoltaic cells, since its optical energy gap of 1.3 eV [1,2] is close to the optimum energy gap 1.5 eV of solar cells, and it has a high absorption coefficient ($> 10^4$ cm^{-1}) and a high conversion efficiency of about 25% [3,4]. In addition, the constituent elements Sn and S are non-toxic and abundant in nature.

In spite of the above advantages, the electrical properties of SnS thin films still need to be improved in order to make good SnS thin film solar cells. W. Albers *et al*. [5] investigated Sb- and Ag-doped SnS single crystals and observed n-type conductivity with carrier concentration of $\sim 10^{19}$ cm^{-3} in Sb-doped SnS crystals and p-type conductivity with $\sim 10^{18}$ cm^{-3} concentration in Ag-doped SnS crystals. Devika *et al.* [6] investigated Ag-doped SnS films grown by thermal evaporation technique and observed that the resistivity of the SnS layers reached a minimum value of 6.98 Ω cm at 15 atom% of Ag. However, some properties of SnS:Ag thin films are unclear and waiting for further study. In particular, how the annealing temperatures affect the microstructure and physical properties of SnS:Ag thin films prepared by vacuum thermal evaporation technique has not been investigated. Therefore, in this paper we investigate the influence of annealing temperatures on the films in order to improve optical and electrical properties of SnS:Ag thin films.

2. EXPERIMENTAL

SnS and Ag films were deposited on glass substrates by vacuum thermal evaporation technique successively. The thermal evaporation system is DMDE-450 deposition equipment (made in China). The SnS powder with 99.5% purity and the Ag grains with 99.9% purity were used as source materials and were loaded onto a ceramic crucible and a molybdenum boat, respectively. The chamber was evacuated down to 5.6×10^{-3} Pa. The source-to-substrate distance was about 10 cm. The as-prepared films were annealed at different temperatures of 210, 260 and 300℃ in N_2 atmosphere for 2h respectively so that Ag-doped SnS films can be obtained.

The structure of the films was characterized by a Philips X'Pert-MPD X-ray diffraction (XRD) system with a Cu K radiation source. The surface roughness was analyzed by a CSPM5000 Scanning Probe Microscopy (AFM), and the thickness of the films was measured by

a Veeco Dektak 6M stylus profiler. The transmission and reflectance spectra were carried out with a Varian Cary 500 UV−VIS−NIR spectrophotometer in the range 400 – 1600 nm. Based on Van der Pauw method, the electrical properties were determined by a HMS-3000 Hall measurement system.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis

Figure 1 (a)-(d) show the XRD patterns of the samples as-prepared and annealed at different temperatures (samples S1-S4 corresponding to unannealing, 210, 260 and 300℃), respectively. It can be seen from **Figure 1 (a)-(c)** that all the diffraction peaks are attributed to SnS (JCPDS39-354) phase with orthorhombic structure. It indicates that the films are polycrystalline SnS with a strong {111} preferred orientation. With the increase of the annealing temperature, the main diffraction peaks of the samples become stronger. Sample S3 exhibits the best crystallization. But the crystallization of sample S4 becomes weaker and there is an obvious SnO_2 peak at 2θ = 33.17°. Maybe a partial of SnS was oxidized into tin dioxide (SnO_2) at the higher annealing temperature because of a low vacuum annealing condition. Therefore, when the annealing temperature is higher, there is probably a SnO_2 phase in the SnS:Ag films.

3.2. Optical Properties

Figure 2 shows absorption coefficient vs photon energy ($h\nu$) curves of the SnS:Ag thin films at different annealing temperatures. As a whole, with the increasing of photon energy, the absorption coefficient increases rapidly and then almost stabilizes at $h\nu > 2.5$ eV. The maximum absorption coefficients of all the films are greater than 1.3×10^5 cm^{-1}. With the increase of the annealing temperature, the absorption coefficient increases correspondingly. Because the improved crystallization and uniformity, and the reduced defect density in the films will make the scattered light loss decrease, thus leading to the increase of the absorption coefficient. However, when the annealing temperature is equal to or greater than 300℃, the absorption coefficient decreases probably due to the presence of SnO_2 in the films.

Figure 3 shows a curve of $(\alpha h\nu)^2$ vs. $h\nu$ for sample S3 and the estimated *E*g value of 1.30 eV (here only show sample S3 for simplicity). The *Eg* values of all the four samples are shown in **Table 1**. With the increase of the annealing temperature, the E_g first drops and then rises. Because, with the increasing of the annealing temperature, Ag atoms are easier to be diffused and doped in the polycrystalline SnS films, and the doped-Ag can drop the band gap [6]. But the *Eg* value of sample S4 is larger than that of sample S3, this is perhaps due to the presence of SnO_2 (3.4 ~ 4.6eV) [7] in sample S4.

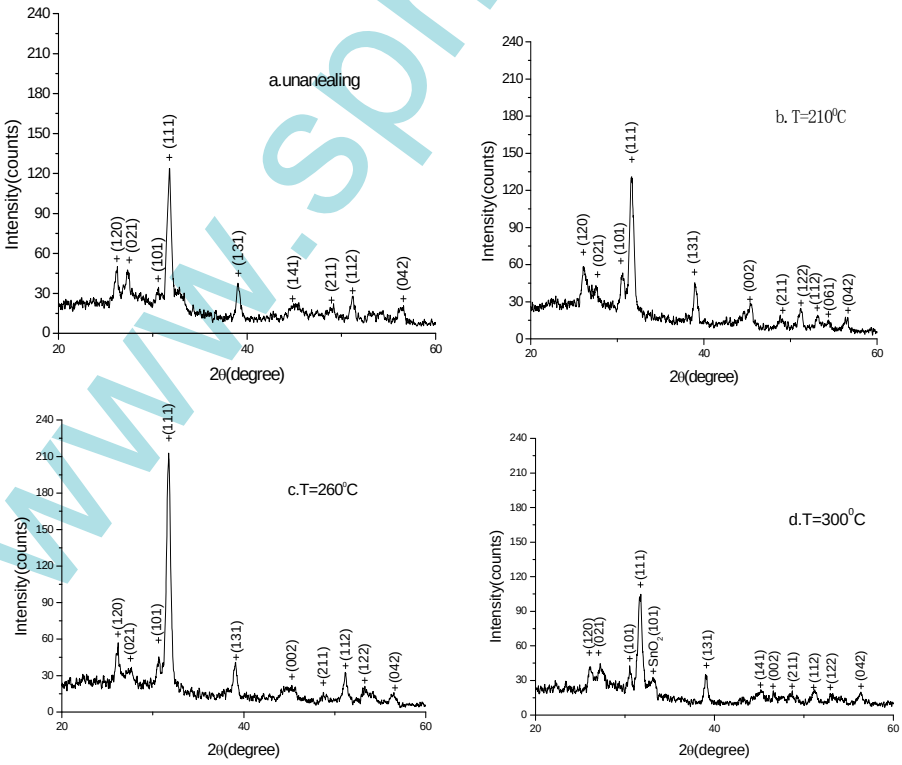

Figure 1. XRD patterns of SnS:Ag thin films at different annealing temperatures.

Table 1. The bandgap and absorption edge of SnS:Ag thin films at different annealing temperatures.

Samples	Annealing Temperature/℃	Band gap Eg /eV	Absorption Edge /nm
S1	unannealed	1.34	925.4
S2	210	1.32	939.4
S3	260	1.30	953.8
S4	300	1.52	815.8

Table 2. Hall measurement results for SnS:Ag thin films at different annealing temperatures.

Samples	temperature/℃	Bulk concentration/cm^{-3}	Mobility/ ($cm^2.v^{-1}.s^{-1}$)	Resistivity/ (Ωcm)	Average Hall Coefficient/(m^2c^{-1})
S1	unannealed	7.242×10^{14}	14.3	601.1	8.631×10^{3}
S2	210	3.212×10^{16}	16.3	11.9	1.945×10^{2}
S3	260	1.132×10^{17}	17.8	3.1	5.522×10^{1}
S4	300	2.601×10^{16}	15.7	15.3	2.402×10^{2}

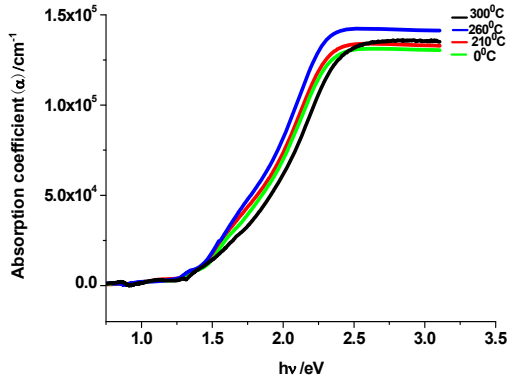

Figure 2. αvs. $h\nu$ curves of SnS:Ag thin films at different annealing temperatures.

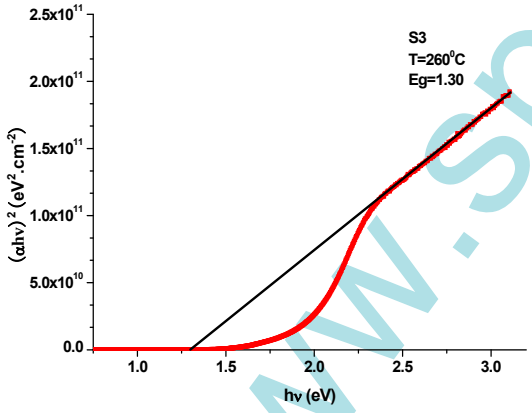

Figure 3. $(\alpha h\nu)^2$ vs. $h\nu$ curve of the SnS:Ag thin film annealed at 260℃.

3.3. Electrical Properties

At room temperature, semiconducting properties of the films were measured by a HMS-3000 Hall measurement system. The results are listed in **Table 2.** Compared with the unannealed sample, the semiconducting properties of the annealed samples have been improved. With the increase of the annealing temperature, the carrier concentration and mobility increase whereas the resistivity decreases except that of films annealed at 300℃. When the annealing temperature equals to 260 ℃, the carrier concentration and mobility reach the maximum values of 1.132×10^{17} cm^{-3} and 17.8 $cm^2.v^{-1}.s^{-1}$, respectively. But, when the annealing temperature is up to 300℃, the carrier concentration decreases to 2.601×10^{16} cm^{-3} with a mobility of 15.7 $cm^2.v^{-1}.s^{-1}$. The phenomenon can be explained by the fact that, with the increase of the annealing temperature, better crystallization and greater grain size in the films lead to the decrease of defects density and crystal-boundary, therefore the resistivity decreases. However, higher temperature urges crystal lattice vibration stronger and results in some crystal lattice defects. These defects become dispersion centers, causing the increase of resistivity of the films. In addition, the presence of SnO_2 can also cause the resistivity of the films increasing. Notably, the average Hall coefficients of all the samples are positive, which proves that the SnS:Ag films are of p-type conduction.

4. CONCLUSIONS

The SnS:Ag thin films were deposited on glass substrates using thermal evaporation technique and post-annealing, and effect of annealing on the films was investigated. The above results indicate that appropriate annealing temperature can increase the grain size of the films, improve the uniformity and crystallization of the films, decrease the resistivities of the films, and increase the absorption coefficients of the films. However, if the annealing temperature is higher than 300℃, crystallization of the films become weaker and the films can be oxidized due to low vacuum, thereby electrical and optical properties of the films become poor. At an annealing temperature of 260℃, the SnS:Ag films have the best properties: the direct bandgap is 1.3eV, the carrier concentration is up to 1.132×10^{17} cm^{-3}, and the resistivity is about 3.1 Ωcm.

5. ACKNOWLEDGMENT

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