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Effect of anneal time on photoelectric properties of SnS:Ag thin films

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Abstract. SnS and Ag films were deposited on glass substrates by vacuum thermal evaporation successively, and then the thin films were annealed at 260℃ in N_2 for different times (60min, 120min, 180min) in order to investigate the influence of annealing time on the silver-doped SnS (SnS:Ag) films. The obtained films annealed at different times are polycrystalline SnS with orthogonal structure, and the crystallites in the films are exclusively oriented along the {111} direction. With the increase of annealing time, the uniformity and crystallization of the films are improved, the carrier concentration and mobility of the films first rise and then drop, whereas their resistivity and direct bandgap energy E_g show the contrary trend.

Introduction

Over the past several years many new and advanced materials were proposed as the potential solar cell materials, tin sulfide (SnS) is one of them. Since its optical energy gap of 1.3 eV [1,2] is close to the optimum energy gap 1.5eV of solar cells, and it has a high absorption coefficient ($>10^4 cm^{-1}$) and a high conversion efficiency of about 25% [3]. In addition, the constituent elements Sn and S are non-toxic and abundant in nature. However, the semiconducting properties of SnS thin films still need to be improved in order to make good SnS thin film solar cells. Doping can improve the semiconducting properties of the films. W. Albers et al. [4] 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. [5] investigated Ag-doped SnS films grown by thermal evaporation technique and observed that the resistivity of the SnS layers reached a minimum value of 6.98Ω•cm at 15 atom% of Ag. But some properties of SnS:Ag thin films are unclear and waiting for further study. We ever reported the effect of anneal temperature on SnS:Ag thin films and obtained that the SnS:Ag film annealed at 260℃ had the best properties[6]. In this paper we investigate the influence of annealing time on the films in order to obtain SnS:Ag thin films with good photoelectric properties.

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 in N_2 atmosphere at a temperature of 260℃ for different times of 60, 120 and 180min 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 Kα 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.

Results and discussion

Structural analysis

Fig.1 show the XRD patterns of the samples as-prepared and annealed at 260℃ in N_2 for different times (samples S1-S4 corresponding to unannealing, 60, 120 and 180 min), respectively. It can be seen from all the samples that the main XRD peaks from planes (120), (101), (111), (131) and (112) 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 anneal time increasing from 0 to 120 min, the intensities of the XRD peaks in the samples become stronger. It indicates that anneal time has a certain effect on SnS:Ag films. Sample S3 exhibits the best crystallization. But when the anneal time is 180 min, the crystallization of the film (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) because of a low vacuum annealing condition. Therefore, when the annealing time is longer, there is probably a SnO_2 phase in the SnS:Ag films .

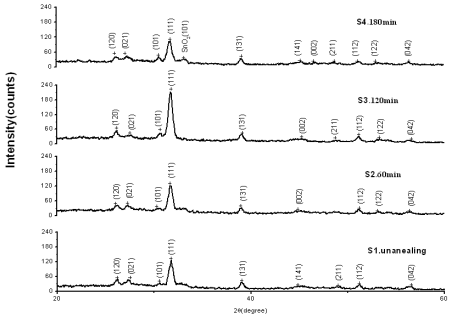

Fig.1 XRD patterns of SnS:Ag thin films annealed at 260℃ in N_2 for different times

Surface morphology

Fig.2 show the AFM images of the SnS:Ag thin films annealed at 260℃ in N_2 for different times. The images were taken in the area of 5×5 μm^2. Table.1 list the RMS and average grain size of SnS:Ag thin films annealed at 260℃ in N_2 for different times. It can be seen that the annealed films (S2-S4) have better uniformity and smoothness than the unannealed film (S1). The evaluated root mean square (RMS) roughness value of samples S2、S3 and S4 is varied between 29.8 and 23.9 nm. However, the evaluated RMS roughness value of sample S1 is 46.5nm. The grain size of the annealed films is larger than the annealed sample (S1).

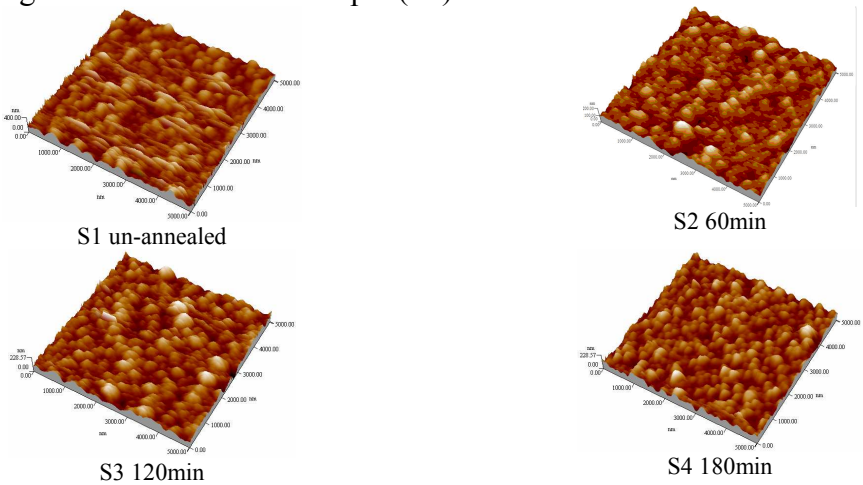

Fig.2 AFM images of the SnS:Ag thin films annealed at 260℃ in N_2 for different times

Table.1 The RMS roughness and grain size of SnS:Ag thin films anneaaled at 260℃ in N_2 for different times

Samples	Time[min]	RMS roughness [nm]	Average grain size [nm]	Average particle height [nm]
S1	0(unannealed)	46.5	115	253
S2	60	23.9	117	125
S3	120	29.8	120	146
S4	180	27	132	145

Optical properties

Fig.3 shows the curves of absorption coefficient (α) vs photon energy (hν) for the four samples. It can be seen that the sharpness and magnitude of curves is increased with the increase of the annealing time from 0 to 120 min , therefore it indicates that the absorbability of the SnS films is increased with increase of annealing time. According to $(\alpha h\nu)^n$ vs. hν relationship [8], we can estimate the bandgap of the samples. For all the samples, each $(\alpha h\nu)^2$ vs. hν curve has a good straight line fit over higher energy range above the absorption edge, indicative of a direct optical transition near the absorption edge. Table.2 lists the direct bandgap (E_g) and absorption coefficients of SnS:Ag thin films annealed at 260℃ in N_2 for different times. With the increase of the annealing time, the E_g value first drops and then rises. Because, with the increasing of the annealing time, Ag atoms have enough time to be diffused and doped in the polycrystalline SnS films. The unsaturated bonds that might be present in the layers are responsible for the formation of some defects, which produce localized states in the band structure reducing the optical bandgap[5]. But sample S4 has larger E_g value than other samples, this is perhaps due to the presence of SnO_2 (3.4 ~ 4.6eV) [7] in sample S4.

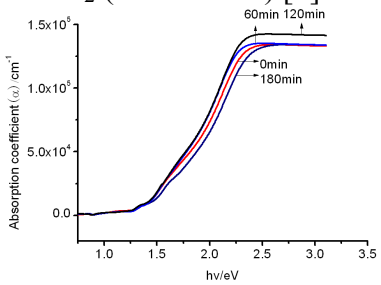

Fig.3 Absorption coefficient vs photon energy plots of SnS:Ag thin films annealed at 260℃ in N_2 for different times

Table.2 The bandgap and absorption coefficients of SnS:Ag thin films annealed at 260℃ in N_2 for different times

Samples	Time[min]	E_g[eV]	λ_c[nm]	$\alpha(\lambda_c)$[cm^{-1}]
S1	0 (unannealed)	1.34	925.4	7.14×10^4
S2	60	1.31	946.5	5.83×10^4
S3	120	1.30	953.8	6.54×10^4
S4	180	1.43	867.1	9.94×10^4

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 3. Compared with the unannealed sample (S1), the semiconducting properties of the annealed samples (S2-S4) have been improved. With the increase of the annealing time from 60 min to 120 min, the carrier concentration increases and the resistivity decreases. When the annealing time equals to 120min, the SnS:Ag films have best properties：the carrier concentration is $1.132\times10^{17}cm^{-3}$ and the resistivity is 3.1Ω·cm. But, when the annealing time is up to 180min, the carrier concentration decreases to $1.730\times10^{16}cm^{-3}$. The phenomenon can be explained by the fact that, with the increase of the annealing time, better crystallization and greater grain size in the films lead to the decrease of defects density and grain boundaries, therefore the resistivity decreases. However, a partial of SnS was oxidized into tin

dioxide (SnO_2) because of a low vacuum annealing condition when annealing time is longer. The presence of SnO_2 can 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.

Table.3 Hall measurement results for SnS:Ag thin films annealed at 260℃ in N_2 for different times

Samples	Time[min]	Bulk concentration[cm^{-3}]	Mobility [$cm^2 \cdot v^{-1} \cdot s^{-1}$]	Resistivity [Ω·cm]	Average Hall Coefficient[$m^2 \cdot c^{-1}$]
S1	0 (unannealed)	7.242×10^{14}	14.3	601.1	8.631×10^{3}
S2	60	7.879×10^{15}	15.1	52.6	7.932×10^{2}
S3	120	1.132×10^{17}	17.8	3.1	5.522×10^{1}
S4	180	1.730×10^{16}	15.5	23.2	3.611×10^{2}

Conclusion

The SnS:Ag thin films were deposited on glass substrates using thermal evaporation technique and post-annealing, and effect of annealing time on the films was investigated. The above results indicate that appropriate annealing time 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 time is longer than 180 min, crystallization of the films become weaker and the films can be oxidized due to low vacuum, thereby photoelectric properties of the films become poor. At an annealing time of 120 min, the SnS:Ag films have the best properties: the direct bandgap is 1.3eV, the carrier concentration is up to $1.132\times10^{17}cm^{-3}$, and the resistivity is about 3.1Ωcm.

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