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Optical and Electrical Properties of SnS: Ag Films as Solar Cell Absorbers

Peimin Lu[a], Hongjie Jia[b] , Shuying Cheng[c]

College of Physics and Information Engineering, and State Key Laboratory Breeding Base of Photocatalysis, Fuzhou University, Fuzhou, 350108, P. R. China

[a]lpm@fzu.edu.cn, [b]jasonhongjie@163.com, [c] corresponding author, email: sycheng@fzu.edu.cn

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Abstract: SnS and Ag films were deposited on glass substrates by vacuum thermal evaporation successively, then they were annealed in N2 ambience at a temperature of 300 ^{o}C for 2h. By controlling the Ag evaporation voltage to roughly alter content of Ag in SnS films, different Ag-doped SnS films were obtained. The microstructures, composition and properties of the films were characterized with X-ray diffraction (XRD), atomic force microscopy(AFM) and some other methods. With the increase of Ag evaporation voltage (V_{Ag}), there exist new phases of Ag_8SnS_6 and Ag_2S, whose intensity of diffraction peaks increases with the increasing Ag-dopant, and the average roughness of the films varies from 18.7nm to 23.6nm, and grain size increases from 192nm to 348nm. With the increase of V_{Ag}, the evaluated direct band gap Eg of the films decreases from 2.28eV(undoped) to 2.05eV (V_{Ag}=70V), the carrier concentration value and Hall mobility of the films diminishes from 2.048×10^{14}cm^{-3} and 25.96 cm^2.v^{-2}.s^{-1} to 1.035×10^{16} cm^{-3} and 5.66 cm^2.v^{-2}.s^{-1}, respectively; while the resistivity of the films decreases sharply from 1174Ω.cm(undoped) to 107Ω.cm (V_{Ag}=70V). All the films are of p-type conductivity. The above results show that the semiconducting properties of the SnS films have been improved by silver-doping.

1 Introduction

Thin monosulphide (SnS) is an interesting potential absorber material in solar cells because of its suitable optical gap (1.3-1.5 eV), high absorption coefficient (a＞10^4cm^{-1}) , appropriate conversion efficiency of ~25％, elementary abundance and non-toxicity in nature[1]. Generally, the films used to fabricate solar cells should possess two basic requiement: high absorption and low electrical resistivity. An effective way to obtain low resistivity metallic-chalcogenide compounds is by creation of excess of metal atoms through incorporation of suitable dopants. Albers, W. et al[2] investigated Sb- and Ag-doped SnS single crystals and observed n-type conductivity with a carrier concentration of ~10^{19} cm^{-3} in Sb-doped SnS crystals and p-type conductivity with ~10^{18} cm^{-3} concentration in Ag-doped SnS crystals. Devika, M. et al[3] 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. Therefore, in this paper, SnS:Ag films were also prepared by vacuum thermal evaporation in order to investigate their optical and electrical properties.

2. Experimental

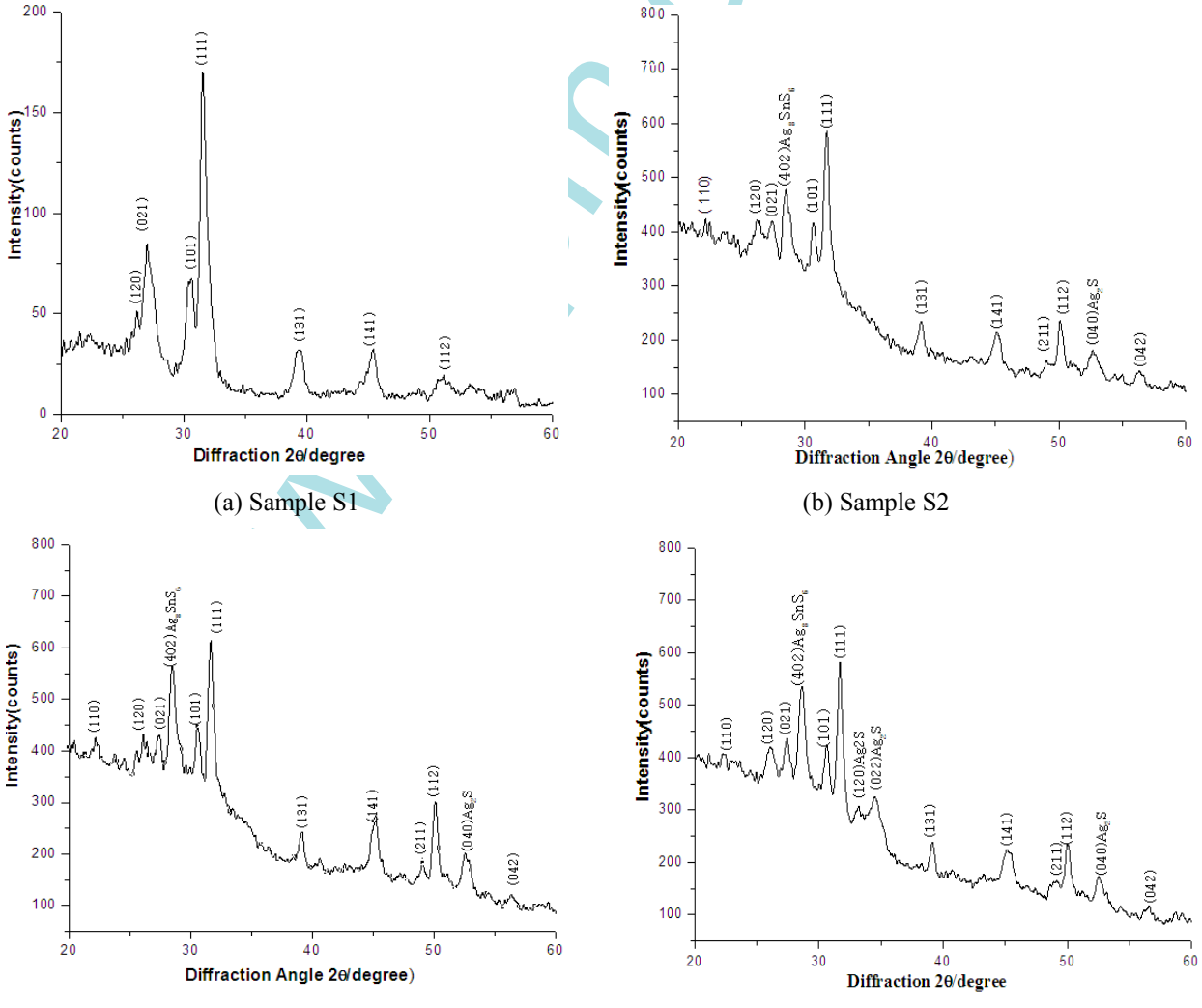
Tin sulphide and silver films were deposited onto glass substrates by a thermal evaporation process successively. The thermal evaporation system is DMDE-450 deposition equipment (made in China). The SnS powder with 99.5 % purity and the Ag grains with 99.9 % purity were used as source materials and were loaded onto a ceramic crucible and a molybdenum boat, respectively.

The chamber was evaculated down to 5.6×10^{-3}Pa. The distance between the source and the substrate was kept constant (12cm) . The films thickness was roughly controlled by evaporation voltage, current and time. At first, SnS films were deposited on glass ssubstrates, and the evaporation voltage, current and time were 95V, 34A and 9min, respectively. Then Ag films were deposited on the SnS films, and the evaporation time was 9min, and the evaporation voltage was 0V, 60V, 65V and 70V, respectively (the corresponding sample names are S1, S2, S3, S4), in order to obtain SnS films with different Ag contents. Finally, the films were annealed in a nitrogen ambience at a temperature of 300 °C for 2h so that Ag can be diffused into the whole films uniformly.

The structure of the films was characterized by a Philips X'Pert-MPD X-ray diffraction (XRD) system . 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 examined using a Varian CARY500 Scan ultraviolet-visible-near infrared spectrophotometer. 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



(a) Sample S1

(b) Sample S2

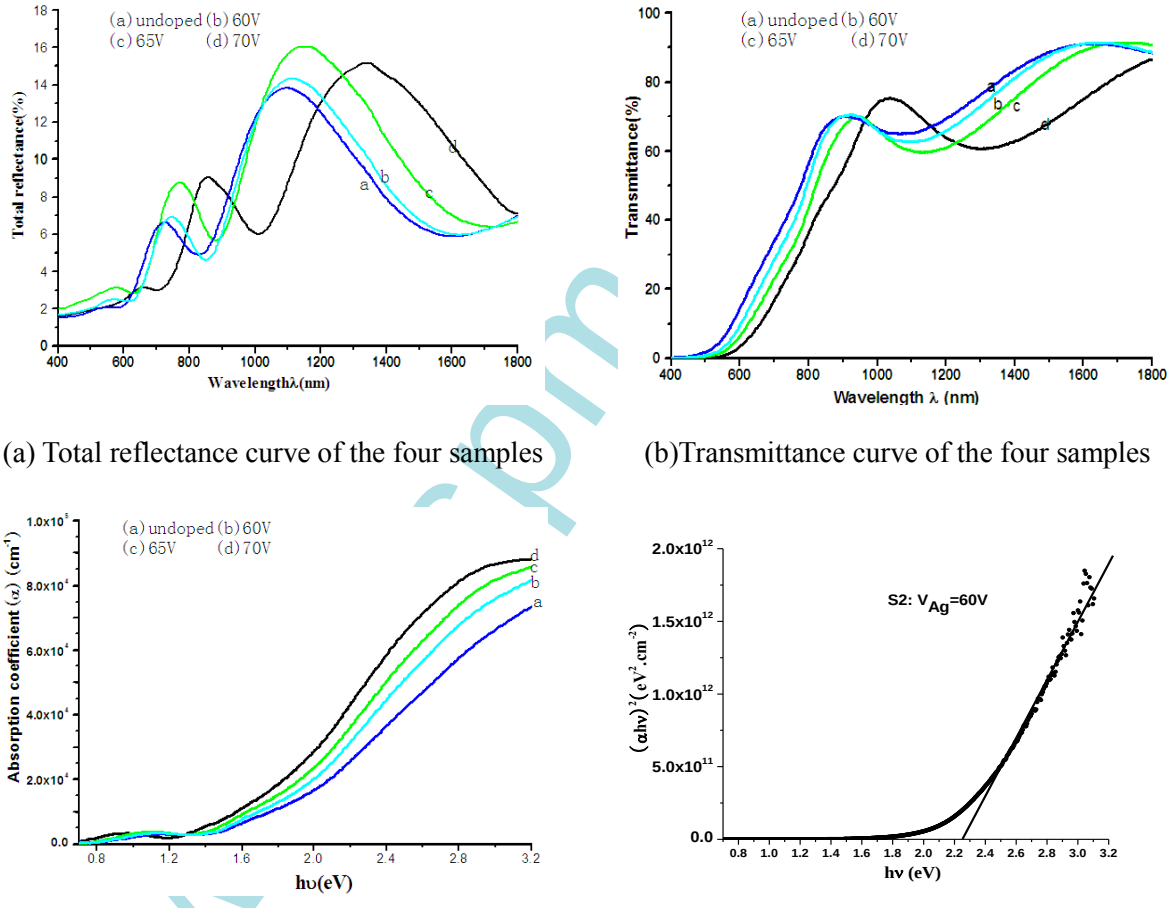
(c) Sample S3

(d) Sample S4

Fig.1 XRD spectra of SnS film and SnS:Ag films at different V_{Ag}

All the films are smooth, pinhole free and strongly adherent to the surface of the substrates. The color of the films is dark brown. It can be seen from AFM pictures (not shown here) that, with the increase of Ag evaporation voltage (V_{Ag}) from 0V to 70V, the average roughness of the films varies from 18.7 nm to 23.6 nm, and the grain size of the films increases from 192 nm to 348 nm. Fig.1(a)-(d) are the XRD patterns of samples S1-S4. All the samples exhibit several obvious XRD peaks corresponding to the planes (120), (021), (101), (111), (131), (141) and (112) of bulk SnS (JCPDS-ICDD No.39-354: orthorhombic structure , its lattice parameters: a=0.4329 nm，b=1.1193 nm, c=0.3984 nm), they are polycrystalline SnS with a strong {111} preferred orientation. From Fig.1 it can be seen that there are some new peaks (2θ＝28.68°，52.83°) which belong to Ag_8SnS_6 (JCPDS 38-434)and Ag_2S (JCPDS 14-072) in Fig.1(b)-(d). That indicates that there exist new phases Ag_8SnS_6 and Ag_2S in the Ag-doped SnS films .

3.2 Optical properties



(a) Total reflectance curve of the four samples (b)Transmittance curve of the four samples

(c) Absorption coefficient curve of the four samples (d) Direct energy badgap of sample S2

Fig.2 Optical properties of SnS and SnS:Ag films deposited at different V_{Ag}

Fig.2 (a) and (b) are plots of the total reflectance and transmittance spectra obtained for the four samples in the wavelength range of 400-1800 nm. These samples have almost similar total reflectance and transmittance spectra curves, but the peaks shift to longer wavelength with the increase of V_{Ag} . This phenomenon may be related with the thickness of the films because the evaporation rate of Ag will increase with the increase of V_{Ag}. Therefore the thickness of SnS:Ag films will be increased during the same deposition time. Though different sample may have different magnitude in total reflectance and transmittance spectra. Generally, for the four samples,

the total reflectance is quite low (less than 16%) in the wavelength range of 400-1800 nm, and the transmittance is very low in the range of 400-600 nm, but the transmittance increases rapidly for wavelengths from 600 nm to 850nm, then it varies slowly in the range of 850-1800nm. The transmittance is larger than about 50% when the wavelength is larger than 900 nm.

With total reflectance R, transmittance T and thickness d of the films (d is about 500~600 nm for the four samples), the absorption coefficient $\alpha(\nu)$ can be calculated according to formula (1)

$$\alpha = \frac{1}{d}\ln(\frac{1-R}{T}) \qquad (1) \qquad\qquad (\alpha h\nu)^2 = A(h\nu - E_g) \qquad (2)$$

Fig.2(c) shows the curves of absorption coefficient α vs hν of the four samples. It can be seen that both the gradient of curves and the magnitude of α increase with the increasing of V_{Ag} . From formula (2), the direct energy gap Eg can be determined [4].

Fig.2(d) shows a curve of $(\alpha h\nu)^2$ vs. $h\nu$ for sample S2 and the calculated Eg value of 2.25eV (here only show sample S2 for simplicity). The Eg value of all the four samples are shown in Table 1. It can be seen from Table 1 that the evaluated Eg of the four films decreases from 2.28eV (undoped) to 2.05eV (V_{Ag}=70V) with the increase of V_{Ag}. The change rule of Eg is in good agreement with reference [3], but the evaluated Eg is larger than 1.3-1.5eV [1] perhaps due to SnO_2 excistence (the films were probably partly oxidized during annealing at 300℃) in the films because the energy badgap of SnO_2 is about 3.59eV.

3.3 Electrical properties

At room temperature, carrier concentration, mobility and resistivity of the films were measured by Hall Measurement System. The results are listed in Table.1. It can be seen from Table 1 that with the increase of V_{Ag} from 0V to 70V, the carrier concentration of the films increases from $2.048\times10^{14}cm^{-3}$ (undoped) to $1.035\times10^{16}cm^{-3}$, wheras their resistivity decreases from $1.174\times10^{3}\Omega.cm$ (undoped) to $1.07\times10^{2}\Omega.cm$. In addition, the carrier concentration of all the samples is positive, which indicates that the SnS:Ag films are of p-type conduction. Therefore, Ag-doping can increase the carrier concentration, reduce the resistivity and optimize the electrical properties of the films.

Table1. Electrical properties of SnS:Ag films deposited at different V_{Ag}

Sample name	V_{Ag} [V]	Carrier concentration [cm^{-3}]	Mobility [$cm^2.v^{-2}.s^{-1}$]	Resistivity [Ω.cm]	Direct energy bandgap [eV]
S1	0	2.048×10^{14}	25.96	1.174×10^{3}	2.28
S2	60	1.271×10^{15}	12.7	3.86×10^{2}	2.25
S3	65	8.549×10^{15}	8.4	2.12×10^{2}	2.15
S4	70	1.035×10^{16}	5.66	1.07×10^{2}	2.05

4 Conclusion

The optical and electrical properties of SnS:Ag films were investigated. It is shown that Ag-doping can improve the morphology of SnS films, increase their carrier concentration and

reduce their resistivity, but the films are still of p-type conduction. The Eg value of the SnS:Ag films decreases with the increasing of V_{Ag}. Therefore, Ag-doping in SnS films can improve the semiconducting properties of the films and lay a good foundation for the development of new kinds of photovoltaic devices.

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