Substrate temperature effects on the structural and photoelectric properties of ZnS:In films*

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Abstract: Indium doped ZnS (ZnS:In) films were prepared on glass substrate using thermal evaporation technology. It was found that the structural, optical and electrical properties of ZnS:In films strongly depend on the substrate temperature (T_s). By X-ray diffraction (XRD), atomic force microscopy (AFM), transmittance spectroscopy, and electric performance measurements, the effect of T_s on ZnS:In film is studied in detail. It reveals that T_s has important effect on ZnS grain size, crystallinity, lattice disorder, etc., which further leads to the obvious influence on its optical and electrical performance. Under the optimized T_s, the performance, especially the conductivity, achieved in this work is far higher than that reported for other n-type ZnS films.

Key words: ZnS; indium; evaporation; photoelectric properties; substrate temperature
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1. Introduction

ZnS has been extensively studied during the past decades and it has obtained important applications in many fields, such as photoconductor and photovoltaic devices[1−3]. In addition, the application of ZnS can be extended if it is of low resistivity. For instance, low resistive ZnS is suitable for acting as a window/buffer layer material of thin film solar cells to significantly improve their response in the blue light zone and simultaneously increase the short-circuit current density to some extent. In addition, ZnS material is cheap and non-toxic. All these merits make low resistivity ZnS an ideal substitute for CdS, a widely used but toxic material, to fabricate high conversion efficiency photovoltaic cells without Cd^{2+} pollution[4].

On the other hand, pure ZnS film is of very high resistivity[5,6]. To improve its conductivity, the most effective way is to dope the layers by suitable dopants which are preferably from III group metals like Al, Ga, and In, which can produce shallow donor levels in ZnS energy structure and further lead to an improvement in the conductivity of the layers. However, up to now, little effort has been made except that Al was doped into ZnS (ZnS:Al) film to achieve a resistivity of about 24 Ω·cm[7]. Despite of that improvement, the resistivity of ZnS film still needs to be further decreased to fulfill its potential application in the thin film solar cell field. Taking into account that an In^{3+} ion has a similar radius with that of a Zn^{2+} (namely In-doped ZnS possibly achieve high performance), together with the extremely important role of substrate temperature (T_s) on ZnS film quality, this paper tries to study In-doped ZnS film and lays it emphasis on analyzing the effect of T_s on the structural, electrical and optical properties of ZnS:In films.

2. Experiment

ZnS:In films were prepared on glass substrates by using the thermal evaporation method. The high purity (99.99%) ZnS and indium bulk materials were used as the source materials, respectively. Firstly, the substrate was ultrasonically cleaned in acetone solution, ethanol solution, and deionized water for 15 min, respectively. Then it was dried and moved into a vacuum chamber to deposit the ZnS (100 nm)/In (5.4 nm)/ZnS (100 nm) (the thickness is measured after annealing) sample based on the following experimental conditions: the vacuum cavity degree was 5×10^{-4} torr, the substrate temperature was kept at 100 ℃, and the deposition rate was 2.5 Å/s. After that, it was naturally cooled and then annealed in Ar atmosphere kept at 500 ℃ for 2.5 h. Then it was naturally cooled to room temperature and characterized by experiments. The structural phase of the ZnS:In samples was measured by XRD experiment using X'Pert Pro MPD X-ray instrument, and the diffraction angle peak is processed by Jade 6.5 software. The electrical performance was analyzed by using a Keithely 4200 semiconductor and a Hall Tester HMS2000. The optical transmittance was recorded by Cary5000 ultraviolet-visible spectrophotometer. The surface morphology was examined with a CSPM5000 atomic force microscope (AFM).

3. Results and analysis

3.1. The effect of T_s on the structural phase of ZnS:In film

Figure 1(a) shows the typical XRD patterns of ZnS:In films. As seen, the film deposited at room temperature has an amorphous structure and the remarkable difference between the XRD spectra at T_s = 27 ℃ and other values clearly indi-

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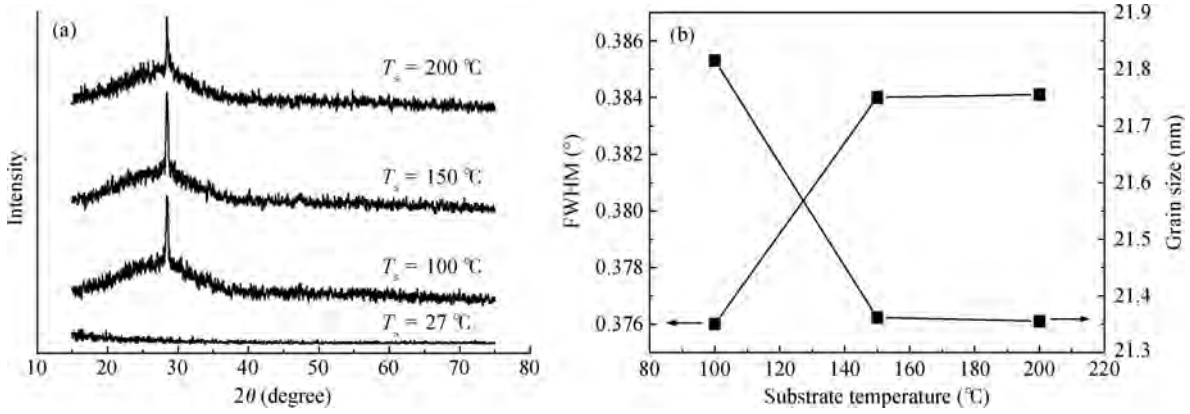

Fig. 1. (a) XRD patterns of ZnS:In film. (b) FWHM/grain size variation with T_s.

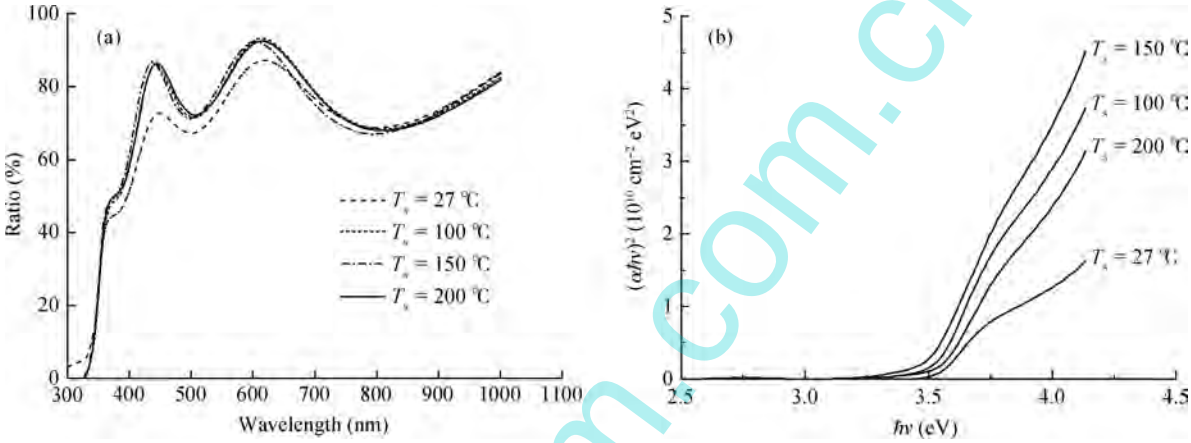

Fig. 2. (a) Transmittance spectra of ZnS:In film. (b) Profile of $(\alpha\hbar\nu)^2$ versus $\hbar\nu$.

cates the important role of T_s in the crystallinity of films. The sole diffraction peak around 28.50° exhibited for other films implies that the films deposited at $T_s \geqslant 100$ ℃ have a cubic structure (JCPD:05-0566) and (111) is the preferred produced plane. Moreover, the intensity of the (111) peak is found to be slowly enhanced with T_s in the range of 100–150 ℃ and then a little decreased at $T_s = 200$ ℃. With regard to the full width at half maximum (FWHM) and the grain size of the films, they are plotted in Fig. 1(b), respectively. It shows that the largest grain size is achieved at $T_s = 100$ ℃ and the films are nanocrystalline with grain sizes ranging from 21.36 to 21.82 nm. Interestingly, Figure 1(b) shows that although the crystallinity decreases obviously, the FWHM and grain size only undergo small changes when T_s increased from 150 to 200 ℃. Based on the Bragg formula and a comparison of (111) diffraction angles (28.473°, 28.478°, 28.463° are ascribed to the films deposited at 100 ℃, 150 ℃ and 200 ℃, respectively) with the standard value (JCPD:05-0566), the lattice is found to suffer a slight expansion in this experiment. The lattice expansion is considered as the result of indium atom transfer from the ideal lattice site to an interstitial site when it gets enough energy from the substrate.

3.2. The effect of T_s on the optical properties of ZnS:In film

Figure 2(a) shows the transmittance spectra of ZnS:In films. It reveals that the film deposited at room temperature has the lowest transmittance, which evidently increases to exceed 80% when higher T_s ($T_s \geqslant 100$ ℃) is applied. The lowest transmittance obtained by amorphous film ($T_s = 27$ ℃) indicates that the crystallinity of ZnS:In film plays some role in the transmittance spectrum. A similar conclusion has been reported in other literatures[7]. In addition, Figure 2(a) only shows a slight difference among the films deposited at 100, 150, and 200 ℃, suggesting that there are some other factors which are more important than crystallinity and other factors (e.g. grain size and lattice deformation, etc.) that affect the transmittance spectrum when T_s is larger than 100 ℃. Here, the factors are derived from the reflectivity at the film surface which is slightly affected by the surface roughness (as will be proved by AFM images).

Figure 2(b) shows the relationship between $(\alpha\hbar\nu)^2$ and $\hbar\nu$ under different T_{rms}. According to the well known formula:

$$(\alpha\hbar\nu)^2 = A(\hbar\nu - E_g), \tag{1}$$

where $\hbar\nu$, E_g, A and α are the photon energy, photonic band gap, constant and the absorption coefficient, the band gaps of 3.55 eV, 3.53 eV, 3.51 eV, 3.58 eV are obtained for the films with $T_s = 27$ ℃, 100 ℃, 150 ℃, 200 ℃, respectively. Interestingly, it is noted that though carrier density increases with T_s until it reaches 150 ℃ (as seen in Section 3.4), E_g is slightly decreased rather than increased as that described by Burstin-Moss effect[8]. The disaccord of the results obtained here with

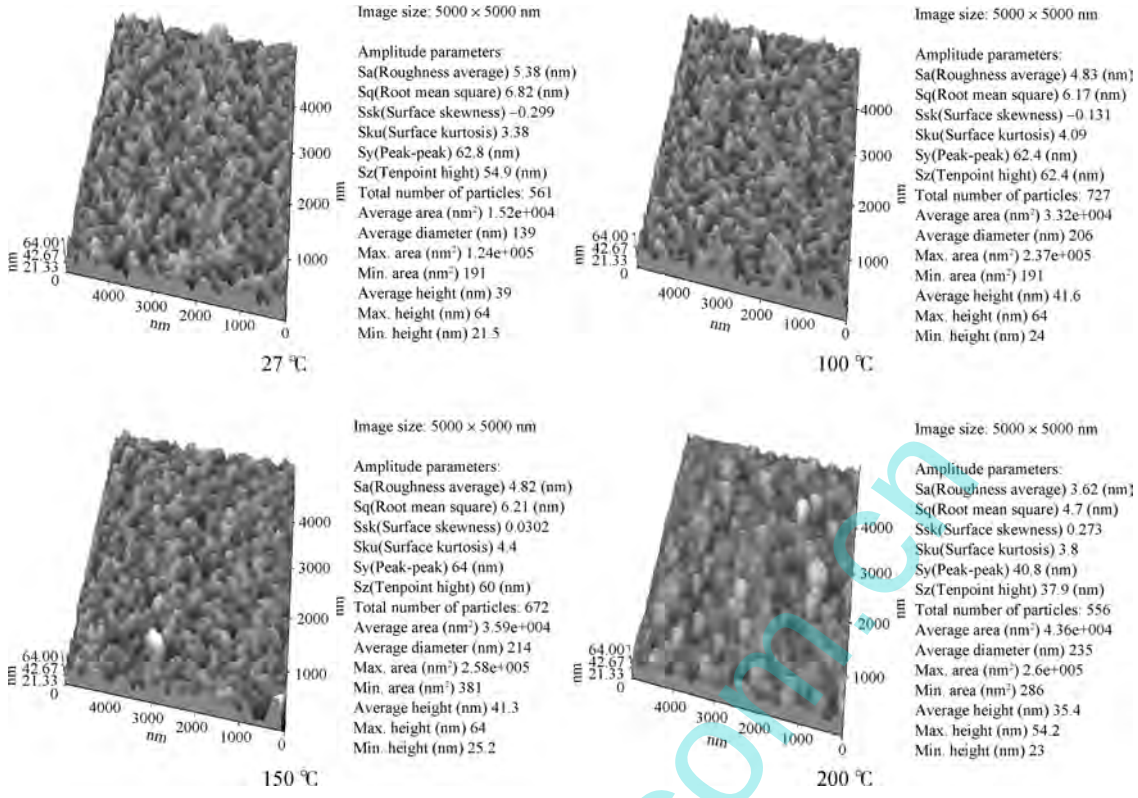

Fig. 3. AFM images of ZnS:In films deposited at different T_s.

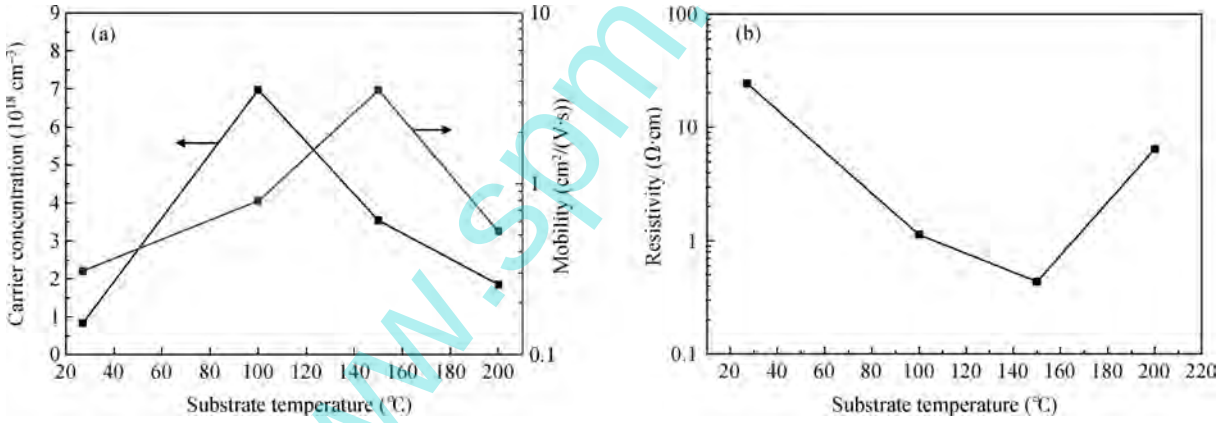

Fig. 4. T_s influence on (a) carrier concentration and mobility and (b) resistivity.

the Burstin-Moss effect indicates that the carrier density is not the sole influential factor and some other factors play a more important role in this case. In fact, the mechanism of E_g variation is very complicated, which may result from the inaction of carriers with donor ions, grain size effect, expansion of dopant energy level, etc[7]. The matter deserves to be further studied later. Nevertheless, the lattice disorder, which has been demonstrated in Section 3.1 by the XRD result, is believed to be one of the important influential factors.

3.3. The effect of T_s on ZnS:In surface morphology

Figure 3 shows the AFM images of ZnS:In films prepared at different T_s. All samples show that ZnS:In particles are homogeneously dispersed in the ZnS layers, indicating that the films are of high quality. In addition, the particle size is increased and surface roughness is decreased with T_s increasing. It seems that higher T_s is beneficial to improve the surface morphology. However, other experimental results show that high T_s will lead to more serious lattice expansion and smaller grain size, and it further results in lower carrier mobility. The former has been analyzed in Section 3.1 and illustrated in Fig. 1. As for the latter, it will be proved in Section 3.4. According to the analysis above, it is necessary to optimize T_s to achieve the high performance.

3.4. The effect of T_s on ZnS:In resistivity

Pure ZnS film is known to have extremely poor conductivity. With In incorporation, the conductivity of ZnS film is significantly improved, which not only results from the higher carrier concentration "*n*" that is derived from the free electrons

released by In atoms, but also from the improvement of carrier mobility "μ". The detailed relationship is plotted in Fig.4.

Figure 4(a) shows the important influence of T_s on "n" and "μ". With T_s increasing, n and μ both increase until they attain the maximum value at $T_s = 100$ ℃ and $T_s = 150$ ℃, respectively. After that, they decrease to some extent. The variations of n and μ with T_s further lead to the variation of resistivity (ρ) with T_s, as shown in Fig. 4(b). Figure 4(b) exhibits the lowest resistivity of 0.435 Ω·cm that is obtained at $T_s = 150$ ℃. In addition, it is noted that the highest carrier density and the highest mobility are not achieved at the same T_s, indicating that there are several factors that simultaneously affect n and μ. By comparing Fig. 4(b) with the structural properties of the films (XRD result in Fig. 1), the grain size and crystallinity seem to play critical role in n and μ in this case. In addition, the decreased E_g of ZnS (less than 3.7 eV) and the similar ionic radius of In^{3+} with Zn^{2+} are also believed to play important role.

4. Conclusions

High-performance ZnS:In is fabricated using vacuum thermal evaporation technology. Substrate temperature shows a significant effect on the grain size, crystallinity, lattice disorder, surface morphology, carrier density, carrier mobility, optical properties, band gap, etc. According to the experimental results, T_s in the range of 100–150 ℃ seems appropriate for achieving high electrical and optical performances. Under $T_s = 150$ ℃, 4 at.% In-doped ZnS:In film obtained resistivity as low as 0.435 Ω·cm and transmittance above 80% simultaneously, which is better than the results reported for n-type ZnS films[7].

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