

Preparation and characterization of cubic lattice ZnS:Na films with (111) preferred orientation*

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ZnS:Na thin films with (111) preferred orientation were deposited on glass substrates by vacuum evaporation method. The as-prepared films were annealed in flowing argon at 400–500 °C to improve the film crystallinity and electrically activate the dopants. The structural, optical and electrical properties of ZnS:Na films are investigated by X-ray diffraction (XRD), photoluminescence (PL), optical transmittance measurements and the four-point probe method. Results show that the as-prepared ZnS:Na films are amorphous, and exhibit (111) preferred orientation after annealing at 400–500 °C. The PL emissions at 414 nm and 439 nm are enhanced due to the increase of the intrinsic defects induced by the thermal annealing. However, all the samples exhibit high resistivity due to the heavy self-compensation.

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Zinc sulphide (ZnS), an important II–VI semiconductor with a variety of good physical and chemical properties, is suitable for many applications like thin film solar cells, light emitting diodes and electroluminescent devices^[1–3]. Up to now, many techniques have been developed to synthesize high-quality ZnS films, such as radio frequency (RF) magnetron sputtering, molecular beam epitaxy, pulsed laser deposition, chemical vapour deposition, chemical bath deposition and electron beam evaporation^[4–8]. Among them, the vacuum evaporation is convenient to prepare ZnS films.

ZnS carries the maximum potentiality for electronic devices due to possible p-type and n-type doping. For the different applications of ZnS, the technique to dope it with suitable impurities to obtain n-type or p-type conductivities is the key. However, recent investigations show either p-type or n-type doping in II–VI semiconductor, but not for both types^[9]. Among ZnS, ZnSe and ZnTe, reliable p-type doping in ZnS is very difficult due to its lower valence band maxima (VBM). Normally, doping ZnS to obtain p-type conductivity with the elements from I_a, I_b and V_b groups is desirable. Recently, there has been a great progress in p-type doping in ZnS^[10–15]. For example, Yuan et al^[10] prepared p-type ZnS thin films by doping them with N. The usually employed dopant elements for p-type conductivity in ZnS are N, Sb, Ag, or combination of In–Ag, In–Ag–N, etc. However, experimental p-type doping with elements from I_a group, such as Li, Na and K, is seldom reported.

In this letter, we have doped ZnS with Na element

from I_a group. ZnS:Na films were prepared with a conventional vacuum evaporation method. The samples were annealed in flowing argon at 400–500 °C. The structural, optical and electrical properties of ZnS:Na films are investigated.

ZnS thin films were deposited on glass substrates by vacuum evaporation method. Before deposition, the glass substrates were first ultrasonically cleaned in acetone for 10 min to remove the organic contamination on the surface, and then washed in deionized water for 5 min. Subsequently, the substrates were again ultrasonically cleaned in alcohol for 10 min to further remove the surface contamination and then were washed in deionized water for 5 min. Then the substrates were rinsed in HF (atom ratio of 5%) solution for 5 min to remove the surface oxide. Finally, the glass substrates were rinsed in deionized water for 5 min and dried in thermal floating air. The substrates were then transferred into vacuum chamber which was pumped to about 1×10^{-4} Pa with a combination of mechanical pump and diffusion pump. To further remove the absorbed gas and residual contamination on the substrate surface, the substrates were heated for 10 min, and then ZnS powder mixed with Na₂S on a tungsten crucible was heated by Joule effect. Na/Zn atomic ratio is 2%. The ZnS films were deposited at a substrate temperature of 200 °C. After the deposition, the films were annealed in flowing argon at different temperatures from 400 °C to 500 °C for 1 h in a quartz tube furnace.

To characterize the structural and optical properties of

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ZnS:Na films, the crystal orientation is investigated using a PHILIPS X'PERT PRO MPD X-ray diffractometer with the radiation source of CuK α . Optical transmittance is measured using a SHIMADZU UV2550 spectrophotometer. Room temperature (RT) photoluminescence (PL) spectra are recorded by a SHIMADZU RF5301PC spectrophotometer with the excitation wavelength of 360 nm. The resistivity of ZnS films is measured by the four-point probe method.

Fig.1 shows that the as-prepared ZnS films have no diffraction peak, suggesting an amorphous nature. It can be seen that only one diffraction peak centered at $2\theta \approx 28.69^\circ$ appears after the samples were annealed at 400 °C. It is well known that ZnS has two commonly available allotropes: one with a zinc blende (ZB) structure and the other with a hexagonal wurtzite (WZ) structure. Whereas the (002) peak of ZB ZnS and the (111) peak of WZ ZnS are very close, the cubic form is the stable low-temperature phase, while the latter is the high-temperature polymorph which forms around 1296 K^[16]. Therefore, the diffraction peak can be indexed to (111) plane of cubic ZnS. Thermal annealing has evident influence on the structural properties of ZnS:Na films. ZnS films exhibit the preferred orientation along (111) plane after annealing at 400 °C for 1 h. The results show that the (111) diffraction peak increases and the full width at half maximum (FWHM) of (111) peak decreases with annealing temperature increasing from 400 °C to 500 °C, suggesting the improvement of crystal quality of ZnS:Na films.

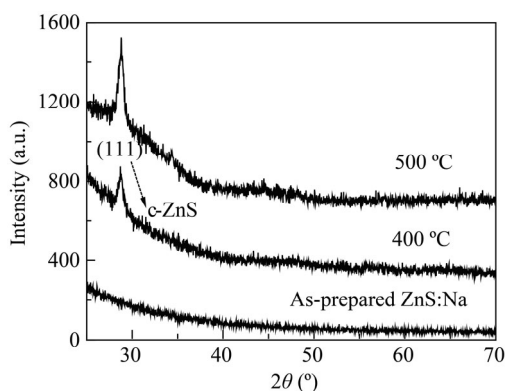


Fig.1 XRD patterns of ZnS:Na films after thermal annealing at different temperatures

Fig.2 shows the influence of thermal annealing on the optical transmittance of ZnS:Na films. It can be seen from Fig.2 that the optical transmittance is slightly enhanced in the visible region by the thermal annealing. It is known that structural defects are easily produced during the preparation process, they will trap photons when irradiated, but can be effectively annealed out by thermal annealing. Therefore, the enhancement of the optical transmittance can be mainly attributed to the improvement of the crystallinity of the ZnS:Na films, as has been confirmed by the XRD analyses.

In addition, thermal annealing also has evident influence on the optical band gaps of ZnS:Na films as shown in the inset of Fig.2. The optical band gaps are determined from the conventional method^[17,18]. It can be seen from Fig.2 that the optical band gap blue-shifts after the thermal annealing. As has been confirmed in the XRD analysis, (111) diffraction peak of ZnS films appears and is enhanced after annealing at 400—500 °C due to the improvement of the crystallinity of ZnS:Na films. It is known that structural defects can form many shallow energy levels near the band edge, which can broaden the absorption edge. Many structural defects are created during the preparation process, further annealing repairs the structural defects, and the defects produced in the growth process are annealed out, which leads to the blue shift of the optical band gaps of ZnS:Na films.

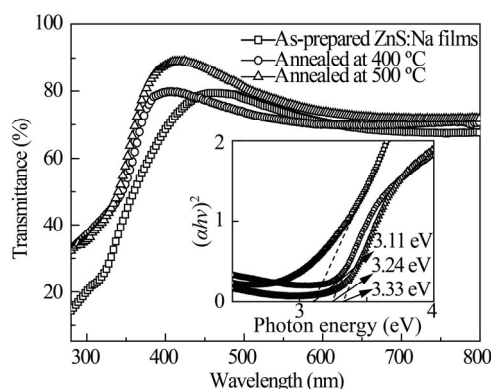


Fig.2 Transmittance spectra of ZnS:Na films before and after thermal annealing (The inset shows the square of absorption coefficient as a function of incident photon energy for ZnS:Na films after thermal annealing.)

It can be seen from Fig.3 that all ZnS:Na PL spectra exhibit two broad emission peaks centered at about 414 nm and 439 nm. The broad emissions are normally ascribed to the intrinsic defects in ZnS. According to the first-principle total-energy calculations of the native defects in ZnS^[19], we find that the transition radiations from Zn interstitial (Zn_i) to Zn vacancy (V_{Zn}) and S vacancy (V_S) to the valence band maximum (VBM) are very close to the 414 nm and 439 nm emissions, respectively. Therefore, we attribute the 414 nm and 439 nm emissions to the transitions of $Zn_i \rightarrow V_{Zn}$ and $V_S \rightarrow VBM$, respectively, as shown in Fig.4. The inset of Fig.3 plots the dependence of the peak intensities of 414 nm and 439 nm emissions on the annealing temperature. It can be seen that the emissions increase with the annealing temperature. The enhancement of the defect related emissions can be explained by the increase of the intrinsic defects, such as Zn_i , V_{Zn} and V_S , produced during the high temperature annealing.

Theoretical investigation reveals that Na is a desirable acceptor dopant in ZnS, and p-type conduction is

more easily realized under Zn-vacancy-rich condition^[19]. To investigate the effects of thermal annealing on the electrical properties of ZnS:Na films, we have measured the resistivity of ZnS:Na films at every processing stage with the four-point probe method. However, we find that ZnS:Na films exhibit high resistivity all the time. Though Zn vacancies produced during annealing, serving as acceptors, are beneficial to the p-type conduction in ZnS, the interstitial Zn produced simultaneously, acting as a donor, causes heavy self-compensation. To obtain p-type conduction, S-rich annealing atmosphere may be more beneficial. On the other hand, higher annealing temperature may be desirable to fully activate the acceptor dopants.

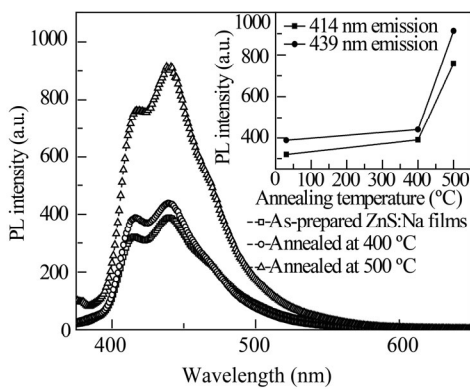


Fig.3 RT PL spectra of ZnS:Na films after thermal annealing

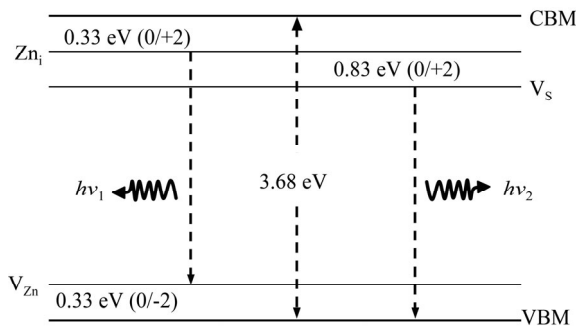


Fig.4 The intrinsic defect levels in ZnS^[19] and the possible transitions between the defect levels

We have prepared ZnS:Na films on glass substrates by the vacuum evaporation method. The as-prepared films show an amorphous nature. After the thermal annealing, (111) diffraction peak appears and is enhanced. Meanwhile, the defect related emissions are enhanced due to

the increase of the intrinsic defects produced during the high temperature annealing. Nevertheless, the ZnS:Na films exhibit high resistivity due to the heavy self-compensation.

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