# Effects of thermal annealing on the properties of N-implanted ZnS films*

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N-ion-implantation to a fluence of $1\times10^{15}$ ions/cm$^2$ was performed on ZnS thin films deposited on glass substrates by using the vacuum evaporation method. The films were annealed in flowing nitrogen at 400 °C–500 °C after N-ion-implantation to repair the ion-beam-induced structural destruction and electrically activate the dopants. Effects of ion-implantation and post-thermal annealing on ZnS films were investigated by X-ray diffraction (XRD), photoluminescence (PL), optical transmittance, and electrical measurements. Results showed that the diffraction peaks and PL intensities were decreased by N-ion-implantation, but fully recovered by further annealing at 500 °C. In this experiment, all films exhibited high resistivity due to the partial dopant activation under 500 °C.

**Keywords:** ZnS thin films, vacuum evaporation, ion implantation, X-ray diffraction

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## 1. Introduction

Zinc sulphide (ZnS), an important II–VI semiconductor with a variety of good physical and chemical properties, is suitable for many applications such as 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.[4–9] Since ZnS thin films are easily grown with high quality using many techniques, annealing ZnS in an oxidative atmosphere has been adopted to produce ZnO.[10–13]

Amongst chalcogenides, ZnS carries the maximum potentiality for electronic devices due to possible p-type and n-type dopings. Though ZnS has great potential applications in electronic devices, the technique to dope it with suitable impurities to obtain n-type or p-type conductivities is the key. Normally, doping ZnS to obtain n-type conductivity with the elements from III group, p-type conductivity with the elements from V group, are desirable. However, recent investigations show a relative ease for either p-type or n-type doping in II–VI semiconductor, but not for both types.[14] Amongst II–VI compounds, ZnS, ZnSe, and ZnTe, reliable p-type doping was not observed in ZnS.

In this work, ZnS films were prepared with a conventional vacuum evaporation method. N-ion-implantation was performed on the films. The effects of ion-implantation and post-thermal annealing on the structural and opto-electrical properties were investigated.

## 2. Experimental

ZnS thin films were deposited on glass substrates by the 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 were washed by deionized water for 5 min. Then the substrates were rinsed in HF (at.5%) solution for 5 min to remove the surface oxide. Finally, the glass substrates were watered in deionized water for 5 min and dried in thermal floating air. The substrates were then transferred into a vacuum chamber, which was pumped to about $1\times10^{-4}$ Pa with a combination of mechanical pumping and diffusion pumping. To further remove the absorbed gas and residual contamination on the substrate surface, the substrates were heated for 10 min, and then the ZnS powders on a tungsten crucible were heated by the Joule effect. The ZnS films were deposited at a substrate temperature of 200 °C.

The as-prepared films were subjected to N ion implantation. N ions were implanted into the as-prepared films at 56 keV to a dose of $1\times10^{15}$ ions/cm$^2$. Figure 1 shows the depth profile of implanted N atoms simulated using the code TRIM 96. The projected range ($R_p$) of the atoms was about 182 nm. After ion implantation, N-implanted films were an-

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nealed in flowing nitrogen, which was used for inhibiting dopant out-diffusion in the films, at different temperatures from 400 °C to 500 °C for 1 h in a quartz tube furnace.

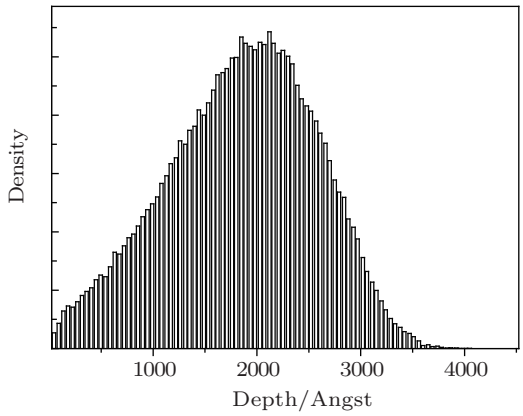



**Fig. 1.** TRIM simulation of the depth profile of implanted N atoms for ZnS films.

To characterize the structural and optical properties of ZnS films after N ion implantation and post-thermal annealing, the crystal orientation was investigated using a PHILIPS X'PERT PRO MPD X-ray diffractometer (XRD) with the radiation source of Cu $K_\alpha$. Optical transmittance was measured using a SHIMADZU UV2550 spectrophotometer. Room temperature (RT) photoluminescence spectra (PL) were recorded by a SHIMADZU RF5301PC spectrophotometer with an excitation wavelength of 360 nm. The resistivity of ZnS films was measured by using the four-point probe method.

## 3. Results and discussion

Ion implantation is the process of depositing chemical dopants into a target by directly bombarding it with high-energy ions of the dopant. This process involves the collision of the highly-energetic bombarding ions with the atoms of the target, and is therefore destructive to the material structure of the target being bombarded. Post-implantation annealing in a protective or neutral environment is usually used to repair the structural destruction and increase the electrical activity of the dopants. To investigate the effects of the annealing temperature on the structural properties of N-implanted ZnS films, the films were annealed after N ion implantation in flowing nitrogen at different temperatures from 400 °C to 500 °C for 1 h. Figure 2 shows the XRD patterns of ZnS films after N ion implantation and annealing at different temperatures. It shows that as-prepared ZnS films have only one diffraction peak at $2\theta \approx 28.8°$. It is well known that ZnS has two commonly available allotropes: one with a zinc blende (ZB) structure and another one 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 at around 1296 K.[15] Therefore, the diffraction peak can be indexed to (111) of cubic ZnS.

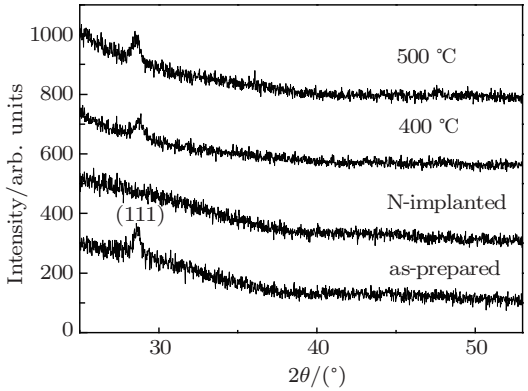



**Fig. 2.** XRD patterns of ZnS films after N ion implantation and post-thermal annealing at different temperatures.

It is found that the (111) diffraction peak is fully suppressed by the N ion implantation. The suppression of the (111) diffraction peak can be attributed to the ion-beam induced lattice disorder. Thermal annealing has evident influences on the structural properties of N-implanted ZnS films. The results show that the (111) diffraction peak increases with annealing temperature increasing from 400 °C to 500 °C. ZnS films exhibit the preferred orientation along the (111) plane after annealing at 400 °C for 1 h. It is noted that significant recovery of the structural properties of N-implanted ZnS films occurs after annealing at 500 °C.

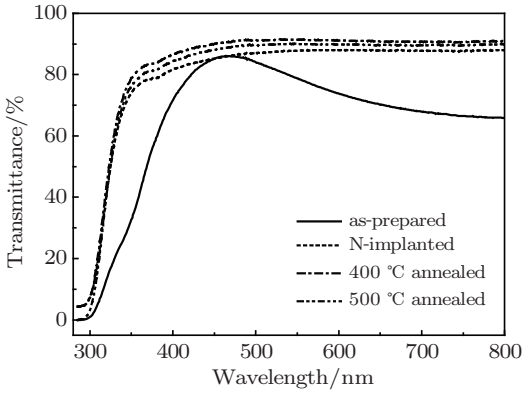



**Fig. 3.** Transmittance spectra of ZnS after N ion implantation and post-thermal annealing at different temperatures.

Figure 3 shows the influences of N ion implantation and post-thermal annealing on the optical transmittances of ZnS films. It can be seen that the average optical transmittance of the as-prepared ZnS films in the visible region is about 80%, and the optical transmittances were enhanced distinctly in the visible region by N ion implantation and post-thermal annealing. It is known that free carriers' concentration can affect the optical absorption. For ZnS films prepared by the vacuum evaporation method, a great deal of S vacancies, which

serve as donors, can be created during preparation. The introduction of the acceptor dopant of N can reduce the concentration of the donors in ZnS films. This results in the increase of the transmittance of ZnS films after N ion implantation. With post-implantation annealing, partial acceptor dopants are electrically activated, which further decreases the concentration of the donors, accompanied by a little increase of the optical transmittance of ZnS films.

In addition, N ion implantation and post-thermal annealing also have evident influences on the optical bandgaps of ZnS films as shown in Fig. 4. The optical bandgaps are determined from the conventional method.[16,17] The band gap of the as-prepared sample is about 3.06 eV. It can be seen from Fig. 4 that the optical bandgap blueshifts after N ion implantation and post-thermal annealing. As has been confirmed in the XRD analysis, the (111) diffraction peak of ZnS films was fully suppressed after N ion implantation due to the ion-beam induced lattice disorder, suggesting that the films have an amorphous nature. Many structural defects are created during the ion implantation, this can result in the redshift of the optical bandgap. Nevertheless, ion implantation can also cause an evident decrease of the crystallite size, which can result in the blueshift of the optical bandgap due to the quantum size effect.[18] Therefore, the quantum size effect may play a dominant role in the blueshift of the optical bandgap of ZnS films after N ion implantation. Further post-implantation annealing repairs the structural destruction by the ion implantation, and the defects produced in the growth process and ion implantation are annealed out, which can also lead to a blueshift of the optical bandgap. After post-ion-implantation annealing, quantum size effect does not play a dominant role due to the growth of ZnS crystallites. We can see that the optical bandgap changes very little.

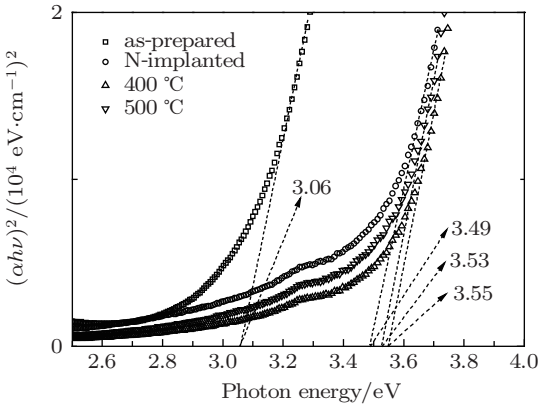



**Fig. 4.** Square of absorption coefficient as a function of incident photon energy for Zns films after N ion implantation and post-thermal annealing.

Figure 5 shows RT PL spectra of ZnS films after ion implantation and annealing at different temperatures. The shape of all the spectra, similar to those reported by others, is featured by a broad defect related deep level emission (DLE) in the visible region. However, the near band edge emission (NBE) relating to exciton in ZnS cannot be detected due to the polycrystalline structure of the samples in this study. It can be seen that all spectra exhibit two emission peaks centered at about 414 nm and 439 nm. In this work, the ZnS films are nominally undoped. Therefore, the observed two emissions must come from the transitions between the intrinsic defect levels or the intrinsic defect levels and band edge. 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 emission to the transition of $Zn_i \rightarrow V_{Zn}$ and 439-nm emission to $V_S \rightarrow$VBM, as shown in Fig. 6.

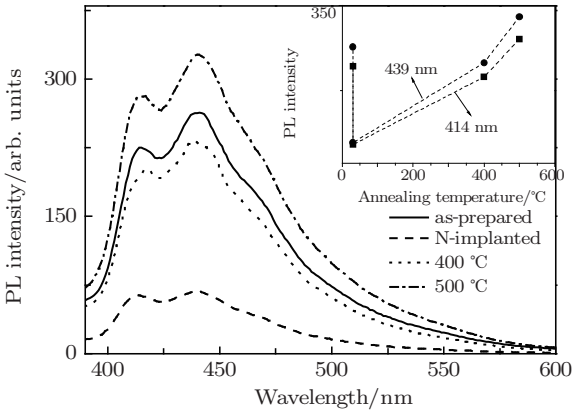



**Fig. 5.** RT PL spectra of ZnS films after N ion implantation and post-thermal annealing.

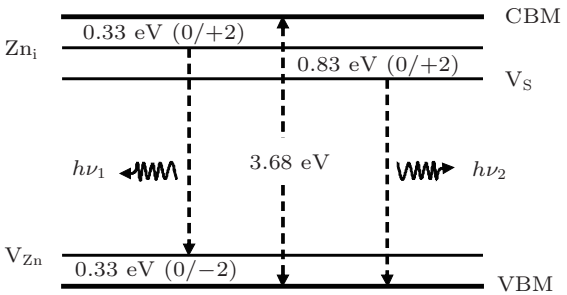



**Fig. 6.** The illustration of the intrinsic defect levels in ZnS[19] and the possible transitions between the defect levels.

The inset of Fig. 5 plots the dependence of the peak intensities of 414-nm and 439-nm emissions on the annealing temperatures. It can be seen that DLE is decreased after N ion implantation. The decreases are mainly due to the ion-beam induced defects which serve as non-radiative centers.[20] In a previous study, we found that the PL emission of ZnS can be fully extinguished by titanium ion implantation.[21] This can be explained by there being a smaller amount of destroyed lattice structure caused by light ion implantation than by heavy ion implantation. After annealing at 400 °C, DLE partially recovers due to the annealing out of the defects produced in N

ion implantation. Further annealing at 500 °C sees that DLE recovers and enhances.

Nitrogen is a desirable acceptor dopant in ZnS.[19] Several groups have reported experimental observations of p-type conduction by doping nitrogen in ZnS,[22,23] but nevertheless theoretical investigations reveal that it is not easy to dope ZnS p-type conduction in most cases due to the heavy self-compensation effect, except in the case of Zn-vacancy-rich condition.[19] To investigate the effects of N-ion-implantation and post-thermal annealing on the electrical properties of ZnS films, we measured the resistivity of ZnS at every processing stage with the four-point probe method. However, we found that the ZnS films exhibit high resistivity at all times. Though Zn vacancies produced during annealing can serve as acceptors, interstitial Zn produced simultaneously acts as a donor. Hence, the observed high resistivity of ZnS films after N ion implantation and post-thermal annealing is mainly due to the dopant not being fully electrically activated during lower temperature annealing. This suggests that higher temperature annealing is needed to obtain p-type conduction.

## 4. Conclusion

We have prepared ZnS on glass substrates by using the vacuum evaporation method. The films show the (111) preferred orientation. After N ion implantation, the (111) diffraction peak is extinguished. DLE is partially suppressed. Post-thermal annealing at 500 °C for 1 h causes the recoveries of the structural and optical properties of ZnS films. Nevertheless, ZnS films exhibit high resistivity.

## References


[1] Berginski M, Hupkes J, Schulte M, Schope G, Stiebig H, Rech B and Wuttig M 2007 *J. Appl. Phys.* **101** 074903
[2] Deulkar S H, Bhosale C H and Sharon M 2004 *J. Phys. Chem. Solids* **65** 1879
[3] Yang H, Holloway P H and Ratna B B 2003 *J. Appl. Phys.* **93** 586
[4] Shao L X, Chang K H and Hwang H L 2003 *Appl. Surf. Sci.* **212** 305
[5] Kunio I, Toshikazu O, Yoichi K, Shizuo F and Shigeo F 1994 *J. Cryst. Growth* **138** 28
[6] McLaughlin M, Sakeek H F, Maguire P, Graham W G, Molloy J, Morrow T, Laverty S and Anderson J 1993 *Appl. Phys. Lett.* **63** 1865
[7] Abounadi A, Blasio M D, Bouchara D, Calas J, Averous M, Briot O, Briot N, Cloitre T, Aulombard R L and Gil B 1994 *Phys. Rev. B* **50** 11677
[8] Vidal J, Melo de O, Vigil O, Lopez N, Contreras-Puente G and Zelaya-Angel O 2002 *Thin Solid Films* **419** 118
[9] Mohamed S H, Ei-Hagary M and Emam-Ismail M 2010 *J. Phys. D: Appl. Phys.* **43** 075401
[10] Zhang X T, Liu Y C, Zhang L G, Zhang J Y, Lu Y M, Shen D Z, Xu W, Zhong G Z, Fan X W and Kong X G 2002 *J. Appl. Phys.* **92** 3293
[11] Chaudhuri T K and Pathak B 2007 *Mater. Lett.* **61** 5243
[12] Li Y, You L, Duan R, Shi P and Qin G 2004 *Solid State Commun.* **129** 233
[13] Zhou P, Yu X, Yang L and Tao Z 2007 *Mater. Lett.* **61** 3870
[14] Chadi D J 1999 *Jpn. J. Appl. Phys.* **38** 2617
[15] Fang X S, Zhai Y T, Gautamb U K, Li L, Wu L M, Bando Y and Golberg D 2011 *Prog. Mater. Sci.* **56** 175
[16] Tauc J 1974 *Amorphous and Liquid Semiconductors* (London: Plenum) p. 159
[17] David E A and Mott N F 1970 *Phil. Mag.* **22** 903
[18] Gupta R, Han K H, Lieb K P, Muller G A, Schaaf P and Zhang K 2005 *J. Appl. Phys.* **97** 073911
[19] Gai Y Q, Li J B, Yao B and Xia J B 2009 *J. Appl. Phys.* **105** 113704
[20] Kumar S S 2006 *Nucl . Instr. Meth. Phys. Res. B* **251** 435
[21] Su H Q, Xue S W, Chen M, Li Z J, Yuan Z L, Fu Y J and Zu X T 2009 *Acta Phys. Sin.* **58** 7108 (in Chinese)
[22] Iida S, Yatabe T and Kinto H 1989 *Jpn. J. Appl. Phys.* **28** L535
[23] Yuan G D, Zhang W J, Zhang W F, Fan X, Bello I and Lee C S 2008 *Appl. Phys. Lett.* **93** 213102