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The effect of zinc encapsulation on the Zn_3P_2-related p-type diffusion in semi-insulated InP substrates

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ABSTRACT

The zinc diffusion technique has been developed as an efficient way to realize the p-type InP material for planar InP-based optoelectronic devices. Herein, Zn_3P_2-related zinc diffusion is carried out on semi-insulated InP substrates by rapid thermal annealing using a zinc film as the encapsulation. The effect of the zinc encapsulation on the p-type diffusion in InP has been investigated in detail. The effect includes both positive and negative aspects, and the related formation mechanism is also clarified.

1. Introduction

It has been proven that planar InP-based optoelectronic devices possess the advantages of higher reliability, lower noise, and higher stability compared with the mesa-type ones [1]. The zinc diffusion technique has been thus developed as an effective way to realize p-type doping in n-type InP materials for p-n junction formation, which is of great significance in developing InP-based planar optoelectronic devices [2–4]. However, during the thermal diffusion, it is accompanied by the decomposition of phosphorus from the InP material, leading to the formation of a large number of phosphorus vacancies in InP [5]. As a result, the diffused zinc atoms not only incorporate into the indium vacancies to become active impurities, but also bond with phosphorus vacancies to form neutral complexes [6]. Moreover, the probability of forming neutral complexes is higher than that of dopant incorporating into the indium vacancy during thermal diffusion, so the carrier concentration turns out to be much lower than the total concentration of diffused zinc [5]. In earlier studies, in order to prevent the decomposition of the InP material during the diffusion, it was conducted in a sealed ampoule using elemental zinc with addition of phosphorus as the dopants [7]. However, the sealed-ampoule method has the disadvantages of complex process, high cost and so on. The subsequent development of open-tube diffusion and rapid thermal annealing (RTA) processes using a zinc phosphate (Zn_3P_2) compound film as the source makes the diffusion more simple and controllable [8,9]. Unfortunately, although additional phosphorus element exists in the Zn_3P_2 source to prevent decomposition of InP, its outward evaporation during thermal diffusion still leads to inefficiency of zinc doping.

In order to prevent the outward evaporation of the Zn_3P_2 source, the insulating material such as SiO_2 or Si_3N_4 is commonly deposited on the surface of Zn_3P_2 layer as the encapsulation [10]. Although the insulating encapsulation can effectively inhibit the loss of the zinc diffusion source, the hole carrier concentration of the p-type InP obtained by RTA method still cannot meet the required concentration (over 10^{18} cm^{-3}) for forming favorable ohmic contact on it. In this letter, the Zn_3P_2-related zinc diffusion in semi-insulated InP (SI-InP) substrates is implemented by RTA method in an N_2 atmosphere. A zinc film is introduced onto the Zn_3P_2 surface as an encapsulation layer instead of the traditional insulating materials, and the effect of zinc encapsulation on the Zn_3P_2-related p-type doping in SI-InP substrates is demonstrated in detail.

2. Experimental procedure

The Zn_3P_2 film was deposited on two commercial (1 0 0)-plane SI-InP substrates by the thermal evaporation. On the Zn_3P_2 film, one was deposited a zinc film by the electron-beam evaporation, the other was deposited a SiO_2 film for comparative study. The zinc diffusion was performed at a rapid thermal annealing system, which had the advantages of rapid heating and short-term cooling. The samples were diffused for two short heating cycles in an N_2 atmosphere. During each cycle, the temperature increased from 300 to 530 °C in 20 s, kept at this temperature for 5 min, and cooled to 300 °C for 2 min. After diffusion, the

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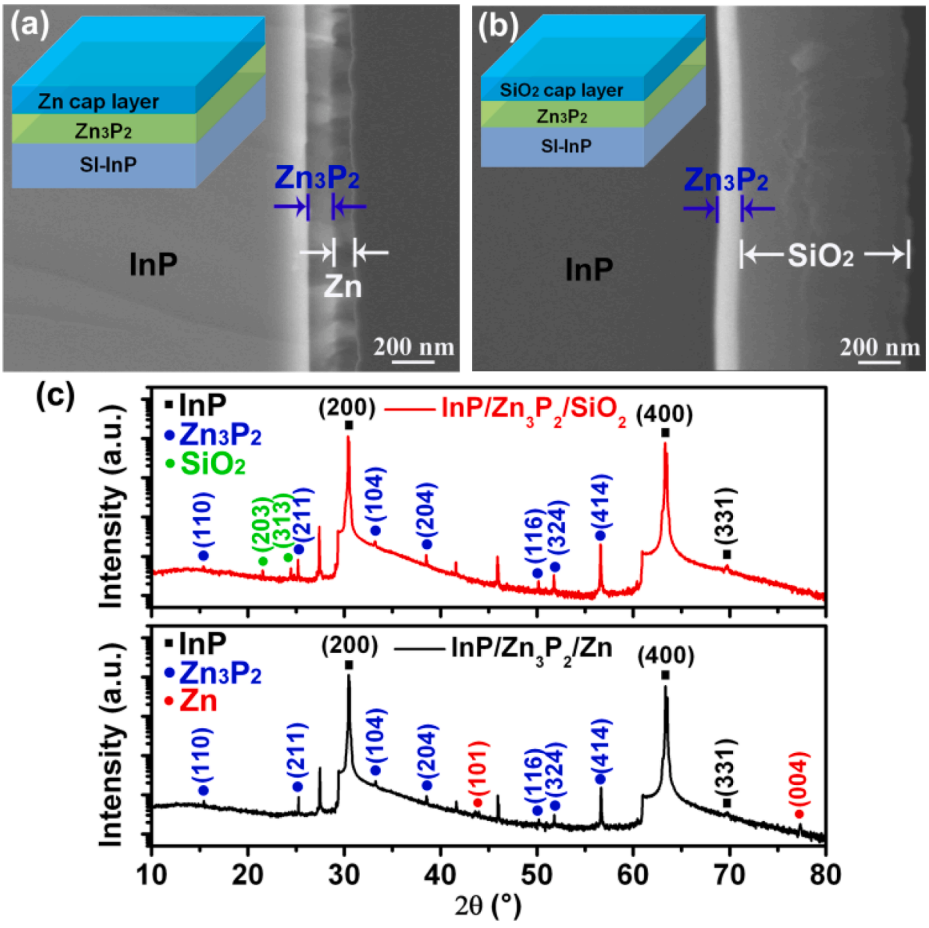

Fig. 1. The SEM cross-sectional images of (a) the InP/Zn_3P_2/Zn structure and (b) the InP/Zn_3P_2/SiO_2 structure. Each inset indicates the corresponding material structure. (c) The X-ray diffraction patterns of both structures.

remaining Zn_3P_2 or Zn_3P_2/Zn source was chemically removed by H_2SO_4:H_2O_2:H_2O (=1:1.5:5) solution at constant temperature of 40 °C. The SiO_2 film was removed by 5% HF solution.

A scanning electron microscope (SEM, Hitachi S4800) and an atomic force microscope (AFM, Veeco multi-mode) were used to characterize the surface and cross-sectional morphologies of the samples. The X-ray diffraction patterns of the two samples were characterized by an X-ray diffractometer (XRD, Bruker D8) with a Cu $K\alpha_1$ radiation of 1.5406 Å. The zinc diffusion profiles were analyzed by an electrochemical capacitance–voltage system (ECV, Nanometrics).

3. Results and discussion

Fig. 1(a) presents the SEM cross-sectional image and corresponding structure of the InP/Zn_3P_2/Zn sample. For comparison, Fig. 1(b) presents those of the InP/Zn_3P_2/SiO_2 sample. As can be seen in the cross-sectional images, both Zn_3P_2 layers are about 100 nm thick. An about 90-nm thick zinc encapsulation is used in comparison with a 700-nm thick SiO_2 encapsulation in the experiment. In order to determine the phase of the composite films, XRD method is used for qualitative analysis. Fig. 1(c) shows the XRD patterns of the two samples. The main peaks located at $2\theta = 30.453°$ and $2\theta = 63.349°$ correspond to the (200) and (400) planes of InP (JCPD card No. 65–5740), respectively. The two peaks for the InP/Zn_3P_2/Zn sample located at 44.636° and 77.335° belong to the (101) and (004) planes of the zinc film (JCPD card No. 65–5973) while the two peaks for the InP/Zn_3P_2/SiO_2 sample located at 21.542° and 24.463° belong to the (203) and (313) planes of the SiO_2 film (JCPD card No. 43–0784). Other peaks of both are the typical diffraction peaks of the Zn_3P_2 film, corresponding to (110), (211), (104), (204), (116), (324), and (414) planes (JCPD card No. 65–9488), respectively.

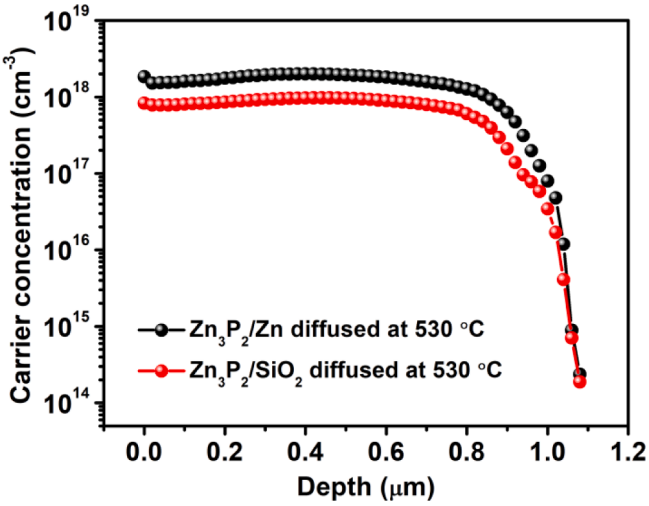

Fig. 2. Comparison of hole carrier concentration distribution in SI-InP substrates with different encapsulation layers.

To evaluate the effect of the zinc encapsulation on the Zn_3P_2-related p-type doping in SI-InP, the hole concentration profiles of the InP/Zn_3P_2/Zn and the InP/Zn_3P_2/SiO_2 samples after the RTA process are presented in Fig. 2. As can be seen, under the same diffusing conditions,

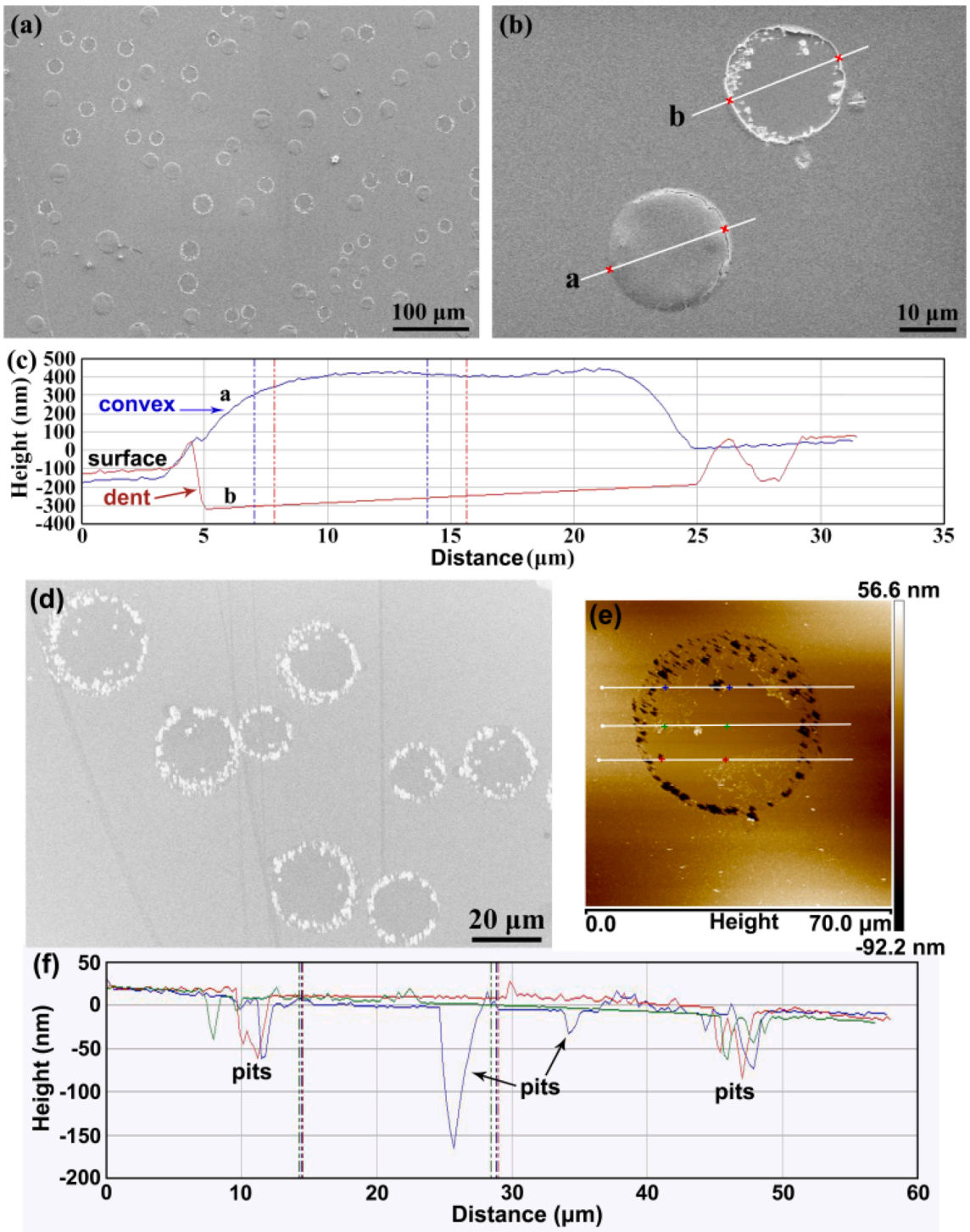

Fig. 3. (a) The surface morphology of the InP/Zn_3P_2/Zn composite material after thermal diffusion. (b) The regional enlarged image of (a). (c) The dimensions of the dent and the convex shown in (b). (d) The surface morphology of the SI-InP substrate after removing the residual Zn_3P_2/Zn composite film. (e) The AFM image corresponding to the surface of (d). (f) The dimensions of the defects in AFM image.

both samples have the same diffusion depth of about 1.1 μm. However, the doped carrier concentration is different. The hole concentration of the zinc encapsulated sample is about 10% higher than that of the SiO_2 encapsulated one. This improvement can be ascribed to the role of the zinc encapsulation, which not only inhibits the outward evaporation of the Zn_3P_2 film, but also provides an additional pure zinc source for diffusion that distinguishes itself from the SiO_2 encapsulation.

Although the positive effect of the zinc encapsulation on the Zn_3P_2-related p-type doping in the SI-InP substrate has been revealed, its negative effect cannot be ignored. The negative effect is directly reflected in the SI-InP surface damage. Fig. 3 (a) and (b) present the surface morphology and regional enlarged images of the zinc encapsulated sample after thermal diffusion. As can be seen from Fig. 3(a), before removing the residual Zn_3P_2/Zn composite film, circular dents and convexes are dispersed on its surface. These dents and convexes are formed in the Zn_3P_2/Zn composite film after the rapid thermal process. In Fig. 3(b), it zooms in to get the typical features of a dent and a convex. The lateral dimensions and shapes for both characterized by AFM are

also shown in Fig. 3(c). It can be estimated that the dent comes from the rupture of the convex film. The Zn_3P_2/Zn composite film swells during thermal treatment and forms a series of circular convexes, which can be mainly originated from the surface tension interaction between the zinc film and the Zn_3P_2 film. It is well known that the melting point of zinc is 420 °C [11]. In the process of rapid annealing at 530 °C, due to the weak van der Waals adsorption between the Zn_3P_2 film deposited by thermal evaporation and the SI-InP substrate, the zinc film shrinks immediately when the instantaneous temperature is higher than its melting point, and the resulting surface tension causes the shrinkage of the Zn_3P_2 film to form a series of convexes.

To further investigate the negative effect on the SI-InP substrate, the residual Zn_3P_2/Zn composite film is removed by wet etching method detailedly described in the experimental section. Fig. 3(d) shows the surface morphology of the SI-InP substrate after removing the residual Zn_3P_2/Zn composite film. As can be seen, the surface of the SI-InP substrate presents a series of annular imprints, which are formed at the boundaries of the convexes. An individual imprint is selected and zoomed in for detailed study, as shown in Fig. 3(e). A series of micro-pits are observed around the boundary, which is confirmed by the AFM image. In Fig. 3(f), the curves corresponding to the mark lines in Fig. 3 (e) represent the surface height distribution at different scanning positions, further proving the existence of micro-pits on the surface of the SI-InP substrate. It should be noted that the etching solution for removing the residual Zn_3P_2/Zn film is highly selective to non-target materials such as InP and has almost no damage to it, so the possibility of forming micro-pits during etching can be ruled out [12,13]. This means that the surface tension generated by the contraction of the Zn_3P_2 film induced by the shrinkage of the zinc film leads to the damage of the SI-InP substrate, and the formation of micro-pits is mainly caused by the boundary stretching interaction during the instantaneous high temperature. This damage is irreversible and will directly have a negative impact on the performance of the relevant optoelectronic devices, such as reducing the voltage resistance and increasing the leakage level.

4. Conclusions

In summary, zinc encapsulation is introduced to the Zn_3P_2-related p-type diffusion doping of SI-InP materials. Distinguished from the traditional insulating encapsulation (e.g. SiO_2), the zinc encapsulation plays a role of inhibiting the outward evaporation of Zn_3P_2 film and supplying additional pure zinc source for diffusion, resulting in the improvement of the hole carrier concentration of the diffused InP. However, conversely, there also exists a negative effect that involves the damage of the InP doping layer, which is originated from the boundary stretching interaction by surface tension generated by the contraction of the Zn_3P_2 film induced by the shrinkage of the zinc film during the instantaneous high temperature.

CRediT authorship contribution statement

Yiren Chen: Conceptualization, Methodology, Data curation, Writing – original draft. **Zhiwei Zhang:** Data curation, Methodology, Investigation. **Guoqing Miao:** Validation, Resources, Visualization. **Hong Jiang:** Project administration, Resources. **Hang Song:** Supervision, Investigation, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2022.132125.

References

[1] P. Kleinow, F. Rutz, R. Aidam, et al., Phys. Status Solidi A 213 (2016) 925–929.
[2] H. Liu, X. Wang, P. Niu, et al., IEEE Photonic Technol. Lett. 33 (2021) 503–506.
[3] J. Zhang, M.A. Itzler, H. Zbinden, J.W. Pan, Light Sci. Appl. 4 (2015), e286.
[4] A.C. Ford, S. Chuang, J.C. Ho, et al., Nano Lett. 10 (2010) 509–513.
[5] M.O. Petrushkov, M.A. Putyato, I.B. Chistokhin, B.R. Semyagin, Tech. Phys. Lett. 44 (2018) 612–614.
[6] B. Tuck, A. Hooper, J. Phys. D Appl. Phys. 8 (1975) 1806–1821.
[7] I. Yun, K. Hyun, Microelectron. J. 31 (2000) 635–639.
[8] Y. Chen, Z. Zhang, G. Miao, et al., Mater. Lett. 308 (2022), 131144.
[9] Z. Chen, M. Segev, eLight 1 (2021) 2.
[10] S. Yang, J. Yoo, Surf. Coat. Tech. 131 (2000) 66–69.
[11] L.C. Tsao, M.J. Chiang, W.H. Lin, et al., Mater. Charact. 48 (2002) 341–346.
[12] X. Duan, Y. Huang, Y. Shang, et al., Opt. Lett. 39 (2014) 2447–2450.
[13] M. Choi, I. Jung, S. Song, C.S. Kim, Mater. Sci. Semi. Proc. 120 (2020), 105252.