ISSN 1027-5495. Functional Materials, 27, No.2 (2020), p. 337-341.
doi:https://doi.org/10.15407/fm27.02.337

Effect of annealing temperature on properties of P–N co-doped ZnO films

Yupeng Xie, Xinhai Li, XianDe Wang

College of Science, Jilin Institute of Chemical Technology,
132022 Jilin, P.R. China

Received February 11, 2020

P–N co-doped ZnO films were grown on a quartz substrate by the radio-frequency magnetron sputtering technique using a mixture of N_2 and Ar gases; then the films were annealed rapidly in air. Effect of annealing temperature on structural, electrical and optical properties of the P–N co-doped films was investigated. Results indicated that the electrical properties of the films were sensitive to the annealing temperature, and the conduction type could be changed from *n*-type to *p*-type with increasing the annealing temperature from 600°C to 800°C. The P–N co-doped *p*-type ZnO film had a resistivity of 32.43 $\Omega\cdot$cm, a hole concentration of $6.09\cdot10^{17}$ cm^{-3} and a mobility of 0.78 $cm^2V^{-1}s^{-1}$, respectively. The ZnO homojunction shows a rectifying characteristic.

Keywords: ZnO, phosphorus, nitrogen, codoping, annealing temperature.

Пленки ZnO, легированные P–N, выращивались на кварцевой подложке методом радиочастотного магнетронного распыления с использованием смеси газов N_2 и Ar, затем они быстро отжигались в воздушной среде. Исследовано влияние температуры отжига на структурные, электрические и оптические свойства пленок, легированных P–N. Результаты показали, что электрические свойства пленок чувствительны к температуре отжига, тип проводимости может быть изменен с *n*-типа на *p*-тип при увеличении температуры отжига от 600 до 800°C. Пленки Z–O *p*-типа, легированные P–N, имели удельное сопротивление 32,43 Ом·см, концентрацию дырок $6{,}09\cdot10^{17}$ $см^{-3}$ и подвижность 0,78 $см^2V^{-1}с^{-1}$, соответственно. Гомопереход ZnO показывает выпрямляющую характеристику.

Вплив температури відпалу на властивості плівок ZnO, легованих P–N. *Yupeng Xie, Xinhai Li, XianDe Wang*

Плівки ZnO, леговані P–N, вирощувалися на кварційве підкладці методом радіочастотного магнетронного розпилення з використанням суміші газів N_2 і Ar, потім їх швидко відпалювали у повітряному середовищі. Досліджено вплив температури відпалу на структурні, електричні та оптичні властивості плівок, легованих P–N. Результати показали, що електричні властивості плівок чутливі до температури відпалу, тип провідності може бути змінений з *n*-типу на *p*-тип при збільшенні температури відпалу від 600 до 800°C. Плівки, що виращено, мали питомий опір 32,43 Ом·см, концентрацію дірок $6{,}09\cdot10^{17}$ $см^{-3}$ і рухливість 0,78 $см^2V^{-1}с^{-1}$ відповідно. Гомоперехід ZnO показує випрямляючу характеристику.

1. Introduction

ZnO is considered a promising material for the fabrication of optoelectronic devices like light-emitting diodes (LED) and photodetectors in the ultraviolet (UV) region, due to its wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature [1–3]. However, ZnO-based devices are difficult to fabricate due to the bottlenecks of reliable and reproducible *p*-type films. The presence of natural defects in ZnO, such as zinc interstitials (Zn_i) and oxygen vacancies (V_O), makes ZnO an intrinsically *n*-type material [4, 5]. Moreover, the low solubility of dopants, their self-compensating nature and lack of stability can further impede the preparation of *p*-type films [6, 7]. So far, many studies have successfully used elements of group V as dopants to overcome the *p*-type doping problem [8–10]. Among the group V dopants, *N* is thought to be a promising candidate, due to its oxygen-like radius and the lowest acceptor level compared to P and As [11]. However, *N* is not suitable for doping due to generation of a deep acceptor level. Therefore, acceptor-donor (In–N, B–N, Ga–N and Al–N) co-doping method is proposed to reduce the acceptor level and increase the acceptor concentration [12–15]. In addition, phosphorus-nitrogen (P–N) dual-acceptor co-doping was conducted to obtain *p*-type ZnO. Complex acceptors can significantly reduce the acceptor level and improve *p*-type conductivity in the ZnO film [16, 17]. To date, P–N co-doped ZnO films were prepared by radio-frequency (rf) magnetron sputtering and pulsed laser deposition [18, 19]. However, P–N co-doped *p*-type ZnO films prepared by rf magnetron sputtering with post-annealing in air were few reported. As is well-known, the post-annealing affects the crystal quality, electrical behavior and luminescent properties of the film. Especially, the annealing temperature can change behavior of the properties.

In this work, P–N co-doped ZnO films were deposited using a ZnO/P_2O_5 target by rf magnetron sputtering with Ar/N_2 and then annealed in air. The effect of annealing temperature on structural, electrical and optical properties of P–N co-doped ZnO films was studied.

2. Experimental

P–N co-doped ZnO thin films were grown on quartz substrates by rf sputtering using high purity Ar and N_2 as sputtering gases. The target for the films was the mixture of ZnO (99.99 %) and 2 wt % P_2O_5 (99.99 %). The quartz substrates were cleaned in an ultrasonic bath with acetone, alcohol and de-ionized water successively. A base pressure of $5\cdot10^{-4}$ Pa was provided in the growth chamber, and then sputtering gases with Ar (30 sccm) and N_2 (10 sccm) were introduced. The total working pressure was fixed at 1 Pa. The films were deposited at 500°C for 60 min with a rf power of 100 W, and then annealed in air for 5 min.

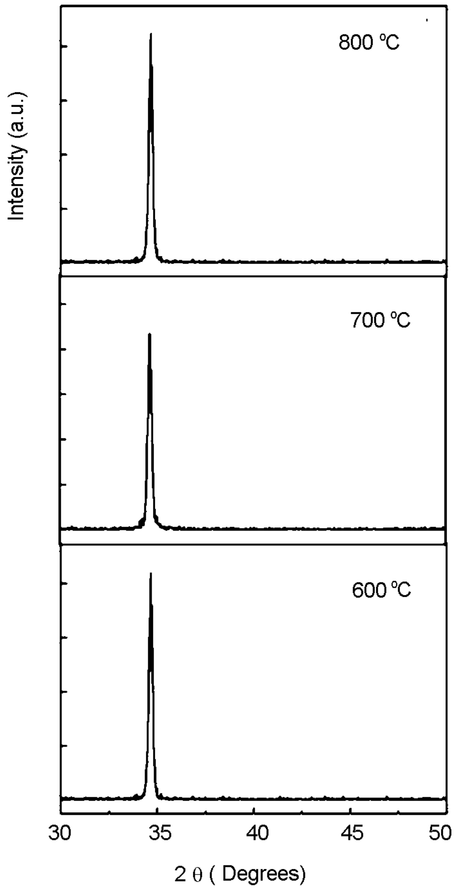

Fig. 1. XRD patterns of P–N co-doped ZnO films annealed respectively at 600°C, 700°C and 800°C.

The structural characteristics of the obtained films were examined by X-ray diffraction (XRD) with Cu $K\alpha_1$ radiation (λ) = 0.15406 nm. The electrical properties of the films were measured in the four-probe van der Pauw configuration by Hall measurements at room temperature. The depth profiles of Zn, O, P and N were investigated by secondary-ion mass-spectrometry (SIMS). Photoluminescence (PL) was carried out at room temperature with a 325 nm He–Cd laser as an excitation source.

3. Results and discussion

The XRD patterns of P–N co-doped films annealed respectively at 600°C, 700°C and 800°C under air atmosphere are shown in Fig. 1. A strong ZnO (002) peak is observed in all patterns without other peaks (e.g. P_2O_5 or Zn_3N_2), indicating that the P–N co-doped films have a good crystalline quality

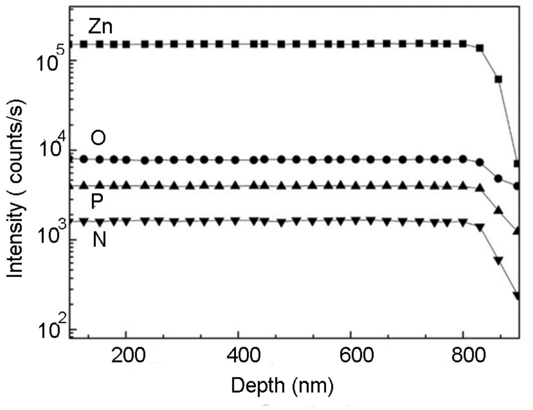

Fig. 2. SIMS depth profiles of P–N co-doped ZnO films annealed at 800°C.

and a preferred orientation along the *c* axis. With increasing the annealing temperature from 600°C to 800°C, the full-width at half-maximum (FWHM) value decreases from 0.38 to 0.29, indicating that the crystal quality of the film is improved. Meanwhile, the (002) peak gradually shifts to the higher diffraction angle with the annealing temperature increasing from 600°C to 800°C, indicating that P substitutes for a Zn site [20].

The SIMS profile curve of the P–N co-doped ZnO film annealed at 800°C is shown in Fig. 2. The film thickness estimated from the curve is about 600–700 nm. P and N can be obviously detected, and their concentrations are quite stable throughout the film depth. The results indicate that P and N were introduced into the ZnO film with a uniform distribution, which leads to the good crystal quality and *p*-type conductivity of the P–N co-doped ZnO film.

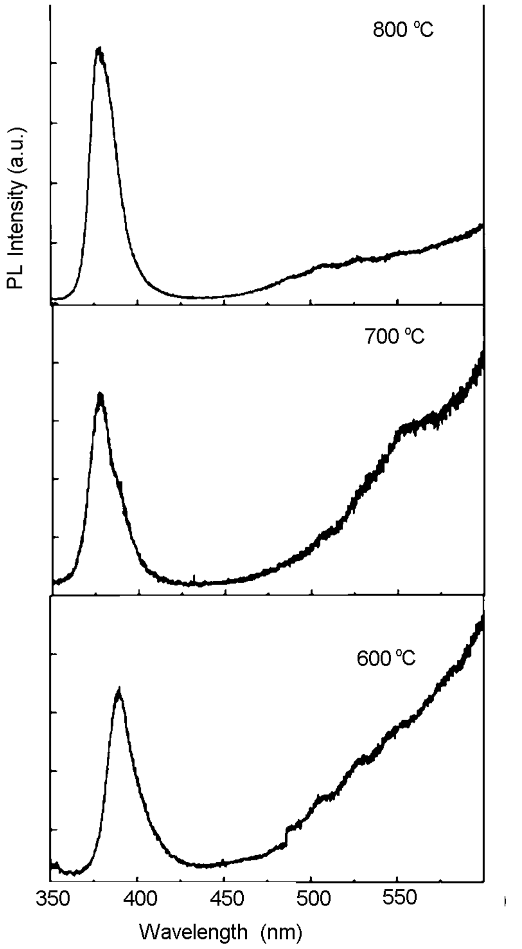

Fig. 3. Room temperature PL spectra of P–N co-doped ZnO films annealed respectively at 600°C, 700°C and 800°C.

The Hall effect measurements were conducted to test the electrical properties of the ZnO films annealed at different temperatures, and the results are listed in Table. It is apparent that the films annealed under different temperatures show different conductivity types, although these films were grown under the same conditions. Under annealing from 600°C to 800°C, the conductivity type of the films was changing from *n*-type to *n*/*p* complex types, and finally changed to *p*-type. When the annealing temperature is 600°C, the donor concentration exceeds the acceptor concentration; the conductivity type shows *n*-type. As the annealing temperature increases to 700°C, Zn and some P and N atoms (as interstitial atoms) leave the films, which leads to the dominance of the acceptor; conductivity type changes from *n*-type to *n*/*p* complex type. When annealing temperature increases to 800°C, some *N* atoms substitute for

Table. Electrical properties of P–N co-doped ZnO thin films

Annealing temperature, °C	Type	Resistivity, Ω·*cm*	Carrier concentration, cm^{-3}	Mobility, cm^2/Vs
600	In	25.70	$1.67 \cdot 10^{18}$	0.39
700	*n*/*p*	28.27	$4.69 \cdot 10^{17}$	0.35
800	*p*	32.43	$6.09 \cdot 10^{17}$	0.78

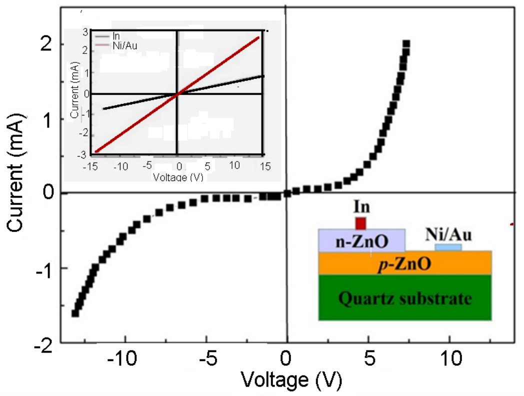

Fig. 4. I–V characteristics of homojunction composed of undoped n–ZnO and P–N co-doped p–ZnO. Lower right inset shows schematic structure of p–n homojunction. Upper left inset shows I–V characteristics of Ni/Au contact on the p–ZnO and In contact on the n–ZnO.

O(NO), these behave as acceptor dopants. In addition, P atoms substituting for Zn(P_{Zn}) are donors, but they can combine with two Zn vacancies (V_{Zn}) or four N substituting for O; that is, V_{Zn}, P_{Zn}–$2V_{Zn}$ and P_{Zn}–$4N_O$ behave also as acceptor dopants. Especially, the P_{Zn}–$4N_O$ acceptor plays an important role in obtaining P–N co-doped p-type ZnO films [18]. Therefore, the conductivity type is converted to p-type.

Fig. 3 shows the room temperature PL spectra of the P–N co-doped films deposited at 500°C and annealed respectively at 600°C, 700°C and 800°C in air. All the curves have the similar features, which contain two parts of a near-band-edge (NBE) UV emission at about 380 nm and a broad emission in the visible region. The broad emission in the visible region is attributed to the transitions from the deep level (intrinsic defects) to the valance band [21]. As shown in Fig. 3, the NBE UV exciton emission peak increases gradually with increasing the annealing temperature; meanwhile, the luminous improves, indicating that crystalline quality of the films are better. These results are in good agreement with the XRD results.

To verify the p-type conduction of the P–N co-doped ZnO films, a ZnO homojunction was synthesized by depositing an undoped n–ZnO layer on the P–N co-doped p–ZnO layer, and its I–V characterization was investigated and shown in Fig. 4. In and Ni/Au metals were respectively used as n-type and p-type electrodes which provide good Ohmic contacts, as shown in the inset of Fig. 4. As shown in Fig. 4, the I–V curves of the ZnO p–n homojunctions exhibit traditional rectifying behavior, indicating that the p-type films can be used in the optoelectronic region.

4. Conclusion

In summary, P–N co-doped ZnO films can be obtained by rf magnetron sputtering after rapid thermal annealing in air. The annealing temperature influences on the properties of the films. With increasing the annealing temperature, the conductivity of the films changes from n-type to n/p complex type, and finally changes to p-type. The P–N co-doped ZnO films have a resistivity of 32.43 Ωcm, a hole concentration of $6.09 \cdot 10^{17}$ cm^{-3} and a mobility of 0.78 cm^{2}V^{-1}s^{-1}, respectively. Meanwhile, the crystal quality of the films is improved, and the NBE UV emission peak increases with increasing annealing temperature. The rectifying characteristic can be observed in the ZnO homojunction.

Acknowledgements. The authors would like to acknowledge the financial support of Science and Technology Project of Jilin Provincial Education Department (JJKH20190832KJ) and Scientific and Technological Innovation Development Plan Project of Jilin City (201831777).

References

1. T.Aoki, Y.Shimizu, A.Miyake et al., *Phys. Stat. Solidi*, **229**, 911 (2002).
2. W.-J.Lee, J.Kang, K.Chang, *Phys. Rev. B*, **73**, 024117 (2006). doi:10.1103/PhysRevB.73.024117.
3. S.Yu, W.Zhang, L.Li et al., *Appl. Surf. Sci.*, **298**, 44 (2014). doi:10.1016/j.apsusc.2014.01.037.
4. Y.Y.Kim, W.S.Han, H.K.Cho, *Appl. Surf. Sci.*, **256**, 4438 (2010). doi:10.1016/j.apsusc.2010.01.035.
5. L.Duan, W.Zhang, X.Yu et al., *Solid State Commun.* **157**, 45 (2013). doi:10.1016/j.ssc.2012.12.029.
6. Q.J.Feng, J.Wang, S.Liu et al., *J. Phys. Chem. Solids*, **74**, 476 (2013). doi:10.1016/j.jpcs.2012.11.013.
7. H.F.Liu, S.J.Chua, *J. Cryst. Growth*, **324**, 31 (2011). doi:10.1016/j.jcrysgro.2011.03.045.
8. D.Hwang, H.Kim, J.Lim et al., *Appl. Phys. Lett.*, **86**, 15917 (2005). doi:10.1063/1.1895480.
9. D.C.Look, G.M.Renlund, R.H.Burgener, J.R.Sizelove, *Appl. Phys. Lett.*, **85**, 5269 (2004). doi:10.1063/1.1825615.
10. W.M.Cho, Y.J.Lin, C.J.Liu et al., *J. Luminescence*, **145**, 884 (2014). doi:10.1016/j.jlumin.2013.09.029.

11. Z.Yu, L.-C.Yin, Y.Xie et al., *J.Colloid Interface Sci.*, **400**, 18 (2013). doi:10.1016/j.jcis.2013.02.046.
12. M.Duta, S.Mihaiu, C.Munteanu et al., *Appl. Surf.Sci.*, **344**, 196 (2015). doi:10.1016/j.apsusc.2015.03.123.
13. T.K.Pathak, V.Kumar, L.P.Purohit, *Optik (Stuttg).*, **127**, 603 (2016). doi:10.1016/j.ijleo.2015.10.013.
14. Y.R.Sui, B.Yao, L.Xiao et al., *Thin Solid Films*, **520**, 5914 (2012). doi:10.1016/j.tsf.2012.04.076.
15. N.Gopalakrishnan, B.C.Shin, H.S.Lim et al., *J.Cryst.Growth*, **294**, 273 (2006). doi:10.1016/j.jcrysgro.2006.06.045.
16. Y.R.Sui, B.Yao, L.Xiao et al., *Appl.Surf.Sci.*, **287**, 484 (2013). doi:10.1016/j.apsusc.2013.10.010.
17. R.Mannam, S.K.Eswaran, N.Dasgupta, M.S.R.Rao, *Appl.Surf.Sci.*, **347**, 96 (2015). doi:10.1016/j.apsusc.2015.04.057.
18. Y.Sui, B.Yao, L.Xiao et al., *J.Appl.Phys.*, 113 (2013). doi:10.1063/1.4798605.
19. R.Mannam, E.S.Kumar, N.DasGupta, M.S.Ramachandra Rao, *Appl.Surf.Sci.*, **400**, 312 (2017). doi:10.1016/j.apsusc.2016.12.146.
20. Y.P.Xie, X.D.Wang, C.Lang, *Surf.Eng.*, **31**, 770 (2015). doi:10.1179/1743294415Y.0000000024.
21. P.Zu, Z.K.Tang, G.K.L.Wong et al., *Solid State Commun.*, **103**, 459 (1997). doi:10.1016/S0038-1098(97)00216-0.