P-type ZnO thin films prepared by *in situ* oxidation of DC sputtered Zn_3N_2:Ga*

Zhang Jun(张军)[1,2], Xue Shuwen(薛书文)[1,2], and Shao Lexi(邵乐喜)[1,2,†]

(1 School of Physical Science and Technology, Zhanjiang Normal University, Zhanjiang 524048, China)
(2 Development Center for New Materials Engineering & Technology, Universities of Guangdong, Zhanjiang 524048, China)

Abstract: The feasibility of a new fabrication route for N and Ga codoped p-type ZnO thin films on glass substrates, consisting of DC sputtering deposition of Zn_3N_2:Ga precursors followed by *in situ* oxidation in high purity oxygen, has been studied. The effects of oxidation temperature on the structural, optical and electrical properties of the samples were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), optical transmittance and Hall effect measurements. The results were compared to a control film without Ga. XRD analyses revealed that the Zn_3N_2 films entirely transformed into ZnO films after annealing Zn_3N_2 films in oxygen over 500 °C for 2 h. Hall effect measurements confirmed p-type conduction in N and Ga codoped ZnO films with a low resistivity of 19.8 Ω·cm, a high hole concentration of 4.6×10^{18} cm^{-3} and a Hall mobility of 0.7 cm^2/(V·s). These results demonstrate a promising approach to fabricate low resistivity p-type ZnO with high hole concentration.

Key words: p-type; ZnO films; Zn_3N_2 films; codoping; magnetron sputtering
DOI: 10.1088/1674-4926/31/4/043001 **EEACC:** 2520

1. Introduction

Zinc compounds have been the subject of intensive research and development efforts during recent decades because of their wide direct bandgaps and potential applications to visible and UV optoelectronic technologies. Among them, zinc oxide (ZnO) has important application potential owing to its unique properties. Its wide bandgap of 3.37 eV and exciton binding energy of 60 meV at room temperature make ZnO suitable for short wavelength opto-electronic devices, including light-emitting diodes (LEDs), laser diodes (LDs) and room-temperature UV laser devices[1, 2]. To realize the light-emitting devices, an important task is the fabrication of p-type ZnO with a high hole concentration, high mobility and a low resistance. Thus, recent ZnO research has been focused on the synthesis of p-type ZnO using various techniques and dopants[3]. It has been suggested that p-type doping in ZnO can be achieved by substituting either group-I elements, such as Li, Na, and K, for Zn sites or group-V elements, like N, P, As, and Sb, for O sites[4−8]. Among these possible dopants for p-type ZnO, N is thought to be the most promising candidate, which has a similar ionic radius to oxygen[9]. By now, many groups have been engaged in the investigations on nitrogen doped p-type ZnO. They have fabricated p-type ZnO thin films by the thermal oxidation of zinc nitride grown by plasma enhanced chemical vapour deposition or by reactive sputtering from elemental Zn target in N_2–Ar plasma. When Zn_3N_2 films are thermally annealed in O_2 ambient, a part of the N atoms in Zn_3N_2 films are replaced by O atoms to form ZnO and the residual N atoms will act as a source of active nitrogen for doping ZnO with acceptor species. However, hydrogen, which acts as a shallow donor in ZnO, often makes it difficult to obtain p-type conduction in ZnO with these methods. So, controlling the conductivity of ZnO requires careful control of hydrogen exposure. In addition, a co-doping method to enhance the acceptor incorporation by simultaneously doping with acceptors (e.g., N) and donors (e.g., Al, Ga, or In) has been proposed, which has drawn intensive attention in recent years[11, 12].

In this paper, DC planar magnetron sputtering was employed to prepare polycrystalline Zn_3N_2:Ga thin films on glass using a metallic zinc disc with Ga grain as the target. After the deposition, the precursors were then oxidized in situ at various temperatures by introducing pure oxygen directly into the deposition chamber. A control sample without Ga was grown by the same route as described above. The physical properties of the two films were investigated. The microstructure and morphology of the films were studied by X-ray diffraction and scanning electron microscopy. Optical and electrical characterizations were performed to obtain the absorption coefficient, carrier concentration and Hall mobility.

2. Experimental procedure

Zn_3N_2:Ga films were prepared on glass substrates by a reactive magnetron sputter process with a conventional sputter set-up. The background pressure of the sputtering chamber was evacuated below 6.6×10^{-4} Pa with a rotary pump and a turbo molecular pump. The substrates were ultrasonically cleaned in acetone for 15 min, in alcohol for 10 min, rinsed in distilled water, and dried in a hot air flow. A metallic zinc disc (purity: 99.999%) with a diameter of 60 mm was used as the target. The different numbers of Ga grain (the diameter is about 2 mm) were put on the zinc disc. The Ga contents of about 0.1 at.% in the resulting films can be calculated from the bare area and the sputtering rate of Ga grain and zinc disc. The target–substrate distance was maintained at 65 mm. Before deposition, the target was sputter-etched in Ar plasma for 30 min to remove target

* Project supported by the National Natural Science Foundation of China (No. 10574106), the Natural Science Foundation of Guangdong Province, China (No. 8452404801021), and the Natural Science Foundation of Zhanjiang Normal University, China (No. 200801).
† Corresponding author. Email: shaolxmail@163.com
Received 9 December 2009
© 2010 Chinese Institute of Electronics

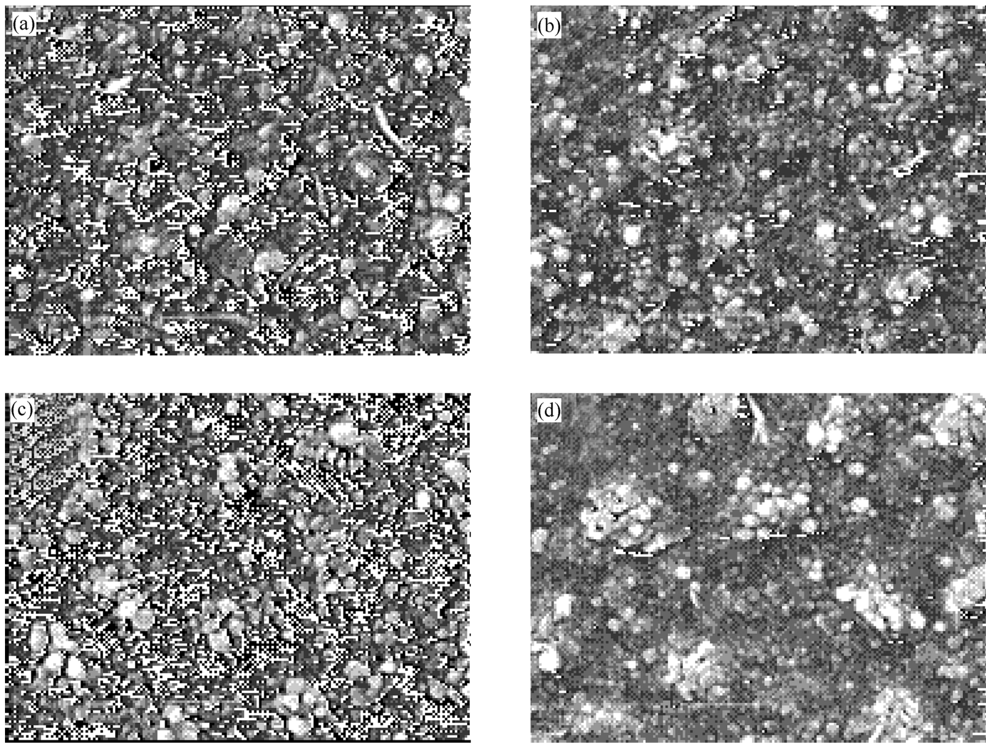

Fig. 1. SEM images of the as-deposited films with and without Ga grains at different temperatures. (a) Without Ga grains at room temperature. (b) Without Ga grains at 200 °C. (c) With 1 Ga grain at room temperature. (d) With 1 Ga grain at 200 °C.

contamination. N_2–Ar mixtures were used as sputtering ambient. The N_2 and Ar gases were introduced into the sputtering chamber through separate mass flow controllers, and the total flow rate was regulated to 40 sccm. The total pressure was kept at 2 Pa. The substrates were heated by a substrate heater set behind the substrate holder and the substrates temperature was estimated from a thermolabel fixed beside the samples. The N_2 concentration was maintained at 50% in the sputtering gas. The substrate temperatures were set at room temperature and 200 °C. The sputtering time was 30 min and the DC power was kept at 120 W. After deposition, the mass flow controllers of N_2 and Ar gases were turned off. The background pressure of the sputtering chamber was evacuated below 1×10^{-4} Pa again. High purity O_2 gas (99.999%) was introduced into the sputtering chamber. The oxidization temperatures were maintained in the range of 500–550 °C for 2 h, respectively. After oxidation, the sample was cooled down to the ambient temperature in the sputtering chamber.

X-ray diffraction (XRD) (Rigaku D/Max-IIIC) analyses were performed to investigate the crystallographic properties. The wavelength of the X-ray beam is 0.1542 nm. The surface morphologies and thickness of the thin films were characterized by SEM (Hitachi S4800). In order to avoid the charge build-up during SEM observations, the samples were coated with gold. The electrical properties of the films were examined by Hall effect measurements using the van der Pauw configuration. The ohmic contacts were fabricated by evaporating aluminium at the four symmetrical corners of the samples, followed by annealing at 350 °C in N_2 flow for one hour. Optical transmission spectra were measured with a double beam UV-VIS spectrometer (UV-3000). Absorption coefficients were calculated from the transmission spectrum with the

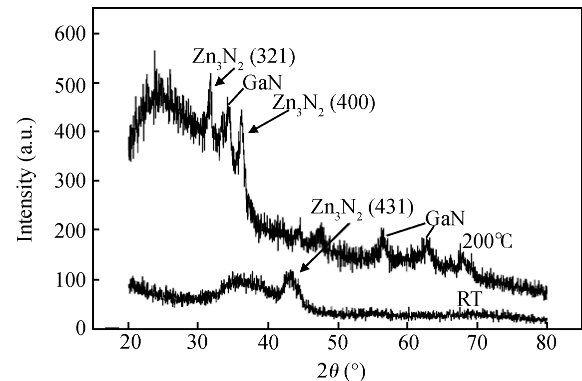

Fig. 2. XRD spectra of samples sputtered at different temperatures with Ga grain.

film thickness. All the above measurements were conducted at room temperature.

3. Results and discussions

To optimize the properties of Zn_3N_2 as a starting material for the fabrication of ZnO, we studied the effects of substrate temperatures on the composition and structure of the deposited films. The films were deposited at various substrate temperatures when the N_2 concentration was maintained at 50% in the sputtering gas. Figure 1 shows the typical SEM images of the as-deposited films with or without Ga grains at different temperatures. It can be seen that the films are composed of uniform particles.

Figure 2 shows the XRD patterns of the films prepared at various substrate temperatures. It can be seen that the Zn_3N_2

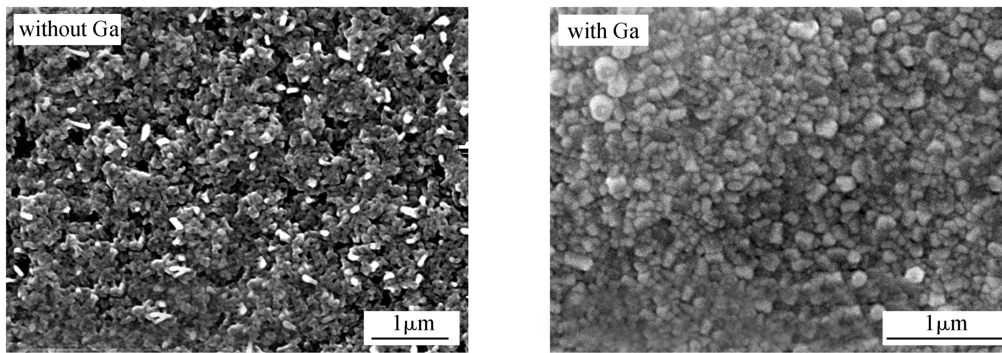

Fig. 3. SEM images of the films oxidized at 550 °C.

Table 1. Electrical properties of ZnO:N and ZnO:(N,Ga) films.

Oxidization temperature (°C)	Resistivity (Ω·cm)	Mobility (cm^2/ (V·s))	Carrier concentration (cm^{-3})	Conduction type	Remark
500	1444.2	1.15	$+6.537 \times 10^{16}$	p	ZnO:N
550	703.6	1.32	$+1.201 \times 10^{17}$	p	ZnO:N
500	253.6	0.32	$+4.201 \times 10^{17}$	p	ZnO:(N,Ga)
550	19.8	0.7	$+4.632 \times 10^{18}$	p	ZnO:(N,Ga)

(431) peak at 2θ = 43.78° appeared in the patterns when the films were deposited at room temperature, which indicated that the deposited Zn_3N_2 thin films were polycrystalline. No secondary phase is observed in XRD spectra, suggesting that no extra phase of Ga was identified in the XRD spectra for the sample. As the substrate temperature increased to 200 °C, sharp peaks in the orientation (321), and (400) are observed. Meanwhile, other little peaks which are the diffraction peaks of GaN can also be seen.

Figure 3 shows the typical SEM images of the films with or without Ga grains oxidized at 550 °C. It can be seen that the surface morphology of the films changes significantly after oxidation, and many nano-grains form on the surfaces of the films. The average diameter of the grains is estimated to be 100 nm.

The crystallinity and orientation of the ZnO thin films were investigated by XRD. Figure 4 shows the XRD spectrum of the films with Ga grain oxidized at 550 °C. In the XRD pattern, the diffraction peaks of ZnO appeared and the Zn_3N_2 and GaN peaks disappear after oxidization, which indicates that the Zn_3N_2 has been completely transformed to ZnO at this stage. It can be also seen from Fig. 4 that the films show a strong peak at 2θ = 36.3°, which corresponds to the (101) diffraction peak of hexagonal ZnO. In addition, some weak peaks at 2θ = 31.9°, 34.4°, 47.5°, 56.6°, and 63.2° also appear in the XRD patterns. These peaks can be attributed to (100), (200), (102), (110) and (103) diffraction peaks of the hexagonal polycrystalline ZnO, respectively.

Electrical property measurements, including resistivity, carrier concentration, and Hall mobility, were performed on the Hall effect measurement system with a magnetic field strength of 0.51 T using the van der Pauw method at RT. Before electrical measurements, ohmic contacts were fabricated by evaporating aluminium at the four symmetrical corners of the samples, followed by annealing at 350 °C in N_2 flow for one

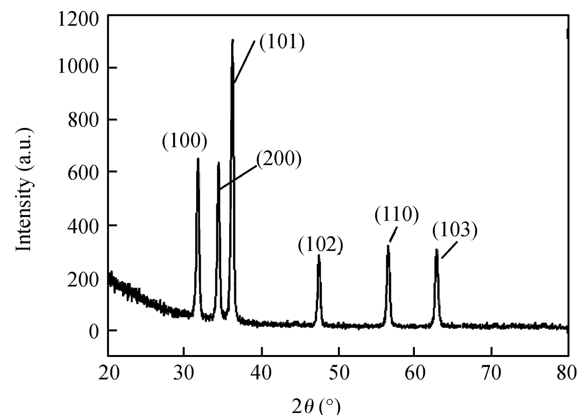

Fig. 4. XRD spectrum of samples with Ga grains oxidized at 550 °C.

hour. P-type ZnO films were obtained by oxidizing Zn_3N_2 and Zn_3N_2:Ga in oxygen atmosphere at 500 °C and 550 °C for 2 h. The sample doped with Ga possesses relative good electrical properties: low resistivity (19.8 Ω·cm), larger hole carrier concentration ($10^{18}cm^{-3}$), moderate Hall mobility (0.7 cm^2/(V·s)). All the films exhibit p-type conductivity. As compared with that of the ZnO:N (about $10^{16}cm^{-3}$), the hole concentrations of ZnO:(Ga,N) are remarkably enhanced. The increase of carrier concentration could be ascribed to the presence of Ga in the films. Thus, the Ga content plays an important role in the p-type behaviours of ZnO. The atomic N would react with Ga to form the GaN precipitates. The concentration of NO can be greatly increased due to the existence of Ga. It is noted that the NO complex acceptor has a shallower energy level than N acceptors. This may be the answer for the realization of good p-type ZnO by the Ga/N co-doping method. The carrier mobility of Ga+N codoped ZnO is only 0.7 cm^2/(V·s) may be due to the inherent defects of GaN.

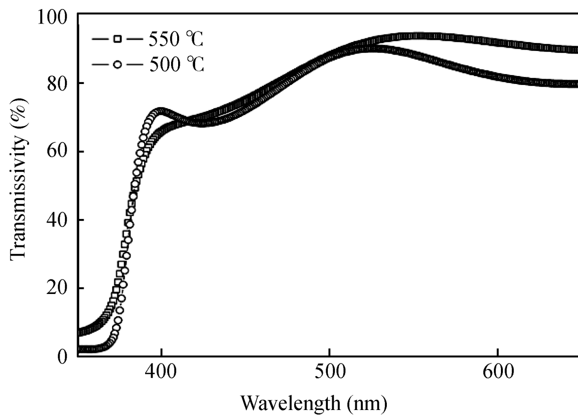

Fig. 5. Transmission spectra of the films oxidized at different temperatures.

The optical properties of the films oxidized at different temperatures are characterized by transmission spectra measured in the wavelength range of 250–900 nm. Figure 5 shows the transmission spectra of the films oxidized at different temperatures. It can be seen that the fundamental absorption edge locates at around 380 nm. The films are highly transparent in the visible region and the average transmittance is over 85%. The optical bandgaps can be determined from a conventional method. It is found that oxidation temperature has evident influences on the optical bandgaps of the films.

4. Conclusion

P-type conduction in N and Ga codoped ZnO films with a low resistivity of 19.8 Ω·cm, a high hole concentration of 4.6×10^{18} cm^{-3} and a Hall mobility of 0.7 $cm^2/(V\cdot s)$ were realized by in situ oxidation of DC sputtered Zn_3N_2:Ga films. These results demonstrate a promising approach to fabricate low resistivity p-type ZnO with high hole concentration. The new technique developed in this work also has many advantages than other methods for fabrication of low resistivity p-type ZnO films, such as easiness in large-area fabrication, high reliability in control processing and no contamination from carbon and hydrogen, and must play a more important role in industrial fields of the ZnO based short wavelength device in the future.

References

[1] Tang Z K, Wong G K L, Yu P. Room-temperature ultraviolet laser emission from self-assembled ZnO microcrystallite thin films. Appl Phys Lett, 1998, 72: 3270

[2] Dzieck E P, Kamiska E, Pasternak I, et al. Photoluminescence study of p-type ZnO:Sb prepared by thermal oxidation of the Zn–Sb starting material. Phys Rev B, 2007, 76: 193303

[3] Futsuhara M, Yoshioka K, Takai O. Structural, electrical and optical properties of zinc nitride thin films prepared by reactive RF magnetron sputtering. Thin Solid Films, 1998, 322: 274

[4] Bian J M, Li X M, Zhang C Y, et al. P-type ZnO films by monodoping of nitrogen and ZnO-based p–n homojunctions. Appl Phys Lett, 2004, 85: 4070

[5] Ji Z, Yang C, Liu K, et al. Fabrication and characterization of p-type ZnO films by pyrolysis of zinc-acetate–ammonia solution. J Cryst Growth, 2003, 253: 239

[6] Ye Z Z, Lu J G, Chen H H, et al. Preparation and characteristics of p-type ZnO films by DC reactive magnetron sputtering. J Cryst Growth, 2003, 253: 258

[7] Look D C, Reynolds D C, Litton C W, et al. Characterization of homoepitaxial p-type ZnO grown by molecular beam epitaxy. Appl Phys Lett, 2002, 81: 1830

[8] Kaminska E, Piotrowska A, Kossut J, et al. Transparent p-type ZnO films obtained by oxidation of sputter-deposited Zn_3N_2. Solid State Commun, 2005, 135: 11

[9] Guo X L, Tabata H, Kawai T. Pulsed laser reactive deposition of p-type ZnO film enhanced by an electron cyclotron resonance source. J Cryst Growth, 2001, 223: 135

[10] Kambilafka V, Voulgaropoulou P, Dounis S, et al. The effect of nitrogen on the properties of zinc nitride thin films and their conversion into p-ZnO:N films. Thin Solid Films, 2007, 515: 8573

[11] Wang C, Ji Z, Liu K, et al. p-type ZnO thin films prepared by oxidation of Zn_3N_2 thin films deposited by DC magnetron sputtering. J Cryst Growth, 2003, 259: 279

[12] Janotti A, van de Walle C G. Fundamentals of zinc oxide as a semiconductor. Rep Prog Phys, 2009, 72: 126501