

Reproducibility and stability of N–Al codoped *p*-type ZnO thin films

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Reproducible and stable *p*-type ZnO thin films have been prepared by the N–Al codoping method. Secondary ion mass spectroscopy measurements demonstrate that N and Al are incorporated into ZnO. The resistivity, carrier concentration, and Hall mobility are typically of 50–100 Ωcm , 1×10^{17} – $8 \times 10^{17} \text{ cm}^{-3}$, and 0.1–0.6 cm^2/Vs , respectively, for the N–Al codoped *p*-type ZnO films. Hall measurement, X-ray diffraction, and optical transmission were carried out to investigate the changes of the properties with the storage period. Results show that the *p*-type characteristics of the N–Al codoped ZnO films are of acceptable reproducibility and stability. In addition, the N–Al codoped *p*-type ZnO films have good crystallinity and optical quality. The properties are time independent. © 2006 Springer Science + Business Media, Inc.

Zinc oxide (ZnO) is a novel compound semiconductor with a direct wide-bandgap of 3.37 eV at room temperature. Recently, it has attracted considerable attention as a potential material for applications in short-wavelength optoelectronic devices, such as light emitting diodes (LEDs) and laser diodes (LDs), due to its large exciton binding energy (60 meV, as compared with 25 meV for GaN and 20 meV for ZnSe) and high optical gain (320 cm^{-1}) at room temperature [1]. For the development of ZnO-based devices, it is necessary to obtain *p*- and *n*-type ZnO. However, ZnO occurs naturally as *n*-type conduction; it is rather difficult to realize *p*-type conduction due to the asymmetric doping limitations. Among possible acceptor dopants, nitrogen was predicted in theory as the best candidate [2]. Considerable efforts have been made to realize *p*-type ZnO by doping nitrogen, but the *p*-type conduction obtained commonly suggests poor reproducibility and stability, the *p*-type conduction sometimes disappearing over period [3–8]. One interesting suggestion, from theoretical analysis, is that “codoping” may be useful in solving the problem [8, 9]. Simultaneous doping with acceptors (e.g., N) and donors (e.g., Al, Ga, or In) will decrease the Madelung energy due to the formation of such N–III–N complex (III = Al, Ga, or In) in ZnO, which enhances the incorporation of N in ZnO and gives rise to a shallower N-acceptor level in the band gap. Moreover, the formation of N–III–N complex can also be expected to stabilize the

properties of *p*-type ZnO films. The growth of codoped *p*-type ZnO has emerged in the recent literatures, indicating the success with this method, such as codoping with nitrogen and gallium (N–Ga) [10, 11], nitrogen and indium (N–In) [12], and nitrogen and aluminum (N–Al) [13, 14]. However, the reproducibility and stability of the codoped ZnO films have not been investigated so far.

In our previous work, *p*-type conduction in ZnO films has been realized by using the N–Al codoping approach [13, 14]. N–Al codoped ZnO films were prepared by dc reactive magnetron sputtering in N_2O or $\text{N}_2\text{O-O}_2$ ambient. Compared with Ga and In, Al has lots of advantages, for example, it is inexpensive and environmentally friendly. In addition, the most important is that the codoping with N–Al should be of the best stability among various codoping techniques, since the corresponding III–N and III–O bonds are strongest for III = Al [8]. The aim of this study is to gain insight into the reproducibility and stability of the properties of the N–Al codoped *p*-type ZnO thin films.

N–Al codoped ZnO films were prepared on glass substrates by dc reactive magnetron sputtering. The target was a disc of Zn metal (99.99% purity) mixed with 0.15 wt% Al (99.99% purity). The chamber was evacuated to a base vacuum of 10^{-3} Pa , and then the sputtering gas, high purity N_2O (99.99%), was introduced into it. The working pressure was kept at about 5 Pa. N_2O acts as both oxygen source and nitrogen doping source. During the

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TABLE I Electrical properties of N-Al codoped ZnO films deposited on glass substrates under the same conditions

Sample no.	Resistivity (Ωcm)	Hall mobility ($\text{cm}^2/\text{V s}$)	Carrier concentration (cm^{-3})	Type
1	6.93e+01	0.210	4.27e+17	<i>p</i>
2	9.43e+01	0.087	7.56e+17	<i>p</i>
3	5.73e+01	0.432	2.52e+17	<i>p</i>
4	8.90e+01	0.201	3.49e+17	<i>p</i>
5	8.47e+01	0.624	1.25e+17	<i>p</i>

deposition process, the substrate temperature was maintained at 500°C according to our optimized results [13, 14]. Films were deposited for 30 min with a sputtering power of 54 W (180V \times 0.3A). Five samples were fabricated under the same conditions as mentioned above, and then measurements were carried out in time to testify the reproducibility of the codoped ZnO films. In order to further investigate the stability of films, the measurements of electrical, structural, and optical properties were also conducted over various periods. Those samples were kept in an ordinary silica-gel desiccator at room temperature under atmospheric conditions.

The structural properties were analyzed by X-ray diffraction (XRD) using a Bede D1 system with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm). The electrical properties were examined by Hall measurements in the van der Pauw configuration (HL5500PC) at room temperature. The optical properties were characterized by transmission spectra with a CARY 100 spectrophotometer. Secondary ion mass spectroscopy (SIMS, CAMECA IMS-6f) was used to investigate the depth profile of main elements in the codoped film.

Table I summarizes the Hall effect measurements for the five samples (labeled as Sample Nos. 1–5, respectively) deposited on glass substrates under the same conditions. The measurements were carried out without delay after film deposition. All the codoped films showed *p*-type

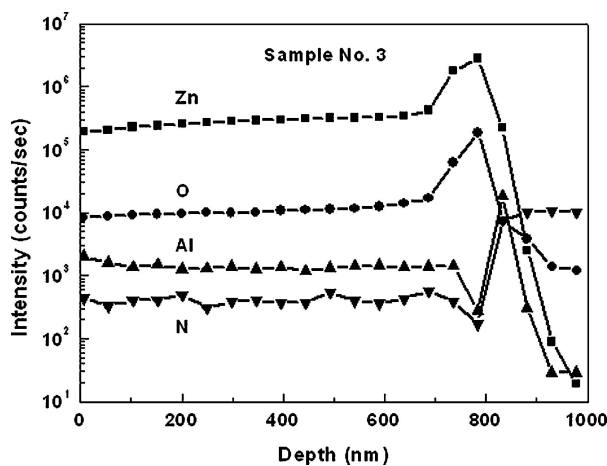


Figure 1 SIMS depth profiles of Zn, O, N, and Al in the N-Al codoped ZnO film (Sample no. 3).

conduction, and much the same results were obtained. The resistivity, carrier concentration, and Hall mobility are typically 50–100 Ωcm , 1×10^{17} – 8×10^{17} cm^{-3} , and 0.1–0.6 cm^2/Vs , respectively. The results suggest the *p*-type conduction is of good reproducibility for the N-Al codoped ZnO films, which is much better than that reported for the *p*-type ZnO films by doping with nitrogen alone [3–8].

SIMS is a very powerful tool for the microdetection of elements, having the ability to measure several ppm order of concentration. It was used in our experiment to testify the presence of nitrogen and aluminum in ZnO. Fig. 1 illustrates the typical depth profiles of the main elements in the N-Al codoped ZnO film (Sample No. 3). The film thickness is about 750 nm. We cannot get the absolute values of the concentrations of N and Al in the codoped ZnO film due to that the standard specimen could not be prepared. However, SIMS measurements clearly indicate that nitrogen and aluminum have been incorporated into ZnO. The distributions of Zn, O, Al, and N are uniform along the film depth. The simultaneous codoping of N and Al is believed to be responsible for the good *p*-type conduction and the reproducibility of the properties for the N-Al codoped ZnO films.

To investigate the stability, Hall measurements were also carried out over various periods for every sample obtained here, respectively. Much at the same tendency was observed with increasing the storage period. Table II lists the electrical properties conducted over a period of 0, 10, 50, 180, and 360 day(s), respectively, after film deposition for the Sample No. 3. They are accordingly named as Serial Nos. 3.1–3.5. It should point out that the Hall data for Serial No. 3.1 are the same as those shown in Table I for Sample No. 3. From Table II, it can be confirmed that as the storage period increases, instead of disappearing for the *p*-type conduction, it shows a good stability. The *p*-type characteristics were still well maintained even after being aged over one year. In contrary, our investigations found that the *p*-type behavior was not stable for the ZnO films by doping with nitrogen alone; their *p*-type conduction was commonly degraded or even disappeared after being aged over three months, which is similar to those recent reports [8, 9]. Therefore, we can conclude that the N-Al codoping method is an effective approach to achieve stable *p*-type ZnO films.

TABLE II Time-dependence of electrical properties for the N-Al codoped ZnO film (Sample No. 3)

Serial no.	Storage period (day(s))	Resistivity (Ωcm)	Hall mobility ($\text{cm}^2/\text{V s}$)	Carrier concentration (cm^{-3})	Type
3.1	0	5.73e+01	0.432	2.52e+17	<i>p</i>
3.2	10	5.58e+01	0.447	2.49e+17	<i>p</i>
3.3	50	4.98e+01	0.412	3.02e+17	<i>p</i>
3.4	180	4.85e+01	0.518	2.47e+17	<i>p</i>
3.5	360	4.12e+01	0.582	2.58e+17	<i>p</i>

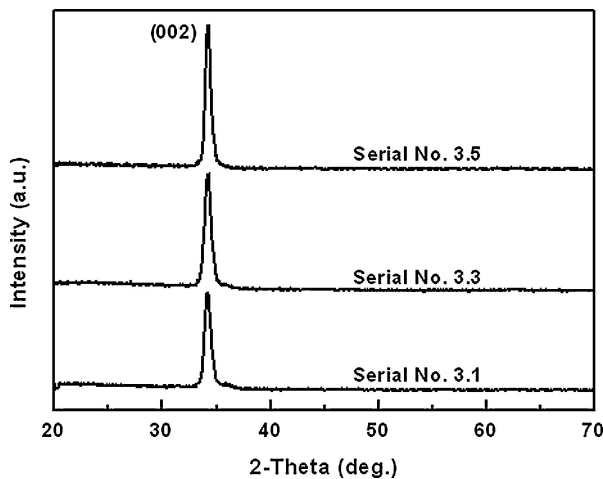


Figure 2 X-ray diffraction profiles of the N–Al codoped ZnO film (Sample No. 3) with its storage period of 0 day (Serial no. 3.1), 50 days (Serial no. 3.3) and 360 days (Serial No. 3.5).

Fig. 2 illustrates the XRD profiles corresponding to Serial Nos. 3.1, 3.3, and 3.5 for the N–Al codoped *p*-type ZnO film (Sample No. 3). Only one peak corresponding to the (002) plane of ZnO is observed in the profile, and no other phases (e.g., AlN, Al₂O₃, or Zn₃N₂) are detected in the film. These suggest that the as-grown *p*-type ZnO film possesses a good crystallinity with a high *c*-axis orientation. In addition, the full width at half-maximum (FWHM) and the 2θ values of the (002) diffraction peak are also investigated. For all the XRD patterns, the FWHM values are in the range of 0.37–0.39°, and the 2θ values are in the range of 34.18–34.25°. The variations are all within the measurement error range. Thus, there should be no change in the XRD patterns, both position and shape, was observed even after being aged over one year, indicating that the structural properties are time independent.

Fig. 3 shows the transmission spectra of Serial Nos. 3.1, 3.3, and 3.5 for the N–Al codoped *p*-type ZnO film

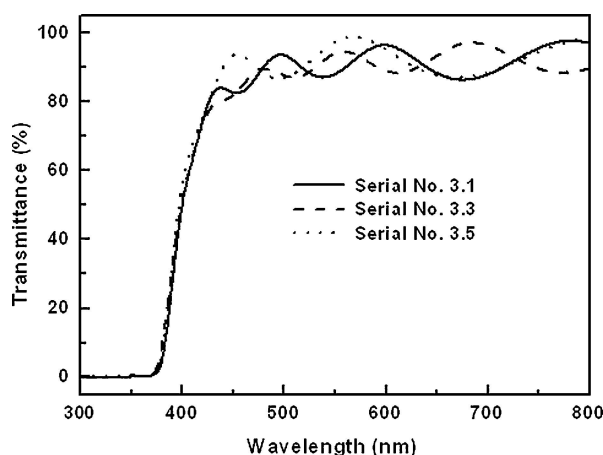


Figure 3 Transmittance spectra of the N–Al codoped ZnO film (Sample No. 3) with its storage period of 0 day (Serial No. 3.1), 50 days (Serial No. 3.3) and 360 days (Serial No. 3.5).

(Sample No. 3). There is also no visible effect of storage period on the optical properties. A high transmittance about 90% in the visible region and a sharp fundamental absorption edge about 395 nm are observed in the spectra. These results are comparable to those reported of Al-doped *n*-type ZnO [15], which is indispensable to provide a transparent *p*-*n* junction. The fundamental adsorption in the transmission spectra corresponds to electron excitation from valance band to conductive band, which can be used to calculate the value of optical band gap of the ZnO film [16]. The band gap E_g is determined to be about 3.12 eV for the N–Al codoped *p*-type ZnO film, lower than that for the intrinsic ZnO (3.37 eV). These optical properties can be well maintained and also show no time dependence.

In summary, we have presented a method to realize reproducible and stable *p*-type ZnO films by codoping with nitrogen and aluminum. The N–Al codoped *p*-type ZnO films obtained by this technique also possess good crystal quality and optical quality. The reproducibility and stability of *p*-type ZnO is the precondition for its applications in various fields. Thus, the advancement presented here certainly will open the door to the fabrication of ZnO-based optoelectronic devices, including LEDs and LDs. There is still room for optimization in both the growth and processing conditions to improve the *p*-type conductivity, and so better properties can be expected in the near future.

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