# Nitridation of Zinc Oxide Film by Pulse Mode Rapid Thermal Annealing

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#### Abstract

In this work, a zinc oxide (ZnO) film deposited at room temperature was subjected to pulse mode rapid thermal annealing at N<sub>2</sub> ambient ie. "nitridation". Then a p-type ZnO film with stable hole-conduction was obtained. A good rectified curve for p-type ZnO/n-Si and linear current-voltage curve for p-type ZnO/p-Si were achieved. The carrier concentration, mobility and resistivity of ZnO:N film in this study were  $1.39 \times 10^{16}$  cm<sup>-3</sup>, 9.5 cm<sup>2</sup>/ V · s and 47.45  $\Omega$ -cm, respectively.

#### 1. Introduction

Recently, ZnO has attracted attention for the fabrication of short-wavelength light emitting diodes (LEDs).[1] Conventionally, the native defects such as zinc interstitials and oxygen vacancies are related to the n-type conduction of ZnO.[2] It is also important to prepare p-type ZnO. However, several issues limit the preparation of p-type ZnO including low dopant solubility, deep acceptor level, and the "self-compensation" of shallow acceptors.[3]

The nitrogen (N) was often used as an acceptor for ZnO (ZnO:N). However, it was difficult to produce p-type conduction repeatedly. J. L. Lyons et al.[4] proposed that N atom nay act as deep acceptor in ZnO. In this study, we used pulse mode rapid thermal annealing (PRTA) to perform nitridation on ZnO:N film to obtain stable p-type conduction.

#### 2. Experimental Procedure

The preparation of ZnO:N film is as follow. First, the ZnO film was deposited on a glass substrate by sputtering the ZnO target (99.995% purity) within a gas mixture of 20 sccm argon (Ar) and 18 sccm nitrogen (N<sub>2</sub>). The deposition temperature, power and pressure were 27 °C, 56 W and  $5 \times 10^{-3}$  Torr, respectively. Next, the as-deposited ZnO:N film was subjected to pulse mode rapid thermal annealing process at N<sub>2</sub>, 570 °C for 5 pulses (the duration time was 5 s/pulse).

#### 3. Results and Discussion

Figure 1 compares the Raman spectra of nitrided and as-deposited ZnO:N and intrinsic ZnO films. A. Kaschner et al. have proposed that the local vibration signals of 275 and 582 cm<sup>-1</sup> are related to the N atom in ZnO:N single crystal bulk.[5] There is no N-related signal observed in the intrinsic ZnO film. On the other hand, the signals of 271.7, 275.1, 576.2 and 579.6 cm<sup>-1</sup> in ZnO:N film verify that the

N atoms are indeed introduced into ZnO film. Comparing with ref. 5, the N-related signals of as-deposited ZnO:N film exhibit shifts of 3.3 and 5.8 cm<sup>-1</sup> away from those of ZnO:N single crystal bulk. It prevails that the bonding between as-deposited ZnO and N atoms is weak. As for nitrided ZnO:N, the N-related signals of 275.1 and 579.3 cm<sup>-1</sup> shows good bonding between ZnO and N atoms.

The SEM images in Fig. 2 show the surface morphology of as-deposited and nitrided ZnO:N films. It is found that the nitrided ZnO:N is crystallized. Besides, ZnO single crystal bulk exhibits a signal of 34.44° in XRD image corresponding to preferential orientation of (002).[6] In Fig. 3, the peak of ZnO:N shifts from 33.86° (as-deposited ZnO) to 34.38° (nitrided ZnO:N) reflects that the physical structure is improved and approaches the ideal ZnO single crystal bulk by nitridation process.

Table I lists the physical properties of various ZnO:N films. The nitridation results in improved carrier concentration and mobility for ZnO:N, which are increased from  $2.72 \times 10^{14}$  to  $1.39 \times 10^{16}$  cm<sup>-3</sup> and 2.09 to 9.50 cm<sup>2</sup>/V · s, respectively. Such an improvement shows that the dopants are activated within ZnO film. The resistivity of ZnO:N film after nitridation process was decreased from  $1.11 \times 10^4$  to  $47.45 \Omega$ -cm.

Finally, the electrical characteristics of nitrided ZnO:N are evaluated in Fig. 4 and 5. A good rectified I-V characteristics with turn-on voltage of 2.25 V is achieved for nitrided ZnO:N/n-Si (Fig. 4). Besides, another linear I-V characteristics of nitrided ZnO:N/p-Si is also observed within small voltage range in Fig.5, which prevails that these introduced N atom may be thought as shallow acceptors in nitrided ZnO:N film.

## 4. Conclusions

We have successfully complete nitridation of the ZnO film to produce p-type ZnO. The bonding between ZnO and N atom was improved by pulse mode rapid thermal annealing. The thermal budget provided by nitridation not only activated the dopant but also drive the processed film being crystallized. The carrier concentration, mobility and resistivity of nitrided ZnO:N were  $1.39 \times 10^{16}$  cm<sup>-3</sup>, 9.5 cm<sup>2</sup>/ V  $\cdot$  s and 47.45  $\Omega$ -cm, respectively.

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### References

- [1] D. K. Hwang, M. S. Oh, J. H. Lim, and S. J. Park: J. Phys. D 40 (2007) R387.
- [2] S. B. Zhang, S. H. Wei, and A. Zunger: Phys. Rev. B 63 (2001) 075205.
- [3] C. H. Park, S. B. Zhang, and S. H. Wei: Phys. Rev. B 66 (2002) 073202.
- [4] J. L. Lyons, A. Janotti, and C. G. Van de Walle: Appl. Phys. Lett. 95 (2009) 252105.
- [5] A. Kaschner, U. Haboeck, M. Strassburg, M. Strassburg, G. Kaczmarczyk, A. Hoffmann, and C. Thomsen: Appl. Phys. Lett. 80 (2002) 1909.
- [6] M. S. Oh, D. K. Hwang, Y. S. Choi, J. W. Kang, S. J. Park, C. S. Hwang, and K. I. Cho: Appl. Phys. Lett. 93 (2008) 111905.

Table I. Electrical properties of various ZnO:N films.

Sample	Carrier concentration	Hall mobility	Resistivity	Grain size
as-deposited ZnO:N	$2.72 \times 10^{14} \mathrm{~cm^{-3}}$	2.09 cm <sup>2</sup> /V • s	$1.11 \times 10^4 \ \Omega$ -cm	20 nm
nitrided ZnO:N	$1.39 \times 10^{16} \text{ cm}^{-3}$	9.50 cm <sup>2</sup> /V • s	47.45 <b>Ω-c</b> m	75 nm



Fig. 1. Raman spectra of various ZnO:N films and intrinsic ZnO.





Fig. 2. SEM images of (a) as-deposited and (b) nitrided ZnO:N.



Fig. 3. XRD images of as-deposited and nitrided ZnO:N films.



Fig. 4. I-V curve of nitrided ZnO:N/n-Si (100).



Fig. 5. I-V curve of nitrided ZnO:N/p-Si (100).