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Fabrication of Nitrogen Doped p-ZnO and ZnO Light-Emitting Diodes on Sapphire

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Nitrogen-doped p-type ZnO thin films were grown on c-plane sapphire (Al_2O_3) substrates by plasma-assistant molecular beam epitaxy, where O_2 and N_2 were introduced via a RF plasma source simultaneously. In situ optical emission spectra of the plasma were employed to monitor the chemical species in the active gas sources, one of the most important growth parameters. By adjusting the growth parameters, we confirm the optimal condition for p-type doping growth. The reproducible p-type ZnO thin films have the hole concentration ($N_A - N_D$) up to $1.0 \times 10^{18} \text{ cm}^{-3}$ and the resistivity of $6 \Omega\text{cm}$. A ZnO LED was fabricated by depositing undoped n-type ZnO on the p-type layer. Electroluminescence spectra centered about 430 nm were obtained even at 350 K.

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I. INTRODUCTION

Since room temperature ultraviolet (UV) stimulated emissions from ZnO thin films have been reported [1], ZnO is now gathering more and more attention for the applications on short wavelength lasers. For realizing the current injection for ZnO-based devices, it is necessary to obtain high-quality ZnO thin films with p-type as well as n-type conductivity. N was established as one of the most soluble group-V impurity. Theoretical calculation predicts that N is an outstanding candidate in current research for p-type doping of ZnO [2]. Potential nitrogen dopant sources include N_2O , N_2 , NO_2 , NO and NH_3 , etc. [3~7]. P-type conductivity ZnO have been fabricated by using NO and N_2 doping, and the electroluminescence (EL) from the p-n junction based on these p-type ZnO was obtained [5,6]. Efficient acceptor doping into ZnO is still a great challenge to achieve controllable p-type dop-

Nitrogen on c-plane molecular substrate to remove (160 °C) was rinsed the blow clean and heated for 30 min under an effusion C₆₀ at 99.999 MHz) at 500 °C for 1 h. The pressure in the Zn beam chamber was fixed by flow of (mass flow rate ratio of 1.0:1.0). The samples were produced to a SiO_2 thickness of 0.154 μm by ellipsometry. The X-ray diffraction patterns were measured with a Philips XRD-6000 diffractometer. The Hall effect was measured with a Hall effect measurement system (EG&G 5500) at 300 K. The optical properties were measured with a Varian V-630 spectrophotometer. The electrical properties were measured with a Keithley 2400 source meter. The atomic force microscopy (AFM) images were obtained with a Nanosurf Nanoscope IIIA instrument. The micrographs of the surface morphology were taken with a JEOL JSM-6360LV scanning electron microscope (SEM).

It really need a detail understand on the nitrogen containing species responsible for ZnO:N formation or an explanation for the wide disparity in nitrogen-doping results.

The purpose of this paper is to optimize the growth condition for efficient nitrogen doping as shallow acceptor. N_2 gas was used as a doping source and was mixed with O_2 gas in a radical source during ZnO growth. In situ optical emission spectra (OES) were measured to ascertain the chemical species in the plasma. The dependences of electric and optical properties upon the chemical species, which changed with the flow ratio of N_2/O_2 , are studied. Additionally, by analyzing the optical emission spectra of radical N_2 and N_2/O_2 mixture in detail, the possible formation mechanism of p-type ZnO can be discussed. The ZnO thin films with maximum hole carrier concentration ($N_A - N_D$) of $1.0 \times 10^{18} \text{ cm}^{-3}$ and resistivity of $6 \Omega\text{cm}$ were obtained. The realization of p-ZnO in our experiment by employing radical N_2 as N dopant seems to open the door for p-type ZnO using N dopant. A ZnO LED was fabricated by depositing

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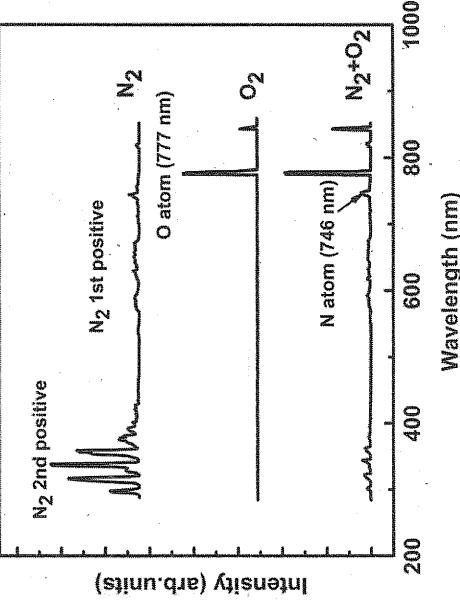


Fig. 1. The optical emission spectra from the plasma of different gas.

Nitrogen-doped p-type ZnO thin films were grown on c-plane sapphire (Al_2O_3) substrates using plasma-molecular beam epitaxy (P-MBE) by simultaneously introducing O_2 and N_2 via a RF plasma source. The substrate was treated by using ethanol in an ultrasonic bath to remove surface contamination, was etched in a hot (160 °C) $\text{H}_2\text{SO}_4:\text{H}_3\text{PO}_4 = 3:1$ solution for 10 minutes, was rinsed in deionized water ($18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$), and was blown dry by using high-purity nitrogen. To obtain a clean and highly crystallized surface, the substrate was heated in vacuum ($\leq 1 \times 10^{-7} \text{ mbar}$) at 800 °C for 30 min in the MBE pretreatment chamber. A Knudsen effusion cell is used to evaporate elemental zinc with 99.999 % purity. The gas sources were activated by using an Oxford Applied Research Model HD25 r.f. (13.56 MHz) atomic source. An electrostatic ion trap operating at 500 V during growth process was employed to suppress interference of ion in the plasma. During growth, Zn beam partial pressure was kept at $4 \times 10^{-6} \text{ mbar}$ by fixed the source temperature at about 245 °C. The flow of O_2 gas and N_2 gas was controlled using separate mass flow controller (MFC) but both gases were simultaneously injected into a single RF plasma. Three samples were prepared at 425 °C using different O_2/N_2 flow rate ratio gas source. The OES of plasma were introduced to the optical spectrometer using a fiber through a SiO_2 window of the rear part of the plasma cell. The thicknesses of all the three obtained samples measured by ellipsometry are about 200 nm.

The crystal structure of sample was characterized by X-ray diffraction (XRD) with Cu $\text{K}_{\alpha 1}$ radiation ($\lambda = 0.15406 \text{ nm}$). The electrical properties of as-grown samples were measured by Hall analysis in the Van der Pauw configuration at room temperature by using a magnetic field of 3200 Gauss and a current automatically set by the Hall system (LakeShore).

III. RESULTS AND DISCUSSION

In order to realize the p-type doping of ZnO, the native donor defects must be compensated. Under proper conditions, it is expected to form nitrogen substitution at the oxygen site (N_O) in ZnO, which is a single shallow acceptor. However, in many cases, ZnO films doped with nitrogen source led to n-type, but not p-type conduction. Yan et al. predict that it is difficult to break N-N bond, so the $(\text{N}_2)_\text{O}$, a shallow double donor in ZnO, was easily formed [8]. It is an important reason why doping with N_2

or N_2O leading to the p-type conducting of ZnO looks so difficult. Generally, a plasma source was used to enhance the dissociation of N_2 . In the present work, a detailed study on the OES from nitrogen-plasmas produced by an Oxford Applied Research radio frequency plasma source was performed to find the optimal experimental condition. The higher plasma power and lower gas pressure can enhance the dissociation degree of N_2 , and similar results were reported in reference [9]. We also find the enhancement of N_2 dissociation degree by mixing with O_2 gas. The OES confirm that the higher N_2 dissociation degree can be obtained at optimal plasma condition.

1. Nitrogen Atoms - Plasma Power and Pressure Dependence

Information about the nitrogen-plasma species responsible for the successful p-type doping, and the optimization of this desired species, are fundamentally important to the pursuit of higher p-type doping levels and improving performance of ZnO light emitting devices [10].

The inductively-coupled 13.56 MHz input energy which generates the nitrogen-plasmas was varied from 200 to 400 W. A variable leak valve was used to carefully control the flow of N_2 gas into the RF plasma source such that the MBE chamber pressure was varied from 1.0×10^{-6} to $5.0 \times 10^{-5} \text{ mbar}$. These conditions provided a variety of stable nitrogen-plasmas for the species analysis.

A representative OES from the Oxford RF plasma source operated at 300 W and $2 \times 10^{-5} \text{ mbar}$ is shown in Figure 1. A variety of nitrogen-plasma emission peaks span the measured spectral region, including emissions from the first-positive and second-positive series transitions of the neutral N_2 molecule, and weak atomic lines at 746 nm [11].

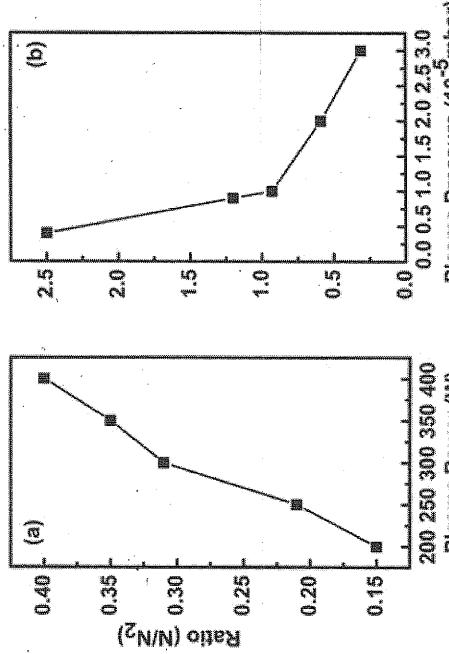


Fig. 2. (a) The effects of dissociation related to the plasma power changing (b) The effects of dissociation related to the N_2 gas flow rate changing.

A series of emission scans recorded from the RF plasma source are measured as the source input power is increased from 200 to 400 W. The MBE chamber pressure was held at 3×10^{-5} mbar. The evolvement of the emission intensity ratio of N atom (represented by 746 nm spectrum) to N_2 (represented by 337 nm spectrum, which is the strongest line of N_2 spectra) is shown in Figure 3(a). The ratio is augmented with increasing the input powers. Besides the intensity increase, the atomic nitrogen emission was found to increase more quickly than the molecular bands. This trend suggests that larger input power brings more efficient breaking of the nitrogen molecules, which generate more nitrogen atoms.

Figure 3(b) shows the effects on dissociation related to changing the N_2 gas flow rate. The input power was adjusted at 300 W. As the N_2 gas flow rate decreases, the overall intensity of the emission is depressed. However, the atomic emission decreases slower than the molecular emission, so the emission ratio increases with decreasing the gas flow rate. It is because that reducing the N_2 gas flow, which reduces the pressure, decreases the probability that two atoms will collide within the plasma and recombine to form molecular N_2 , hence favoring the net generation of atomic nitrogen [12]. Thus, low-pressure and high-power nitrogen-plasmas generate a higher amount of nitrogen atoms in plasma of the gas source.

Comparing to the gas flow rate, *i.e.* pressure of the plasma, the input power influence on the ratio of plasma species was limited. The pressure at 6×10^{-6} mbar and the power at 300 W was believed to be the preferable growth condition.

2. Nitrogen Atoms - Mixture Composition Dependence

However, it is obvious that dissociation degree is still too low for p-type growth even in optimized condition.

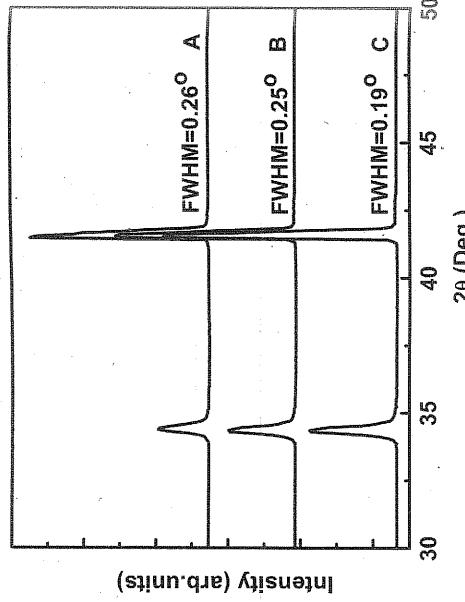


Fig. 3. The XRD spectra of the three samples (labeled as A, B and C).

Figure 1 shows the OES spectrum obtained from the plasma of N_2 and mixture gas with different composition with the chamber pressure fixed at 6×10^{-6} mbar and the power held at 300 W. The dissociation ratio of nitrogen in the O_2 - N_2 mixture gas plasma was enhanced significantly as same as the hydrogen or argon introducing in the plasma. [13,14].

For the O_2 - N_2 gas mixture, the O atomic peaks around 777, and 841 nm were observed clearly, the intensities of the N-related emissions appear stronger compared to those of pure N_2 . The intensity ratio between the nitrogen atomic emission at 746 nm and the nitrogen molecule emission at 337 nm increases obviously. The most received reaction pathways discussed in the literature for the dissociation ratio of nitrogen in mixture gas plasma are enhanced in reactions (1)–(3).



When the plasma is generated in pure N_2 , the dissociation ratio is small due to the highly stable N_2 bond (the N_2 dissociation energy is bigger as 9.60 eV) [15]. While the O_2 dissociation energy is only 5.6 eV [16], so the dissociation of O_2 is easier. When the mixture gas introduced into the plasma firstly, a mount of O atoms and electrons are produced in the plasma, which accelerates the reaction (2), (3) by impacting with N_2 . No emission from NO was detected in this system because NO emit primarily in the deep UV [17].

The emission spectrum in Figure 1(c) is dominated by the sharp atomic nitrogen emission peaks at 746, 821, 869 nm. It indicates that co-activation of O_2 - N_2 mixture is a practicable technology for producing an appreciable flux of neutral nitrogen atoms. Therefore, the O_2 - N_2 mixture was used in the growth of p-type ZnO .

Table 1. Plasma spectra properties and Electrical properties of ZnO films grown by different O₂/N₂ ratio.

Sample	Gas O ₂ :N ₂	N ₂ :N	N:O	Carrier type	Resistivity Ω·cm	Mobility cmV ⁻¹ s ⁻¹	Carrier concentration(cm ⁻³)
A	1:2	1:2.0	1:3	n	1200	0.20	2.4 × 10 ¹⁶
B	1:1	1:2.5	1:5	p	1410	0.53	8.4 × 10 ¹⁵
C	2:1	1:3.5	1:8	p	5.83	0.94	1.2 × 10 ¹⁸

3. ZnO Film Properties

Precise control of supply ratio is essential for epitaxial growth of compound semiconductors, especially for low temperature growth. For nitrogen-doped p-type ZnO growth, the nitrogen/oxygen ratio is very important. The optimized ratio can supply enough oxygen to reduce the intrinsic defect, and assure a certain N-doping level at the same time.

ZnO:N films were grown by different O₂/N₂ flow rate mixed gas. To ascertain the best ratio, the OES spectra were measured at various O₂/N₂ flow ratio. The total flow rate was fixed at 0.45 sccm and the O₂ and N₂ flow rate was changed with the O₂/N₂ flow rate ratio fixed at 1/2, 1/1, 2/1. In these conditions, the pressure of growth chamber was held at 4 × 10⁻⁶ mbar. The RF power was 300 W for all the growth processes. The samples are labeled as A, B and C, respectively.

Table 1 shows the N/N₂, N/O ratio of plasma source and electrical properties of the films with different O₂/N₂ flow rate ratio. In the case of high nitrogen content, the sample shows n-type conduction with carrier concentration of 2.4 × 10¹⁶ cm⁻³ and mobility of 0.2 cm²V⁻¹s⁻¹. Besides the desirable acceptors N_O, large amounts of (N₂)_O and intrinsic defects (V_O, etc.) also exist in the film, which are donor impurity. When O₂/N₂ flow rate ratio was decreased to 1:1, the mobility increase to 0.53 cm²V⁻¹s⁻¹ and carrier conductivity become to p-type (1) with hole concentration 8.4 × 10¹⁵ cm⁻³, which means the crystal quality was improved and donor impurity (2) (N₂)_O, V_O was depressed in a certain degree. When (3) O₂/N₂ flow rate ratio fixed at 2/1, Sample C shows p-type with carrier concentration of 1.2 × 10¹⁸ cm⁻³ and mobility of 0.94 cm²V⁻¹s⁻¹. The improvement of the sample crystal quality can be testified by the X-ray diffraction (XRD) measurements. As shown in Figure 3, the full width at half maximum (FWHM) of these samples are 0.26°, 0.25°, 0.19°, respectively. Sample C has the best crystal quality. It shows that the growth parameters for Sample C are a set of parameters for p-type ZnO emit growth.

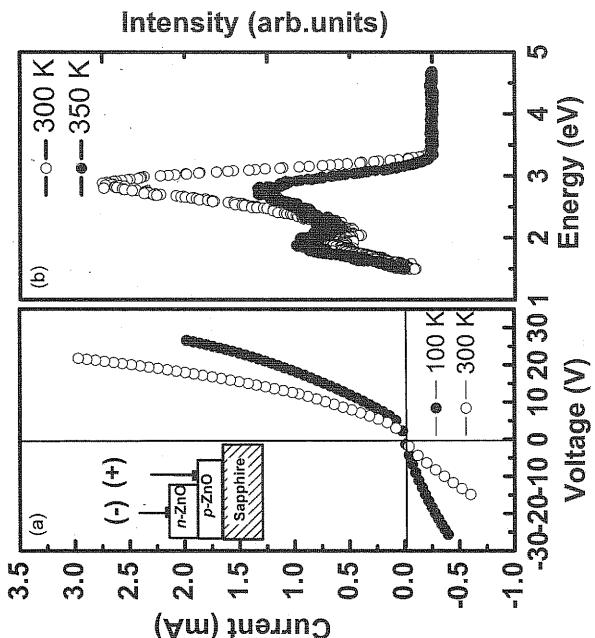


Fig. 4. (a) The I-V curve measured at 100 and 300 K. Inset is the LED structure sketched (b) The EL spectrum measured at 300 and 350 K.

sketched in inset of Figure 4(a). The electron concentration and mobility of the n-type layer are at 10¹⁸ cm⁻³ or 40 cm²V⁻¹s⁻¹, respectively. Indium and Ni-Au electrodes were used to obtain Ohmic contacts to the n-type and p-type layers, respectively. The I-V curve measured at about 100 and 300 K is shown in Figure 4(a). As seen, the LED shows a clear rectification effect. The turn on voltage is about 4.0 V, which approaches the band gap of ZnO. Figure 4(b) is the EL spectrum measured at about 300 and 350 K. At 300 K, the EL spectrum is dominated by the emission band in the blue-violet region (2.84 eV) with an emission band in the red region (1.92 eV). With increasing temperature to 350 K, the blue-violet emission band slightly shifted from 2.84 to 2.75 eV, accompanied with decrease in emission intensity, and the whole spectrum was gradually dominated by the red emission band. The EL can even be observed at 400 K by naked eye.

4. Electroluminescence from ZnO LED

A p-n junction LED was fabricated by directly covering an undoped n-type ZnO film on the p-type layer by masking an area for electrode. The LED structure is

IV. CONCLUSION

By adjusting the plasma condition, the Nitrogen-doped p-type ZnO thin films were grown on c-plane sapphire (Al₂O₃) substrates by plasma-assistant molecular

beam epitaxy (P-MBE) by simultaneously introducing O₂ and N₂ via a RF plasma source. In situ optical emission spectra (OES) from the plasma were characterized the chemical species in the gas source plasma, one of the most important growth parameters for p-type doping for ZnO. It confirms that p-type ZnO can be obtained through depressing (N₂)₀ defect in optimal condition. Electroluminescence spectra centered about 430 nm were obtained from the ZnO LED fabricated by the p-type layer even above 350 K.

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With a binding energy of 1.6 eV, it is considered that short-wavelength ultraviolet LEDs with p-type Zn_xAl_{1-x} has larger bandgap than n-type Zn_xAl_{1-x} with a wider bandgap.

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