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Dominant Factor Determining the Conduction-Type of Nitrogen-Doped ZnO Film

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Nitrogen-doped zinc oxide (ZnO) film has been grown by molecular beam epitaxy. The as-grown sample showed *p*-type conduction with a hole concentration of 3.1×10^{17} cm^{-3}. After an annealing process in O_2 at 600 °C for 30 min, *p*-type conduction was still remained, and the hole concentration of the film decreased to 6.8×10^{16} cm^{-3}. Secondary ion mass spectroscopy revealed that the concentration of both nitrogen and hydrogen decreased after the annealing process. It is demonstrated that the intrinsic compensation source has been decreased after the annealing process. Because the variation trend of the hole concentration in the ZnO:N film is opposite to that of hydrogen and intrinsic defects, but in good accordance with nitrogen, the extrinsically substituted nitrogen (N_O) should be the dominant factor that determines the conduction-type of the ZnO:N film.

Keywords: Molecular Beam Epitaxy, ZnO, Doping, SIMS.

1. INTRODUCTION

Due to its large exciton binding energy (60 meV) and wide direct bandgap (3.37 eV), ZnO has attracted much attention for its potential applications in solar cells,[1,2] biomedical,[3,4] transistors,[5–7] especially short wavelength optoelectronic devices, such as light-emitting-devices, laser diodes, and photodetectors, etc.[8–15] However, such applications are drastically hindered by the difficulty in achieving *p*-type ZnO. In recent years, many efforts have been devoted to fabricating *p*-type ZnO using different dopants, such as group I elements (Li, Na), group V elements (N, P, As, Sb) or co-doped groups I–V elements (Li–N).[15,16] Amongst these dopants, nitrogen (N) has been considered as one of the effective candidates for the *p*-type doping of ZnO both theoretically and experimentally.[17,18] However, the reproducibility of *N*-doped *p*-type ZnO films is still far from acceptable. The main complications that prevent the formation of reproducible *p*-ZnO have been ascribed to hydrogen or intrinsic donors. Some groups[19–24] demonstrated that hydrogen acts as a hole "killer" that passivates or compensates acceptors in ZnO:N, and it can be removed from the film via an annealing process at 600 °C or above.[25–27] Meanwhile, intrinsic donors, such as oxygen vacancy (V_O) and interstitial zinc (Zn_i), have also been considered as compensation source that prevents the formation of *p*-ZnO.[28] It is of great significance to clarify the effect of hydrogen and intrinsic donors on the conduction of nitrogen-doped ZnO films. However, none of such a fundamental report can be found to the best of our knowledge.

In this paper, nitrogen-doped ZnO film has been prepared. Hall measurements show that the hole concentration in the film decreases for around half an order after an annealing process in in O_2 at 600 °C for 30 min, and secondary ion mass spectroscopy (SIMS) reveals that the concentration of both nitrogen and hydrogen has decreased distinctively after the annealing process. It has also been demonstrated that the compensation source has decreased after annealing. Because hydrogen and intrinsic defects have an opposite variation trend, while nitrogen has the same concentration with that of the hole, extrinsic nitrogen

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dopant can be attributed to the dominating factor that determines the conduction-type of ZnO, while hydrogen and intrinsic defects may play a minor role.

2. EXPERIMENTAL DETAILS

The nitrogen-doped and undoped ZnO thin films studied in this paper were grown on *c*-plane sapphire (Al_2O_3) substrate by a plasma-assisted molecular beam epitaxy (MBE) technique. The cleaning process of the substrate can be found in our previous publication.[29] In brief, after being chemically etched, the substrates were pretreated in vacuum ($\leq 1 \times 10^{-7}$ mbar) at 750 °C for 30 min to obtain a clean fresh surface. After that, the substrates were loaded into the growth chamber. Nitric oxide (NO) (99.99%) was used as N dopant and O source for the growth of nitrogen-doped ZnO film, and oxygen gas (99.9999%) was used as O source for that of undoped ZnO. Note that oxygen was activated by a radio-frequency (rf) plasma cell (Oxford Applied Research, Model HD25) operating at 13.56 MHz. The power of the plasma cell was maintained at 350 W during the growth process. High purity (99.9999%) metallic zinc contained in a Knudsen-cell was used as the zinc source. The pressure in the MBE chamber was maintained at 2×10^{-5} mbar, and the substrate temperature was kept at 575 °C during the growth process. We note that the a relatively low temperature employed is helpful for the incorporation of N into ZnO. In this way, N-doped ZnO and undoped ZnO films were prepared. Both the as-grown ZnO:N and the undoped ZnO films were cut into two pieces for the post-annealing study. They were annealed at 600 °C for 30 min in a tube furnace in O_2. The structure of the films was characterized using a Rigaku D/max-RA X-ray diffractometer (XRD) using Cu Kα ($\lambda = 1.54$ Å) as the irradiation source. The carrier concentration and mobility of the films were studied by Hall measurement (Lakeshore 7707) under Van der Pauw configuration. The composition depth profile of the ZnO:N films was measured using a time of flight SIMS setup (IONTOF TOF-SIMS IV) with Ga^+ as the analysis source and Cs^+ as the sputtered source, the primary beam energy (Cs^+) was set at 3 kV, the current was approximately 16 nA, and the analyzing area is 200×200 μm^2.

3. RESULTS AND DISCUSSION

Figure 1 shows a typical XRD pattern of the as-grown N-doped ZnO film. Besides the peak from the Al_2O_3 substrate, only a single peak located at 34.43° can be observed from the pattern, which can be indexed to the diffraction from the (002) facet of wurtzite ZnO. The XRD pattern reveals that the as-grown film is of wurtzite structure with (002) preferential orientation.

The electrical characteristics of the ZnO:N samples are summarized in Table I. As can be seen, both the as-grown and the annealed ZnO:N films behave *p*-type conduction.

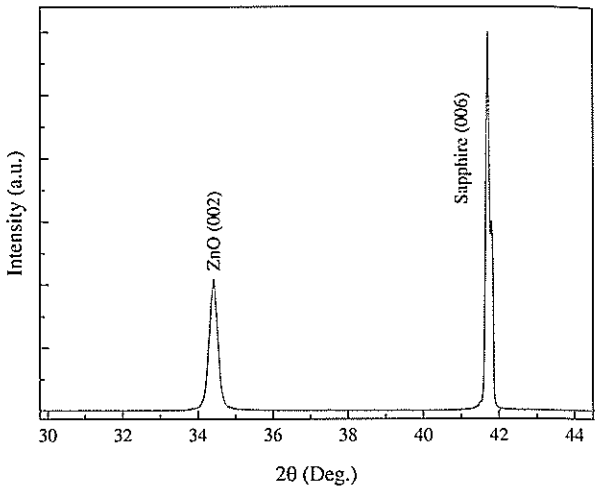

Figure 1. A typical XRD pattern of the as-grown nitrogen-doped ZnO sample.

However, after the as-grown ZnO:N film was annealed in O_2 ambient at 600 °C for 30 min, the hole concentration is reduced from 3.1×10^{17} cm^{-3} to 6.8×10^{16} cm^{-3}. In order to understand the effect of the annealing on the hole concentration of the ZnO:N film in more details, SIMS measurements on the ZnO:N films before and after the annealing process were conducted. An undoped ZnO film fabricated in our MBE system was used as a benchmark for the SIMS measurement. Figure 2 shows the SIMS profiles of the main elements in the as-grown and annealed ZnO:N films. For both films, nitrogen and hydrogen have been well detected, and the flat concentration profile of nitrogen indicates that the nitrogen was doped uniformly in the as-grown ZnO:N film. However, the SIMS spectrum of the annealed ZnO:N film shows that the concentration profiles of both hydrogen and nitrogen decreased gradually with the ZnO:N film depth, which may be due to the thermal diffusion of the elements. The reduction of hydrogen from the ZnO:N film can be observed readily after the annealing process. Although there is plenty of hydrogen in the as-grown and annealed ZnO:N films, both films behave the *p*-type conduction. In addition, the concentration of hydrogen is reduced while the hole concentration in the film is decreased after the annealing process, which means that there must be some other factors that dominate the conduction-type of nitrogen-doped ZnO instead of hydrogen. Another possible dominant factor is the intrinsic defects in ZnO, such as oxygen vacancy, interstitial zinc,

Table I. Electrical characteristics of the ZnO:N samples before and after the annealing process in O_2 ambient.

Sample	Carrier density (cm^{-3})	Hall mobility (cm^2/VS)	Resistivity (ohm cm)	Conduction type
ZnO:N				
As-grown	3.1×10^{17}	1.1	19	*p*
Annealed at 600 °C	6.8×10^{16}	1.1	100	*p*

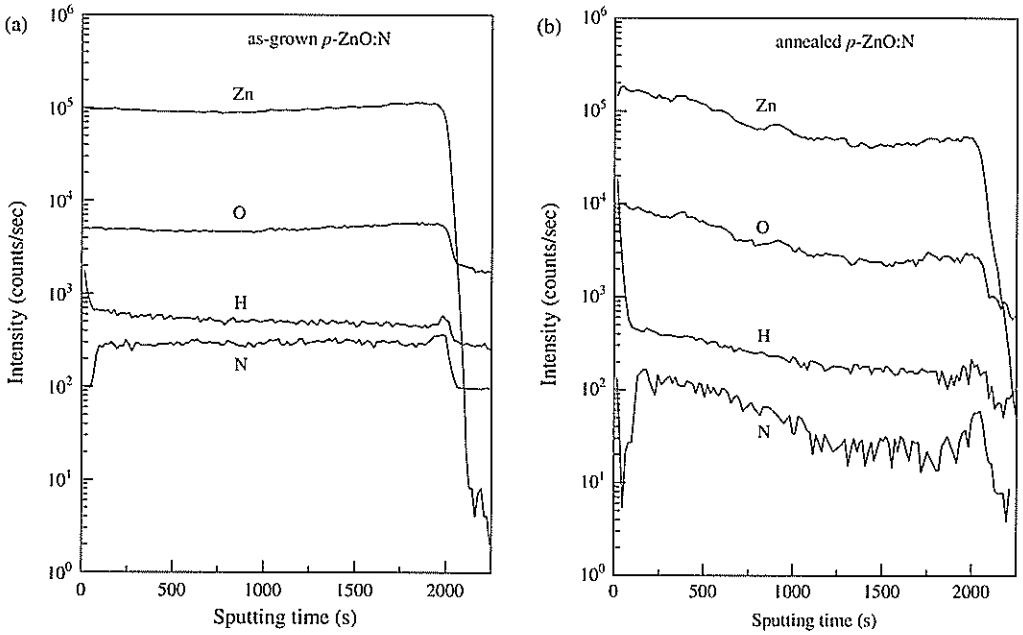

Figure 2. Representative atomic profiles of Zn, O, H and N in ZnO:N for the as-grown (a) and the annealed film (b).

or zinc vacancy. However, it is widely accepted that the density of this kind of intrinsic defects are well beyond the detection limit of SIMS. Therefore, other methods have to be adopted to characterize the effect of the intrinsic defects on the Hall data of the ZnO:N film.

Herein an undoped ZnO film were annealed at the same conditions (O_2 atmosphere, 600 °C, 30 min) in order to test the effect of these intrinsic defects on the conduction type of the ZnO:N film,. The Hall data of the as-grown and annealed undoped ZnO films are listed in Table II. As can be seen, the electron concentration decreased nearly half an order of magnitude after the annealing process. It is noted that the above variations are not occasional since three similar experiments have been designed and carried out, and very similar variation trend was obtained. The above phenomenon can be understood as below: after an annealing process in O_2 at 600 °C, the concentration of hydrogen will decrease, as confirmed by our SIMS data. Meanwhile the intrinsic donors (V_o, Zn_i) will also greatly decrease,[21] while the intrinsic acceptor, such as zinc vacancy, will increase. As a result, the electron concentration will decrease. One can deduce from the above results that for the ZnO:N film, the compensation source, such as hydrogen, V_O and Zn_i, will decrease after the annealing process. Consequently, the hole concentration will increase if there is no other factors contributing to the conduction of the film. However, the hole concentration shows an opposite variation trend. Therefore, there must be a factor that dominant the conduction type of the ZnO:N film instead of hydrogen and intrinsic defects.

Table II. The electrical properties of the as-grown ZnO film and those of the film after an annealing process at 600 °C in oxygen ambient for 30 min.

Annealing ambient	Carrier density (cm^{-3})	Hall mobility ($cm^2\ V^{-1}\ S^{-1}$)	Resistivity (ohm cm)	Conduction type
As-grown	2.6×10^{18}	36.4	0.07	*n*
O_2	5.5×10^{17}	23.4	0.48	*n*

One can see from the SIMS data that after the annealing process, the concentration of extrinsic dopant of nitrogen has decreased, which has the same variation trend with the hole concentration in the film. Hence, it is speculated that the dominant factor of the variation of the hole concentration is the extrinsic dopant.

A clue for the above deduction is that the average concentration of the nitrogen decreases about half an order of magnitude after the annealing process, which has the same variation trend with the hole concentration in the film. The relationship between hole concentration and the concentration of N_O, the main acceptor in the ZnO:N film, can be expressed approximately as follows:

$$n_p = N_A \times \exp\left(-\frac{E_A}{KT}\right) \quad (1)$$

Here, n_p and N_A are the hole concentration and the N_O concentration in the as-grown ZnO:N film, respectively. E_A is the activation energy of the acceptor. Likewise, the hole concentration can also be expressed in the annealed ZnO:N film:

$$n'_p = N'_A \times \exp\left(-\frac{E_A}{KT}\right) \quad (2)$$

Here, n'_p and N'_A are the hole concentration and N_O concentration of the annealed ZnO:N film, respectively. The ratio of N_A/N'_A is roughly equal to the ratio of

nitrogen concentration in the as-grown and the annealed ZnO:N films. It can be seen that the average concentration of nitrogen decreased about half an order of magnitude in the ZnO:N film after the annealing process. With an assumption that the donor's compensation in ZnO:N films is constant, the hole concentration n'_p should be about 5.5×10^{16} cm^{-3} after the annealing process. However, the hole concentration in the annealed film is 6.8×10^{16} cm^{-3}, which is very close to the assumed value (5.5×10^{16} cm^{-3}). It also confirmed that the dominant factors of the conduction-type in N-doped ZnO film is extrinsic dopant, while the hydrogen and intrinsic donors play a minor role in nitrogen-doped *p*-ZnO.

4. CONCLUSION

In summary, the SIMS spectra of the *p*-ZnO:N films show that the concentration of the hydrogen decreased after an annealing process in O_2 gas at 600 °C. By analyzing the variation of electron concentration in undoped ZnO film after the same annealing process, it is speculated that the deduction of the concentration of the hydrogen and intrinsic donors (V_o, Zn_i) will greatly increase the hole concentration in the annealed *p*-ZnO:N film. However, the hole concentration has an opposite change. Hence, it is concluded that the dominant factor that determines the conduction-type of nitrogen-doped ZnO is the extrinsic dopants instead of hydrogen and intrinsic donors (V_o, Zn_i), and we also confirmed that the hydrogen and intrinsic donors play a minor role in the N-doped *p*-ZnO film. Therefore, one can deduce from the above results that by properly optimizing the doping conditions, *p*-ZnO should be attainable.

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