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Abstract
Nitrogen doped zinc oxide (ZnO) films have been prepared by molecular beam epitaxy. The
as-grown samples show n-type conduction, but they convert to p-type after being annealed in
O_2 atmosphere. X-ray photoelectron spectroscopy reveals that the conversion is mainly caused
by the escaping of substituted N molecule $(N_2)_O$ donors from the films, and
photoluminescence spectroscopy confirms the extraction of $(N_2)_O$. The work shown in this
paper reveals experimentally that the main compensation source in nitrogen doped ZnO is
$(N_2)_O$ donors instead of intrinsic donors or background impurities, and annealing in oxygen
may be a promising route to p-ZnO.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Due to its large binding energy (60 meV), excitons in ZnO are
thermally stable at room temperature, which is a significant
advantage in light emitting devices and laser diodes [1, 2].
However, one of the major obstacles in the development of
ZnO is the difficulty in realizing p-type conduction. Up to now,
nitrogen (N) has been proven to be one of the effective p-type
dopants for ZnO [3, 4]. Although some groups have obtained
N-doped p-type ZnO films and realized electroluminescence in
ZnO homojunction [5–8], there are still some severe problems
to be solved, such as low reproducibility and poor stability of
N-doped p-ZnO. It is widely accepted that the main reason
for the difficulties in p-type doping of ZnO lies in the strong
compensation. As for the compensation source, some thought
that the intrinsic donor defects (Zn_i, V_O) or background
impurities in ZnO played a key role [9–13]. However, both
theoretical and experimental works confirm that nitrogen is
in the form of both substituted N atom $(N)_O$ (acting as
acceptors) and substituted N molecule $(N_2)_O$ (acting as donors)
in as-grown ZnO : N [14–17], and the introduced $(N_2)_O$ donors

can compensate the $(N)_O$ acceptors [14, 16]. However, what
is the real compensation source in ZnO : N? No experimental
work has been demonstrated to the best of our knowledge.

In this paper, experiments have been designed and carried
out to reveal the compensation source in N-doped ZnO. It
is concluded that $(N_2)_O$ donors instead of intrinsic donors
or background impurities play a key role in hindering the
formation of p-type ZnO, and post-annealing in oxygen can
suppress $(N_2)_O$ donors and thus may be an effective route to
p-ZnO.

2. Experiments

All the samples mentioned in this study were grown on c-plane
sapphire (Al_2O_3) by plasma-assisted molecular beam epitaxy
(MBE). To obtain a clean fresh surface, the substrates were
chemically etched in $H_2SO_4 : H_3PO_4 = 3 : 1$ at 160 °C for
15 min, then they were thermally pre-treated at 750 °C for
30 min before being loaded into the growth chamber, which
was expected to remove the surface contaminants of the
Al_2O_3 substrates. Nitric oxide (NO) (99.99%) and O_2 gas
(99.9999%) were used as the N dopant and the O source,

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respectively, and they were activated by two separate radio-frequency (rf) plasma cells (Oxford Applied Research Model HD25) operating at 13.56 MHz. The rf power of the O_2 and NO plasma was maintained at 300 W and 400 W, respectively. High purity (6N) metallic zinc contained in a Knudsen cell was used as the zinc source. The pressure in the MBE chamber was maintained at 1.5×10^{-5} mbar, and the substrate temperature was fixed at 380 °C during the growth process. We note that the low temperature is necessary for the incorporation of N into ZnO. In this way, N-doped ZnO samples were prepared; for comparison, an undoped ZnO sample was also prepared under the same conditions. The as-grown ZnO : N and undoped ZnO films were cut into small pieces for the post-annealing study, and they were annealed at 400, 500 and 600 °C for 30 min in a tube furnace in O_2 ambient. X-ray diffraction (XRD) was carried out in a Rigaku O/max-RA x-ray system using Cu Kα ($\lambda = 1.5418$ Å) as the irradiation source. Chemical bonding states of the films were measured by x-ray photoelectron spectroscopy (XPS, ESCALAB 250) with an Al K$_\alpha$ ($h\nu = 1486.6$ eV) line as the irradiation source. The optical properties were characterized by photoluminescence (PL) spectroscopy excited by the 325 nm line of a He–Cd laser. The electrical properties of the samples were studied by Hall measurement (Lakeshore 7707) under Van der Pauw configuration. Recently, Ohgaki *et al* [18] reported that a false positive Hall coefficient could be obtained due to the non-uniform electrical properties of the ZnO sample. For our samples, the electrical properties are confirmed to be uniform before the Hall measurements. Hence, the false positive Hall coefficient can be avoided in our experiments.

3. Results and discussions

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 the ZnO(0 0 2) diffraction peak can be observed, indicating that the as-grown N-doped ZnO film is of wurtzite structure with (0 0 2) preferential orientation. The electrical characteristics of the samples are summarized in table 1. In order to reveal the effect of the annealing temperature on the carrier concentration of the samples clearly, a plot is made, as
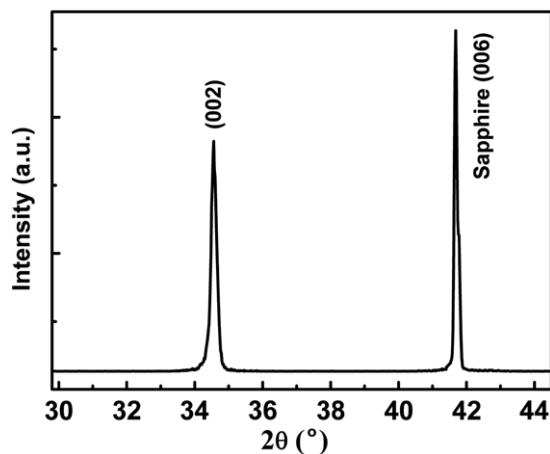

Figure 1. XRD pattern of the as-grown N-doped ZnO sample.

shown in figure 2. Hall measurements indicate that both the undoped ZnO and the as-grown ZnO : N films show n-type conduction, and the electron concentration of the as-grown ZnO : N (6.00×10^{19} cm^{-3}) is much higher than that of the undoped ZnO (5.41×10^{18} cm^{-3}), which indicates that many donors have been introduced during the doping process. After being annealed, the ZnO : N sample converts to p-type conduction, and the hole concentration decreases from 2.85×10^{18} to 1.95×10^{15} cm^{-3} as the annealing temperature is increased from 400 to 600 °C, which indicates that the introduced donors may be greatly suppressed, and the introduced acceptors dominate the conduction of ZnO : N after the annealing process. For the undoped samples, the carrier concentration remains almost unchanged after annealing. The above facts clearly reveal that the main compensation source in ZnO : N is the introduced donors instead of the intrinsic ones. Furthermore, some groups reported that the as-grown ZnO often contains a significant concentration of optically and electrically inactive hydrogen that can be converted into shallow donors by annealing at about 400 °C [19, 20]. However, in our case, the role of hydrogen should be negligible because since hydrogen is ubiquitous, if it is the dominant donor source in our films, annealing will not affect the carrier concentration greatly.

The variation of the carrier concentration and conduction type of the ZnO films with annealing temperature can be understood as follows: as stated above, it is reported that nitrogen exists in two forms, $(N)_O$ acting as acceptors and $(N_2)_O$ acting as donors in ZnO : N [14–17]. Theoretical calculation indicates that $(N_2)_O$ has a smaller formation energy than $(N)_O$ [14, 16], which may be the reason why the as-grown ZnO : N sample shows an even higher electron concentration than undoped ZnO in our case. The N–N bond is very strong, whereas the interactions between the N and surrounding Zn atoms are extremely weak [14, 16]. As a result, the introduced donors $(N_2)_O$ can be removed by thermal treatment; this may be the reason for p-type conduction of ZnO : N after the annealing process. To confirm the above speculations, two representative XPS spectra taken on the as-grown ZnO : N sample and the sample annealed at 500 °C are shown in figure 3. The spectrum of the as-grown film shows three peaks located at 396.1 eV, 399.8 eV and 403.9 eV, respectively. The peak at 399.8 eV has been frequently observed in nitrogen doped ZnO, and its origin is controversial [21, 22]. Many publications have indicated that the peaks at 396.1 eV and 403.9 eV are characteristic peaks of $(N)_O$ and $(N_2)_O$ in N-doped ZnO [17, 23, 24], respectively. The appearance of the 396.1 and 403.9 eV peaks confirms that both $(N)_O$ and $(N_2)_O$ are formed in the as-grown ZnO : N film. These $(N_2)_O$ should be responsible for the very high electron concentration up to 6.00×10^{19} cm^{-3} in the as-grown ZnO : N film. For the annealed sample, the relative intensity of $(N_2)_O$ decreases significantly compared with that of the as-grown sample. One can then conclude that many $(N_2)_O$ donors have escaped from the ZnO : N film, and $(N)_O$ acceptors dominate the conduction of the film after the annealing process; consequently p-ZnO results. At a higher annealing temperature, $(N)_O$ will also be replaced by O gradually; as a result, the hole concentration
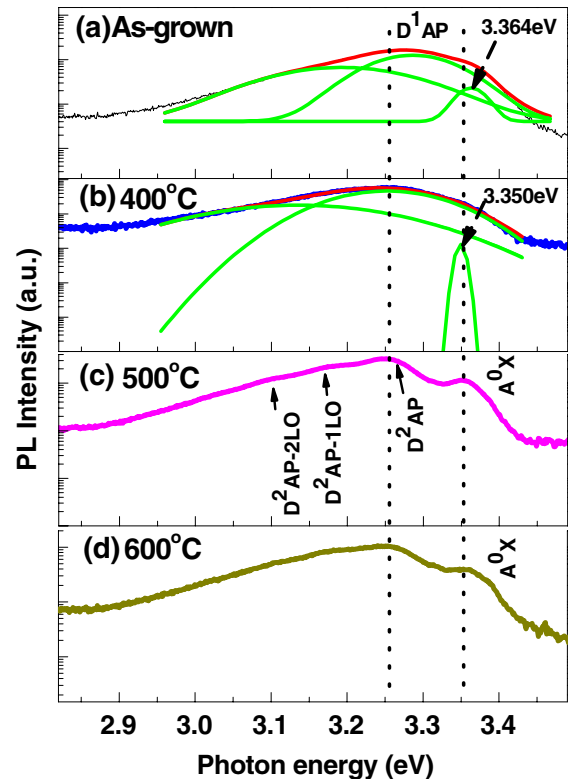
Table 1. Electrical characteristics of the samples before and after the annealing process in O_2 ambient.

	Sample	Resistivity (Ω cm)	Hall mobility ($cm^2\ V^{-1}\ s^{-1}$)	Carrier concentration (cm^{-3})	Conduction type
ZnO : N	As-grown	0.39	0.26	6.00×10^{19}	n
	Annealed at 400 °C	18.47	0.12	2.85×10^{18}	p
	Annealed at 500 °C	62.12	3.11	4.25×10^{16}	p
	Annealed at 600 °C	12 000	0.16	3.25×10^{15}	p
Undoped ZnO	As-grown	1.09	1.83	3.23×10^{18}	n
	Annealed at 400 °C	2.98	1.56	4.85×10^{18}	n
	Annealed at 500 °C	1.34	1.88	2.56×10^{18}	n
	Annealed at 600 °C	6.40	3.87	6.40×10^{18}	n
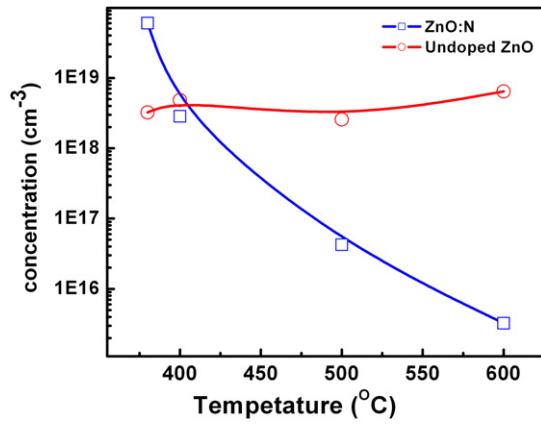
Figure 2. Effect of the annealing temperature on the conduction type and carrier concentration of ZnO : N and undoped ZnO sample.
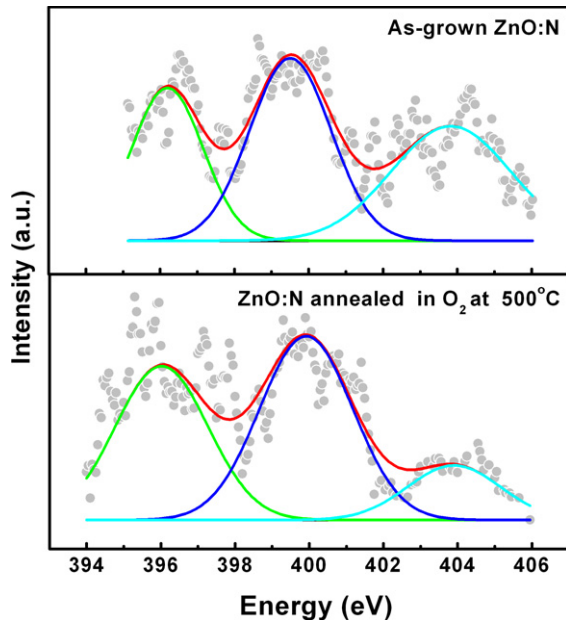
Figure 3. N 1s XPS spectra of the as-grown ZnO : N and the annealed ZnO : N sample at 500 °C.

Figure 4. The 80 K PL spectra of the as-grown ZnO : N film and the film annealed at 400, 500 and 600 °C. The spectra of the as-grown ZnO : N and the sample annealed at 400 °C can be best fitted by three Gaussian curves.

of the ZnO films decreases by increasing the annealing temperature further. The above conclusion is supported by the following PL data.

Figure 4 illustrates the 80 K PL spectra of the as-grown and annealed ZnO : N samples. The PL spectrum of the as-grown ZnO : N can be well fitted by three Gaussian peaks, and the

dominant sharp peak is located at 3.28 eV, which is the donor–acceptor pair (labelled as D^1AP) emission in ZnO [25, 26]. There also appears one peak at about 3.364 eV, and the position of this peak is in good accord with the neutral donor-bound excitons (D^0X) in ZnO [27]. After being annealed at 400 °C, the PL spectrum can also be well fitted by three Gaussian peaks, and the dominant peak lies at 3.25 eV, which may come from another donor–acceptor emission (labelled as D^2AP). The peak at the high energy side shifts to 3.350 eV, which is in good accord with the neutral acceptor-bound excitons (A^0X) in ZnO [28]. For the ZnO : N samples annealed at 500 and 600 °C, their PL spectra have a similar shape. Note that all the three annealed samples have a DAP emission peak at 3.25 eV, while the as-grown sample has a DAP emission at 3.28 eV, which leads us to think that the D^1AP peak at 3.28 eV may

come from the recombination between $(N_2)_O$ donors and $(N)_O$ acceptors, while the D^2AP at 3.25 eV from the recombination between intrinsic donors and $(N)_O$ acceptors.

The above PL data can be understood as follows: for the as-grown ZnO : N, many shallow donors $(N_2)_O$ were created; this is the reason why the as-grown ZnO : N sample shows n-type conductivity with a very high electron concentration. In the PL spectrum, there appears an emission coming from D^0X, and the PL spectrum was dominated by the DAP emission coming from the recombination between $(N_2)_O$ donors and $(N)_O$ acceptors (D^1AP). While after annealing, many $(N_2)_O$ donors escape from the ZnO films, thus $(N)_O$ acceptors dominated the conductivity, consequently, the ZnO film converted to p-type conduction. In addition, there appeared an emission from acceptor-bound excitons, and the DAP emission coming from the recombination between intrinsic donors and $(N)_O$ acceptors (D^2AP) dominated the PL spectrum.

4. Conclusions

In conclusion, the compensation source in N-doped ZnO films has been studied. It is found that the as-grown ZnO : N sample shows n-type conductivity with a very high electron concentration, which is caused by the introduction of $(N_2)_O$ donors during the doping process. While after annealing in O_2, many $(N_2)_O$ donors escape from the film, and the conduction of the films converts to p-type, the conduction type and carrier concentration of the undoped ZnO films remain almost unchanged after the annealing process. We can then draw the conclusion that the main compensation source in ZnO : N films is the introduced $(N_2)_O$ donors instead of the intrinsic ones or residual H, and annealing in O_2 may be a feasible route to p-type ZnO. The results presented in this paper may provide a clue to obtaining reproducible N-doped p-type ZnO.

Acknowledgments

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