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Optical and Electrical Properties of p-type ZnO:N Films Grown by N-plasma Assisted Pulsed Laser Deposition

WANG Lei, XU Hai-yang*, LI Xing-hua, LIU Yi-chun

(Center for Advanced Optoelectronic Functional Materials Research and Key Laboratory for UV Light-Emitting Materials and Technology of Ministry of Education, Northeast Normal University, Changchun 130024, *China)*

Abstract: Nitrogen-doped ZnO (ZnO:N) films were grown by N-plasma assisted pulsed laser deposition. The p-type conductivities were achieved by post low-temperature rapid thermal annealing (RTA). The N chemical states, optical and electrical properties of ZnO:N films were systematically studied by X-ray photoelectron spectroscopy (XPS), photoluminescence (PL) and Hall measurements. The results revealed that the obtained p-type ZnO:N films are highly compensated semiconductor, and the RTA process can activate more N acceptors and reduce the self-compensation of intrinsic donor defects. Three N acceptor-related emissions were observed in low-temperature PL spectra. The ionization energy of N acceptor was determined as about 128 meV from free-electron-to-acceptor (FA) transition. Interestingly, donor-acceptor pair (DAP) emission showed a slight redshift with increasing annealing temperature. This phenomenon was understood in terms of a potential fluctuation model.

Key words: p-type; ZnO:N films; PLD; optical and electrical properties
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1 Introduction

With a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, ZnO becomes a focus of intense research as a promising material for short-wavelength optoelectronic devices that suitable for high-temperature operation, such as ultraviolet (UV) photodetectors, UV light emitting diodes and laser diodes[1-2]. However, ZnO still suffers from the asymmetric doping limitation. The realization of a stable and high-quality p-type ZnO, which is crucial for practical device applications, has be proved to be very difficult due to the self-compensation effect, low solubility[3-4] and high ionization energy of acceptor impurities. In recent years, the research on p-type ZnO has proceeded at a more rapid pace. Various group-I and -V dopant, have been employed to fabricate p-type ZnO. Among them, N is regarded as one of the most promising p-type dopants for ZnO because it has a similar ionic radius to O and the N^{3-} ion substitution for O sublattice (N_O) can introduce a shallow acceptor level in ZnO[5]. Nitrogen gas (N_2) is an environmentally friendly N doping source. Although the N_2 would inevitably introduce the substitutional $N_2[(N_2)_O]$ donors into ZnO films[3,6], this negative effect can be minimized by choosing suitable growth techniques and conditions[7-8]. Plasma assisted pulsed laser deposition (PLD), as a nonequilibrium technique, is an effective method to grow alloy or doped films. High-power radio-frequency (RF) plasma source can ionize the N_2 molecule and generate N-plasma, which can

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Biography: WANG Lei, born in 1982, male, Jilin Province. His work focuses on wide-band-gap semiconductor materials and devices.
E-mail: wangl055@nenu.edu.cn
*: Corresponding Author; E-mail: hyxu@nenu.edu.cn

increase the solubility of N in ZnO over 8 orders of magnitude, as reported in Ref. [8]. However, reports on PLD growth of p-type ZnO∶N film are very limited[9]. In this work, we used N-plasma assisted PLD technique to grow ZnO∶N films, their p-type conductivities were achieved just via post low-temperature rapid thermal annealing (RTA). Detailed studies have been given on the chemical states, electrical and optical properties of the p-type ZnO∶N films.

2 Experiments

ZnO∶N films were grown on *c*-sapphire substrates by N-plasma assisted PLD technique. A Nd∶YAG pulsed laser (355 nm, 5 ns, 10 Hz) was employed to ablate a ZnO ceramic target (4N purity). Prior to the deposition, the growth chamber was evacuated to a base pressure of 7.5×10^{-5} Pa with a turbo molecular pump. And then, ultrapure O_2 and N_2 gases were introduced into the chamber. The total pressure was kept at 20 Pa, and the partial pressure ratio of N_2 to O_2 is 9∶1. The N-plasma, which was generated by an RF plasma source with a power of 100 W, serves as the doping source. The substrate temperature was maintained at 500 ℃. The film thickness was about 120 nm. To activate more N acceptors, the as-grown ZnO∶N films are rapidly annealed at 200 and 400 ℃ in N_2 atmosphere, respectively. The chemical states of the elements in ZnO∶N films were identified by X-ray photoelectron spectroscopy (XPS, VG ESCALAB MK-Ⅱ system, UK). The electrical property was examined by Hall measurements (Lakeshore 7704 system) in the van der Pauw configuration. Their optical properties were investigated by temperature-dependent photoluminescence (PL) measurements (Jobin-Yvon HR800 UV spectrometer), in which the 325 nm He-Cd laser line was used as the excitation source.

3 Results and Discussion

Table 1 lists the resistivity, net carrier concentration and mobility of ZnO∶N films. The resistance of the as-grown ZnO∶N film was so high as to exceed the detection limit of Hall system. After the RTA treatment, the films show weak p-type conduction. As the annealing temperature increase from 200 to 400 ℃, the net carrier concentration increases from 3.24×10^{13} to 2.68×10^{15} cm^{-3}, but the mobility decreases significantly. The low carrier concentration and mobility are attributed to the strong self-compensation effect. The observation of RTA-induced p-type conversion indicated that the low-temperature RTA process helps to activate more N acceptors and decrease the donor species adsorbed on the grain boundaries and film surface, which will be further demonstrated by the following XPS results.

Table 1 Hall measurement results of as-grown and RTA-treated ZnO∶N films

t_{RTA}/℃	Resistivity/(Ω · cm)	Type	C/cm^{-3}	Mobility/($cm^2\cdot V^{-1}\cdot s^{-1}$)
as-grown	High ρ	–	–	–
200	8.05×10^3	p	3.24×10^{13}	26.0
400	1.57×10^3	p	2.68×10^{15}	1.49

Fig. 1 shows the N 1s and O 1s core-level XPS spectra of the as-grown and annealed ZnO∶N films, respectively. The binding energy scale was calibrated by using the C 1s line at 284.6 eV. In Fig. 1(a), a broad band at about 400 eV dominates all the N 1s core-level XPS spectra, which can be deconvoluted into two Gaussian peaks at about 399 and 401 eV. The former is attributed to the substitutional N^{3-} ion (N_O)[10-11], which has been investigated in our previous report by temperature-dependent XPS[12] and is an effective acceptor dopant. The latter is associated with N—O species, such as $(NO_2)^-$[10]. They may be adsorbed on the grain boundary, and impose a negative effect on p-type conductivity. With the increasing annealing temperature, the integrated intensity ratio of N_O to N—O peak increases. This confirms that the RTA treatment can decrease the undesirable N—O species and activate more N_O acceptors. As a result, the p-type conductivity of ZnO∶N films is achieved. Another weak N

1s peak at 405 eV was also observed. The origin of this peak can be considered as the N_2 molecule occupying O site [$(N_2)_O$], which is a shallow double donor and usually exists in the heavily doped ZnO: N[3,13]. However, the XPS results indicate that it is difficult to remove the $(N_2)_O$ component via a low-temperature RTA treatment. The presence of the $(N_2)_O$ donors partly compensates the N_O acceptors[3,13], which leading to a very low net carrier concentration in the ZnO: N films. Fig. 1(b) exhibits the O 1s core-level XPS spectra. Obviously, the O 1s band is overlapped by two peaks with binding energies of 530.5 and 532.2 eV, which corresponding to the O-Zn bond and the loosely bound oxygen adsorbed on the grain boundaries and film surface, respectively[14]. The latter was labeled as Ads. O. In general, they play a negative role in p-type conductivity[15]. After ZnO: N films were RTA-treated in N_2 atmosphere, the intensity ratio of the adsorbed oxygen peak to the lattice O peak decreases significantly

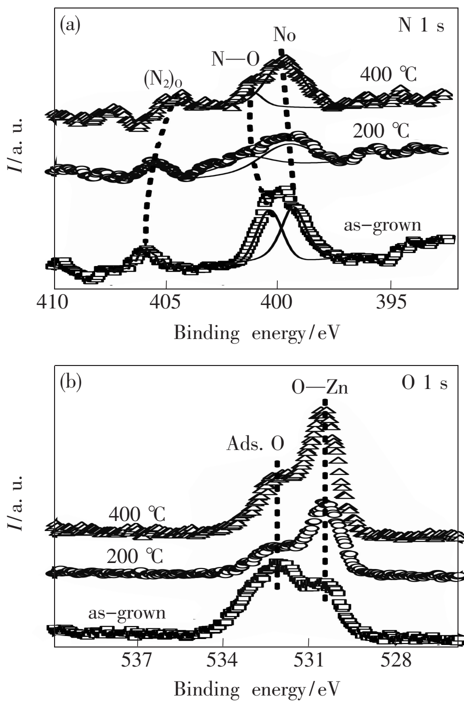

Fig. 1 (a) N 1s and (b) O 1s core-level XPS spectra of ZnO: N films. The rectangle (□), circle (○) and triangle (△) experimental data corresponds to the as-grown, 200 and 400 ℃ annealed ZnO: N films, respectively. The XPS spectra have been smoothed in order to reduce the noise level.

and suggesting a relative reduction in the adsorbed oxygen species, which partly contributes to p-type conversion. Similar phenomenon of RTA-induced oxygen desorption has also been observed in the previous reports[14]. To study N-doping effects on the optical properties of ZnO films, PL spectra of RTA-treated ZnO: N films were measured at 80 K, as shown in Fig. 2(a). The UV emission band can be well fitted by five peaks. By comparing the reported peak positions, we tentatively assign the three main peaks at about 3.35, 3.31 and 3.25 eV to neutral acceptor bound exciton (A^0X) emission, free-electron-to-acceptor transition (FA) and donor-acceptor pair (DAP) recombination, respectively[16-17]. Another two weak peaks at about 3.17 and 3.10 eV are attributed to the longitudinal optical (LO) phonons replicas of DAP emission, since their energy separations are close to the LO phonon energy of ZnO (72 meV). The appearance of these acceptor-related emissions further confirms the N incorporation. One can determine the ionization energy of N acceptor (E_A) from the FA emission energy (E_{FA}), using the following equation[16]:

$$E_A = E_g - E_{FA} + k_B T/2, \quad (1)$$

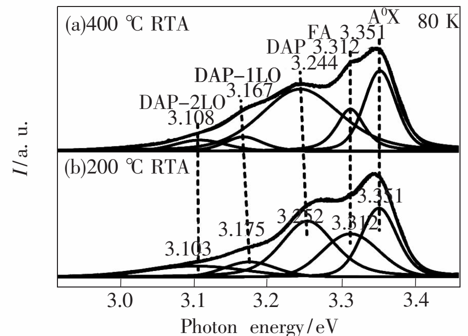

Fig. 2 Low-temperature (80 K) PL spectra of RTA-treated ZnO: N films. (a) 400 ℃ and (b) 200 ℃. The UV emission bands are well fitted by five Gaussian peaks.

With intrinsic band gap $E_g = 3.377$ eV, E_A can be calculated to be about 128 meV at 80 K. It is very agreement with the theoretical value of 132 meV predicted by a hydrogen-like acceptor model and the experimental value of about 120 meV reported in ZnO: N films grown by molecular beam epitaxy[18]. The lower N ionization energy indicated its shallow

acceptor nature. It was worth noting that the DAP emission slightly redshifts from 3.252 to 3.244 eV with increasing RTA-temperature from 200 to 400 ℃. This DAP shift suggests a high compensation in the heavily doped ZnO:N films, and can be understood in terms of a potential fluctuation model[19-20]. In a heavily doped, strongly compensated semiconductor, a high density of charged donors and acceptors can create strong local electrical fields, which inducing Coulomb-potential fluctuations of the band edges and impurity levels. In this case, the photon energy of DAP recombination (E_{DAP}) is expressed as:

$$E_{DAP} = E_g - (E_D + E_A) - 2\sigma, \qquad (2)$$

where E_g, E_D and E_A are the band gap of ZnO, the donor and acceptor ionization energies, respectively. The σ represents the average potential-well depth, which is proportional to the charged impurities concentration and the screening radius. Hall and XPS studies have revealed that increasing RTA-temperature can activate more N acceptors. The increase in ionized acceptor concentration deepens the potential well (σ), thus leading to the redshift of DAP emission. Similar observation has also been reported in heavily doped ZnSe:N and GaAs:Li films[19-20]. To support the PL assignments, the temperature-dependent PL spectra of the two RTA-treated ZnO:N films were measured in the range of 80 ~ 290 K. Both films exhibit similar temperature evolution.

Fig. 3 show the temperature-dependent PL spectra of the film annealed at 400 ℃. As the temperature increasing, the DAP emission loses its intensity rapidly, and merges into the FA emission peak, due to the relatively lower donor ionization energy. This feature is typical for DAP recombination. The A^0X emission also shows a thermal quenching behavior,

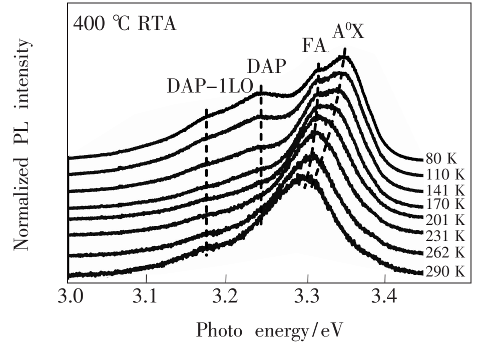

Fig. 3 Temperature-dependent PL spectra of ZnO:N films annealed at 400 ℃

which may be attributed to the dissociation of A^0X to free exciton. Moreover, the FA emission gradually shifts to the low energy side with the temperature increasing. This redshift is dominated by the ordinary temperature-induced band gap shrinkage.

4 Conclusion

The p-type ZnO:N films were fabricated by N-plasma assisted PLD technique combined with a low-temperature RTA process. Different types of N local states, including N_O acceptor, $(N_2)_O$ donor and N-O species, were observed in the ZnO:N films. Though the weak p-type conductivity is realized, the strong self-compensation of $(N_2)_O$ and native donors results in the low net carrier concentration and mobility. N acceptor-related emissions dominate the low-temperature PL spectra of ZnO:N films. The ionization energy of N acceptor was estimated to be about 128 meV from the PL studies. The mechanisms of DAP redshift were discussed. It is expected that the detailed investigations on the physical properties of ZnO:N films are helpful for achieving reproducible, high-quality and stoble p-type ZnO films.

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氮等离子体辅助脉冲激光沉积生长 p 型 ZnO: N 薄膜的光学和电学性质

王　雷, 徐海阳*, 李兴华, 刘益春
(东北师范大学 先进光电子功能材料研究中心 紫外光发射材料与技术教育部重点实验室, 吉林 长春　130024)

摘要: 通过氮气等离子体辅助脉冲激光沉积(PLD)技术制备了氮掺杂氧化锌(ZnO: N)薄膜。经过低温快速热退火(RTA)处理后,ZnO: N 薄膜呈现 p 型导电特性。利用 X 射线光电子能谱(XPS)、光致发光(PL)和霍尔测量对 ZnO: N 薄膜中 N 的化学状态及其光学和电学性质进行了系列的研究。结果表明:所制得的 p 型 ZnO: N 薄膜为高度补偿半导体;RTA 工艺不仅可以激活薄膜中更多的 N 受主,还可以弱化由薄膜中的施主缺陷造成

的自补偿效应。在低温 PL 光谱中观察到了 3 种与氮受主相关的光发射,并且通过自由电子-受主(FA)辐射复合光发射确定了薄膜中 N 受主的离化能(128 meV)。随着退火温度的升高,施主-受主对发射峰呈现了略微的红移现象,这可以通过势能波动模型加以理解。

关　键　词: p 型; ZnO: N 薄膜; PLD; 光学和电学性质

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作者简介: 王雷(1982 -), 男, 吉林德惠人, 主要从事宽带隙半导体材料与器件的研究。
E-mail: wangl055@nenu.edu.cn

*: 通讯联系人; E-mail: hyxu@nenu.edu.cn, ycliu@nenu.edu.cn

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