Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thin Solid Films 435 (2003) 49–55
thin solid films
www.elsevier.com/locate/tsf

Synthesis of p-type ZnO thin films using co-doping techniques based on KrF excimer laser deposition

Tamiko Ohshima[a,*], Tomoaki Ikegami[a], Kenji Ebihara[a], Jes Asmussen[a], RajK. Thareja[b]

[a]*Graduate School of Science and Technology, Department of Electrical and Computer Engineering, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555 Japan*
[b]*Department of Physics and Center of Laser Technology, Indian Institute of Technology, Kanpur 208-016 (U.P.), India*

Abstract

Preparation of N-doped ZnO thin films was attempted using various co-doping methods. A ZnO:Ga (Ga_2O_3 of 5 wt.%) target was ablated in NO gas by pulsed laser deposition (PLD). In addition, a nitrogen ion gun and an ECR nitrogen plasma source were used as post-N-doping treatment of undoped ZnO films. Optical emission from elemental Zn I, Ga I and O I, as well as from N_2 molecules, was identified in the plasma plume. The structural, optical and electrical properties of these synthesized films were investigated. All films show n-type conduction, with resistivity in the range 10^{-3}–10^{-2} Ω cm and carrier density from 10^{17} to 10^{20} cm^{-3}.
© 2003 Elsevier Science B.V. All rights reserved.

Keywords: p-Type ZnO; Co-doping; Pulsed laser deposition (PLD); NO gas

1. Introduction

ZnO, a II–VI compound semiconductor, has a wide bandgap of 3.37 eV at room temperature (RT) and has some unique properties. In particular, ZnO has an exciton binding energy of approximately 60 meV at RT in comparison with ZnSe (22 meV) and GaN (25 meV), which have been widely used [1]. ZnO is a candidate for short-wavelength optoelectrical applications such as ultraviolet (UV) laser, light-emitting diodes (LEDs) and laser diodes (LDs). Recently, an excitonic laser action at RT from optically pumped ZnO thin films with hexagonally shaped nanocrystals was demonstrated [2].

For future realization of optical devices based on ZnO, it is necessary to grow both p- and n-type ZnO. However, most II–VI semiconductors naturally show n-type conduction. The difficulty of p-type doping in ZnO is due to the deep donor level, the low solubility of the dopant and the self-compensating processing on doping. The fabrication of p-type ZnO films has been attempted by many researchers so far, but there have only been a few successes. These are N doping using NH_3 gas by chemical vapor deposition (CVD), Ga and N co-doping using a N_2O ECR plasma source for ablation of ZnO:Ga target by PLD, and As doping by preparation of ZnO films on GaAs substrates using the PLD method [3–5]. For the last two reports, ZnO-based p–n junctions were successfully fabricated [6,7]. Work is still in progress to improve the structural and other properties of ZnO p–n junctions.

In this paper we have attempted to fabricate p-type ZnO films using several co-doping techniques. The ablation of a ZnO:Ga (Ga_2O_3 of 5 wt.%) target was carried out in an atmosphere of high-purity NO gas (99.5%). NO has a lower dissociation energy of 6.1 eV than that of N_2 (9.1 eV), and the ionization potential of NO is lower than that of N_2 and N_2O. We have succeeded in the fabrication of carbon nitride (CN_x) thin films with a maximum nitrogen/carbon (N/C) ratio of 1.0 by ablating a graphite target in NO gas [8]. This suggests that incorporating N into ZnO can be easily attained without supplying radicals from some excited plasma source.

We have also used two other techniques for the post-doping of undoped ZnO films. One is N^+ or N_2^+ ion implantation by an ion gun and the other is treatment using nitrogen plasma generated by an ECR plasma

*Corresponding author. Tel.: +81-96-342-3620; fax: +81-96-342-3630.
E-mail address: tamiko@st.eecs.kumamoto-u.ac.jp (T. Ohshima).

0040-6090/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0040-6090(03)00383-3

Table 1
Deposition conditions

Sample	Target	Substrate	Laser fluence E_L (J/cm^2)	Gas pressure (Pa)		Substrate temperature T_s (°C)	Number of laser pulses
				P_{O_2}	P_{NO}		
#1	ZnO	Al_2O_3(0001)	2	0.7		550	9000
#2	ZnO:Ga	Al_2O_3(0001)	2	0.7		550	9000
#3	ZnO:Ga	Amorphous quartz glass	3.2		6.7	400	9000
#4	ZnO:Ga	Al_2O_3(0001)	4		13	400	9000

The ZnO target was 99.99% pure. The ZnO:Ga target contained 5 wt.% Ga_2O_3. The O_2 gas was 99.95% pure and NO was 99.5%.

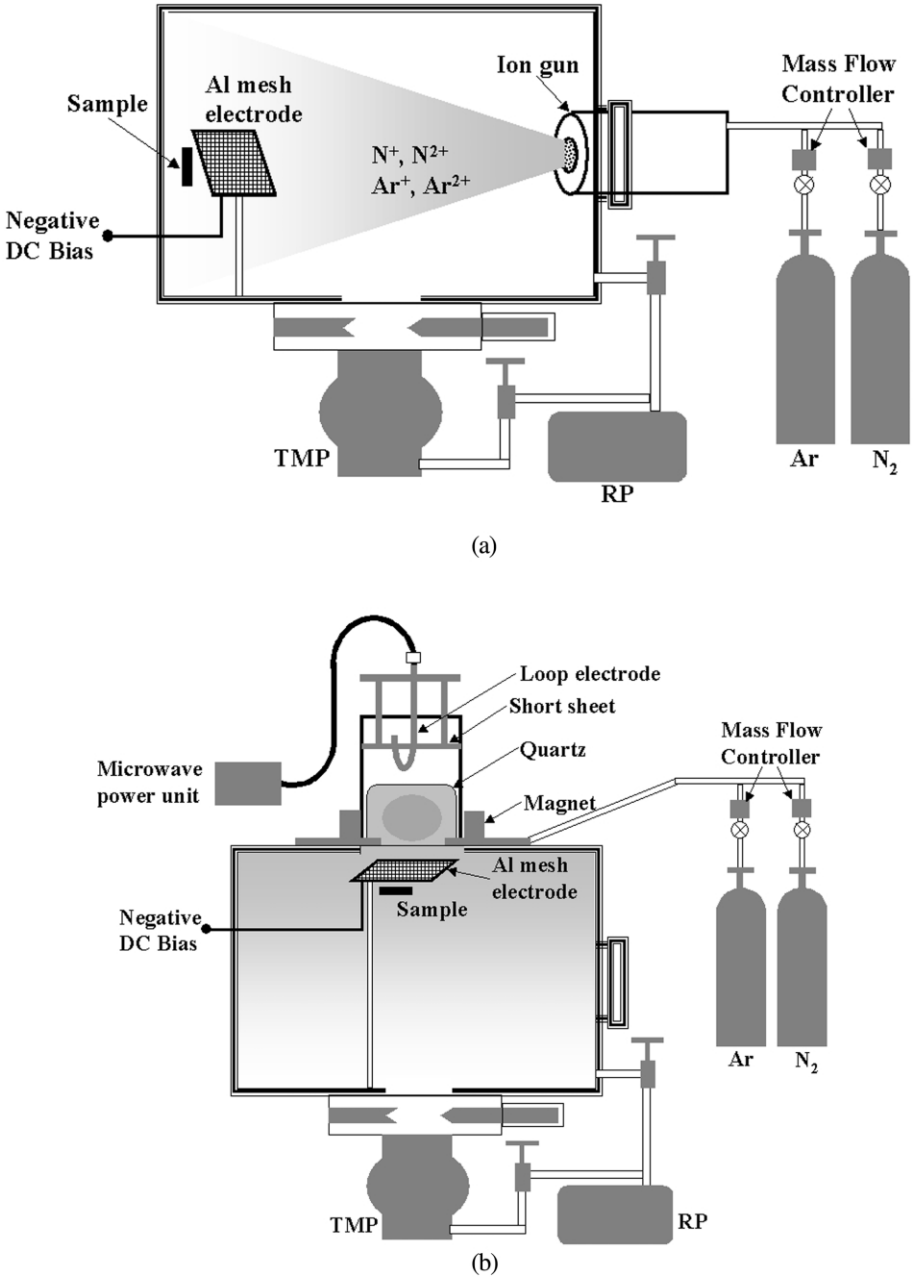

Fig. 1. Co-doping system consisting of (a) ion gun and (b) microwave ECR plasma source.

Table 2
Doping conditions

Sample	Doping conditions
#1-I	Ion gun Total pressure, 0.2 Pa N_2/Ar=6:4 sccm Ion energy, 256 eV Al mesh bias, −100 V
#1-II	Microwave ECR Total pressure, 3.5 Pa N_2/Ar=13:2 sccm Microwave power, 150 W Al mesh bias, −10 V 10 min
#2-1	Ion gun Total pressure, 0.2 Pa N_2/Ar=3:2 sccm Ion energy, 500 eV Al mesh bias, 0 V 10 min
#2-II	Microwave ECR Same as #1 II

source. We have investigated the structural properties of these synthesized N-doped ZnO films by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Optical and electrical characteristics of the films were also studied by UV–visible photometry, photoluminescence (PL) and Hall measurement by the van der Pauw method.

2. Experimental

A detailed description of the PLD system is reported elsewhere [9]. Film deposition was carried out in a stainless steel vacuum chamber that can be evacuated to a base pressure of 6.7×10^{-4} Pa. A KrF excimer laser (Lambda Physik, COMPex205, $\lambda=248$ nm, pulse duration of 25 ns, repetition rate of 10 Hz, maximum energy of 650 mJ/pulse) was used to ablate the target. Films with a thickness of ~400 nm were grown on Al_2O_3(0001) and amorphous quartz glass substrates placed 5 cm away from the target. The deposition conditions for the films are listed in Table 1. After deposition of samples #1 and #2, we prepared N-doped ZnO films at RT using two kinds of co-doping methods: (I) an ion gun (Anatech, IG30/IS3000); and (II) a microwave ECR plasma source, as shown in Fig. 1 and Table 2. Here we have used Al as a donor dopant. Negative DC bias was applied to the Al mesh electrode placed in front of the samples. As ions such as Ar^+, Ar^{2+}, N^+ and N_2^+ are accelerated and the Al mesh electrode is sputtered by ions, we can expect both Al and N elements to be incorporated in the ZnO film. After this doping process, annealing was carried out at a temperature of 850 °C in N_2 atmosphere for 30 min.

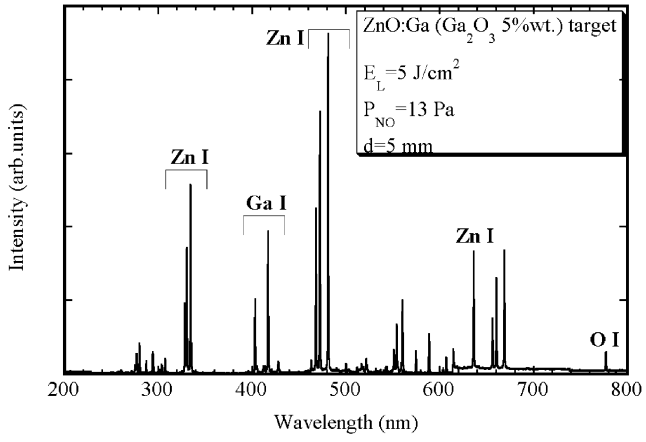

Fig. 2. Optical emission spectrum of the plasma plume generated by laser ablating a ZnO:Ga target at $E_L=5$ J cm^{-2} and $P_{NO}=13$ Pa.

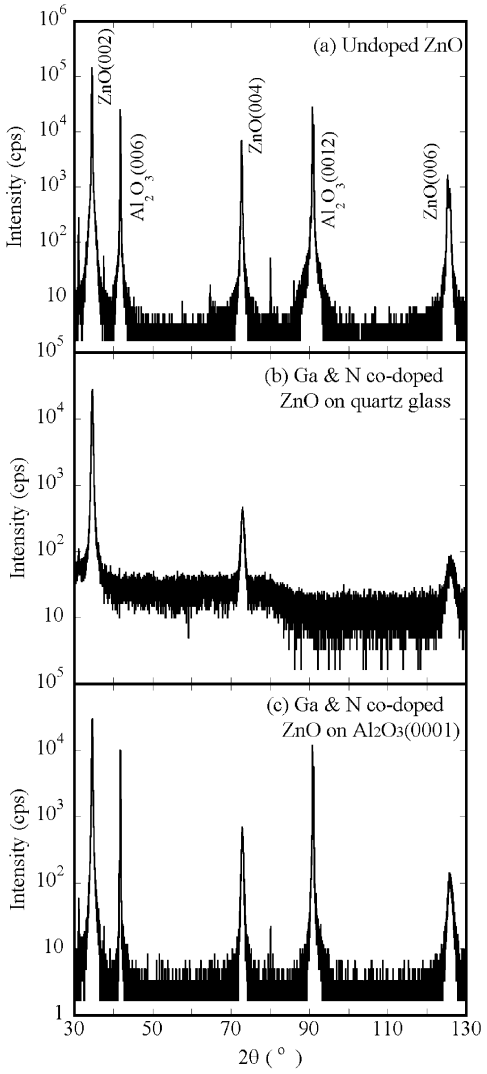

Fig. 3. XRD patterns of: (a) sample #1, undoped ZnO; (b) sample #3, Ga- and N-co-doped ZnO on amorphous quartz glass; and (c) sample #4, Ga- and N-co-doped ZnO on Al_2O_3(0001).

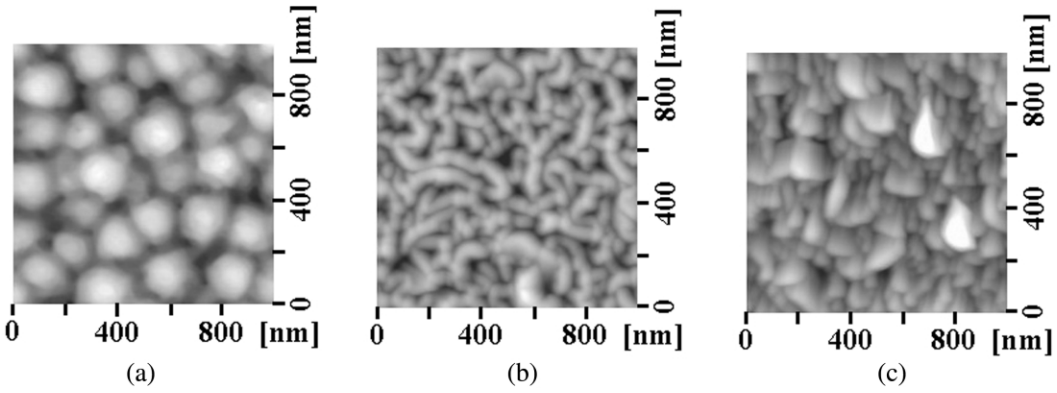

Fig. 4. AFM images of: (a) sample #1, undoped ZnO; (b) sample #3, Ga- and N-co-doped ZnO on amorphous quartz glass; and (c) sample #4, Ga- and N-co-doped ZnO on $Al_2O_3(0001)$.

The structural properties of films were investigated using XRD (Rigaku, RINT2100/PC) with a CuK_α ($\lambda = 1.5406$ Å) source and AFM (Seiko Instruments, SPI3800N). XPS (VG Scientific, Sigma Probe) measurements with an AlK_α (1486.6 eV) source were made to identify the chemical state. The optical transparency was measured by UV–visible photometry (Shimadzu, UV-160). Hall measurements (electrical resistivity, carrier density, mobility and the major conduction type) were performed by a four-probe van der Pauw method in a magnetic field of 3 kG. Au contacts on the film surface were deposited by vacuum vapor deposition. For the PL measurement, an area with a diameter of 1 mm of the sample was irradiated by the third-harmonic light of a Nd:YAG laser (355 nm, 6 ns, 10 Hz). PL emission spectra were taken using a spectrograph (Acton Research, SpectraPro-308i) equipped with an ICCD camera (Princeton Inc, ICCD-576G) and a detector controller (Princeton Inc, ST-138S).

3. Results and discussion

3.1. Characteristics of films grown by ablating ZnO:Ga target in NO gas

The optical emission of a plasma plume generated by ablating a ZnO:Ga target was measured at a distance $d = 5$ mm from the target surface. Fig. 2 shows the spectrum of ZnO:Ga plasma produced at laser fluence of $E_L = 5$ J/cm^2 and NO gas pressure of $P_{NO} = 13$ Pa. Strong emission lines at 328.2, 330.3, 334.6, 468.0, 472.2, 481.1, 518.2 and 636.2 nm are due to the Zn atomic lines (Zn I). Emission from the Ga atomic lines (Ga I) at 403.3 and 417.2 nm, and O (O I) at 777.2 nm was also observed. Since this O I line was found in the ablation plume in vacuum (9×10^{-4} Pa), most of oxygen radicals seem to originate from material ablated from the ZnO:Ga target. NO molecular emission lines were not observed. Weak emission centered at approximately 300 and 500–600 nm is likely molecular emission lines, such as first-positive or second-positive N_2

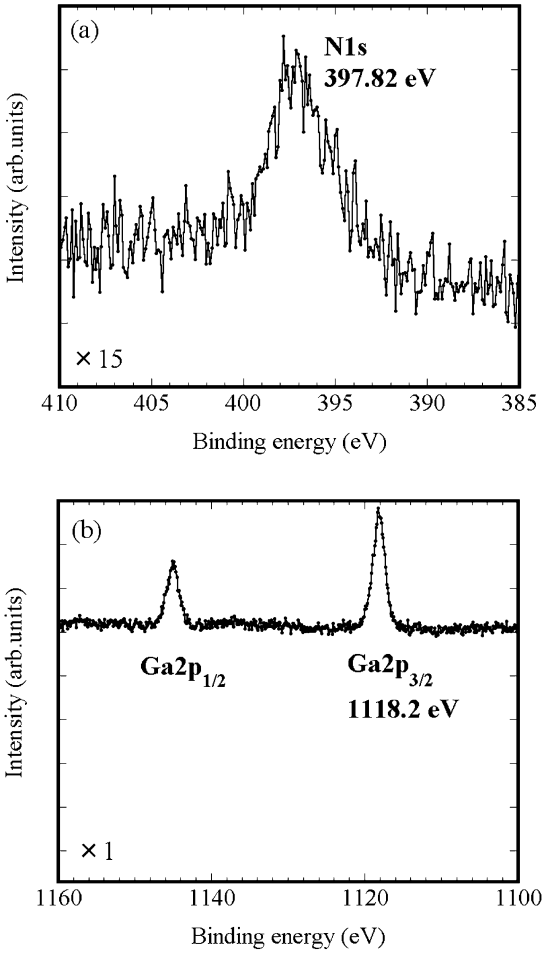

Fig. 5. XPS spectra for (a) N 1s and (b) Ga 2p of sample #3, Ga- and N-co-doped ZnO on amorphous quartz glass.

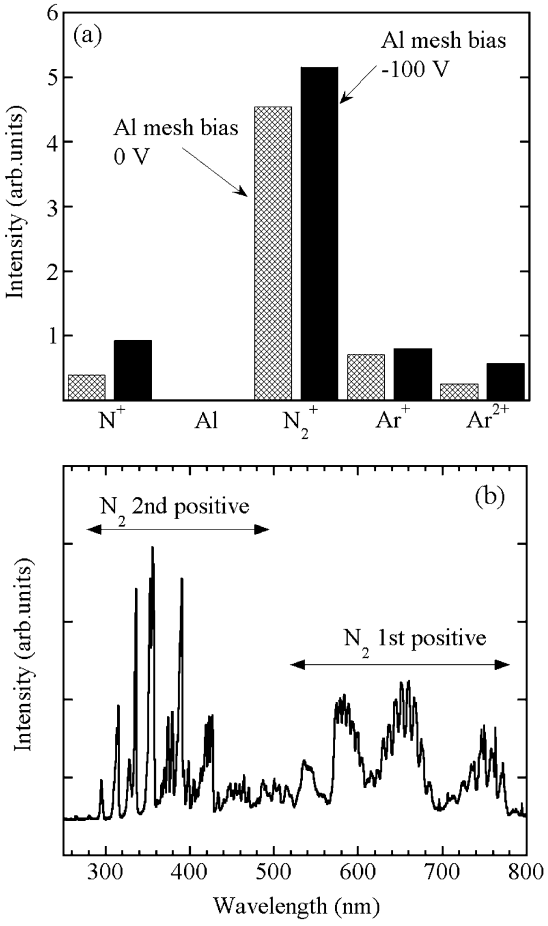

Fig. 6. Plasma status results: (a) mass spectrum by QMS, on applying Al mesh bias of 0 or −100 V using an ion gun in mixed Ar/N_2 = 2:3 sccm; and (b) optical emission spectrum of a microwave ECR mixed Ar/N_2 = 13:2 sccm plasma.

transitions. Although specific lines for NO species were not observed, N radicals were generated through the dissociation of NO.

Fig. 3 shows XRD patterns of undoped ZnO and Ga- and N-co-doped ZnO films. We have studied the dependence of film crystallinity on deposition conditions, such as the oxygen gas pressure and substrate temperature, in previous experiments [10]. Undoped ZnO films on Al_2O_3(0001), which were deposited under optimum conditions (E_L = 2 J/cm^2, P_{O_2} = 0.7 Pa, T_s = 550 °C), have a high *c*-axis (002) orientation, as shown in Fig. 3a. XRD for Ga- and N-co-doped ZnO films (Fig. 3b,c) shows (002), (004) and (006) planes, indicating *c*-axis orientation. Fig. 4 shows 1×1-μm^2 AFM images of the films shown in Fig. 3. Ga- and N-co-doped ZnO films shown in Fig. 4b,c consist of slender-shaped grains having roughness of approximately 90 nm, while the undoped ZnO film shown in Fig. 4a has hexagonally shaped grains with a uniform sizes of approximately 150–200 nm.

In order to investigate the chemical state of Ga and N in ZnO, we carried out XPS measurements. Fig. 5 displays the XPS spectra of N 1s and Ga 2p for sample #3. As shown in Fig. 5, a relatively weak N 1s peak centered at 397.82 eV and a Ga $2p_{3/2}$ peak centered at 1118.2 eV were observed. Joseph et al. [11] reported that the peak positions of N 1s at 397.84 eV and Ga 2p at 1118.8 eV, which were measured on their Ga- and N-co-doped p-type ZnO film, indicate the presence of Ga–N bonding, because these two peak positions are in agreement with those of XPS spectra on GaN. Therefore, our Ga- and N-co-doped ZnO film, which was synthesized by ablating a ZnO:Ga target in NO gas, also has Ga–N bonding. The relative ratio of Ga/N estimated from the area of Ga $2p_{3/2}$ and N 1s peaks is 1:2.67 at the film surface. Moreover, the Ga/N ratio changed to 1:0.98, 1:0.77 and 1:0.76 with increasing Ar^+ ion etching time (60, 120 and 180 s, respectively). However, a Ga/N ratio of 1:6 was reported by Joseph et al. [11]. A value corresponding to Ga/N = 1:2 was predicted by theoretical calculations for p-type ZnO grown by a co-doping process [12]. We confirmed the presence of Ga–N bonding in the co-doped ZnO film, but only low incorporation of N in the film was observed.

3.2. Characteristics of N-doped ZnO films using an ion gun and a microwave ECR plasma source

In our current co-doping method, the Al mesh electrode was placed in front of an undoped ZnO film to generate Al elements via sputtering by Ar^+, Ar^{2+}, N^+

Table 3
Electrical properties

Sample	Resistivity (Ω cm)	Mobility (cm^2 V^{-1} s^{-1})	Carrier density (cm^{-3})	Carrier type
Undoped ZnO (sample #1)	0.48	2.18×10^{3}	4.59×10^{15}	n
#1 I	5.75×10^{-2}	1.67×10^{3}	6.51×10^{17}	n
#1 II	3.98×10^{-2}	49.7	3.16×10^{18}	n
#2 I	1.72×10^{-3}	26.3	1.38×10^{20}	n
#2 II	1.59×10^{-3}	60.9	6.44×10^{19}	n
#3	8.01×10^{-3}	1.40×10^{2}	5.57×10^{18}	n
#4	2.85×10^{-3}	30.9	7.09×10^{19}	n

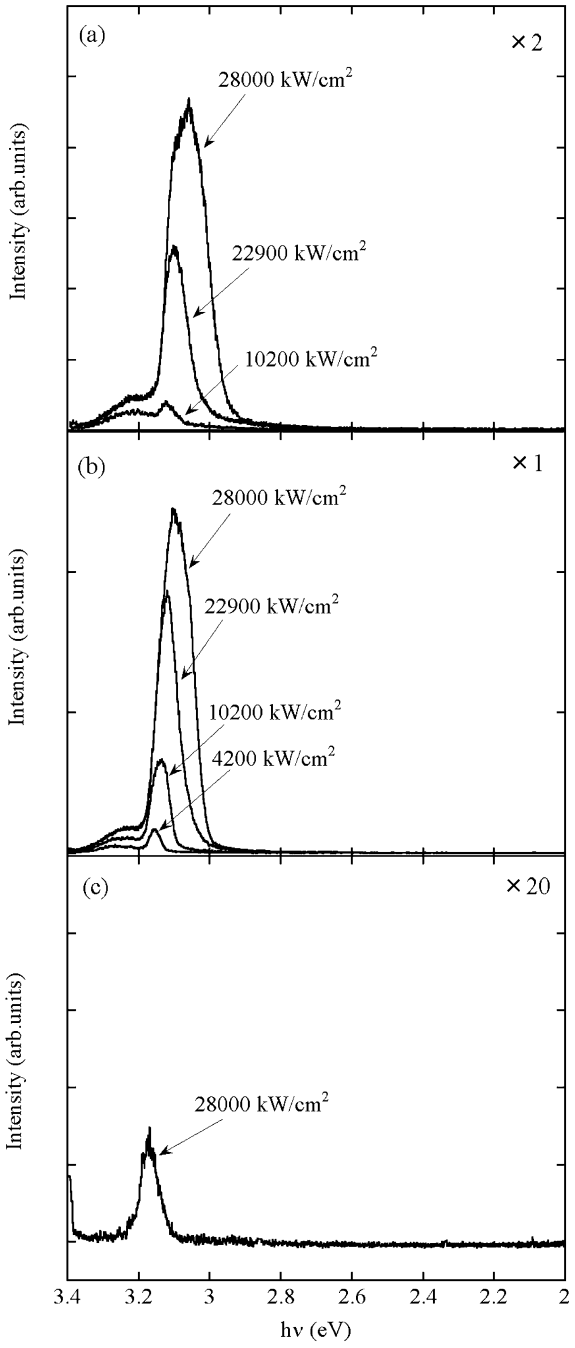

Fig. 7. PL spectra of: (a) sample #1 (undoped ZnO); (b) sample #1-I; and (c) sample #2-II.

and N_2^+ ions. The mass spectrum measured by a quadrupole mass spectrometer (QMS; Anelva, AQA-200) under the co-doping condition I is shown in Fig. 6a. The optical emission spectrum under the co-doping condition II is shown in Fig. 6b. However, no atomic or ionic species of Al were observed in the plasma by either QMS or optical emission measurements, as shown in Fig. 6. As a result, no remarkable N 1s peaks in the XPS spectra of Al- and N-co-doped ZnO films (samples #1-I and #1-II) were observed. Kumatsu et al. have reported the difficulty of N doping because N is a very insoluble element in ZnO [13].

3.3. Electrical properties

Table 3 shows the electrical properties measured by Hall effect measurements using a four-probe van der Pauw method. In this paper, p-type ZnO films were not obtained using our co-doping methods. The resistivity of co-doped ZnO films is lower than that of the undoped ZnO film, and the carrier density for the doped samples increased. The undoped ZnO films (samples #1-I and -II) have low resistivity and high carrier (electron) density due to the annealing procedure. Other films (samples #2–#4) have Ga–N bonding with a small amount of N. Thus, in order to grow p-type ZnO material, it is necessary to suppress the doping level of Ga and control the ratio of Ga and N.

3.4. Photoluminescence

Fig. 7 shows PL spectra of optically pumped samples #1 (undoped ZnO), #1-II and #2-II at RT. Fig. 7a for undoped ZnO film indicates a broad PL spectrum centered at 3.24 eV, attributed to the free-exciton spontaneous emission at low pumping power. When the pumping power is increased, new PL peaks appear at low photon energy of approximately 3.05–3.10 eV, which is lower than that of the spontaneous free-exciton emission peak. This peak corresponds to an exciton–exciton scattering process. In Fig. 7b for doped ZnO films, the PL intensity is enhanced due to the effect of annealing. The very weak PL peak of sample #2-II is shown in Fig. 7c. Another peak, different from those in Fig. 7a,b, is observed at approximately 3.17 eV. Ga- and N-co-doped ZnO films (sample #3 and #4) grown by ablating a ZnO:Ga target in NO gas showed no PL peak, in spite of increased pumping power.

4. Conclusion

We have attempted to synthesize p-type ZnO films using various co-doping methods. We have identified the presence of Ga–N bonding in ZnO films, but could not obtain Ga- and N-co-doped p-type ZnO film. However, our proposal for a co-doping method by ablating a ZnO:Ga target in NO gas is a very simple technique and may possibly be successfully used for the fabrication of high-quality p-type ZnO.

References

[1] B. Lin, Z. Fu, Y. Jia, Appl. Phys. Lett. 79 (2001) 943.
[2] M. Kawasaki, A. Ohtomo, U. Ohkubo, H. Koinuma, Z.K. Thang, P. Yu, G.K.L. Wong, B.P. Zhang, Y. Segawa, Mater. Sci. Eng. B 56 (1998) 239.
[3] X.L. Guo, H. Tabata, T. Kawai, J. Cryst. Growth 223 (2001) 135.

[4] K. Minegishi, Y. Koiwai, Y. Kikuchi, K. Yano, M. Kasuga, A. Shimizu, Jpn. J. Appl. Phys. 36 (1997) L1453.
[5] Y.R. Ryu, S. Zhu, D.C. Look, J.M. Wrobel, H.M. Jeong, H.W. White, J. Cryst. Growth 216 (2000) 330.
[6] X.L. Guo, J.H. Choi, H. Tabata, T. Kawai, Jpn. J. Appl. Phys. 40 (2001) L177.
[7] Y.R. Ryu, W.J. Kim, H.W. White, J. Cryst. Growth 219 (2000) 419.
[8] S. Aoqui, T. Ohshima, T. Ikegami, K. Ebihara, Sci. Technol. Adv. Mater. 2 (2001) 533.
[9] T. Ohshima, R.K. Thareja, T. Ikegami, K. Ebihara, J. Narayan, Sci. Technol. Adv. Mater. 2 (2001) 517.
[10] T. Ohshima, R.K. Thareja, T. Ikegami, K. Ebihara, Surf. Corros. Mater., submitted for publication.
[11] M. Joseph, H. Tabata, T. Kawai, Jpn. J. Appl. Phys. 38 (1999) L1205.
[12] T. Yamamoto, H.K. Yoshida, Jpn. J. Appl. Phys. 38 (1999) L166.
[13] M. Kumatsu, N. Ohashi, I. Sakaguchi, S. Hishita, H. Haneda, Appl. Surf. Sci. 7760 (2002) 1.