/

Article / Book Information

Title	Nitrogen doped Mg_x_Zn_1-x_O/ZnO single heterostructure ultraviolet light-emitting diodes on ZnO substrates
Authors	K. Nakahara,S. Akasaka,H. Yuji,K. Tamura,T. Fujii,Y. Nishimoto,D. Takamizu,A. Sasaki,T. Tanabe,H. Takasu,H. Amaike,T. Onuma,S. F. Chichibu,A. Tsukazaki,A. Ohtomo,M. Kawasaki
Citation	Applied Physics Letters, Vol. 97, No. 1,
Pub. date	2010, 7
URL	http://scitation.aip.org/content/aip/journal/apl
Copyright	Copyright (c) 2010 American Institute of Physics

Nitrogen doped Mg$_x$Zn$_{1-x}$O/ZnO single heterostructure ultraviolet light-emitting diodes on ZnO substrates

K. Nakahara,[1,a)] S. Akasaka,[1] H. Yuji,[1] K. Tamura,[1] T. Fujii,[1] Y. Nishimoto,[1] D. Takamizu,[1] A. Sasaki,[1] T. Tanabe,[1] H. Takasu,[1] H. Amaike,[2] T. Onuma,[2] S. F. Chichibu,[2] A. Tsukazaki,[3] A. Ohtomo,[3] and M. Kawasaki[3,4,b)]

[1]*Interdisciplinary Devices R&D Center, ROHM Co. Ltd., Kyoto 615-8585, Japan*
[2]*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan*
[3]*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[4]*WPI Advanced Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan and CREST, Japan Science and Technology Agency, Tokyo 102-0075, Japan*

We have grown nitrogen-doped Mg$_x$Zn$_{1-x}$O:N films on Zn-polar ZnO single crystal substrates by molecular beam epitaxy. As N-sources, we employed NO-plasma or NH$_3$ gas itself. As x increased, optimum growth temperature window for smooth film morphology shifted to higher temperatures, while maintaining high N-concentration ($\sim 1 \times 10^{19}$ cm^{-3}). The heterostructures of Mg$_x$Zn$_{1-x}$O:N ($0.1 \leq x \leq 0.4$)/ZnO were fabricated into light emitting diodes of 500-μm-diameter. We observed ultraviolet near-band-edge emission ($\lambda \sim 382$ nm) with an output power of 0.1 μW for a NO-plasma-doped LED and 70 μW for a NH$_3$-doped one at a bias current of 30 mA. © *2010 American Institute of Physics*. [doi:10.1063/1.3459139]

ZnO, with a room-temperature direct band gap of 3.37 eV ($\lambda = 369$ nm) and a large exciton binding energy (60 meV), is a promising candidate for making cost-competitive ultraviolet light emitting diodes (LEDs).[1–4] ZnO is an as-grown n-type semiconductor due to crystalline defects serving as donors.[5] Tsukazaki *et al.*[6,7] clearly indicated that the major carrier type can be turned into p-type and demonstrated p-n junction LEDs. However, the experiments reported previously involved certain challenges in extending the technology to industrial mass-production.

First, Tsukazaki *et al.* employed ScAlMgO$_4$ (SCAM) substrates to grow high-quality ZnO films. One advantage of SCAM as a substrate material is that it has an excellent lattice-matched condition. However, SCAM has some problems; for example, it is an expensive compound because Sc is a rare element, it is difficult to grow large crystals,[8] and it is an insulator, which results in a complicated LED structure because the device geometry requires two electrical contacts fabricated on one side of the substrate (this is also the case for GaN-based LEDs on sapphire).[9,10] Second, Tsukazaki *et al.* utilized a pulsed-laser deposition (PLD) technique that involves the critical difficulty that impurities in the starting materials (targets) are inevitably transferred into the grown films. Single-crystal ZnO with high purity can be used for PLD-ZnO growth but the unavoidable choice of a sintered "ceramic" Mg$_x$Zn$_{1-x}$O target to produce p-type Mg$_x$Zn$_{1-x}$O gives rise to contamination with typical donor elements such as Si and Al at a level of a few hundred ppm.[11] Third, the growth temperature (T_g) was repeatedly modulated between low (~ 400 °C) and high (~ 1000 °C) levels while growing N-doped ZnO (ZnO:N) films for doping and activating N as an acceptor. This process is not suited for production because it is difficult to keep both low and high T_g stable simultaneously throughout the entire growth pro-cess. Note that the need for this process is due to the less efficient N-incorporation for the O-polar surface of ZnO films than for the Zn-polar surface.[12]

Our solution to the first problem is to adopt n-type single crystalline ZnO substrates, which facilitate a vertical contact geometry (a standard configuration of LEDs). Recently, ZnO bulk crystal substrates of up to 3 in. in diameter have become commercially available due to the advancement of a modified hydrothermal method.[13] For the second problem, we have employed molecular beam epitaxy, a mature technology in the field of III-V and II-V compound semiconductors. The authors have overcome the third problem by utilizing Zn-polar ZnO substrates, which allow N-doping even at a high T_g,[14] leading to an optimal growth conditions for N-doping where deterioration of the N-doped film crystalline quality can be avoided.

We selected ZnO substrates from which Li was eliminated by thermal annealing (Tokyo Denpa Co. Ltd.).[13] Their Zn-polar surfaces were chemomechanically polished so that 0.26 nm high steps (half of the c-axis lattice constant of a ZnO unit cell) and atomically flat terraces were clearly observed by atomic force microscopy (AFM) inspection (Mitsubishi Chemical Corporation). The source materials were 7N Zn, 6N Mg, 6N O$_2$ gas, 4N NO gas, and 5N NH$_3$ gas. The growth conditions of Mg$_x$Zn$_{1-x}$O:N on Zn-polar c-plane ZnO substrates were optimized at the highest allowable temperature, while maintaining an atomically smooth surface and a nitrogen concentration as high as 1×10^{19} cm^{-3}. Radio-frequency plasma sources were used to crack O$_2$ and NO molecules into O radicals and mixture of O and N radicals, respectively. NH$_3$ gas was directly supplied through a nozzle to the growing surface without any thermal or plasma cracking. The MgO molar fraction x, relating to the band gap energy of the Mg$_x$Zn$_{1-x}$O, was controlled by adjusting the Mg/Zn flux ratio and was calibrated using x-ray diffraction, photoluminescence characteristics, and Auger electron

a)Electronic mail: ken.nakahara@dsn.rohm.co.jp.
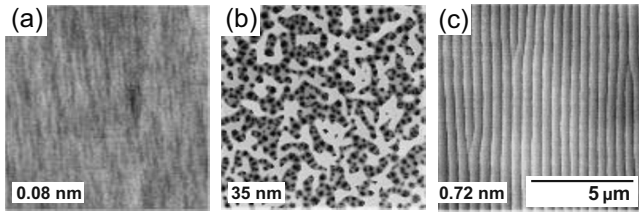b)Electronic mail: kawasaki@imr.tohoku.ac.jp.

FIG. 1. AFM images (10×10 μm^2) of the films (a) undoped ZnO grown at 750 °C, (b) N-doped ZnO grown at 750 °C, and (c) N-doped $Mg_{0.1}Zn_{0.9}O$ grown at 870 °C. The root-mean-square value of roughness is given in each image.
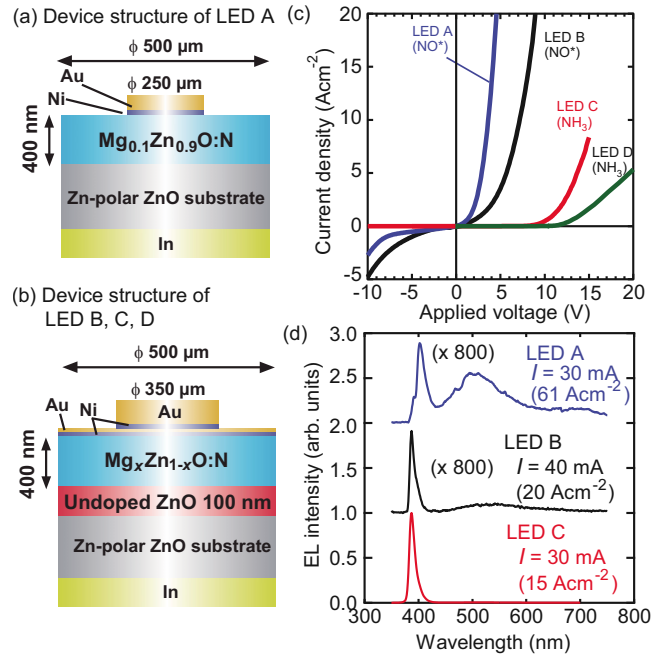

FIG. 2. (Color online) (a) and (b) depict cross-sectional schematics for LED A and those of B–D, respectively. The device was 500 μm in diameter and the back side of the ZnO substrates was bonded to a metal plate with In. The top electrode in (a) was formed as Au (200 nm)/Ni (10 nm) with a diameter of 250 μm. That of (b) consists of a semitransparent electrode of Au (4 nm)/Ni (2 nm) with a diameter of 500 μm and a contact pad of Au (500 nm)/Ni (2 nm) with a diameter of 350 μm. (c) The rectifying *I*-*V* curve measured for LEDs A, B, C, and D. (d) EL spectra from LEDs A–C. All spectra were measured at room temperature. Forward bias operation conditions are also shown.

spectroscopy.[14,15] Nitrogen concentration was determined by secondary ion mass spectroscopy.

We first focused our efforts on growing highly crystalline $Mg_xZn_{1-x}O$ films on ZnO substrates. The most critical condition for the substrate was found to be adjustment of the miscut angle: 0.5° off toward the $[10\bar{1}0]$ direction.[16] The straight step edges remained intact after growth for this particular condition but tended to meander and bunch for the other conditions, indicating stable crystallinity with the $\{10\bar{1}0\}$ *m*-plane. Figure 1(a) shows an AFM image of the ZnO film grown under the optimum conditions [T_g =750 °C with O_2 radical at a flow rate [$FL(O_2)$] of 1.0 standard cubic centimeter per minute (SCCM)]. The surface morphology is very similar to that of the substrate (not shown). When we switched the gas source from O_2 to NO (FL =0.5 SCCM) for making the ZnO:N at T_g=750 °C, the surface became rough [Fig. 1(b)], although a high level (3×10^{19} cm^{-3}) of N was incorporated. With this gas condition, we found that higher T_g was necessary to obtain a flat surface (not shown) similar to that of original substrate. The increase in *x* in $Mg_xZn_{1-x}O$ tended to shift the optimum T_g upward.[14] This trend resembles those for $Al_xGa_{1-x}As$ and $Al_xGa_{1-x}N$ alloy growths, where Al has lower surface diffusivity than Ga due to larger bond energy with As or N.[17,18] This scenario is thought to be applied in case of $Mg_xZn_{1-x}O$ as well. When we grew undoped $Mg_xZn_{1-x}O$ films ($x \le 0.12$) at T_g=870 °C, the surfaces remained smooth (not shown). The excellent quality of the $Mg_xZn_{1-x}O$ films was confirmed by the observation of a high-mobility two-dimensional electron gas (2DEG) confined at the ZnO/$Mg_xZn_{1-x}O$ interfaces.[19,20]

We now show the results for $Mg_xZn_{1-x}O$:N films grown using NO gas at T_g=870 °C. As stated above, smooth $Mg_xZn_{1-x}O$:N films could be grown at such a high T_g value, as shown in Fig. 1(c). The surfaces exhibited many coarse step edges, indicating that step bunching took place while growing in a step-flow mode. A typical terrace width was 300 nm, ruled by ~3 nm high bunched steps. The N-concentration was kept at reasonably high level of 8 $\times 10^{18}$ cm^{-3}, demonstrating a significant advantage of Zn-plane growth. We also examined the possibility of NH_3 as a N-dopant in view of the proposal by Van de Walle who claimed that the use of NH_3 lead to easier incorporation of N in ZnO.[21] Optimization of film growth processes were carried out to identify a set of conditions ($FL(NH_3)$=3 SCCM, $FL(O_2)$=3 SCCM, and T_g=870 °C) resulting in films with smooth surface similar to that shown in Fig. 1(c) and N-concentration of 1×10^{19} cm^{-3}. It was not possible to prove the *p*-type conduction in our $Mg_{1-x}Zn_xO$:N films by such conventional measurements as Hall or Seebeck effects

due to the parallel conduction path in the *n*-type substrates. If it were *n*-type, we should have observed high in-plane conductivity due to 2DEG at the ZnO/$Mg_xZn_{1-x}O$ interfaces.[20] We have never observed 2DEG in the $Mg_{1-x}Zn_xO$:N/ZnO using above mentioned films, supporting the depletion of 2DEG by the presence of *p*-type $Mg_{1-x}Zn_xO$:N.

We employed 400 nm thick $Mg_{0.1}Zn_{0.9}O$:N films shown in Fig. 1(c) for fabricating LEDs A and B whose structures are schematically illustrated in Figs. 2(a) and 2(b), respectively. The current-voltage (*I*-*V*) characteristics of the LEDs A and B exhibited a rectifying property with a turn-on voltage of approximately 3 V, as shown in Fig. 2(c). The electroluminescence (EL) spectra of these devices are shown in Fig. 2(d). Both LEDs showed a sharp EL peak at the near-band-edge (NBE, λ=380–400 nm), which was sharper and shorter in wavelength than that of a ZnO *p*-*n* junction reported previously (λ=430 nm).[7] The result implies an effective blocking of electrons by the wide band gap $Mg_{0.1}Zn_{0.9}O$:N layers, leading to efficient exciton recombination in the *n*-type ZnO layers. In fact, a characteristic orange emission (λ=610 nm) observed in the PL spectrum (not shown) of the $Mg_{0.1}Zn_{0.9}O$:N film was absent in the EL spectra of the LEDs. Another characteristic green emission around 500 nm, however, was observed in the EL spectra. A similar emission band was also observed in the PL spectrum of the ZnO substrate. By inserting an undoped ZnO epitaxial film, the green emission was considerably suppressed, indicating that the homoepitaxial ZnO was of better quality than the ZnO substrates and most of the radiative recombination took place in the ZnO film.
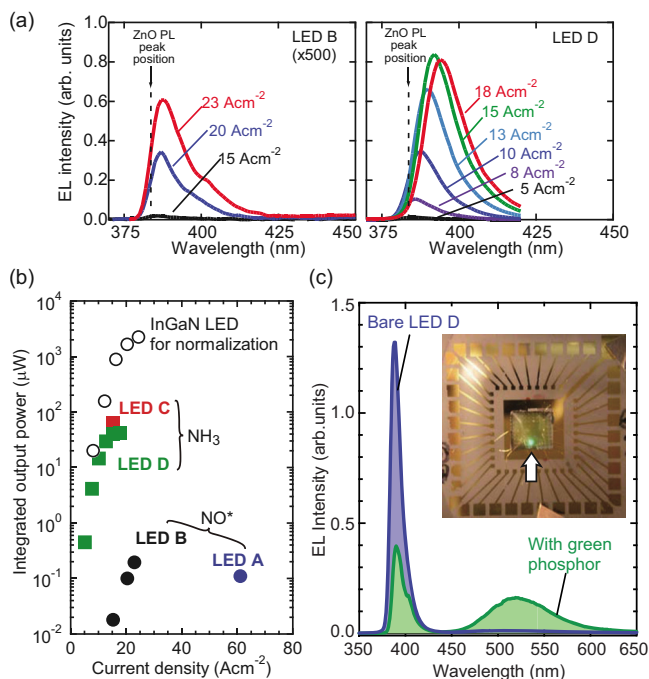
FIG. 3. (Color online) (a) EL spectra of the LEDs B and D operated with various current densities. (b) Integrated EL intensity for the spectra shown in (a) (LEDs B and D) as a function of applied current density. The data for LEDs A and C are also shown. The integration was conducted in a wavelength range from 350 to 450 nm. (c) EL spectra for bare and with a green phosphor coating for LED D at an operation current of 40 mA. Inset is a picture taken under standard laboratory illumination. Emission from the phosphor can be clearly seen as indicated by an arrow.

We also fabricated LED C and D whose structure is shown in Fig. 2(b) with employing $Mg_{0.4}Zn_{0.6}O$:N grown with NH_3. Although the turn-on voltage is as high as 10 V as shown in Fig. 2(c), presumably due to poor electrical contact with Ni and highly resistive $Mg_{0.4}Zn_{0.6}O$:N layer, clear rectification was observed as shown in Fig. 2(c). The EL of LED C was much more intense by a factor of 800 than those of LED A and B and the spectral weight was more concentrated in NBE emission.

The NBE emission spectra of LEDs B and D are shown in Fig. 3(a). The EL peak energies were slightly lower than the PL peak energy of ZnO (broken line). One of the reasons is self-absorption of the ZnO emission in the thick ZnO substrate. In addition, both LEDs showed a clear redshift tendency as the operating current increased. Therefore, a heating effect is also likely. Actually, the PL peak shifted to longer wavelengths at 0.06 nm/°C, yielding device temperatures of 67 °C at 23 A cm^{-2} operation in LED B and 175 °C at 18 A cm^{-2} operation in LED D. These devices broke down when we were measuring spectra at higher currents. We assume that the severe heating was due to the high contact resistance at the Ni/$Mg_{0.1}Zn_{0.9}O$:N interfaces. Reducing the contact resistance is an essential pathway for improving device performance. Figure 3(b) shows the integrated NBE emission of these LEDs as a function of the forward current density. Our EL measurement system was calibrated by using a commercial $In_xGa_{1-x}N$ based LED having similar peak wavelength, whose output power was measured by a calibrated integrating sphere system. The output power ranged from 0.1 to 70 μW at the maximum attainable operation current (typically 30–40 mA).

The LED D was coated with a 0.1-mm-thick epoxy resin containing 5 wt % $(BaEu)(MgMn)Al_{10}O_{17}$ (LP-G3, Mitsubishi Chemical) green phosphor. This structure is similar to the combination of commercial white LED composed of 470 nm blue (InGa)N LED and a garnet yellow phosphor, the only material choice with a high excitation efficiency by the blue LED. As shown in Fig. 3(c), a part of ultraviolet NBE was converted into green. The UV emission of ZnO LED will make it possible to excite many existing phosphors developed for fluorescent tube, enabling better color rendering.

In conclusion, we have optimized the MBE conditions of N-doped $Mg_xZn_{1-x}O$ films on Zn-polar ZnO substrates to obtain smooth surface films with a nitrogen concentration of $\sim 1 \times 10^{19}$ cm^{-3}. NBE emission was clearly observed in the EL spectra from LEDs. Further improvements in material quality, LED design, and processing are of interest. It is a promising fact that NH_3 worked as N dopant because NH_3 is more suitable than radical nitrogen sources for the future challenge of making ZnO based LEDs by use of an industry-suited growth method of metal organic chemical vapor deposition.

[1]Ü. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho, and H. Morkoc, J. Appl. Phys. **98**, 041301 (2005).
[2]C. Klingshirn, Phys. Status Solidi B **244**, 3027 (2007).
[3]D. M. Bagnall, Y. F. Chen, Z. Zhu, T. Yao, S. Koyama, M. Y. Shen, and T. Goto, Appl. Phys. Lett. **70**, 2230 (1997).
[4]P. Zu, Z. K. Tang, G. K. L. Wong, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, Solid State Commun. **103**, 459 (1997).
[5]D. C. Look, J. W. Hemsky, and J. R. Sizelove, Phys. Rev. Lett. **82**, 2552 (1999).
[6]A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, and M. Kawasaki, Nature Mater. **4**, 42 (2005).
[7]A. Tsukazaki, M. Kubota, A. Ohtomo, T. Onuma, K. Ohtani, H. Ohno, S. F. Chichibu, and M. Kawasaki, Jpn. J. Appl. Phys., Part 2 **44**, L643 (2005).
[8]E. S. Hellman, C. D. Brandle, L. F. Schneemeyer, D. Wiesmann, I. Brener, T. Siegrist, D. N. E. Buchanan, and E. H. Hartfold, MRS Internet J. Nitride Semicond. Res. **1**, 1 (1996).
[9]S. Nakamura and G. Fasol, *The Blue Laser Diode* (Springer, New York, 1997).
[10]F. A. Ponce and D. P. Bour, Nature (London) **386**, 351 (1997).
[11]M. Sumiya, S. Fuke, A. Tsukazaki, K. Tamura, A. Ohtomo, M. Kawasaki, and H. Koinuma, J. Appl. Phys. **93**, 2562 (2003).
[12]K. Nakahara, H. Takasu, P. Fons, A. Yamada, K. Iwata, K. Matsubara, R. Hunger, and S. Niki, J. Cryst. Growth **237–239**, 503 (2002).
[13]K. Maeda, M. Sato, I. Niikura, and T. Fukuda, Semicond. Sci. Technol. **20**, S49 (2005).
[14]A. Ohtomo, M. Kawasaki, T. Koida, K. Masubuchi, H. Koinuma, Y. Sakurai, Y. Yoshida, T. Yasuda, and Y. Segawa, Appl. Phys. Lett. **72**, 2466 (1998).
[15]Y. Nishimoto, K. Nakahara, D. Takamizu, A. Sasaki, K. Tamura, S. Akasaka, H. Yuji, T. Fujii, T. Tanabe, H. Takasu, A. Tsukazaki, A. Ohtomo, T. Onuma, S. F. Chichibu, and M. Kawasaki, Appl. Phys. Express **1**, 091202 (2008).
[16]H. Yuji, K. Nakahara, K. Tamura, S. Akasaka, A. Sasaki, T. Tanabe, H. Takasu, T. Onuma, S. F. Chichibu, A. Tsukazaki, A. Ohotomo, and M. Kawasaki, *Proceedings of Zinc Oxide Materials and Devices III*, Son Jose, edited by F. H. Teherani and C. W. Litton (SPIE, Bellingham, WA, 2008), Vol. 6895, p. 68950D.
[17]F. Alexandre, L. Goldstein, G. Leroux, M. C. Joncour, H. Thibierge, and E. V. K. Rao, J. Vac. Sci. Technol. B **3**, 950 (1985).
[18]C. R. Elsass, C. Poblenz, B. Heying, P. Fini, P. M. Petroff, S. P. DenBaars, U. K. Mishra, and J. S. Speck, J. Cryst. Growth **233**, 709 (2001).
[19]A. Tsukazaki, A. Ohtomo, T. Kita, Y. Ohno, H. Ohno, and M. Kawasaki, Science **315**, 1388 (2007).
[20]A. Tsukazaki, A. Ohtomo, M. Kawasaki, S. Akasaka, H. Yuji, K. Tamura, K. Nakahara, T. Tanabe, A. Kamisawa, T. Gokmen, J. Shabani, and M. Shayegan, Phys. Rev. B **78**, 233308 (2008).
[21]C. G. Van de Walle, Phys. Status Solidi B **229**, 221 (2002).