APPLIED PHYSICS LETTERS **93**, 132113 (2008)

Dominant ultraviolet light emissions in packed ZnO columnar homojunction diodes

Jieying Kong, Sheng Chu, Mario Olmedo, Lin Li, Zheng Yang, and Jianlin Liu[a)]
Quantum Structures Laboratory, Department of Electrical Engineering, University of California at Riverside, Riverside, California 92521, USA

(Received 11 July 2008; accepted 9 September 2008; published online 2 October 2008)

The growth of Sb-doped p-type ZnO/Ga-doped n-type ZnO homojunction on Si (100) substrate by molecular beam epitaxy led to closely packed vertical ZnO columns with lateral diameters ranging from 100 to 400 nm. Mesa structures were defined and Ohmic contact of both n-type ZnO and p-type ZnO was realized with Au/Ti and Au/NiO, respectively. I-V and C-V curves present typical electrical properties of a diode, indicating that reliable p-type ZnO was formed. Electroluminescence shows dominant ultraviolet emissions with insignificant deep-level related yellow/green band emissions at different drive currents from 60 to 100 mA at room temperature. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2992629]

ZnO is considered to be a promising material for ultraviolet (UV) light emitting diodes (LEDs) and laser diodes due to its direct band gap of 3.37 eV and large exciton binding energy of 60 meV.[1–3] Nevertheless, unlike n-type ZnO,[4] reliable p-type doping is difficult to achieve due to the possibility of holes getting compensated by the intrinsic donors such as zinc interstitials and oxygen vacancies. Therefore, previous efforts on ZnO p-n junctions are mostly made from n-type ZnO and other p-type semiconductors such as SiC, GaN, $SrCu_2O_2$, and so on.[5–7] The benefit of making those heterojunction LEDs is that it is easy to obtain a device, however, the chemical and crystallographic differences between ZnO and dissimilar materials give rise to the formation of interfacial defects, which makes negative impact on optical and electrical properties of diodes. With the development of p-type doping techniques, several groups recently reported LEDs based on ZnO p-n homojunction structures.[8–13] All of those devices, however, yield deep-level related emissions with much larger intensity than near band edge emissions. The fundamental reasons are radiative recombination associated with high-density inactive dopants, high-density Zn or O point defects, and poor material quality. To resolve some of these problems and achieve dominant near band edge emissions over deep-level emissions for possible practical applications, in this letter, we report our fabrication and characterization of Sb-doped p-type ZnO/Ga-doped n-type ZnO closely packed columnar structure LEDs on Si that show dominant UV emissions at room temperature. The reason of insignificant deep-level emissions in our devices is discussed.

ZnO p-n junction was grown on n-type Si (100) substrate (1–20 Ω cm) using molecular beam epitaxy system. A thin magnesium oxide (MgO) buffer layer was deposited at 350 °C to reduce the lattice mismatch between Si and ZnO, followed by 410 nm Ga-doped n-ZnO and 410 nm Sb-doped p-ZnO. X-ray diffraction (XRD) $\theta/2\theta$ scans show that the diode film grows preferentially along the c-direction of the ZnO wurtzite lattice [Fig. 1(a)]. Surface morphology and cross section of ZnO film were studied by scanning electron microscope (SEM). Figure 1(b) shows the top-view image of the ZnO film on Si substrate. It is evident that ZnO grains with in-plane size from 100 to 400 nm are formed, which is the typical result of oriented nucleation process due to the large lattice mismatch between ZnO and Si substrate.[14] Fig-

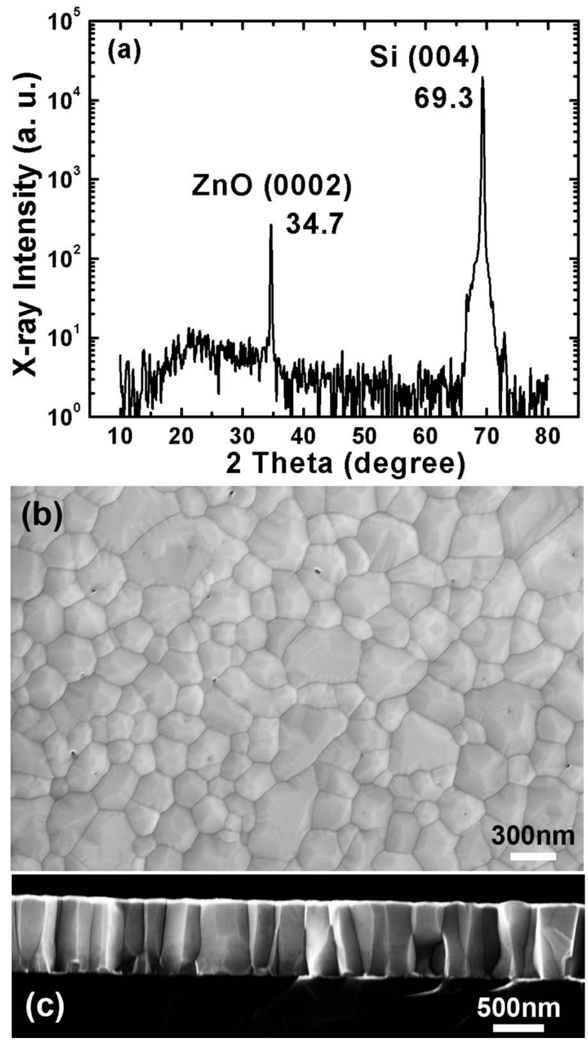

FIG. 1. (a) XRD spectrum of ZnO p-n junction on Si (100) substrate, (b) SEM image of sample surface, and (c) cross-sectional SEM image of the ZnO diode.

[a)]Electronic mail: jianlin@ee.ucr.edu.

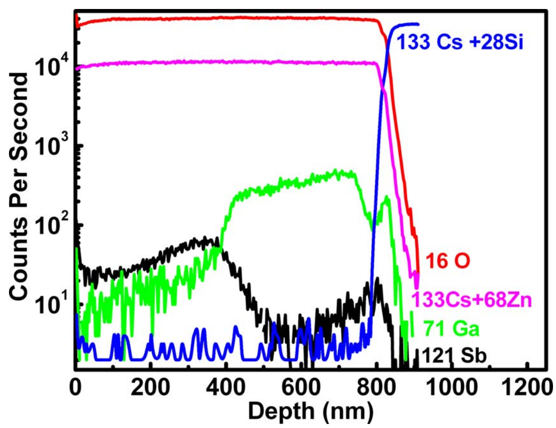

FIG. 2. (Color online) SIMS result of ZnO *p-n* junction on Si (100) substrate. The elemental profiles of Sb, Ga dopants, Zn, O, and Si substrate can be seen.

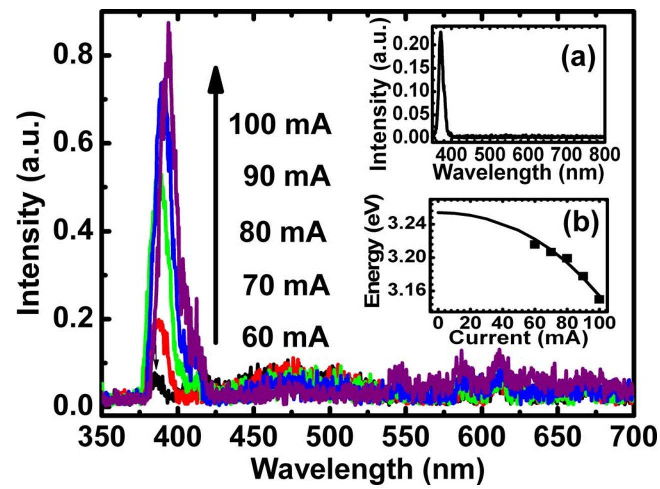

FIG. 4. (Color online) EL spectra of *p-n* ZnO diode at room temperature, with increasing injection current from 60 to 100 mA. (a) The inset is PL spectrum of the same device at room temperature; (b) is the fitting using Varshni's equation for near band emission energy at different temperatures. Here $\alpha=8.2\times10^{-4}$, $\beta=1060$.

ure 1(c) is the image in the cross-sectional configuration of the film, which clearly presents nanocolumnar structures. The elemental distribution of Zn, O, Sb, Ga, and Si was obtained by performing secondary ion mass spectroscopy (SIMS) measurements, as shown in Fig. 2. Dominant distribution of Sb and Ga dopants are in *p*-type and *n*-type layers, respectively, leading to relatively sharp *p-n* junction interface.

The *p-n* junction diodes with defined mesa size $800\times800\ \mu\text{m}^2$ were fabricated by employing standard photolithography techniques. Au/NiO (500/30 nm) and Au/Ti (200/30 nm) were then deposited on *p*-type ZnO and *n*-type ZnO, respectively, by lift-off process. The contacts were annealed at 550 °C for Au/NiO and 850 °C for Au/Ti to form Ohmic contact, as shown in the left inset of Fig. 3. The specific contact resistivity of *p*-layer was calculated to be $9.3\times10^{-5}\ \Omega\ \text{cm}^2$. The device was packaged onto TO5 can using conductive epoxy resin. Current-voltage (*I-V*) and capacitance-voltage (*C-V*) characteristics were measured using Agilent 4155C semiconductor parameter analyzer and Agilent 4284A precision *LCR* meter. Figure 3 shows *I-V* characteristics of the *p-n* junction and the right inset is *C-V* characteristics. The diode shows fairly good rectification behavior with a threshold voltage of about 2.5 V. These results suggest that we have formed ZnO *p-n* junction diodes.

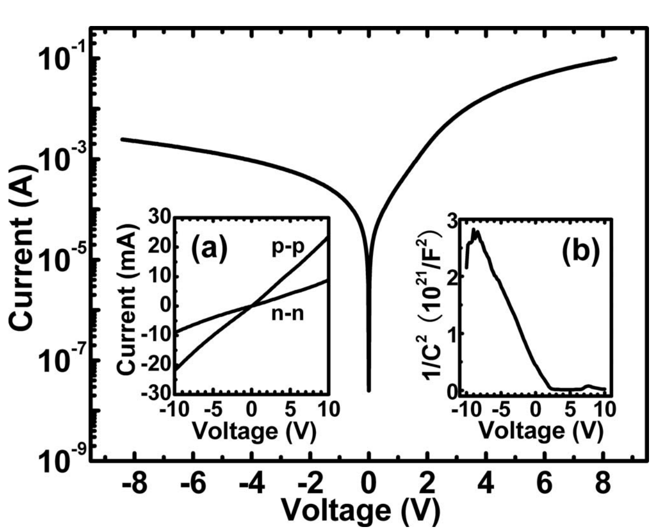

FIG. 3. *I-V* characteristics of the *p-n* homojunction diode, showing typical rectifying characteristics. (a) The left inset shows the *I-V* curve of both *n*-type and *p*-type contacts. (b) The right inset shows $1/C^2$-V characteristics confirming *p-n* junction with built-in potential of about 2.5 V.

Electroluminescence (EL) measurements were performed using an Oriel monochromator and photomultiplier tube at room temperature. The diode was biased under dc forward voltages. Figure 4 shows the EL spectra obtained at different injection currents. Near band edge emission at 3.2 eV started to appear when the current is 60 mA. Afterwards, the intensity of this emission increases as the injection current increases from 60 to 100 mA. Moreover, the intensity of this emission peak increases evidently from 60 to 80 mA while it changes less significantly from 80 to 100 mA, which is due to the heat effect as a result of the increasing current through the diode. Several other deep-level emission peaks near 475 nm (green band) and 610 nm (yellow band) were routinely reported in literatures, related to O vacancy and O interstitial in *n*-type and *p*-type ZnO, respectively.[15–17] In this case, experimental results show that UV near band edge emissions are always dominant in the emission spectra while defect-related yellow and green band emissions are very weak. Moreover, the dominance of UV emission is much clearer at higher injection currents. While injection current increases from 60 to 100 mA, the UV emission peak also slightly redshifts from 385 to 393 nm. This is typical in a radiative recombination process for direct band gap material because heat induced by increased injection current will decrease its effective band gap.[18] Fitting the experimental result by using Varshni's equation, $E_g(T)=E_0-\alpha\times T^2/(T+\beta)$, and assuming $(T-300\text{ K})\sim I^2$, we obtain α and β to be 8.2×10^{-4} and 1060, respectively, and E_g at 300 K for ZnO to be 3.25 eV. α and β values are consistent with what were reported.[19,20]

To understand the dominant UV emissions, we realized that the "film" consists of a great deal of vertical nanocolumns, which connect closely to each other. Therefore, the whole structure is a collection of packed ZnO *p-n* homojunction columns and the detected EL spectrum is a sum of emissions from each one of these columns. The stress from the lattice mismatch between ZnO and Si substrate is released by the formation of these columnar structures, whose sidewalls terminate a great deal of threading dislocations generated at column/substrate interface. With lower dislocation density in the upper diode portion of each column, nonradiative recombinations are reduced and UV near band edge emission is dominant. Deep-level radiative yellow/green band recombinations, which were routinely observed in other reported ZnO LEDs, are also reduced. This is also verified in the photoluminescence (PL) spectrum in the upper inset of Fig. 4 where no visible emissions are seen. Since the yellow/green band emissions are associated with oxygen interstitial/vacancy point defects, respectively,[8–13] our results suggest that ZnO on Si can achieve insignificant amount of point defects via the formation of columnar structures under appropriate growth conditions. The output power of this LED is estimated to be only 1 nW at drive current of 100 mA, calibrated by a commercial GaN based UV LED using Ocean Optics integrating sphere. The low output is due to a large amount of defects/dislocations existing in this structure, contributing to phonon-assisted nonradiative recombinations. To improve the efficiency, ZnO *pn* junctions with higher crystal quality are in progress.

In summary, UV ZnO LED on Si (100) substrate has been realized. Reliable *p*-type ZnO is formed and microscopically the *p-n* homojunction consists of column nanostructures. Au/NiO and Au/Ti make good Ohmic contacts to *p*-type and *n*-type portions of the ZnO nanocolumns for the formation of LED devices. *I-V* and *C-V* measurements show good rectification behavior and EL experiments demonstrate dominant UV emissions.

This work was supported by the ONR/DMEA through the center for NanoScience and Innovation for Defense (CNID) under Grant No. H94003-07-2-0703 and DOE under Grant No. DE-FG02-08ER46520.

[1]S. J. Pearton, D. P. Norton, K. Ip, Y. W. Heo, and T. Steiner, J. Vac. Sci. Technol. B **22**, 932 (2004).
[2]D. C. Look, Mater. Sci. Eng., B **80**, 383 (2001).
[3]D. C. Look, B. Claflin, Y. I. Alivov, and S. J. Park, Phys. Status Solidi A **201**, 2203 (2004).
[4]S. B. Zhang, S. H. Wei, and A. Zunger, Phys. Rev. B **63**, 075205 (2001).
[5]H. Ohta, M. Orita, M. Hirano, and H. Hosono, Appl. Phys. Lett. **77**, 475 (2000).
[6]Y. I. Alivov, J. E. V. Nostrand, D. C. Look, M. V. Chukichev, and B. M. Ataev, Appl. Phys. Lett. **83**, 2943 (2003).
[7]Ya. I. Alivov, U. Ozgur, S. Dogan, D. Johnstone, V. Avrutin, N. Onojima, C. Liu, J. Xie, Q. Fan, and H. Morkoç, Appl. Phys. Lett. **86**, 241108 (2005).
[8]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).
[9]W. Liu, S. L. Gu, J. D. Ye, S. M. Zhu, S. M. Liu, X. Zhou, R. Zhang, Y. Shi, Y. D. Zheng, Y. Hang, and C. L. Zhang, Appl. Phys. Lett. **88**, 092101 (2006).
[10]J. C. Sun, J. Z. Zhao, H. W. Liang, J. M. Bian, L. Z. Hu, H. Q. Zhang, X. P. Liang, W. F. Liu, and G. T. Du, Appl. Phys. Lett. **90**, 121128 (2007).
[11]J. H. Lim, C. K. Kang, K. K. Kim, I. K. Park, D. K. Hwang, and S. J. Park, Adv. Mater. (Weinheim, Ger.) **18**, 2720 (2006).
[12]F. X. Xiu, Z. Yang, L. J. Mandalapu, D. T. Zhao, J. L. Liu, and W. P. Beyermann, Appl. Phys. Lett. **87**, 152101 (2005).
[13]S. Chu, J. H. Lim, L. J. Mandalapu, Z. Yang, L. Li, and J. L. Liu, Appl. Phys. Lett. **92**, 152103 (2008).
[14]J. W. Shin, J. Y. Lee, Y. S. No, T. W. Kim, and W. K. Choi, J. Appl. Phys. **100**, 013526 (2006).
[15]X. L. Wu, G. G. Siu, C. L. Fu, and H. C. Ong, Appl. Phys. Lett. **78**, 2285 (2001).
[16]S. A. Studenikin, N. Golego, and M. Cocivera, J. Appl. Phys. **84**, 2287 (1999).
[17]Z. Z. Ye, J. G. Lu, Y. Z. Zhang, Y. J. Zeng, L. L. Chen, F. Zhuge, G. D. Yuan, H. P. He, L. P. Zhu, J. Y. Huang, and B. H. Zhao, Appl. Phys. Lett. **91**, 113503 (2007).
[18]D. W. Hamby, D. A. Lucca, M. J. Klopfstein, and G. Cantwell, J. Appl. Phys. **93**, 3214 (2003).
[19]B. Cao, W. Cai, and H. Zeng, Appl. Phys. Lett. **88**, 161101 (2006).
[20]H. J. Ko, Y. F. Chen, Z. Zhu, I. Kobayashi, and H. Uchiki, Appl. Phys. Lett. **76**, 1905 (2000).