Demonstration of NOx gas sensing for Pd/ZnO/GaN heterojunction diodes

Makoto Miyoshi, Shu Fujita, and Takashi Egawa

Citation: Journal of Vacuum Science & Technology B **33**, 013001 (2015); doi: 10.1116/1.4906032
View online: http://dx.doi.org/10.1116/1.4906032
View Table of Contents: http://scitation.aip.org/content/avs/journal/jvstb/33/1?ver=pdfcov
Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

Articles you may be interested in

Effects of rapid thermal annealing on properties of Ga-doped MgxZn1−xO films and Ga-doped MgxZn1−xO/AlGaN heterojunction diodes
J. Appl. Phys. **116**, 063501 (2014); 10.1063/1.4892591

Slanted n-ZnO/p-GaN nanorod arrays light-emitting diodes grown by oblique-angle deposition
APL Mater. **2**, 056101 (2014); 10.1063/1.4874455

Nitrogen doped-ZnO/n-GaN heterojunctions
J. Appl. Phys. **109**, 084330 (2011); 10.1063/1.3575178

Electroluminescence at 375 nm from a Zn O ⁄ Ga N : Mg ⁄ c - Al 2 O 3 heterojunction light emitting diode
Appl. Phys. Lett. **88**, 141918 (2006); 10.1063/1.2195009

Characterization of bulk GaN rectifiers for hydrogen gas sensing
J. Vac. Sci. Technol. B **23**, 2373 (2005); 10.1116/1.2110343

AVS
www.avs.org
AVS 63RD International Symposium & Exhibition
MUSIC CITY CENTER
Symposium: November 6-11, 2016 | Exhibit: November 8-10, 2016

Redistribution subject to AVS license or copyright; see http://scitation.aip.org/termsconditions. IP: 133.68.232.179 On: Thu, 04 Aug 2016 06:34:43

CrossMark click for updates

BRIEF REPORTS AND COMMENTS

This section is intended for the publication of (1) brief reports which do not require the formal structure of regular journal articles, and (2) comments on items previously published in the journal.

Demonstration of NOx gas sensing for Pd/ZnO/GaN heterojunction diodes

Makoto Miyoshi,[a] Shu Fujita, and Takashi Egawa
Research Center for Nano-Device and System, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

(Received 21 August 2014; accepted 23 December 2014; published 14 January 2015)

In this study, planar Pd/ZnO/GaN heterojunction diodes (HJDs) are fabricated and their capabilities for NO_x (NO and NO_2) gas-sensing is evaluated. The fabricated HJDs exhibit good rectifying properties at a high temperature of 250 °C and, in addition, they exhibit obvious current changes even under low-concentration 10 ppm NO_x gases and respond to the on/off switching of the gas introduction. It is considered that the sensor action is owing to the electron depletion around the heterojunction caused by the absorbed gas molecules. The current changes reached relatively high values of approximately 1 mA even under exposure to a low-concentration 10 ppm NO_2 gas. © *2015 American Vacuum Society*. [http://dx.doi.org/10.1116/1.4906032]

I. INTRODUCTION

Gallium nitride (GaN) and the related group-III nitrides have been attracting much interest as materials not only for light-emitting devices,[1,2] but also for high-power and/or high-frequency electronic devices.[3,4] In addition, they are known to be applicable for some sensor devices, such as ultraviolet photodetectors[5,6] and gas sensors,[7–13] where their innate ability to operate even at a high temperature is a significant advantage. For the past several decades, field-effect transistors (FETs) using gas-sensitive materials as gate electrodes[14,15] have been viewed as advanced gas-sensing devices adaptable to the highly networked information society. This is because the FET gas sensors have superior features compared to other types of sensors in terms of integration and signal amplification capabilities. In fact, wireless gas sensor network systems based on Si-FET sensors with microprocessors have already been proposed.[16] Although Si is a commonly employed material in FET gas sensors, improving the gas sensitivity of these sensors is problematic because Si-FETs cannot operate properly at high temperatures over 150 °C, whereas many gas-sensitive materials, such as catalyst metals and oxide semiconductors, exhibit innate potential at a temperature over 200 °C. In Ref. 16, for example, Si-FETs were operated at 100 °C. Taking this into consideration, the wide bandgap semiconductors including the group-III nitrides seem to be more suitable for FET gas sensors than do conventional Si.

In the literature, some researchers have reported GaN-based gas sensors that include Schottky barrier diodes (SBDs) and high-electron-mobility transistors (HEMTs),[7–13] but many of those reports discuss only Schottky contacts with Pt or Pd metals and there are only a few reports on metal–oxide–semiconductor (MOS) structures.[9,10] We believe, however, that MOS structures using oxides possessing good gas selectivity will expand the applications of GaN-based sensor devices. Furthermore, past studies on GaN-based gas sensors have been limited almost entirely to H_2 or CO gas-sensing evaluations.[7–13] However, NO_x gases (NO and NO_2) are known to be typical environmental pollutants that should be reduced to lower than 20 ppm environmental concentration, and the regulations governing NO_x gases, especially in automobiles, will become increasingly strict. Therefore, we attempt to apply GaN-based MOS structures to NO_x-sensing evaluations. In this study, Pd/ZnO/GaN heterojunction diodes (HJDs) are employed as a first trial prior to applying them to MOS-HEMT structures. Zinc oxide (ZnO) is known to be a good gas-sensitive semiconductor[17] and is also stable at a high temperature owing to its wide bandgap nature. Moreover, it has been reported that ZnO polycrystalline films can detect NO_x gases with a high selectivity against H_2 and CO gases.[17] Therefore, ZnO/GaN-based MOS-HEMT structures are expected to produce high-performance gas sensors owing to their signal amplification capability. This report presents the basic results on the current–voltage (I–V) characteristics of Pd/ZnO/GaN HJDs under NO_x gas exposure at a temperature of 250 °C. The on/off responses of the HJDs are also measured under exposure to NO_x gases with gas concentrations ranging from 10 to 100 ppm.

II. EXPERIMENT

Figure 1 shows schematic drawings of the planar Pd/ZnO/GaN HJDs fabricated in this study [Fig. 1(a)] and of the band lineup around the heterojunctions [Fig. 1(b)]. Figure 1(b), which was drawn with reference to the physical parameters reported for single-crystalline semiconductors,[18–23] implies

[a]Electronic mail: miyoshi.makoto@nitech.ac.jp

 2166-2746/2015/33(1)/013001/4/$30.00 © 2015 American Vacuum Society

Redistribution subject to AVS license or copyright; see http://scitation.aip.org/termsconditions. IP: 133.68.232.179 On: Thu, 04 Aug 2016 06:34:43

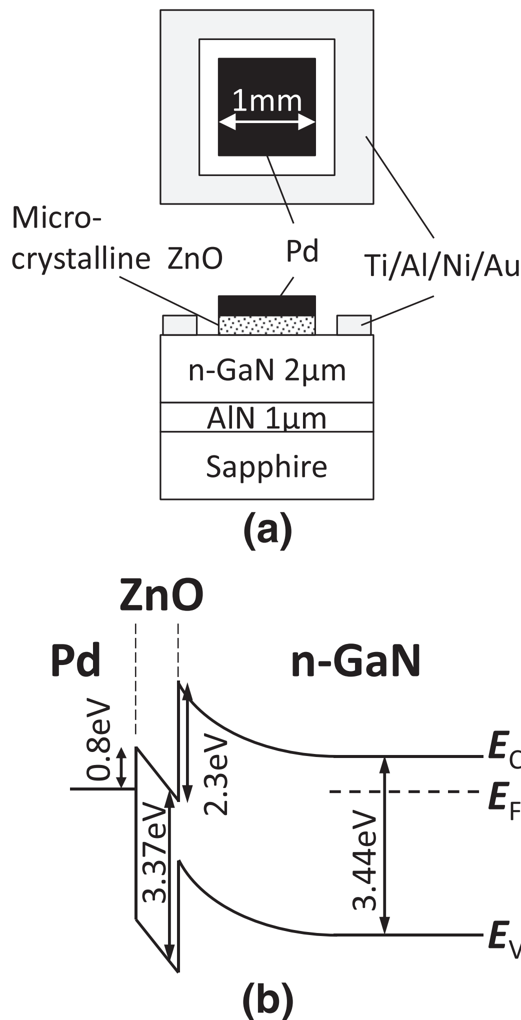

FIG. 1. Schematic drawings of (a) a planar Pd/Zn/GaN heterojunction diode and (b) the band lineup around the heterojunction.

the existence of a large band offset between ZnO and GaN owing to the difference of their electron affinities. Thus, if an ideal junction is realized, the forward voltage drop will reach a value higher than 2 V in the *I–V* characteristics. For application to HJDs, 2 μm-thick n-type epitaxial GaN films with a Si concentration of approximately $2 \times 10^{17}\,\text{cm}^{-3}$ were grown on 2 in.-diameter AlN/sapphire templates in a horizontal metalorganic chemical vapor deposition (MOCVD) system (Taiyo Nippon Sanso, SR-2000), where trimethylgallium and NH_3 were used as the gallium source and the nitrogen source, respectively, and where SiH_4 was used for Si doping. The AlN/sapphire template consisted of a 1 μm-thick epitaxial AlN film on a *c*-face sapphire. Planar HJDs with a square-shaped anode of $1.0 \times 1.0\,\text{mm}^2$ were fabricated on MOCVD-grown epitaxial wafers using a conventional photolithographic lift-off method. Cathode ohmic contacts were formed on the n-type GaN surface by evaporation of Ti/Al/Ni/Au (15/60/12/40 nm), and were subsequently subjected to an annealing process at a temperature of 875 °C for 30 s in a nitrogen atmosphere. A 10 nm-thick microcrystalline ZnO film was formed using the atomic layer deposition (ALD) technique, where diethyl-zinc and H_2O were used as precursors.[24] During the ALD process, the chamber temperature

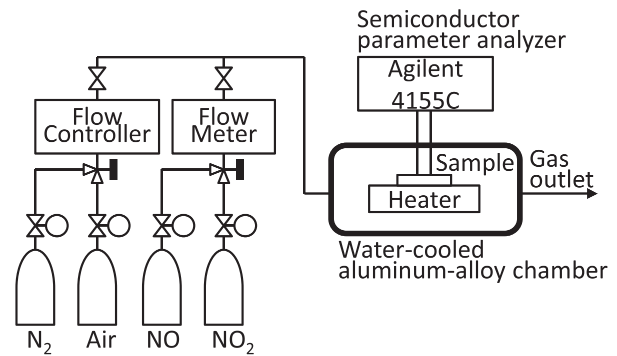

FIG. 2. Schematic diagram of the *I–V* measurement and gas-sensing system.

and pressure were maintained at 200 °C and at 0.28 Torr, respectively. The electron density of the ALD-grown ZnO films was measured to be approximately $1 \times 10^{20}\,\text{cm}^{-3}$ at room temperature (RT) using Hall effect measurements. Finally, anode contacts were formed on the ZnO film via evaporation of a 10 nm-thick Pd film, which was expected to act as an absorbent window for the sampling gases.

Figure 2 shows the schematic diagram of the system used to characterize the HJDs, where the *I–V* characteristics were measured with a semiconductor parameter analyzer (Agilent 4155C). Gas-sensing properties were evaluated by introducing mixed gases into a water-cooled aluminum-alloy chamber, where the HJDs were placed on a heating susceptor and annealed up to a temperature of 250 °C under atmospheric pressure. The NO_x gases used in this experiment were N_2-based and diluted and, during the gas-sensing evaluation, the total flow rate of the sampling gases was maintained at 5 SLM (standard liters per minute). The on/off responses of the HJDs were measured under exposure to the NO_x gases with gas concentrations ranging from 10 to 100 ppm.

III. RESULTS AND DISCUSSION

Figure 3(a) plots typical *I–V* characteristics of the Pd/ZnO/GaN HJDs measured at RT and at 250 °C, where the lower graph is the semilogarithmic plot of the data. As seen in these graphs, the fabricated HJD exhibits a good rectifying property even at the high temperature of 250 °C and, with respect to temperature dependence, a negative temperature coefficient is clearly observed in the forward drift region (>1 V), which is a typical property of majority-carrier diodes. It is therefore confirmed that the fabricated HJDs act like SBDs. The forward voltage drop, V_F, is observed to be approximately 1 V, which is somewhat lower than that estimated from the band lineup, as seen in Fig. 1(b). This indicates that the present HJDs do not have ideal junctions, which is probably because the ALD-grown ZnO films consist of micropolycrystals, and not epitaxially grown single crystals.

Figures 3(b) and 3(c) show the changes in the *I–V* characteristics measured at 250 °C under exposure to NO gas and NO_2 gas, respectively, at a gas concentration of 100 ppm, where the lower graphs are the semilogarithmic plots of the data, and all of the *I–V* measurements are conducted 5 min after introducing the gases. The results clearly show that the

Redistribution subject to AVS license or copyright; see http://scitation.aip.org/termsconditions. IP: 133.68.232.179 On: Thu, 04 Aug 2016 06:34:43

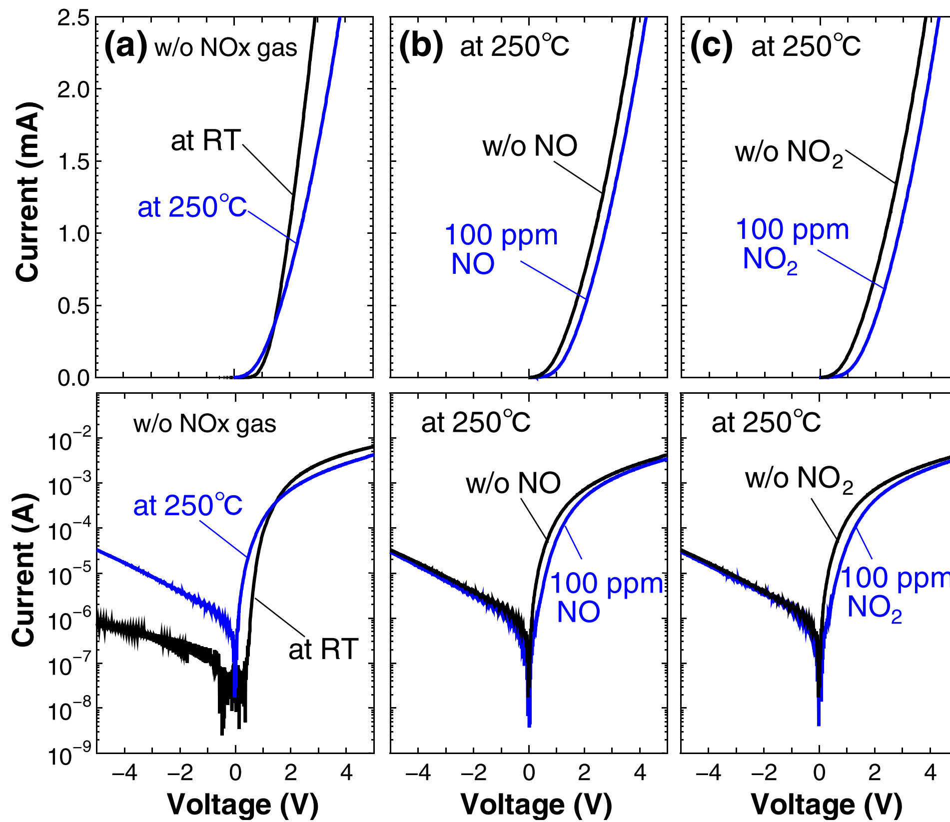

FIG. 3. (Color online) (a) Typical *I–V* characteristics of heterojunction diodes measured at room temperature and at 250 °C. (b) Changes in the *I–V* characteristics of a heterojunction diode measured at 250 °C with and without the exposure to NO gas. (c) Changes in the *I–V* characteristics of a heterojunction diode measured at 250 °C with and without exposure to NO_2 gas. The lower graphs are the semilogarithmic expressions of the upper graphs.

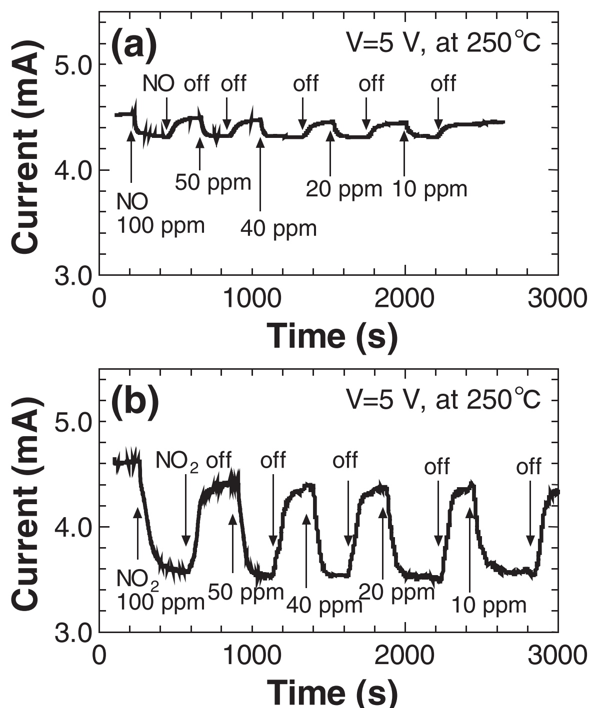

FIG. 4. On/off responses of HJDs under exposure to various concentrations of (a) NO gas and of (b) NO_2 gas.

forward currents decrease with exposure to NO_x gases and, from the upper graphs, it is observed that the changes in the drift resistance are not so large. The current changes are therefore considered to be caused mainly in the diffusion region (<1 V) rather than in the drift region. This indicates that the absorbed gas molecules increase the effective barrier height and/or the tunneling length around the heterojunction. This is likely owing to the dissociatively absorbed molecules depleting the carriers around the heterojunction because they are negatively charged themselves, as is seen in many oxide semiconductors.[25] As a result, the fabricated HJDs exhibit clear current changes under NO_x gas exposure.

Figure 4 shows the on/off responses of the forward HJD currents under exposure to the NO gas [Fig. 4(a)] and to the NO_2 gas [Fig. 4(b)] with different gas concentrations measured at a constant forward voltage of 5 V and at a temperature of 250 °C. The results show clear current changes in response to the gas introduction switching exhibiting a stabilizing time within 1 min and a recovery time within 2 min, where the times are estimated by reading out the rise times to 90% of the final values. These current changes are confirmed to be as high as approximately 1 mA in the case of NO_2 exposure, which is a positive indication because this current change is large enough for actual sensor device applications. However, the current changes are not greatly dependent upon the NO_x gas concentrations, which means that the amount of the absorption charges reach a saturation

Redistribution subject to AVS license or copyright; see http://scitation.aip.org/termsconditions. IP: 133.68.232.179 On: Thu, 04 Aug 2016 06:34:43

state even with the low-concentration 10 ppm NO_x gases. In addition, Fig. 4 implies that the current changes under NO exposure are somewhat smaller than those under NO_2 exposure. This may be owing to the number of dissociatively absorbed molecules and/or the phenomenon of positively charged NO molecules. Further research will be needed to understand these phenomena.

IV. SUMMARY AND CONCLUSIONS

Planar Pd/ZnO/GaN HJDs are fabricated, and their NO_x-sensing capability is evaluated. The fabricated HJDs exhibit good rectifying properties at a high temperature of 250 °C. In addition, the HJD exhibits obvious current changes even under low-concentration 10 ppm NO_x gases, and they respond to the on/off switching of the gas introduction. The cause of this current change appears to be the extraction of electrons in the vicinity of the surface of the HJDs by the absorbed molecules. We believe that the present results will contribute to the future development of high-sensitivity gas sensors. In future, we will conduct a more detailed study that will include the heterojunction characteristics, gas-sensing capability, and selectivity over a wider gas concentration range and dependency upon the ZnO thicknesses, as well as evaluation using MOS-HEMTs.

ACKNOWLEDGMENT

This work was partially supported by the Japan Science and Technology Agency (JST) Super Cluster Program.

[1]S. Nakamura, T. Mukai, and M. Senoh, Jpn. J. Appl. Phys., Part 2 **30**, L1998 (1991).
[2]S. P. DenBaars *et al.*, Acta Mater. **61**, 945 (2013).
[3]T. Egawa, "Heteroepitaxial growth and power electronics using AlGaN/GaN HEMT on Si," IEEE Electron Devices Meet. 2012, 27.1.1.
[4]T. Kikkawa, M. Kanamura, T. Ohkita, K. Imanishi, K. Watanabe, and K. Joshin, ECS Trans. **50**, 323 (2013).
[5]A. Osinsky, S. Gangopadhyay, B. W. Lim, M. Z. Anwar, M. A. Khan, D. V. Kuksenkov, and H. Temkin, Appl. Phys. Lett. **72**, 742 (1998).
[6]L. Sang, M. Liao, and M. Sumiya, Sensors **13**, 10482 (2013).
[7]P. Luther, S. D. Wolter, and S. E. Mohney, Sens. Actuators, B **56**, 164 (1999).
[8]J. Schalwig, G. Müller, M. Eickhoff, O. Ambacher, and M. Stutzmann, Sens. Actuators, B **87**, 425 (2002).
[9]B. S. Kang, F. Ren, B. P. Gila, C. R. Abernathy, and S. J. Pearton, Appl. Phys. Lett. **84**, 1123 (2004).
[10]S. J. Pearton, B. S. Kang, S. Kim, F. Ren, B. P. Gila, C. R. Abernathy, J. Lin, and S. N. G. Chu, J. Phys.: Condens. Matter **16**, R961 (2004).
[11]K. Matsuo, T. Hashizume, and H. Hasegawa, Appl. Surf. Sci. **244**, 273 (2005).
[12]M. Miyoshi, Y. Kuraoka, K. Asai, T. Shibata, and M. Tanaka, J. Vac. Sci. Technol., B **25**, 1231 (2007).
[13]H. Okada, A. Naruse, Y. Furukawa, and A. Wakahara, Jpn. J. Appl. Phys., Part 1 **50**, 01AD08 (2011).
[14]L. Stiblert and C. Svensson, Rev. Sci. Instrum. **46**, 1206 (1975).
[15]I. Lundstrom, S. Shivaraman, C. Svensson, and L. Lundkvist, Appl. Phys. Lett. **26**, 55 (1975).
[16]S. Nakano, Y. Goto, K. Yokosawa, and K. Tsukada, IEEE Sens. **2005**, 159.
[17]N. Koshizaki and T. Oyama, Sens. Actuators, B **66**, 119 (2000).
[18]M. Shur, M. Shatalov, A. Dobrinsky, and R. Gaska, *GaN and ZnO-Based Materials and Devices*, Springer Series in Materials Science, edited by S. Pearton (Springer, New York, 2012), Vol. 156, p. 83.
[19]V. Bougrov, M. E. Levinshtein, S. L. Rumyantsev, and A. Zubrilov, *Properties of Advanced Semiconductor Materials GaN, AlN, InN, BN, SiC, SiGe*, edited by M. E. Levinshtein, S. L. Rumyantsev, and M. S. Shur (Wiley, New York, 2001), pp. 1–30.
[20]H. B. Michaelson, Appl. Phys. Lett. **48**, 4729 (1977).
[21]H. Moormann, D. Kohl, and G. Heiland, Surf. Sci. **80**, 261 (1979).
[22]H. Moormann, D. Kohl, and G. Heiland, Surf. Sci. **100**, 302 (1980).
[23]K. Jacobi, G. Zwicker, and A. Gutmann, Surf. Sci. **141**, 109 (1984).
[24]T. Tynell and M. Karppinen, Semicond. Sci. Technol. **29**, 043001 (2014).
[25]Y. Shimizu and M. Egashira, MRS Bull. **24**, 18 (1999).

Redistribution subject to AVS license or copyright; see http://scitation.aip.org/termsconditions. IP: 133.68.232.179 On: Thu, 04 Aug 2016 06:34:43