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<table>
<thead>
<tr>
<th>論文タイトル</th>
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<tbody>
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</table>

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Demonstration of NOx gas sensing for Pd/ZnO/GaN heterojunction diodes
Makoto Miyoshi, Shu Fujita, and Takashi Egawa

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

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In this study, planar Pd/ZnO/GaN heterojunction diodes (HJDs) are fabricated and their capabilities for NOx (NO and NO2) 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 NOx 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 NO2 gas.

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, implies...
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 $\mu$m-thick n-type epitaxial GaN films with a Si concentration of approximately $2 \times 10^{17}$ 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 $\mu$m-thick epitaxial AlN film on a $c$-face sapphire. Planar HJDs with a square-shaped anode of 1.0 $\times$ 1.0 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 $^\circ$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$_2$O were used as precursors. During the ALD process, the chamber temperature and pressure were maintained at 200 $^\circ$C and at 0.28 Torr, respectively. The electron density of the ALD-grown ZnO films was measured to be approximately $1 \times 10^{20}$ 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.

FIG. 2. 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 $^\circ$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 $^\circ$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 $^\circ$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 $^\circ$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
forward currents decrease with exposure to NOx 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 NOx gas exposure.

Figure 4 shows the on/off responses of the forward HJD currents under exposure to various concentrations of NO gas and NO2 gas. 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 NO2 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 NOx gas concentrations, which means that the amount of the absorption charges reach a saturation

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**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 NO2 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) NO2 gas.
state even with the low-concentration 10 ppm NOx gases. In addition, Fig. 4 implies that the current changes under NO exposure are somewhat smaller than those under NO2 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 NOx-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 NOx 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.

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