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Hydrogen sensing of N-polar and Ga-polar GaN Schottky diodes

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ABSTRACT

N-polar and Ga-polar GaN grown on *c*-plane sapphire were used to fabricate platinum deposited Schottky contacts for hydrogen sensing at room temperature. After exposure to hydrogen, Ga-polar GaN Schottky barrier reduced by 3–4 meV, while the N-polar GaN Schottky contacts became fully Ohmic. The N-polar GaN Schottky diodes showed stronger and faster response to 4% hydrogen than that of Ga-polar Schottky diodes. The abrupt current increase from N-polar GaN Schottky exposure to hydrogen was attributed to the high reactivity of the N-face surface termination. The surface termination dominates the sensitivity and response time of the hydrogen sensors made of GaN Schottky diodes.

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There is great interest in detection of hydrogen sensors for use in hydrogen-fuelled automobiles and with proton-exchange membrane (PEM) and solid oxide fuel cells for spacecraft and other long-term sensing applications. These sensors are required to detect hydrogen near room temperature with minimal power consumption and weight and with a low rate of false alarms. Due to their low intrinsic carrier concentrations, GaN- and SiC-based wide bandgap semiconductor sensors can be operated at lower current levels than conventional Si-based devices and offer the capability of detection to ~600 °C [1–10]. The ability of electronic devices fabricated in these materials to function in high temperature, high power and high flux/energy radiation conditions enable performance enhancements in a wide variety of spacecraft, satellite, homeland defense, mining, automobile, nuclear power, and radar applications.

Wurtzite GaN is a polar material. Therefore, along the *c*-axis, there are N-face (N-polar) or Ga-face (Ga-polar) orientations on the GaN surface. The polarity determined by the GaN surface has been used to improve performance of AlGaN/GaN high electron mobility transistors (HEMTs) [11]. The Ga-polar surface is intentionally grown to make the spontaneous polarization compatible with the piezoelectric polarization to enhance the two-dimensional electron gas in AlGaN/GaN HEMTs [11]. Since there are different reactivities for the N-face and Ga-faces [12–14], it is interesting that how these different surfaces react with different chemicals. Our previously published result shows the improved hydrogen sensing through N-polar GaN Schottky diodes [15]. Since GaN Schottky diodes have been widely used to fabricate hydrogen sensors, it is important to investigate the surface termination effect in detail on the hydrogen sensors made of GaN Schottky diodes.

In this paper, we study the hydrogen sensing with N-face and Ga-face GaN Schottky diodes. Four epi structures with different surface termination, film thickness and carrier concentration were employed. Current–voltage characteristics and the real-time detection of the sensor for hydrogen were investigated.

The Ga- and N-GaN layer structures were grown on *c*-plane sapphire substrates by a metal-organic chemical vapor deposition (MOCVD) system. Four different epi structures were grown and fabricated as Schottky diodes. The layer structures included an initial thin undoped GaN buffer for all the four structures then followed by different active GaN layers with different surface termination or thickness. Fig. 1 (top) shows the schematic of the hydrogen sensor and four different epi structures. The first (#1) and the second (#2) epi structures both have nitrogen face and have 25 nm and 1.1 μm undoped GaN, respectively. The third (#3) and the fourth (#4) structures both have Ga-face. The third has 1.5 μm undoped GaN on a buffer layer. The fourth has 0.7 μm undoped GaN on a buffer layer, followed by 1 μm Si-doped GaN. These four structures have carrier concentration of 2.8×10^{18}, 1.5×10^{18}, 1.2×10^{17}, and 1.4×10^{18} cm^{-3}, respectively, obtained by Hall measurements. The high background carrier concentrations were due to the oxygen incorporation during the growth and the details of the materials

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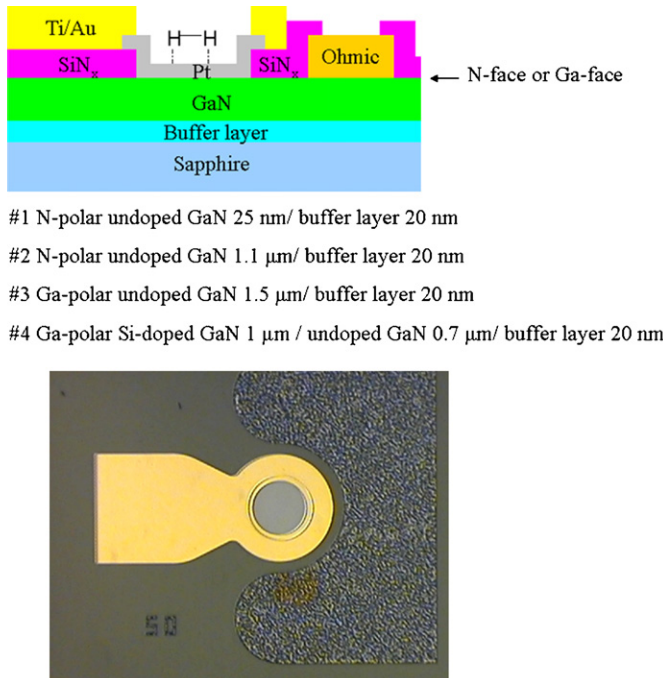

Fig. 1. (Top) Top view of a GaN Schottky diode hydrogen sensor. (Bottom) Schematic of the hydrogen sensor and four different epi structures.

growth can be found elsewhere [16,17]. The Ohmic contacts were formed by lift-off of e-beam deposited Ti (200 Å)/Al (1000 Å)/Ni (400 Å)/Au (1200 Å). The contacts were annealed at 850 °C for 45 s under a flowing N_2 ambient in a Heatpulse 610T system. Isolation was achieved with 2000 Å plasma enhanced chemical vapor deposited SiN_x formed at 300 °C. A window was opened for etching SiN_x where a 100 Å of Pt was deposited by e-beam evaporation to form Schottky contacts. Final metal of e-beam deposited Ti/Au (200 Å/1200 Å) interconnection contacts were employed on the Schottky diodes. Fig. 1 (bottom) shows an optical microscope image of the completed devices. The current–voltage characteristics and real-time detection of these Schottky diodes were measured at 25 °C to detect 4% hydrogen in nitrogen using an Agilent 4156C parameter analyzer with the Schottky contact exposed.

Fig. 2 shows the current–voltage characteristics of the four different hydrogen sensors in pure nitrogen or in 4% hydrogen for

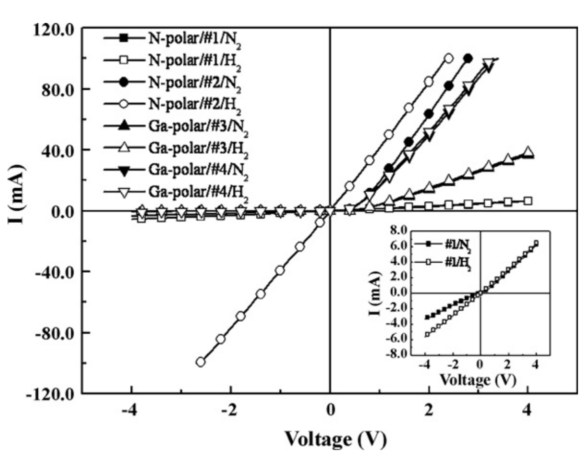

Fig. 2. IV characteristics of the hydrogen sensors with four different structures in pure nitrogen and 4% hydrogen gas, respectively. The inset shows the IV characteristics of the sensor with #1 structure in enlarged scale.

10 min. The N-polar Schottky diodes (#1 and #2) become fully Ohmic when exposed to 4% hydrogen. However, the Ga-polar (#3 and #4) Schottky diodes still maintain rectifying contacts when exposed to 4% hydrogen. The current change of the Ga-polar Schottky diodes before and after exposure to hydrogen is comparable to our published results [8,9] and the current change of Ga-polar Schottky diode was much smaller than that of the N-polar Schottky diodes. This phenomena is even more significant in the reverse bias region where the N-polar Schottky diodes have a current change from μA to mA while the Ga-polar Schottky diodes have current change in the same order of magnitude. The #1 sensor has a much thinner GaN layer of 250 Å, compared to the other three. Therefore it has a higher resistance than the others. The inset of Fig. 2 shows the IV characteristics of #1 sensor. The high leakage current of the #1 sensor may result from a high density of defects in the interface between the thin GaN and sapphire substrate. The #2 sensor has much thicker thickness and does not have this problem. However, the #1 sensor can also shows completely Ohmic behavior when exposed in hydrogen due to its N-polar surface termination. Hydrogen sensing with Pt-deposited GaN Schottky diodes is usually explained by a mechanism in which the dipole formed on the Pt/GaN interface lowers the Schottky barrier height [18,19]. By using the thermoionic emission transport mechanism, the Schottky barrier heights were approximately evaluated as 0.4366, 0.5568 and 0.4247 eV for #2, #3 and #4, respectively, in pure nitrogen at room temperature (298 K). After these sensors were exposed to 4% hydrogen, the effective Schottky barrier heights were reduced by 3.65 and 4.69 meV for #3 and #4, respectively. However, the change for the N-polar Schottky diodes (#2) is huge because it becomes Ohmic. The only difference among #2, #3 and #4 is the surface termination. Therefore, the surface potential change or the dipole forming on the surface is the most likely mechanism. High resolution electron energy loss spectroscopy (HREELS) showed a strong preference of N sites for the adsorption of hydrogen gas or atomic H [12]. The strong affinity of hydrogen with N-polar surfaces was also reported [13]. It was also shown that below 820 °C, N-polar GaN has much faster reaction rate than that of Ga-polar GaN surface [14]. These experiments can explain why N-polar Schottky diodes have stronger response than Ga-polar ones.

Fig. 3 (top) shows the real-time test of sensor #1 in pure nitrogen or in 4% hydrogen at room temperature with the applied voltage at 1 V. The abrupt increase of current shows when 4% hydrogen was exposed to sensor #1, the current suddenly rose and quickly saturated. Fig. 3 (bottom) shows the real-time test of sensor #2 in pure nitrogen or in 4% hydrogen at room temperature with the applied voltage at 0.75 V. It shows a very strong and very fast response to hydrogen. However, when the sensor was purged with pure nitrogen again, the current did not move back to the original baseline. It is possible that some hydrogen was strongly bonded with nitrogen, with the thermal energy at room temperature not being high enough to break the bonding.

Fig. 4 (top) and (bottom) shows the real-time test of the sensor #3 and #4, respectively, at room temperature in pure nitrogen or 4% hydrogen at 1 V. Comparing with N-polar GaN Schottky diodes, the Ga-polar Schottky diodes have weaker and slower response to hydrogen. This demonstrates that the abrupt current increase from the N-polar GaN Schottky diodes was indeed determined by the surface termination, not by the bulk GaN. Therefore, the slower response to hydrogen for the Ga-polar Schottky diodes proved that the Ga-polar surface has lower reactivity to hydrogen than that of N-polar surface. Note the second response to hydrogen is faster than that of the first one for Ga-polar Schottky diodes. This indicates that in the beginning, the Ga surface is contaminated with other elements, such as oxygen, which may form Ga–O bonds (bond energy 282 ± 62.7 kJ/mole) [20]. However, hydrogen may replace